TABLE II

Compound	Melting point, °C. Reported	Melting point, °C. Found	Sublm. temp., °C. (at ~ 10^{-5} mm.)	Ultraviolet spectral data Reported λ_{max}	log ϵ	Solvent[b]	Found λ_{max}	log ϵ	N, Analyses,[a] % Calcd.	Found
Cytosine	320–325 (dec.)[c]	313–315 (dec.)	200	265[h]	3.79	H_2O	265[m]	3.81	37.8	37.6
Uracil	335 (dec.)[c]	339 (dec.)	140	260[h]	3.95	H_2O	260[n]	3.90	25.0	25.0
Thymine	321 (dec.)[c]	320 (dec.)	100	263[h]	3.93	H_2O	265[m]	3.90	22.3	21.9
Adenine	360 (dec.)[d]	354 (dec.)	160	262[i]	4.09[j]	0.05 *N* NaOH	268[n]	4.08	51.8	51.7
Guanine	Not given[c]	>400 turns black	255	248	4.10	0.1 *N* HCl	248[m]	4.05	46.4	45.3
				274[h]	3.89		272	3.87		
Hypoxanthine	Not given[c]	>400 turns black	230	260[k]	4.04	0.1 *N* NaOH	263[n]	4.03	41.2	41.3
Xanthine	Not given[c]	379 (dec.)	200	278[k]	3.99	0.1 *N* NaOH	280[m]	3.99	30.3[o]	30.6[o]
Theophylline	264[e]	269–271	110			H_2O	272[n]	4.00	31.1	31.3
Theobromine	351[f]	354–355	115			H_2O	272[n]	4.01	31.1	30.8
Caffeine	235[g]	235–236	80	275[l]	4.03	0.1 *N* HAc	275[n]	3.99	28.9	28.7

[a] We are greatly indebted to Dr. Earl D. Stewart of the Schwarz Laboratories for supplying us with some of the nitrogen analyses. [b] When no superscript appears with the log ϵ value under Reported, the solvent was the same as used in this investigation. [c] For references to the original literature, see Levene and Bass, "Nucleic Acids," A. C. S. Mon. Series, Reinhold Publ. Corp., New York, N. Y., 1931. [d] Traube, *Ann.*, **331**, 64 (1904). [e] Kossel, *Ber.*, **21**, 2164 (1888). [f] Kempf, *J. prakt. Chem.*, [2], **78**, 246 (1908). [g] Fischer and Bromberg, *Ber.*, **30**, 219 (1897). [h] Heyroth and Loofbourow, THIS JOURNAL, **56**, 1728 (1934). [i] Cavalieri, Bendich, Tinker and Brown, *ibid.*, **70**, 3875 (1948). [j] At *p*H 8.99. [k] Stimson and Reuter, THIS JOURNAL, **65**, 154 (1943). [l] Loofbourow, Stimson and Hart, *ibid.*, **65**, 148 (1943). [m] Spectral data on crystallized sample before sublimation. [n] Spectral data on sublimed sample. [o] With one molecule of water.

ment Company recording potentiometer. For initial observation, a complete spectrum from 1 to 15 μ was recorded continuously. For drawing the final curves in Figs. 1 to 4, the data were obtained on a point-to-point basis, the points being taken from 5 to 10 cm.$^{-1}$ apart at frequencies up to 1900 cm.$^{-1}$ (5.2 μ) and at larger intervals at higher frequencies.

Summary

The infrared spectra of the pyrimidines and purines obtainable by the hydrolysis of nucleic acids have been determined over the spectral region 2 to 15 μ. The infrared spectra of the related purines, hypoxanthine, xanthine, theophylline, theobromine and caffeine have also been determined. On the basis of these measurements, suggestions have been made concerning the molecular structure of certain of the compounds in the solid state.

Infrared spectroscopy offers a convenient method for the identification and differentiation of this class of compounds.

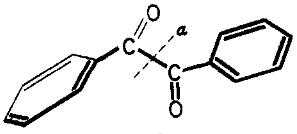
CAMBRIDGE 39, MASSACHUSETTS RECEIVED JUNE 9, 1949

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

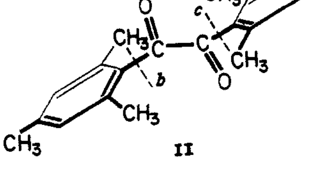
The Ultraviolet Absorption Spectra of Hindered Benzils

BY NELSON J. LEONARD AND ELKAN R. BLOUT*

In a previous paper[1] it was shown that the ultraviolet absorption maxima of certain alkoxy- and hydroxybenzils and the correspondingly substituted benzaldehydes lie at closely comparable wave lengths. This fact is consistent with the skew structure of benzil in which the two benzoyl units lie in planes approximately at right angles to each other (I) and the dicarbonyl system is not coplanar. Presumably the dicarbonyl absorbing unit would make a greater contribution to the total spectrum if the carbonyl groups could become coplanar. One method of permitting such coplanarity to develop is to provide hindering groups on the *ortho* carbons of benzil, thereby throwing each carbonyl group out of the plane of the attached ring. Thus, in contrast to the benzil molecule (I), which is twisted about *a*, the mesitil molecule (II) will be twisted about *b* and *c* and the dicarbonyl system is not prevented from becoming coplanar. Determination of the ultraviolet absorp-



I



II

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[*] Harvard University National Research Fellow, 1942–1943.

[1] Leonard, Rapala, Herzog and Blout, THIS JOURNAL, **71**, 2997 (1949).

TABLE I

HINDERED BENZALDEHYDES AND BENZILS

No.	Compound	M. p.,[a] °C.	λmax. mμ	log ε	mμ[b]	log ε
1	Benzil[1]	94–95	259	4.31	370	1.89[1]
2	2,4,6-Trimethylbenzaldehyde[2]	118–121 (16)	265	4.10	~300	3.24
3	Mesityl phenyl diketone[3]	136–137	265	4.22	400	1.89
4	Mesityl *p*-tolyl diketone[4]	103–104	278	4.26	400	1.97
5	Mesityl 2,4-xylyl diketone[4]	84.5–85	275	4.24	400	1.94
6	Mesitil[5]	115–115.5	255–290	3.41	467 493	1.69 1.71
7	2,4,6-Triethylbenzaldehyde[2]	147–148 (20)	265	4.13	~298	3.35
8	Phenyl 2,4,6-triethylphenyl diketone[6]	48.2–50	268	4.10	405	1.82
9	2,2′,4,4′,6,6′-Hexaethylbenzil[7]	78–79	310	3.26	467 493	1.77 1.76
10	2,4,6-Triisopropylbenzaldehyde[2]	123–126 (4)	265	4.02	~298	3.31
11	2,2′,4,4′,6,6′-Hexaisopropylbenzil[8]	155–156	310	3.03	468 491	1.61 1.63
12	Duryl phenyl diketone[9]	62.5–63.5	268	4.11	405	1.71
13	Duril[10]	243.5–244.5	267	3.63		
14	2,3,4,6-Tetramethylbenzaldehyde[11]	112–114 (3)	267	4.09	~306	3.32
15	Isoduryl phenyl diketone[12]	65–66	265	4.35	402	1.88
16	Isoduril[10]	180–180.5	265 310	3.45 3.22	470 490	1.69 1.66

[a] Figures in parentheses indicate pressure in mm. when a boiling point is reported. [b] ~ Indicates an inflection point

tion spectra of mesitil and a number of related hindered benzils now shows that the dicarbonyl absorption is shifted to longer wave lengths with increasing hindrance at the *ortho* carbons.

Experimental

Compounds.—The authors are deeply indebted to Dr. R. C. Fuson, whose generous donation of samples made this investigation possible.

Apparatus.—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 and spectrometric data for the compounds studied, and in the accompanying figures, the ultraviolet absorption curves for these compounds.

The authors wish to acknowledge the technical assistance of the Spectrophotometric Group of Polaroid Corporation in the determination of the absorption spectra.

Discussion

The most striking feature of the ultraviolet spectra of this series of benzils is the strong bathochromic effect of *ortho*-hindrance on the dicarbonyl absorption maximum. The peak assigned to dicarbonyl absorption in benzil lies at 370 mμ, whereas hindrance in one ring (mesityl phenyl diketone, mesityl *p*-tolyl diketone, phenyl 2,4,6-triethylphenyl diketone, duryl phenyl diketone, and isoduryl phenyl diketone) causes a shift in maximum to the 400-mμ region, and hindrance in both rings (mesitil, 2,2′,4,4′,6,6′-hexaethylbenzil, 2,2′,4,4′,6,6′-hexaisopropylbenzil and isoduril) causes a further and relatively greater shift in maximum to the 470–490-mμ region.[13] The dicarbonyl absorption maximum for the coplanar *trans* molecules glyoxal and biacetyl lies in the 430–450-mμ region, at lower intensity.[1] Strong indication that hindrance at the *ortho* carbons is the cause of the shift in maximum toward longer wave length is found in a comparison of the position of the dicarbonyl maxima for mesityl phenyl diketone, mesityl *p*-tolyl diketone and mesityl 2,4-xylyl diketone. The maxima for all three compounds lie at 400 mμ, and no effect on the wave length of the dicarbonyl absorption is realized until the final *o*-methyl group has been introduced, as in mesitil (maxima at 467 and 493 mμ).

The effect of hindrance on absorption would appear to be traceable to a change in spatial configuration of the dicarbonyl grouping in these molecules. From the arrangement in benzil (I), in which the carbonyl groups are supposed to be ap-

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(2) Fuson, Horning, Rowland and Ward, "Organic Syntheses," **23**, 57 (1943).

(3) Gray and Fuson, THIS JOURNAL, **56**, 739 (1934).

(4) Fuson, Emerson and Weinstock, *ibid.*, **61**, 412 (1939).

(5) Fuson, McKeever and Corse, *ibid.*, **62**, 600 (1940).

(6) P. E. Hoch, Thesis, Doctor of Philosophy, University of Illinois, 1948.

(7) Fuson Corse and McKeever, THIS JOURNAL, **61**, 2010 (1939).

(8) Fuson and Horning, *ibid.*, **62**, 2962 (1940).

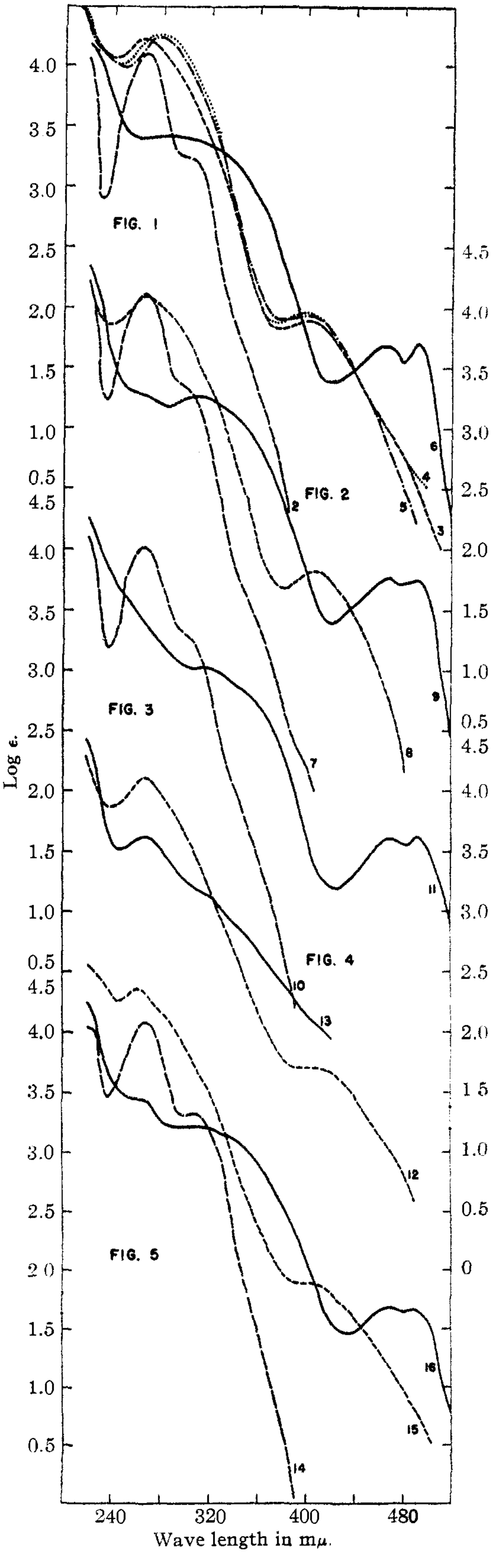
(9) Fuson, Byers, Sperati, Foster and Warfield, *J. Org. Chem.*, **10**, 69 (1945).

(10) Fuson and Kelton, THIS JOURNAL, **63**, 1500 (1941).

(11) Fuson, Southwick and Rowland, *ibid.*, **66**, 1109 (1944).

(12) Fuson, Armstrong, Wallace and Kneisley, *ibid.*, **66**, 1274 (1944).

(13) The solubility of duril in 95% ethyl alcohol is too low for accurate spectral determinations at wave lengths longer than 420 mμ in the path lengths used.



proximately at right angles to each other,[14,15,16] either contraction of the interplanar angle toward the *cis* or expansion of the angle toward the *trans* arrangement of the dicarbonyl system should shift the absorption maxima. In general, the introduction of coplanarity will increase the energy of the ground state relative to that of the excited state, and the corresponding absorption will occur at lower frequencies or longer wave lengths.[17] Whether, in mesitil (II), the carbonyl groups are predominantly in the *cis* or the *trans* position has not been established, but expansion of the angle between the carbonyls toward the *trans* position is favored because of the electrostatic repulsion between the similar groupings. A study of scale models indicates that in mesitil it is possible to accommodate the carbonyl groups most readily in the *trans* position, with the phenyl rings making an angle of 45–90° with the individual carbonyls. The bathochromic shift of approximately 100 mμ in dicarbonyl absorption maximum from benzil to mesitil therefore corresponds most likely to a twisting of the angle between carbonyls from approximately 90° to approximately 180°. In a molecule of intermediate hindrance, such as mesityl phenyl diketone (no. 3), in which the benzoyl unit tends to be coplanar and the mesitoyl unit cannot be coplanar, the carbonyls will be joined at an angle intermediate between 90 and 180°. The observed shift in the dicarbonyl absorption maximum for no. 3 from that in benzil (30 mμ) is correspondingly less than that observed for mesitil. This is in accordance with the principle developed by Klevens and Platt,[18] in their study of substituted dimethylanilines, that changes in spectrum are quantitatively related to the angle of twist between potentially conjugable groups. The same explanation applies to the spectra exhibited by the pairs: phenyl 2,4,6-triethylphenyl diketone (no. 8) and 2,2′,4,4′,6,6′-hexaethylbenzil (no. 9); isoduryl phenyl diketone (no. 15) and isoduril (no. 16).

Fig. 1.—2, 2,4,6-trimethylbenzaldehyde, — — — —; 3, mesityl phenyl diketone, - - - - - - - -; 4, mesityl *p*-tolyl diketone, ...; 5, mesityl 2,4-xylyl diketone, —·—·—·—; 6, mesitil, ———.

Fig. 2.—7, 2,4,6-triethylbenzaldehyde, — — — —; 8, phenyl 2,4,6-triethylphenyl diketone, - - - - - - - -; 9, 2,2′4,4′,6,6′-hexaethylbenzil, ———.

Fig. 3.—10, 2,4,6-triisopropylbenzaldehyde, — — —; 11, 2,2′,4,4′,6,6′-hexaisopropylbenzil, ———.

Fig. 4.—12, Duryl phenyl diketone, - - - - - - - -; 13 duril, ———.

Fig. 5.—14, 2,3,4,6-Tetramethylbenzaldehyde, — — —; 15, isoduryl phenyl diketone, - - - - - - - -; 16, isoduril, ———.

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[14] Knaggs and Lonsdale, *Nature*, **143**, 1023 (1939).

[15] Caldwell and LeFèvre, *ibid.*, **143**, 803 (1939); *J. Chem. Soc.*, 1614 (1939).

[16] Gibling, *ibid.*, 661 (1942).

[17] Remington, THIS JOURNAL, **67**, 1838 (1945).

[18] Klevens and Platt, *ibid.*, **71**, 1714 (1949).

Between the spectra of the hindered benzils and the spectra of the corresponding hindered benzaldehydes there does not exist the similarity which was observed for the non-hindered alkoxybenzils and alkoxybenzaldehydes.[1] For the non-hindered substituted benzils, it was observed that the spectral absorption was more or less like that of the individual substitued benzoyl units present, as represented by the spectra of the corresponding benzaldehydes. In contrast, the long wave length absorption band exhibited by the hindered benzils is not present in the spectra of the corresponding hindered benzaldehydes, and the short wave length absorption band is altered in intensity. 2,4,6-Trimethylbenzaldehyde (no. 2) has a maximum at 265 mμ, log ϵ = 4.10, and an inflection point at 300 mμ, log ϵ = 3.24; whereas mesitil (no. 6) has a broad maximum at 255–290 mμ, log ϵ = 3.41. A comparison of the short wave length absorption maxima for 2,4,6-triethylbenzaldehyde (no. 7) and 2,2',4,4',6,6'-hexaethylbenzil (no. 9), 2,4,6-triisopropylbenzaldehyde (no. 10) and 2,2',4,4',6,6'-hexaisopropylbenzil (no. 11), indicates a shift in wave length of 45 mμ toward the red and approximately a tenfold decrease in intensity (ϵ) in proceeding from the benzaldehyde to the benzil. In proceeding from 2,3,4,6-tetramethylbenzaldehyde (no. 14) to isoduril (no. 16), the principal changes noted are a decrease in intensity of absorption in the short wave length maximum and the presence of a maximum at the same place ($\lambda \sim 310$ mμ) noted above. The intensity of the absorption maxima (*circa* 310 mμ) found with all of the hindered benzils may represent a decreased probability of the excitation[17] responsible for the phenyl–carbonyl absorption or may be associated with carbonyl absorption alone. In the hindered benzils, the preferred configurations for the molecule will be those in which the carbonyl group is not in the plane of the attached substituted phenyl ring. The twist about *b* away from coplanarity in mesitil (II), for example, would be expected to be comparable with that observed in the non-coplanar compounds, 6,9-dimethylbenzosuberone and acetomesitylene.[19] The second mesitoyl group in mesitil must exert hindrance at least as great as that of the terminal methyl group of acetomesitylene, the non-coplanarity of which has been demonstrated by dipole moment[20] and spectral measurements.[21,22] In 2,4,6-trimethylbenzaldehyde, since the aldehyde group is probably too small to be blocked from the coplanar position by the two *ortho* methyl groups,[19] the coplanar form will make more contribution to the structure of the aldehyde than it can to that of mesitil, in which the aldehyde hydrogen is replaced by a mesitoyl grouping. The spectral differences (short wave length maxima) between nos. 7 and 9, 10 and 11, 14 and 16 are likewise traceable to the possibility of phenyl–carbonyl coplanarity in the substituted aldehydes and the comparative lack of such coplanarity in the substituted benzils. . The partially hindered benzils, *i. e.*, those possessing a benzoyl unit which can exhibit coplanarity, have short wave length absorption maxima which correspond closely with those of the substituted aldehydes (*cf.* nos. 3 with 2, 8 with 7, 12 and 15 with 14).

Summary

The ultraviolet absorption spectra of a number of polyalkyl-substituted benzaldehydes and benzils have been determined.

Dicarbonyl absorption is shifted to longer wave length with increasing hindrance at the *ortho* carbons of benzil, corresponding to increasing tendency to coplanarity of the two carbonyl groups.

Phenyl–carbonyl absorption is decreased in intensity (and may be shifted) with increasing hindrance at the *ortho* carbons of benzil, corresponding to decreasing tendency to coplanarity of the phenyl and carbonyl groups.

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(19) Kadesch, THIS JOURNAL, **66**, 1207 (1944).

(20) Kadesch and Weller, *ibid.*, **63**, 1310 (1941).

(21) O'Shaughnessy and Rodebush, *ibid.*, **62**, 2906 (1940).

(22) Saunders, Murray and Cleveland, *ibid.*, **63**, 3121 (1941)