more recent investigations too numerous to list here. As might be expected the effect is slight in the case of strong acids but the dissociation constants of weak acids may be 10^4 to 10^6 times smaller in absolute ethanol than in water.[16]

Diffusion Current Data and Calculation of Diffusion Coefficient.—The diffusion current behavior illustrated in Fig. 4 may be attributed mainly to the effect of the viscosity of the medium on the diffusion coefficient. No viscosity data for the electrolyte solutions studied are available but if the viscosities of water–ethanol mixtures[17] are plotted against ethanol content, the curve shows a flat maximum over a region coinciding roughly with that of the minimum in the curves of Fig. 4. A similar effect was observed by Pasternack and Halban in the reduction of two ketones[4] and by Zlotowski and Kolthoff in the reduction of barium and strontium.[3]

The electroreduction of *p*-nitroaniline at a mercury electrode has been found to involve 6 electrons.[18] Assuming $n = 6$ in the Ilkovic equation, it is possible to calculate the diffusion coefficient (D) for the *p*-nitroaniline molecule from the polarographic data. In the aqueous phosphate buffer of *p*H 6.8 (no. 7, Table II), such a calculation yields a value of $D = 8.79 \times 10^{-6}$ cm.^{2}sec.$^{-1}$. No data permitting a direct calculation of a diffusion coefficient value for this molecule could be found in the literature; an approximate value can be obtained, however, by assuming, as suggested by Kolthoff and Lingane,[19] that the required diffusion coefficient is equal to that of an organic ion of similar size and shape for which conductivity data are available and applying the equation

$$D^\circ = 2.67 \times 10^{-7}\ (\lambda^\circ/\text{valence})$$

Thus, the diffusion coefficient for the *p*-aminobenzoate ion, for which $\lambda^\circ = 32$ mhos.,[20] is 8.54×10^{-6} cm.^{2}sec.$^{-1}$, a value in good agreement with that calculated from the polarographic data above and tending to confirm the assumption that six electrons are indeed involved in the reduction. Using the value $n = 6$, together with the $m^{2/3}t^{1/6}$ values given above, and applying the Ilkovic equation, values for the diffusion coefficient, D, in all buffer solutions studied can be obtained from the data of Table II.[21]

Summary

1. "Apparent" *p*H values have been determined for a series of commonly used buffer systems in water and 6 ethanol–water mixtures and the polarographic reduction of *p*-nitroaniline in these buffers has been investigated.

2. The Ilkovic equation has been shown to hold for the reduction and evidence that 6 electrons are involved has been given.

3. Equations relating half-wave potentials to apparent *p*H in each solvent medium have been given.

4. Data showing the effect of ethanol on (a) the equation for the polarographic waves, (b) the magnitude of the half wave potential and (c) the various terms in the Ilkovic equation have been presented and discussed.

5. The polarographic data given affords a means of obtaining diffusion coefficient values for *p*-nitroaniline in the solutions studied.

---

[16] Kolthoff and Rosenbloom, ref. 15, p. 97.

[17] "Handbook of Chemistry and Physics," 24th ed., Chem. Rubber Co., Cleveland, O., 1940.

[18] Glasstone and Hickling, "Electrolytic Oxidation and Reduction," D. Van Nostrand Co., New York, N. Y., 1936, p. 204.

[19] Ref. 2, p. 51.

[20] "International Critical Tables," Vol. VI, p. 278.

[21] Such calculations will of course involve the assumption that ethanol does not affect the validity of the Ilkovic equation or the value of n.

CHAPEL HILL, N. C. RECEIVED OCTOBER 27, 1948

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION]

The Ultraviolet Absorption Spectra of Alkoxy- and Hydroxybenzils

BY NELSON J. LEONARD, RICHARD T. RAPALA,[1] HERSHEL L. HERZOG[2] AND ELKAN R. BLOUT

The yellow color of glyoxal and benzil was contrasted by Robinson[3] with the absence of color in ethyl oxalate and crystalline 4,4′-diethoxybenzil. The difference was explained on the basis that ethyl oxalate possesses a neutralized system (an electron-donating group attached to an electron-accepting group) and that the ethoxyl groups in 4,4′-diethoxybenzil have an influence on the diketone system of benzil through the benzene nuclei similar to that which obtains by direct union in ethyl oxalate. A quantitative comparison of the color of these compounds can be found in the determination of their absorption spectra.

The ultraviolet absorption maximum for ethyl oxalate[4] has been shown to lie at much shorter wave length than the maxima of glyoxal,[5] methyl-

---

[1] Present address: Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

[2] Present address: Department of Chemistry, University of Southern California, Los Angeles, California.

[3] Robinson, "Outline of an Electrochemical Theory of the Course of Organic Reactions," Institute of Chemistry of Great Britain and Ireland, London, 1932, p. 30.

[4] Scheibe, *Z. Elektrochem.*, **34**, 497 (1928), reported $\lambda_{\max.} = 250$ mμ and $\log \epsilon = 1.35$ in methanol.

[5] Lüthy, *Z. physik. Chem.*, **107**, 285 (1923), reported $\lambda_{\max.} = 450$ mμ and $\log \epsilon = 0.50$ in ethanol.

TABLE I

SUBSTITUTED BENZILS

Benzil	Color of solid[e]	M. p., °C.	Yield	λmax.						Formula	Analyses, %			
											Carbon		Hydrogen	
				mμ	log ε	mμ	log ε[g]	mμ	log ε		Calcd.	Found	Calcd.	Found
Unsubstituted[8]	y	94–95	93[a]	259	4.31			370	1.89	$C_{14}H_{10}O_2$				
2-Methoxy[12]	y	71–72	60[a]	257	4.28	323	3.64			$C_{15}H_{12}O_3$				
3-Methoxy	y	87–88	30[b]	255	3.90	319	4.12	365	3.26	$C_{15}H_{12}O_3$	74.98	74.91	5.04	5.36
4-Methoxy[13]	y	64–65	68[a]	255	4.18	291	4.26	~380	2.08	$C_{15}H_{12}O_3$				
2-Ethoxy	p	101–102	60[a]	253	4.19	326	3.63			$C_{16}H_{14}O_3$	75.57	75.72	5.55	5.66
4-Ethoxy	p	70–71	60[a]	260	4.30	292 277	4.34 4.31	~390	2.0	$C_{16}H_{14}O_3$	75.57	75.31	5.55	5.67
2,2′-Dihydroxy[14]	p	154–155	50[d]	257	4.22	332	3.86			$C_{14}H_{10}O_4$				
4,4′-Dihydroxy[11]	y	244–246	87[d]			299	4.52	~400(?)	2.0	$C_{14}H_{10}O_4$				
2,2′-Dimethoxy[15]	0	128–129	40[a]	254	4.29	318	3.92			$C_{16}H_{14}O_4$				
3,3′-Dimethoxy[16]	y	82–83	60[a]	262	4.06	322	4.18	~380	2.67	$C_{16}H_{14}O_4$				
4,4′-Dimethoxy[17]	y	132–133	52[a]			298	4.35	~380(?)	2.16	$C_{16}H_{14}O_4$				
2,2′-Diethoxy[16]	0	157–158	50[a]	255	4.29	317	3.98			$C_{18}H_{18}O_4$				
3,3′-Diethoxy	p	55–56	50[a]	262	3.97	321	3.97	~375	2.97	$C_{18}H_{18}O_4$	72.47	72.05	6.08	6.19
4,4′-Diethoxy[18]	0[f]	148–149	62[c]			300	4.51			$C_{18}H_{18}O_4$	72.47	72.46	6.08	6.27
3,3′,4,4′-bis-Methylenedioxy[11]	y	171–172	54[a]	235	4.28	281	3.98	324	4.12	$C_{16}H_{10}O_6$				
3,3′,4,4′-Tetraethoxy	0	162–163	40[a]	232	4.40	285	4.29	323	4.30	$C_{22}H_{26}O_6$	68.38	68.34	6.78	6.70
2,2′,3,3′-Tetramethoxy	0	143–144	37[a]	261	4.29	320	3.70			$C_{18}H_{18}O_6$	65.45	65.69	5.49	5.98
5,5′-Dibromo-2,2′-dimethoxy[14]	0	231–232	53[a]	250	4.29	331	3.86			$C_{16}H_{12}Br_2O_4$				

[a] Benzoin condensation (symmetrical or unsymmetrical) followed by oxidation of the benzoin with copper sulfate–pyridine. Over-all yield is based on the original aldehyde. [b] Formation of the benzyl phenyl ketone by reaction between a substituted benzamide and benzylmagnesium chloride, followed by oxidation of the substituted benzyl phenyl ketone with selenium dioxide. Over-all yield is based on the substituted benzamide. [c] Friedel–Crafts reaction between oxalyl chloride and phenetole with aluminum chloride. Over-all yield is based on the oxalyl chloride. [d] Hydrolysis of the corresponding dialkoxybenzyl. [e] y = yellow; p = pale yellow; 0 = colorless. [f] Yellow in 95% ethanol or in chloroform solution. [g] ~ Indicates an inflection point.

glyoxal,[6] and biacetyl,[7] which is consistent with Robinson's theory. However, our investigation shows that the absorption spectra of 4,4′-diethoxybenzil and of a series of alkoxy- and hydroxybenzils do not have an analogous relationship when compared with that of benzil. We have found that the introduction of alkoxyl and hydroxyl groups into the benzil molecule produces a bathochromic shift in ultraviolet absorption, and we have observed that, whereas crystalline 4,4′-diethoxybenzil is colorless, solutions of the compound are yellow.

Experimental

Preparation of Substituted Benzils: Method A

Preparation of Symmetrical Benzoins.—One-tenth mole of the aldehyde was dissolved in 30 ml. of ethanol and 15 ml. of water. Two grams of potassium cyanide was added and the solution was heated under reflux for one and one-half hours. After the material had been allowed to cool and to stand for three hours, it was poured into two volumes of water. The oil which separated was extracted with ether. The ether was removed and the residual oil was used directly in the oxidation.

Preparation of Unsymmetrical Benzoins.—Five hundredths mole of the substituted benzaldehyde and 0.05 mole of benzaldehyde were dissolved in 30 ml. of ethanol and 15 ml. of water. The condensation and isolation methods were identical with those employed for the symmetrical benzoins.

Oxidation of Benzoins to Benzils.[8]—To 0.05 mole of impure benzoin was added a solution of 20 g. of copper sulfate in 30 ml. of pyridine and 10 ml. of water. The mixture was heated under reflux for two hours, after which it was poured into three volumes of water. The product was extracted with ether and the ether was removed. The residue was recrystallized at least five times from aqueous ethanol.

Method B

Preparation of *m*-Alkoxyphenyl Benzyl Ketones.—The reaction between the *m*-alkoxybenzamide and benzyl magnesium chloride was conducted according to the method of Jenkins[9] to obtain the corresponding *m*-alkoxyphenyl benzyl ketone.

Oxidation of *m*-Alkoxyphenyl Benzyl Ketones to Benzils.—The oxidation was carried out according to the method of Hatt, Pilgrim and Hurran.[10] The benzil was recrystallized five times from aqueous ethanol.

Method C

Friedel–Crafts Reaction. Preparation of 4,4′-Diethoxybenzil.—To a well-stirred, ice-cooled solution of 0.2 mole of phenetole and 0.1 mole of oxalyl chloride in 100 ml. of carbon disulfide, 30 g. of aluminum chloride was added in small portions over a period of two hours. The reaction mixture was then warmed gently on the steam-bath for thirty minutes. The complex was decomposed by means of hydrochloric acid and ice. The carbon disulfide was removed by distillation and the residue was filtered. The 4,4′-diethoxybenzil thus collected was recrystallized first from glacial acetic acid and then several times from aqueous ethanol.

Method D

Hydrolysis, Preparation of 4,4′-Dihydroxybenzil.[11]—A solution of 20.2 g. (0.074 mole) of 4,4′-dimethoxybenzil in

---

(6) Woo and Chang, *Trans. Faraday Soc.*, **41**, 157 (1945), reported $\lambda_{max.}$ = 440 mμ and log ε = 1.14 in ether.

(7) Lüthy, *Compt. rend.*, **176**, 1547 (1923), Lardy, *ibid.*, **176**, 1548 (1923), and Herold, *Z. physik. Chem.*, **B18**, 265 (1932), reported $\lambda_{max._1}$ = 430 mμ and log ε = 1.3, $\lambda_{max._2}$ = 280 mμ and log ε = 1.2 in hexane. Henri, "Études de Photochimie," Paris, 1919, reported the same values in ethanol.

(8) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, pp. 80, 88.

(9) Jenkins, THIS JOURNAL, **55**, 703 (1933).

(10) Hatt, Pilgrim and Hurran, *J. Chem. Soc.*, 93 (1936).

(11) Schönberg and Kraemer, *Ber.*, **55**, 1174 (1922).

(12) Brass, Willig and Hanssen, *ibid.*, **63**, 2613 (1930).

(13) Tiffeneau and Lévy, *Bull. soc. chim.*, [4] **49**, 725 (1931).

(14) Kuhn, Birkofer and Moller, *Ber.*, **76**, 900 (1943).

(15) Irvine, *J. Chem. Soc.*, **79**, 668 (1901).

(16) Schönberg and Malchow, *Ber.*, **55**, 3746 (1922).

(17) Irvine and Moodie, *J. Chem. Soc.*, **91**, 536 (1907).

(18) Vorländer, *Ber.*, **44**, 2455 (1911).

150 ml. of acetic acid was heated to boiling, and 48% hydrobromic acid was added in portions until the solution became turbid. Boiling was continued for two hours, after which the mixture was cooled and poured into water. The crude product (15.6 g.) was recrystallized five times from nitroethane.

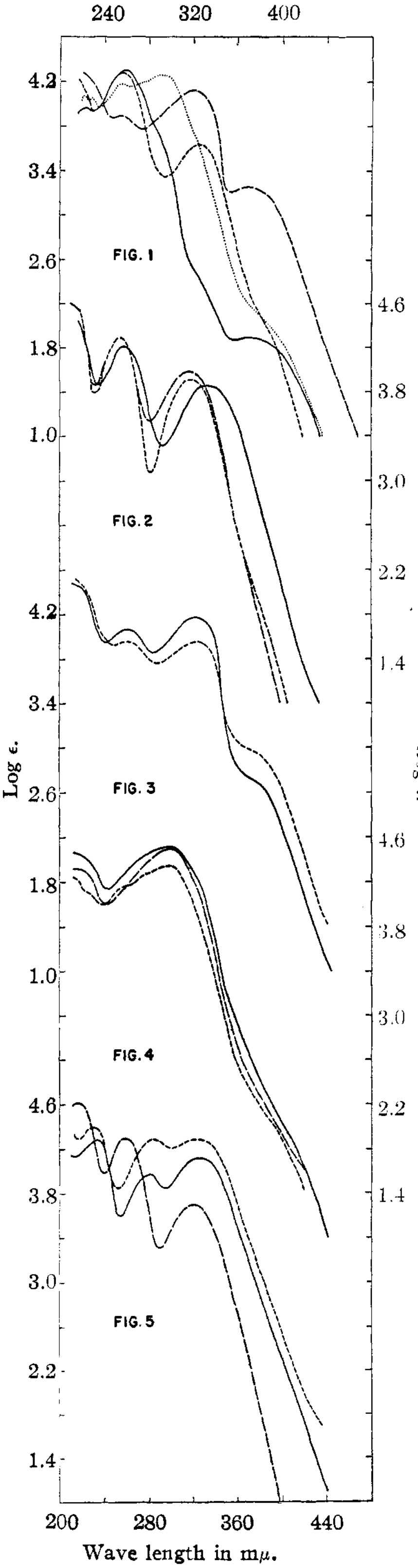
The absorption spectra measurements were made with a Beckman quartz spectrophotometer model DU using a 1-cm. quartz cell and a hydrogen discharge tube as the ultraviolet source. Ninety-five per cent. ethanol was used as the solvent throughout. In Table I are reported the physical, analytical and spectrographic data for the compounds studied, and in Figs. 1 through 5, the ultraviolet absorption curves for these compounds.

Discussion

Macroscopic examination of the colors of the 4,4′-disubstituted benzils in the crystalline state shows that the diethoxy compound is colorless whereas the dihydroxy and dimethoxy compounds are definitely yellow. Microscopic examination of the crystals of these compounds, as obtained from aqueous ethanol, indicates that 4,4′-dimethoxy- and 4,4′-diethoxybenzil crystals are orthorhombic, although probably not isomorphous because of the different orientation of the index ellipsoid axes with respect to the prism axis. 4,4′-Dihydroxybenzil crystals are monoclinic.[19]

In all three compounds, the resonance configurations should be similar, which would lead us to expect that the absorption spectra should be similar. This is, in fact, the case, as the ultraviolet absorption determination shows. All three compounds are characterized essentially by one high-intensity absorption peak at 300 mμ (Fig. 4). This is a similar bathochromic shift of 30–40 mμ (compared to benzil) to that observed with the *p*,*p*′-disubstituted benzalazines.[20] In the wave length region above 410 mμ, the curves for the 4,4′-disubstituted benzils are also similar and resemble closely that of benzil. The prediction from these absorption curves that all of the ethanolic solutions should be yellow is verified simply by visual examination. Since the diethoxy compound is similar to the dimethoxy and dihydroxy compounds in ultraviolet absorption and visible absorption in solution, the lack of color in the 4,4′-diethoxybenzil solid is related to the crystalline habit of the material and is not an effect directly attributable to the electron-donating property of the ethoxyl group, as has been proposed. This seems to be another example of the relatively well-known fact that the color of crystals does not indicate necessarily the color of the molecules in solution.

The inconsistency between color of solid and color of solutions is not exhibited by the corresponding 2,2′-disubstituted benzils. 2,2′-Diethoxybenzil and 2,2′-dimethoxybenzil are colorless as solids and colorless in solution; 2,2′-dihydroxybenzil is pale yellow as a solid and yellow in ethanol solution. As would be expected



Benzil, ——; 2-methoxy-, ----; 3-, ——; 4-, ····.

2,2′-Dihydroxybenzil, ——; 2,2′-dimethoxy, ----; 2,2′-diethoxy-, ——.

3,3′-Dimethoxybenzil, ——; 3,3′-diethoxy, ——.

4,4′-Dihydroxybenzil, ——; 4,4′-dimethoxy-, ----; 4,4′-diethoxy-, ——.

3,3′,4,4′-bis-Methylenedioxybenzil, ——; 3,3′,4,4′-tetraethoxy-, ----; 2,2′,3,3′-tetramethoxy-, ——.

Figs. 1–5.—Absorption spectra of benzils.

---

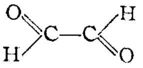
[19] The authors are indebted to Miss E. J. Weichel for the crystallographic and optical analyses.

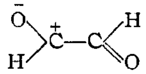
[20] Blout and Gofstein, THIS JOURNAL, 67, 13 (1945).

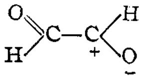
because of their similar electronic configurations, the first two compounds exhibit similar absorption maxima at 254 and 318 mμ; the dihydroxy compound likewise has a maximum at 257 mμ, but the second maximum has shifted to 332 mμ (Fig. 2). The end absorption, above 380 mμ, is less for 2,2′-diethoxybenzil and 2,2′-dimethoxybenzil (colorless in solution) than it is for benzil, while the end absorption of 2,2′-dihydroxybenzil (yellow in solution) is similar to that of benzil. The spectral determination is thus, in this case, consistent with visual examination of the solids and solutions.

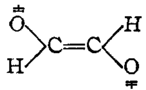
While comparison of light absorption of different benzils is warranted, similar comparison of absorption of aromatic 1,2-diketones with that of aliphatic 1,2-diketones has less meaning. Since the time when Robinson proposed the common basis for the yellow color of benzil and glyoxal and for the lack of color of 4,4′-diethoxybenzil and ethyl oxalate,[8] the spacial configuration of the dicarbonyl groups in these molecules has been elucidated. The accumulated evidence indicates that the dicarbonyl system in benzil has a skew configuration, whereas the carbonyl groups in glyoxal and biacetyl have a coplanar, *trans* configuration. The conclusion that the benzil molecule has a skew structure, in which the two benzoyl units lie in planes approximately at right angles to each other, has been reached from X-ray examination of crystals by Knaggs and Lonsdale,[21] from dipole moment measurement of benzil in solution by Caldwell and LeFèvre,[22] and from parachor determination by Gibling.[23] For glyoxal and biacetyl, LuValle and Schomaker[24] have found that the electron diffraction, dipole moment, and chemical data indicate uniformly that both molecules are planar with the *trans* configuration and that rotation about the C—C bond (1.47 ± 0.02 Å.) connecting the adjacent carbonyls is restricted. Observations by Gaydon[25] on the spectrum resulting from a Tesla discharge through glyoxal vapor are best explained on the assumption that the glyoxal molecule has the planar, *trans* form. The bond orders in glyoxal, as calculated by the method of molecular orbitals,[26] are also consistent with the molecular structure of glyoxal as advanced by LuValle and Schomaker.

The exact chemical state of glyoxal can be considered most adequately as a resonance hybrid of a number of contributing structures (I, II, III, IVa, IVb). The fact that structures IVa and IVb contribute to the ground state of the molecule is evidenced by the shortened distance, 1.47 Å., between the carbonyl carbon atoms.


I

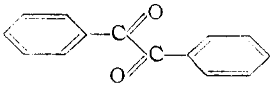

II

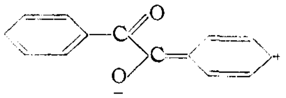

III

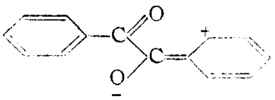

IVa,b

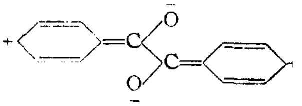
It has been suggested[27,28] that the absorption (and therefore the visible yellow color) of such an aliphatic 1,2-dicarbonyl compound is due to excitation of the electronic oscillations represented mainly by the formulas IVa and IVb.

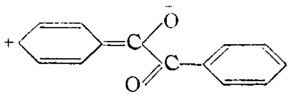
In the benzil molecule, structures of type IV should make much less contribution to the resonance hybrid because the molecule is skew and will resist the coplanarity demanded by such contributing structures. The more likely resonance structures for benzil are indicated by formulas V-X. The absorption spectra observations are consistent with the known differences in the structure of glyoxal and benzil. The wave length (450 mμ) and magnitude (log ε = 0.50)[29] of absorption by glyoxal[5] are not commensurate with the wave length (259, 370 mμ) and magnitude (log ε = 4.31, 1.89) of absorption by benzil (Fig. 1). The "dicarbonyl" absorption has been greatly modified in the benzil molecule.

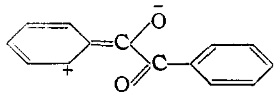

V


VI


VII


VIII


IX


X

Since we must consider the 1,2-dicarbonyl systems in the aliphatic and aromatic compounds as essentially different, we cannot expect hydroxyl or alkoxyl groups on the benzil molecule to have an effect on the absorption spectra analogous to that found in going from glyoxal to oxalic acid and its esters. Because of the skew structure of benzil, the absorbing units must act more or less like individual benzoyl groups (V-X), and the spectral effect of substitution of alkoxyl or hydroxyl groups on benzil should be similar to that of analogous substitution on benzaldehyde or acetophenone. The spectra of such compounds in ethanol have been previously deter-

---

(21) Knaggs and Lonsdale, *Nature*, **143**, 1023 (1939).

(22) Caldwell and LeFèvre, *J. Chem. Soc.*, 1614 (1939); *Nature*, **143**, 803 (1939).

(23) Gibling, *J. Chem. Soc.*, 661 (1942).

(24) LuValle and Schomaker, THIS JOURNAL, **61**, 3520 (1939).

(25) Gaydon, *Trans. Faraday Soc.*, **43**, 36 (1947).

(26) Coulson, *ibid.*, **42**, 106 (1946).

(27) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

(28) Calvin and Wood, THIS JOURNAL, **62**, 3152 (1940).

(29) Methylglyoxal[6] and biacetyl[7] show maxima of greater intensity.

mined, but in order to facilitate comparison of the ultraviolet absorption maxima of benzaldehydes and benzils, the pertinent data are collected and reproduced in Table II.

TABLE II

SUBSTITUTED BENZALDEHYDES

Compound	λmax.					
	mμ	log ε	mμ	log ε	mμ	log ε
Benzaldehyde[30]	240	4.12	278	3.02	320	1.7
Acetophenone[30]	240	4.12	278	3.02		
Propiophenone[31]	245	4.1	~280	3.05		
o-Hydroxybenzaldehyde[30]	255	4.00	325	3.48		
p-Hydroxybenzaldehyde[30]	221	4.14	284	4.24	~332	2.25
o-Methoxybenzaldehyde[30,32]	253	4.07	319	3.62		
m-Methoxybenzaldehyde[30,32]	252	3.92	314	3.45		
p-Methoxybenzaldehyde[30]			277	4.17		
Piperonal[33]			275	3.8	315	4.0

It can be seen from Tables I and II that the effect of *o*-, *m*- and *p*-hydroxy- and alkoxy-substitution in benzaldehyde are indeed parallel to the effects of analogous substitution in both rings of benzil. In general, such substitution shifts the absorption maxima to longer wave lengths. In both series, *ortho*- and *meta*-substituted compounds exhibit two main peaks and *para*-substituted compounds have essentially one absorption band in the ultraviolet.[34] The wave lengths of the maxima are proximate for the benzaldehyde and benzil analogs. The closest agreement is found for the maxima exhibited by *o*-methoxybenzaldehyde and 2,2′-dimethoxybenzil. The wave lengths of the maxima are practically identical and the extinction coefficients of the 2,2′-dimethoxybenzil maxima are about double those of *o*-methoxybenzaldehyde. Thus, the transitions to the excited states responsible for absorption must be similar for the two compounds. There is also close agreement between the maxima of *o*-methoxybenzaldehyde and 2,2′-diethoxybenzil (Fig. 2) and good agreement between the maxima of *o*-hydroxybenzaldehyde and 2,2′-dihydroxybenzil. The maxima for *m*-methoxybenzaldehyde and 3,3′-dimethoxy- and 3,3′-diethoxybenzil (Fig. 3) differ only by 8–10 mμ in wave length, but the long wave length absorption of benzil (370 mμ) appears as an inflection point (380 mμ) in the 3,3′-dialkoxybenzils, indicating that additional electronic transitions are possible in this molecule. The greatest difference of wave length for comparative maxima is found between *p*-hydroxybenzaldehyde and 4,4′-dihydroxybenzil (15 mμ), between *p*-methoxybenzaldehyde and 4,4′-dimethoxybenzil (21 *mμ*). The shift of the maxima toward longer wave lengths with these *para*-substituted benzils can be due either to an increase in the number of configurations for the excited state or to an increase in the electron density of such states. Because two adjacent carbonyl groups are not very effective in transmitting conjugation through a molecule, it is difficult to see how the length of the absorbing system can be increased over that which exists in *p*-hydroxy- or *p*-alkoxybenzaldehydes.

When the absorption curves of different benzils are compared, we observe that there is close correspondence between those of 4,4′-dihydroxybenzil and 4,4′-dimethoxybenzil, whereas the longer wave length maximum of 2,2′-dihydroxybenzil undergoes a 14 mμ bathochromic shift compared to that of 2,2′-dimethoxybenzil (*cf.* Figs. 2 and 4). Morton and Stubbs[30] observed a similar displacement of 18 mμ between the absorption maxima of *o*-hydroxybenzaldehyde and *o*-methoxybenzaldehyde in hexane solution. They attributed this to chelation in the *o*-hydroxybenzaldehyde, an explanation which is also admissible for 2,2′-dihydroxybenzil.

As mentioned previously, the long wave length maximum of benzil appears as an inflection point in the absorption curves of 3,3′-dialkoxybenzils (Fig. 3), but is not present in the curves of the 2,2′- or 4,4′-dialkoxybenzils (Figs. 2 and 4).[35] This maximum, present in benzil, either has disappeared or has shifted toward shorter wave length and lost its identity in the 2,2′- and 4,4′-disubstituted compounds.

The absorption curves of the 2-, 3- and 4-alkoxybenzils are intermediate between those of benzil and the corresponding disubstituted benzils (*cf.* Figs. 1, 2, 3, 4), as expected. The curves of 3,3′,4,4′-bis-methylenedioxybenzil and 3,3′,4,4′-tetraethoxybenzil (Fig. 5) are a composite of those of 3,3′- and 4,4′-dialkoxybenzil and that of 2,2′,-3,3′-tetramethoxybenzil (Table I) is a composite of those of 2,2′- and 3,3′-dimethoxybenzil.

Summary

The ultraviolet absorption spectra of benzil and seventeen alkoxy- and hydroxybenzils have been determined.

The absorption maxima and the color of series of *o*-, *m*- and *p*-substituted benzils in ethanol solution show regularities which are not exhibited by these compounds in the crystalline state.

The absorption maxima of the substituted benzils and the correspondingly substituted benzaldehydes have been shown to lie at closely comparable wave lengths. This is consistent with the skew structure of benzil, likewise to be expected for the substituted benzils, and is an in-

---

(30) Morton and Stubbs, *J. Chem. Soc.*, 1347 (1940).

(31) Zucker and Hammett, THIS JOURNAL, **61**, 2785 (1939).

(32) Valiasko, *J. Russ. Phys.-Chem. Soc.*, **42**, 751 (1910).

(33) Hilmer and Schorning, *Z. physik. Chem.*, **168A**, 81 (1934).

(34) The gross structure of the main ultraviolet absorption bands in the benzil series seems to parallel closely that observed with the similarly substituted benzalazines.[20] In particular, it should be pointed out that in both series the symmetrically *para*-substituted compounds exhibit but a single maximum in the region examined, whereas two main absorption peaks become increasingly evident as one proceeds from the symmetrically substituted *meta* to the symmetrically substituted *ortho* compounds.

(35) The presence of a true inflection point at 380–400 mμ in the 4,4′-dihydroxy- and 4,4′-dimethoxybenzil is certainly open to question.

dication that the excited structures which give the major contribution to absorption are closely related to those which contribute to the absorption of the substituted benzaldehydes.

URBANA, ILLINOIS
CAMBRIDGE 39, MASSACHUSETTS
RECEIVED MARCH 22, 1948

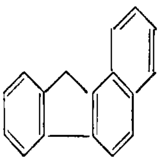
[CONTRIBUTION FROM THE WEIZMANN RESEARCH CENTER, REHOVOTH, ISRAEL, AND THE U. S. BUREAU OF MINES PITTSBURGH, PENNA.]

Structure of the Benzfluorenes and Benzfluorenones

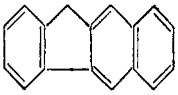
BY MILTON ORCHIN[1] AND ROBERT A. FRIEDEL[2]

Introduction

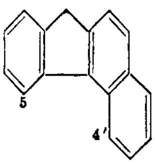
Of the three possible benzfluorenes, I–III, 1,2-benzfluorene, I, and 2,3-benzfluorene, II, have strikingly similar chemical and physical properties and ultraviolet spectra. 3,4-Benzfluorene, III, is however considerably different from its isomers. The benzfluorenes, I and II, are high melting, difficult to separate and relatively insoluble. They both form unstable picrates and trinitrobenzene complexes in the ratio of 2 moles of polynitro compound to 1 mole of hydrocarbon. The benzfluorene, III, is much lower melting, relatively soluble, easily separated from its isomers and forms stable molecular complexes in a molar ratio of 1:1.



I



II



III

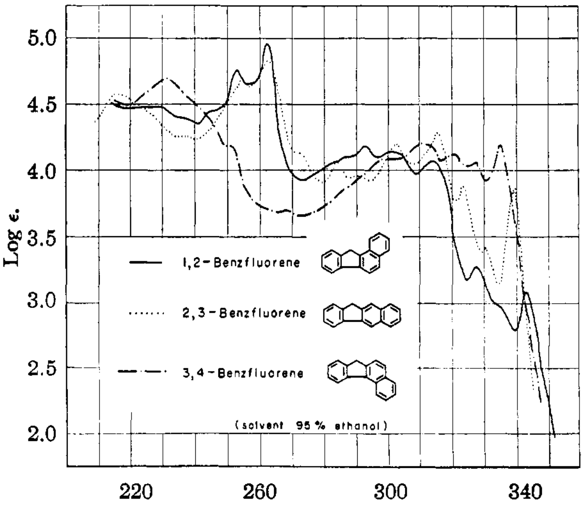


Fig. 1.—Ultraviolet spectra of the benzfluorenes.

Discussion

A possible explanation of the contrasting properties of the benzfluorenes is revealed in a comparison of them with the phenylnaphthalenes. Both I and II may be considered as 2-phenylnaphthalene derivatives while III may be considered as a derivative of 1-phenylnaphthalene. The ultraviolet absorption spectra of the three isomers (Fig. 1) show that although some dissimilarity exists between the spectra of I and II in the 270–300 mμ region, on the whole the spectra of I and II are quite similar and differ from that of III in a manner analogous to the difference in spectra between 1- and 2-phenylnaphthalene.[3] Thus it will be noted that I and II have strong absorption bands in the 260 mμ region, a feature also characteristic of the spectrum of 2-phenylnaphthalene, while the spectrum of the 3,4-benzfluorene, III, exhibits a minimum in this region similar to that shown by 1-phenylnaphthalene.

In 1-phenylnaphthalene there is unquestionably

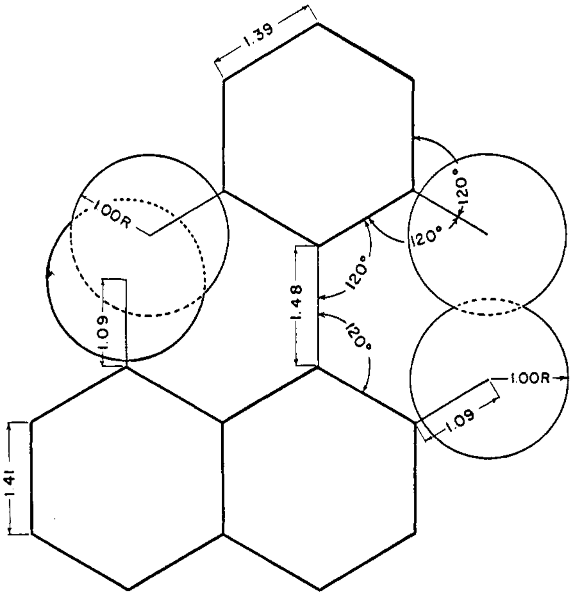


Fig. 2.—Planar representation of 1-phenylnaphthalene.

---

[1] Present address, U. S. Bureau of Mines, Pittsburgh, Penna. We wish to thank the John Simon Guggenheim Memorial Foundation for a fellowship grant to one of us (M. O.) which helped make this work possible.

[2] Physical chemist, Central Experiment Station, U. S. Bureau of Mines, Pittsburgh, Penna.

[3] Friedel, Orchin and Reggel, THIS JOURNAL, **70**, 199 (1948). The relationship of the spectra of the benzfluorenes and the phenylnaphthalenes has been commented on previously by Jacobs, Craig and Lavin, *J. Biol. Chem.*, **141**, 51 (1941).