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ELECTRONIC SPECTRA OF ORGANIC MOLECULES AND THEIR INTERPRETATION—X†

THE ELECTRONIC SPECTRA OF THIOBENZOPHENONE

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Abstract—As would be expected hydrogen bonding solvents and others of high polarity cause the K- and R-Bands of thiobenzophenone to shift to longer and shorter wavelengths, respectively. However, some solvents behave in an anomalous manner, suggesting the formation of a specific, and perhaps novel, association between the solute and solvent.

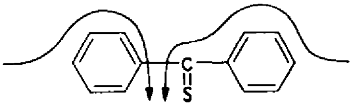
INTRODUCTION

ALTHOUGH the electronic spectra of a considerable number of organic compounds have been determined and reported in the literature, the data for the thioketones, despite Brocklehurst's[1] extensive work, is still incomplete. In particular, little is known about the affect of solvents on the spectra of thiobenzophenone and its derivatives. In this paper, the first of a trilogy, the spectra of thiobenzophenone is studied in a variety of hydrogen bonding and non-hydrogen bonding solvents.

1. *The Absorption Spectrum of Thiobenzophenone*

In hexane

a. A K-Band of fairly high intensity (ε, 17800) at 3145 Å which originates in a transition involving an electron migration along the conjugated system as indicated in I. The two electron migrations, illustrated in I, are equivalent and give



I

rise to two superposed absorption bands, which separate only if the electronic system becomes unbalanced due to the introduction of other substituents.

b. An R-Band of low intensity (ε, 184) at 6092 Å. Whether this band originates from an n → π* or a singlet-triplet transition is not yet certain, but it is a characteristic of the thiocarbonyl group.

c. An absorption band at much shorter wavelengths, i.e. at 2330 Å (ε, 8000). The origin of which is not known.

The band corresponding to the 2600 Å band system of benzene is not observed as it is masked by the K-Band absorption of higher intensity. This masked band,

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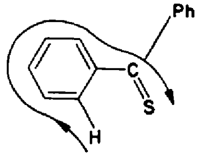
† Part VIII: *Tetrahedron* **10,** 118 (1960).

‡ Present Address: Leicester, Lovell and Co. Ltd., Southampton, Hants.

[1] P. Brocklehurst and A. Burawoy, *Tetrahedron* **10,** 118 (1960).

the B-Band,[2] corresponds to an electron migration around the benzene ring as illustrated in II.

In hexane solution benzophenone exhibits both an R- (λ_{max}, 3280 Å; ε, 100) and a K-Band (λ_{max}, 2480 Å; ε, 20800) together with an inflexion at 2800 Å which arises from a similar type of transition to that causing the masked B-Band of thiobenzophenone itself.[3]



II

2. The Effect of Solvents on the Absorption Spectrum of Thiobenzophenone

a. *K-Band*

It is, at first, convenient to discuss the influence of hydrogen bonding and non-bonding solvents separately. Of the solvents investigated, about half are capable of hydrogen bonding provided that there is a *suitable* solute hydrogen with which to bond. In the case of thiobenzophenone this is not so, and consequently only ethanol and ethyl acetate, which can exist in equilibrium with ethanol and acetic acid, are considered to be hydrogen bonding solvents.

i. *Non-bonding solvents.* Table 1 illustrates the effect of non-bonding solvents, arranged in order of increasing dielectric constant (DE), upon the spectrum of thiobenzophenone. The movement to longer wavelengths of the band maximum with increase in dielectric constant is typical K-Band behaviour. The rather inconsistent size of the shifts relative to the change in dielectric is caused by the low polarity of the solute and the consequent over riding of polar solvent effects by the cumulative result of lesser effects such as dispersion forces. However it is noteworthy that the shift caused by acetonitrile is very small.

ii. *Hydrogen bonding solvents.* Table 2 illustrates the effect of the hydrogen bond. It is immediately apparent that far from having the expected strongly bathochromic displacement due to the mutually reinforcing effects of polar solvent and increase in solute polarity, caused by intermolecular hydrogen bonding, the absorption maximum has moved only slightly to longer wavelengths in both ethanol and ethyl acetate. This displacement, moreover, is smaller than that observed in the non-bonding solvents, particularly benzene. In this connection, it is interesting to compare a related absorption system by means of the wave number, ν cm^{-1}, which is a measure of the change in transition energy. Table 3 illustrates the effect of hexane and ethanol on the spectra of 4-nitrosobiphenyl.

Comparison of Tables 1–3 shows that the bathochromic shift caused by a hydrogen bonding solvent, ethanol, is much greater for the nitroso compound than it is for the thiocarbonyl. The shift of the nitroso compound is similar to that found for

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[2] E. A. Braude, *Ann. Rep. Chem. Soc.* **42,** 105 (1945).

[3] G. Scheibe, *Ber. Dtsch. Chem. Ges.* **59,** 2617 (1926).

other structurally related compounds. Thus, it can be said that the small shift in thiobenzophenone is anomalous.

b. *R-Bands*

It is convenient to discuss the effect of solvents on the same basis as for the K-Bands.

TABLE 1. MAXIMA (IN Å AND CM^{-1}) OF THE K-BAND OF THIOBENZOPHENONE IN NON-HYDROGEN BONDING SOLVENTS

Solvent	DE	D(DE)	λ_{max}	ε	D(λ) (H → solv)	ν_{max}	D(ν) (H → solv)
(H)exane	1·9	—	3145	17800	—	31797	—
(B)enzene	2·3	·4	3195	17600	50	31298	−499
(C)hloroform[4]	5·0	3·1	3195	16800	50	31298	−499
(E)thyl (B)enzoate	6·0	4·1	3218	15600	73	31077	−720
(P)yridine	12·3	10·4	3220	17400	75	31056	−741
(B)enzo-(N)itrile	25·2	23·3	3220	15200	75	31056	−741
(A)ceto-(N)itrile	37·5	35·6	3190	14200	45	31348	−449
(ET)her†	4·3	2·4	—	—	—	—	—
(A)ceto-† (P)henone	17·4	15·5	—	—	—	—	—
(AC)etone†	20·7	18·8	—	—	—	—	—
(N)itro-† (B)enzene	34·8	32·9	—	—	—	—	—
(N)irto-† (M)ethane	35·9	34·0	—	—	—	—	—

† Given for convenience.

[4] P. Brocklehurst, Ph.D. Thesis, Manchester University (1956).

i. *Non-bonding solvents.* Table 4 illustrates the effect of non-bonding solvents, arranged in order of increasing dielectric constant (DE).

Comparison of Tables 1 and 4 shows that the R-Bands have been moved to shorter wavelengths in their characteristic manner by an increase of solvent polarity. It is important, however, that direct comparisons should be made on the basis of the change in ν, D(ν).

The hypsochromic shift shown by benzonitrile, acetonitrile and nitromethane is somewhat larger than would normally have been expected.

Generally, the change in D(ν) with dielectric constant is much more regular than for the K-Band. Since the R-Band corresponds to an entirely different type of

TABLE 2. MAXIMA (IN Å AND CM^{-1}) OF THE K-BAND OF THIOBENZOPHENONE IN HYDROGEN BONDING SOLVENTS

Solvent	DE	D(DE)	λ_{max}	ε	D(λ) (H → solv)	ν_{max}	D(ν). (H → solv)
(H)exane	1·9	—	3145	17800	—	31797	—
(E)thyl- (A)cetate	6·0	4·1	3167	16100	22	31575	−220
(E)thanol	24·3	22·4	3157	16700	12	31675	−122

TABLE 3. MAXIMA (IN Å AND CM^{-1}) OF THE K-BAND OF 4-NITROSOBIPHENYL IN HEXANE AND ETHANOL

Solvent	D(DE)	λ_{max}	ε	D(λ) (H → solv)	ν_{max}	D(ν) (H → solv)
H	—	3275	13800	—	30533	—
E	22·4	3402	14340	127	29403	−1130

MAXIMA (IN Å AND CM^{-1}) OF THE B-BAND OF 4-NITROSOBIPHENYL IN HEXANE AND ETHANOL

Solvent	D(DE)	λ_{max}	ε	D(λ) (H → solv)	ν_{max}	D(ν) (H → solv)
H	—	2285	9790	—	43763	—
E	22·4	2315	9490	30	43198	−565

TABLE 4. MAXIMA (IN Å AND CM^{-1}) OF THE R-BAND OF THIOBENZOPHENONE IN NON-HYDROGEN BONDING SOLVENTS

Solvent	D(DE)	λ_{max}	ε	D(λ) (H → solv)	ν_{max}	D(ν) (H → solv)
H	—	6092	184	—	16414	—
B	·4	6040	200	−52	16556	142
ET	2·4	6055	200	−37	16515	101
EB	4·1	6053	206	−39	16521	107
P	10·4	6000	207	−92	16667	253
AP	15·5	5990	198	−102	16694	280
AC	18·8	6010	193	−82	16639	225
BN	23·3	5985	190	−107	16708	294
NB	32·9	5995	202	−97	16680	266
NM	34·0	5915	196	−177	16906	492
AN	35·6	5920	170	−172	16892	478

transition, it is hardly surprising that other solvent effects should be involved to a different degree.

ii. *Hydrogen bonding solvents.* Table 5 illustrates and compares the effect of hydrogen bonding solvents on the spectrum of thiobenzophenone, nitrosobenzene and 4-nitrosobiphenyl.

By comparison with the two nitroso compounds, the influence of a hydrogen bonding solvent on the R-Band of thiobenzophenone has increased by ten fold over its effect on the K-Band. Further, the R-Band spectrum of thiobenzophenone in ethanol and ethyl acetate is much closer to its expected position, i.e. at shorter wavelengths than in benzene.

TABLE 5. MAXIMA OF R-BANDS (IN Å AND CM^{-1})

Solvent	D(DE)	λ_{max}	ε	D(λ) (H → solv)	ν_{max}	D(ν) (H → solv)
Thiobenzophenone						
H	—	6092	184	—	16414	—
EA	4·1	6005	189	−87	16653	239
E	22·4	5990	201	−102	16694	280
Nitrosobenzene						
H	—	7763	46	—	12882	—
E	22·4	7675	45	−88	13029	147
4-Nitrosobiphenyl						
H	—	7750	33·5	—	12903	—
E	22·4	7687	33·8	−63	13009	106

It should be noted that both solvent polarity and the increase in polarity of the solute, due to hydrogen bond formation, are mutually reinforcing, but here, unlike their effect on the electron migration corresponding to a K-Band transition, they serve to oppose the R-Band transition. For it is a well-known fact that any increase in the polarity or polarizability of a solute-solvent system which involves an R-Band, causes the R-Band to move to shorter wavelengths.[5]

3. *Discussion*

The anomalous effect of hydrogen bonding solvents and others of high dielectric constant upon the K- and R-Bands of thiobenzophenone is indicative of an unexpected association between this solute and the various solvents used in this study. As both the K- and R-Bands are affected it is reasonable to suggest that if an "association" exists then it must be centered on the thiocarbonyl group. Unfortunately, the evidence presented here is only sufficient to direct further work rather than justify a conclusion.

[5] A. Burawoy, *Hydrogen Bonding* p. 259. Pergamon Press, London (1959).

EXPERIMENTAL

Spectra were determined with a Hilger Uvispek Photoelectric Spectrophotometer, using quartz cells. Maxima above 4000 Å were obtained with a glass prism, those below, with a quartz prism. All solvents were purified and their absorption spectra checked against published values.

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A special tribute is due to the late Dr. A. Burawoy who supervised this work, in which he was actively engaged before his sudden and untimely death.