Tetrahedron, 1964, Vol. 20, pp. 2229 to 2236. Pergamon Press Ltd. Printed in Northern Ireland

ELECTRONIC SPECTRA OF ORGANIC MOLECULES AND THEIR INTERPRETATION—XII*

THE EFFECT OF SOLVENTS ON THE ELECTRONIC SPECTRA OF THIOBENZOPHENONE AND ITS DERIVATIVES

W. A. LEES† and the late A. BURAWOY
Manchester College of Science and Technology

(*Received* 3 *July* 1963; *in revised form* 2 *February* 1964)

Abstract—The electronic spectra of thiobenzophenone derivatives have been studied in a number of solvents of varying polarity. It has been found that both the K_1- and K_2-Bands of 4-monosubstituted derivatives move to longer wavelengths with the increasing polarity of the solvent, thus, supporting the view that the electron migration, corresponding to the K_2-Band, is reversed in these compounds relative to its direction in thiobenzophenone itself. However, in some solvents, of very high dielectric constant, e.g. acetonitrile, the bathochromic shift, relative to hexane, is very small. The reverse effect is noted with the thiocarbonyl R-Band. Although, there is a movement to shorter wavelengths with increase in solvent polarity, some solvents have an effect much greater than consideration of solvent polarity alone would allow. The relatively large and small movements of these R- and K-Bands in the presence of solvents of high polarity confirms the earlier observation on the anomalous behaviour of the spectra of thiobenzophenone and furnishes more evidence for the formation of a specific "association" between solvents of high polarity and the thiocarbonyl group.

INTRODUCTION

In the first two papers of this trilogy the effect of solvents and substituents on the electronic spectra of thiobenzophenone were examined. It is appropriate to conclude by studying the effect of solvents on its derivatives.

The effect of solvents on the electronic spectra of thiobenzophenone and its derivatives

K- and R-Bands. For comparative purposes the data obtained will be presented in six tables, K_1-, K_2- and R-Bands, non-bonding or hydrogen bonding solvents respectively. Again, for ease of discussion and clarity, an arbitrary distinction is made between hydrogen bonding solvents and non-hydrogen bonding solvents in that the former contain an oxygen atom which may form a hydrogen bond with a suitable hydrogen atom.

The molecular extinction coefficients (ε) are not included in Tables 1–6 as they make reference more complex.

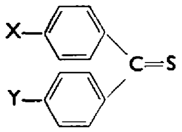
It has already been pointed out in the first two papers that there are two anomalies observed in the spectra of thiobenzophenone in solutions of ethanol and other solvents of very high dielectric constant, such as nitromethane and acetonitrile.

The data, of the diarylthioketones examined, in Tables 1–6 also illustrates this

---

* Part XI: *Tetrahedron* **20,** 1533 (1964).

† Present address: Leicester, Lovell and Co. Ltd., Southampton, Hants.

TABLE 1. MAXIMA (IN Å AND CM^{-1}) OF THE $K_{(1)}$-BANDS OF  IN NON-HYDROGEN BONDING SOLVENTS

Substituents		Solvents							
X	Y	H	B	C	P	BN	NM	AN	
		—	·4	3·1	10·4	23·3	34	35·6	D(DE)
H	H	3145	3195	3195	3220	3220	—	3190	λ_{max}
		31797	31298	31298	31056	31056	—	31348	ν_{max}
		—	−499	−499	−741	−741	—	−449	Dν (H → solv)
Ph	H	3482	3577	3565	3612	3597	—	3536	λ_{max}
		28719	27955	28050	27686	27799	—	28329	ν_{max}
		—	−764	−699	−1033	−920	—	−390	Dν (H → solv)
Ph	Ph	3510	3597	3605	3635	3645	—	3575	λ_{max}
		28490	27799	27740	27510	27435	—	27971	ν_{max}
		—	−691	−750	−980	−1055	—	−519	Dν (H → solv)
BzO	H	3536	3633	3680	3687	3683	3665	3637	λ_{max}
		28291	27525	27174	27121	27151	27284	27495	λ_{max}
		—	−766	−1117	−1170	−1140	−1007	−796	Dν (H → solv)
HO	H	—	3567	3700	3778	3690	3648	3645	λ_{max}
		—	28034	27027	26468	27100	27413	27445	ν_{max}
		—	—	−1007	−1566	−934	−621	−589	Dν (B → solv)
MeO	MeO	3455	3550	3575	3588	3605	3656	3550	λ_{max}
		28944	28169	27971	27870	27740	27352	28169	ν_{max}
		—	−775	−973	−1074	−1204	−1592	−775	Dν (H → solv)
HO	HO	—	3481	3590	3675	3590	3628	3544	λ_{max}
		—	28727	27855	27210	27855	27564	28217	ν_{max}
		—	—	−872	−1517	−872	−1163	−510	Dν (B → solv)
NM_2	H	4130	4367	4480	4503	4528	4492	4468	λ_{max}
		24213	22899	22321	22207	22086	22262	22382	ν_{max}
		—	−1314	−1892	−2006	−2127	−1951	−1831	Dν (H → solv)
NMe_2	NMe_2	—	4330	4420	4480	4485	—	4466	λ_{max}
		—	23095	22624	22321	22276	—	22392	ν_{max}
		—	—	−471	−774	−799	—	−703	Dν (B → solv)

(H)exane, (B)enzene, (C)hloroform, (P)yridene, (B)enzo(N)itrile, (N)itro(M)ethane, (A)ceto(N)itrile, (and for later convenience) (E)thyl(B)enzoate, (E)ther, (A)ceto(P)henone, (AC)etone, (N)itro(B)enzene.

TABLE 2. MAXIMA (IN Å AND CM^{-1}) OF THE K_2-BANDS OF THE COMPOUNDS IN TABLE 1 IN NON-HYDROGEN BONDING SOLVENTS

Substituent		Solvents						
		H	B	C	P	BN	AN	
		—	·4	3·1	10·4	23·3	35·6	D(DE)
H	H	3145	3195	3195	3220	3220	3190	λ_{max}
		31797	31298	31298	31056	31056	31348	ν_{max}
		—	−499	−499	−741	−741	−449	$D\nu$ (H → solv)
Ph	H	3315	3375	3415	3370*	3410	—	λ_{max}
		30166	29629	29284	29674	29326	—	ν_{max}
		—	−573	−882	−492	−440	—	$D\nu$ (H → solv)
BzO	H	3190	3254	3260	3260*	3275	3253	λ_{max}
		31348	30731	30675	30675	30533	30741	ν_{max}
		—	−617	−673	−673	−815	−607	$D\nu$ (H → solv)
HO	H	—	3238	3240	—	3235	3242	λ_{max}
		—	30884	30864	—	30912	30845	ν_{max}
		—	—	−20	—	28	−39	$D\nu$ (B → solv)
NMe_2	H	3233	3315	—	3398	3230*	3375	λ_{max}
		30932	30166	—	29428	30960	29629	ν_{max}
		—	−766	—	−1504	28	−1303	$D\nu$ (H → solv)

* It is doubtful if the maxima figures are accurate since these peaks are affected by either or both the absorption of the solvent and the absorption of the K_1-Band.

anomaly and extends it, quite clearly, to other solvents. The data allows the following observations to be made:

i. With non-hydrogen bonding solvents of low polarity, the K_1- and R-Bands move progressively to longer and shorter wavelengths respectively, in the order of increasing dielectric constant—hexane < benzene < pyridine < nitrobenzene—though progressive increments in the dielectric constant have a decreasing effect.

ii. With non-hydrogen bonding solvents of high polarity *both* the K_1- and R-Bands *display strong hypsochromic* shifts in order of *increasing polarity* and *dielectric* constant—chloroform ~ benzonitrile < nitromethane < acetonitrile.

iii. In hydrogen bonding solvents, especially ethanol and ethyl acetate (equilibrium), the diarylthioketones, except for the hydroxy derivatives, display bathochromic shifts for the K_1-Band which are smaller than consideration of the dielectric constant alone would imply. The opposite effect is observed for the R-Bands.

iv. The view that the electron migration corresponding to the K_2-Bands investigated is away from the thiocarbonyl group is confirmed, since the movement of the K_2-Band in various solvents, though smaller, is similar to that of the K_1-Band.

Since both a reduction in a bathochromic shift and an increase in a hypsochromic shift indicate an increase in the energy required for excitation it would appear that

TABLE 3. MAXIMA (IN Å AND CM^{-1}) OF THE R-BAND OF THE COMPOUNDS IN TABLE 1 IN NON-HYDROGEN BONDING SOLVENTS

Substituents		Solvents								
X	Y	H	B	C	P	BN	NB	NM	AN	
		—	·4	3·1	10·4	23·3	32·9	34	35·6	D(DE)
H	H	6092	6040	5970	6000	5985	5995	5915	5920	λ_{max}
		16414	16556	16750	16667	16708	16680	16906	16892	ν_{max}
		—	142	340	253	294	276	492	478	$D\nu$ (H → solv)
Ph	H	6100	6057	5975	6027	6030	6030	5940	5945	λ_{max}
		16393	16510	16736	16592	16584	16584	16835	16821	ν_{max}
		—	117	343	199	191	191	442	428	$D\nu$ (H → solv)
Ph	Ph	6140	6087	5990	6060	6050	6065	5970	5980	λ_{max}
		16287	16428	16694	16502	16529	16488	16750	16722	ν_{max}
		—	141	407	215	242	201	463	535	$D\nu$ (H → solv)
BzO	H	5985	5960	5800	5921	5975	5914	5830	5835	λ_{max}
		16708	16779	17241	16889	16736	16909	17153	17138	ν_{max}
		—	71	533	181	28	201	445	430	$D\nu$ (H → solv)
HO	H	—	5949	5775	5860	5865	—	5790	5810	λ_{max}
		—	16810	17316	17065	17050	—	17271	17212	ν_{max}
		—	—	506	255	240	—	461	402	$D\nu$ (B → solv)
MeO	MeO	5895	5870	5720	5842	5830	5832	5742	5865	λ_{max}
		16963	17036	17483	17117	17153	17416	17147	17050	ν_{max}
		—	73	520	154	190	184	453	87	$D\nu$ (H → solv)
HO	HO	—	5865	5665	5775	5800	5820	5737	5735	λ_{max}
		—	17050	17652	17316	17241	17182	17431	17437	ν_{max}
		—	—	602	266	191	132	381	387	$D\nu$ (B → solv)
NMe_2	H	5880	5815	5637	5700	5752	5675	5510	5580	λ_{max}
		17007	17197	17740	17544	17385	17621	18149	17921	ν_{max}
		—	190	733	534	378	614	1142	914	$D\nu$ (H → solv)
$N(Me)_2$	$N(Me)_2$	—	5730	—	5630	5615	5620	5450	5520	λ_{max}
		—	17452	—	17762	17809	17794	18349	18116	ν_{max}
		—	—	—	310	357	342	897	664	$D\nu$ (B → solv)
2-MeO	2′-MeO	6034	5975	—	5925	5916	5920	—	5855	λ_{max}
		16573	16736	—	16878	16903	16892	—	17079	ν_{max}
		—	163	—	305	330	319	—	506	$D\nu$ (H → solv)
4-NO_2	H	6220	6175	—	—	6125	6155	6065	6060	λ_{max}
		16077	16194	—	—	16327	16354	16488	16502	ν_{max}
		—	117	—	—	250	277	411	425	$D\nu$ (H → solv)

TABLE 4. MAXIMA (IN Å AND CM^{-1}) OF THE $K_{(1)}$-BANDS OF THE COMPOUNDS IN TABLE 1 IN HYDROGEN BONDING SOLVENTS

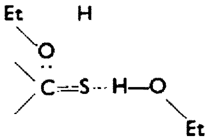
Substituents		Solvents							
X	Y	H or (B)	ET	EB	EA	AP	AC	E	
		—	2·4	4·1	4·1	15·5	18·8	22·4	D(DE)
H	H	3145	3145	3218	3167	—	—	3157	λ_{max}
		31797	31797	31077	31575	—	—	31675	ν_{max}
		—	0	−720	−222	—	—	−122	Dν (H → solv)
Ph	H	3482	3520	3585	3537	—	3565	3522	λ_{max}
		28719	28409	27893	28273	—	28050	28393	ν_{max}
		—	−310	−826	−446	—	−609	−326	Dν (H → solv)
Ph	Ph	3510	3535	3625	3560	—	3587	3562	λ_{max}
		28490	28289	27586	28090	—	27877	28074	ν_{max}
		—	−201	−904	−400	—	−613	−416	Dν (H → solv)
BzO	H	3536	3580	3660	3632	3732	3647	3621	λ_{max}
		28291	27933	27322	27533	26789	27420	27617	ν_{max}
		—	−358	−969	−758	−1052	−871	−674	Dν (H → solv)
HO	H	(3567)	3635	3665	3638	3728	3660	3690	λ_{max}
		28034	27510	27284	27488	26825	27322	27100	ν_{max}
		—	−524	−750	−546	−1209	−712	−934	Dν (B → solv)
MeO	MeO	3455	3530	3570	3530	—	3545	3530	λ_{max}
		28944	28329	28011	28329	—	28209	28329	ν_{max}
		—	−615	−933	−615	—	−735	−615	Dν (H → solv)
HO	HO	(3481)	3530	3567	3537	3693	3580	3582	λ_{max}
		28727	28329	28034	28273	27077	27933	27917	ν_{max}
		—	−398	−693	−454	−1650	−794	−810	Dν (B → solv)
NMe_2	NMe_2	(4330)	—	4395	4295	4483	4405	4335	λ_{max}
		23095	—	22752	23282	22306	22702	23068	ν_{max}
		—	—	−343	187	−689	−393	−27	Dν (B → solv)
NMe_2	H	4130	4310	4424	4342	4527	4435	4372	λ_{max}
		24213	23202	22604	23030	22090	22548	22872	ν_{max}
		—	−1011	−1609	−1183	−2123	−1665	−1341	Dν (H → solv)

Table 5. Maxima (in Å and cm^{-1}) of the K_2-Bands of the compounds in Table 1 in hydrogen bonding solvents

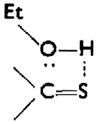
Substituent		Solvents						
X	Y	H or (B)	ET	EB	EA	AC	E	
		—	2·4	4·1	4·1	18·8	22·4	D(DE)
H	H	3145	3145	3218	3167	—	3157	λ_{max}
		31797	31797	31077	31575	—	31675	ν_{max}
		—	0	- 720	- 222	—	−122	Dν (H → solv)
Ph	H	3315	—	—	3345	—	3332	λ_{max}
		30166	—	—	29895	—	30012	ν_{max}
		—	—	—	- 271	—	−154	Dν (H → solv)
BzO	H	3190	3220	3250	3235	—	3234	λ_{max}
		31348	31056	30769	30912	—	30922	ν_{max}
		—	−292	−579	- 436	—	−426	Dν (H → solv)
HO	H	(3238)	3187	3226	3180	—	3150	λ_{max}
		30884	31376	30999	31447	—	31746	ν_{max}
		—	492	115	563	—	862	Dν (B → solv)
NMe_2	H	3233	3280	3340	3327	3370	3440	λ_{max}
		30932	30488	29940	30058	29674	29070	ν_{max}
		—	−444	−992	−874	−1258	−1862	Dν (H → solv)

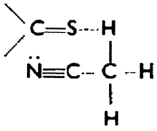
some property common to both solvents of high polarity and those which can hydrogen bond is reducing either or both the polarity and polarizability of the K-Band system and increasing either or both for the R-Band system.

A possible explanation is that the solvent and the thiocarbonyl group of the solute "associate." Typical associations are illustrated in I and II. Such "associations"



I





II

would certainly inhibit the electron migration corresponding to the K-Band, since they would effectively increase the electron density at the carbon atom of the thiocarbonyl group. In the case of the R-Band, the increase in electron density at the carbon atom of the thiocarbonyl group would inhibit the perturbation into the rest of the molecule. This factor would increase the transition energy requirements

TABLE 6. MAXIMA (IN Å AND CM^{-1}) OF THE R-BANDS OF THE COMPOUNDS IN TABLE 1 IN HYDROGEN BONDING SOLVENTS

Substituents		Solvents							
X	Y	H or (B)	ET	EB	EA	AP	AC	E	
		—	2·4	4·1	4·1	15·5	18·8	22·4	D(DE)
H	H	6092	6055	6053	6005	5990	6010	5990	λ_{max}
		16414	16515	16521	16653	16694	16639	16694	ν_{max}
		—	101	107	239	280	225	280	Dν (H → solv)
Ph	H	6100	6035	6040	6020	6030	6030	5980	λ_{max}
		16393	16570	16556	16611	16584	16584	16722	ν_{max}
		—	177	163	218	191	191	329	Dν (H → solv)
Ph	Ph	6140	6045	6070	6050	6070	6037	6025	λ_{max}
		16287	16542	16474	16529	16474	16565	16597	ν_{max}
		—	255	187	242	187	278	310	Dν (H → solv)
BzO	H	5985	5933	5940	5915	5907	5900	5875	λ_{max}
		16708	16855	16835	16906	16929	16949	17020	ν_{max}
		—	147	127	198	221	241	313	Dν (H → solv)
HO	H	(5949)	5910	5906	5890	5885	5868	5760	λ_{max}
		16810	16920	16932	16978	16992	17043	17361	ν_{max}
		—	110	122	168	182	232	551	Dν (B → solv)
MeO	MeO	5895	5835	5875	5850	5850	5827	5760	λ_{max}
		16963	17138	17021	17094	17094	17162	17361	ν_{max}
		—	175	58	131	131	199	398	Dν (H → solv)
HO	HO	(5865)	5800	5830	5815	5815	5787	5618	λ_{max}
		17050	17241	17153	17197	17197	17280	17800	ν_{max}
		—	191	103	147	147	230	750	Dν (B → solv)
NMe_2	H	5880	—	5750	5764	5695	5680	5387	λ_{max}
		17007	—	17391	17349	17559	17606	18562	ν_{max}
		—	—	384	342	552	599	1555	Dν (H → solv)
NMe_2	NMe_2	(5730)	5700	5750	5700	5650	5622	—*	λ_{max}
		17452	17544	17391	17544	17699	17788	—	ν_{max}
		—	92	−61	92	274	336	—	Dν (B → solv)
2-MeO	2′-MeO	6034	6000	5940	5935	5930	5920	5880	λ_{max}
		16573	16667	16835	16849	16863	16892	17007	ν_{max}
		—	94	262	276	290	319	434	Dν (H → solv)
4-NO_2	H	6220	—	6170	6140	6150	6125	6150	λ_{max}
		16077	—	16207	16287	16260	16327	16260	ν_{max}
		—	—	130	210	183	250	183	Dν (H → solv)

* Inflection.

However, if the transition were n $\rightarrow \pi^*$ and not singlet-triplet as has been assumed above, then such an increase in the electron density of the carbon atom would have facilitated the electron migration into the rest of the molecule, and in consequence a bathochromic shift of the R-Band *might* well be expected, such a shift is not observed.

In the case of the 4-hydroxy- and 4,4′-hydroxy-thiobenzophenones in ethanolic (ethyl acetate) solution, the "association" effect is partially over-ridden by the formation of a strong hydrogen bond between the hydroxyl group(s) and the solvent, giving, in consequence, a greater bathochromic shift to the K-Bands.

The hypsochromic shift of the R-Band, due to "association" is assisted by the formation of the hydrogen bond between the hydroxyl group(s) and the solvent.

Molecular models have shown that these associations are physically possible. Moreover, work by Franzosini (1) though interpreted on a differing basis (excited states and the R-Band represented by an n $\rightarrow \pi^*$ transition) to that offered here, has shown in the case of symmetrical thio- and seleno-γ-pyrones that there is a distinction between the solvent effect of non-hydrogen bonding and hydrogen bonding solvents. His observations concur with those made here.

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.

The absorption spectra of unstable compounds were determined by making up and maintaining solutions under appropriate conditions. Weak acids were ionized by the addition of NaOH aq. Care was taken to ensure that there was no adverse effect upon the absortpion spectrum of the compound concerned.

4-Nitrothiobenzophenone is unstable unless its solutions are saturated with HCl and H_2S. Further, attempts to purify it led to instantaneous decomposition. Accordingly, the R-Band spectra in solvents other than benzene, in which it was prepared (part XI), were determined by analysing solutions made up from benzene mother liquor (2%) and benzonitrile, nitrobenzene, nitromethane and acetonitrile (98%). Each solution was saturated with HCl and H_2S. The spectra of other thiobenzophenones were re-determined in order to check the effect of the benzene and the gases. No significant differences were observed.

Acknowledgements—The authors wish to thank Professors H. N. Rydon and R. N. Haszeldine for the facilities provided in the College and the laboratory staff for their unfailing assistance.

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

(1) P. Franzosini, *Gazz. Chim. Ital.*, **88**, 1109 (1958).