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Study of Organic Scintillators*†

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The scintillation counting behavior of a group of fifty-five pure crystalline organic compounds has been extensively studied. The data obtained have been analyzed with the goal of developing a better understanding of the scintillation process and of scintillator behavior.

The materials were carefully purified, and massive crystals were grown. Relative scintillation average-pulse-height efficiencies at 30°C and −70°C for cobalt-60 gamma-ray excitation, gamma-ray excited scintillation decay times, and 2537 A ultraviolet-excited reflection and transmission photofluorescence spectra have been determined. A few solutions were also studied for comparison purposes. The purification and properties of the different materials are discussed in detail.

The experimental data have been analyzed on the basis of Birks' photon cascade theory of the scintillation process. The ratio of the scintillation efficiency to the integrated photofluorescence intensity is shown to be a measure of Birks' primary photon production efficiency. The primary photon efficiencies vary over a relatively narrow range, so that there is a rough general correlation between the scintillation efficiencies and the integrated photofluorescence intensities. The best phosphors are those with rigid molecular and crystal bonding so that both the primary photon production and photofluorescence efficiencies are reasonably high. There is a tendency for the best scintillators to have the simplest and most sharply defined photofluorescence spectra.

The scintillation efficiencies have been correlated with molecular structures and the mobility of the π electrons (or with the resonance interactions) within the molecules. In the simpler cases, consideration of singly charged quinoid structures permits the calculation of parameters which can be directly correlated with the scintillation efficiencies. In more complex cases, steric hindrance, hyperconjugation, "unshared" and "nonbonding" electron pairs, five-membered aromatic rings, heavy atom (triplet-state) effects, and quinoid (quenching) ground states must be considered. In all cases, the effects of thermal (vibrational) perturbations are present. "Bond density" and "bound valence" values have proved to be useful in correlating scintillation phenomena and molecular structure effects.

Strongly colored compounds are usually poor scintillators. Earlier predictions of high scintillation efficiency for quinquephenyl and sexiphenyl are reaffirmed, and coronene, benzo[ghi]-perylene, and 1,2,5,6-dibenzanthracene are also predicted to be significantly better than the presently known organic scintillators. The further study of compounds containing five-membered aromatic rings appears promising.

A generally good correlation has been found between the scintillation efficiencies and molecular diamagnetic anisotropy values. Some relationships between the scintillation decay times and the molecular structures can also be seen.

The best crystalline organic scintillators are colorless substances of high melting point possessing molecules of simple structure and low atomic number in which there is extensive resonance conjugation of rings, ethylenic double bonds, and other groups to give extended, rigidly interlocked systems.

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† Part of this work was submitted by R. C. Sangster in partial fulfillment of the requirements for the degree of Doctor of Philophy in Chemistry at the Massachusetts Institute of Technology.

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INTRODUCTION

SCINTILLATION counting has been the subject of numerous technical articles and of several books. The modern techniques of scintillation counting have nearly the same importance for experimental nuclear physics as the older techniques[1] had during the classical period of the science. Comprehensive treatments of this subject can be found in the recent books of Birks[2] and Curran.[3] No effort will be made to deal with the subject as a whole in this paper.

The objective of the work reported in this paper has been to study the scintillation process in organic substances. With the external physical conditions held constant, the results of the scintillation process were studied while the chemical nature or the physical state of the scintillating medium was varied. The materials studied were almost exclusively pure crystalline solids.

Several earlier reports have been made on this work.[4–7] In any respects in which the present paper conflicts with the earlier publications, it is to be understood that it completely supersedes them and that the earlier work is to be disregarded. On the other hand, a number of valid details not appropriate for this paper were included in the Technical Report.[4]

Studies of this sort are by no means all recent. As just one example, Newcomer[8] in 1920 studied the x-ray induced fluorescence of nearly five hundred commercial organic compounds. However, very little of the older work was of such a nature as to yield much insight into the relation between the luminescence properties studied and the chemical structures of the compounds.

The term *scintillator* will be used throughout this paper to describe a scintillating medium or a substance presumed capable of being a scintillating medium. A scintillator may be defined as any material which will emit a brief pulse of fluorescent light, or *scintillation*, when it interacts with a high energy particle or quantum. The more conventional term *phosphor* is often used in this connection interchangeably with *scintillator*. The scintillating medium may be solid, liquid, or gaseous,[9,10] crystalline or plastic, pure, a solution, or a mixture.

A note about the nomenclature of the compounds studied here is in order. For the most part, the internationally accepted chemical names have been used. The principal exceptions are these: (1) The higher diphenylpolyenes have not been explicitly named; however, if it is understood hereafter that in this paper all polyene chains are completely conjugated, with neither cumulated nor isolated double bonds, no confusion will result. (2) The term *terphenyl* has been used for *p*-diphenylbenzene (*p*-terphenyl); the terms *m*-terphenyl and *o*-terphenyl have not been used at all. Conventional structural diagrams for the compounds to be discussed are given in Figs. 17–21 with the fluorescence spectra. The order of grouping of the compounds may seem rather arbitrary and capricious; however, this is only partly true, since this order has been selected to permit the most effective comparison of differences in properties with differences in structure. The same sequence has been used throughout the paper.

The experimental work is described in the first part of the paper, while the interpretation and correlation of the empirical data is handled in the second part.

PART I. EXPERIMENTAL

A. Preparation of Materials

1. Purification

Since all fluorescence phenomena, particularly those occurring in crystalline materials, may be strongly influenced by minute traces of impurities,[11] extreme care in the purification of materials has been necessary.

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[1] J. Chariton and C. A. Lea, Proc. Roy. Soc. (London) **122**, 304–352 (1929).

[2] J. B. Birks, *Scintillation Counters* (McGraw-Hill Book Company, Inc., New York, 1953).

[3] S. C. Curran, *Luminescence and the Scintillation Counter* (Academic Press, Inc., New York, 1953).

[4] R. C. Sangster, Technical Report No. 55, Laboratory for Nuclear Science, Massachusetts Institute of Technology, Cambridge, Massachusetts (January 1, 1952).

[5] J. W. Irvine, Jr., and R. C. Sangster, Phys. Rev. **75**, 1460 (A) (1949).

[6] R. C. Sangster and J. W. Irvine, Jr., Phys. Rev. **83**, 241 (A) (1951).

[7] R. C. Sangster and J. W. Irvine, Jr., Nucleonics **10**, No. 3, 36 (A) (1952); see also *erratum*, Nucleonics **10**, No. 4, 29 (1952).

[8] H. S. Newcomer, J. Am. Chem. Soc. **42**, 1997 (1920).

[9] C. O. Muehlhause, Phys. Rev. **91**, 495 (A) (1953).

[10] A. E. Grün, Z. Naturforsch. **9A**, 55–63 (1954).

[11] P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949).

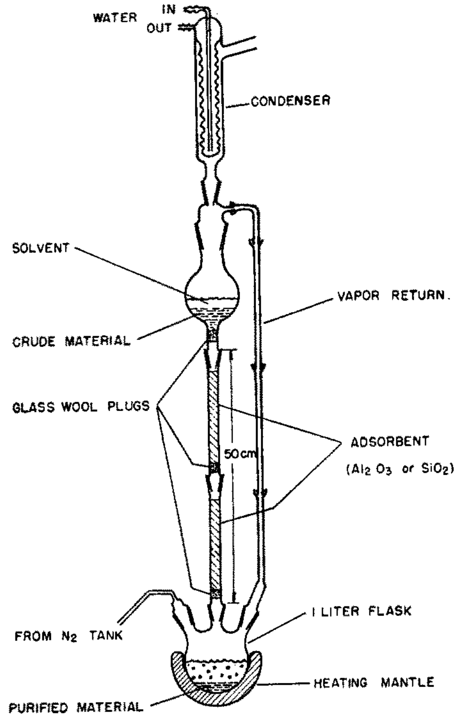

FIG. 1. Adsorption purification apparatus.

While many specific techniques have been used for special cases, an effective general purification procedure has been found to be multiple recrystallizations from appropriate solvents followed by repeated treatments in the adsorption purification[12,13] apparatus illustrated in Fig. 1. A similar procedure was used by Rosahl.[14]

In the apparatus shown in Fig. 1 the solvent in the upper reservoir seeps through the crude material extracting the more soluble components to form a solution which then enters the multiple adsorption column. On the column the more highly adsorbed impurities are retained so that a purified solution enters the bottom reservoir. The solvent is distilled from the bottom reservoir into the upper one to complete the solvent cycle and to cause the purified solute to crystallize out below. Extraction, filtration, adsorption, and recrystallization thus take place simultaneously in this apparatus.

When the top unit in a segmented column becomes saturated with impurities, it can be removed and a fresh unit added at the bottom with a minimum interruption of the process. By replacement of components in this fashion the operation of the apparatus can be continued almost indefinitely with only minor interruptions and with very little attention. Units of this type were first put in operation by the authors in December, 1948 and have been used extensively by them since that time.

Alcoa activated alumina (grade F-1, 48–100 mesh) and Davison silica-gel (commercial grade, 28–200 mesh) are the only adsorbents that have been used. The most generally effective type of column segment is one with silica-gel in the upper half and activated alumina in the lower one. While alumina seems usually to possess the greatest adsorptive powers, there are some cases in which silica-gel is a much more effective purifying medium. Normal-pentane is in most cases the best solvent for this adsorption work. Benzene and other solvents can be used for special cases and are particularly appropriate when the solubility in pentane of the material to be purified is low (i.e., less than about 1 g/l).

Conventional Soxlet-type extractors or the apparatus of Fig. 1 with the adsorption column removed can be used for extraction-recrystallization purifications. The solvents are usually those giving fairly high solubilities. A given material is recrystallized from a variety of solvents[15] until no further purification can be observed before it is put onto an adsorption column. It seems to be generally true that the impurities left by recrystallization are those most readily removed by adsorption and that traces of almost any impurity can be removed by the adsorption procedure.

A further purification is effected during the crystal growing process (see below), since impurities usually will be rejected by the growing crystal and therefore segregated into the last part of the melt to solidify (see, for example, the papers by Bridgman[16] and Wright[17]).

The criteria that have been used to judge purity are melting points, changes in the appearance of materials and residues as the materials are purified, the appearance of crystalline samples grown from the purified materials, the consistency of the scintillation counting data, the consistency and appearance of the fluorescence spectra, and the consistency between the results obtained for different lots of a substance prepared from different sources by different purification methods.

The presence of impurities segregated at the top of the crystallized melt is one of the most important criteria. These segregated impurities may be detected by analysis of the scintillation counting results, or they may be evident visually, either through discoloration effects or through changes in the nature of the crystals. Lack of any evidence for segregated impurities usually implies high purity; apparently complete segregation usually implies satisfactory purity for the lower portions of the melt; obviously incomplete or unsatisfactory segregation implies inadequate purity.

The purification procedures used, the melting points, and other observations made on the materials studied are described in Sec. I-E.

2. Sample Preparation

For reliable comparison among different substances of the light produced during the scintillation process, it is necessary to use samples of comparable optical condition. The crystalline materials have been as nearly perfect and identically mounted monocrystalline samples as could be obtained. The inherently homogeneous

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[12] H. H. Strain, *Chromatographic Adsorption Analysis* (Interscience Publishers, Inc., New York, 1942).

[13] A. Winterstein and K. Schön, Z. physiolog. Chem. **230**, 146 (1934).

[14] D. Rosahl, Ann. Physik (Series 6) **12**, 35 (1953).

[15] A. Seidell, *Solubilities of Organic Compounds* (D. Van Nostrand Company, Inc., New York, 1941), third edition, Vol. 2.

[16] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **60**, 305 (1925).

[17] G. T. Wright, Proc. Phys. Soc. (London) **A66**, 777–783 (1953).

liquids were mounted and tested in essentially the same fashion as the crystalline samples.

Crystalline samples.—Crystals were grown from purified materials using the furnace shown in Fig. 2. The method is basically that of Bridgman.[16] The apparatus is similar to that of Teazel and Smith.[18] While the crystal rods obtained were often single crystals of high quality, normally they were moderately polycrystalline in cross section with the individual crystals extending most of the length of the rod. The crystal diameters were held within a ±2% range about two standard values, 0.49 in. and 0.245 in., by careful selection of the tubing in which the crystals were grown. The one-half inch diameter crystals were preferred, since they gave more precise results. The crystal samples were disks, 0.25±0.01 in. thick, cut from the crystal rods by using a glass saw to cut the sample—glass tube, crystal, and all. The surfaces left from the cut were carefully shaved and polished until fairly good (though microscopically rough) optical surfaces were obtained. Use of slightly rough surfaces probably helped minimize trapping of scintillation photons by total internal reflection.[19] Since the light output was studied through the circular faces, flaws parallel to the axes of the disks had relatively little effect. Fragile crystals were tested without removing them from the glass rings left by the saw.

One to ten grams of the purified materials were sealed under vacuum or $\frac{1}{3}$ atmos prepurified nitrogen into the glass sample tubes, great care being taken to avoid any thermal decomposition of the materials or their vapors. (No significant differences between crystals grown under vacuum or under nitrogen have been detected.) The sample tubes were slowly lowered (1 cm/hr) through the temperature gradient set up by the heating coils in the crystal-growing furnace. As they emerged from the hot zone, crystallization began in the bulb tips and proceeded up through the capillaries in which usually all seed crystals but one were eliminated. A thyratron temperature controller was used to stabilize the temperatures within the furnace; no significant fluctuations were ever noted. The few exceptional materials studied which melt below room temperature were crystallized by lowering sample tubes through a heating coil into an ice bath.

The finished samples were mounted in aluminum holders of the type shown at the lower right of Fig. 4. The 0.25-in. diameter samples were first mounted in aluminum rings which then fitted the standard holders. Shiny aluminum foil was used as a reflector behind all samples.

Several materials were studied both with and without the glass retaining rings and as crystals of both diameters. No reliable correction factor could be assigned to the use of the glass retaining rings; at the most, their effect was no greater than ±5%. Reliable (±2%) correction factors were deduced for normalizing the behavior of the 0.25-in. samples to the same basis as that of the 0.50-in. samples. The size of the crystal is important for gamma rays of the energies used, due at least in part to leakage of high-energy electrons from the crystal surfaces and the consequent reduction in the intensity of the scintillation pulse.[20] These corrections have been applied in all the material that follows.

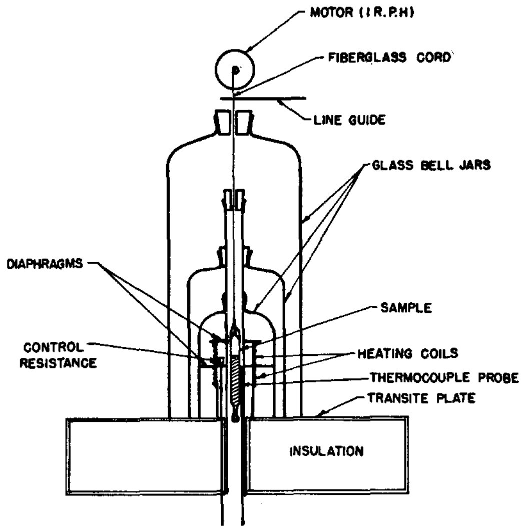

FIG. 2. Crystal-growing furnace.

The one sodium iodide crystal[21] was sealed behind a quartz window in a modified sample holder. Two standard anthracene crystals were mounted with the same geometry and tested to permit the correction of the sodium iodide data to the standard geometry. No attempt was made to correct for the optical effects of the quartz window.

Liquids.—Several pure liquids and solutions were tested, both to obtain new data and to determine a calibration factor for liquids *versus* solids. In order to accomplish this latter end, the liquids were tested under conditions as nearly comparable to those for the solids as possible. The standard aluminum sample holders were used as cups to contain the liquid scintillators. Thin mica sheets were used as cover glasses. Standard anthracene crystals covered with thin films of Nujol or glycerine were tested with and without mica cover glasses to determine an average correction factor for the effect of the mica. This factor was applied to all the results obtained and was consistent with the transmission spectrum shown in Fig. 3.

B. Study of Scintillation Counting Behavior

1. *Testing Equipment and Procedures*

The apparatus in which the scintillation counting behavior of the mounted samples was studied is shown in Fig. 4.

The samples in their holders were stacked in the hopper at the right and were pushed through the channel one by one for testing. A ball and slot arrangement served to position the samples ac-

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[18] C. E. Teazel and C. D. Smith, Rev. Sci. Instr. 19, 817 (1948).

[19] W. A. Shurcliff and R. C. Jones, J. Opt. Soc. Am. 39, 912–916 (1949).

[20] Prestwich, Colvin, and Hine, Phys. Rev. 87, 1031 (1952).

[21] Purchased from the Harshaw Chemical Company.

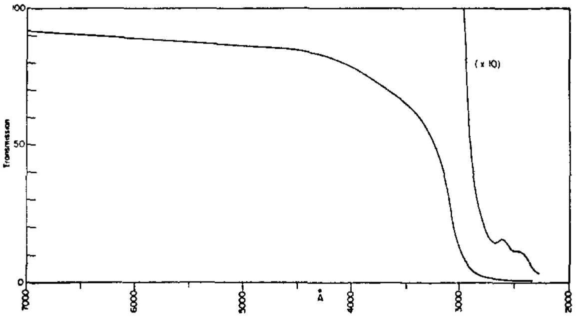

FIG. 3. Transmission spectrum of mica cover glasses used in testing liquid scintillators: percent transmission *versus* the wave-ength in angstroms.

curately beneath the photomultiplier. The spectral response curve[22] of the 5819-type end-window RCA C-7140 photomultiplier tube used for all of the work described here is shown in Fig. 5, together with an average curve for C-7140 photomultiplier tubes given in the literature which accompanied the tube. Cobalt-60 gamma rays were used to excite the scintillations. All of the data reported here have been reduced to the values corresponding to the standard cobalt-60 source with which most of the work was done and have been corrected for the radioactive decay of the source. The scintillation counting behavior of the samples was studied at 30°C, at −70°C, and in exceptional cases at 0°C; the temperature was held within a ±0.5°C range at the two higher temperatures and within a ±2°C range at the lower. Since the temperatures of photomultiplier and phosphor could not be independently controlled, it has been assumed in interpreting the results that any variation in the behavior of the photomultiplier could be ignored. When dry-ice cooling was used, a steady flow from right to left through the channel of dry carbon dioxide gas minimized frosting problems.

A positive high voltage power supply furnished the photomultiplier high voltage, which was arbitrarily held at 640±1 volts. The photomultiplier output pulses were fed through a preamplifier into a precision linear amplifier with a one microsecond time constant. Following the linear amplifier were three units—a scale-of-256 scaler with an integral discriminator, a differential discriminator unit with built-in scaler, and a precision counting-rate meter with integral discriminator—which could be connected in parallel or in series. The counting-rate meter together with its associated recording milliammeter was used at constant settings as a monitoring instrument, while the experimental data were taken with the other two units. A Sola constant-voltage transformer was used to power all of the electronic apparatus, except for the differential discriminator whose functioning depended upon both the peak and rms voltages.

The discriminator circuits were so arranged that the zero-pulse bias voltages ("flop points") and the operating bias voltages could be read and adjusted to within ±0.1 volt. With the flop point set at 72 volts, the discriminators would function properly for pulses with peak voltages ranging from 72 volts down to somewhat less than 2 volts. The gain of the linear amplifier was adjusted to make optimum use of this working range.

Short period fluctuations were detected by the counting-rate meter monitoring unit. Long-range fluctuations were detected both by this unit and by running standard anthracene crystals at about two-hour intervals. The results of these standard runs were used to adjust all of the data obtained to standard conditions. Difficulties introduced by such factors as changing tubes were thus also eliminated. During one period of about a month when the apparatus was on continuously and in frequent use, the total amplification factor (photomultiplier plus linear amplifier) remained constant within a ±1% range.

The standard testing time for a single sample was about fifteen minutes. The pulse distribution curves were normally based on from nine to twelve points, most closely spaced on the high counting rate portion of the curve. The shortest counting time was twenty seconds. The counting time was made long enough to give sufficient counts to permit a statistical accuracy of at least one percent, until a counting time of one hundred seconds was reached, after which it was held constant.

2. *Pulse Distribution Curves*

The types of pulse distribution curve obtained are illustrated in Fig. 6 for an anthracene and a thallium-activated sodium iodide crystal. The integral distribution curves—*integral bias curves*—indicate the number of pulses per second whose pulse heights are greater than the value plotted. The differential distribution curves show as a function of pulse height the number of counts per second per unit of pulse height.

For the inorganic phosphors such as sodium iodide, the differential curves are useful in bringing out fine structure. However, for the organic phosphors under the conditions existing during these experiments, they were generally quite featureless. Therefore the more easily obtained integral bias curves were chosen as the form in which the primary scintillation counting data were to be recorded.

Averaged and normalized integral bias curves are shown in Figs. 7–10 for all of the crystalline materials studied, for temperatures of 30°C (in exceptional cases 0°C) and −70°C. The structural formulas of the compounds named in the figures are shown with the fluorescence spectra in Sec. I-D. The background[23] curves observed are shown in Fig. 11.

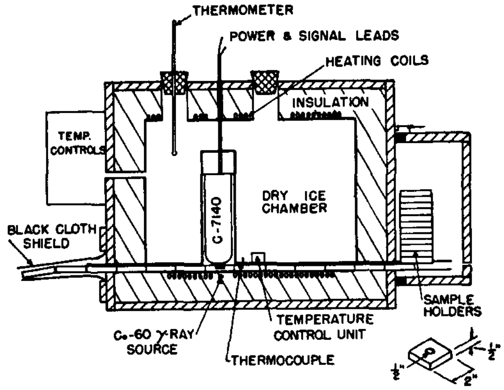

FIG. 4. Scintillation counting test apparatus.

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[22] Determined by the National Bureau of Standards.

[23] J. B. Birks and J. W. King, Proc. Phys. Soc. (London) **B66**, 81 (1953).

The shapes of the distribution curves shown in Figs. 6 and 7–11 are consistent with theoretical expectations. The 1.1- and 1.3-Mev cobalt-60 gamma rays interact with organic media primarily by the Compton process which produces recoil electrons (the agents which actually produce the scintillations) possessing a continuous range of energies from zero up to maximum values somewhat less than the gamma-ray energies. The type of Compton distribution which would be obtained under essentially ideal conditions is shown in Fig. 12. The curve of that figure was derived from those given by Maeder, Müller, and Wintersteiger.[24–26] It is computed for ideal collimation and is broadened out by a Gaussian distribution corresponding to 1000 multiplier photoelectrons per Mev of energy dissipated in the crystal. When the dispersive effects of the following factors—no collimation of the primary gamma-ray beam, back-scattered radiation, excited electrons both leaving and entering the crystal, bremsstrahlung losses, randomness in the collection of light, and the greater statistical spread due to 100 or fewer photoelectrons being produced per Mev of energy dissipated in the crystal instead of the 1000 Mev assumed for the theoretical calculations—are superimposed on this distribution, the generally featureless character of the curves for the organic phosphors is to be expected.

The better phosphors such as anthracene show curves which gradually diminish until a pulse-height value corresponding approximately to the maximum energy of the Compton electrons is reached, after which the curves fall off much more rapidly. For the poorer organic phosphors the statistical spread in the detection and amplification of the pulses is so large that all structure is lost and the curves on a semilog plot approximate straight lines. On the other hand the inorganic phosphors may interact with gamma rays of these energies to give photoelectrons of sharply defined energy, and despite the dispersive effects mentioned above, at least some traces of this structure persist in the low and broad peaks evident on the differential distribution curve for sodium iodide.

3. *Analysis of Integral Bias Curves*

Three main parameters have been used to describe the integral bias curves; the intercept I or I_g, the average pulse height $\bar{v}_n$, and the shape factor β.

Intercept.—The intercept I is the counting rate found by extrapolating the empirical integral bias curve back to the zero pulse-height axis. It normally represents the total number of scintillations of all sizes greater than zero that take place in the crystal per unit time. The organic crystals usually are composed only of low atomic number atoms and vary little in atomic composition, so that the stopping power for gamma rays is usually for all practical purposes dependent only on the mass of the crystal. The intercept I should thus be essentially directly proportional to the mass of crystal, and the intercept divided by the mass of the crystal, or I_g, should be a constant, independent of either the mass or the nature of the crystal, dependent basically only on the source intensity and the geometry and composition of the apparatus. Although there is a small mass-independent contribution to I due to energetic electrons entering the crystal from the surrounding material, over the ranges of mass usually encountered I_g is for all practical purposes a constant, $I_g{}^0$, in the normal cases. It has not been possible to find any dependence of I_g on the geometrical parameters of the crystal samples for those approximating a given standard size. Similarly, no dependence of variations in I_g on variations in the other scintillation parameters has been found.

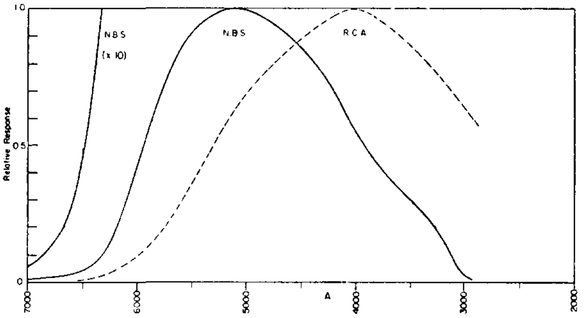

FIG. 5. Photomultiplier response curves showing the relative response to equal amounts of radiant energy incident at different wavelengths. The NBS curve was determined by the National Bureau of Standards for the C-7140 photomultiplier used in this work. The RCA curve was taken from an RCA data sheet supplied with this photomultiplier.

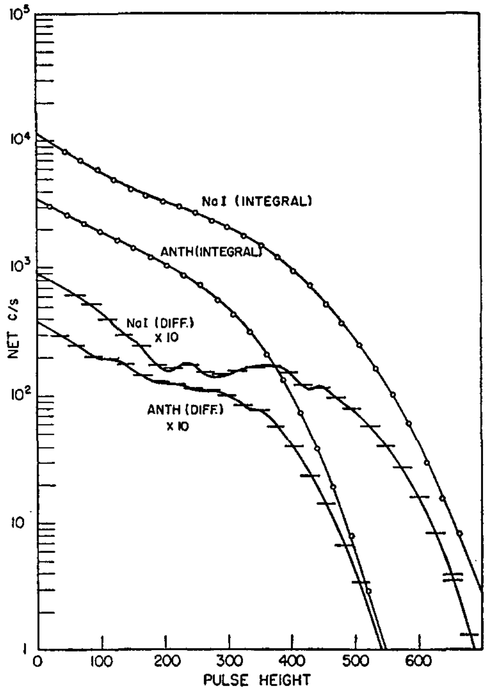

FIG. 6. Integral and differential pulse distribution curves for anthracene and thallium-activated sodium iodide crystals.

Although I_g is normally the constant $I_g{}^0$, there are exceptional cases in which I_g may be either much larger or much smaller. When the average number of photons per scintillation is small, the statistical probability that some scintillations will fail to produce any photoelectrons in the photomultiplier may be large and the total number of pulses produced in the photomultiplier may be much less than the total number of scintilla-

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[24] Maeder, Müller, and Wintersteiger, Helv. Phys. Acta 27, 3–44 (1954).

[25] D. Maeder and V. Wintersteiger, Phys. Rev. 87, 537 (1952).

[26] D. Maeder and V. Wintersteiger, Physica 18, 1147–50 (1952).

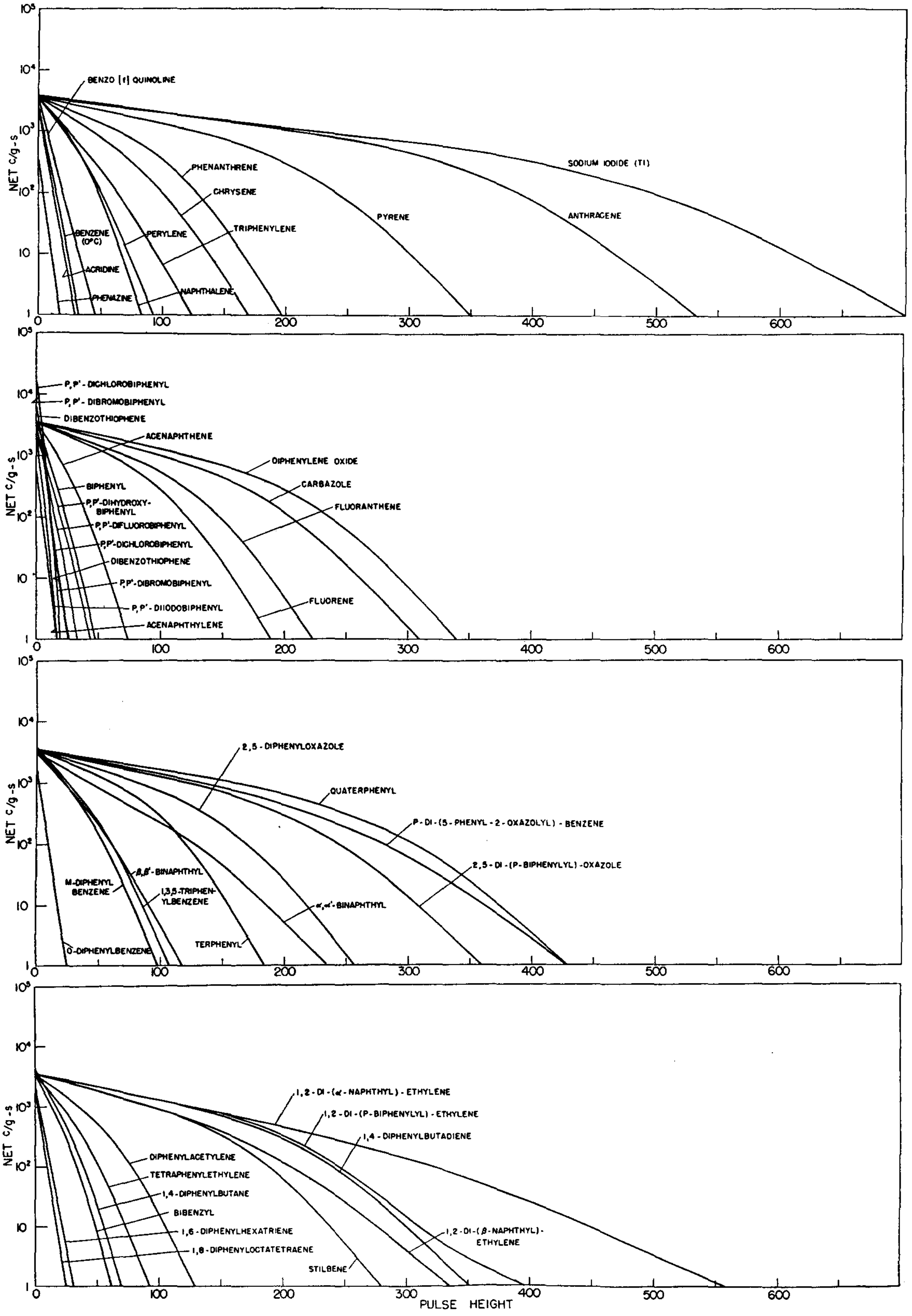

FIG. 7. Integral bias curves for 30°C except where indicated for 0°C.

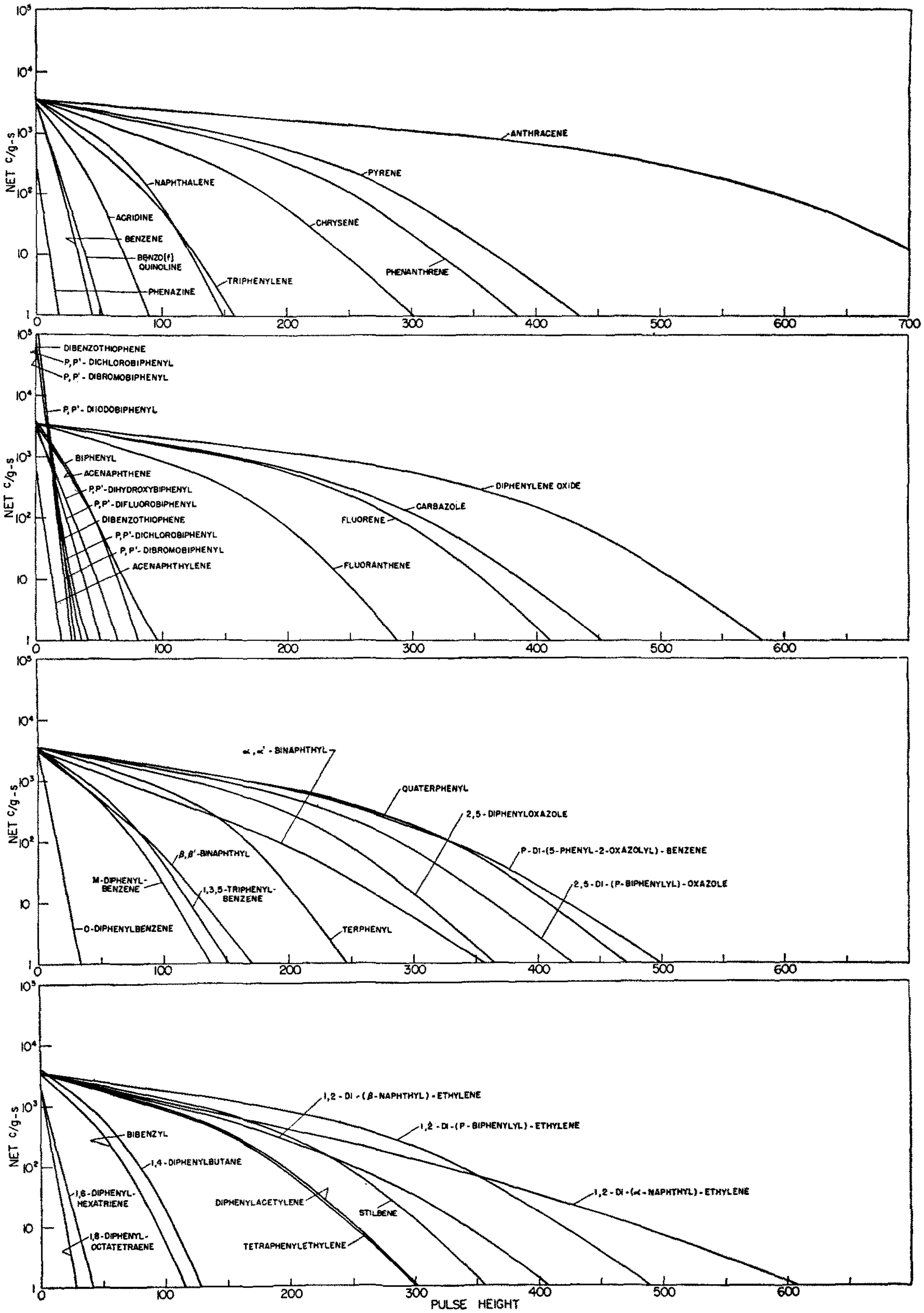

FIG. 8. Integral bias curves for −70°C.

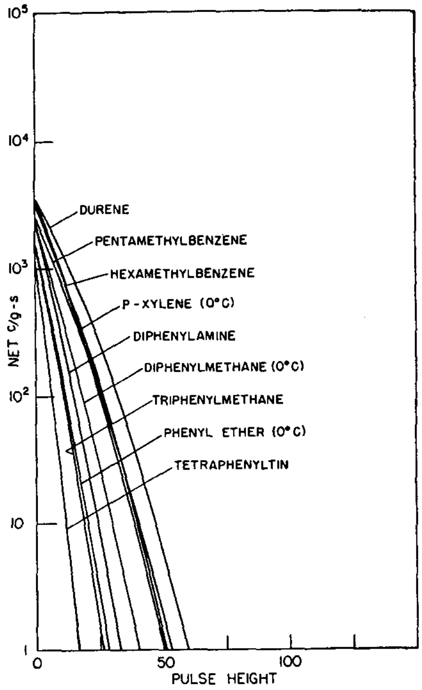

FIG. 9. Integral bias curves for 30°C except where indicated for 0°C.

tions actually occurring in the crystal.[27,28] The normalized intercept I_g is thus less than I_g^0. On the other hand, if the photons produced during a given scintillation are emitted so slowly that the single photoelectron pulses from the photomultiplier look like separate pulses to the linear amplifier (with its one microsecond time constant), then a very large number of very small pulses may be recorded.[29,30] In the limiting case, all of the pulses observed will correspond to single photoelectron pulses in the photomultiplier; this makes it possible to calibrate the pulse-height scale in terms of the number of photoelectrons produced in the photomultiplier, and thus roughly in terms of the total number of photons produced in the crystal.

Some deviations in I_g due to the difference in gamma-ray stopping power of light and heavy atoms will be expected for the materials containing heavy atoms. However, I_g for sodium iodide does not differ much from that found for the normal organic compounds, so that this effect can probably be ignored.

Average pulse height.—In the usual case, the (normalized) average pulse height $\bar{v}_n$, the parameter of primary importance, can be found directly from the (normalized) integral bias curve by a process of numerical integration. (*All of the pulse-height values reported in this paper have been normalized so that anthracene at 30°C shows an average pulse height of 100.*) In the exceptional cases, the apparent average pulse heights $\bar{v}_n'$ found by integration must be multiplied by the factor I_g/I_g^0 to give the true average over all of the scintillations actually produced within the crystals. Normally, the average pulse heights are independent of the intercept values. Likewise, in a group of crystals approximating a given size, the average pulse height values are experimentally independent of the exact sizes or masses of the crystals.

For mathematical purposes the integral bias curves may be regarded as plots of the function $c=c(v)$ where c is the counting rate corresponding to v, the minimum pulse height passed by the discriminator. For small v, $c(v)$ is linear on a semilog plot. As v increases, $c(v)$ falls off from the initial straight line to approach linearity again with a steeper slope, for large v. The function $c(v)$ cannot be accurately determined when c is less than about one count per second. It is physically permissable and mathematically convenient to assume that $c(v)$ approaches zero exponentially along the limiting semilog straight line that it approaches or approximates as c approaches one count per second. Then the product $v\cdot c(v)$ also approaches zero as v becomes very large.

Application of elementary calculus indicates that the number of pulses per unit time with voltages between v and $v+dv$ is given by $-(dc/dv)_v dv$ and that the average pulse height $\bar{v}$ is given by

$$\bar{v}=\int_{v=0}^{v=\infty} v\left[-\left(\frac{dc}{dv}\right)dv\right]\Big/\int_{v=0}^{v=\infty}-\left(\frac{dc}{dv}\right)dv$$

$$=-\frac{1}{I}\int_{v=0}^{v=\infty} v\,dc$$

$$=-\frac{1}{I}\left[v\cdot c\Big|_{v=0}^{v=\infty}-\int_{v=0}^{v=\infty} c\,dv\right]$$

$$=\frac{1}{I}\int_{v=0}^{v=\infty} c\,dv.$$

An approximate value for this last integral can be obtained as follows:

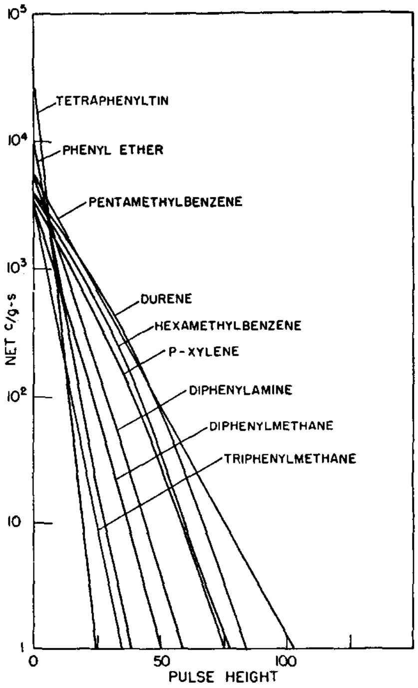

FIG. 10. Integral bias curves for −70°C.

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[27] F. Seitz and D. W. Muller, Phys. Rev. **78**, 605 (1950).
[28] W. V. Mayneord and E. H. Belcher, Nature **165**, 930 (1950).
[29] W. G. Cross, Phys. Rev. **78**, 185 (1950).
[30] E. H. Belcher, Nature **166**, 742 (1950).

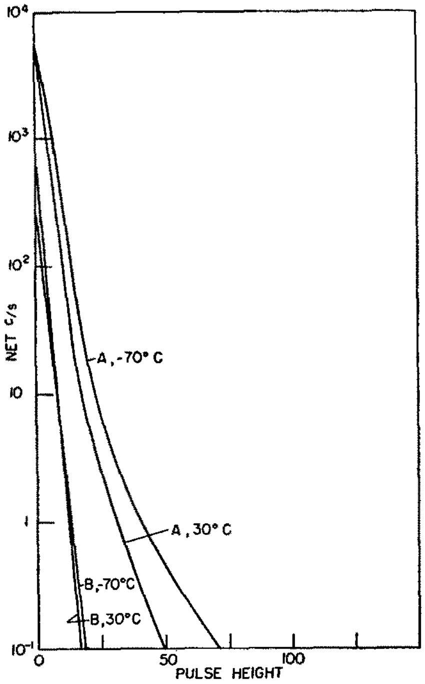

FIG. 11. Background integral bias curves. The *A* curves were determined with the cobalt-60 gamma-ray source present and the phosphor absent. The *B* curves were determined with both source and phosphor absent. The difference between the *A* and *B* curves is probably due primarily to fluorescent scintillations in the air and the glass of the photomultiplier.[23] Direct excitation of the multiplier by the gamma rays may also occur.

A set of voltage values, v_j, $j \geq 0$, are obtained such that

$$v_0 = 0,$$

and

$$c(v_j) = \tfrac{1}{2}c(v_{j-1}) = I(\tfrac{1}{2})^j.$$

Intervals Δv_j are defined by $\Delta v_j = v_j - v_{j-1}$, with $j \geq 1$. The approximate values for the integral can be obtained by connecting the points $(v_j, c(v_j))$ by straight line segments, and integrating over the resulting broken-line curves. Inspection of the experimental curves will show that if the straight lines are drawn on a straight algebraic plot of $c(v)$ *versus* v, the segments will in every case lie above the smooth curve, and that if they are drawn on a semilog plot of $c(v)$ *versus* v, the segments will coincide with or lie below the smooth curve. (The conclusion for the algebraic plot depends on the fact that $\Delta v_j = \frac{1}{2}\Delta v_{j-1}$ for an algebraic straight line while experimentally $\Delta v_j > \frac{1}{2}\Delta v_{j-1}$ in every case, so that $c(v)$ falls off at a decreasing rate and must therefore be concave upwards on the algebraic plot.) Integration over these two different broken-line curves will yield upper and lower limits for the value of $\bar{v}$. For the straight algebraic plot,

$$\bar{v} = 1.5 \sum_{j=1}^{\infty} \Delta v_j (\tfrac{1}{2})^j.$$

For the semilog plot,

$$\bar{v} = \frac{1}{\ln 2} \sum_{j=1}^{\infty} \Delta v_j (\tfrac{1}{2})^j = 1.442 \sum_{j=1}^{\infty} \Delta v_j (\tfrac{1}{2})^j.$$

By interpolation a second-order correction can be found for the latter case, which is much the better of the two approximations, to give as exact a value for $\bar{v}$ as the precision of the data will warrant. This second-order correction $\delta\bar{v}$ is given by

$$0.058 \sum_{j=1}^{\infty} -\Delta(\Delta v_j)(\tfrac{1}{2})^j,$$

where $-\Delta(\Delta v_j) = \Delta v_{j-1} - \Delta v_j$.

Inspection of the series used to approximate $\bar{v}$ will show that the initial term contributes over one-half of the total integral, and that its value is one-half of the negative reciprocal of the initial slope of the curve, which quantity can thus be used as a useful approximate measure of $\bar{v}$. Since each term of the summation for $\bar{v}$ is normally less than or equal to one-half of the previous term $(\Delta v_j \leq \Delta v_{j-1})$, and since

$$\sum_{m+1}^{\infty} (\tfrac{1}{2})^j = (\tfrac{1}{2})^m,$$

the summation of all terms with $j > m$ is normally less than or equal to the value of the mth term itself. The empirical curves are valid out to at least the tenth interval, which contributes no more than $(\frac{1}{2})^{10} = 0.1\%$ of the total; the contribution of the extrapolated tail is of a similar magnitude and is unimportant so that any empirical or mathematical difficulties which might have been implied by carrying the summations and integrations to infinity are of no practical consequence.

Shape factor.—The arbitrary shape factor β is essentially the ratio of the limiting slope of the integral bias curve to the initial slope. In practice, β has been defined as $\Delta v_1/\Delta v_m$; where Δv_m is the smallest interval Δv_j, usually Δv_{10}. The fractional second-order correction factor for the average pulse height, $\delta\bar{v}/\bar{v}$, is roughly equal to $(\beta - 1) \times 10^{-3}$.

Discussion.—Both I_g and β are primarily functions of the average pulse height (except for those scintillators giving abnormally high I values). This can readily be seen from Figs. 13, 14, and 15. In Fig. 13 the integral bias curves have been plotted for the pulses produced by an anthracene crystal with white translucent paper between the crystal and photomultiplier. As the optical absorber reduces the size of the pulses reaching the photomultiplier, both I_g and β diminish. In Fig. 14 the intercepts I_g have been plotted against the apparent average pulse heights $\bar{v}_n'$. The rapid drop off of I_g

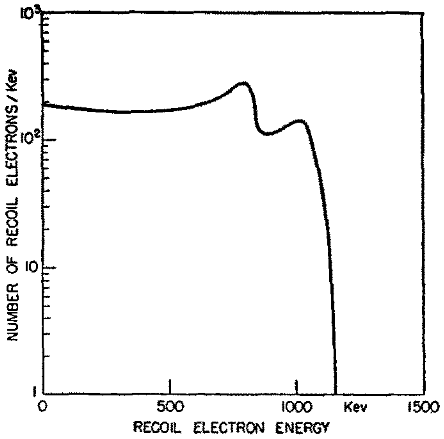

FIG. 12. Theoretical shape of the differential Compton distribution for equal numbers (10^6 each) of 1.022- and 1.28-Mev gamma rays incident upon a cylindrical NaI(Tl) crystal of 0.5-cm radius and thickness.

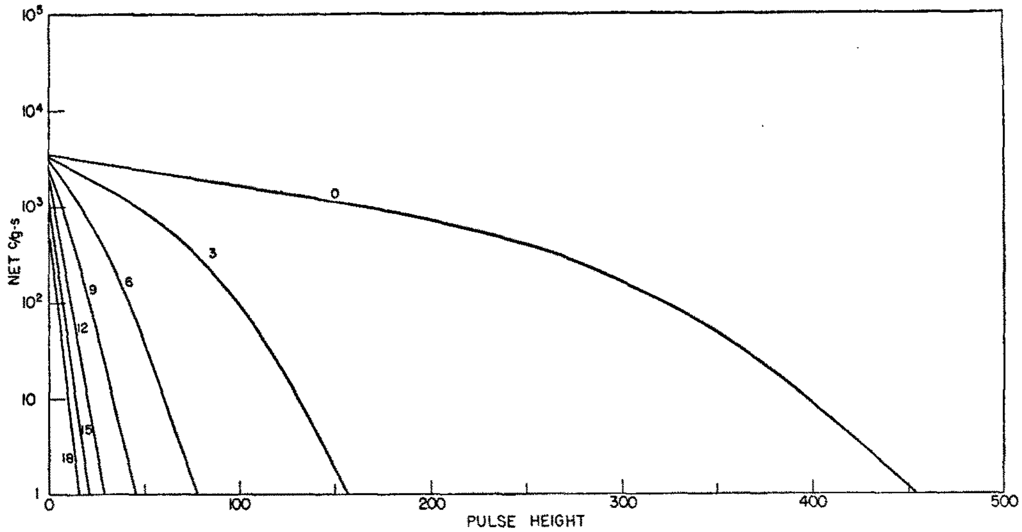

FIG. 13. Integral bias curves for an anthracene crystal with the indicated numbers of layers of a white translucent paper between the crystal and the photomultiplier.

when $\bar{\nu}_n'$ becomes small is readily apparent. The limiting value of $\bar{\nu}_n'$ corresponding to single photoelectron pulses is indicated and could be used to renormalize all of the pulse-height values in terms of the single photoelectron average pulse height. In Fig. 15 the shape factors β have been plotted against the true average pulse heights $\bar{\nu}_n$. The shape factors are functions of both the average pulse height and the perfection of the crystals; the poorest crystals and the smallest pulses give the distribution curves with the poorest resolution.

Aside from the top samples from the melts, there are very few exceptions to the statement that no correlation has been noted between the scintillation parameters and the position of a crystal in the crystal rod from which it was cut. The scintillation properties of the top samples are often abnormal, indicating the presence of impurities segregated into them during the freezing process. The failure to observe any such segregation effects lower down in the crystal rods is good evidence that no impurities are present that have any direct or appreciable influence upon the scintillation response. In the few exceptional cases, where such effects were noted, repurification was usually attempted and usually led to more consistent results.

4. *Scintillation Counting Data*

In Tables I–VI averaged and normalized scintillation counting parameters are presented for all of the materials that have been studied. The intercepts I_g, average pulse heights $\bar{\nu}_n$, and apparent average pulse heights $\bar{\nu}_n'$ have been defined in the preceding section. The temperature coefficients α are defined by the equa-

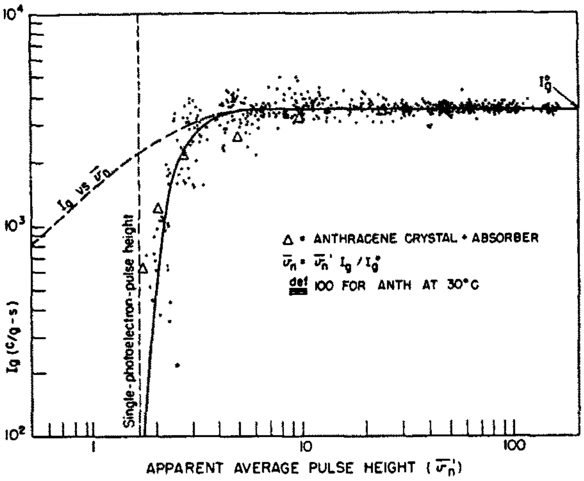

FIG. 14. Intercepts normalized to constant weight plotted against the apparent average pulse heights, for all of the individual experimental curves showing negligible evidence of spurious pulses.

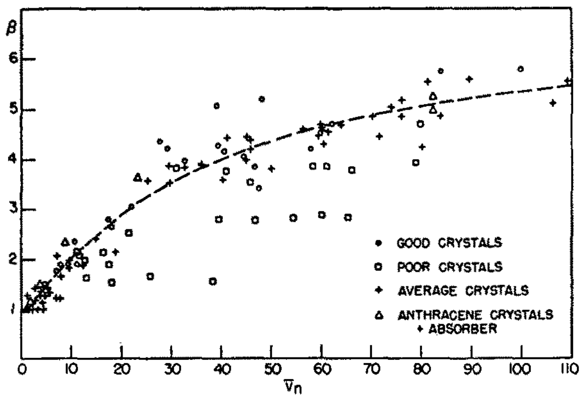

FIG. 15. Shape factors β plotted against the true average pulse heights $\bar{\nu}_n$. A qualitative estimate of the perfection of the crystal is indicated for each of the points plotted.

TABLE I. Scintillation counting parameters—crystalline solids.

Substance	Intercept[a] I_0 (c/g-sec)	Average pulse height[a] $\bar{v}_n$ (p.h. units)	Temperature coefficient of $\bar{v}_n$ α $(\times 10^2)$	Number of samples and melts	Crystal transmission factor[b] (ν)
Benzene (0°C)	2765±345	2.33±0.26	−1.33 ±0.04	6,2	(0.9)
Naphthalene	3660±40	10.75±0.12	−1.06 ±0.03	9,3	(1.0)
Anthracene	3505±20	100.0 ±0.7	−0.540±0.003	29,8	1.00 (def.)
Phenanthrene	3510±25	31.2 ±0.2	−0.96 ±0.03	10,3	0.80±0.01
Chrysene	3490±80	21.6 ±0.6	−0.85 ±0.03	3,1	0.67±0.01
Pyrene	[f]3590±35	60.0 ±0.9	−0.20 ±0.03	9,3	0.78±0.01
Triphenylene[c]	3370±100	12.7 ±1.2	−0.39 ±0.14	3,1	1.00
Perylene[c]	3180	10.6	+0.25?	(2,1)[d]	0.80
Acridine	2360±30	1.78±0.03	−4.20 ±0.40	5,2	(1.0)
Phenazine	416±30	0.24±0.02	+0.17 ±0.13	2,1	(0.6)
Benzo[f]quinoline	3685±130	2.84±0.03	−0.61 ±0.01	5,2	0.78±0.01
Acenaphthene	3410±105	9.0 ±0.2	−0.10 ±0.05	3,3	(1.0)
Acenaphthylene	620±105	0.32±0.02	−0.43 ±0.35	2,1	(1.0)
Fluoranthene	3550±70	36.0 ±0.4	−0.26 ±0.03	3,1	(0.95)
Fluorene	3585±40	29.7 ±0.8	−1.49 ±0.03	5,2	0.85
Carbazole	3410±20	49.9 ±0.5	−0.52 ±0.01	6,2	(0.95)
Diphenylene oxide	3590±35	60.0 ±0.4	−0.82 ±0.03	5,2	0.95±0.05
Dibenzothiophene	8700±400	4.38±0.16	−12.6 ±4.8	4,2	0.93±0.05
Biphenyl	3830±55	5.05±0.16	−1.10 ±0.08	9,3	(1.0)
p,p′-Difluorobiphenyl	3060±60	2.65±0.05	−0.92 ±0.05	6,2	(1.0)
p,p′-Dichlorobiphenyl	22 650±1600	10.3 ±0.6	−3.28 ±0.04	5,2	0.90±0.03
p,p′-Dibromobiphenyl	20 000±800	10.2 ±1.2	−2.43 ±0.16	(7,3)[d]	0.77±0.02
p,p′-Diiodobiphenyl	2305±130	1.22±0.05	−56±7	5,2	(0.9)
p,p′-Dihydroxybiphenyl[c]	2180±180	3.64±0.27	−0.87 ±0.14	5,2	0.65±0.10
p,p′-Dinitrobiphenyl		0		2,1	(1.0)
o-Diphenylbenzene	1800±75	1.16±0.05	−1.34 ±0.06	4,2	0.73
m-Diphenylbenzene	3770±45	12.5 ±0.3	−0.32 ±0.04	6,3	0.76±0.01
1,3,5-Triphenylbenzene[c]	3970±80	13.8 ±0.4	−0.38 ±0.06	6,2	1.00
Terphenyl	3515±55	29.7 ±0.5	−0.40 ±0.05	7,3	1.00
Quaterphenyl	3480±25	75.9 ±0.7	−0.054±0.012	7,2	0.81±0.01
2,5-Diphenyloxazole	3415±20	40.9 ±0.6	−0.42 ±0.01	5,2	0.75±0.04
2,5-Di-(*p*-biphenylyl)-oxazole[c]	3550±85	59.3 ±2.2	−0.18 ±0.05	3,1	0.97±0.01
p,Di-(5-phenyl-2-oxazolyl)-benzene[c]	3560±125	66.1 ±2.6	−0.19 ±0.02	3,1	0.93±0.01
α,α'-Binaphthyl[c]	3230±85	25.7 ±0.6	−0.49 ±0.02	5,2	0.48±0.01
β,β'-Binaphthyl[c]	3140±45	13.0 ±0.7	−0.39 ±0.05	5,2	0.79±0.04
Diphenylacetylene	3555±45	25.4 ±0.6	−1.41 ±0.01	7,4	0.80±0.02
Stilbene	3650±25	45.7 ±0.7	−0.31 ±0.01	16,4	1.00
1,4-Diphenylbutadiene	3450±20	60.0 ±0.5	−0.08 ±0.01	5,2	0.71
1,6-Diphenylhexatriene	2500±255	1.92±0.27	−0.18 ±0.11	2,2	(0.6)
1,8-Diphenyloctatetraene	2220±235	1.37±0.15	−0.17 ±0.09	2,2	(0.6)
1,2-Di-(*p*-biphenylyl)-ethylene	3550	60	−0.35	(2,1)[d]	(0.8)
Tetraphenylethylene	3600±65	11.2 ±0.2	−3.10 ±0.15	5,2	(0.8)
1,2-Di-(α-naphthyl)-ethylene[c]	3515±65	65.4 ±1.3	+0.11 ±0.04?	5,2	0.52±0.03
1,2-Di-(β-naphthyl)-ethylene	3620±40	46.8 ±2.5	−0.16 ±0.03	6,2	(0.8)
Bibenzyl	3575±70	7.1 ±0.3	−1.15 ±0.09	5,2	(1.0)
1,4-Diphenylbutane	4230±100	9.4 ±0.7	−1.16 ±0.12	3,3	1.00
Diphenylmethane (0°C)	2310±40	2.74±0.03	−0.80 ±0.01	3,2	(0.9)
Diphenylamine	2655±110	2.34±0.12	−2.28 ±0.33	6,3	0.78
Phenyl ether (0°C)	1615±55	1.32±0.02	−7.04 ±0.50	4,2	(0.9)
Triphenylmethane	1650±50	1.28±0.03	−1.15 ±0.27	6,2	0.85±0.04
Tetraphenyltin	1300±70	0.58±0.03	−23.7 ±2.1	7,2	0.83±0.13
p-Xylene (0°C)	3480±145	5.00±0.07	−0.86 ±0.15	3,1	(0.9)
Durene	3680±30	7.11±0.20	−0.58 ±0.12	5,2	(1.0)
Pentamethylbenzene[c]	2640±170	4.04±0.26	−2.25 ±0.08	5,2	(0.9)
Hexamethylbenzene	3260±75	5.26±0.17	−0.79 ±0.03	5,2	0.86±0.01
Sodium iodide (Tl activated)	3730±30	108.7 ±1.3		1	(1.00)

[a] Values for 30°C, except 0°C where noted after substance name. $\bar{v}_n$ is in normalized pulse height units, so that for anthracene at 30°C $\bar{v}_n \equiv 100$.

[b] Melts and samples 0.25 in. in diameter; otherwise, 0.50 in. in diameter

[c] The crystal transmission factor is approximately the average fractional amount of light escaping per scintillation, relative to the fraction escaping from such standard "good" crystals as anthracene. The values in parentheses are estimates.

[d] The data reported here were selected or computed from those obtained for the indicated number of samples.

tion $\alpha=[\bar{v}_{t0}-\bar{v}_{-70}]/[\bar{v}_{t0}(t_0+70)]$, where $t_0=30$°C or 0°C, so that, approximately, $\bar{v}_{t2}=\bar{v}_{t1}[1+\alpha(t_2-t_1)]$. The crystal transmission factor ν is the ratio of the average fraction of the scintillation light escaping from a crystal to the average fraction escaping from a "good" crystal such as anthracene. The other quantities in the tables are either self-explanatory or adequately explained in the legends.

Table I contains the scintillation counting data of primary importance, those describing the behavior of the pure crystalline solids. Table II contains data which supplement those of Table I, describing the behavior

TABLE II. Scintillation counting parameters—slow scintillators.

Temperature	30°C		−70°C	
Substance	I_g	$\bar{v}_n'$	I_g	$\bar{v}_n'$
Dibenzothiophene	8700±400	1.78±0.02	125 000±50 000	1.70
Biphenyl	3830±55	4.67±0.10	4020±120	9.34
p,*p*′-Difluorobiphenyl	3060±60	3.08	4170±90	4.33
p,*p*′-Dichlorobiphenyl	22 650±1600	1.61	84 000±6000	1.86
p,*p*′-Dibromobiphenyl	20 000±800	1.76	57 000±3000	2.18
p,*p*′-Diiodobiphenyl	2305±130	1.88	144 000±16 000	1.71
m-Diphenylbenzene	3770±45	11.8±0.2	3560±120	16.5
1,3,5-Triphenylbenzene	3970±80	12.3±0.2	3650±130	19.0
1,4-Diphenylbutane	4230±100	7.9±0.5	4125±15	17.5
Diphenylamine	2655±110	3.14	5440±150	5.01
Phenyl ether	1615±55(0°C)	2.90(0°C)	11 100±700	2.50
Tetraphenyltin	1300±70	1.60	30 700±3000	1.66
Durene	3680±30	6.85	4100±100	9.70
Pentamethylbenzene	2640±170	5.44	5600±400	8.30
Hexamethylbenzene	3260±75	5.73	3870±120	8.65

I_g is the intercept, in c/g-sec (counts per gram-second).
$\bar{v}_n'$ is the apparent average pulse height, in normalized pulse height units.
$\bar{v}_n' = \bar{v}_n(I_g^0/I_g)$.
Standard deviations have been given only for the quantities determined directly from the experimental curves. The other values were computed from the directly determined ones.

of the "slow" scintillators in more detail. Table III summarizes the work done to establish the reliability of the scintillation counting data for anthracene. Table IV indicates the variation—or the lack of it—in the results obtained with different preparations of some of the other materials in Table I. Table V presents data obtained for some liquid scintillators. Table VI contains miscellaneous values for some relatively impure and polycrystalline materials, for what value they may be to future investigators contemplating work with these compounds.

Averaging and normalizing methods.—The intercept values, average pulse heights, and temperature coefficients were determined for the individual samples

TABLE III. Scintillation counting parameters—anthracene preparations.[a]

Preparation symbol[b]	Melting range[c] (°C)	Average pulse height $\bar{v}_n$ (p.h. units)	Temperature coefficient α (×10²)	Number of samples and melts
RSG	215.5–219.2	73.2±3.4	−0.489	3,1
RSG-Pent	217.0–220.5	94.9±0.7	−0.556	3,1
RSG-Acet	217.5–220.5	83.5±1.4		3,1
**RSG-(Al_2O_3, pent*)	216.5–219.8	102.0±2.5	−0.558±0.011	3,1
**RSG-(SiO_2, pent*)	216.2–219.7	99.7±1.0	−0.534±0.004	7,1
RSG-(Al_2O_3, pent)-IV	218.0–220.1	96.9±1.8		4,1
*RSG-(Al_2O_3, pent)-$(CH_2OH)_2$-Acet	217.3–219.9	97.0±1.0	−0.524±0.008	6,2
**RSG-(Al_2O_3, pent)-$(CH_2OH)_2$-Acet-(Al_2O_3, pent*)	218.0–221.0	99.5±0.6	−0.542±0.012	3,1
RSG-Dianthracene	(249.7–254.2)	94.0±1.4	−0.505±0.024	2,1
EKC	215.2–218.7	∼40		1
EKC-Acet	216.4–219.9	90.5±1.2	−0.543±0.018	3,1
*EKC-(Al_2O_3, pent)	215.8–219.5	96.8±1.2		3,1
JTB-(SiO_2 pent)-(Al_2O_3, pent)^2-(Al_2O_3, pent*)	215.4–219.5	74.2±4.4		3,1
**JTB-(Al_2O_3, Bz)^3	217.0–220.2	103.0±2.1	−0.524±0.008	3,1
JTB-(Al_2O_3, Bz)^3-$(CH_2OH)_2$-Acet-Bz	217.0–220.6	91.0±4.7		2,1
Weighted Average[d]		100.0±0.7	−0.540±0.003	29,8
Radiac[e]		100.2	−0.53	1
Brookhaven[f]		101.2±0.8	−0.62	3,1

[a] The intercept values do not differ significantly from one preparation to the next, and have been omitted from the table.

[b] The preparation code symbols describe both the source and the purification procedure. RSG refers to Reilly Tar and Chemical Corporation scintillation-grade anthracene. EKC refers to Eastman Kodak Company blue-violet fluorescence grade anthracene; this material apparently contains ethylene glycol as a contaminant. JTB refers to J. T. Baker Company technical grade (95%) anthracene. Pent, Acet, and Bz refer to recrystallization from commercial normal-pentane, reagent grade acetone, and reagent grade benzene, respectively. Pent* refers to olefine-free normal pentane. In the bracketed symbols, the first component is an adsorbent, either activated alumina or silica gel, while the second is the solvent. $(CH_2OH)_2$ refers to codistillation with ethylene glycol.[120,121] Dianthracene refers to anthracene regenerated by melting dianthracene[107,108] which was precipitated by intense ultraviolet irradiation of a refluxing benzene solution of highly purified anthracene.

[c] The recorded literature melting point of pure anthracene is 216.6°C,[106] of dianthracene, 244°C.[108,109]

[d] The weight given to each preparation in determining the mean average pulse height is indicated by the number of stars before the preparation symbol. The mean temperature coefficient was determined in a similar manner. The weighting factors were assigned on the basis of the purity of the materials and the precision of the data.

[e] Furnished by the courtesy of Mr. J. L. Zar, National Radiac, Inc.

[f] Furnished by the courtesy of Brookhaven National Laboratory.

TABLE IV. Scintillation counting parameters—miscellaneous preparations.

Preparation[a]	Intercept I_g (c/g-sec)	Average pulse height, $\bar{v}_n$ (p.h. units)	Temperature coefficient α ($\times 10^2$)	Number of samples and melts
Fluoranthene I	3525±35	31.3 ±0.6	−0.23±0.06	6,2
* II	3570±35	32.8 ±0.6	−0.24±0.002	6,2
III	3550±70	36.0 ±0.4	−0.26±0.03	3,1
Carbazole I	3615±40	60.4 ±1.0	−0.75±0.02	6,2
* II	3410±20	49.9 ±0.5	−0.52±0.01	6,2
o-Diphenylbenzene I	1012±20	0.64±0.02	−2.63±0.30	5,3
* II	1800±75	1.16±0.05	−1.34±0.06	4,2
m-Diphenylbenzene I	3460±40	13.3 ±0.2	−0.49	2,1
* II	3770±45	12.5 ±0.3	−0.32±0.04	6,3
Terphenyl I	3500±55	27.9 ±0.3	−0.49	3,1
* II	3515±55	29.7 ±0.5	−0.40±0.05	7,3
III	3590±90	29.6 ±0.3		3,1
Radiac	3540±15	32.8 ±0.2	−0.21	1
2,5-Diphenyloxazole I	3340±10	31.5 ±0.9	−0.54	2,1
* II	3415±20	40.9 ±0.6	−0.42±0.01	5,2
α,α'-Binaphthyl I	3045±155	20.9 ±0.5	−0.42±0.01	6,2
* II	3230±85	25.7 ±0.6	−0.49±0.02	5,2
β,β'-Binaphthyl I	2800±80	7.16±0.09	−0.41±0.03	4,2
* II	3140±45	13.0 ±0.7	−0.39±0.05	5,2
*Diphenylacetylene I	3555±45	25.4 ±0.6	−1.41±0.01	7,4
II	3580±20	18.0 ±0.3	−1.64±0.18	6,2
Radiac I	3550	29.2 ±0.1	−0.40±0.02	1
II[b]	3590	30.6	−0.65	1
Stilbene I	3475±50	45.2 ±0.8	−0.25±0.01	8,2
II	3470±130	31.3 ±0.6		2,1
III	3610±20	45.7 ±0.5	−0.40±0.03	11,3
* A	3645±30	44.7 ±0.5	−0.30±0.01	8,2
* B	3660±25	46.6 ±1.2	−0.33±0.02	8,2
Radiac	3750±30	39.1 ±0.7	−0.21	1
Tracerlab I[c]	3615±15	38.3 ±1.6	−0.31	2
Tracerlab II[c]	3670	34.9	−0.40	1

[a] The nature of each preparation is discussed in Sec. I-E.

[b] By courtesy of Mr. J. L. Zar, National Radiac Inc.

[c] By courtesy of Tracerlab, Inc.

* The preparation or preparations which are regarded as most typical of the pure compound, in each case. The bases for these evaluations are discussed in Sec. I-E.

from the appropriate integral bias curves. They were then reduced to standard conditions, the pulse heights normalized to anthracene at 30°C = 100, and the quantities averaged. The standard deviations of the mean have also been determined and are reported in the tables. Average pulse heights for −70°C have been

TABLE V. Scintillation counting parameters—liquids.

Solvent	Solute	Conc. (g/l)	Av. pulse height $\bar{v}_n$ (p.h. units)	Pract. scint. eff. (K and F)[a]	Ratio $\frac{\text{K and F}}{\bar{v}_n}$	Fluor. spectral range[b] (A)
Benzene	(Reagent)		0.3	1.0–1.2	3	
	(Reagent, purified)		0.4			
	Anthracene	1.5	3.3	7.1	2.15	(3900–4700)
	Naphthacene	Sat.	0.6			
	Perylene	Sat.	5.9			4500–5200
	Fluoranthene	3	6.7	11	1.65	(4300–6100)
	Terphenyl	4.5	7.8	37	4.75	
	2,5-Di-(*p*-biphenylyl)-oxazole	Sat.	10.1			3900–4900
	p-Di-(5-phenyl-2-oxazolyl)-benzene	Sat.	7.3			3900–4900
	1,2-Di-(*p*-biphenylyl)-ethylene	Sat.	4.6			3800–4800
	1,2-Di-(α-naphthyl)-ethylene	1.5	12.3			4000–4900
	1,2-Di-(β-naphthyl)-ethylene	Sat.	7.6			3800–4600
Toluene	(Reagent)		0.4	1.2–1.5	3.5	
	Anthracene	1.5	3.4	8.1	2.4	
	Terphenyl	4	9.3	42	4.5	(3500–4500)
p-Xylene	(Purified)		0.4			
Diphenylmethane	(Purified)		0.6	0.9	1.5	
Phenyl ether	(Purified)		0.4	4.3	11	
	Terphenyl	3.5	8.2	52	6.5	
	1,2-Diphenylhexatriene	1	12.4	37	3.0	4100–5200
Phenylcyclohexane	(Purified)		1.5	2.0–1.7	1	2700–3100[a]
	Terphenyl	3	7.9	52	6.5	3200–4100[a]

[a] Data taken from Kallmann and Furst, Nucleonics **8**, No. 3, 32 (1951).

[b] Values determined by the present authors unless otherwise noted. The bracketed values are uncertain. All data were taken, and the saturated solutions prepared, at room temperature (25–30°C).

TABLE VI. Scintillation counting parameters—miscellaneous materials.

Substance	Average pulse height $\bar{v}_n$ (p.h. units)	Comments[a]
Anthranilic acid	~ 0.75	EKC.[b]
Azobenzene	0	Purity and source unknown.
Benzidine	~ 2.5	EKC partially purified.
Benzil	0	Matheson.
Cadmium anthranilate	0	Recrystallized.
Diphenyldiacetylene[c]	0	Through Al_2O_3 in pentane. Decomposed when melted.
Diphenyl sulfone	0	Unknown source and purity.
2-(2-Iodophenyl)-5-phenyloxazole[d]	0	Through Al_2O_3 in pentane. Impure.
α-Methylnaphthalene (liquid)	2	Through Al_2O_3 in hexane.
β-Methylnaphthalene	5	Matheson.
Naphthacene	0	Through Al_2O_3 in benzene. Decomposed when melted.
β-Naphthol	0	Unknown source and purity.
Paraffin	~ 0.85	Through Al_2O_3 as liquid.
p-Phenylphenacyl chloride	0	Unknown source and purity.
Salicylic acid	~ 1.5	EKC.
1,2,4,5-Tetrabromobenzene	0	EKC.
Tri-*p*-cresyl phosphate	5	EKC.
Triphenylbismuthine	1	Unknown source and purity.
Triphenylcarbinol	5	EKC.
Triphenyl phosphate	5	Unknown source and purity.

[a] The purity and crystalline nature of these materials were usually poor. All determinations were made at room temperature.

[b] Eastman Kodak Company.

[c] By courtesy of Professor W. S. Koski, Johns Hopkins University.

[d] By courtesy of Dr. F. N. Hayes, Los Alamos Scientific Laboratory.

determined by applying the mean temperature coefficients α to the mean average pulse heights for 30°C (or 0°C) (see Table XI and Fig. 24); in this fashion the influence of the chance selection of better or poorer samples for testing at -70°C has been minimized. Usually only two or three samples of a given material were studied at -70°C.

The averaged and normalized integral bias curves reported in Figs. 7–11 have been derived in a similar fashion.

Precision.—The standard deviations of the mean are consistently about 0.2% for the mean, corrected, average-pulse-height values determined for series of from ten to forty, nonconsecutive runs on single, constantly-mounted, anthracene crystals. The percentage standard deviations in I_g are usually about twice as large. The standard deviations of the mean for the average pulse height values obtained for a given substance by averaging over runs for several different crystals are usually ±1% or larger. Since determinate factors may be involved, particularly those due to the small number of preparations tested for each substance (usually one) and to the small number of crystal rods grown (usually two or three), the calculated standard deviations for the different substances which are presented in the tables may be misleading. In general, average pulse height values for different substances or preparations differing by less than 5% cannot be considered significantly different, values differing by 10% are on the borderline, and values differing by 20% are definitely different.

Anthracene standards.—The average pulse-height value for anthracene used for normalization was determined by averaging over the preparations starred in Table III, weighting the doubly starred preparations twice as much as the others. The ±0.7% standard deviation is probably significant. In any case, the value selected is completely reliable within a ±5% range. The Radiac and Brookhaven samples were run *after* the basic normalization factor had been chosen; the agreement between these samples and the weighted average is highly satisfactory.

A serious aging effect exists for anthracene crystals. Over a period of several months a surface film forms which reduces the light output by 15–25%. Washing with benzene or toluene or mechanically shaving the surface exposed to the photomultiplier restores the original efficiency of the crystal. The cause of this film is probably surface oxidation, but it could also be photochemical.

When the standard crystals were in constant use, the routine wiping and polishing to which they were subjected apparently prevented the aging effect from perturbing the results; however, when the crystals were stored for extended periods, they aged and approached a constant efficiency much lower than the original value. The original group of standard crystals fortunately contained both aged and unaged crystals, and the effect was discovered when these crystals were used in a later series of runs. A series of fresh anthracene samples was then prepared to establish the stability of the originally aged standards and thus to validate the whole correction and normalization procedure that had been used in working up the raw experimental data.

Another surface effect was discovered which could perhaps account for some of the discrepancies between this work and that done by other authors. The presence of a film of Nujol (a heavy paraffin oil) or glycerin on the surface of an anthracene crystal will reduce the light output by about 20%. Standing for extended periods of time does not restore the original efficiency. Thorough washing with a volatile solvent such as pentane and standing in air for several hours restores perhaps one-third of the lost response. The probable explanation of these phenomena is that the nonvolatile liquid fills in the minute surface irregularities of the crystal so that a much greater fraction of the light incident on the surface is totally reflected and trapped in the crystal,[19] where it is ultimately absorbed or lost through the other faces. The liquid and crystal have similar indices of refraction, so that the surface film has much the same effect as an optically high quality crystal surface.

Aging effects.—In addition to the aging effects noted above for anthracene, such effects have also been found for the higher diphenylpolyenes and, apparently, perylene and 1,2-di-(α-naphthyl)-ethylene. These phenomena are described in some detail during the discussion of the individual materials.

Absolute scintillation efficiency of anthracene.—The single photoelectron pulse height value of Fig. 14 implies that for anthracene in this particular apparatus 60 photoelectrons are produced at the photocathode and collected by the photomultiplier per average pulse. Since the C-7140 used in this work was an early model, its photoelectron production efficiency quite possibly was no higher than 2–5% (see reference 2, p. 28). The average collection efficiency for this type of tube is about 60%. A combined value of 2% for the collected photoelectron efficiency seems reasonable. This then implies that 3000 photons were intercepted by the photomultiplier. Assumption of a 1.5π geometry factor implies that 8000 photons were produced in the anthracene crystals, per gamma ray intercepted, on the average. For anthracene, the average uv-excited fluorescence photon energy is about 2.7 ev, so that about 22 kev of fluorescence energy is produced in the crystal. The gamma rays from cobalt-60 consist of equal numbers of 1.17- and 1.33-Mev quanta.[31] Figure 12 suggests that a reasonable average energy dissipation per incident gamma ray is about 600 kev. On this basis, the absolute energy conversion scintillation efficiency of anthracene (i.e., the fraction of the energy dissipated in an anthracene crystal which is converted into usable light) for cobalt-60 gamma-rays is about 3.5%, in good agreement with the values reported in the literature for gamma- or beta-ray bombardment: 4.2%,[32] 3.76%,[33] 3.5%,[34] 1–2%,[35] 10%.[36] However, while it is justified to state that the data determined during the course of this work are consistent with what appears to be the best value for the absolute efficiency for anthracene, about 4%, the factors leading to this agreement were rather arbitrarily selected, and they could be almost as reasonably chosen to give efficiencies differing by a factor of two or four either way.

Optical transmission factors.—The optical transmission factors ν of Table I were calculated from experimentally determined values μ by the formula $\nu=(\mu-1)/\ln\mu$. The μ values were determined by measuring the diminution of the apparent intensity of a diffuse light source when the scintillation crystals were interposed between the source and a spectrograph slit. (The grating spectrograph was set for the central maximum.) The intensity passed by anthracene and similar "good" crystals was used as the reference point. The formula above was derived on the assumption that all points in a crystal are equally likely places of origin for a scintillation photon, that the average probability of a photon's escaping from a crystal is an exponential function of the distance from its point of origin to the face nearest the photomultiplier or spectrograph slit, and that photons from the diffuse light source which enter the crystal behave thereafter as though they were scintillation photons produced just within the crystal at the face away from the photomultiplier. In examination of both the scintillation and the transmission fluorescence data in connection with Part II of this paper, it has been found that the use of the appropriate transmission factors to correct the primary data increases the consistency of the results. The consistency achieved is about the maximum to be expected in view of the probable errors in the primary data. Thus, while the transmission factors are not known with all the precision and completeness which could be desired, they are definitely useful and do not seem to introduce any significant additional uncertainties.

The corrected average pulse heights $\bar{v}_n/\nu$ have been denoted as "the scintillation efficiencies ϵ." For the liquids or where no corrections are possible, the quantities ϵ and $\bar{v}_n$ are synonymous. The scintillation efficiencies ϵ for the substances of Table I are presented in Table XI and Fig. 24. They will be used extensively in Part II of this paper.

Discussion and criticisms.—The ways in which the scintillation data have been obtained and handled have not been completely ideal:

First, all of the data obtained are "technical" values which may be significant only for macroscopic crystals. They do not necessarily bear any constant relationship to "true molecular values."

Second, while the optical transmission factors can be used to eliminate in part the perturbations due to the differing degrees of crystal perfection, they are not too precisely known.

Third, the temperature variation has not been thoroughly studied. This deficiency is particularly serious, since there is no reason to expect the data obtained at any temperature other than absolute zero to be fundamentally more significant than that obtained at any other temperature, and since rather slight temperature changes will alter the relative response of different phosphors quite markedly.

Fourth, the effects of temperature changes on photomultiplier and phosphor have not been separated. This defect may not be too important, since it has been reported[37] that the photomultiplier gain is not appreciably affected by cooling, at least for the tubes with uv-transparent envelopes.[38] This conclusion is supported by the fact that quite small (negative) values of α have been reliably observed for some of the present cases, but no really reliable positive values; there are theoretical reasons for believing that $-\alpha$ can become very small, but never less than zero.

Fifth, the influence of the variation in the response of the photomultiplier tube with wavelength has not been eliminated from the values presented. This deficiency was originally thought not to be too important, since the C-7140 photomultiplier involved in this work was throught to possess at least approximately the "RCA" sensitivity curve of Fig. 5; most of the experimentally determined spectra have maxima which fall within the 80%-of-maximum-response limits on this curve. However, the curve determined by the National Bureau of Standards for the tube is quite different, although within the manufacturing limits observed by

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[31] Hollander, Perlman, and Seaborg, Revs. Modern Phys. **25**, 469–651 (1953).

[32] F. B. Harrison, Nucleonics **10**, No. 6, 40–45 (1952).

[33] J. B. Birks and M. E. Szendrei, Phys. Rev. **91**, 197 (1953).

[34] D. K. Butt, Proc. Roy. Soc. (London) **A66**, 940 (1953).

[35] J. I. Hopkins, Rev. Sci. Instr. **22**, 29–33 (1951).

[36] Furst, Kallman, and Kramer, Phys. Rev. **89**, 416–417 (1953).

[37] W. H. Jordan and P. R. Bell, Nucleonics **5**, No. 4, 30–41 (1949).

[38] G. G. Kelley and M. Goodrich, Phys. Rev. **77**, 138 (1950).

RCA,[39] and indicates that a serious bias exists against the scintillators with the shorter emission wavelengths. This bias can be approximately eliminated by taking a weighted average wavelength of a fluorescence spectrum to determine an appropriate relative sensitivity factor. The results of such computations are shown in the ϵ_{30}^* column of Table XI. For several reasons, these corrected values have been discarded and the uncorrected values used in the later analysis: First, there exists some doubt as to the proper sensitivity curve to be used in making this correction. While the NBS curve indicates very low uv sensitivity, the information furnished by RCA indicates a high uv transparency for the envelope, which should mean a high uv sensitivity. Second, the corrected values indicate that the simpler compounds—benzene, diphenylmethane, durene, etc.—have scintillation efficiencies that are equal to or greater than corresponding higher homologs, or that they are otherwise out of line. While *a priori* one cannot exclude the possibility that these results are valid, the general picture of the scintillation and fluorescence process in aromatic compounds strongly indicates that they should be regarded with suspicion. Therefore, provisionally at least, the relative spectral response of the photomultiplier will for the most part be disregarded in the sections to follow. In any case, it appears probable that the true relative scintillation efficiencies of the different compounds lie somewhere between the uncorrected (ϵ) and "corrected" (ϵ^*) values.

An exact correction for the relative spectral response of the photomultipler can be calculated as indicated in Sec. I-D in a fairly simple though extremely tedious fashion by making use of the fluorescence spectra and the curves of Fig. 23.

5. *Comparison with the Literature*

Pure organic crystals.—It has often been difficult to reconcile the scintillation response values determined during this work with those reported by other workers for supposedly pure organic crystals. In many cases, this is clearly due to their use of impure materials, or of microcrystalline powders.[40] Differing definitions of scintillation efficiency or the use of different types of photomultipliers have also produced confusion. Then too, efficiency sequences determined with heavy particle excitation[41] may not be the same as those determined with beta or gamma rays. In addition there is good reason to suspect the reliability of the anthracene standards used in much of the work reported in the literature. Often, the readjustment of the anthracene value to 75 or perhaps even lower gives relative figures that agree much better with those reported here.[42] However, differences in order often exist which cannot be eliminated by any readjustment of the response scale.

The paper of Koski and Thomas[43] of all those in the literature most closely parallels this one. It is gratifying that both their experimental data and their theoretical interpretation are in generally good agreement with those presented here. Approximate average pulse-height values calculated from the data of Koski and Thomas are shown in Table VII for comparison with the values determined during this work.

Relatively little information is available concerning the temperature variation of the scintillation efficiency. The following estimates of α values have been made from the available literature data, for comparison with the ones determined here: for anthracene, -0.4,[44,45] -0.25,[46] ~ -0.3;[47] for naphthalene, -0.6,[44,45] -0.8;[46] for stilbene[46] and sodium iodide (Tl),[47] 0.0; and for calcium tungstate, ~ -0.6.[47]

Additional literature data for individual compounds will be discussed in Sec. I-E.

Liquids and plastics.—Table V describes the results obtained with the few liquid compounds and solutions studied. In this table have been included the scintillation efficiencies determined by Kallmann and Furst, multiplied by a factor of 100 to correspond to setting the response of their standard anthracene crystal equal to 100. The "practical" efficiencies[48] have been used rather than the "physical" efficiencies,[49] since the former were determined using reflecting containers more closely approximating those used in this work than the non-reflecting containers used in the latter case. In the final column, the ratios of the efficiencies of Kallmann and Furst to those of the present authors are given.

While there is a strong tendency for ratios in the last column to be larger for the solutions fluorescing at the shorter wavelengths, presumably because of differences in spectral response of the photomultipliers and similar factors, there is still a real discrepancy by a factor of two or more between the two sets of data. This discrepancy can probably be attributed in large part to determinate errors by Kallmann and Furst in referring the response of their solutions to that of anthracene. First, the experimental arrangement used by those authors was such that the solutions and crystals were not tested under completely identical conditions; second, flaws in their massive anthracene crystal would be more important than those in the smaller crystals used in this work; and finally, lack of awareness of the

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[42] Anonymous (R. Hofstadter), Nucleonics **6**, No. 5, 70–73 (1950).

[43] W. S. Koski and C. O. Thomas, J. Chem. Phys. **19**, 1286 (1951).

[44] S. H. Liebson, Nucleonics **10**, No. 7, 41 (1952).

[45] S. H. Liebson and R. T. Farrar, Phys. Rev. **79**, 733 (1950).

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[47] W. L. Minarik and H. G. Drickamer, Rev. Sci. Instr. **22**, 704–5 (1951).

[48] H. Kallmann and M. Furst, Nucleonics **8**, No. 3, 32 (1951).

[49] M. Furst and H. Kallmann, Phys. Rev. **85**, 816 (1952).

aging effect of anthracene crystal surfaces could account for an appreciable part of the discrepancy. The work of Pringle *et al.*[50] also suggests that the values determined by Kallmann and Furst are too high by a factor of two. The data of Reynolds *et al.*[51,52] indicate that simple solutions of terphenyl in such solvents as benzene, toluene, and xylene are slightly less efficient than naphthalene, in good agreement with the present data; this comparison is particularly significant, since wavelength differences should not be important in this case.

Pringle *et al.*[50] demonstrate that solutions with about three times the efficiency of the normal terphenyl solutions can be produced, and quote values of 70% or better for the efficiencies relative to anthracene. Applying their factor of three to the values in Table V for simple terphenyl solutions yields an efficiency for the best liquids of about 30 relative to anthracene = 100. The discrepancy between this value and theirs is probably due to photomultiplier spectral sensitivity effects. It seems probable that the true efficiency relative to anthracene of the best solutions so far tested lies somewhere between 30 and 75.

Some preliminary work with plastics was carried out by Mr. P. J. Drevinsky in this laboratory. The most important conclusion reached was that polyvinylcarbazole plastics, first used by Cassen and Curtis,[53] appear to be superior to polystyrene plastics by a factor of about five, and that they are at least as good as naphthalene. Only phenanthrene and stilbene were tried as solutes. It seems quite probable that further development of this material would be worthwhile. The highest efficiency relative to anthracene reported for a plastic is about 45%.[54–56]

Aging effects.—Scintillator aging effects have been noted by several authors, in organic liquids[57,58] and crystals.[14,59,60] The aging of the liquids is probably closely related to the quenching effect of oxygen in liquid scintillators which has been described by Pringle, *et al.*[50]; the effect is ascribed by the authors to possible photo-oxidation or photodimerization. Birks and Black[59,60] have described the aging of organic crystals under prolonged bombardment by heavy particles; they detected no changes due to electron bombardment.

TABLE VII. Comparison of the data of Koski and Thomas[43] with those of the present authors.

Substance	Scintillation efficiencies Koski and Thomas (approximate)	Sangster and Irvine
Anthracene	100.0	100.0
Biphenyl	5.2	5.0
Diphenylacetylene	68	32
Stilbene	62	46
1,4-Diphenylbutadiene	78	85
1,6-Diphenylhexatriene	2.5	3.2
1,8-Diphenyloctatetraene	1.5	2.3
Bibenzyl	26	7.1

Chynoweth[61] has found evidence for a two-step photo-oxidation process with anthracene crystals. Black[61] noted aging effects due to irradiation with 3650 A ultraviolet light; naphthalene and stilbene recovered on standing, anthracene did not. Rosahl[14] described difficulties due to surface oxidation of organic materials under ultraviolet irradiation, stating that oxidation became serious in a few seconds to a few minutes, depending upon the irradiation intensity and the particle size.

Sodium iodide (Tl).—The generally accepted value for the scintillation efficiency of sodium iodide—see reference 2, p. 52, for example—is about twice that of anthracene. A reasonably careful search of the literature has given the impression that this is an approximate estimate made rather early in the development of the modern scintillation counter, which has been quoted and requoted until it has assumed the status of revealed fact. No reliable experimental data to support this value have been found in the literature. The only such data known to the authors other than their own are those of Hofstadter.[62] The curves presented by Hofstadter indicate an average pulse height of about 160 relative to anthracene = 100. McIntyre and Hofstadter[63] estimate a 6% absolute efficiency, which is quite compatible with this relative efficiency. It seems to the present authors probable that the value 160 is an upper limit on the range of uncertainty in knowledge of the true relative efficiency of sodium iodide (Tl). Their own value, about 110, is quite possibly too low, primarily because no corrections have been made for the smoothness of the quartz window to which the sodium iodide crystal was cemented; undoubtedly a disproportionate amount of radiation was trapped by total internal reflection. Most of the other factors which may account for the discrepancy between these two values have been discussed above in connection with organic crystals. The only new one which may be involved in discussions of data for NaI(Tl) is that due to the significant amount of photoelectric interaction between the cobalt-60 gamma rays and sodium iodide, the average energy dissipated per incident gamma ray is higher for NaI(Tl) than for anthracene; therefore the

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[59] J. B. Birks and F. A. Black, Proc. Phys. Soc. (London) **A64**, 511 (1951).

[60] F. A. Black, Phil. Mag. (Series 7) **44**, 263 (1953).

[61] A. G. Chynoweth, J. Chem. Phys. **22**, 1029 (1954).

[62] R. Hofstadter, Phys. Rev. **75**, 796 (1949).

[63] J. A. McIntyre and R. Hofstadter, Phys. Rev. **78**, 617 (1950).

TABLE VIII. Scintillation decay times.

Substance	Decay constants[a] (in mμsec)					
	MIT[b]	S+B[c]	LBE[d]		Misc.[e]	
	γ	x	uv	γ	γ	uv
Naphthalene	81.0±4.5	~144			68±10[f,g,h]	
Anthracene	30.0±0.7	29.9	17	30	31±2[c,f,h–l]	13.5±0.5[m,n,o]
Anthracene (−196°C)			8	13	10±2[i]	
Phenanthrene	12.1±0.3	7.8	5.2			13.5[o]
Chrysene	40.0±1.7	30.5	22	26		
Pyrene	82.0±3.5	~97				
Perylene			12			
Fluoranthene	43.0±2.0	~46	46			
Fluorene	27.5±1.3	14.9	8.8			15[o]
Carbazole (I)	14.5±0.4					
(II)	17.0*	10.9	7	13		
Diphenylene oxide	15.1±0.6	10.7				
m-Diphenylbenzene	29.0±1.7	9.8(24)				
1,3,5-Triphenylbenzene	32*					
Terphenyl	11.5±0.7	4.5	11	6	4.2	
Quaterphenyl	8.5±0.3	4.2	3.8	7		
2,5-Diphenyloxazole	12.1*	5.7				
2,5-Di-(*p*-biphenylyl)-oxazole	9.8*					
p-Di-(5-phenyl-2-oxazolyl)-benzene	10.8*					
β,β′-Binaphthyl	90*	~29(~74)				
Diphenylacetylene (I)	7.3±0.3	3.5	2.5	4	6.2±0.8(*x*)[c,j]	15[o]
(II)	5.5*					
Stilbene	8.1±0.2	⩽3.0	3.1	8	7.2±0.6[c,f,h–j,l]	6[o]
1,4-Diphenylbutadiene	8.0±0.2	4.1	2	6	4.2[f]	
1,2-Di-(*p*-biphenylyl)-ethylene	11.6*	6.6				
Tetraphenylbutadiene					4.0[c]	
1,2-Di-(α-naphthyl)-ethylene	13.0*	7.6				
1,2-Di-(β-naphthyl)-ethylene	6.2*	4.0				
Bibenzyl		43.5				
Hexamethylbenzene	10.2*	~120				
Sodium iodide (Tl)					250±50[p]	
Calcium tungstate					25 000[q]	
Calcium fluoride					150±10[r]	
Cesium fluoride					5±1[s]	
Liquid solutions					2–4[c,d,t]	5–10[h]
Plastic solutions					2–4[c,u]	

* Precision unknown.

[a] Calculated for the regions, or on the assumption, of exponential decay of the scintillation pulse.

[b] Data obtained by Mr. Howard Kimball and Mr. Jerome Tiemann working with Professor W. L. Kraushaar in this laboratory. Cobalt-60 gamma rays were used to excite the scintillations. All measurements were made at room temperature, as were also all others reported in the table, except for those specifically indicated otherwise.

[c] Data obtained by R. K. Swank and W. L. Buck for samples furnished by the present authors, using a pulsed 7.5 kv x-ray technique. (See reference 70.)

[d] Data obtained by Liebson, Bishop, and Elliot (see reference 71) at the Naval Research Laboratory, using for the first column modulated ultraviolet irradiation and for the second column gamma-ray excitation.

[e] Data due to miscellaneous authors, for gamma-ray excited and uv-excited fluorescence decay times. Where more than one value was available for a given quantity, the average value and its standard deviation have been tabulated. On a few occasions, x-ray values have been included with the gamma-ray data; only in the case of diphenyl-acetylene was it thought necessary to note this specifically.

[f–j] See references 73–77, respectively.

[k] See reference 38.

[l–o] See references 78–81, respectively.

[p] See reference 62.

[q,r] See references 82 and 83, respectively.

[s] See reference 64.

[t,u] See references 84 and 85, respectively.

ratio of the absolute efficiencies of NaI(Tl) and anthracene will be lower than that of the average pulse heights. In conclusion, it seems probable that the true relative average pulse height of NaI(Tl) is about 130±10.

Other inorganics.—Of the other inorganic scintillators which have been reported in the literature, CsF and CsI are perhaps the most interesting. CsF has been reported[64] to give scintillation pulse heights about1/10 those of anthracene with cobalt-60 gammas and a C7140A photomultiplier; the decay time is about 5×10^{-9} second; it has a blue-ultraviolet fluorescence emission. It closely approximates the organic scintillators in three respects: (1) it apparently scintillates in the pure state, (2) the decay time is of the order of allowed atomic transitions, and (3) it has a lower relative efficiency for alpha-particle than for electron-produced pulses.

CsI[65–67] likewise apparently requires no activator. It is reported to possess an absolute energy conversion efficiency for gamma-ray excitation of about 40%, at about 100°K, with a decay time of about 0.5 μsec and a blue emission. While the value 40% is based on other absolute efficiencies that are probably not too well established, so that the true value may be ap-

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[64] W. Van Sciver and R. Hofstadter, Phys. Rev. **87**, 522 (1952).

[65] B. Hahn and J. Rossel, Helv. Phys. Acta **26**, 803–810 (1953).

[66] B. Hahn and J. Rossel, Helv. Phys. Acta **26**, 271–280 (1953).

[67] B. Hahn, Phys. Rev. **91**, 772 (1953).

preciably lower, it still appears probable that the true response would be almost as remarkable. Other advantages are that it is not hygroscopic and that both ionic constituents give strong photoelectric effects with gamma rays. The most important disadvantage is that it gives almost no response at all at room temperature.

Among the other inorganic phosphors, calcium tunstate has been used to some extent, primarily because of its high density (6.06 g/cm^3).[42] It appears to give pulses somewhat smaller than those of anthracene,[42,68,69] perhaps by a factor of as much as three or four.

C. Scintillation Decay Times

The available scintillation and photofluorescence decay time data are summarized in Table VIII. The data in the first column were obtained in this laboratory. The remaining values were compiled from the literature.

The MIT data were obtained using crystals selected from those on which the work of the previous section was based. Only one crystal per compound was tested, and no attempt was made to check impurity or crystal-flaw effects. All of the substances in Table I were checked, but many gave pulses either too small or too long to permit determination of the decay times. Scintillations were excited by cobalt-60 gamma rays, and the resulting charge pulses from a 1P21 photomultiplier were fed directly onto the deflection plates of a high writing-speed oscilloscope. The pulses were scanned at random with about two one-microsecond sweeps per second and were photographed on a continuously moving film. The time scale was established using a 12.5 megacycle crystal oscillator. The pulses were assumed to rise exponentially. In the cases where the standard deviations of the mean have been presented, the times required for twenty-five pulses (a purely arbitrary number) to rise to 63% (i.e., $1-1/e$) of the maximum deflection were measured and averaged to get the rise-time constant, the scintillation decay constant. The only arbitrary element in the selection of pulses was the omission of those near the ends of the sweeps and those difficult to measure because of their small amplitude. The remaining values in the first column of Table VIII were obtained at a later date and are of less certain precision. None of the values have been corrected for the observed millimicrosecond single-electron-pulse rise time or for other possible systematic instrumental errors.

The numbers in the second column of data were determined by Swank and Buck[70] using samples furnished by the present authors. Values determined by these authors using samples from other sources have been included in the data given in the final, miscellaneous column. These decay times were determined (at 25°C) using pulsed x-rays, mostly the 7.5 kv Ni K_α radiation. Unless otherwise noted (by an approximation sign), the determinations are accurate to about $\pm 1\%$. Two components were found for the fluorescent decay of *m*-diphenylbenzene and β,β'-binaphthyl. Swank and Buck suggest that this implies the presence of appreciable impurities in these materials. The present authors tend to agree, particularly since there is additional evidence to support this suspicion in at least the first case (see the discussion in Sec. I-E, below).

The third column of figures in Table VIII contains the results of Liebson, Bishop, and Elliot[71] for the decay times of both ultraviolet and gamma-ray excited fluorescence. The ultraviolet excited decay times were determined from the phase shift between the modulated ultraviolet radiation and the resulting fluorescence. Shorted-line techniques were used for the determination of the gamma-ray excited decay times. Data were also obtained for 80-kv x-ray excitation; they unexpectedly agree well with those found for the ultraviolet excited fluorescence. Ravilious, Farrar, and Liebson[72] have recently redetermined some of the photofluorescence decay data by a fluorescence depolarization method, obtaining results in good agreement with those of the fluorometer method.

In the final, miscellaneous column, other significant decay times determined by various authors[38,62,64,70,71,73–85] have been summarized. Where more than one measurement of a given quantity has been available, the average value and its standard deviation have been presented.

It appears from the data in Table VIII that the fluorescence decay times for 7.5-kv x-ray excitation are in general intermediate between those determined for high energy beta- and gamma-ray excitation and those for uv-excited photofluorescence, sometimes agreeing very well with one limit, sometimes with the other. This is a curious situation which it would be interesting to see rationalized.

Birks and Little[80] have shown that the photofluorescence decay times are functions of the size of the crystals being studied. The existence of a temperature

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[68] R. H. Gillette, Rev. Sci. Instr. **21**, 294–301 (1950).

[69] M. Furst and H. Kallmann, Phys. Rev. **91**, 766 (1953).

[70] R. K. Swank and W. L. Buck, Rev. Sci. Instr. **26**, 15 (1955).

[71] Liebson, Bishop, and Elliot, Phys. Rev. **80**, 907 (1950).

[72] Ravilious, Farrar, and Liebson, J. Opt. Soc. Am. **44**, 238–241 (1954).

[73] A. Lundby, Phys. Rev. **80**, 477 (1950).

[74] G. B. Collins, Phys. Rev. **74**, 1543 (1948).

[75] Bittman, Furst, and Kallmann, Phys. Rev. **87**, 83 (1952).

[76] R. F. Post and N. S. Shiren, Phys. Rev. **78**, 80 (1950).

[77] H. B. Phillips and R. K. Swank, Rev. Sci. Instr. **24**, 611–616 (1953).

[78] G. G. Kelley, Oak Ridge Natl. Lab. Report No. 366 (1949).

[79] Schmillen, Schmillen, and Rohde, Z. Naturforsch. **8A**, 213–14 (1953).

[80] J. B. Birks and W. A. Little, Proc. Phys. Soc. (London) **A66**, 921–928 (1953).

[81] Hanle, Kotschak, and Scharmann, Z. Naturforsch. **6A**, 202–206 (1951).

[82] Gobrecht, Hahn, and Dammann, Z. Physik **132**, 239–247 (1952).

[83] W. J. MacIntyre, Phys. Rev. **75**, 1439 (1949).

[84] R. F. Post, Phys. Rev. **79**, 735 (1950).

[85] W. J. MacIntyre, Phys. Rev. **76**, 312 (1949).

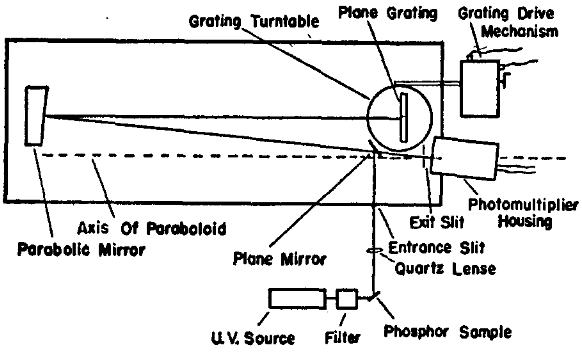

FIG. 16. Automatic-recording fluorescence spectrograph.

dependence for the fluorescence decay times has been established by, among others, Elmore and Hofstadter[86] and Liebson and coworkers.[44,87] Schmillen and coworkers[79,88] have shown that photofluorescence decay times can be quite sensitive to impurities. As one example, the curve displayed for the decay time of the anthracene emission from naphthacene-anthracene mixtures indicates that the anthracene decay time decreases linearly with the logarithm of the mole fraction of naphthacene, over the range from 10^{-7} to 10^{-3} mole fraction, at least.

In addition to the fast fluorescence decay times listed in Table VIII, longer-lived phosphorescent components have been resolved in the decay of the luminescence excited by light, x-rays, γ rays, or β rays in anthracene,[29,89,90] stilbene,[29,89,90] terphenyl,[89] plastics,[89] sodium iodide (Tl),[89,91,92] and other scintillators (see also Table X). Slow decay times up to more than 100 μsec have been measured for anthracene, stilbene, and terphenyl. For sodium iodide (Tl), decay times up to 90 minutes have been measured at room temperature.

TABLE IX. Relative intensities of the spectral lines in the filtered mercury radiation with which the scintillator crystals were excited to obtain the spectra of Figs. 17–21.

Wavelength (A)	Intensity (% of total)
2483	0.12
2537	88.0
2652	1.0
2699	0.02
2753	0.17
2804	0.15
2894	0.52
2967	2.0
3021	1.8
3126	2.5
3132	3.4
3341	0.32
4358	0.0005
5461	0.0017
	100.0

D. Spectroscopic Observations

1. *Fluorescence Spectra*

Fluorescence spectra excited by the ultraviolet irradiation of selected samples of organic scintillators have been determined with the apparatus schematically indicated in Fig. 16. Representative "transmission" and "reflection" fluorescence spectra are presented in Figs. 17–21, for the compounds listed in Table I. With a few exceptions, spectra were obtained for at least two crystals of each substance. Where, due to low melting points or weak fluorescence, no spectra were obtained, only the names and structural formulas are indicated.

Experimental techniques.—The instrument diagrammed in Fig. 16 was designed to be an automatic-recording Raman and fluorescence spectrograph.[93] It operates in the following manner:

> The light emitted by a sample is focused on the entrance slit. The rays diverging from the entrance slit are deflected by a small plane mirror toward an off-axis paraboloidal mirror. The paraboloid reflects the light back toward an echellette plane grating. The beam of defracted light returned by the grating is focused above the deflecting mirror onto the exit slit. The output current from the C-7140A photomultiplier behind the exit slit is amplified and recorded by a modified Brown recorder. Dry-ice cooling is used to reduce the photomultiplier dark current. As the grating drive mechanism causes the spectrograph to scan the appropriate spectral regions, the spectrum is recorded on the recorder chart. The standard scanning speed used in this work was approximately 400 A per minute. The slit widths were 200μ, corresponding to about 3.2 A in the first order. Lines 5 A apart were resolved.
>
> A four-watt Sylvania Type E germicidal lamp was used as the source of mercury radiation to excite the fluorescence. Two centimeters of a cobalt-nickel sulfate solution[94] contained in quartz cells and a one millimeter thick red-purple Corex (Corning No. 9863) glass filter were used to isolate the 2537–3126–3132 A region of the mercury spectrum. The true intensities of the lines in the exciting radiation are given in Table IX. The germicidal lamp gave an output stable for periods of several days of continuous operation.

When the exciting radiation was incident upon the crystal face whose fluorescence was being studied, as in Fig. 16, the *reflection* fluorescence spectrum was obtained. When the face being studied was opposite to that being excited (as with the sample in the figure rotated 90°), the *transmission* fluorescence was recorded. The transmission fluorescence is essentially the reflection fluorescence filtered through the crystal, so that the shorter wavelength peaks are reduced in intensity or missing entirely. Since the scintillation fluorescence excited by gamma rays may originate anywhere within a crystal, of the two ultraviolet-excited fluorescence

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[86] W. C. Elmore and R. Hofstadter, Phys. Rev. **75**, 203 (1949).

[87] Elliot, Liebson, and Ravilious, Phys. Rev. **79**, 393 (1950).

[88] A. Schmillen, Z. Physik **135**, 294–308 (1953).

[89] F. B. Harrison, Nucleonics **12**, No. 3, 24–25 (1954).

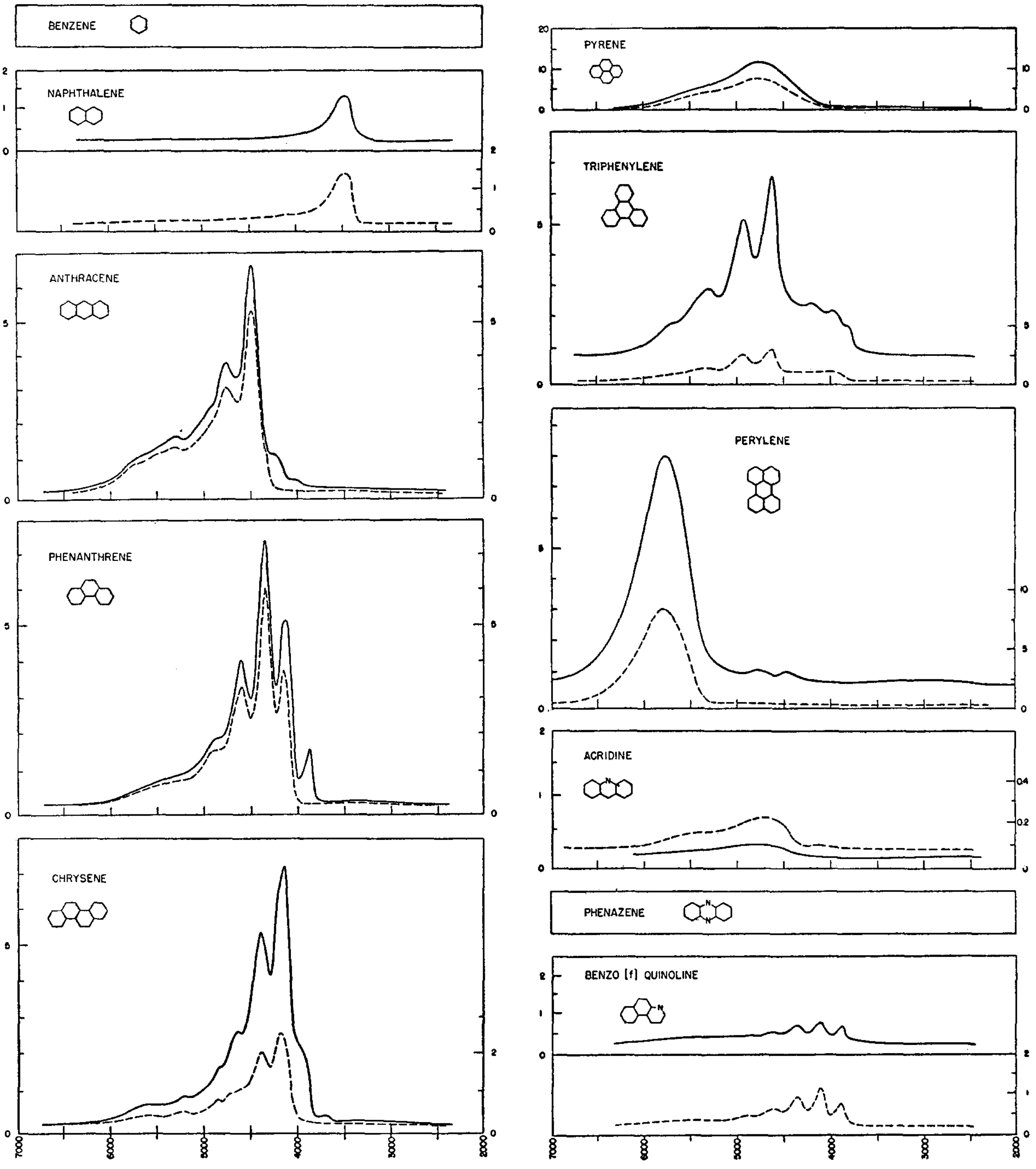
[90] K. P. Meyer and A. Maier, Helv. Phys. Acta **26**, 411 (1953).

[91] C. R. Emigh and L. R. Megill, Phys. Rev. **93**, 1190–1194 (1954).

[92] H. Neuert and T. Retz-Schmidt, Z. Phys. **134**, 165–172 (1953).

[93] Harrison, Lord, and Loofbourow, *Practical Spectroscopy* (Prentice-Hall, Inc., New York, 1948), pp. 515–517.

[94] M. Kasba, J. Opt. Soc. Am. **38**, 929–934 (1948).

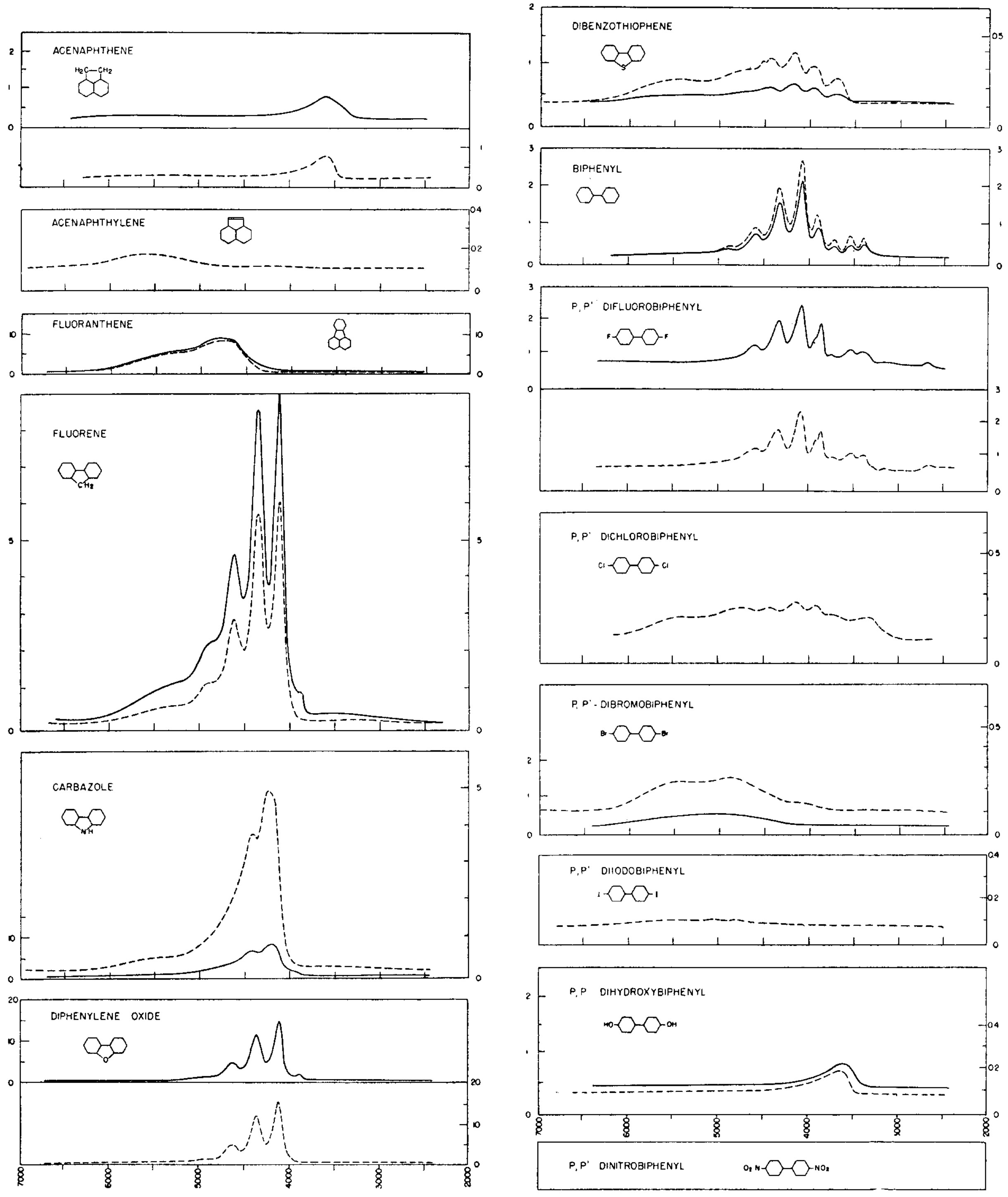


(a) (b)

FIG. 17. Fluorescence spectra of crystalline organic scintillators, I. All spectra were excited by ultraviolet radiation (see Table IX). For the solid curves, the "reflection" spectra, the fluorescent radiation studied was that emitted by the faces of the crystals directly excited; the relative intensities are given by the left-hand scales. The dashed curves or "transmission" spectra were obtained by studying the radiation emitted by the faces opposite to those directly excited; the right-hand scales give the relative intensities in these cases. The scales on the horizontal axes give the wavelengths in Angstrom units. The name and structural formula are indicated for each of the compounds studied. Where no spectrum was obtained due to a low melting point or very weak fluorescence, only the name and formula are given.

spectra the transmission spectrum should most nearly resemble the scintillation fluorescence.

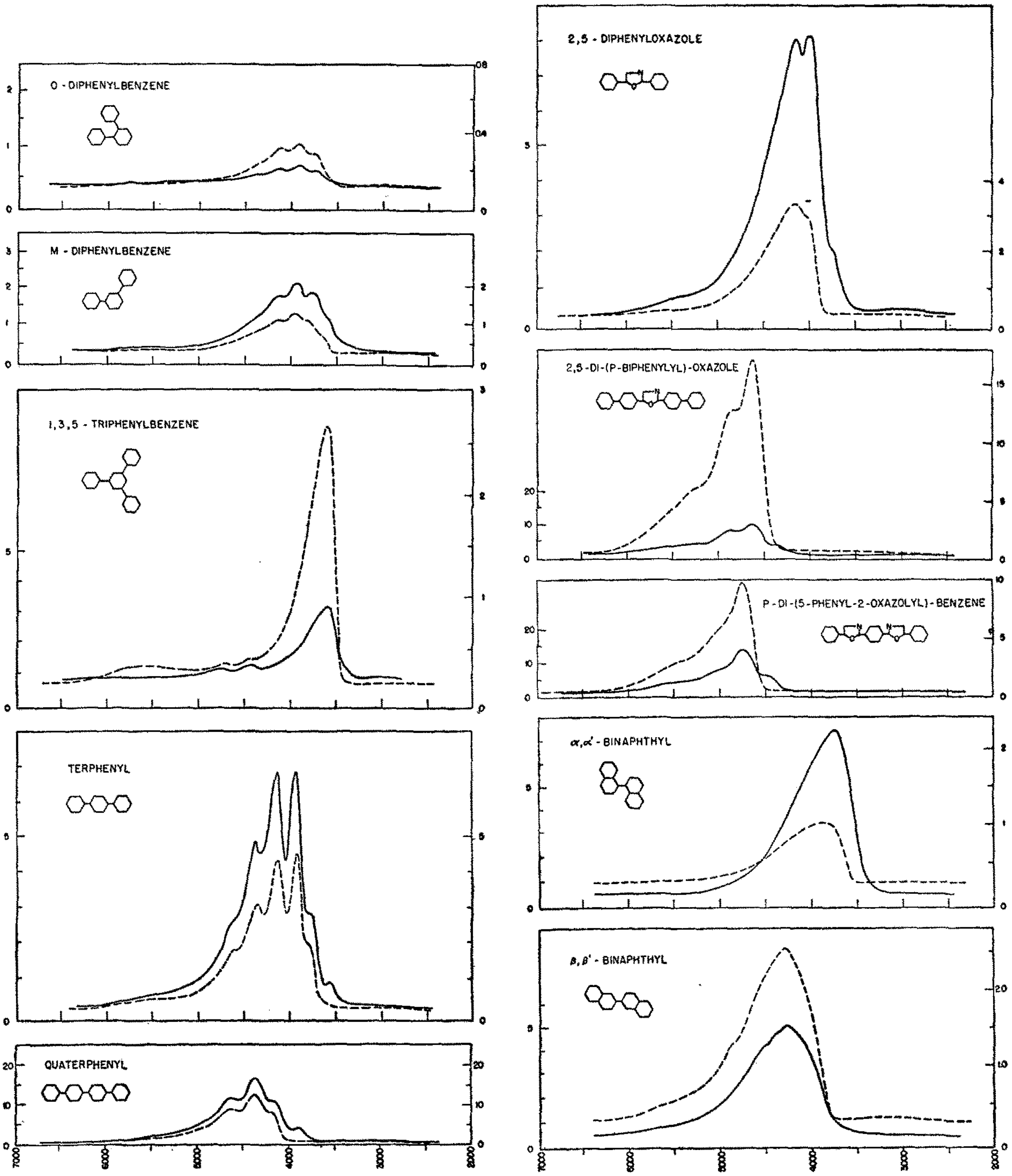
The originals of the curves presented in Figs. 17–21 were traced directly from curves on the recorder charts. The scattered radiation background level has not been subtracted. The apparatus was arranged so that at least some of the mercury emission lines were recorded with the fluorescence spectra, and these lines were used to



(a) (b)

FIG. 18. Fluorescence spectra of crystalline organic scintillators, II.

establish the wavelength scale, which is linear and accurate to ±5 A. The intensity units are, very approximately, millimicroamperes of photomultiplier current, and are quantum intensities rather than energy intensities. By the use of standard samples, all intensity scales have been corrected as far as possible for the time variation in the response of the spectrograph and for the differences in size and position of the samples studied. The basic correlation of the transmission and fluorescence intensities was effected by mounting



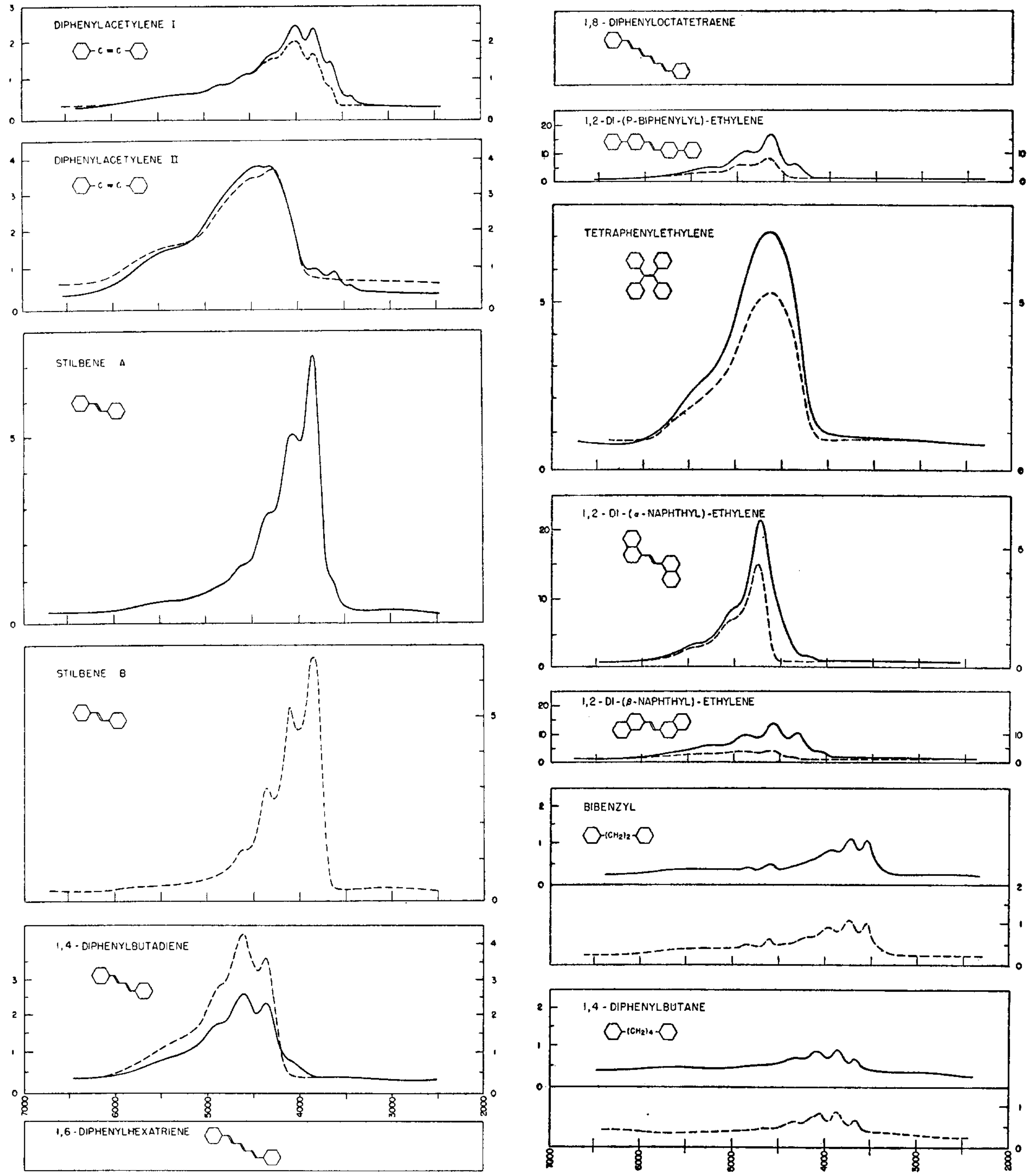
(a)

(b)

FIG. 19. Fluorescence spectra of crystalline organic scintillators, III.

crystals in as nearly equivalent optical positions as possible for both cases. The intensity scales are significant only to ±10–20% in going from one curve to another. In a given spectrum, the intensity scale varies (decreases) by no more than 5% as the wavelength increases by 1000 A.

Correction curves.—The spectrograph response curve (Fig. 22) was determined from recordings of the spectra of light sources having known absolute spectral energy distributions. For most of the range covered, ordinary tungsten filament bulbs were used. An Eastman color-temperature meter and Variac control of the filament voltages were used to set the color-temperatures of the filaments at predetermined values. The true absolute



(a) (b)

FIG. 20. Fluorescence spectra of crystalline organic scintillators, IV.

spectral distributions were obtained by combining the values for the emissivity of tungsten at different wavelengths with the intensities of the blackbody radiation corresponding to the selected temperatures.[95] Most of Fig. 22 was derived from the results from a total of six runs with three different tungsten lamps. Below 3000 A the continuous spectrum from a Beckman hydrogen-discharge lamp, calibrated by the National Bureau of Standards, was used to determine the response curve. An overlap region from 3000 A to 3600 A permitted the joining of the two portions of the curve.

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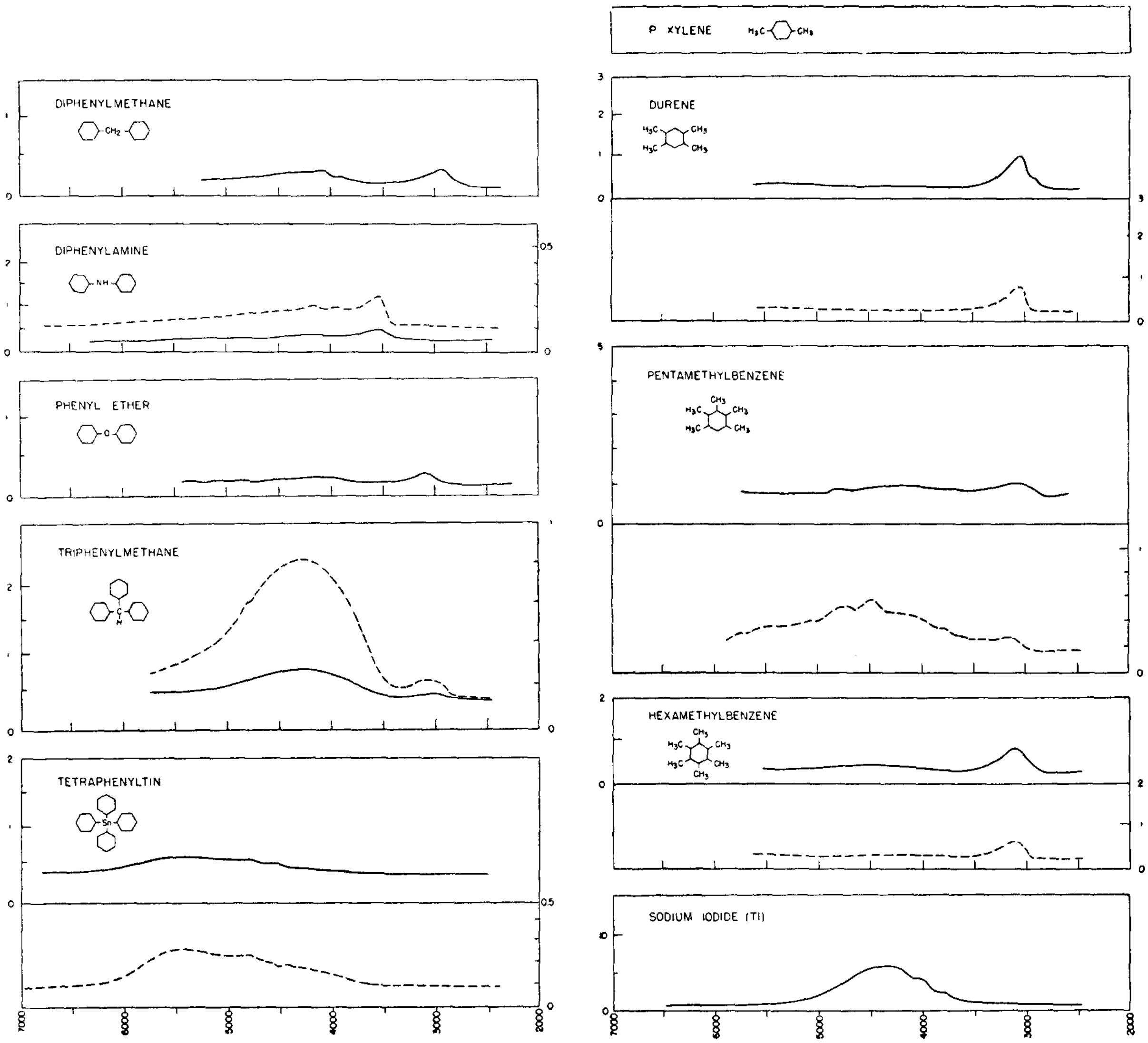
[95] P. H. Moon, *The Scientific Basis of Illuminating Engineering* (McGraw-Hill Book Company, Inc., New York, 1936), p. 123 and App. C.



(a) (b)

FIG. 21. Fluorescence spectra of crystalline organic scintillators, V.

The standard deviation of the curve at any point is about ±0.3% of the maximum deflection (0.003 scale unit).

The recorded spectral intensities can readily be converted into true relative intensities by use of the curves of Fig. 23. Multiplying by the appropriate values from the $1/S$ curve, which is the reciprocal of the spectrograph resonse curve, will yield the relative energy intensities. The values from the $(\lambda/\lambda_0)(1/S)$ curves give the relative quantum intensities. The integrated energy intensity of a spectrum can be found by multiplying the spectrum by the $1/S$ curve and integrating. The integrated quantum intensity can be found in a similar manner by using the $(\lambda/\lambda_0)(1/S)$ curves. The portion of this quantum intensity that will affect the photomultiplier whose response curve is given in Fig. 5 is given by multiplying the empirical spectrum by the P/S curve and integrating. The fraction that is effective then is

$$k\int_\lambda (sp)(P/S)d\lambda \Big/ \int_\lambda (sp)(\lambda/\lambda_0)(1/S)d\lambda,$$

where (sp) is the empirical spectral intensity and k is a normalization constant. Thus, to the extent that the transmission fluorescence spectra of Figs. 17–21 coincide with the scintillation fluorescence spectra, all of the scintillation pulse-height intensity data could be put on an absolute basis relative to a given compound.

Comparison with literature.—A fair amount of work has been done on the fluorescence spectra of organic scintillators excited by high energy radiation. In particular Roth[96] has shown that copper K_α x-rays, radium-beryllium neutrons, and 10-Mev deuterons

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[96] L. Roth, Phys. Rev. 75, 983 (1949).

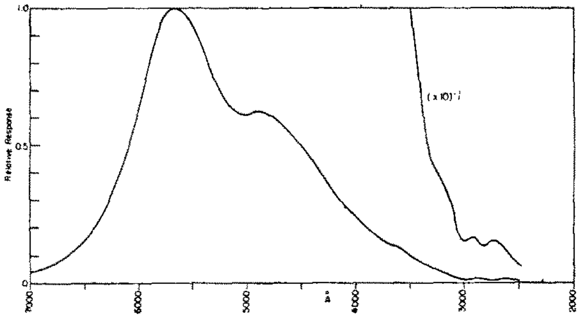

FIG. 22. Spectrograph response curve, showing the relative response of the spectrograph of Fig. 16 to equal amounts of radiant energy incident at different wavelengths.

give the same anthracene spectra (bands at 4240, 4440, and 4700 A) and that the bands found are responsible for the scintillation properties. Koski[97] has reported fluorescence spectra excited by copper x-rays for anthracene and stilbene. The band positions—4475 and 4740 A for anthracene, 3830 and 4035 A for stilbene—and the general appearance of the spectra check well with those reported here. The work of Koski and Thomas[98] on the fluorescence of bibenzyl, stilbene, diphenylacetylene, and diphenylbutadiene excited by α, γ, or x-rays likewise gave the same spectra for each mode of excitation; the band positions and intensities agree fairly well with those reported in Figs. 17–21. The agreement found with the spectra reported in a later paper[43] for copper x-ray excitation of diphenyl, stilbene, diphenylbutadiene, diphenylhexatriene, diphenyloctatetraene, bibenzyl, and diphenylacetylene ranges from good for bibenzyl to very poor for biphenyl. Other workers[99–102] have reported spectra excited by high-energy radiation for naphthalene, anthracene, phenanthrene, terphenyl, stilbene, and NaI(Tl), giving band positions in from fair to good agreement with those reported here for ultraviolet excitation.

While most of the papers referred to above seem to indicate that essentially the same fluorescence spectra are obtained regardless of the nature of the excitation, the work of Bose *et al.*[103] on the luminescence of some organic phosphors under excitation by copper x-rays and 2–5 kev cathode rays demonstrates that the luminescence spectra are not always or necessarily independent of the nature of the excitation. In general, a larger number of bands are emitted for x-ray or cathode-ray excitation than for uv excitation. Except for napthalene, the x-rays and cathode rays yielded the same spectrum. All three modes of excitation yielded the same spectrum for anthracene, a spectrum in good agreement with those observed by the present authors and others referred to above. Phenanthrene likewise has the same spectrum for all three modes of excitation, one which agrees fairly well with that of Fig. 17. Phenanthrene showed a long period afterglow. Biphenyl gives more bands with excitation by x-rays and cathode rays than for uv-excitation; Bose *et al.* surmise that the additional emission bands are due to some changes induced in the crystal by the method of excitation; however, at least some of the bands missing from their uv-excited spectrum can be seen in the uv-excited spectrum of Fig. 18. For triphenylmethane, approximately the same spectrum is observed in all three cases, except that there is more band structure for the high energy bombardment, and at 90°K a group of bands, apparently due to a long period phosphorescence (~3 sec decay time), appear between 5170 A and 6310 A. The bands in Fig. 21 at about 3000 A are not detected at all.

2. *Slow Fluorescence or Phosphorescence*

Slow fluorescence or phosphorescence has been observed visually for many of the compounds studied. References to published descriptions of similar phenomena have been given during the discussions of the decay times and the fluorescence spectra, and can be found in abundance in such compendia as Pringsheim's book,[11] The results of these observations are given in Table X. The experimental technique was very crude, consisting of holding a sample in a beam of ultraviolet radiation for a few seconds before removing it to inspect it visually for phosphorescent afterglow. The colors and

TABLE X. Visual observations on phosphorescence or slow fluorescence of scintillator crystals excited by ultraviolet radiation.

Substance	Strength of afterglow	Color	Approximate decay time (sec)
Triphenylene		Yellow	1
Benzo[f]quinoline	weak		2
Fluorene		Greenish-yellow	1
Carbazole	strong	Yellow	2
Diphenylene oxide		Yellowish-white	1.5
Dibenzothiophene		Yellow	0.5
Biphenyl	weak		0.3
p,p'-Difluorobiphenyl	very weak		slow
p,p'-Dichlorobiphenyl	weak		0.5
m-Diphenylbenzene	weak		0.5
1,4-Diphenylbutadiene	weak		4
Bibenzyl	strong	Green	2
1,4-Diphenylbutane	strong	Green	4
Diphenylamine	weak		0.5
Tetraphenyltin		Greenish-white	1.5
Durene		Dirty green	1
Pentamethylbenzene		Greenish-white	1
Hexamethylbenzene	strong	Yellowish	1

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[97] W. S. Koski, Phys. Rev. **82**, 230 (1951).

[98] W. S. Koski and C. O. Thomas, Phys. Rev. **79**, 217 (A) (1950).

[99] J. C. D. Milton and R. Hofstadter, Phys. Rev. **75**, 1289 (A) (1949).

[100] F. B. Harrison and G. T. Reynolds, Phys. Rev. **79**, 732 (1950).

[101] H. O. Albrecht and C. E. Mandeville, Rev. Sci. Instr. **22**, 855–856 (1951).

[102] K. Hengst, Z. Naturforsch. **6A**, 540 (1951).

[103] Bose, Sharma, and Chatterjee, Proc. Natl. Inst. Sci. India **18**, 389–398 (1952).

decay times were estimated roughly from these observations. All of the highly purified materials included in Table I (except the higher di-aryl-ethylenes) were inspected in this manner.

E. Preparation and Other Data on Individual Substances

In the paragraphs which follow, information is given on the sources, methods of preparation, purity, and other properties of the materials referred to in Tables I and IV. The best general reference for many of these compounds is Clar, *Aromatische Kohlenwasserstoffe*,[104] for both practical and theoretical principles and details.

The first item in each case is the source of the raw material. This is followed by a condensed description of the purification procedure: Each unit step in the procedure is enclosed within parentheses. An exponent denotes the number of successive times the step was carried out. The name of a solvent, or a mixture of solvents, inside the parentheses denotes recrystallization from that solvent or mixture. The name of an adsorbent or of a combination of adsorbents (e.g., silica-alumina) followed by a solvent denotes adsorption purification on that adsorbent from a solution in that solvent. The inclusion of temperature or other data provides information about the conditions of the recrystallization or adsorption processes in the abnormal cases. Other self-explanatory purification steps are listed for particular cases. See Sec. I-A for a general description of the purification procedures.

Following the description of the purification of the materials is information about their purity. The experimental melting points are presented, followed by literature values in parentheses. In the cases in which melting ranges are given, the data were obtained using a copper-block apparatus. In the other cases, an oil bath was used. Next comes a description of the scintillation response of the top sample(s) from the crystallized melts, the samples in which impurity effects are normally most pronounced. Then the quality and nature of the crystalline samples is described. Finally, miscellaneous observations, literature data, and discussions are presented.

Benzene.—Mallinckrodt, analytical reagent. (Alumina, pure liquid, 1st portion discarded.) (5.5)[105] Crystals grown by lowering sample tube into ice bath, milky with small bubbles.

Naphthalene.—Baker, cp, recrystallized from alcohol. (Alumina, pentane)^2. 79.6–81.2 (80.0).[106] Top samples normal. Crystals were colorless and clear except for traces of small bubbles.

Anthracene.—See Table III and previous discussions. Spectra of twenty or more different anthracene samples were obtained. Qualitatively there were all identical with those of Fig. 17. Quantitatively, there was an extreme variation in the absolute intensities, which was probably due to the surface aging effects previously discussed. There was a slight tendency toward more intense tails with the less pure samples; otherwise, the shapes of the spectra were constant within experimental error, and the positions of the maxima coincided to within ±5 A. For information on dianthracene, see the papers by Bradley and Marsh,[107] Orndorff and Cameron,[108] and Nechaeva, Faidysh, and Kharitonova.[109]

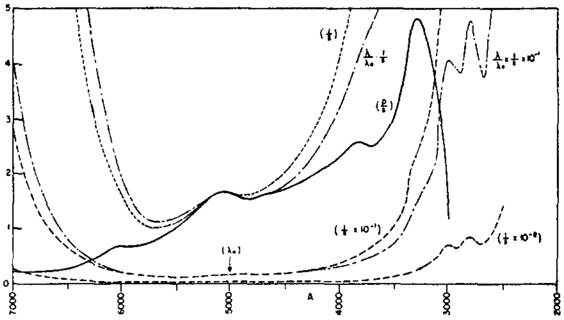

FIG. 23. Correction curves. The $1/S$ curves are reciprocals of the spectrograph response curve. True plots of energy intensity *versus* wavelength are obtained by multiplying the experimental spectra by these curves. The $(\lambda/\lambda_0)(1/S)$ curves applied in a similar fashion will yield plots of quantum intensity *versus* wavelength. The P/S curve is a plot of the ratio of the photomultiplier (NBS) and spectrograph response curves of Figs. 5 and 22.

Phenanthrene.—Gesellschaft für Teerverwertung m.b.h. Duisberg Meidrich (1932), "rein." (Alumina, hexane), (alumina, pentane). 97.8–99.5 (100.3).[106] Top crystals slightly below average. Crystal habits apparently unfavorable, crystals translucent.

The purity of this material was determined by the Bureau of Mines Laboratory at Bruceton, Pennsylvania, as not greater than 97.7 mole percent.[110] Anthracene and fluorene were stated to be the probable impurities. From the fluorescence spectra and knowledge of the purification techniques, it seems very improbable that anthracene is present. Fluorene could well be present. Fortunately, fluorene is similar to phenanthrene in fluorescence and scintillation properties, so that aside from causing the crystalline samples to be of poor quality, it probably has relatively little perturbing effect.

Pringsheim (see reference 11, pp. 399, 409, 412) states that phenanthrene, biphenyl, and fluorene fluoresce exclusively in the ultraviolet, and ascribes the blue fluorescence usually observed to impurities. It is not clear whether he is talking of solution or of crystal fluorescence. Along this same line, recent work by Pesteil and Pesteil[111] indicates that the true ultraviolet-excited fluorescence spectrum of crystalline fluorene at 20°C lies between 3235 and 3750 A. These statements throw doubt on the work reported here. On the other hand, photofluorescence spectra are described in some other recent work[112] which agree quite well with the spectra presented here for phenanthrene and chrysene (although not quite so well for pyrene and anthracene). The similarity of the spectra found here for biphenyl, *p,p′*-difluorobiphenyl, *p,p′*-dichloribiphenyl, phenanthrene, chrysene, benzo[f]quinoline, fluorene, diphenylene oxide, and dibenzothiophene (see Figs. 17–21) seems to indicate either a basic similarity in the fluorescence energy level structures or a common fluorescing impurity. It is somewhat difficult to see anthracene as this impurity, as is usually stated to be the case (see reference 11). The positions of the anthracene maxima do not agree well with those observed for the other substances, being considerably further toward the red. Any common impurity, in the nine different substances, of different properties and different origins, all highly purified, seems improbable. The only possible source would seem to be the dust in the laboratory air.

Chrysene.—Reilly[113] highly purified. (Silica, pentane.) 254.8–256.9 (252).[106] Top sample better than average. Samples fairly translucent, but far from clear, crystal habits apparently unfavorable. Chrysene has been variously reported as about equal

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[104] E. Clar, *Aromatische Kohlenwasserstoffe* (Springer-Verlag, Berlin, 1952), second edition.

[105] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, 1944), twenty-eighth edition.

[106] G. Egloff, *Physical Constants of Hydrocarbons* (Reinhold Publishing Comporation, New York, 1939), Volumes III and IV.

[107] G. Bradley and J. K. Marsh, J. Chem. Soc. 650–652 (1933).

[108] W. R. Orndorff and F. K. Cameron, Am. Chem. J. **17**, 658–681 (1895).

[109] Nechaeva, Faidysh, and Kharitonova, Zhur. Eksptl. i Teort. Fiz. **22**, 380–381 (1952).

[110] Dr. Milton Orchin (private communication).

[111] P. Pesteil and L. Pesteil, Compt. rend. **238**, 75–77 (1954).

[112] S. C. Ganguly and N. K. Choudhury, Z. Physik **135**, 255–259 (1953).

[113] By courtesy of Dr. F. E. Cislak, Reilly Tar and Chemical Corporation.

to anthracene,[114] and to have a beta response approximately 60% of that of anthracene.[42] The analyses of Part II (see Sec. II-C-13) suggest that even the corrected scintillation efficiency ϵ for chrysene is less than the true value, which appears to be about 65. The purity of the samples is thought to have been adequate; the poor crystal quality is the most likely cause for the low results.

Pyrene.—Reilly, technical. (Silica, pentane)^2, (ethyl acetate)^2, (silica, pentane), yielding beautiful white crystals. (Recrystallization, codistillation with ethylene glycol, and repeated adsorption on alumina yielded beautiful yellow crystals. Only adsorption on silica would remove the yellow color.) 153.2–155.2 (149.5).[106] Top sample 6% low. Crystals shattered badly while annealing and were therefore not removed from the glass sample-tube rings. The value reported by Hofstadter for an impure crystal[42] is in fair agreement with the value found during this work for similar impure crystals.

Triphenylene.—Organic Specialties. (Silica-alumina, pentane)^3. 199.0–202.4 (196.5).[106] Top samples normal. Good crystals.

Perylene.—Organic Specialties. (Alumina, pentane; first fraction discarded), (alumina, benzene, nitrogen). 268.5 (273–4).[104] Response of top sample very low. Crystals clear, yellow, good quality, but brittle and hard to mount. There seemed to be some evidence of aging. This was the only material observed which showed a strong yellow fluorescence.

Acridine.—Eastman. (Dissolved in H_2SO_4, filtered), (precipitated as dichromate[115]), (washed, regenerated with ammonia), (recrystallized as chloride from dilute HCl)^2, (regenerated with ammonia, dried), (silica-alumina, pentane). 111.0–113.6 (108).[116] Top samples average. Crystals large, clear, slightly yellowish with what appears to be an intrinsic color. Material photodimerizes.[108,115]

Phenazine.—Synthesized from 2-nitrodiphenylamine by method of Watermann and Vivian.[117] (Silica-alumina, pentane), (dissolved[118] conc H_2SO_4, filtered, and precipitated by dilution with water), (chloride formed and recrystallized from hot, dilute HCl), (regenerated with ammonia, dried), (silica-alumina, pentane). 176.2–179.9 (171).[116] Crystals bright, clear yellow; fair quality. The fluorescence and scintillation properties are practically undetectable.

Benzo[f]quinoline.—Eastman. (Ethyl acetate), (chloride generated and extracted with benzene), (regenerated with ammonia), (ethyl acetate, −70°), (hexane, −70°), (silica-alumina, pentane). 91.6 (93).[105] Top samples normal. Crystals soft and translucent.

Acenaphthene.—Eastman. (Ethyl acetate)^4, (silica-alumina, pentane)^2. 92.5–95.2 (95.4).[106] The crystals were clear and of good quality. A regular progression in the average pulse-height values from the top to the bottom of the melt was found: 5.1, 6.4, 7.3, 9.0. A similar progression in the fluorescence spectra exists. Both phenomena can be attributed to impurity quenching. The fluorescence spectra presented agree well with those reported recently,[119] if it is assumed that the lower wavelength bands reported there are reabsorbed in the crystal here, either by acenaphthene molecules or by impurities.

Acenaphthylene.—Monomer-Polymer, Inc. (Silica-alumina, pentane). 90.8–93.2 (93).[106] Clear, bright yellow crystals, with little fluorescence or scintillation response.

Fluoranthene.—Reilly, technical. (Silica, pentane), (ethyl acetate)^3, (benzene), (hexane), (silica-alumina, pentane), yielding Fluoranthene I. 111.0–113.8 (110).[106]

Fluoranthene I. (Codistillation with ethylene glycol[120,121])^2, (wash with water), (acetone), (alumina, pentane), yielding Fluoranthene III. 110.9–113.2 (110).[106]

Residue from preparation of Fluoranthene III. (Codistillation with ethylene glycol), (water wash), (acetone), (alumina, pentane), yielding Fluoranthene II. 110.8–113.6 (110).[106]

For all three materials, the crystals were of only fair quality, rather badly cracked and flawed, but cohesive. They were not removed from their glass rings. The material apparently has an inherently greenish-yellow color.

Fluorene.—Eastman. (Ethyl acetate)^2, (silica-alumina, pentane)^2. 115.0–117.5 (114).[106] Top samples normal. Crystals clear, fairly good quality.

Carbazole.—Reilly, synthetic technical. (Ethyl acetate)^2, (benzene), (hexane), (ethyl acetate), (silica-alumina, benzene), (alumina, benzene), yielding Carbazole I. 246.2–249 (244.8).[116] Top crystal discolored, fluorescence spectra distorted toward red, scintillation response about 75% of average.

Carbazole I. (Silica-alumina, decalin, 180°, nitrogen), (alumina, benzene, nitrogen), yielding Carbazole II. 247.6 (244.8).[116] Top sample less than 10% low, only slightly discolored. Crystals tough, fairly good quality.

The fluorescence spectra of Carbazole I appeared, relative to those of fluorene, to be distorted toward the red, indicating the presence of impurities. This was particularly true for the discolored top sample of Carbazole I. In contrast, the spectra of Carbazole II appear to be compressed toward shorter wavelengths. The positions of the first true maxima are about the same. It appears that the fluorescence of carbazole is significantly different from that of fluorene, biphenyl, etc. (see discussion under *Phenanthrene* above). This may be due to the asymmetry introduced by the lone hydrogen atom in the NH group, or may be a spurious effect due to impurities either here or in the other substances.

Diphenylene Oxide.—Eastman. (Ethyl acetate)^3, (hexane), (silica-alumina, pentane). 82.0–83.9 (87).[116] Top samples normal. Crystals very clear.

Dibenzothiophene.—Eastman. (Ethyl acetate)^3, (hexane), (silica-alumina, pentane). 98.8–101.2 (97).[122] Top sample normal. Crystals very clear.

Biphenyl.—Eastman. (Alumina, hexane), (alumina, pentane). 68.8–70.0 (70.0).[106] Top sample slightly low. Crystals clear and nearly flawless.

p,p′-Difluorobiphenyl.—Eastman. (Ethyl acetate, −70°), (trichloroethylene, −70°), (pentane, −70°), (silica-alumina, pentane). 89.9 (94–5).[123] Top sample normal. Crystal quality very good.

p,p′-Dichlorobiphenyl.—Solvay Process Division, Allied Chemical and Dye Corporation.[124] (Ethyl acetate), (alumina, pentane). 149.3 (148–9).[105] Top sample 20% low. Crystals clear and colorless, but cracked somewhat in cooling.

p,p′-Dibromobiphenyl.—Eastman. (Ethyl acetate)^2, (carbon tetrachloride), (toluene), (silica-alumina, pentane). 169 (164).[105] Top samples normal. Crystals cracked badly during cooling.

p,p′-Diiodobiphenyl.—Synthesized via diazotization of benzidine. (Ethyl acetate)^2, (trichloroethylene), (toluene-benzene), (silica-alumina, pentane). 208 (202).[125] Top sample 20% low. Crystals of fairly good quality, pale greenish yellow.

p,p′-Dihydroxybiphenyl.—Eastman. (Ethyl alcohol, −70°)^2, (silica-alumina, pentane+25% ethyl ether). 272.6 (274–5).[105] Top sample normal. Crystals clear, but very hard, brittle, and difficult to mount.

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[114] Schillinger, Waldman, and Miller, Phys. Rev. **75**, 900 (1949).

[115] *Thorpe's Dictionary of Applied Chemistry* (Longmans, Green, and Company, London, 1939), fourth edition, Vol. I, p. 126.

[116] *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1926), Vol. I.

[117] H. C. Watermann and D. L. Vivian, J. Org. Chem. **14**, 289–297 (1949).

[118] Beilstein, *Handbuch der organischen Chemie* (Julius Springer, Berlin, 1936), fourth edition, Vol. XXIII, p. 223.

[119] P. Pesteil, Compt. rend. **237**, 235–237 (1953).

[120] L. F. Fieser, *Experiments in Organic Chemistry* (D. C. Heath and Company, Boston, 1941), second edition, p. 345.

[121] Harding, Flowers, and Eppstein, Nature **163**, 990 (1949).

[122] Beilstein, reference 118, Vol. XVII, p. 72.

[123] I. Heilbron, *Dictionary of Organic Compounds* (Oxford University Press, New York, 1953).

[124] Gift of H. W. McNulty, Allied Chemical and Dye Corporation.

[125] Beilstein, reference 118, Vol. V, p. 581.

p,p′-Dinitrobiphenyl.—Eastman. (Ethyl acetate), (toluene), (alumina, benzene). 241 (237–43).[105] Good crystals, yellow, tough. No fluorescence or scintillation properties observable at all.

o-Diphenylbenzene.—Eastman. (Alumina, pentane), yielding preparation I. 56.0–57.4 (57).[106] Top sample normal. Crystals heavily flawed.

Eastman. (Ethyl acetate)^2, (hexane)^2, (alumina, pentane), yielding preparation II. 55.5–57.4 (57).[106] Top normal, crystals translucent.

Preparation II was selected in preference to I, primarily because of the greater care taken in the purification.

m-Diphenylbenzene.—Eastman. (Alumina, pentane), yielding preparation I. 84.9–139 (87).[106] (With sixteen to twenty minutes of heating, melting was rapid for the first few degrees, then very slow.) A violet-fluorescing impurity was observed to precede the *m*-diphenylbenzene down the column and was discarded insofar as possible. A darker-blue-fluorescing impurity was held up in the column. The crystals were of low translucence and low quality. The spectral data imply that terphenyl (*p*-diphenylbenzene) is the principal impurity. *o*-Diphenylbenzene is also possible.

Eastman. (Ethyl acetate)^4, (silica-alumina, pentane), yielding preparation II. 85.2–90.2 (87),[106] with a small amount of material still undissolved at the upper temperature limit. There was a possibility of contamination by terphenyl due to overly prolonged running of the column. Top samples 90% of average. Transluscence and quality of crystals fair, much better than for preparation I.

The melting point and spectral data imply that preparation II was much purer than I. However, observations made during purification and the melting point determinations indicate a residual contamination with terphenyl. This is consistent with the poor crystal quality, the wide melting range, the two component fluorescence decay curve (see Sec. I–C), and the scintillation pulse-height data (see the discussions which follow in Part II).

1,3,5-Triphenylbenzene.—Jasonols Chemical Company (gift). (Silica-alumina, pentane), (ethyl acetate)^3, (silica-alumina, pentane). 174.8–179.1 (174).[106] Top sample normal. Crystals clear, of very good quality.

Terphenyl (p-diphenylbenzene).—Eastman. (Alumina, pentane), yielding preparation I. 212.6–216.0 (210).[106] Top sample 10% low. Crystals clear, very high quality.

Terphenyl I (Silica, pentane), yielding Terphenyl II. 213.6–216.2 (210).[106] Top sample 17% low. Crystals clear, very high quality.

Terphenyl III was a sample of Terphenyl II which was grown in an air atmosphere. The top of the melt was discolored and 35% low in scintillation response, but otherwise the samples were about the same as those of Terphenyl II in both scintillation response and fluorescence spectra.

A considerable amount of variation in the relative intensities of the different bands were observed for the several terphenyl spectra run. The spectra presented in Fig. 19 were more or less arbitrarily chosen.

Quaterphenyl.—Synthesized from *p*-dibromobiphenyl by the method of Bowden[126] in 35% yield. (CuCl in reaction mixture leached out with conc. HCl and water), (wash with ethyl alcohol and ether), (benzene)^2, (silica-alumina, benzene), (aniline)^2, (wash with benzene), (wash with pentane), yielding fine, yellow crystals; (silica-alumina, decalin, 180°), yielding white product; (wash with benzene), (benzene)^2, (wash with benzene and ether), yielding a white material that gave a melt seriously discolored for most of its length. The sequence of average pulse heights from top to bottom was 66, 68, 81.5, 84.1. M.p., 315.0–318.1 (318).[106]

Product and melt from above. (Dichlorobenzene)^2, (benzene), (silica-alumina, purified decalin, 180°), (benzene). M.p. 308.4 (318).[106] Discoloration of frozen melt negligible. Top sample 20% low. The crystals are clear but of only fair quality as a result of cracks forming during the cooling process; they are very tough and rugged.

The average pulse height found for quaterphenyl is consistent with and higher than a previously reported value.[42]

Quarterphenyl has a number of advantages as a crystalline organic scintillator: a high melting point, high chemical and thermal stability, low vapor pressure, the formation of tough, clear crystals, a short decay time, a fluorescence spectrum matching the photomultiplier sensitivity curves well, a very low scintillation temperature coefficient, and a high scintillation efficiency. The microcrystalline material is now available commercially, reportedly in high purity.

2,5-Diphenyloxazole.—Gift of F. N. Hayes, Los Alamos Scientific Laboratory.[127–129] (Preparation I). M.p. 71–72.[130] Preparation II was prepared from Hayes' material. (Silica-alumina, pentane). 71.8 (71–72),[130] (74).[123] Top samples normal. Crystals milky, translucent, tough.

2,5-Di-(p-biphenylyl)-oxazole.—Gift of F. N. Hayes, Los Alamos Scientific Laboratory. (Silica-alumina, benzene). 240.3 (232–33).[130] Top sample normal. Crystal quality fairly good.

p-Di-(5-phenyl-2-oxazolyl)-benzene.—Gift of F. N. Hayes, Los Alamos Scientific Laboratory. (Silica-alumina, benzene). 245.4 (237–238).[130] Top sample normal. Crystal quality fairly good.

α,α′-Binaphthyl.—Organic Specialties. (Silica-alumina, pentane)^2, yielding preparation I. 147.1–149.5 (157),[106] (160.5).[105] Top samples normal. Crystals poor.

Preparation I. (Ethyl acetate, −70°)^2, (toluene, −70°)^2, (ethyl acetate, −70°), (alumina, pentane), yielding preparation II. 160.6 (157),[106] (160.5).[105] Top sample 15% low. Crystal quality poor.

β,β′-Binaphthyl.—Organic Specialties. (Silica-alumina, pentane), yielding preparation I. 187.2–190.2 (187–9).[106] Top sample 20% low. Crystal quality poor.

Preparation I. (Ethyl acetate-ethyl alcohol, −70°), (ethyl acetate, −70°), (toluene, −70°), (ethyl acetate, −70°), (alumina, pentane), yielding preparation II. 187.6 (187–9).[106] Top 15% high. Crystal quality fair.

Diphenylacetylene.—Synthesized according to the procedure in *Organic Syntheses*.[131] (Alumina, pentane), (ethyl alcohol, denatured), (ethyl alcohol, absolute), (wash with pentane), (silica-alumina, pentane), yielding preparation I. 59.0–62.2 (60.9).[106] Top samples approximately normal. Crystals very clear, of good quality.

Jasonols Chemical Company. (Ethyl alcohol)^2, (trichloroethylene), (ethyl alcohol), (pentane), (silica-alumina, olefine-free pentane) (all with Dry Ice cooling, 62% over-all yield), yielding preparation II. 64 (60.9).[106] Crystals clear, fair quality. Top samples normal.

The true scintillation behavior of diphenylacetylene is somewhat controversial, one group[43,132] claiming it to be better than stilbene, the present authors and others[42,133] claiming the opposite. Both sides have used impurity arguments to explain the other's results. Koski and Thomas suggest sterically hindered impurities, such as tetraphenylethylene or bromide derivatives of stilbene, which could be produced during the synthesis of diphenyl acetylene, as the explanation of the low response materials. On the other hand, the data of Koski and Thomas are consistent with the view that their diphenyl acetylene contains a trace of stilbene which is enhancing the fluorescence and scintillation properties of the material. Their diphenylacetylene spectrum shows maxima at the same wavelengths as does the stilbene spectrum, plus another shorter wavelength peak which could be a stilbene maximum which is completely reab-

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[126] S. T. Bowden, J. Chem. Soc. 1111–1114 (1931).

[127] F. N. Hayes, Nucleonics **10**, No. 3, 36 (A) (1952).

[128] Hayes, Hiebert, and Schuch, Science **116**, 140 (1952).

[129] F. N. Hayes, Nucleonics **12**, No. 3, 27 (1954).

[130] F. N. Hayes (private communication).

[131] L. I. Smith, Ed., *Organic Syntheses* (John Wiley and Sons, Inc., New York, 1942), Vol. 22, pp. 50–51.

[132] Ravilious, Elliot, and Liebson, Phys. Rev. **77**, 851 (1950).

[133] Allen, Beghian, and Calvert, Proc. Phys. Soc. (London) **A65**, 295–296 (1952).

sorbed in massive crystals but which becomes visible when the stilbene is in low concentration in a medium transparent at this wavelength; the spectra in Fig. 20 indicate that there exists a "normally suppressed" stilbene maximum at a wavelength at which diphenyl acetylene is transparent. It seems more probable that the purification techniques used in the present work would remove the sterically hindered substances referred to above than that the purification techniques used by the other authors would remove stilbene.

The three different preparations tested here (including the Radiac crystals—see Table IV) were each internally consistent in their scintillation properties, but differed appreciably from one another. All, however, gave average pulse heights lower than those of any of the stilbene preparations tested. Since stilbene and diphenylacetylene have been found to have spectra of very similar wavelengths, the photomultipliers used in any tests on these materials should not perturb the comparative results.

The fluorescence spectra are erratic. Those obtained for diphenylacetylene II are fairly consistent from sample to sample, but the shorter wavelength bands observed for all of the other preparations are suppressed (see Fig. 20). The spectra for diphenylacetylene I vary considerably from sample to sample; the sample whose spectra are reproduced in Fig. 20 was chosen rather arbitrarily; in part, however, because the Radiac II samples give quite similar spectra. Mainly from consideration of these spectra, diphenylacetylene I has been judged to be better than the second preparation: impurities can shift the fluorescence spectra toward longer wavelengths, but not appreciably toward shorter ones. The Radiac samples, particularly Radiac II, may actually be the most characteristic of the compound. Those crystals were of excellent quality. However, the temperature coefficients found do not agree with those apparently characteristic of I and II, and there seems to be reason to expect the higher α values to be valid (see discussion in Sec. II-C-10). Also, when the values found for preparation I are corrected for the poorer quality of the crystals by use of the appropriate transmission factors, they are apparently slightly better than the Radiac samples.

Stilbene.—Eastman. (Alumina, pentane), yielding Stilbene I. 124.0–127.6 (124.2).[106] Top samples normal. Crystals of good quality.

Organic Specialties, (Alumina, pentane), (ethyl acetate), (alumina, pentane), (ethyl acetate), yielding Stilbene II. 124.8–127.9 (124.2).[106] Melt very cloudy, crystals of poor quality.

Stilbene II. (Silica-alumina, pentane), yielding Stilbene III. 125.0–127.9 (124.2).[106] Top samples slightly below normal. Crystals clear but noncohesive along crystal boundaries.

Stilbene III. (Ethyl alcohol), (ethyl acetate), (trichloroethylene), (toluene), (acetone), (hexane), (silica-alumina, olefine-free pentane), (Dry-Ice cooling of all solutions), giving an 85% yield of Stilbene A. 125.7 (124.2).[106] Top samples normal. Crystals clear, of very good quality.

Stilbene I. (Ethyl acetate), (ethyl alcohol), (trichloroethylene), (toluene), (acetone), (hexane), (silica-alumina, olefine-free pentane), (Dry-Ice cooling of all solutions), giving a 90% yield of Stilbene B. 125.4 (124.2).[106] Top samples normal, crystals clear, of very good quality.

The fluorescent spectra from samples of Stilbene I and III were for both materials far from consistent; this was one of the principal reasons for repurifying these materials. The spectra presented for Stilbene A and B in Fig. 20 fairly represent the degree of reproducibility that has now been attained. In both scintillation and fluorescence properties, Stilbene A and B appear to be identical and to be representative of pure stilbene.

1,4-Diphenylbutadiene.—Synthesized in 31% yield by the procedure of Kuhn and Winterstein.[134] (Alumina, pentane), (ethyl acetate)^2, (silica-alumina, pentane). 151.3–154.2 (149.7).[106] The material produced consisted of clear white crystals with a strong "daylight" fluorescence. Contrary to some reports[11, 134] there was no trace of yellow color visible in either the microcrystalline powder or in the crystals produced in the crystal-growing furnace. The material grew as sheets parallel to each other and to the axis of the tube. It stuck badly to the glass, so that it had to be tested in the glass rings left by the slicing operation. The samples were of only moderate clarity. The top sample was slightly subnormal. Serious overheating and aging effects were noted. Samples aged one day gave an average pulse height of 60.0±0.5; three days, at −70°C, 56.4; three weeks, 42.0±1.5 at 30° and 45.3 at −70°. Samples that had been overheated during the crystal growing process gave at one day, 31.0±0.2. The spectra given in Fig. 20 are of an aged sample and must therefore be regarded as of only provisional significance. The decay time data are also uncertain for the same reason.

1,6-Diphenylhexatriene.—Synthesized in 4% yield by the method of Kuhn and Winterstein.[134] (Wash with methyl alcohol), (alumina, pentane). 199.8–204.2 (200–202).[106] The crystals were poor, stuck to the glass, and were tested in the glass rings. The substance decomposes rapidly if heated more than a few degrees above the melting point.

1,8-Diphenyloctatetraene.—Synthesized in 13.7% yield by the method of Kuhn and Winterstein.[134] (Alumina, benzene). 230–234.2 (232–37).[106] The odor of one of the reactants, succinaldehyde, could be detected above the final product, but the fluorescence and scintillation response of the material were sufficiently low that it was not felt necessary to repurify it. The crystals were of low quality and stuck to the glass; they were tested in the glass rings. The substance decomposes to a dark golden tar when heated appreciably above the melting point.

1,2-Di-(p-biphenylyl)-ethylene.—Synthesized by the pyrolysis of *p*-phenylpolythiobenzaldehyde.[135] (Ethyl acetate), (benzene), (ethyl acetate-ethyl alcohol), (alumina, decalin, 180°), (alumina. benzene). 295.8 (302–303).[136] Top samples low by a factor of four, Crystals of fair quality, discolored badly toward top of melt, apparently due in part to thermal decomposition. Tested in glass rings.

Tetraphenylethylene.—Synthesized by method of Norris, Thomas, and Brown.[137] (Reaction mixture extracted with ethyl ether), (ethyl ether), (benzene, pentane), giving a 71% yield of brown powder; (silica-alumina, pentane), (ethyl acetate), (acetone), (silica-alumina, pentane), giving an over-all 51% yield of white crystals. 224.1–228.0 (222.4).[106] Large clear crystals formed from solutions. Crystals formed from melt were clear, but cracked during annealing and crumbled badly when cut into samples. They were tested while mounted in the glass rings.

1,2-Di-(α-naphthyl)-ethylene.—Synthesized by pyrolysis of polythionaphthaldehyde-1.[135] (Silica-alumina, pentane), (ethyl acetate)^2, (trichoroethylene, −70°). (toluene, −70°), (silica-alumina, pentane). 165 (161).[123] Top sample 10% low. Samples quite opaque and polycrystalline, very poor quality. Some evidence of aging.

1,2-Di-(β-naphthyl)-ethylene.—Synthesized by pyrolysis of polythionaphthaldehyde-2.[135] (Ethyl acetate)^2, (benzene), (ethyl acetate-ethyl alcohol), (alumina, benzene), (alumina, decalin, 180°), (benzene). 249 (254-5).[123] Top sample normal. Crystals yellowish, poor quality.

Bibenzyl.—Eastman. (Alumina, pentane), (pentane, −70°). 50.2–52.5 (52) [106] Top samples slightly subnormal. Crystals very clear though not completely flawless.

Bibenzyl has been reported[138] to be as good as stilbene and

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[134] R. Kuhn and A. Winterstein, Helv. Chim. Acta 11, 87–116 (1928).

[135] Synthesis developed and carried out by Mr. Roscoe A. Pike of the Chemistry Department, Massachusetts Institute of Technology.

[136] R. Kuhn and T. Wagner-Jauregg, Chem. Abstracts **25**, 1514^8 (1931).

[137] Norris, Thomas, and Brown, Ber. deut. chem. Ges. **43**, 2940 (1910).

[138] Hofstadter, Liebson, and Elliot, Phys. Rev. **78**, 81 (1950).

terphenyl. A crystal obtained from R. Hofstadter had an excellent appearance and gave an average pulse height of 23.5 ± 1.0 with a temperature coefficient of -0.47×10^{-2}. This average pulse-height value agrees quite well with that calculated from Koski and Thomas' data (see Table VII), and is not too far from the values found for terphenyl and stilbene. Hofstadter's crystal was prepared without special purification of the raw material and undoubtedly contains such substances as stilbene as impurities. Koski and Thomas' material was recrystallized three times from appropriate solvents and then vacuum distilled. It appears possible that stilbene or other impurities would not be completely removed by this procedure. The present authors feel that their preparation is more likely to be representative of pure bibenzyl.

1,4-Diphenylbutane.—Synthesized by method of Barbot.[139] (Pentane, −70°)^3, (alumina, pentane), yielding a clear crystalline product. Neither distillation nor column adsorption procedures were effective in removing the principal contaminants; it was not even possible to crystallize any of the material until Dry-Ice cooling of suitable solutions was tried. 52–53.2 (52).[106] Crystals clear, of good quality.

Diphenylmethane.—Eastman. (Pentane, −70°)^3, (alumina, pentane) (26–27).[105] Crystals were formed by lowering sample tubes into an ice-bath. They were milky with small bubbles, especially around the core of the samples.

Diphenylamine.—Eastman. (Pentane)^3, (wash with water and 5*N* HCl), (ethyl alcohol-water, 3:1)^3, (silica-alumina, pentane). 54.2 (53).[105] Top sample normal. Crystal quality fair.

Phenyl ether.—Eastman. (Pentane, −70°)^3, (alumina, pentane) (28).[105] Crystals were formed by lowering sample tubes into an ice-bath. They were milky with small bubbles, especially around the core.

Triphenylmethane.—Eastman. (Toluene)^2, (ethyl acetate), (hexane), (silica-alumina, pentane). 94.6 (92.5).[105] Top sample 15% low. Clear crystals, fair quality, too brittle and noncohesive to remove from glass rings.

Tetraphenyltin.—Matheson. (Alumina, benzene), (benzene). 228.5–231.5 (226).[105] Top sample normal. Clear crystals, fair quality, tested in glass rings.

p-Xylene.—Eastman. (Pentane, −70°)^3, (alumina, pentane). (13.2).[105] Crystals formed by lowering sample tube into ice-bath, milky with small bubbles around core.

Durene.—Eastman. (Toluene, −70°), (ethyl acetate, −70°), (hexane, −70°), (silica-alumina, pentane). 80.2 (80).[105] Top sample 15% low. Very good crystals.

Pentamethylbenzene.—Eastman. (Pentane, −70°)^3, (alumina, pentane). 55.8 (53).[105] Top sample 20% low. Clear, fairly good crystal. Penta- and hexa-methylbenzene are relatively good phosphors for scintillation Geiger counters[140] (which are strongly far-uv-sensitive), much better than NaI(Tl), for instance.

Hexamethylbenzene.—Eastman. (Toluene, −70°)^2, (hexane, −70°), (silica-alumina, pentane). 167.6 (166).[105] Top sample slightly low. Crystal quality fair—cracked during annealing.

Sodium Iodide (Tl).—Harshaw crystal mounted on quartz window in aluminum sample holder. Very good crystal.

F. Summary

In Table XI is presented a summary of the scintillation counting and fluorescence behavior of the compounds listed in Table I. The scintillation efficiencies at 30° and −70°C, and in a few cases 0°C, are presented graphically in Fig. 24.

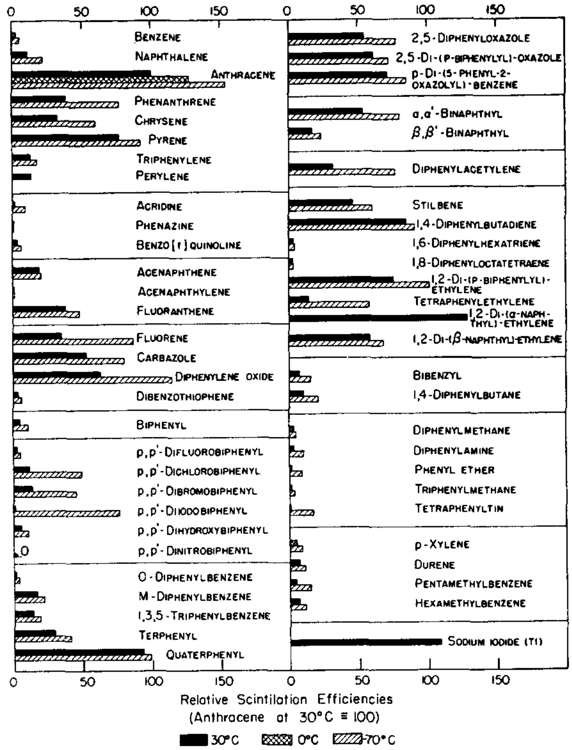

FIG. 24. Scintillation efficiencies ϵ for 30°C, −70°C, and in a few cases 0°C, for the materials listed in Tables I and XI.

The *R* and *T* values were obtained by tracing on a uniform white paper the reflection and transmission fluorescence spectra, respectively, with the stray light backgrounds subtracted; the appropriate areas were cut out and weighed to obtain a measure of the integrated fluorescence intensities. The numbers thus obtained were in each case corrected for the variations in intensity-scale amplitudes. The *T* values were further corrected by dividing them by the μ values, the experimental crystal transmission factors for radiation passing through the total thickness of the crystal.

Analysis of the *R* and *T* data has yielded the following facts:

The geometrical mean value for R/T is approximately 1.10, indicating that the reflection values are on the average about 10% higher than the transmission values. This could be due to a failure of the correction by the crystal transmission factors: for example, they were all referred to the transmission of "good" crystals like anthracene as unity, and even a "good" crystal may perhaps diminish the light passing through it by 10%. However, the figure is scarcely significant in view of the very approximate, mechanical equation of the reflection and transmission intensities, and of the variation in response from sample to sample or with orientation of a given sample.

The mean value of $\exp(|\ln R/T|)$, an average value of the ratio of the two intensities, is 1.32, a somewhat larger value than that expected from a preliminary examination of the spectra. Elimination of the 10% bias between the reflection and transmission values reduces this figure only to 1.29.

A scatter plot of $\log R/T$ *versus* the transmission coefficients μ reveals no discernible correlation. (The μ values ranged from 0.18 to 1.0 and averaged about 0.65.) Thus there does not appear to be any systematic error in the determination (or assignment) and use of the μ transmission factors. This scatter plot also reveals a bias for positive $\log R/T$ values which is in good agreement with the computed geometrical mean value of R/T mentioned above.

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[139] A. Barbot, Bull. Soc. Chem. France **47**, 1314 (1930).

[140] H. O. Albrecht and C. E. Mandeville, Phys. Rev. **81**, 163 (1951).

TABLE XI. Summary of scintillation and fluorescence data. The ϵ_{30} values in the second column denote the scintillation efficiencies at 30°C of crystals of the substances listed in the first column, computed by dividing the appropriate average pulse-height values of Table I by the transmission factors also listed in that table. The alternate values for *m*-diphenylbenzene and chrysene are those suggested by the analyses of Part II as the probable true values. The units are defined by ϵ_{30} for anthracene$\equiv$100.0. The α values in the third column are temperature coefficients taken from Table I, while the ϵ_{-70} values are scintillation efficiencies computed from the ϵ_{30} and the α values according to the formulas given in Sec. I-B-4. The ϵ_{30}^* values are the ϵ_{30} numbers approximately corrected for the photomultiplier spectral response characteristics according to the NBS curve of Fig. 5. (See Sec. 1-B-4, *Discussion and criticism.*)

The T and R values denote the integrated transmission and reflection fluorescence intensities, in purely arbitrary units. (See accompanying text.) The F values are averages of the corresponding T and R values, or average "fluorescence efficiencies." The ϵ_{30}/F ratios are self-explanatory. (However, see Sec. II-B-1 for an analysis of their meanings.) The ordinal numbers n denote approximate classes into which the ϵ_{30}/F values can be grouped. λ_{peak} is the approximate wavelength of the highest maximum in the (transmission) fluorescence spectrum, while $\lambda_{\min}$ denotes the wavelength of the head of the transmission spectrum. $\Delta\lambda_{\min}$ is the difference between the position of the head of the transmission spectrum and that of the reflection spectrum. All wavelengths are in Angstrom units. In the "No. of peaks" column is listed the approximate number of distinctly defined maxima in the transmission fluorescence spectrum for each substance.

A figure in parentheses in the ϵ_{30}^* column indicates that the spectral correction factor could not be directly estimated. A zero in parentheses in the T or R column indicates that under the given experimental conditions the fluorescence spectrum could not be detected. The values in parentheses in the $\lambda_{\min}$ column refer to the reflection spectra: no transmission spectra were obtained in these cases. For the places which are blank, no reliable data of any sort were obtained.

Substance	ϵ_{30}	ϵ_{-70}	$-\alpha\times10^2$	ϵ_{30}^*	T	R	$F\cong\frac{1}{2}(R+T)$	$\frac{\epsilon_{30}}{F}$	n	λ_{peak}	$\lambda_{\min}$ (T)	$\Delta\lambda_{\min}$ ($T-R$)	No. of peaks
Benzene	1.5	5.0	1.33	28	...	...	...	...	...	...	...	...	...
Naphthalene	10.8	22	1.06	32	7.6	5.9	6.8	1.6	7	3480	3340	120	1
Anthracene	100.0	154	0.54	100.0	40	50	45	2.2	8	4480	4250	350	3
Phenanthrene	39	76	0.96	45	62	55	58	0.65	4	4340	3980	200	3
Chrysene	32(65)	60(120)	0.85	40(80)	45	57	51	0.65	4	4170	3840	210	4
Pyrene	77	92	0.20	77	150	182	166	0.45	4	4770	4060	30	1
Triphenylene	12.7	17.6	0.4	13	30	65	48	0.26	2	4620	3790	190	3
Perylene	13.2	...	...	20	106	67	86	0.16	1	5790	5280	980	1
Acridine	1.8	9.2	4.2	1.8	2.0	3.2	2.6	0.7	5	4700	4300	−20	1
Phenazine	0.4	...	...	(0.6)	(0)	(0)	(0)	...	...	...	...	...	...
Benzo[f]quinoline	3.6	5.8	0.61	5.5	17.2	9.2	13.2	0.28	2	4100	3710	110	4
Acenaphthene	9.0	9.9	0.1	24	3.1	4.8	4.0	2.2	8	3590	3440	180	1
Acenaphthylene	0.32	0.46	0.4	0.4	0.9	(0)	0.9	0.35	3	5600	4900	...	1
Fluoranthene	38	48	0.26	38	123	122	122	0.32	3	4750	4300	260	1
Fluorene	35	87	1.49	40	56	71	63	0.55	4	4100	3860	50	3
Carbazole	52	80	0.52	65	38	70	54	1.0	6	4220	3880	20	2
Diphenylene oxide	63	115	0.82	75	83	87	85	0.75	5	4110	3900	70	3
Dibenzothiophene	4.7	64	12.6	5.6	5.7	5.2	5.4	0.9	6	4170	3550	50	5
Biphenyl	5.0	10.6	1.1	7.0	15.6	12.7	14.2	0.35	3	4080	3290	−30	8
p,p′-Difluorobiphenyl	2.6	5.1	0.9	3.6	15.5	14.4	15.0	0.17	1	4080	3210	−20	8
p,p′-Dichlorobiphenyl	11.4	49	3.3	16	5.0	(0)	5.0	2.3	8	4140	3000	...	6
p,p′-Dibromobiphenyl	13.2	45	2.4	13	5.2	7.0	6.1	2.2	8	4850	3800	−100	2
p,p′-Diiodobiphenyl	1.4	77	56	1.5	0.8	(0)	0.8	1.7	7	5000	4600	...	1
p,p′-Dihydroxybiphenyl	5.6	10.5	0.9	14	1.7	2.6	2.2	2.5	8	3650	3450	150	1
p,p′-Dinitrobiphenyl	0	0	...	0	(0)	(0)	(0)	...	...	...	...	...	...
o-Diphenylbenzene	1.6	3.7	1.3	28	4.6	4.7	4.6	0.35	3	3910	3440	−10	3
m-Diphenylbenzene	16.4(12)	21.7(16)	0.32	30(22)	17.3	23.3	20.3	0.8	5	3950	3530	330	3
1,3,5-Triphenylbenzene	13.8	19.0	0.4	36	15.8	17.5	16.6	0.8	5	3590	3410	140	4
Terphenyl	30	42	0.4	40	39	69	54	0.55	4	3910	3510	160	3
Quaterphenyl	94	99	0.05	105	175	174	175	0.55	4	4370	3950	330	3
2,5-Diphenyloxazole	55	78	0.42	75	48	80	64	0.9	6	4160	3800	320	2
2,5-Di-(*p*-biphenylyl)-oxazole	61	72	0.2	60	154	96	125	0.5	4	4630	4300	200	2
p-Di-(5-phenyl-2-oxazolyl)-benzene	71	84	0.19	70	85	114	100	0.7	5	4740	4460	220	1
α,α'-Binaphthyl	54	80	0.49	95	44	70	57	1.0	6	3880	3540	300	1
β,β'-Binaphthyl	16.5	23	0.4	20	41	60	50	0.32	3	4280	3770	220	1
Diphenylacetylene	32	77	1.41	50	34	30	32	1.0	6	4020	3540	240	5
Stilbene	46	60	0.31	75	45	54	50	0.9	6	3840	3630	230	3
1,4-Diphenylbutadiene	84	91	0.08	85	84	27	55	1.5	7	4630	4090	240	2
1,6-Diphenylhexatriene	3.2	3.8	0.2	(3.8)	(0)	(0)	(0)	...	...	...	...	...	...
1,8-Diphenyloctatetraene	2.3	2.7	0.2	(3.4)	(0)	(0)	(0)	...	...	...	...	...	...
1,2-Di-(*p*-biphenylyl)-ethylene	75	101	0.35	75	100	121	110	0.7	5	4670	4300	200	4
Tetraphenylethylene	14	57	3.1	14	75	71	73	0.20	1	4640	4100	200	1
1,2-Di-(α-naphthyl)-ethylene	125	...	...	125	111	142	126	1.0	6	4750	4530	470	1
1,2-Di-(β-naphthyl)-ethylene	58	68	0.16	60	88	175	132	0.45	4	4600	4290	360	2
Bibenzyl	7.1	15.3	1.2	16	10.6	12.3	11.4	0.60	4	3740	3290	10	5
1,4-Diphenylbutane	9.4	20.3	1.2	17	5.2	7.5	6.4	1.5	7	3870	3550	50	4
Diphenylmethane	2.3	4.8	0.80	40	...	4.8	4.8	0.48	4	2930	(2700-R)	..	2
Diphenylamine	3.0	9.8	2.3	7.5	2.9	3.1	3.0	1.0	6	3530	3420	80	3
Phenyl ether	1	8.7	7	18	...	3.3	3.3	0.30	3	3060	(2800-R)	...	2
Triphenylmethane	1.5	3.2	1.2	1.9	17.7	9.3	13.5	0.11	0	4280	2870	120	2
Tetraphenyltin	0.7	17.2	24	0.7	5.4	4.4	4.9	0.14	0	5500	3600	0	3
p-Xylene	4.1	8.9	0.9	(75)	...	...	...	...	...	...	...	...	...
Durene	7.1	11.2	0.6	120	2.4	3.3	2.8	2.5	8	3050	2940	150	1
Pentamethylbenzene	4.5	14.5	2.3	5	9.9	7.5	8.7	0.5	4	4480	2960	100	4
Hexamethylbenzene	6.1	11.0	0.8	90	2.6	7.5	5.0	1.2	6	3100	2960	120	1
Sodium iodide (Tl)	108.7	...	...	120	...	62	62	1.7	7	4370	(3560-R)	...	3

PART II. INTERPRETATION AND CORRELATION

A. The Scintillation Process

1. The Photon Cascade Theory

For the sake of completeness and for later reference, a current picture of the scintillation process will be described briefly at this point. This picture is due in great part to J. B. Birks, and the interested reader is referred to his book[2] and papers[141,142] for justification. (The two papers referred to here are by no means Birks' only journal publications on this topic. The other articles, however, can be approached most efficiently via the references given here.) For present purposes, the photon-cascade theory appears to be the most complete, simple, adaptable, and generally satisfactory theoretical approach which has been published. Also, it seems probable that any interpretations made using it can be readily modified to fit any other theory that may ultimately be adopted.

This paper is not a review of the facts and theories of the scintillation mechanism *per se*; for such discussions other sources must be consulted.[2,3,143]

The scintillation process in organic materials can be divided into a number of successive phases. One such division is the following:

(1) High-energy radiation incident upon an organic material is capable of producing scintillations if it either consists of ionizing particles or reacts within the medium to yield such particles.

(2) The ionizing particles, whatever their origin, dissipate their energy to produce highly excited molecules.

(3) The highly excited molecules very rapidly emit primary photons, the primary fluorescence radiation.

(4) The primary photons are absorbed with high probability by unexcited molecules.

(5) The secondarily excited molecules emit true molecular fluorescence radiation, the molecular radiation produced by ordinary ultraviolet excitation.

(6) The true molecular fluorescence radiation is reabsorbed in part in the medium and the portion absorbed is either dissipated as heat or degraded and reemitted, and this process is repeated until ultimately only the radiation to which the massive medium is transparent escapes to be detected by the photomultiplier or other light sensitive device.

According to Birks' theory, primary photon emission is a fundamental molecular property. The primary photon energy is approximately the molecular ionization energy. The mean free path of a primary photon in an anthracene crystal is about 7 microns. The energy saturation effects observed for densely ionizing particles are due to quenching of the primary photon emission in the ionization column. The decrease in energy response for particles of range less than one primary photon mean free path in a crystal is due at least in part to the escape of primary photons from the crystal.

The radiation emitted by secondarily excited molecules is essentially the true molecular fluorescence radiation. Any emission and reabsorption of radiation of energy intermediate between that of "ordinary" fluorescence and that of the primary fluorescence occurs so extremely rapidly and with such high efficiency that this step can be neglected for the present purposes. The true molecular fluorescence radiation is reabsorbed in the medium in the spectral region where the molecular absorption and emission spectra overlap. The absorption and partial dissipation of the molecular fluorescence energy depends critically on the amount of this overlap. As the temperature decreases, the vibrational perturbations decrease and the overlap decreases. As a result the efficiencies of both photofluorescence and the scintillation process rise. Simultaneously, the observed scintillation decay time decreases, approaching the true molecular scintillation decay time.

The scintillation decay time is the resultant of the decay times (or mean lives) of all of the processes involved in the over-all scintillation process. Since the photofluorescence process is only one of these, the scintillation decay time is inherently longer than the (ultraviolet-excited) photofluorescence decay time. The primary photon emission and the photofluorescence probabilities are roughly comparable, and the remaining processes much more rapid, so that the scintillation decay times are approximately twice as large as those for photofluorescence.

The over-all scintillation efficiency of an organic crystal is determined by (a) the primary photon production efficiency, (b) the true molecular photofluorescence quantum efficiency, and (c) the degree of overlap of the absorption and emission spectra, which determines the number of photon exchanges which occur. As corollaries of this observation of Birks, the following statements can be made: Both (a) and (b) depend at least in part upon the transition dipole moments of the molecular photon emission processes. These transition dipole moments are at least qualitatively dependent upon both the geometry of the molecules of the scintillating species and the mobility of the electrons in these molecules. Therefore, one can expect to find a correlation between the scintillation efficiency and both molecular geometry and electron mobility.

2. Scintillation Mechanisms and Photo- and Semiconduction Properties

Some characteristics of organic scintillators which to the best of the authors' knowledge have never been considered in the development of theories of the scintillation process are the photoconduction and semiconduc-

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[141] J. B. Birks, Phys. Rev. **94**, 1567 (1954).

[142] J. B. Birks, Phys. Rev. **95**, 277 (1954).

[143] R. K. Swank, Nucleonics **12**, No. 3, 14–19 (1954).

tion properties of these materials.[61,144–150] According to the information in the literature, materials such as anthracene appear to be intrinsic semi- and photoconductors. For anthracene the plot of the photocurrent *versus* the wavelength of the exciting light parallels the uv absorption spectrum of the crystal, reproducing all of the inflections of that curve. The semiconduction energy gap for anthracene is about 1.6 ev. Both electrons and holes participate in the conduction process. The magnitudes of the currents are quite small; normally these materials are regarded as insulators. The semiconduction is quite possibly associated with a singlet-triplet transition. The activation energy in general decreases with an increase in the number of aromatic rings in the molecule. The semiconductivity is anisotropic.

Two comments seem in order regarding the relation of the photo- and semiconduction properties to the scintillation mechanism. First, it has on occasion been mistakenly stated in this connection that anthracene and similar compounds do not show photoconductivity. Second, the semiconduction properties imply the existence of energy transfer mechanisms independent of the photon transfer mechanism used by Birks; these mechanisms may also be involved in the scintillation process.

B. Scintillation Efficiencies and Fluorescence Spectra

The correlation between the scintillation efficiencies ϵ and data abstracted from the uv-excited fluorescence spectra can best be seen by an examination of the data in Table XI.

1. Scintillation Efficiencies and Integrated Fluorescence Intensities

Theoretical analysis.—To restate a conclusion given in a preceding section, the scintillation efficiency of a crystal can for our present purposes be resolved into the following two factors: the primary photon production efficiency of the molecules, and the photofluorescence emission efficiency of the crystal. For the "ultraviolet-excited photofluorescence efficiency" there are also two factors: the ultraviolet fluorescence-excitation efficiency, and the fluorescence emission efficiency of the crystal. For ultraviolet radiation of energy between and not too near either the long wavelength absorption edge or the ionization limit, as in this work, the first factor here can be assumed to be unity. The ratio of the scintillation efficiency to the uv-excited photofluorescence efficiency should therefore be (proportional to) the primary photon production efficiency. Thus the ϵ_{30}/F values in Table XI should be a measure of the primary photon production efficiencies. (In studying these values it must be remembered that any determinate factors reducing the apparent fluorescence intensity, such as an absorbing film on an anthracene crystal or fluorescence radiation in a region to which the spectrograph is not sensitive, will lead to anomalously high values.)

Casual inspection of the ϵ_{30}/F values seems to indicate that these numbers cluster around a regular sequence of favored values. Closer examination of both these values and R/ϵ_{30} and T/ϵ_{30} data gives the consistent and definite impression that there are favored ratios which can be represented by the expression

$$(\epsilon/F)_{\text{favored}}=(0.127)2^{n/2},$$

where n is a small integer. The nearest n number is given for each substance in Table XI in the column following the ϵ/F figures. Calculation of the average deviation of the logarithms to the base 10 of the empirical ratios from the logarithms of the nearest "favored" values gave 0.0342 ± 0.0038, where 0.0038 is the standard deviation of the mean deviation value. Randomly, i.e., essentially uniformly, distributed values would give an average deviation of 0.0379. These computations thus indicate that there is about a two to one chance that the apparent clustering is real.

Experimental correlations.—A scatter plot of the n or ϵ/F values *versus* ϵ shows a slight positive correlation. The average value of n rises from about 4 for $\epsilon=0$ to 6 at $\epsilon=100$, corresponding to a rise by a factor of 2 in the ϵ/F ratios. In other words, the better phosphors tend to have the larger primary photon production efficiencies. In a similar plot of n *versus* the temperature coefficient α, no correlation could be seen.

There is a tendency for members of series of similar compounds to have approximately the same ϵ/F values.

The total range of the ϵ/F values corresponds to a factor of about 20. The corresponding figure for the scintillation efficiency ϵ is about 400, while that for the fluorescence efficiency F is of the same order. Thus there is a general correlation, good to within about a factor of five, between the scintillation and uv-excited fluorescence responses for crystalline organic scintillators. That is, for some purposes, the primary photon production efficiency may be regarded as roughly the same from compound to compound and the normal photofluorescence emission efficiency as the only important factor.

A scatter plot of n *versus* F indicates that the materials with the greater photofluorescence intensities tend to have the smaller primary photon production efficiencies. This implies that to some extent high primary photon production efficiencies and high uv emission efficiencies are mutually contradictory. This is not

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[144] N. S. Bayliss and J. C. Riviere, Nature **163**, 765 (1949).
[145] D. J. Carswell, J. Chem. Phys. **21**, 1890 (1953).
[146] Carswell, Ferguson, and Lyons, Nature **173**, 736 (1954).
[147] A. G. Chynoweth and W. G. Schneider, J. Chem. Phys. **22**, 1021 (1954).
[148] G. J. Goldsmith, Phys. Rev. **93**, 929 (A) (1954).
[149] S. H. Inokuchi, Bull. Chem. Soc. Japan **24**, 222 (1951).
[150] H. Mette and H. Pick, Z. Physik **134**, 566–575 (1953).

too surprising, since those molecular configurations which are most conducive to high efficiency for one process are not likely to be the same as those conducive to the other. The best scintillators are those materials for which both factors are reasonably high (i.e., in each case, $\geq\sim 25\%$ of the maximum observed values). For both factors to be reasonably high, neither the primary photon production process nor the photofluorescence emission process can require or result in much shift of the nuclei from their ground-state equilibrium positions, which is equivalent to saying that there must be relatively little opportunity for internal-conversion energy loss in either process. Normally, very rigid binding is necessary if a molecule is to meet these requirements. The best scintillators thus should be and are characterized by very rigidly bound molecules. A rigid crystal structure will also tend to favor good scintillation and fluorescence response, for similar reasons, so that the best scintillators tend to have high melting points. Reynolds[151] has suggested that the relatively better energy response of the inorganic scintillators may be due to the existence of stronger binding forces in those materials.

2. *Other Spectral Considerations*

Effect of variation of photomultiplier and spectrograph response with wavelength.—A plot of ϵ/F or n *versus* λ_{peak} shows a slight correlation which roughly parallels the P/S curve of Fig. 23, the curve which shows the ratio of the photomultiplier and spectrograph response curves. Most of the spectra have λ_{peak} values between 3500 and 5200 A, and in this range P/S varies only by a factor of two, while the ϵ/F values are varying randomly over a 16-fold range. Only for λ_{peak} below 3700 A and above 5200 A does there seem to be any clear-cut perturbation of the ϵ/F values. A reduction of the n values on the low end by two units and an increase by two or three units on the upper end would appear to be justifiable corrections. A similar plot of n *versus* λ_{min} shows no correlation.

Spectral overlap.—To the extent that the reflection fluorescence spectra determined during the course of this work approximate the true molecular emission spectra, the $\Delta\lambda_{\text{min}}$ values in the next to the last column of Table XI can be used as a measure of the overlap of the absorption and scintillation emission spectra. However, there is good evidence that the degree of approximation is not very high,[3,80,141] so that it is not too surprising that these $\Delta\lambda$ values do not show the behavior expected for the true overlap factors (see below). The fact that the reflection fluorescence spectra do not show the behavior expected of the true molecular fluorescence spectra implies that the incident exciting radiation penetrates the crystals to a depth such that extensive reabsorption of the molecular fluorescence radiation occurs before it can escape from the crystal. This may in part be due to the approximately 4π distribution and backscattering effects for the emitted radiation, compared with the fair degree of collimation of the incident radiation, which results in its travelling on the average through more of the crystal than did the radiation which excited the fluorescence, and in part to the enhanced reabsorption resulting from polarization effects (see reference 2, pp. 73–74).

The true overlap values are expected to show a negative correlation with the scintillation efficiency and a positive correlation with the absolute value of the temperature coefficient of the scintillation average pulse height, α. In the first case, the greater the overlap, the greater the amount of radiation which is reabsorbed and dissipated as heat, thus reducing the scintillation efficiency. In the second case, the greater overlap values and the larger $|\alpha|$ values can both be correlated with large vibrational perturbations of the molecular absorption and emission spectra. In contrast to expectations, appropriate scatter plots reveal that the tabulated $\Delta\lambda$ values show a rather definite *positive* correlation with both the scintillation and fluorescence efficiencies, and a distinct inverse correlation with the temperature coefficient values.

Spectral complexity.—A scatter plot of the approximate number of peaks in the transmission fluorescence spectrum *versus* the scintillation efficiency yields a slight negative correlation; i.e., there is a tendency for the best scintillators to have the simplest (and most sharply defined) fluorescence spectra. This is to be expected, since a simple and well-defined fluorescence spectrum implies a tendency toward a similarly simple and well-defined fluorescence emission process, which is therefore likely to have a high efficiency. In good agreement with this analysis, the fluorescence efficiency F shows a similar negative correlation with the number of peaks, while no correlation either positive or negative can be discerned for the primary photon production efficiency ϵ/F.

C. Correlation of Scintillation Efficiencies and Molecular Structures

1. *Introduction*

It seems well established and generally accepted that the fluorescence and scintillation properties of a crystalline organic compound are determined primarily by the nature of the molecules of that compound, and that they are only secondarily affected by the arrangement of the molecules in the crystal or by other properties specifically connected with the crystal lattice. While no explicit effort will be made to justify this statement, much evidence supporting it is implicit in the discussions which follow. An interesting bit of additional confirming evidence,[152] moreover, is furnished by the

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[151] G. T. Reynolds, Nucleonics **10**, No. 7, 46 (1952).

[152] A. J. Reinsch and H. G. Drickamer, J. Appl. Phys. **23**, 152–153 (1952).

fact that while a pressure of 10 000 atmos reduces the scintillation efficiency of the inorganic, crystal scintillator $CdWO_4$ by 15–20% and causes the emission band to shift toward longer wavelengths, a similar pressure does not affect the scintillation behavior of anthracene.

The scintillation efficiency or average pulse height of a crystal of a given molecular species has been found empirically to be primarily a function of the mobility of the π electrons in, and of the geometry of, the molecules of that species. High π-electron mobility is dependent upon or equivalent to large resonance interactions, or large amounts of conjugation, between the different portions of the molecule. In the simpler cases, the effective amount of mobility or conjugation can be perceived from a study of the number and the nature of molecular structures that can be written out on paper, and can be correlated directly with the scintillation efficiency of the respective crystals. In more complex cases, the following factors must be considered: (a) Steric hindrance effects. (b) Hyperconjugation. (c) "Unshared" electron pairs. (d) "Nonbonding-electron" energy levels. (e) Effects of five-membered aromatic rings. (f) Presence of heavy atoms, allowing singlet-triplet transitions. (g) The possibility of predominantly quinoid rather than Kekule ground state structures. In all cases, the effects of thermal (vibrational) perturbations will be present.

It should be noted that quite independent (although less extensive and less detailed) discussions[127,153–155] of the correlation of scintillation efficiency and molecular structure have been published by other authors which are basically similar to and in agreement with the one to be presented here.

2. π-Electron Mobility in the Kekule Hydrocarbons

Formal approach.—In the case of the Kekule hydrocarbons (hydrocarbons for which it is possible to write structures such that every carbon atom has a share in exactly one double and two single bonds),[156] it is possible to make some crude but semiquantitative calculations of the relative scintillation efficiencies of different substances. While the procedure is far from elegant or well justified theoretically, and while it is somewhat difficult to see why it should work as well as it does, still it is of some practical value, and it may be of help in guiding more satisfactory theoretical approaches. It appears to be basically related to McWeeny's valence-bond theory[157–159] with its "charge hops" across bonds, particularly since the valence-bond theory was developed originally in connection with computations of diamagnetic susceptibilities (see Sec. II-C-13). This valence bond theory will probably be the most useful for any basic theoretical computations of the correlation of scintillation efficiencies and molecular structures.

It has been assumed in the development that follows that the molecules being discussed are planar. In general this is probably true.[160–163] The known exceptions will be noted and discussed later.

In the procedure that has been developed, attention has been focused on all the quinoid structures[164] with a single separation of charge that can be drawn for the molecular species under consideration. The justification for considering only such structures is this: First, since the scintillation efficiency will be connected with a transition dipole moment, any correlation of scintillation efficiency with molecular electronic structures must involve structures having a separation of charge. Second, the lowest excited electronic states play an important part in the scintillation process, at least in the photofluorescence stage, and to these states the singly-charged quinoid structures normally make a predominating contribution. Third, the effects of structures with a multiple separation of charge can be at least approximately resolved into a combination of the effects of a number of singly-charged structures, so that only singly-charged structures need be considered.

In the first step of this procedure, numerical structural parameters are derived by considering every quinoid structure with a single separation of charge that can be drawn for the molecule in question. For each such structure two numbers are obtained—the squares of the components along two arbitrary, perpendicular axes of the charge separation vectors, in arbitrary units. (An average carbon atomic radius is a convenient unit.) These squared components are then summed for each axis over all of the structures involved, and the axes are rotated (if necessary) to yield the maximum and minimum sums of such squared components that can be obtained for the molecules involved. The justification for this process is the following: Components along some axes must be used, since interaction with the electromagnetic field of a light quantum is a vector process; the charge separation vectors must be added vectorially. Secondly, the structures with the greater charge separations will contribute with dis-

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[153] E. J. Bowen, Nucleonics **10**, No. 7, 14 (1952).

[154] L. Herforth and D. Rosahl, Ann. Physik (Series 6) **12**, 340–347 (1953).

[155] O. Neunhoeffer and D. Rosahl, Z. Elektrochem. **57**, 81 (1953).

[156] M. Gordon and W. H. T. Davison, J. Chem. Phys. **20**, 428 (1952).

[157] R. McWeeny, Proc. Phys. Soc. (London) **A66**, 714–720 (1953).

[158] R. McWeeny, Proc. Roy. Soc. (London) **A223**, 63–79 (1954).

[159] R. McWeeny, Proc. Roy. Soc. (London) **A223**, 306–323 (1954).

[160] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1945), second edition.

[161] K. Lonsdale, Z. Krist. **97**, 91 (1937).

[162] J. M. Robertson and I. Woodward, Proc. Roy. Soc. (London) **A162**, 568 (1937).

[163] Mukeril, Singh, and Singh, Indian J. Phys. **27**, 341–346 (1953).

[164] The authors are indebted to Dr. Harvey Winston of Hughes Aircraft Company, Culver City, California, for the original suggestion that attention be focused on quinoid structures in developing a mathematical theory of the scintillation behavior of these compounds.

proportionate strength to the transition probability, and summing the squares of the components is a simple way of weighting the contributions of each structure in direct proportion to their probable importance. Third, the sense of the charge separation vectors is not important, just the direction and magnitude; summing squares of components automatically disregards the sense of the vectors.

On examination of the numbers thus obtained, it has been found that in any given series, such as benzene-naphthalene-anthracene, or the polyphenyls, the maximum "sum of squared components" can be correlated directly with the scintillation efficiency along a reasonably smooth curve. While the different types of compounds have different correlation curves, the differences are of such a nature that by reasonable though arbitrary assumptions the parameters for the different series can be reduced to a common basis so that they fit a common curve. The curve for the essentially "circular" fused-ring compounds—benzene, naphthalene, anthracene, and pyrene—was adopted as a provisional standard. Then arbitrary but consistent factors were devised to reduce the maximum "sums of squared components" for the other compounds to the common basis.

The reduction factors (f) were constructed for each molecule according to the following formula:

$$f=[n\sqrt{2}+2m+2l+(\sqrt{2})^k+s]^{-1},$$

where n = the number of "indentations" of the type shown by phenanthrene, chrysene, perylene, and triphenylene; m = the number of "single" bonds connecting conjugated benzene rings in the polyphenyl series, or other aromatic systems in such compounds as the binaphthyls (in m-diphenylbenzene and 1,3,5-triphenylbenzene, the longest chains of mutually conjugated benzene rings consist of only two such groups, so that $m=1$ as in biphenyl and the binaphthyls; for o-diphenylbenzene, terphenyl, and quaterphenyl $m=2$, 3, and 3, respectively); l = the number of five-membered aromatic rings in the molecule (one each in fluoranthene and acenaphthylene); k = the number of olefinic double bonds connecting aromatic ring systems; s = a structural parameter assigned to different pairs of aromatic ring systems which are connected by "single" bonds or olefinic chains ($s=0$ for phenyl groups, 4 for biphenylyl, $\sqrt{2}$ for α-naphthyl, and 5 for β-naphthyl).

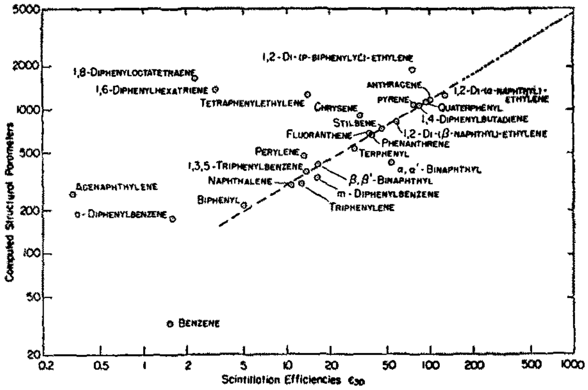

FIG. 25. Computed structural parameters *versus* scintillation efficiencies.

The reduction factors can be qualitatively justified. In the case of the phenanthrene-type "indentations," qualitative application of a "free electron in a channel" theory indicates that this indentation must act as some sort of an impediment to the flow of electrons around the molecule in comparison with the flow to be found in a "circular" molecule like anthracene. McWeeny[157] has more or less rigorously established the existence of such an effect. Similar arguments can be applied to the effects of single bonds or olefinic chains linking aromatic ring systems: in addition, in these cases a clear-cut argument can be made that thermal vibrations will have an abnormally strong effect in reducing the effective electron mobilities below computed values. The use of different ring system building blocks will likewise introduce perturbations; e.g., it is well known that bonds to the α and β positions on naphthalene are not equivalent, and the introduction of a five membered ring as in fluoranthene both makes new types of quinoid structures possible and produces steric strain in the molecule.

No correlation was found between the scintillation efficiencies and the minimum "sums of squared components," or between the scintillation efficiencies and any other combinations or permutations of these "sums of squared components." This is reasonable, since it is to be expected that scintillation photon emission or absorption will depend primarily upon the maximum polarizability or transition dipole moment that a molecule can show, particularly in the organic crystals where the molecules are oriented so that the absolute spatial polarizations favored in emission processes are also those favored in reabsorption processes.

The structural parameters calculated in the fashion indicated above are shown in Fig. 25, plotted against the appropriate scintillation efficiency values ϵ. It is evident that for most of the compounds the points fall more closely on a common straight line in the logarithmic plot than can reasonably be expected in view of the many possible sources of error in both quantities. Moreover, in most cases, the deviations are quite significant.

The low value for α,α'-binaphthyl and the high value for 1,2-di-(p-biphenylyl)-ethylene are thought to be due to failures in the procedure used in reducing the calculated values to a common scale. In each case, any reasonable excuse for dividing the ratio between the parameters for the diarylethylene and the corresponding diaryl by a factor of two would make it possible to being these two points onto the common curve.

The deviation of triphenylene and biphenyl are felt to be more or less random and not significant. The deviation of *m*-diphenylbenzene is probably real and due to the traces of terphenyl previously mentioned as a probable impurity (see Sec. I-E). The true scintillation efficiency of *m*-diphenylbenzene at 30°C is probably about 12 or 12.5.

The departure of benzene from the curve may or may not be real. First, the straight line relationship may break down in this region. Second, the scintillation efficiency for crystalline benzene at 30°C is a value extrapolated from that at 0° and −70°C; besides being essentially hypothetical in nature, since 30°C is so far above the melting point of benzene, it may be appreciably in error due to the crudity of the extrapolation.

The behavior of the point for chrysene is anomalous and is not well understood (see Sec. II-C-13).

The remaining deviant compounds will be discussed in the sections which follow.

Intuitive approach.—It will probably be instructive to depart from the rather abstract, formalized approach above to examine the behavior of some of these compounds more closely and in a perhaps more intuitive fashion. The polyphenyl series is a good subject for such an approach. The substances involved are benzene, *o*-diphenylbenzene, *m*-diphenylbenzene, 1,3,5-triphenylbenzene, *p*-diphenylbenzene or terphenyl, and quaterphenyl.

When two benzene rings are joined to form a biphenyl molecule, it can readily be shown that quinoid resonance forms can exist which involve the interaction of one ring with the other. As a result of this resonance interaction, biphenyl is a considerably better scintillator than benzene.

In *ortho*-diphenylbenzene, due to steric interference (see the next section), there is little or no interaction between the rings and the scintillation behavior approximates that of benzene.

In *meta*-diphenylbenzene, trial and error soon shows that either end ring can interact with the middle ring, but that no singly-charged quinoid structures can be written with all three rings interacting at once. Likewise, in 1,3,5-triphenylbenzene, only two rings may interact in any one structure with a single separation of charge. The picture derived in the previous subsection suggests that the combination of the different two-ring interactions in these compounds will be vectorial, not algebraic, with the scintillation efficiency proportional to the magnitude of the maximum resultant which can be obtained by arbitrarily assigning directions to the vectors. By assigning each biphenyl group a unit vector parallel to the axis of the group, it is not difficult to derive the ratio of the scintillation efficiencies for biphenyl, *m*-diphenylbenzene, and 1,3,5-triphenylbenzene as $1:\sqrt{3}:2$. Using the estimated true values for *m*-diphenylbenzene (see Table XI), the ratio found at 30°C is $0.7:\sqrt{3}:2$, and at -70°C $1.1:\sqrt{3}:2$.

In the case of terphenyl (*para*-diphenylbenzene) and quaterphenyl, singly-charged quinoid resonance structures can be written which involve interactions of all of the rings simultaneously. This is reflected in the large increase in scintillation efficiency in the series biphenyl-terphenyl-quaterphenyl.

Spectroscopic study of the *meta*- and *para*-linked polyphenyls[165] has led to conclusions paralleling those mentioned in the previous paragraphs. In the *meta*-series, it was found that the absorption spectra differed little in position or intensity. The theoretical analysis indicated that the absorption was due to separate biphenyl, or "half-biphenyl," units in the molecules and that these units interacted with each other only slightly. In contrast, both the positions of the maxima and the extinction coefficients shift rapidly in going up the *para*-polyphenyl series, where all of the rings interact so that the absorbing unit is the molecule as a whole.

3. *Steric Hindrance*

The computations described in the preceding section were all based upon planar carbon skeleton structures drawn out on paper. While in most cases such a procedure is valid, it is not without perils. Specifically, the molecules being considered consist of carbon skeletons attached to which are hydrogen atoms, and the hydrogen atoms cannot be completely ignored. For example, even in biphenyl and similar compounds there is computed to be some steric interference between the ortho hydrogen atoms of the adjacent rings (see reference 160, p. 220). In the case of *ortho*-diphenylbenzene, writing a planar structure for the molecules implies not only overlap of adjacent hydrogen atoms on the two substituent rings, but also overlap of these hydrogen atoms with carbon atoms on the neighboring rings. Thus *o*-diphenylbenzene cannot be a planar molecule. It seems experimentally well established that none of the benzene rings in the molecule are coplanar.[161,166,167] This view of *o*-diphenylbenzene suggests that its scintillation behavior should be due to isolated benzene rings, since adjacent rings can interact strongly only when they are coplanar. It is therefore reasonable that its scintillation efficiency is about the same as or somewhat smaller than that of benzene. These steric considerations account for the anomalous position of *o*-diphenylbenzene in Fig. 25, since the parameter of that figure was based upon the planar configuration.

In a similar fashion steric interference between adjacent rings in the tetraphenylethylene molecule precludes a planar configuration—the molecule is known to be nonplanar[168]—and causes the scintillation efficiency to be anomalously low. The resonance interactions in this molecule appear to be very strong,

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[165] A. E. Gillam and D. H. Hey, J. Chem. Soc. 1170–1177 (1939).

[166] I. L. Karle and L. O. Brockway, J. Am. Chem. Soc. **66**, 1974 (1944).

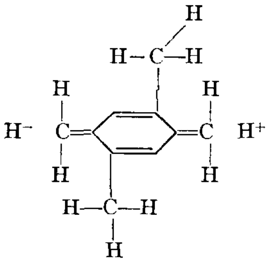
[167] C. J. B. Clews and K. Lonsdale, Proc. Roy. Soc. (London) **A161**, 493 (1937).

[168] M. N. Datta, Indian J. Phys. **27**, 126–128 (1953).

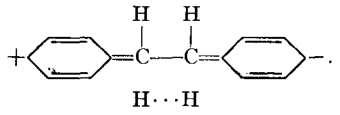
however, even if the molecule can never be completely planar; a small decrease in temperature and vibrational perturbation apparently permits a closer approximation to the planar configuration and increases the resonance interactions greatly, so that the temperature coefficient $-\alpha$ is unusually large.

4. Hyperconjugation

While ordinary resonance conjugation can qualitatively account for the behavior of the alternate single and double bond hydrocarbons, it cannot account for the behavior of bibenzyl, diphenylbutane, and the multi-methylbenzenes. In at least first order theory, the scintillation behavior of all of these materials should be essentially due to isolated benzene rings, and their scintillation efficiency should approximate that of benzene or orthodiphenylbenzene. To account for the systematically observed, much larger values actually found, it is necessary to introduce the concept of hyperconjugation,[169–172] which permits resonance contributions from structures of the types



or



In this fashion the necessary electron mobility and transition dipole moments can be accounted for.

It should perhaps be noted here that bibenzyl is known to be nonplanar, with the planes of the benzene rings parallel to each other and perpendicular to the zig-zag of the connecting CH_2 groups.[173]

Hyperconjugation will also be present in diphenylmethane and similar compounds. However, there is no way in which a separation of charge involving both phenyl groups can be created without requiring the existence of two double bonds to the linking atom, an unstable and improbable situation. Therefore diphenylmethane, diphenylamine, phenyl ether, and triphenylmethane all approximate benzene in their behavior.

5. "Unshared" Electron Pairs

The series biphenyl—fluorene—carbazole—diphenylene-oxide—dibenzothiophene requires for the explanation of its behavior the invoking of most of the principles outlined at the beginning of this present Sec. II-C.

The structural parameters originally computed for biphenyl and its homologs were found to be high in comparison with those for the anthracene series. The reason in part was felt to be the vibrational perturbations associated with the existence of free rotation in solution or the vapor of the phenyl groups about the phenyl-phenyl bond. If this vibration of biphenyl could be frozen out to give a molecule with a rigidity comparable to that of anthracene, then the computed parameter should fit better than the reduced one. In at least first-order theory, bridging across the phenyl groups with a CH_2 group, as in fluorene, should have this stabilizing effect. Fluorene[174] would then be expected to have a scintillation efficiency of about 10 or 11, or perhaps 18 or 20, at 30°C, depending upon whether the parameter was handled like that of phenanthrene or that of anthracene. The much higher value observed suggests that other effects are also at work. One of these is probably hyperconjugation, which allows resonance interaction of the CH_2 group with the two benzene rings. Another is the "enhanced resonance" of five membered rings (see the following).

In the case of carbazole and diphenylene oxide, still another factor is involved. In both of these compounds the bridging atom possesses "unshared" electron pairs which permit ready interaction of the bridging atom with the benzene rings, the more so with diphenylene oxide with its two pairs of "unshared" electrons than with carbazole which has only one pair. Since the computed structural parameters (calculated on the basis of Sec. II-C-2) for carbazole and diphenylene oxide give considerably smaller scintillation efficiencies than those observed, it appears that the interaction of the unshared electrons of the bridging groups with the π electrons of the biphenyl ring systems is stronger than the ordinary interactions of the π electrons with each other.

When a bridging atom shares its "unshared" electrons with the biphenyl ring, it can have only a positive formal charge. For a negative formal charge on the group some sort of hyperconjugation or use of a *d*-type electronic orbital is necessary. One implication is that these molecules will possess permanent dipole moments, and these permanent dipole moments will be expected to affect the scintillation properties. They may be responsible for enhancing the scintillation efficiencies of these compounds.

Dibenzothiophene shows the behavior typical of compounds containing heavy atoms (see below).

The somewhat greater response of diphenylamine and phenyl ether compared with that of diphenyl-

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[169] V. A. Crawford, Quart. Revs. **3**, 226 (1949).

[170] C. A. Coulson and V. A. Crawford, J. Chem. Soc. 2052–2058 (1953).

[171] V. A. Crawford, J. Chem. Soc. 2058–2061 (1953).

[172] V. A. Crawford, J. Chem. Soc. 2061–2065 (1953).

[173] J. M. Robertson, Proc. Roy. Soc. (London) **A146**, 473 (1934).

[174] Fluorene is known to have a planar molecule; see D. M. Burns and J. Iball, Science **173**, 635 (1954).

methane is probably associated with the unshared electron pairs of the former compounds.

6. *"Nonbonding-electron" Energy Levels*

Acridine, phenazine, and benzo[f]quinoline contain unshared electron pairs which superficially at least resemble the "unshared" pairs in carbazole and diphenylene oxide. However, these electron pairs differ fundamentally from those in carbazole, etc., in that the atoms to which they are attached are already fully conjugated in the atomatic ring system. Thus these electrons are truly unshared and "nonbonding."[175,176]

Acridine structurally resembles anthracene very closely. In essence, the two differ only in the position of a proton: in the first case it is part of a nitrogen nucleus, in the second it is the H nucleus in a CH group. Electronically the structures of the two compounds are almost identical. However, shifting (mathematically, or with the aid of a super-Maxwell demon) of a proton from being bound by a pair of electrons to being bound in a nucleus leaves behind a loosely bound "nonbonding" electron pair which in many cases has an energy level lying below the π electron energy levels of the molecule.[176] Such is thought to be the case for acridine and phenazine,[176] and appears to be true for benzo[f]quinoline. Associated with the presence of these nonbonding levels appear to be dissipative processes, so that while in most respects the energy level structures of anthracene and acridine are very similar, the fluorescence and scintillation properties are greatly different.

It appears that a nonbonding electron pair does not necessarily imply a low fluorescence or scintillation efficiency: in the oxazole compounds, the oxazole nitrogen has such a pair, with no apparent deleterious effects.

7. *Five-Membered Aromatic Rings*

Five membered aromatic rings have the interesting property that quinoid structures with single separations of charge can be written for any two atoms as bearers of the charges. In six-membered rings, only atoms *ortho* or *para* to each other can be the centers for such separate charges. As a result, there are more quinoid resonance forms possible with a five-membered ring present than with a six-membered ring. For example, in oxazolylbenzene there will be one-third more quinoid structures with interaction between the two rings than with phenylbenzene. It is apparently at least in part a result of such factors that 2,5-diphenyloxazole is a better scintillator than terphenyl, and *p*-di-(5-phenyl-2-oxazolyl)-benzene is better than 2,5-di-(*p*-biphenylyl)-oxazole. The failure of either five-ring system to be better than quaterphenyl at room temperature may be due in part to the apparently larger temperature coefficients of the former, which imply greater vibrational perturbations, or to the zig-zag or bent shapes of the molecules (that almost certainly are not linear), which result in effective separations of charge between end rings that are not as large as they at first sight appear to be.

The properties of five-membered rings are also involved in the behavior of the "bridged biphenyls"—carbazole, etc.—and of fluoranthene and acenaphthylene. In the case of fluoranthene it was necessary to use a smaller reduction factor than application of the "indentation" rule would yield. In the case of acenaphthylene, either the strain or the quinoid properties associated with the five-membered ring apparently has led to thorough quenching of fluorescence.

8. *Heavy Atoms and Triplet States*

In atomic spectroscopy as the weight or atomic number of an atom increases, the type of spin-orbital interaction shifts from Russell-Saunders to $j-j$ coupling. One result is that singlet-triplet transitions become less forbidden. A similar phenomenon is observed in molecular spectroscopy:[175] the presence of heavy atoms in or substituted on an aromatic ring system makes π electron singlet-triplet transitions less forbidden.

Characteristically, singlet-triplet transition energies are lower than those for corresponding singlet-singlet transitions. Thus, when the singlet-triplet transition probability becomes appreciable, a new lowest "effective" excited state, a triplet state, is observed. The absorption and emission spectra tend to shift toward the red and to change in character. The fluorescence radiation will be at least in part singlet-triplet in nature, and the fluorescence decay time will tend to be increased toward the value associated with the partially forbidden singlet-triplet transition. Furthermore, if energy is trapped in a triplet state and held an abnormmally long time before being radiated, the probability of its being dissipated by nonradiative processes will tend to be increased. However, since new types of dissipative processes may be involved, and the old ones may no longer be important, the scintillation efficiency could be either larger or smaller than that which would otherwise be expected.

To summarize then, when heavy atoms are introduced into or onto an aromatic ring system, the scintillation decay time will be expected to increase, while the integrated scintillation efficiency may either increase or decrease. If the scintillation decay time is much longer than the resolving time of the electronic equipment with which the observations are made, the scintillation photons may be observed individually as separate single photoelectron pulses, so that highly anomalous counting rates may be found. Since the probability of the slow singlet-triplet transition relative to that for radiationless processes is strongly influenced by vibrational

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[175] J. R. Platt, J. Opt. Soc. Am. **43**, 252–257 (1953).
[176] J. R. Platt, J. Chem. Phys. **19**, 101 (1951).

perturbations, the temperature coefficient of the scintillation efficiency may be very large.

The *p,p'*-dihalogenated-biphenyl series illustrates the points discussed above very well. Substituting a light atom, fluorine, for each *para* hydrogen atom of biphenyl has relatively little effect on the scintillation or fluorescence properties. The fifty percent drop in scintillation efficiency observed may be, but is not obviously, due to the introduction of a slight amount of singlet-triplet character into the biphenyl emission processes. With the introduction of two chlorine atoms into the para positions, singlet-triplet character is clearly introduced. The apparent counting rate has become very large, the integrated scintillation efficiency has increased sharply, and the temperature coefficient $-\alpha$ has become large. Replacement of the chlorine atoms by bromine atoms has relatively little effect, aside from a significant drop in the temperature coefficient which suggests that the probability of the singlet-triplet transition has appreciably increased. Introduction of two iodine atoms has profound consequences. In contrast to the preceding compounds, *p,p'*-diiodobiphenyl has a visible color, a pale greenish-yellow. The scintillation efficiency is low, the temperature coefficient very high. Apparently the iodine atoms have broken down the usual coupling enough to introduce appreciable triplet character into the ground state of the molecule, or at least have in this or some other fashion produced a highly temperature-sensitive quenching process. Similar phenomena seem to occur with tetraphenyltin.

In the case of *p,p'*-dihydroxybiphenyl, a number of factors seem to have cancelled each other out, so that the apparent scintillation efficiency is about the same as that of biphenyl. In the case of strongly colored *p,p'*-dinitrobiphenyl, the nitro groups have apparently introduced strong quinoid character into the ground state of the molecule (see Sec. II-C-9) to cause complete quenching.

Replacement of the oxygen atom in diphenylene oxide by a sulfur atom, to get dibenzothiophene, apparently introduces triplet character into the fluorescence processes and simultaneously increases the probability of the dissipative processes. The scintillation efficiency is strongly lowered, and spurious pulses are introduced. The apparent shift of the fluorescence spectrum toward the blue probably reflects a shift toward the blue of the long wavelength edge of the absorption spectrum, a shift caused by the difference in the vibrational perturbations of the singlet and triplet electronic energy levels.

Heavy atoms can make singlet-triplet transitions allowed in solutions and hence act as quenchers of fluorescence even when not present themselves in the fluorescing molecules.[176,177] The study of Colgate[178] of the effect of adding a large variety of materials to liquid scintillators bears this out quite well. On the other hand, Hanle and Schneider[179] apparently find that some chlorine containing solvents can be used successfully. Pichat *et al.*[54] have introduced up to 7–9% by weight of lead and bismuth into transparent plastic scintillators without excessive loss of scintillation efficiency, and Rosahl *et al.*[154,155] have introduced chlorine, bromine, and iodine into their compounds without strongly quenching the fluorescence.

It is not necessary to have heavy atoms in a molecule to be able to observe triplet state phenomena. The long period phosphorescences reported in Table X are more than likely in part connected with forbidden singlet-triplet transitions. Over half of the slow scintillators listed in Table II contain only atoms from the first and second rows of the periodic table.

9. Quinoid Ground States

It is known that in many series of fused-ring hydrocarbons, as one progresses to larger and larger molecules, the molecules become increasingly quinoid in nature, often with a rather abrupt transition from a basically nonquinoid nature to basically quinoid.[104] This transition can often be correlated with a shift from a colorless to a strongly colored nature. Since similar abrupt transitions are observed in fluorescence and scintillation phenomena as one progresses up a homologous series, it seems probable that these phenomena are causally related. It appears that strong quinoid character of the ground state of a molecule implies strong dissipative processes and quenching of the fluorescence and scintillation emission processes. The "rule of thumb" that strongly colored compounds are usually very poor scintillators is apparently just a corollary of this statement. Thus in Fig. 25, biphenyl, stilbene, and 1,4-diphenylbutadiene fall on the regular curve, but the strongly colored compounds 1,6-diphenylhexatriene and 1,8-diphenyloctatetraene are strongly quenched. The fluorescence of yellow acenaphthylene is probably suppressed for similar reasons. The apparent scintillation efficiency of golden-yellow perylene may be low due to "quinoid" quenching processes, or merely due to the inefficiency with which its yellow fluorescence radiation is detected by the photomultiplier used. The pale yellow compound fluoranthene is a definite exception to the rule that colored compounds are poor scintillators.

10. Acetylenic Bonds

In view of the somewhat controversial nature of the experimental data for diphenylacetylene (see Sec. I-E), it is rather hazardous to attempt to construct any extensive theory explaining the behavior of this material. However, writing out a few quinoid structures for this molecule soon shows that any such structure in-

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[177] M. Kasha, J. Chem. Phys. **20**, 71–74 (1952).

[178] S. A. Colgate, Rev. Sci. Instr. **22**, 346 (1951).

[179] W. Hanle and H. Schneider, Z. Naturforsch. **6A**, 290–293 (1951).

volving both benzene rings contains three cumulated double bonds in the chain linking the rings. Such a structure is electronically less stable than the type of conjugated structure shown by stilbene. Thus it does not seem unreasonable that diphenyl acetylene should be a poorer scintillator than stilbene. The poor scintillation properties found[180] and predicted (see Sec. II-C-13) for diphenyldiacetylene, which would have five cumulated double bonds in any extended quinoid structure, would appear to confirm this interpretation.

11. Bond Densities and Bound Valences

The bond densities and bound valences defined and calculated by Scherr[181] can be used to provide additional insight into the behavior of some of the Kekule hydrocarbons.

The "bound valence" of a carbon atom in an aromatic hydrocarbon is essentially a measure of the π-electron density on or about that atom. The bound valence of a carbon atom in benzene is 2.000; of an α atom in naphthalene, 1.873; of a β atom in naphthalene, 2.015; of a "joint" or linking atom in biphenyl, 2.215; of a joint atom in a benzene ring in stilbene, 2.350. The bound valences of joint atoms (i.e., those bonded to three other carbon atoms) are normally about 2.3. The joint atoms on the naphthalene rings in the binaphthyls and the dinaphthylethylenes can be expected to have about this value.

From an inspection of the values quoted above, it seems plausible that two naphthalene residues should unite to form β,β'-binaphthyl with but little change in the energy level structure of the combined molecule relative to that of two separate naphthalene molecules, while union at the α position requires considerably greater readjustment in the energy level structures. This interpretation agrees well with the tendency of β,β'-binaphthyl to display about the same scintillation behavior as naphthalene, with α,α'-binaphthyl being quite different, and generally speaking, much better. For the dinaphthylethylenes the readjustment will be more profound than for the dinaphthyls, for either α or β linking, but should still be less for β than for α. This is consistent with the greater resonance interactions implied by the scintillation efficiency data for di-(α-naphthyl)-ethylene than for the di-(β-naphthyl) compound. (See also the discussion in Sec. II-D.)

When two naphthalene residues are joined at both α positions to give a perylene molecule, it is not surprising on the basis of the considerations of the previous paragraphs that very profound changes should occur. As evidence that a "strained" situation exists in this case, the joint α atoms in perylene are calculated[181] to have bound valences of only 2.111, appreciably less than the normal values for joint atoms.

Consideration of these bound valences can also help justify the "structural" factors used in Sec. II-C-2 above. For example, since the bound valence of a *para* carbon atom in biphenyl is 1.998, it seems reasonable that the structural factor for the biphenylyl group should be intermediate between those for the two naphthyl groups and much closer to that of the β-naphthyl group.

The "bond density" is a measure of the π-electron density in the region of a given bond. It is 1.000 for the benzene bonds, 0.515 for the linking bond in biphenyl, 0.602 for the "linking" bond in phenanthrene (the one joining the two end rings), 0.676 for the corresponding bond in pyrene, 0.575 for the ring-linking bonds in triphenylene, 0.683 for the other central bonds in triphenylene, 0.560 for the bonds linking the two naphthalene residues in perylene, 0.634 and 0.603, respectively, for the "interior," cross-linking bonds in naphthalene and anthracene, and 0.682 for the bonds linking the phenyl groups with the ethylene nucleus in stilbene. The non-cross-linking bonds in these molecules have bond densities in the range 0.75–1.2. The point of this recitation of numbers is to demonstrate that many bonds usually thought of as single and nonaromatic have π-electron densities equal to or not much less than other bonds usually thought of as fully aromatic. A further conclusion is that these bond density values support the use of such concepts as regarding phenanthrene, fluorene, carbazole, etc. as "bridged" biphenyls, regarding triphenylene as built up from three benzene rings, and so forth.

12. Prediction of Scintillation Efficiency of Crystals of Unexamined Compounds

In a previous report[4] predictions were made that quinquephenyl should show an average pulse height of the order of 150 relative to anthracene=100 at 30°C, and that sexiphenyl should have one in the region 200–250. These values were obtained by a combination of the results of several methods of rough numerical extrapolation of the data for biphenyl, terphenyl, and quaterphenyl. The known lack of color as solids and the known solution absorption spectra suggest that the dissipative processes associated with the higher, colored members of other homologous series are not yet present in these compounds, and thus lend credibility to these predictions.

Computations made following the procedure of Sec. II-C-2 above suggest that the earlier predictions were conservative; the parameter values obtained correspond on a linear extrapolation of the line in Fig. 25 to scintillation efficiencies in the neighborhood of 260 and 600 for quinquephenyl and sexiphenyl, respectively. However, in evaluating these predictions and those

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[180] Private communication from Professor W. S. Koski, Johns Hopkins University, and some preliminary experiments by the present authors.

[181] C. W. Scherr, J. Chem. Phys. 21, 1582–1596 (1953).

which follow, it must be kept in mind that the linear extrapolation may not be valid. Harrison's data[32] on the energy expended per electron and Birks' evaluation (see reference 2, p. 98) of these figures as well as Birks' figures for the over-all quenching factor in massive anthracene crystals imply that anthracene is within a factor of about 2.5 of the ultimate limiting efficiency of organic scintillators. If this be so, then the line of Fig. 25 must curve upward and approach asymptotically a line corresponding to a scintillation efficiency of about 250. In this case the original predictions for the higher parapolyphenyls are probably most nearly correct.

An extensive effort was made to have the compounds quinquephenyl and sexiphenyl prepared for examination of their scintillation behavior. However, it was not possible to prepare enough of either material in a high enough purity for testing. Not only are the syntheses difficult and inefficient, but the materials are very difficult to handle in any purification or crystal growing processes due to their high melting points and extremely low solubilities in any solvents at room temperature. Normal octadecane ($C_{18}H_{38}$), which boils at 317°C, was used in the absorption purification at that temperature of the end product of one of the syntheses attempted. While it would be very interesting to have experimental data on these compounds, the experimental difficulties in preparing and handling them are by no means negligible.

It was also predicted in the previous report[4] (from the behavior of biphenyl, stilbene, and tetraphenylethylene) that the higher di-aryl-ethylenes should be good scintillators, with the thought being implied that they might possibly be better than anthracene. This prediction has been verified with the di-naphthylethylenes and di-(*p*-biphenylyl)-ethylene. Another compound of closely related structure, 1,1,4,4-tetraphenylbutadiene, has been reported to be a very effective scintillator in plastic or liquid solutions.[54–56,182] It is probable that still other effective scintillators can be found in this group of compounds, but it is unlikely that any will be anthracene derivatives or will have more than two double bonds, since in either case the fluorescence will probably be quenched: diphenylhexatriene is a poor scintillator as a crystalline solid, and dianthranyl is known to be a yellowish substance.

Scintillation efficiencies computed by the method of Sec. II-C-2 and the curve of Fig. 25 are listed in Fig. 26 together with the structural formulas of the compounds involved. The interpolated values are probably of greater validity than the extrapolated ones (see the discussion in the second paragraph of this section). Quite possibly all the higher values should be rounded off to values below 250, to fit some sort of curve asymptotically approaching the value 250.

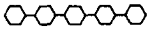
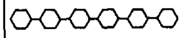
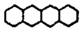
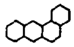
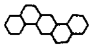
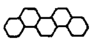
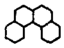
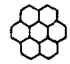
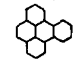
SUBSTANCE	STRUCTURE	COMPUTED SCINTILLATION EFFICIENCY (ϵ_{30})
Quinquephenyl		260
Sexiphenyl		600
Naphthacene		(540)
1,2-Benzanthracene		120
1,2,5,6-Dibenzanthracene		225
Picene		120
3,4-Benzophenanthrene		35
Coronene		400
Benzo[ghi] perylene		200
Benzo [e] pyrene		40

Fig. 26. Computed scintillation efficiencies. Note: Since there may be a natural upper limit on the scintillation efficiency, at about 250, the higher values in this table may have to be modified accordingly.

Naphthacene has been computed to possess an (extrapolated) scintillation efficiency of 540. Experimentally, it is known to be an efficiently fluorescing material in dilute liquid or solid solution. However, the pure, orange-yellow crystals show almost no fluorescence under ultraviolet irradiations. A quantity of naphthacene was purified and an attempt was made to grow suitable scintillation crystals. The molten material charred so that the crystalline masses that were obtained were of extremely low quality; molten naphthacene appears to be thermally unstable. No scintillation response could be detected from the samples which were prepared. In any case, quite independent of the poor character of these samples, there appear to be strong dissipative processes which quench the scintillation and photofluorescence responses of pure crystalline naphthacene (see the discussion of quinoid effects in Sec. II-C-9).

The commercially available carcinogenic compounds 1,2-benzanthracene and 1,2,5,6-dibenzanthracene were for several reasons not studied. They are white solids with medium high melting points (158–59° and 262°, respectively).[104] Both can therefore be expected to be normal, relatively good scintillators. The computed scintillation efficiencies are 120 and 225, respectively.

The compound coronene forms pale yellow needles of mp 438–440°C.[104] The material is expensive and not readily available in this country. Computation yields a scintillation efficiency value of 400. The similar compound benzo[ghi]perylene forms pale yellow-green plates (mp 273°C)[104] and is computed to have a scintillation efficiency of the order of 200. From the reported crystal colors, absorption spectra, and fluorescence

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[182] L. Pichat and Y. Koechlin, J. Chim. Phys. 48, 225 (1951).

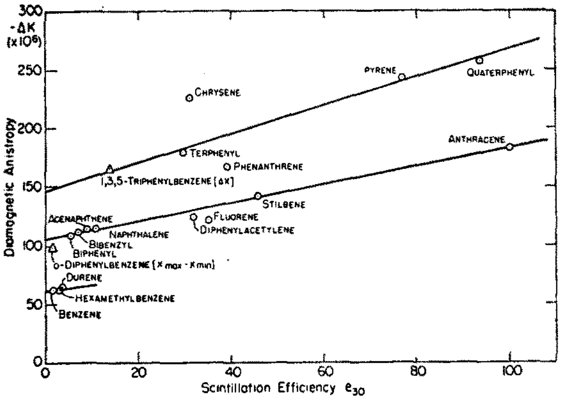
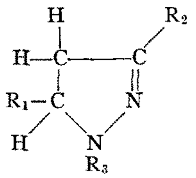


FIG. 27. Diamagnetic anisotropies *versus* scintillation efficiencies. $\Delta K = K_3 - (K_1 + K_2)/2$, where K_3 is the component of the molecular diamagnetic susceptibility perpendicular to the plane of the molecule, and K_1 and K_2 are the components lying in that plane. The χ values refer to crystal susceptibilities. Both K and χ values are in cgs units.

properties, it appears probable that both compounds would be normal scintillators and might therefore be expected to possess scintillation efficiencies of the magnitude predicted. This statement also applies to picene, 3,4-benzophenanthrene, and benzo[e]perylene; however, only the first is of any particular potential interest, and the experimental difficulties experienced with chrysene do not encourage interest here.

Aside from the polycyclic hydrocarbons or the multiaryl-polyene series, there appear to be few possibilities for new good scintillators, except in the field of compounds containing five-membered heterocyclic rings, a field which has been ably pioneered by F. N. Hayes[127] and Rosahl *et al.*[154,155] In the sequence of compounds studied by the latter workers the central ring is the five-membered pyrazoline ring, and the aromatic substituents were introduced in three places:



Some of these compounds could be very useful scintillators. Kirkbride's work[183] with borazole suggests some interesting possibilities for pseudo-organic scintillators.

13. *Scintillation Efficiencies and Molecular Diamagnetic Anisotropies*

Partial confirmation of the general picture presented in the preceding sections—the correlation of the scintillation efficiency with the effective electron mobility in aromatic molecules—can be had by comparing the scintillation efficiency with molecular diamagnetic anisotropy values computed from data in the literature.[167,184–189] Inasmuch as it is well established that molecular diamagnetic susceptibilities are directly connected with equivalent molecular electronic current loops, or with the mobility of the electrons in a molecule,[157,190–194] there should if the previous discussions are valid be some correlation between the diamagnetic susceptibilities of a molecule and its scintillation efficiency.[42,195] This correlation is shown in Fig. 27 for all of the compounds for which data could be found. The diamagnetic anisotropy ΔK is the difference between the susceptibility in a direction normal to the plane of the molecule and the average of the two in the plane of the molecule. The two latter susceptibilities are due primarily to electronic current loops of atomic dimensions (those associated with the σ electrons and those in inner shells), while the former will have contributions from both these atomic current loops and π-electron molecular ring loops. ΔK is therefore a measure of the π-electron mobility alone.

ΔK has been plotted in Figs. 27 and 28 against the scintillation efficiency ϵ and the integrated fluorescence intensity F. There is a fairly good correlation in each case. There appear to be three separate well-defined correlation lines in Fig. 27, but this may be illusory and the true correlation may be similar to that of Fig. 28.

Chrysene is anomalous in both Figs. 25 and 27. It looks as though the scintillation response measured for this substance is much smaller than the true value, which appears to be about 65. It seems more likely that poor crystals are responsible for this than impurities. Phenanthrene is anomalous for unknown reasons in Fig. 27; the diamagnetic data could possibly be in error.

ΔK data are available for diphenyl diacetylene[196] and azobenzene.[187] The value for the former (114.3) implies a scintillation efficiency of about 12, which is much lower than that of diphenylacetylene, in good agreement with the statements of Sec. II-C-10 above. ΔK for azobenzene has a value of 128.2, corresponding to an ϵ value of 30. Azobenzene is very highly colored and is known to give no scintillation response (see Table

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[183] J. Kirkbride, Nature **171**, 564 (1953).

[184] Krishnan, Guha, and Banerjee, Phil. Trans. Roy. Soc. (London) **A231**, 235 (1933).

[185] K. S. Krishnan and S. Banerjee, Phil. Trans. Roy. Soc. (London) **A234**, 265 (1935).

[186] K. Lonsdale and K. S. Krishnan, Proc. Roy. Soc. (London) **A156**, 597 (1936).

[187] K. Lonsdale, J. Chem. Soc. 364 (1938).

[188] J. Shanker and M. Praesad, Current Sci. (India) **6**, 554 (1938).

[189] K. Lonsdale, Proc. Roy. Soc. (London) **A171**, 541 (1939).

[190] L. Pauling, J. Chem. Phys. **4**, 673 (1936).

[191] K. Lonsdale, Proc. Roy. Soc. (London) **A159**, 149 (1937).

[192] R. McWeeny, Proc. Phys. Soc. (London) **A64**, 261–275 (1951).

[193] R. McWeeny, Proc. Phys. Soc. (London) **A64**, 921–930 (1951).

[194] R. McWeeny, Proc. Phys. Soc. (London) **A65**, 839–844 (1952).

[195] The existence of such a rough correlation was first pointed out to the authors in late 1948 or early 1949 by an individual from Harvard University who is, at this late date, unfortunately anonymous.

[196] K. Lonsdale, Nature **145**, 148–149 (1940).

VII). If a quinoid or other quenching ground state is responsible for this lack of response, there could be a high electron mobility and a high diamagnetic anisotropy and still be immeasurably little scintillation response.

D. Scintillation Decay Times

Very few significant statements of the sort pertinent to this part of the paper can be made about the scintillation decay times. No distinct correlations can be seen between the decay time and the scintillation efficiency ϵ_{30}, the average integrated fluorescence intensity F, the temperature coefficient of the scintillation efficiency α, the wavelength of the peak of the fluorescence spectrum λ_{peak}, or the primary photon production efficiency ϵ/F. There may be a slight inverse correlation between the decay time and the scintillation efficiency, but it is not very clear-cut. There is a fairly well defined inverse correlation between the decay times and the intervals $\Delta\lambda_{\min}$; here again (see Sec. II-B-2)) the correlation is inverse to the anticipated relationship, since a large overlap interval presumably should imply a relatively large amount of cascaded fluorescence radiation and therefore a long decay time.

At least some rudimentary correlations can be made between the decay time values and molecular structures.

Naphthalene and β,β'-binaphthyl have essentially the same decay time, while that for α,α'-binaphthyl is apparently so much longer that the instantaneous pulse intensities were so low that the pulses were not detected when the decay time measurements were attempted. This is consistent with the scintillation efficiency values and other independent data (see Sec. II-C-11) which imply that the interaction between the two naphthyl groups is much greater in the α,α'-compound than in the other one. Indeed, for β,β'-binaphthyl both the scintillation efficiency data and the scintillation decay times suggest that the two naphthyl groups behave essentially like independent naphthalene molecules. The scintillation efficiency and decay time data for the di-naphthylethylenes are also consistent with this picture. (This apparent much greater interaction of α-naphthyl groups with each other than for β-naphthyl groups is rather curious from one point of view, since there should be much more steric strain in α,α'-binaphthyl opposing the resonance conjugation than in β,β'-binaphthyl.)

M-diphenylbenzene and 1,3,5-triphenylbenzene have experimentally identical decay times, a fact which is in agreement with the close basic similarity of these materials. It is probable that biphenyl would give a similar value (see the discussion of Sec. II-C-2).

The bridged biphenyls with resonance interaction through the bridge—phenanthrene, carbazole, and diphenylene oxide—have similar decay times, while fluorene, without strong interactions of this sort, has about the same decay time as *m*-diphenylbenzene 1,3,5-triphenylbenzene, and presumably, therefore, biphenyl.

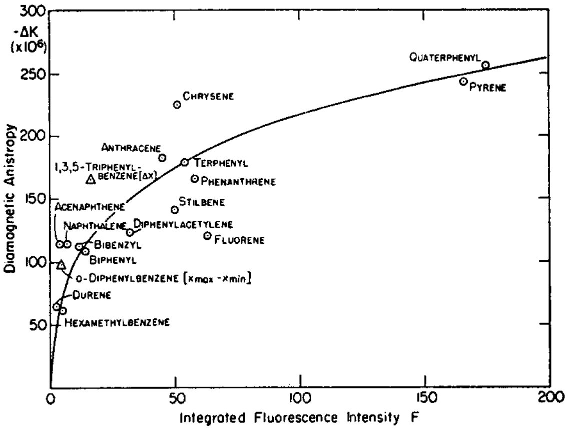

FIG. 28. Diamagnetic anisotropies *versus* integrated fluorescence intensities. K and χ have the same meanings as for Fig. 27.

There appears to be a regular decrease in decay time in going from biphenyl to terphenyl to quaterphenyl. It seems likely that quinquephenyl and sexiphenyl will have even shorter decay times.

SUMMARY

The scintillation and photofluorescence behavior of a large group of organic scintillators, for the most part in a pure crystalline state, have been studied and analyzed.

The utility of Birks' photon-cascade theory of the scintillation process has been demonstrated.

The theory of the correlation of scintillation behavior and molecular structure has been placed on a qualitatively firm basis, and semiquantitative computations have been made for the behavior of as yet untested materials.

The best crystalline organic scintillators are essentially colorless substances of high melting point possessing molecules of simple structure and low atomic number in which there is extensive resonance conjugation of rings, ethylenic double bonds, and other groups to give extended, rigidly interlocked systems.

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