Acknowledgments. This work was supported by a grant from the National Science Foundation. Computer time was provided by the Office of General Research, The University of Georgia. The authors gratefully acknowledge illuminating conversations and correspondences with colleagues at the University of Georgia, especially G. S. Handler, P. L. Olympia, Jr., and E. G. Larson, and with workers in CIDNP, particularly F. J. Adrian, G. L. Closs, H. Fischer, S. H. Glarum, and R. Lawler, several of whom provided us with unpublished manuscripts referred to in footnotes to this paper.

ketone in CCl_4), and that they have been able to obtain a good fit for the observed variation by means of their calculations. We are grateful to Dr. Kaptein for providing us with a copy of his thesis, which represents a magnificent body of work.

(25) NOTE ADDED IN PROOF. Fischer and Lehnig[14a] have determined the esr parameters of $Cl_2CH\cdot$ as $g = 2.00829 \pm 0.00010$ and $A = 16.79 \pm 0.05$ G. See H. Fischer and M. Lehnig, *J. Phys. Chem.*, **75**, 3410 1971); this paper reports the work cited in our ref 14a.

Fluorescence of Aromatic Benzoxazole Derivatives

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Abstract: Absorption spectra, emission spectra, and fluorescence yields were measured for a group of benzoxazolyl-substituted aromatic hydrocarbons. From the data, radiative and nonradiative lifetimes of the first-excited singlet state are calculated and compared to those of the unsubstituted molecules. It is found that benzoxazolyl groups enhance fluorescence by increasing the rate of the radiative process without too much affecting the probability of the nonradiative transitions. Stilbene and tolan are exceptions in this respect; the introduction of benzoxazolyl groups in these molecules considerably decreases the rate of nonradiative deactivation. This behavior is connected with the configurational changes which occur in stilbene and in tolan on optical excitation. From flash spectrometric experiments on fluorescent benzoxazole derivatives in polystyrene matrices it can be inferred that the nonradiative deactivation of the excited singlet state of these molecules proceeds mainly by intersystem crossing to the triplet; internal conversion to the ground state is of minor importance. Direct spin–orbit coupling between the excited $\pi\pi^*$ singlet state and a $n\pi^*$ triplet state leads to fast intersystem crossing in benzoxazole and to a short nonradiative lifetime (0.8 nsec). In the composite heteroaromatic fluorescers direct spin–orbit coupling is eliminated by a change in the relative positions of the $\pi\pi^*$ and the $n\pi^*$ levels. Intersystem crossing proceeds here by spin–vibronic coupling, an effect similar to "intensity borrowing" in radiative transitions.

With the advent of fluorescent whitening agents, wavelength converters, and scintillators, the synthesis of highly fluorescent compounds has gained new impetus. Currently a whole subsection of *Chemical Abstracts* is devoted to the subject.[1] The great majority of the new fluorescers are composite aromatic systems containing one or several heteroaromatic components. Some heterocycles such as furan, oxazole, oxadiazole, and thiazole recur particularly often in industrial fluorescers. They do not fluoresce themselves but have a powerful fluorescence enhancing effect when coupled to aromatic hydrocarbons or other conjugated systems.

Although this effect is responsible for the fluorescence capability of a whole class of substances, it has not attracted attention because of a lack of experimental data. The syntheses of large numbers of industrial fluorescers have been described, but their spectra are rarely given and quantum yields of fluorescence are reported for only a few.[2] It seemed therefore of interest to investigate a representative group of composite heteroaromatics in some detail. We have chosen a series of aromatic derivatives of benzoxazole. The compounds listed in Table I were prepared as described in the Experimental Section, their absorption and emission spectra were measured, and their fluorescence efficiencies determined. The rate (k_R) of the radiative depopulation of the first-excited singlet state of the molecules was calculated from the integrated absorption spectra by the method of Förster.[3] The sum of the rates of the nonradiative processes (k_N) was obtained from the radiative rate and the fluorescence yield (φ_f) by the relation

$$\varphi_f = k_R/(k_R + k_N) \qquad (1)$$

We have compared the rates of the radiative and the nonradiative transitions in the composite fluorescers with the corresponding rates in the parent hydrocarbons and in benzoxazole, and we have attempted a qualitative interpretation of the effect of structure on these rates. The results are reported in the present communication.

Results and Discussion

Experimental results relating to the singlet state of the fluorescent benzoxazole derivatives are collected in Table I. Apart from a reference number and the structural formula, Table I indicates the wavelength of the 0,0 band and the wavelength of maximum

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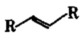
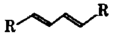
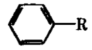
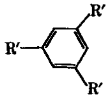
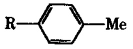
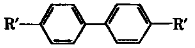
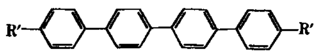
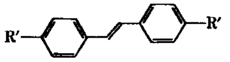
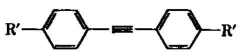
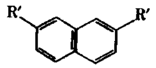
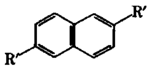
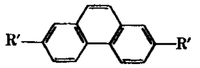
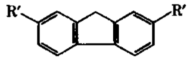
(1) See section 40 of *Chemical Abstracts*, "Fluorescent Whitening Agents."

(2) I. D. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965.

(3) Th. Förster, "Fluoreszenz Organischer Verbindungen," Göttingen, 1951.

Table I. Absorption and Fluorescence Data of Benzoxazolyl-Substituted Hydrocarbons

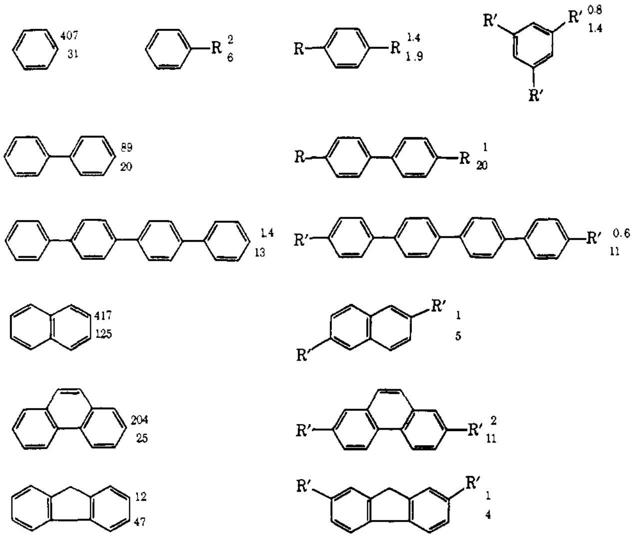
Ref no.	Compd[a]	Solvent	Absorption characteristics: 0,0 band, nm	Absorption characteristics: λ_{max}, nm	Absorption characteristics: ϵ_{max}, $\times 10^{-3}$	Emission characteristics[b]: Principal maxima, nm	Emission characteristics[b]: Fluor yield, ϕ_f	Radiative lifetime, τ_R (nsec)	Nonradiative lifetime, τ_N (nsec)
I	R—H	Cyclohexane	277	277	3.59	280 (s), *286*, 293 (s)	⩽0.05	16	⩽0.8
II	R—Me	Cyclohexane	277	277	4.64	279 (s), *286*, 294	⩽0.05	13	⩽0.7
III	R′—R′	Chloroform	352	335	31.7	363, *382*, 401	0.79	2.1	7.9
IV		Chloroform	374	354	42.2	394 (s), *413*	0.76	1.8	5.8
V		Chloroform	394	373	49.1	416 (s), *436*, 460	0.58	1.9	2.7
VI		Cyclohexane	314	300	26.9	316, *330*, 348	0.78	1.8	6.3
VII		Chloroform	360	341	53.3	377, *397*, 417	0.90	1.4	19
VIII		Cyclohexane	334	318	71.5	343 (s), *300*, 376	0.65	0.8	1.4
IX		Cyclohexane	316	302	28.0	318, *400*, 423	0.70	1.7	4.3
X		Cyclohexane	Not resolved	339	65.0	380, *400*, 423	0.96	1.1	20
		Chloroform	Not resolved	344	56.9	*393*, 413, 433	1.01	1.1	>20
XI		Cyclohexane	Not resolved	339	125.0	*390*, 410	0.96	0.6	13
		Chloroform	Not resolved	343	97.9	*402*, 420	0.99	0.9	>20
XII		Cyclohexane	396	375	99.7	408, *433*, 461	0.72	0.8	2.0
		Chloroform	395 (s)	377	83.2	413, *438*, 465	0.79	1.1	4.2
XIII		Cyclohexane	379	349	71.3	*383*, 402	0.90	0.9	10
		Chloroform	379	356	69.7	*402*, 420	0.93	1.1	14
XIV		Cyclohexane	368	324	68.7	*368*, 390, 411	0.42		
		Chloroform	369	326	62.4	*379*, 398	0.51		
XV		Cyclohexane	374	353	64.5	378, *398*, 421	0.79	1.4	5.2
		Chloroform	376	356	63.8	391, *412*, 437 (s)	0.87	1.4	9.5
XVI		Cyclohexane	371	352	44.8	379, *400*, 424	0.86	1.8	11
		Chloroform	376	356	36.5	385, *407*, 430	0.93	2.2	29
XVII		Cyclohexane	378	358	98.5	382, *405*, 430	0.82	1.0	4.4
		Chloroform	380	360	84.2	390, *412*, 446	0.87	1.1	7.4

[a] R = benzoxazol-2-yl; R′ = 5,7-di-*tert*-pentylbenzoxazol-2-yl. [b] The symbol (s) after a wavelength value indicates a shoulder. The italicized wavelength in the emission column is the wavelength of maximum emission intensity.

extinction of the absorption spectrum, the extinction at this maximum, the principal vibrational maxima of the emission spectrum, and the fluorescence yield. In keeping with common practice the rates of the radiative and nonradiative processes originating in the first-excited singlet state are characterized by lifetimes (reciprocal rate constants) in units of nanoseconds. In some cases *tert*-pentyl groups have been introduced into the 5 and 7 positions of the benzoxazole nucleus to make the compounds more soluble, and this is indicated in Table I (R′ instead of R). The presence of these alkyl groups does not affect the fluorescence yield of the molecules appreciably.

The lifetimes of the composite fluorescers are compared with those of the unsubstituted hydrocarbons in Table II. It can be seen immediately that benzoxazolyl groups enhance the fluorescence yield of the molecule by increasing the rate of the radiative transition, without affecting the rates of the nonradiative processes to the same degree. Only two exceptions to this rule have been observed, stilbene and tolan, and these are discussed at the end of the paper.

Table II. Effect of Benzoxazolyl Groups on the Lifetimes of the First-Excited Singlet State of Some Aromatic Hydrocarbons[a]



[a] Upper number, radiative lifetime in nanoseconds; lower number, nonradiative lifetime in nanoseconds.

Radiative Transition. In some systems the increase in the rate of the radiative transition on introducing benzoxazolyl groups is quite dramatic: in benzene and in phenanthrene the radiative rate increases by a factor of 200, in biphenyl by a factor of 100, and in naphthalene by a factor of 400. This effect is well understood and requires little comment (see, *e.g.*, Murrell[4]). The benzoxazole nucleus extends the π system of the hydrocarbon and provides room for a larger charge displacement (transition dipole moment) in absorption and in emission. This increases the radiative transition probability and hence decreases the radiative lifetime of the excited state. In short, the heteroaromatic component acts as a chromophore.

The chromophoric effect of the benzoxazolyl group completely overshadows any symmetry considerations. For example, 2-phenylbenzoxazole (VI) has a radiative lifetime of 1.8 nsec, 1,4-dibenzoxazolylbenzene (VII) a radiative lifetime of 1.4 nsec, and 1,3,5-tribenzoxazolylbenzene (VIII) a radiative lifetime of 0.8 nsec. The rate of the radiative transition is clearly more affected by the number than by the positions of the heteroaromatic components. In this respect benzoxazole behaves as a mesomeric substituent.[5]

While the chromophoric effect of benzoxazole is considerable in small aromatic systems, it is less important in large hydrocarbons which already have short radiative lifetimes. For example, in quaterphenyl (XI) the radiative lifetime changes on substitution only by a factor of two, from 1.4 to 0.6 nsec. Here the natural limit of the rate of a spontaneous radiative transition has been reached. It will be recalled that the radiative rate is linked to the oscillator strength (f) of a transition by the relation

$$k_R \equiv 1/\tau_R = 0.67\omega^2 f \qquad (2)$$

where ω is the frequency (wave number) of emission. If the ideal radiator has an oscillator strength of unity, its radiative lifetime for emission at 400 nm is about 1 nsec. The radiative lifetimes of all our strong emitters converge to this limit.

Similar considerations are not limited to benzoxazole. Quite generally, heteroaromatic groups enhance the efficiency of the radiative process in the composite system, and it is not difficult to devise structures with radiative rates close to the natural limit of 10^9 sec^{-1}. Whether such potentially fast radiators will fluoresce or not depends then entirely on the rates of the nonradiative processes which depopulate the excited singlet state.

Nonradiative Transitions. Neglecting small variations between individual molecules it may be concluded from the data in Table II that in aromatic systems nonradiative transitions are not much affected by the presence of the benzoxazole nucleus. With one exception the nonradiative lifetime changes by less than a factor of ten when benzoxazolyl groups are introduced into the molecule.

An interpretation of this behavior must depend on the nature of the processes involved. We recall that the nonradiative deactivation of the excited singlet state can take at least two different routes: intersystem crossing from the singlet excited state S_1* to a triplet state T*, and the direct nonradiative return from S_1* to the ground state (internal conversion). We have tried to assess the relative importance of these two processes in fluorescent benzoxazole derivatives by estimating triplet yields with a flash-spectrometric technique. Five of the fluorescers in Table I were incorporated at low concentration in polystyrene matrices and exposed to an argon flash of 130 J and about 5-μsec duration. Strong transient absorptions were observed in the region between 400 and 500 nm. From the location and general form of their spectra the transients were assigned to the triplet states of the fluorescers. Also, the initial intensity of the transients did not decrease on repeated flashing (no irreversible photoreaction) and the signals decayed accurately with first-order kinetics (time constants of about 100 sec^{-1}).

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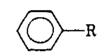
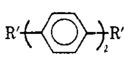
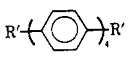
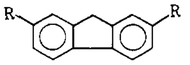
(4) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen, London, 1963, p 211.

(5) A. R. Horrocks, T. Medinger, and F. Wilkinson, *Photochem. Photobiol.*, 6, 21 (1967), and references cited therein.

Triplet yields were estimated from the initial intensity of the transient signal at the maximum of the absorption band by calibrating the quantum output of the flash lamp (see Experimental Section) and assuming a common value of 50,000 for the extinction coefficient of the triplet–triplet transition. Results obtained in this way (see Table III) are of necessity crude. Nevertheless, the fact that the triplet yield and fluorescence yield complement each other to unity is an indication that in the aromatic benzoxazole derivatives internal conversion is not an important process.

Table III. Triplet Yields and Lifetimes from Flash Experiments

		φ_T	$\varphi_T + \varphi_F$	τ_T, 10^{-3} sec
III	R′—R′	0.21 ± 0.07	1.00	32
VI		0.28 ± 0.10	1.06	41
X		0.03 ± 0.01	1.01	52
XI		0.03 ± 0.01	0.99	55
XVII		0.20 ± 0.07	1.07	42

This finding agrees with general experience. Internal conversion in polynuclear aromatic systems is usually too slow to compete successfully with the radiative process and with intersystem crossing.[5] Also, the rate of the nonradiative transition $S_1^*(0) \rightarrow S_0(v)$ is determined essentially by its Frank–Condon factor which, for the large energy gap E_{S_1}–E_{S_0}, is dominated by high frequency CH modes.[6,7] These are little affected by the presence of heteroatoms, and for this reason the rate of internal conversion in heteroaromatics is not expected to be very different from that in similar homoaromatic systems. We conclude tentatively that the nonradiative lifetimes in Table II are mainly determined by the rate of the intersystem crossing process $S_1^* \rightarrow T^*$.

Intersystem crossing is brought about by spin–orbit coupling, the interaction between two molecular states of different multiplicity being determined by the matrix of the spin–orbit operator. El Sayed has shown[8] that for reasons of local symmetry this matrix vanishes to a good approximation between states of the same orbital character. Direct spin–orbit coupling between aromatic singlet and triplet states of ππ* character is therefore weak; it is stronger between the ππ* and the nπ* states of heteroaromatics.

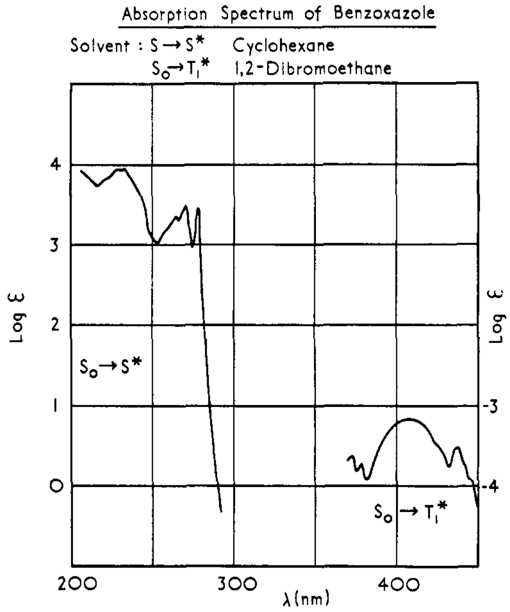


Figure 1. Singlet–singlet and singlet–triplet absorption spectrum of benzoxazole. Solvent: cyclohexane for $S_0 \rightarrow S^*$, 1,2-dibromoethane for $S_0 \rightarrow T_1^*$.

Let us apply El Sayed's rule to the case of benzoxazole. It can be seen from the spectrum in Figure 1 that the absorption band corresponding to the transition $S_0 \rightarrow S_1^*$ has a high extinction coefficient, indicating that in benzoxazole the first-excited singlet state has ππ* character. Its energy relative to the ground state is 130 kcal. An nπ* singlet state corresponding to promotion of a nonbonding electron from nitrogen into an antibonding π* orbital lies not more than a few kilocalories above the level of $S_{\pi\pi^*}$. This follows from a comparison with the spectrum of quinoline where the singlet ππ* and nπ* states are so close together that their order is inverted by a change of solvent.[9] The lowest (ππ*) triplet state of benzoxazole has been located by heavy-atom-perturbed absorption measurements at 64 kcal (see also ref 10). Heteroaromatic nπ* states have singlet–triplet splittings typical of the order of 5–8 kcal; an nπ* triplet state is therefore expected at about 97 kcal, that is, *below* the level of $S_{\pi\pi^*}$. In such a case direct spin-orbit coupling between $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ will lead to fast intersystem crossing. In agreement with this the nonradiative lifetime of benzoxazole is short (0.8 nsec) and the substance is a poor fluorescer in solution ($\varphi_f < 0.05$). Quinoline[9] behaves in very much the same way ($\varphi_f = 0.02$).

The situation is different when two benzoxazole groups are joined together to form 2,2′-bisbenzoxazolyl (III). Here the $S_{\pi\pi^*}$ level is lowered from 103 to 81 kcal (see Figure 2) and the $S_{\pi\pi^*}$ level is expected to decrease to about 95 kcal. With a singlet–triplet splitting (nπ*) of 5–8 kcal, the nπ* triplet state lies now *above* the $S_{\pi\pi^*}$ level, direct spin–orbit coupling is ruled out, and intersystem crossing should be comparatively slow. The nonradiative lifetime of III is indeed an order of magnitude longer than that of benzoxazole (I) or 2-methylbenzoxazole (II), and the fluorescence yield is increased from less than 0.05 to 0.79. The vinylogs of bisbenzoxazolyl, compounds IV and V, show a similar behavior. In fact, direct spin-orbit coupling is eliminated in all the composite fluorescers of Table I because the nπ* triplet states of the molecules are located well above the level of the lowest ππ* singlet excited state. That, ultimately, is the reason why the nonfluorescent

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(6) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); **38**, 1187 (1963).

(7) B. R. Henry and M. Kasha, *Annu. Rev. Phys. Chem.*, **19**, 161 (1968).

(8) M. A. El Sayed, *J. Chem. Phys.*, **38**, 2834 (1963).

(9) M. A. El Sayed and M. Kasha, *Spectrochim. Acta*, **15**, 758 (1960).

(10) H. D. Scharf, private communication quoted by W. Metzner and D. Wendisch, *Justus Liebigs Ann. Chem.*, **730**, 111 (1969).

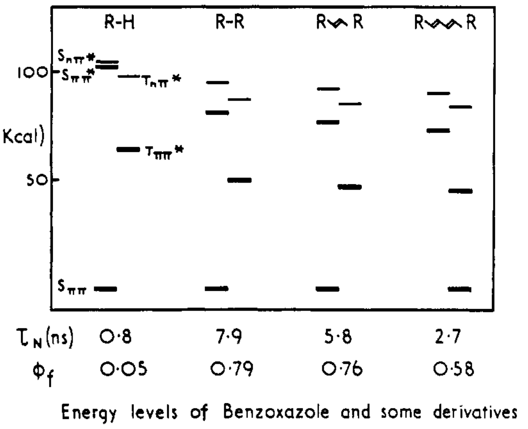


Figure 2. Energy levels of singlet and triplet excited states of benzoxazole and 2,2′-bisbenzoxazolyl and its vinylogs IV and V. τ_N is the nonradiative lifetime of the excited singlet state $S_{\pi\pi^*}$, φ_f the fluorescence yield.

benzoxazole nucleus is able to enhance the fluorescence yield of aromatic systems.

In large heteroaromatics, as indeed in aromatic hydrocarbons where direct spin–orbit coupling is not effective, intersystem crossing proceeds by virtue of the vibronic mixing between $\pi\pi^*$, $\sigma\pi^*$, $\pi\sigma^*$, and $n\pi^*$ states of the same multiplicity, an effect similar to "intensity borrowing" in symmetry-forbidden radiative transitions.[4] Henry and Siebrand[11] and Veeman and Van der Waals[12] have recently produced convincing evidence for such a mechanism in the phosphorescent transition of several aromatic and heteroaromatic systems. In Siebrand's formulation[13] the rate of a spin–vibronic transition of this kind depends, apart from an overall Frank–Condon factor, on terms of the form

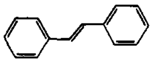
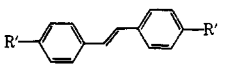
$$\frac{\langle T_{\pi\pi^*}|H_{so}|S_{n\pi^*}\rangle\langle S_{n\pi^*}|H_k|S_{\pi\pi^*}\rangle}{E_{n\pi^*} - E}$$

Here $S_{\pi\pi^*}$, etc., stand for the electronic wave functions of the states, $E_{n\pi^*}$ for their energies, H_{so} and H_k are the spin–orbit and the nuclear kinetic energy operators, and E is the energy of the crossing level (the lowest vibration level of $S_{\pi\pi^*}$). All states containing atomic orbitals orthogonal to the p_z orbitals of the aromatic π system will contribute such terms to the overall interaction matrix. In aromatic hydrocarbons the "perpendicular" levels are those of the $\sigma\pi^*$ and $\pi\sigma^*$ states with high excitation energies (200 kcal and more). Heteroaromatics have in addition lower lying $n\pi^*$ states with energy gaps of 5–40 kcal which will contribute larger terms. The smaller size of the $\sigma\pi^*$ and $\pi\sigma^*$ contributions is, however, compensated by their greater number (there are usually many more CC and CH bonds in the molecule than heteroatoms). For this reason intersystem crossing in large heteroaromatics (*i.e.*, in the absence of direct spin–orbit coupling) is not expected to be much faster than in the corresponding hydrocarbons. This agrees on the whole with the results obtained on the aromatic benzoxazole derivatives.

The physical basis for spin–vibronic coupling which induces intersystem crossing in these molecules is a transient out-of-plane deformation. Experimental conditions which restrict the freedom of motion of the system may therefore reduce the rate of intersystem crossing and have indeed been observed to enhance the fluorescence yield.[14] Equally, structural features which prevent or hinder the deformation of the aromatic plane tend to stabilize the excited singlet state against nonradiative deactivation. Lewis and Calvin[15] have noted this fact in 1939; it has since been widely exploited in the design of industrial fluorescers.

Stilbene and Tolan. Two systems do not fit the general pattern: stilbene and tolan. Here the benzoxazolyl groups are particularly successful in enhancing the fluorescence efficiency of the molecule, but they do so not by increasing the radiatve rate but by decreasing the rates of the nonradiative processes (see Table IV).

Table IV. Effect of Benzoxazolyl Groups on the Lifetime of the First-Excited Singlet State of *trans*-Stilbene and Tolan

	τ_R, nsec	τ_N, nsec
	1.6	0.1
	0.8	2
	1.4	0.01
	0.9	10

The fluorescence of stilbene originates in the excited singlet state of transoid configuration. The main competition to the radiative process comes here from the well known trans–cis isomerization[16] of stilbene which proceeds by conversion of S_1^* (trans) into a twisted configuration where the phenyl rings are perpendicular to each other.[17] In this configuration rapid internal conversion leads to a vibrationally excited ground state which may then relax into the trans or the cis isomer.[18] This mechanism accounts for the short nonradiative lifetime of singlet excited stilbene and *mutatis mutandis* for the short lifetime of stilbene triplet.[19] If nonradiative deactivation depends on a change of molecular geometry in the excited state, any factor which tends to prevent such a change will be expected to stabilize the excited state and hence lead to a longer nonradiative lifetime. The introduction of benzoxazolyl groups into stilbene has such an effect. This may be due partly to the higher resistance to rotation which the larger molecule now offers in a viscous medium, partly to a reduced incentive to rotation, the antibonding electron density located at the central ethylene bond being reduced by "dilution" in the much enlarged aromatic system. This view is supported by the effect on triplet

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lifetimes of the viscosity of the solvent[20] and by solvent and substituent effects on the quantum yield of photoisomerization in stilbene derivatives.[21]

The case of tolan is even more striking. Here the introduction of benzoxazolyl groups increases the nonradiative lifetime by a factor of 1000. It is tempting to interpret this effect by a mechanism similar to that described for stilbene. The lower excited states of acetylene are known[22,23] to have a nonlinear configuration, and the basic argument for a change in geometry on excitation (relief of repulsive orbital overlap in the excited state) is equally valid for tolan. There is evidence for a tolan "phantom triplet,"[19] *i.e.*, a triplet state accessible by energy transfer and of lower energy (51 kcal mol^{-1}) than the spectroscopic triplet described by Evans[24] (62 kcal mol^{-1}). On introduction of benzoxazolyl groups into tolan the mesomeric effect of the substituents will impart some double bond character to the links between the phenyl rings and acetylene. In the larger π system the fraction of antibonding overlap in the acetylene unit will be smaller and so presumably will be the tendency for configurational changes in the excited state. More experimental work is clearly required before the case of tolan can be properly understood, but there is little doubt that the anomalous behavior of stilbene and tolan is connected with the configurational changes which occur in these molecules on optical excitation.

Summary

In summarizing our results we note that the rates of the radiative and nonradiative processes allow a better insight into the relation between structure and fluorescence than quantum efficiency data alone. The benzoxazolyl group is seen to enhance fluorescence by increasing the rate of the radiative process without too much affecting the probabilities of the nonradiative transitions. Stilbene and tolan are exceptions in this respect; the introduction of benzoxazolyl groups in these molecules considerably decreases the rate of nonradiative deactivation. This behavior is connected with the configurational changes which occur in stilbene and in tolan on optical excitation.

In the fluorescent benzoxazole derivatives as in benzoxazole itself, the nonradiative deactivation of the excited singlet state proceeds mainly by intersystem crossing to the triplet state; internal conversion to the ground state is of minor importance. Direct spin–orbit coupling between the excited $\pi\pi^*$ singlet state and a nπ^* triplet state leads to fast intersystem crossing in benzoxazole and to a short nonradiative lifetime (0.8 nsec). In the composite heteroaromatic fluorescers direct spin–orbit coupling is eliminated by a change in the relative positions of the $\pi\pi^*$ and the nπ^* levels. Intersystem crossing proceeds here by spin–vibronic coupling, an effect similar to "intensity borrowing" in radiative transitions.

Experimental Section

Spectral Measurements. Absorption spectra were taken with a Unicam SP 800 spectrophotometer, recording on a wavelength scale. Emission spectra were recorded on a spectrofluorimeter constructed in this laboratory and similar in design to that described by Calvert and Pitts.[25] The irradiating unit was a Bausch and Lomb high intensity monochromator coupled to a Wotan XBO 150 W/1 high-pressure xenon arc. Fluorescent light from the rectangular sample cell was collimated onto the entrance slit of the analyzing monochromator (Bausch and Lomb, 500 mm, grating) and monitored by a photomultiplier (EMI Type 9558, quartz window). The photomultiplier output was fed into a "Servoscribe" chart recorder (Goertz-Electro, Austria, 2-mV full scale). The wavelength calibration of both monochromators was checked against the principal mercury lines.

The recorder trace of the emission spectrum was corrected for spectral changes in photomultiplier sensitivity and for optical losses by a procedure similar to that described by Melhuish.[26] The principal bands of the emission spectra are listed in Table I.

Fluorescence Efficiency. Following Parker and Rees,[27] the quantum yield of fluorescence was determined by comparison with a reference substance of known fluorescence yield. Quinine sulfate in 1 *N* sulfuric acid was used as standard (φ_s = 0.51).[28] Solutions of the sample and of the standard were made up from degassed solvents and their optical densities carefully matched at the wavelength of excitation. The solutions were accurately diluted to an optical density of not more than 0.1 to eliminate self-absorption. The emission spectra of sample and of standard were then recorded and the quantum yield of fluorescence of the sample was obtained as the ratio of the areas under the corrected emission curves.

We have investigated the effect of sample purity on fluorescence yield in solution. Compounds IV, VII, X, XII, and XVII were measured before and after repeated chromatography on neutral alumina plates. The results were unchanged by this operation.

We estimate the accuracy of our results at ±5%. One source of uncertainty is the matching of optical densities and hence of the intensities of absorbed radiation in sample and standard; another is the limited accuracy of the photomultiplier corrections. To check the overall reliability of the procedure we have measured a group of compounds covering a range of fluorescence yields from 0.1 to 0.9. Our results are compared with literature values given in Table V.

Table V

	Fluorescence yield
9,10-Dibromoanthracene	0.12 (0.103)[29]
Toluene	0.17 (0.17)[3]
Naphthalene	0.22 (0.23)[3]
p-Xylene	0.41 (0.40)[3]
Acridone	0.76 (0.78)[29]
p-Terphenyl	0.87 (0.94)[3]

Triplet Energies. Triplet energies were obtained where possible by phosphorescence measurements. The triplet energy of benzoxazole was obtained from heavy-atom-perturbed $S_0 \rightarrow T_1$ absorption spectra.[29] Benzoxazole was purified by chromatography and by low-temperature sublimation in a stream of nitrogen. The pure sample was mixed in a 1:1 ratio with (a) carbon tetrachloride and (b) 1,2-dibromoethane. The absorption spectra of the mixtures were taken in 10-cm quartz cells on the Unicam SP 800 spectrophotometer which had been fitted with a device allowing an up to 20-fold expansion of the absorbance scale. The singlet-to-triplet absorption was found to be significantly enhanced by the presence of the heavy-atom solvent. The total absorption spectrum of benzoxazole is shown in Figure 1.

Triplet Yield. The fluorescent compounds and the required amount of polystyrene (Styron K27, Distrene Ltd.) were dissolved in

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Table VI. Results of Lamp Calibration Experiment

	φ_T	ϵ_{TT}, l. mol^{-1} cm^{-1}	Lamp output $\bar{Q}$, einstein cm^{-2}
Triphenylene	0.95	16,500	2.70×10^{-5}
Naphthalene	0.75	45,000	1.4×10^{-5}
Phenanthrene	0.76	41,500	1.4×10^{-5}
Anthracene	0.75	75,000	1.3×10^{-5}
1,2-Benzanthracene	0.77	43,600	1.4×10^{-5}

toluene, and the viscous solutions were coated on glass and dried under nitrogen. The dry coatings were lifted from the glass supports and were mounted against the inner wall of a rectangular quartz cell. The cell was placed between two upright flash tubes dissipating together some 130 J per flash. The transient absorption of the sample was followed with a flash photolysis apparatus described earlier.[30] The absorption spectrum of the transient was scanned point by point in intervals of 5 nm.

Triplet yields φ_T were estimated from the initial value of the absorbance (D, t = 0) at the peak of the triplet–triplet transition using the expression

$$\varphi_T = D(t = 0)/\epsilon_{TT}\bar{Q}A$$

Here ϵ_{TT} is the extinction coefficient at the absorption maximum, $\bar{Q}$ the mean quantum output of the lamp over the spectral region of sample absorption, and A is the total absorption of the sample.

The absorption of the sample was obtained from its spectral transmission curve; for the extinction coefficient we have assumed a common value of 50,000. The radiative output of the lamp was determined by measuring in the same conditions the triplet signals of a group of hydrocarbons for which the triplet yield φ_T and the extinction coefficient ϵ_{T_u} are known.[31] The results of this calibration in terms of the mean number of einsteins supplied to the sample in a single flash are collected in Table VI. The constancy of the value of $\bar{Q}$ over most of the frequency range is some indication of the overall reliability of the experimental procedure.

Table VII. Preparative Details of Benzoxazole Derivatives

Compd[a]	Cyclization conditions	Purification	Mp, °C	Ref
III	*b*	Chromatography	190–192	
IV	Chlorobenzene, 270°	Recrystn from benzene	245–246	32
V	*b*	Recrystn from dioxane	264–266	
VII	Ethanol	Recrystn from benzene	361–366	
VIII	*o*-Dichlorobenzene	Recrystn from ethanol	283–286	
X	*o*-Dichlorobenzene, 250°	Recrystn from ethanol	179–180	
XI	*b*	Recrystn from petroleum ether (60–80°)	265–269	
XII	Chlorobenzene, 280°	Aqueous pyridine	182–185	Prepn of acid[33]
XIII	*b*	Recrystn from aqueous pyridine	212–213	Prepn of acid[34]
XIV	Chlorobenzene, 300°	Chromatography, benzene	217–220	
XV	Chlorobenzene, 300°	Chromatography, benzene	218	
XVI	*o*-Dichlorobenzene, 250°	Chromatography, benzene	165–167	35
XVII	Chlorobenzene	Chromatography, petroleum ether (40–60°)	203–205	Prepn of acid[36]

[a] Compounds I, II, VI, and IX were obtained from Eastman Organic Chemicals, Rochester, N. Y. [b] The preparation of these compounds did not follow the general procedure and is described below.

Preparation of Compounds. Most of the benzoxazole derivatives were prepared from the acid chlorides. These were obtained by the action of thionyl chloride on the carboxylic acids, in the presence of catalytic amounts of dimethylformamide. Those acids which were not available commercially were prepared according to the literature references in Table VII.[32–36]

The intermediate amides were prepared by refluxing the acid chlorides with an equivalent of the appropriate *o*-aminophenol in a suitable solvent. The crude amides, after removal of the solvent, were cyclized by heating under reduced pressure (10 mm). The method of purification and the melting points of the final products are indicated in Table VII. All new compounds gave satisfactory elemental analyses.

2-Amino-4,6-di-*tert*-pentylphenol. This was prepared *via* the corresponding nitro compound. 2,4-Di-*tert*-pentylphenol (460 g) was stirred rapidly in benzene (840 ml) while nitric acid (157 ml, d 1.42) was dripped into the solution, the temperature being kept between 25 and 35°. After the addition, which took 45 min, more benzene was added and after separation the organic layer was thoroughly washed with water and dried over anhydrous magnesium sulfate. The solvent was removed and the residue was distilled through a Vigreux column. The product, 2-nitro-4,6-di-*tert*-pentylphenol, distilled, bp 134–150° (0.4–0.7 mm), as a viscous red liquid (274 g, 50%).

2-Nitro-4,6-di-*tert*-pentylphenol (42 g) was dissolved in sodium hydroxide solution (1200 ml, 10%) with stirring in a 5-l. beaker and heated to 65° on the steam bath. Sodium dithionite (114 g) was then added all at once. The temperature rose to 80°, and stirring was continued until the red color disappeared (about 3–4 min). Heating was stopped and the mixture was neutralized with acetic acid (about 120 ml). Ice was added to bring the temperature down to 10° and the precipitate was collected and washed with water under an atmosphere of nitrogen. It was dried in a vacuum desiccator. Dark oxidation products were removed from the precipitate by washing it quickly with chilled (5–10°) petroleum ether (bp 40–60°, 300–500 ml, under nitrogen). A pale-pink solid (33 g, 86%), mp 131–134°, remained.

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2,2′-Di(5,7-di-*tert*-pentylbenzoxazolyl) (III). This was obtained as a by-product of the attempted synthesis of 2,4,5-tri(5,7-di-*tert*-pentylbenzoxazol-2-yl)triazine from 3 mol of 2-amino-4,6-di-*tert*-pentylphenol and 1 mol of *s*-triazine-1,3,5-carbonyl chloride.

1,4-Di(benzoxazol-2-yl)buta-1,3-diene (V). Muconyl chloride (1 g) and *o*-aminophenol (1.2 g) in dioxane (14 ml) containing triethylamine (1.7 ml) were heated for 30 min on a steam bath. On cooling, the solid was collected and recrystallized from 50% aqueous pyridine to give muconoyl di(2-hydroxy)anilide (1.3 g, 57%), mp 275–276°. This compound (1 g) was added over 20 min to zinc chloride (anhydrous, 10 g) and water (0.7 ml), stirred, and heated in an oil bath at 160–170° for 1 hr. The stirring was then stopped and the heating was continued overnight. Subsequently the mixture was cooled to about 120° and water (10 ml) was added with stirring to give a smooth slurry. The mixture was cooled to 80° and poured into water (20 ml) containing concentrated hydrochloric acid (1.4 ml). After standing, with occasional stirring, for 1 hr the precipitate was collected and recrystallized from dioxane to give a pale-yellow solid (0.53 g, 60%), mp 264–266°.

4,4′-Di(5,7-di-*tert*-pentylbenzoxazol-2-yl)-1,1′:4′,1′′:4′′,1′′-quaterphenyl (XI). 4-Carboxy-4′-iodobiphenyl prepared from biphenyl[36-38] was converted by the standard procedure to the corresponding acid chloride, mp 149–150°.

4-Iodo-4′-(5,7-di-*tert*-pentylbenzoxazol-2-yl)biphenyl. 2-Amino-4,6-di-*tert*-pentylphenol (1.3 g) and 4-chlorocarbonyl-4′-iodobiphenyl (1.8 g) were heated under reflux for 2 hr in chlorobenzene (35 ml). The solvent was distilled off and the residue was heated under water-pump vacuum in an oil bath at 240–260° for 15 min. The product was recrystallized from petroleum ether (bp 60–80°) to give pale-yellow crystals (1.97 g, 73%), mp 171–174°.

4-Iodo-4′-(5,7-di-*tert*-pentylbenzoxazol-2-yl)biphenyl (4 g) was throughly mixed with copper powder (8 g) and plunged into an oil bath (N_2 atmosphere) at 270–280° for 15 min. The product was extracted with benzene overnight, the solvent evaporated, and the residue extracted with petroleum ether (bp 40–60°). Concentration and cooling of this solution gave pale-yellow crystals (0.76 g, 27%), mp 261–266°. A second recrystallization from the same solvent gave an analysis sample, mp 265–269°.

4,4′-Di(5,7-di-*tert*-pentylbenzoxazol-2-yl)diphenylacetylene (XIII). Diethyl diphenylacetylene-4-4′-diimidate dihydrochloride[34] (2 g) was thoroughly mixed with 2-amino-4,6-di-*tert*-pentylphenol and immersed under vacuum in a preheated oil bath at 240°. After the solid had melted and gas evolution subsided (about 10 min) the mixture was cooled to room temperature, still under vacuum. The product (2.3 g) was twice recrystallized from pyridine–water and finally from pyridine to give a white solid, mp 212–213°.

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Excited Dimer Luminescence of Pairs of Phenanthrene Molecules

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Abstract: A phenanthrene sandwich dimer has been prepared by photolytic dissociation of the cis syn dimer of 9-hydroxymethylphenanthrene in a rigid matrix at 77°K. The fluorescence of this species is that of an excited dimer rather than an excimer; the phosphorescence similarly indicates a weak interaction in the triplet state. The luminescence of the partially overlapping pair formed by photolytic dissociation of the trans dimer of 4,5-methylenephenanthrene shows a very weak interaction. Previous reports of excimer luminescence for phenanthrene are suggested to be in error.

Most aromatic hydrocarbons which are not encumbered by bulky substituents have been found to form fluorescent excimers under some condition of temperature and/or concentration.[1,2] The binding energies are typically 6–10 kcal mol^{-1}. Phenanthrene is the only hydrocarbon of the four containing three or fewer rings which has not been shown unambiguously to form an excimer under any of the usual conditions. There is a brief report of what appeared to be delayed excimer fluorescence from phenanthrene in a hydrocarbon glass at 77°K[3] as well as a more recent report of luminescence in fluid solution at low temperatures which was interpreted as excimer phosphorescence.[4] It has also been said that the electrochemiluminescence spectrum of phenanthrene contained an excimer component.[5] We have examined the luminescence of a pair of phenanthrene molecules by the sandwich dimer technique[6] and found only weak interaction in both singlet and triplet states. These results suggest that the previous reports of excimer luminescence for phenanthrene are probably in error.

The determination of the fluorescence of a phenanthrene sandwich pair requires the photolytic dissociation of a phenanthrene photodimer (**1**) which must have a cis configuration. Phenanthrene itself does not photodimerize; the trans dimer (**2**, R = H; X = 2 H) has been prepared by a thermal route.[7] The failure of phenanthrene, with its stilbenoid double bond, to dimerize implies that the excimer is not long-lived at room temperature. This has also been suggested by Stevens and Dubois, who found phenanthrene to show negligible self-quenching of fluorescence at room temperature.[8]

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