# ELECTRONIC SPECTRA OF ORGANIC MOLECULES AND THEIR INTERPRETATION—VIII\*

## THE ELECTRONIC SPECTRA OF THIOBENZOPHENONE AND ITS DERIVATIVES

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Abstract—The effect of the hydroxyl, methoxy, dimethylamino groups as well as the charged  $O^-$  atom at the end of the conjugated system (1) of thiobenzophenone on the positions of the corresponding K-bands and R-bands is discussed.

(1) p-X  $C_{4}H_{4}-C(Ph) = S$  X = HO, MeO, NMe<sub>3</sub>, and  $\tilde{O}$ 

THE effect of substituting the previously mentioned groups in the *para* position of the unsubstituted phenyl group (i.e. in the side chain of the main conjugated system) on the R-bands and K-bands is also discussed and shown to be similar.

The direction of the electronic transition in the excited state in the side-chain phenyl group of the conjugated system is shown to be away from the thiocarbonyl group.

## INTRODUCTION

Although the electronic spectra of a considerable number of organic compounds have been determined and reported in the literature, the data (mostly incomplete) for only a few thicketones is available.

It was considered, therefore, that a systematic examination of the ultra-violet spectra of these compounds would produce information about several aspects of the electronic spectra of organic compounds, such as the similar effect of side-chain substituents on the positions of K-bands and R-bands, and the effect of substituents on the position of R- and K-bands in general.

#### 1. The spectrum of thiobenzophenone

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The spectrum of thiobenzophenone in ethanol shows three regions of absorption:

(i) A K-band of fairly high intensity ( $\lambda_{max} \text{ Å 3165 } \epsilon_{max} 15,600$ ) which originates in a transition involving an electronic migration along the conjugated system as indicated in (a).



(ii) An R-band of low intensity ( $\lambda_{max}$  Å 5990  $\varepsilon_{max}$  185) characteristic of the thiocarbonyl group.

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(iii) An absorption band at much shorter wavelengths ( $\lambda_{max}$  Å 2350  $\varepsilon_{max}$  9000), the origin of which is uncertain.

The B-band<sup>1</sup> corresponding to the 2600 Å band system of benzene is not observed as it is masked by the K-band absorption of higher intensity. The K-band (as will be shown later) must be considered as arising from the two equivalent electronic transitions along the two conjugated systems present in the molecule.

## 2. K-bands

(i) The effect of terminal groups of the conjugated system. The K-band of thiobenzophenone in ethanol is displaced to longer wavelengths in the spectra of p-methoxy, p-benzyloxy, p-hydroxy, p-dimethylamino, p-phenylthiobenzophenone, and the sodium salt of p-hydroxythiobenzophenone. (Table 1). The substituents in the para position to the thio-carbonyl group are terminal groups of the absorbing conjugated system (b):

(b) 
$$X \longrightarrow C(Ph) \Longrightarrow S$$
 where  $X = OR, OH, NMe_2, Ph, \delta$ .

Recent work<sup>2</sup> has shown that the effect of such groups on the position of the K-band are twofold. The K-band is displaced to longer wavelengths as the length of the absorbing system is increased, i.e. more precisely, as the *polarizability* of the electrons of the terminal group increases. The higher this polarizability becomes, the greater is the displacement to longer wavelengths. Secondly, as the *polarity* of the absorbing system is increased, the greater is the displacement of the K-band concerned to longer wavelengths. Influences that increase the polarity of the substituted system facilitate the electron migration and stabilize the excited state.

The former factor is predominant in p-phenyl-thiobenzophenone whereas, in the p-hydroxy-, and p-amino-substituted derivatives the increased polarity of the absorbing system makes a large contribution. This would account for the much greater effect of the p-dimethylamino group and the negatively charged oxygen atom compared with the p-hydroxyl, and alkoxyl groups.

(ii) Secondary K-bands. Thiobenzophenone contains two equivalent conjugated systems, both making a contribution to the observed K-band. If, however, one of the para positions only is substituted, the two absorbing conjugated systems become unequal, and hence two K-bands could be expected, resulting from the different electronic systems (c) and (d). They should be observable if the bands are sufficiently separated.



The spectra of the investigated p-mono-substituted thiobenzophenone derivatives show either two separated K-bands or an inflexion superimposed on the more

<sup>&</sup>lt;sup>1</sup> E. A. Braude, Ann. Rep. Chem. Soc. 42, 105 (1945).

<sup>&</sup>lt;sup>2</sup> A. Burawoy and E. Spinner, J. Chem. Soc. 2557 (1955); A. Burawoy, J. P. Critchley and A. R. Thompson, Tetrahedron 4, 403 (1958).

pronounced K-band at longer wavelengths. Their maxima are given in Table 1 where they are denoted as  $K_1$  and  $K_2$  bands. This is analogous to earlier observations<sup>3</sup> that the spectra of p:p'-disubstituted triphenyl-methyl cations show two K-bands which can be attributed to transitions involving an electronic migration along the axes of the two conjugated systems present (e) and (f).



where X=OH, OMs, NMs,, SMs

Substituent X—	<b>K</b> 1-1	Band	$K_{1}$ -Band		
	max Å	max	max Å	max	
н—	3165	15,600			
СН,О—	3595	12,100	3220	9000	
C <sub>4</sub> H <sub>4</sub> CH <sub>2</sub> O—	3610	17,000	3210	12,400	
HO-	3685	16,000	3175	10,800	
Mc <sub>2</sub> N	4390	23,600	3320	10,400	
Ō—	4500	32,600	3060	6600	
C <sub>4</sub> H <sub>4</sub>	3545	17,800	3370	inflexion	

(iii) The effect of side-chain substituents of conjugated systems. Substituents (in the para position) such as phenyl, hydroxyl, methoxyl, dimethylamino, and the anion O as terminal groups of the absorbing conjugated system displace the K-band of thiobenzophenone to considerably longer wavelengths. If, however, a second substituent is introduced into the unsubstituted phenyl group (representing a branch of the conjugated system) only a small effect is observed. Thus the K-band of p:p'-diphenylthiobenzophenone appears at only slightly longer wavelengths than the K1-band of the p-phenyl-thiobenzophenone (Table 2). Similarly, the K-bands of p:p'-dimethoxy, p:p'-dihydroxy-, and p:p'-tetramethyldiaminothiobenzophenones as well as the sodium salt of p:p'-dihydroxy-thiobenzophenone absorb at slightly shorter wavelengths than the corresponding mono-substituted derivatives (Table 2). Similar observations have been made by Burawoy<sup>3</sup> in the di- and tri-substituted triphenylmethyl cations. Moreover, since the two absorbing conjugated systems in the p:p'-disubstituted thiobenzophenones are once more equivalent, only one K-band of increased intensity is now observed.

It is also of interest that the K<sub>2</sub>-bands of all the investigated mono-substituted thiobenzophenones appear at similar wavelengths to the K-band of thiobenzophenone

<sup>&</sup>lt;sup>8</sup> A. Burawoy, Ber. Disch. Chem. Ges. 66, 228 (1933); G. N. Lewis and J. Bigeleisen, J. Amer. Chem. Soc. 65, 2102 (1943).

Substituents		K <sub>1</sub> -Band			K <sub>2</sub> -Band		
<i>p</i> ∙X	ρ'-Υ	max Å	max	Å	max Å	max	
McO	н	3595	12,100		3220	9000	
McO	MeO	3525	20,000	75		<u> </u>	
но	н	3685	17,000		3170	12,400	
но	но	3595	24,000	90		_	
Mc,N	Н	4390	23,600		3320	10,400	
Mc <sub>1</sub> N	Mc <sub>2</sub> N	4330	37,000	60			
Ō	H ·	4500	32,600		3060	6600	
ō	ō	4440	36,000	60		_	
C <sub>4</sub> H <sub>5</sub>	н	3545	17,800		3370	inflexior	
C <sub>H</sub>	C <sub>4</sub> H <sub>4</sub>	3568	25,000	, 23			

D displacement of K<sub>1</sub>-band due to substituent in the side-chain.

itself (Table 2). The substituted phenyl group, in this case, is the side-chain of the absorbing system and, thus, the substituent has only a small effect.

The effect of side-chain substituents on the position of the K-bands should involve the same two factors that are responsible for the effect of terminal groups. They will cause changes in the polarity of the substituted system in the ground state, resulting in changes of its polarizability, and they will participate in the electronic migration of the transition. These factors will now be of greater complexity. Thus, in the substances investigated, an electron repelling group such as OMe, NMe<sub>2</sub>, or  $\overline{O}$  [as substituent X in (g)] will cause electron displacements in the ground state towards both the aryl and thio-carbonyl groups. This will inhibit the electron migration of the transition as indicated in (g) in the former, and facilitate it in the latter part of the principal absorbing system.



It is probable that the hypsochromic displacement by these side-chain groups arises from a somewhat greater effect in the Ar—C bond than in the C= S linkage. The participation of the electrons of the side-chain in the electronic migration of the transition will also make some contribution, but the resultant effect should be rather complex and would need more extensive investigation.

However, the observations of two K-bands in the mono-substituted compounds indicates that in the excited state the direction of the electronic migration in the sidechain phenyl group is away from the thiocarbonyl group.<sup>4</sup>

<sup>4</sup> A. Burawoy, Ber. Disch. Chem. Ges. 63, 3164 (1930); Tetrahedron 2, 122 (1958).

In a system such as A - C(X). B, in which the effective electronic migration is directed from A towards B, a migration in the branch C-X towards the carbon atom would allow for only *one* electronic transition (h). In the alternative case, two similar electronic transitions (i and j) could be expected. They would be responsible for two K-bands, which in favourable conditions could be observed.

This is indeed the case in the *p*-substituted thiobenzophenones and in the p:p' substituted-triphenyl-methyl ions. When two *para* substituents are present branches A



and X become equivalent and only one K-band of high intensity is observed. This does not exclude the possible existence of a K-band corresponding to excited state (h) at considerably shorter wavelengths.

### 3. R-Bands

As previously shown by Burawoy<sup>4</sup>, the observations related to R-bands can be reduced to two simple generalisations:

(a) Substituents of the chromophoric double bonds have the same qualitative effects on R-bands as substituents (in a side-chain) of an absorbing system on K-bands.

(b) R-Bands are displaced to shorter wavelengths by influences (solvent effect, proton addition, substituents, hydrogen-bond formation) which increase the polarity of the chromophoric double bond.

The considerable separation of the R- and K-bands in the spectra of thiobenzophenone and its derivatives allows, amongst other effects, a comparison of the effect of substituents on both R- and K-bands in the same molecule. This is in contrast to the ketones and azo compounds where the separation of the bands is usually incomplete, the R-band being partly or completely masked by the more intense K-band.

Data for the effect of substituents on the position of the R-band of thiobenzonone are summarized in Table 3 and compared with the effects of these substituents on the K-bands.

It can be seen from Table 3 that the displacement of the R-band to shorter wavelengths increases with the increasing electron donating character of the substituent, i.e. in the order  $H < OMe(OH) < NMe_2$ .

The effect of phenyl groups introduced into the *para*-positions of thiobenzophenone is quite characteristic. Whilst the K-band in *p*-phenyl-thiobenzophenone is displaced appreciably to longer wavelengths (by 380 Å) by the first phenyl group, the R-band is only slightly displaced to longer wavelengths ( $\pm 15$  Å). But, because the second *p*-phenyl substituent in p:p'-di-phenylthiobenzophenone is in the side-chain of the absorbing conjugated system it is again responsible for a slight shift of the R-band to longer wavelengths ( $\pm 20$  Å) and a slight displacement of the K-band to longer wavelengths ( $\pm 23$  Å). This shift is negligible compared with the displacement of the K-band to longer wavelengths caused by the first phenyl group.

When a p-hydroxy group is substituted into thiobenzophenone the K-band is displaced to longer wavelengths (+520 Å) and the R-band to shorter wavelengths

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Substituents		R-Band		D	K <sub>1</sub> -Band		D
<i>p</i> -X	p-X'	max Å	max	Å	max Å	max	Å
н	н	5990	185		3165	15,600	
H	но	5800	254	· · 190	3685	16,000	÷ 520
но	но	5662	370	- 128	3595	25,000	+ 430
CH3O	н	5800	175	190	3595	12,100	-i 430
C <sub>4</sub> H <sub>4</sub> -CH <sub>2</sub> O	н	5875	275	-115	3610	17,000	• 445
CH'0	CH <sub>1</sub> O	5770	288	120	3580	20,000	- 415
(CH <sub>3</sub> ) <sub>3</sub> N	н	5475 i	452	515	4390	23,600	- 1225
(CH,),N	(CH <sub>1</sub> ),N	inflexion	_	_	4330	37,000	- 1165
C.H.	н	6005	246	• 15	3545	17,800	• 380
C.H.	C.H.	6025	318	.: 35	3568	25.000	+ 403

TABLE 3. EFFECT OF SUBSTITUENTS ON R- and K-bands of thiobenzophenone (in ethanol)

D Displacement due to substituent

(190 Å). When a second hydroxyl group is substituted in the vacant *para*-position (i.e. in the side-chain of the absorbing system) the displacements observed (compared with thiobenzophenone) are 128 Å for the R-band, and 430 Å for the K-band. Compared with *p*-hydroxythiobenzophenone, therefore, both bands are displaced towards their original positions in thiobenzophenone when the second hydroxyl group is substituted in the side-chain, the R-band by (190–128 Å) 62 Å, and the K-band by (520–430 Å) 90 Å. Similar results obtain for the *p*-methoxy substituted compounds but unfortunately the data for the *p*-dimethylamino substituted compounds is incomplete due to the inflexion observed in the R-band of p:p'-dimethylamino-thiobenzophenone.

These observations confirm that the effect of substituents of the chromophoric double bond on the position of the R-bands is similar to that of these substituents (in a side-chain) of the absorbing system on K-bands.

#### EXPERIMENTAL

All the spectra included in this publication were determined using a Hilger Uvispek Photoelectric Spectrophotometer. All the compounds were obtained in a high state of purity. p-Hydroxy, p:p'-dihydroxy, p-methoxy, and p-benzyloxy thiobenzophenones have not been previously described.

p-Hydroxy-thiobenzophenone. p-Hydroxybenzophenone (5.0 g) dissolved in ethanol (50 ml) was treated with dry hydrogen chloride and hydrogen sulphide for 3 days. The thioketone precipitated as red plates on pouring the reaction mixture into water. The compound was crystallized from a 1:1 mixture of chloroform and pet ether (b.p. 60-80°), m.p. 139°. Yield: 4.3 g; 78%. (Found: C, 73.0; H, 4.6; C<sub>13</sub>H<sub>10</sub>OS requires: C, 73.1; H, 4.67%).

p:p'-Dihydroxythiobenzophenone. p:p'-Dihydroxythiobenzophenone (5.0 g) was dissolved in ethanol (50 ml) and treated with dry hydrogen chloride and hydrogen sulphide for 3 days. The thioketone precipitated as red plates when the reaction mixture was poured into water. The compound was crystallized from water giving red plates and needles of the monohydrate (m. p. 114° dec). After drying over phosphorus pentoxide *in vacuo*, the thioketone had a m.p. 190°. Yield: 4.5 g; 83%. (Found: C, 68.1; H, 4.3; C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>S requires: C, 67.8; H, 4.4%).

p-Methoxy-thiobenzophenone. p-Methoxybenzophenone (5.0 g) was dissolved in ethanol (50 ml) and treated with dry hydrogen sulphide and hydrogen chloride for 3 days, and the reaction mixture then poured into water. A blue oil separated which was extracted with ether. After drying over anhydrous sodium sulphate and removal of the ether, a viscous blue oil remained which resisted all attempts to purify it. The sample was finally used for spectral determination without further purification. (Found: C, 72.5; H, 5.4;  $C_{14}H_{12}OS$  requires: C, 73.7; H, 5.3%).

To overcome this difficulty, *p*-benzyloxythiobenzophenone was prepared, its spectra determined, and the figures used throughout the discussion. No appreciable difference was observed between the spectra of *p*-methoxy, and *p*-benzyloxythiobenzophenone.

p-Benzyloxythiobenzophenone. p-Benzyloxybenzophenone (5.0 g) was dissolved in ethanol (50 ml) and dry hydrogen sulphide and hydrogen chloride passed in. After 10 hr the thioketone crystallized out as blue plates which on recrystallization from ethanol had m. p. 110-111°. Yield: 4.3 g: 90%. (Found: C, 79.2; H, 5.3. C<sub>20</sub>H<sub>10</sub>OS requires: C, 78.9; H, 5.3%).

p:p'-Diphenyl-thiobenzophenone. p:p'-Diphenylbenzophenone (2.0 g) was refluxed for 10 hr with phosphorus pentachloride (5.0 g) in toluene (10 ml). The reaction mixture was distilled under reduced pressure to remove the toluene and phosphorus oxychloride. The residual keto-dichloride was dissolved in dry light petroleum (b. p. 60 80°, 50 ml) and refluxed with thioacetic acid (14 g) for 30 min. p:p'-Diphenylthiobenzophenone crystallized out and was filtered off. On recrystallization from pet ether (b. p. 100 120°) blue plates m. p. 189° were obtained (Schönberg et al.\* give m.p. 228°). Yield: 1.2 g 56%. (Found: C, 86·0; H, 5·0. Calc. for C<sub>15</sub>H<sub>16</sub>S. C, 85·7, H, 5·1%).

A. Schönberg, O. Schutz and S. Nickel, Ber. Disch. Chem. Ges. 61, 2175 (1928).