

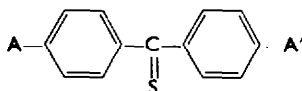
## ELECTRONIC SPECTRA OF ORGANIC MOLECULES AND THEIR INTERPRETATION—XI\*

### THE EFFECT OF SUBSTITUENTS ON THE ELECTRONIC SPECTRA OF THIOBENZOPHENONE

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**Abstract**—1. Thiobenzophenone ( $A=A'=H$ ), and a series of 4-monosubstituted derivatives ( $I, A=H; A'=Ph, OH, O-CH_2-Ph, NMe_2, NO_2$ ) and 4,4'-disubstituted derivatives ( $A=A'=Ph, OH, OMe, NMe_2$ ) and 2-iodo- and 2,2'-dimethoxythiobenzophenone have been prepared.



2. The electronic spectra of these compounds has been determined in either, or both, benzene or hexane, as necessary. In addition, data for 2-hydroxy- and 2-methoxythiobenzophenone are given for a number of solvents.

3. The K-Band of thiobenzophenone is displaced to longer wavelengths on the substitution into thiobenzophenone of a terminal 4-group(s) which increases the polarity and/or polarizability of the molecule.

4. In contrast to the considerable, and always bathochromic, effect of substituents in the terminal 4-position, the introduction of this same substituent into the unsubstituted phenyl group in the "side-chain" of the thiobenzophenone molecule has a much smaller, and usually hypsochromic, effect.

5. The introduction of an electron donating group into the 4-position causes the (thiocarbonyl) R-Band of thiobenzophenone to move to shorter wavelengths.

6. The introduction of an electron withdrawing nitro group into the 4-position causes the (thiocarbonyl) R-Band of thiobenzophenone to move to longer wavelengths.

7. On the basis of the experimental results, the benzene nucleus, when substituted into the thiobenzophenone system, appears to act as an electron acceptor.

8. The 4-monosubstituted thiobenzophenones display two K-Bands, both at longer wavelengths than that of thiobenzophenone itself. An interpretation, based on the possible reversal of the electron migration, corresponding to the  $K_2$ -Band, in the unsubstituted branch of the absorbing system, caused by the introduction of a terminal 4-electron donating group into the relatively non-polar molecule of thiobenzophenone, is offered.

9. The effect of intra- and inter-molecular (solute-solvent) hydrogen bonding on the R-Bands of 2- and 4-hydroxythiobenzophenones is examined.

10. The possible nature of the R-Band transition is discussed.

#### INTRODUCTION

VERY little is known about the effect of solvents on the electronic spectra of the thiobenzophenones. In this paper, the second of a trilogy, the effect of substituents on the K- and R-Bands of thiobenzophenone are studied as an intermediate step before considering the general case of substituents and solvents.

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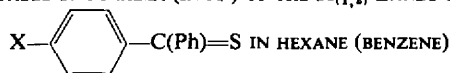
1. *K*-Bands

For the purpose of this discussion, substituents are conveniently divided into those which are electron donating, electron withdrawing, and those which form internal hydrogen bonds.

i. *Electron donating substituents.* The *K*-Band of thiobenzophenone is actually composed of two superimposed band systems. It is convenient to discuss the mono-substituted derivatives separately from the disubstituted derivatives, since in the former the two *K*-Band systems separate.

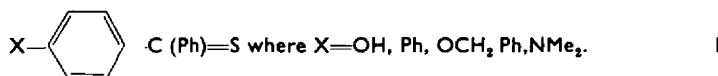
(1) *Monosubstituted thiobenzophenone*

The  $K_1$ -Band of thiobenzophenone in hexane (benzene) is progressively displaced to longer wavelengths in the spectra of 4-hydroxythiobenzophenone, 4-phenylthiobenzophenone, 4-benzyloxythiobenzophenone and 4-dimethylaminothiobenzophenone, cf. Table 1.

TABLE 1. MAXIMA (IN Å) OF THE  $K_{(1,2)}$ -BANDS OF

X	$\lambda_{\max}$	$K_1$ -Band		D(H → X)	$K_2$ -Band	
		$\epsilon$	D(H → X)		$\lambda_{\max}$	$\epsilon$
H	3145	17800	—	3145	17800	—
	(3195)	17600	—	(3195)	17600	—
HO	(3567)	14738	372	(3238)	11940	43
Ph	3482	18400	337	3315	16800	170
C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> O	3536	17700	391	3190	12380	45
Me <sub>2</sub> N	4130	21000	985	3233	12720	88

The substituents in the 4-position to the thiocarbonyl group are terminal groups of the primary absorbing conjugated system,  $K_1$ -I.



Burawoy and Spinner<sup>1</sup> have shown that the effect of such groups on the position of the *K*-Band are two-fold. The *K*-Band is displaced to longer wavelengths:

(a) 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 the greater the displacement to longer wavelengths.

(b) As the *polarity* of the absorbing system is increased, i.e. influences that increase the polarity of the substituted system facilitate the electron migration and stabilize the excited state.

Indubitably, the former factor is predominant in 4-phenylthiobenzophenone whereas, in the 4-hydroxy- and 4-amino-substituted derivatives, the increased polarity of the absorbing system also makes a considerable contribution. This would account for the much greater effect of the 4-aminodimethyl group as compared with the 4-hydroxy and 4-benzyloxy groups.

<sup>1</sup> A. Burawoy and E. Spinner, *J. Chem. Soc.* 2557 (1955).

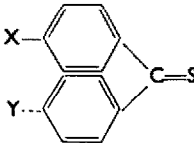
Burawoy and Brocklehurst<sup>2,3</sup> have also investigated the corresponding benzophenones and have found that they behave in an analogous manner.

The absorption spectra of the unsubstituted K-Band system, the secondary K-Band,  $K_2$ , is also affected by this introduction of a substituent and is moved, though to a much smaller extent than the  $K_1$ -Band, to longer wavelengths.

It must be *emphasized* that this bathochromic shift of the  $K_2$ -Band is the *reverse* of the hypsochromic shift normally obtained when an electron donating group is substituted into a benzene nucleus which is itself in the side-chain of the absorbing conjugated system. This phenomenon will be discussed later, but the effect on other systems has been investigated by Burawoy<sup>4</sup> and Brandt.<sup>5</sup>

## (2) Disubstituted thiobenzophenones

On the introduction of a second identical substituent into the terminal 4'-position, the  $K_1$ -Band moves to shorter wavelengths, as the substituent is in the side-chain of the absorbing system, while the  $K_2$ -Band moves to longer wavelengths, since the substituent is in the terminal position of this system. As a consequence of this substitution the two K-Bands are equivalent, and their individual shifts are such as to produce two superposed bands which together have a higher molecular extinction coefficient than observed for either band in the monosubstituted derivatives, cf. Table 2.

TABLE 2. MAXIMA (IN Å) OF THE  $K_{1,2}$ -BANDS OF X- IN BENZENE

Substituents		$K_1$ -Band			$K_2$ -Band		
X	Y	$\lambda_{\max}$	$\epsilon$	D*	$\lambda_{\max}$	$\epsilon$	D*
H	H	3195	17600	—	3195	17600	—
HO	H	3567	14738	—	3238	11900	—
HO	HO	3481	24460	-86	3481	24460	243
Ph	H	3577	16720	—	3375	15940	—
Ph	Ph	3597	31560	20	3597	31560	222
MeO	H†	3595	12100	—	3220	90000	—
MeO	MeO	3550	22500	-45	3550	22500	330
Me <sub>2</sub> N	H	4367	23340	—	3315	11200	—
Me <sub>2</sub> N	Me <sub>2</sub> N	4330	44000	-37	4330	44000	985
and 2:2'-dimethoxythiobenzophenone:—							
		3126	8760	-69	(from $K_2$ -Band of thiobenzophenone)		

\* Displacement due to second substituent

† Values due to Brocklehurst<sup>3</sup>

<sup>2</sup> P. Brocklehurst and A. Burawoy, *Tetrahedron* **10**, 118 (1960).

<sup>3</sup> P. Brocklehurst, Ph.D. Thesis, Manchester University (1956).

<sup>4</sup> A. Burawoy, *Ber. Dtsch. Chem. Ges.* **66**, 228 (1933).

<sup>5</sup> W. Brandt, *J. Prakt. Chem.* **109**, 1 (1925).

### (3) *Mono- and disubstituted thiobenzophenone and side-chain substitution*

Consideration of the spectra of mono- and disubstituted thiobenzophenone offers further information on the effect of substituents in the branch (side-chain) of an absorbing conjugated system on the corresponding K-Bands. This has represented an important part of the evidence advanced by Burawoy<sup>6</sup> for his original classification of electronic spectra, but in more recent years this effect has been almost completely neglected.

Substituents (in the 4-position) such as phenyl, hydroxyl, benzyloxy and dimethyl-amino, when terminal groups of the absorbing conjugated system, displace the K-Band of thiobenzophenone to considerably longer wavelengths. If, however, the same substituent is now introduced into the second unsubstituted phenyl group (representing a branch of the conjugated system), only a small effect is noted. Thus, the K-Bands of 4,4'-dihydroxy-, 4,4'-dimethoxy- and 4,4'-tetramethyldiaminothiobenzophenone are at slightly shorter wavelengths, and 4,4'-diphenylthiobenzophenone at slightly longer wavelengths, than the corresponding monosubstituted derivatives, cf. Table 2. This is analogous to the observation by Burawoy,<sup>4</sup> that the K-Band of 4,4'-disubstituted triphenylmethyl cations display either a zero or hypso-chromic shift on introduction of a corresponding substituent into the third (branching) phenyl group in the 4,4',4''-trisubstituted triphenyl-methyl cations. Reference to this matter will be made later.

The data for 2,2'-dimethoxythiobenzophenone has also been included in Table 2 since this compound illustrates the effect of introducing a substituent into another position in the side-chain benzene nucleus of the thiobenzophenone molecule. The K-Band shift compared with thiobenzophenone itself, is to shorter wavelengths.

Burawoy<sup>7</sup> has shown that the effect of side-chain substituents on the position of the K-Band should involve the same two factors that are responsible for the effect of terminal groups. Such substituents 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 electron migration of the transition. These factors will now be of greater complexity. Thus, in the substances investigated, an electron repelling group such as NMe<sub>2</sub> (as substituent Y in II) will cause electron displacements in the ground state towards both the aryl and thiocarbonyl groups. This will inhibit the electron migration of the transition as indicated in III in the former, and facilitate it in the latter part of the principal absorbing system.

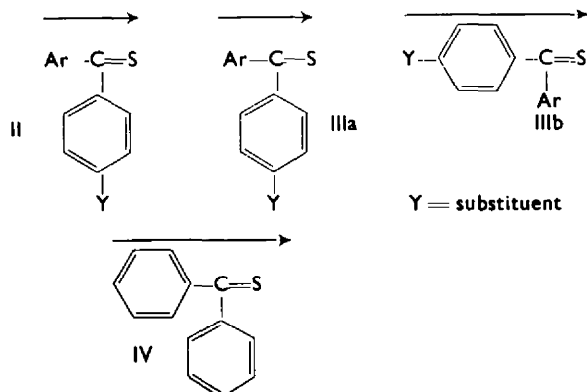
These considerations explain both the *normal* bathochromic shift for the K<sub>1</sub>-Band on the introduction of the first substituent in the terminal 4-position and the hypso-chromic displacement on the introduction of the second (identical) substituent into the 4'-position, but fail to explain why the introduction of the first substituent (into the benzene nucleus in the side-chain for the K<sub>2</sub>-transition) causes an anomalous *bathochromic* displacement of the K<sub>2</sub>-Band. One possible interpretation may now be considered. That is, that the direction of the electron migration in thiobenzophenone itself (IV), (i.e. towards the thiocarbonyl group) is reversed in the electron migration corresponding to the K<sub>2</sub>-Band transition. It is possible that this reversal could be caused by the change in the system brought about by the introduction of

<sup>6</sup> A. Burawoy, *Ber. Dtsch. Chem. Ges.* **63**, 3155 (1930).

<sup>7</sup> A. Burawoy, *Tetrahedron* **2**, 122 (1958).

the electron donating substituent in the benzene nucleus in the "side-chain". Alternatively, one might say that the 'complementary' electron migration plays a much more significant part in this relatively non-polar  $\text{Ph}-\text{C}=\text{S}$  system.

A final decision as to the validity of this postulate might be drawn from the effect of solvents on the  $\text{K}_2$ -Bands of monosubstituted thiobenzophenone derivatives.



ii. *Electron withdrawing substituents.* To date it has not been possible to isolate 4-nitrothiobenzophenone except in a contaminated form, consequently it has not been possible to investigate the effect of an electron withdrawing substituent on a K-Band, although a sample of sufficient purity to allow only an investigation of the R-Band has been obtained.

iii. *Substituents which form internal hydrogen bonds.* To date, it has not been possible to isolate any one of the 2-hydroxythiobenzophenone derivatives prepared, except in a contaminated form. Consequently, again, it has not been possible to investigate any band system other than the R-Band.

However, the effect on K- and B-Bands of intra-molecular hydrogen bonding is well known and is discussed in considerable detail elsewhere in the literature.

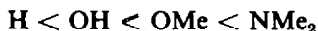
## 2. R-Bands

For the purpose of this discussion substituents are conveniently divided into those headings under which they were discussed in relation to K-Bands.

i. *Electron donating substituents.* Data for the effect of 4-methoxy-,<sup>3</sup> 4,4'-dimethoxy-, 4-benzyloxy-, 4-hydroxy-, 4,4'-dihydroxy-, 4-dimethylamino-, 4,4'-tetramethyldiamino-, 4-phenyl-, 4,4'-diphenyl-, 2-methoxy-,<sup>3</sup> and 2,2'-dimethoxy groups on the position of the R-Band of thiobenzophenone are summarized in Table 3, and compared with the effects of these substituents on the  $\text{K}_1$ -Bands.

The data listed in Table 3 allows the following observations to be made:

(1) That the R-Band moves progressively to shorter wavelengths with the increase in electron donating character of the substituent, i.e. in the order

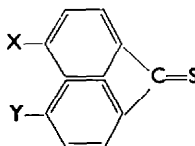


(2) That on the introduction of an unsaturated phenyl group into both thiobenzophenone and the methoxy group of 4-methoxythiobenzophenone, the R-Band moves to longer wavelengths. This displacement, which is far smaller than the corresponding bathochromic shift of the K-Band, is a further instance of the general rule that an

unsaturated group moves R-Bands to longer wavelengths.<sup>9-11</sup> However, the introduction of a diphenyl group moves the R-Band to shorter wavelengths. This will be referred to later.

(3) The introduction of a second electron donating group into the equivalent 4'-position, causes the R-Band to move once again to shorter wavelengths, although the introduction of a second phenyl group again gives a small bathochromic shift.

TABLE 3. MAXIMA (IN Å AND CM<sup>-1</sup>) OF THE K- AND R-BANDS OF X-  
IN BENZENE



Substituent		R-Band						K <sub>(1)</sub> -Band					
X	Y	$\lambda_{\max}$	$\epsilon$	D( $\lambda$ )*	$\nu_{\max}$	D( $\nu$ )*	$\lambda_{\max}$	$\epsilon$	D( $\lambda$ )*	$\nu_{\max}$	D( $\nu$ )*		
H	H	6040	200	—	16556	—	3195	17640	—	31298	—		
MeO	H	5912	177	-128	16914	358	3610	11200	415	27701	-3597		
MeO	MeO	5870	300	-170	17036	480	3550	22500	355	28169	-3129		
PhCH <sub>2</sub> O	H	5960	280	-80	16779	223	3633	17900	438	27525	-3773		
HO	H	5949	239	-91	16810	254	3567	14700	372	28034	-3264		
HO	HO	5865	330	-175	17050	494	3481	24640	286	28727	-2571		
Me <sub>2</sub> N	H	5815	366	-225	17197	641	4367	23340	1172	22899	-5700		
Me <sub>2</sub> N	Me <sub>2</sub> N	5730	94	-310	17452	896	4330	44000	1135	16428	-4870		
Ph	H	6057	246	17	16510	-46	3577	16720	382	27955	-920		
Ph-Ph†	H	5925	—	-115	16878	322	3700	—	505	27027	-4271		
Ph	Ph	6087	317	47	16428	-128	3597	31560	402	27799	-3499		
and in the 2- and 2':2'-position:—													
MeO	H	6030	172	-10	16584	28	3245	14400	50	30816	--482		
MeO	MeO	5975	245	-65	16736	180	3126	8760	-69	31990	692		
							3630‡	9400	—	27548	—		

\* the displacement due to substituent

† Values due to Brocklehurst and Burawoy<sup>8</sup>

‡ B-Band

(4) The numerical ratio of the energy change D( $\nu$ ), for both K- and R-Bands, on the introduction of the first and second substituent is remarkably similar.

(5) The effect of a 2-methoxy group in the side-chain, although small, is still hypsochromic, the introduction of a second 2'-methoxy group causes the R-Band to move again to slightly shorter wavelengths.

(6) Although the introduction of the 2-methoxy group is 'sidechain' with respect to the K-Band absorption system and therefore only moves it slightly to shorter wavelengths, the introduction of a second methoxy group in the 2'-position moves the K-Band to shorter wavelengths relative to both the 2-methoxythiobenzophenone and thiobenzophenone itself, in agreement with previous observations.

(7) The introduction of the second terminal 4'-phenyl substituent causes the K-Band to move to longer wavelengths. Thus, once again, the introduction of a

<sup>8</sup> P. Brocklehurst and A. Burawoy, Private Communication.

<sup>9</sup> A. Behr, *Ber. Dtsch. Chem. Ges.* **5**, 970 (1872).

<sup>10</sup> J. C. V. Brand and J. R. Davidson, *J. Chem. Soc.* **15** (1956).

<sup>11</sup> A. Schonberg et alia *Ber. Dtsch. Chem. Ges.* **61**, 2175 (1928).

phenyl group has caused what appears to be an *anomalous* bathochromic shift, though this time of the K-Band.

It is convenient to consider and discuss these observations together with a general review of current opinion on the nature of the R-Band transition.

There is no general agreement on the nature of the corresponding electronic transition. These bands have been assigned to transitions involving an excited triplet (radical) state, i.e. originating in the bonding electrons,<sup>6,12-19</sup> or to an  $n \rightarrow \pi^*$  transition, i.e. excitations of non-bonding electrons into the lowest unoccupied  $\pi$  state.<sup>20-24</sup> Burawoy<sup>16</sup> concluded, after a critical analysis of the available experimental data, that R-Bands originate in the bonding electrons, and that this is certain in ethylene and its derivatives.

It has recently been suggested<sup>25,26</sup> that the blue shift (hypsochromic) of an R-Band, interpreted as an  $n \rightarrow \pi^*$  transition, brought about by solvents such as ethanol can be taken as a direct measure of the strength of the external hydrogen bond formed, since, on excitation of the non-bonding electron into the excited state, the hydrogen bond will be disrupted, i.e. the transition energy would be greater by an amount corresponding to the strength of this bond than would have been the case in its absence.

Superficially, the disappearance of these bands on proton addition to the non-bonding electron pair of an oxygen or other atom, or the displacement to shorter wavelengths on hydrogen bond formation may appear to support the view that the excitation originates in the non-bonding electrons, since the bonding energy of the lone pair would considerably increase, but one can equally argue that proton addition and hydrogen bond formation will also increase the bonding energy of the bonding electrons of the double bond. Obviously, these observations do not allow a decision between these two possibilities.

However, the effect of proton addition and hydrogen bond formation on the R-Band is only a special instance of the general rule that these bands are displaced to shorter wavelengths as the polarity of the absorbing system increases. Substitution by electron-repelling groups, such as the dimethylamino group, or the use of solvents of high polarity, such as nitrobenzene, which contain no, or only very weakly hydrogen bonding hydrogen atoms, cause similar displacements to shorter wavelengths. This is illustrated here by Table 3 and by Tables 4 and 5 in the first paper of the trilogy.

It is not easy to reconcile the latter observations with the suggested  $n \rightarrow \pi^*$

<sup>12</sup> A. Burawoy, *Ber. Dtsch. Chem. Ges.* **64**, 464 (1931).

<sup>13</sup> A. Burawoy, *Ber. Dtsch. Chem. Ges.* **65**, 941 (1932).

<sup>14</sup> A. Burawoy, *J. Chem. Soc.* 1865 (1937).

<sup>15</sup> A. Burawoy, *J. Chem. Soc.* 1177 (1939).

<sup>16</sup> A. Burawoy, *Disc. Faraday Soc.* **9**, 78 (1950).

<sup>17</sup> E. P. Carr, *Chem. Revs.* **41**, 293 (1947).

<sup>18</sup> M. Kasha, *Chem. Revs.* **41**, 401 (1947).

<sup>19</sup> G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.* **67**, 934 (1945).

<sup>20</sup> M. Kasha, *Disc. Faraday Soc.* **9**, 14 (1950).

<sup>21</sup> H. L. McMurry, *J. Chem. Phys.* **9**, 231 (1941).

<sup>22</sup> H. L. McMurry and R. S. Mulliken, *Proc. Nat. Acad. Sci.* **26**, 312 (1940).

<sup>23</sup> R. S. Mulliken, *J. Chem. Phys.* **3**, 564 (1935).

<sup>24</sup> J. R. Platt, *J. Chem. Phys.* **19**, 101 (1951).

<sup>25</sup> G. J. Brealey and M. Kasha, *J. Amer. Chem. Soc.* **77**, 4462 (1955).

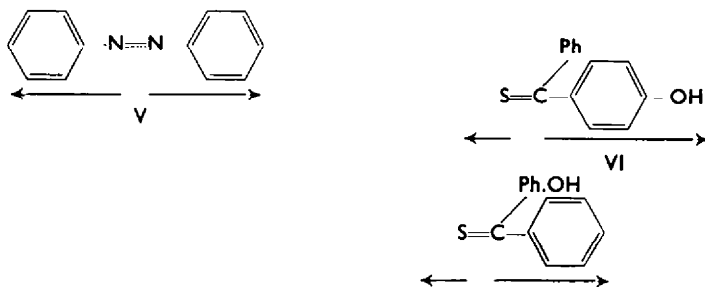
<sup>26</sup> C. A. Coulson, *Research* **10**, 149 (1957).

transition, since these factors will increase the negative charge at the 'O', 'S' or other atom, will reduce the binding energy and, thus, the ionization potential of the non-bonding electrons. Almost certainly, the stability of the excited  $\pi$  state will also increase. Both factors would require a displacement of the R-Band to longer wavelengths, whereas the reverse is observed.

However, the most compelling objection to this interpretation of the R-Bands arises from the fact that it requires an appreciable displacement to longer wavelengths as the length of the conjugated system increases, since at least the excited  $\pi$  state should become increasingly more stable.<sup>21,22</sup> In contrast to the well known displacements of the K-Bands to much longer wavelengths, this is not observed for the R-Bands as can be seen in Table 3.

Similar large K-Band and small R-Band shifts are noted for 4-phenyl-substituted azobenzene<sup>27</sup> and conjugated aldehydes and ketones.<sup>28</sup>

Thus whatever the reason, the observed slight bathochromic shift of an R-Band, caused by the introduction of a terminal 4-phenyl group, is not due to an increase in the length of the absorbing system, but it may be explained if the phenyl group acts as an electron acceptor, i.e. "an electron sink". That the transition originates in the bonding electrons of the double bond is borne out by the fact that on the introduction of a biphenyl group into the terminal 4-position the R-Band moves to shorter wavelengths, indicating that the effect of polarity has overcome the "sink" effect, while the K-Band still moves bathochromically, though to a smaller extent due to the decreasing effect of progressive increments in chain length, i.e. polarity and polarizability.<sup>23</sup> Qualitatively, it involves a charge migration (in phase) towards both atoms of this bond, the perturbation extending into the substituents (cf. V and VI). There are two possibilities: (1) only one pair of electrons, e.g. the  $\pi$  electrons, participate. This would correspond to a singlet-triplet transition, forbidden both by spin requirements and by a small transition moment.



(2) An alternative and more likely interpretation would be that the electron pairs of the double bond are equivalent, a view that is supported both by Burawoy<sup>7,29-33</sup> and Pauling<sup>34</sup> on theoretical and experimental grounds, and that they both participate

<sup>27</sup> A. Burawoy, *Hydrogen Bonding* p. 259. Pergamon Press, London (1959).

<sup>28</sup> A. Burawoy, *J. Chem. Soc.* 20 (1941).

<sup>29</sup> A. Burawoy, *Trans. Faraday Soc.* 40, 537 (1944).

<sup>30</sup> A. Burawoy, *Contribution à l'Étude de la Structure Moléculaire*. Desoer, Liège, 73 (1947/48).

<sup>31</sup> A. Burawoy, *Disc. Faraday Soc.* 10, 104 (1951); *Tetrahedron* 2, 122 (1958).

<sup>32</sup> A. Burawoy and J. P. Critchley, *Tetrahedron* 5, 340 (1959).

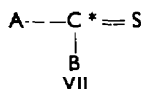
<sup>33</sup> A. Burawoy, J. P. Critchley and A. R. Thompson, *Tetrahedron* 4, 403 (1958).

<sup>34</sup> L. Pauling, *The Kekulé Symposium on Theoretical Organic Chemistry*. Butterworths (1958).



in the transition. This would correspond to a charge migration around a two-membered ring system, the transition being "forbidden," as in the case of the B-Bands, only by the comparatively small transition moment. These qualitatively similar interpretations account for the small intensities and low transition energies characteristic of the R-Bands. They also explain their displacements to shorter wavelengths by all influences which increase the polarity of the absorbing system, since the electron-shifts in the ground state, at least in the substituents, are opposite to the direction of the effective charge migration. Thus, the introduction of one or more electron donating substituents into either the 2- or 4-position causes the R-Band to move to shorter wavelengths for exactly the same reason that a  $K_1$ -Band moves to shorter wavelengths on the introduction of an electron donating substituent into the 'side-chain' absorbing system.

The effect on the K- and R-Bands of the introduction of the first 4- and second 4' terminal electron donating groups, and the fact that the observed effects were due to a change in electron density of the central common carbon atom ( $C^*$ , VII) has already been discussed. It would be idle to speculate on the proportional effect of this change in electron density on the electronic migrations corresponding to the K- and R-Bands, but from a consideration of the energy ratios of the symmetrically 4,4'-disubstituted thiobenzophenones, cf. Table 3, it is quite certain that the effect of the substituent on the position of the K- and R-Band is very much the same in each of these diarylthioiketones investigated.



where A is the first substituent system  
B is the second (identical)  
substituent system

To date the consideration of the absolute value of the R-Band extinction coefficient has received rather less attention than might otherwise have been expected. Kasha<sup>20</sup> pointed out that as a result of McClure's work<sup>35</sup> one could expect that if the R-Band were in fact a singlet-triplet transition then the molecular extinction coefficient ought to increase with an increase in the atomic number of the substituent, while the singlet-singlet,  $n \rightarrow \pi^*$ , transition would be unaffected. Kasha pointed out that the 'weak' absorption bands of investigated N-heterocyclics were unaffected by change in atomic number of the substituents and concluded, therefore, that these bands were not singlet-triplet, but singlet-singlet,  $n \rightarrow \pi^*$ .

Burawoy<sup>16</sup> pointed out that data for halogen substituted carbonyl compounds were reported in the literature, and that contrary to Kasha's claim, a considerable increase of the intensity in the order of substituents  $\text{H} < \text{Cl} < \text{Br} < \text{I}$  is, indeed, observed and thus should apparently represent strong additional evidence for the singlet-triplet character of the carbonyl and thus thiocarbonyl band as discussed above.

However, the molecular extinction coefficient of the R-Band of 2-iodothiobenzophenone, far from being larger or even the same as that of thiobenzophenone itself ( $\epsilon$ , 184), is much smaller ( $\epsilon$ , 103). (It is not certain whether the 2-iodothiobenzophenone was absolutely pure (Experimental)). This reversal of the effect expected from a molecule of high substituent atomic number, does not necessarily imply that

<sup>35</sup> D. S. McClure *J. Chem. Phys.* **17**, 905 (1949).

the singlet-triplet transition interpretation of the R-Band is incorrect, since a consideration of the molecular structure would indicate that the triplet state would be sterically involved with the electronic shell of the substituent. Further, in this connection, Franzosini<sup>36</sup> has found that the R-Band of 2,6-dimethyl-4-seleno- $\gamma$ -pyrone has a molecular extinction coefficient ( $\epsilon$ , 302) much higher than the corresponding thiopyrone ( $\epsilon$ , 18).

It should be possible to make a firmer decision when data for the other five 2- and 4-chloro-, bromo- and iodothiobenzophenones are available.

The actual position of the R-Band of 2-iodothiobenzophenone is ( $\lambda_{\max}$ , 6085;  $\epsilon$ , 103) in hexane, which would indicate that the iodo substituent is acting as a very weak electron donor.

ii. *Electron withdrawing substituents.* It has already been explained that the R-Band moves to shorter wavelengths on the introduction of an electron donating group, because the perturbation resulting from the R-Band transition extends into the rest of the absorbing system and is directly opposed by the electron migration from the electron donating group.

Consequently, it is hardly surprising to find that when an electron withdrawing substituent is introduced the reverse effect is noted, as is shown in Table 4 for 4-nitrothiobenzophenone.

TABLE 4. MAXIMA OF R-BANDS IN Å AND  $\text{CM}^{-1}$  IN HEXANE

Compound	$\lambda_{\max}$	$\nu_{\max}$	D( $\lambda$ )	D( $\nu$ )
Thiobenzophenone	6092 (6040)*	16414 —	— —	— —
4-Nitrothiobenzophenone	6220†	16077	128	-337

\* Benzene

† This solution contained 2% benzene and impurities which did not contaminate this region of the absorption spectrum.

Energetically, the displacement is similar to that of the electron donating substituents and is very much less than that which would have been obtained for a typical K-Band or, more precisely, for an  $n \rightarrow \pi^*$  transition. Again an indication, if not absolute proof, of the correct interpretation of the R-Band as a singlet-triplet transition involving the bonding electrons.

iii. *Substituents which form internal hydrogen bonds.* In Table 5 the position of the R-Bands of 2-nitrosoanisole and 2-nitrosophenol in various solvents are compared. They show the considerable displacement, due to internal hydrogen bond formation, which is smallest in ethanol.

Attempts were made to extend this work to the 2-hydroxythiobenzophenones, but it was impossible to obtain a pure sample. However, as the ketone itself does not absorb in the region above 5000 Å, samples of 2-hydroxythiobenzophenone of sufficient purity for the determination of the R-Band have been obtained. The data obtained for various solvents are shown in Table 5 and are compared with those of 2-methoxythiobenzophenone. They show that an internal hydrogen bond exists between the thiocarbonyl group and the 2-hydroxyl group, and that this bond is

<sup>36</sup> P. Franzosini, *Gazz. Chim. Ital.* **88**, 1109 (1958).

responsible for a very appreciable displacement of the R-Band to shorter wavelengths (500–600 Å).

The anomalous behaviour of the alcoholic solution of 2-hydroxythiobenzophenone can be clearly seen in Table 5. Not only is the displacement to shorter wavelengths (as compared with the 2-methoxyderivative) smaller than in other solvents, but the R-Band appears at longer wavelengths in this solvent than in benzene and

TABLE 5. MAXIMA OF R-BANDS IN Å

2-Methoxythiobenzophenone			2-Hydroxythiobenzophenone†		
Solvent	$\lambda_{\max}$	$\epsilon$	$\lambda_{\max}$	$\epsilon$	Displacement (Å)
Hexane	6110	161	5460	71	–650
Ether	6015	165	5400	90	–615
Benzene	6030	172	5350	90	–680
Ethanol	5975	166	5420	60	–555
Chloroform	5870	120	5300	93	–570
2-Nitrosoanisole			2-Nitrosophenol*		
Benzene	7760	54	6975	60	–785
Chloroform	7660	49	6830	55	–810
Ethanol	7610	41	7150	53	–460
Water	7450	23	6730	31	–720

\* The values for the nitroso compounds are due to Burawoy *et al.*<sup>42</sup>

† The values for the thioketone compounds are due to Brocklehurst.<sup>2,3</sup>

ether, thus suggesting that this anomalous solvent effect is partly due to a cleavage of the internal hydrogen bond and the alternative formation of an external hydrogen bond.

An interesting example of solute-solute hydrogen bonding is found in solutions of 4-hydroxythiobenzophenone. This compound is a red solid, and in dilute solutions of all solvents it gives a blue colour; however in very concentrated solutions (when the first drop of solvent is added to the crystals) it gives a red colour. This is probably due to the presence of a comparatively strong hydrogen bond between the thiocarbonyl and hydroxyl groups in both the solid state and concentrated solution, in the latter case, there is not enough solvent to give complete dispersion of the solute.

## EXPERIMENTAL

*Spectra* were determined with a Hilger Uvispek Photoelectric Spectrophotometer, using quartz cells. Maxima above 4000 Å were determined 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 oxidizing-reducing and pH conditions and, when necessary, in the dark. Care was taken to ensure that deliberate pH changes did not have any adverse effect upon the absorption spectrum of the compound concerned.

## PREPARATIONS

### a. 2-Iodobenzophenone

2-Iodobenzoylchloride, prepared from anthranilic acid by the methods of Koopal<sup>37</sup> and Cohen and Raper,<sup>38</sup> was used for the preparation of 2-iodobenzophenone. There appears to be some

<sup>37</sup> S. A. Koopal, *Rec. Trav. Chim.* **34**, 156 (1915).

<sup>38</sup> J. B. Cohen and H. S. Raper, *J. Chem. Soc.* **85**, 1271 (1904).

confusion in the literature over the purification of the latter. Koopal<sup>37</sup> and Wachter<sup>38</sup> state that the compound can only be purified by the formation of the oxime, due to the breakdown of the 'phenone' itself. However, Koopal also refers (no details given) to a M. Montagne, and says that the latter succeeded in purifying by distillation. The course of the reaction was followed closely and the product was purified by distillation and not by the formation of the oxime.

Aluminium trichloride (45 g, 0.36 mole) was added in small quantities to 2-iodobenzoylchloride (48 g, 0.18 mole) in refluxing benzene (400 ml). The temp was maintained for 15 min after the addition of the  $AlCl_3$ . Ice was then added to the cooled solution, but decomposition did not always occur. This may explain why Koopal thought that the compound could not be purified by distillation (cf. below).

i. *When breakdown did occur.* The filtered water and benzene layers were separated. The water layer was extracted with ether which was added to the benzene layer which was then dried. Distillation gave a crude iodine stained oil. Further distillation (210–211°, 13 mm) gave a light yellow oil which did not solidify. Crystallization from ethanol gave small white rhomboids, m.p. 31–32° (mixed m.ps with 2-iodobenzoylchloride depressed), yield, 37.6 g, 66.8%.

ii. *When breakdown did not occur.* The reaction mixture formed a creamy yellow sludge. Steam distillation and extraction with ethanol did not leave an inorganic residue. On cooling, the alcohol extract formed an oil. The supernatant alcohol was distilled, when a sludge very similar to that already experienced was reformed.

However, on distilling further the sludge broke down to give an oil and a solid. The solid was inorganic and contained aluminium, the oil was worked up as in (i) to pure iodobenzophenone. The oil formed from the alcohol extract was similarly distilled, forming an inorganic solid and a further quantity of oil which was again worked up as in (i).

It can only be concluded that the aluminium complex is very stable and is alcohol-soluble. The exact course of the reaction requires fuller investigation.

M.p. 31–32° (mixed m.p. with the product of stage (1) gave no depression); Koopal,<sup>37</sup> 31–32°; yield, 26 g, 47%.

#### b. 2-Iodothiobenzophenone

2-Iodobenzophenone was dissolved in ethanol (50 ml) at 5°, previously saturated with dry HCl and dry  $H_2S$ . The solution turned blue immediately. The dry gases were passed into the solution for 3 days, and the solution was then poured through a layer of light-petroleum (40–60°, 200 ml) into water (500 ml), the upper layer decanted off quickly and the aqueous layer discarded, no attempt being made to extract it. The light-petroleum was dried by swirling with  $MgSO_4$  under an atm. of HCl and concentrated by distillation under red. press. in an tm of HCl, the temp. never being allowed to exceed 30°. A thick blue-black oil was precipitated, care being taken to maintain a supernatant layer of petroleum. This oil was crystallized by dissolving in a minimum of ethanol at 30° and freezing out with solid  $CO_2$ . The mixture was warmed until the crude precipitate had almost dissolved and then placed in an ice salt freezing mixture. This technique formed a light blue needles of m.p. 37–38°. Examination under a microscope showed that the needles were all blue and not mixed crystals. The crystals were dried *in vacuo* over  $CaCl_2$  for 2 weeks at 2° and then analysed. The analysis showed that there was still about 20% of the parent benzophenone present. The seeding of a cold (2°) ethanolic solution produced a few large blue rhomboids, m.p. 53°, after 5 weeks. There was not by this time enough compound for both spectroscopic and quantitative elemental analysis, and therefore the absorption spectra was determined. Suitable comparison showed that the absorption spectra of 2-iodobenzophenone was not observed.

Further attempts to obtain a higher yield were unsuccessful and an analysis together with an absorption spectra, was never obtained.

<sup>38</sup> W. Wachter, *Ber. Dtsch. Chem. Ges.* **26**, 1744 (1893).

<sup>40</sup> R. Adams and R. L. Jenkins, *Organic Synthesis* Vol. 1, p. 394. Chapman and Hall, London.

<sup>41</sup> C. Furlani and G. Sartori, *Annal. Chim. Roma* **44**, 95 (1954).

<sup>42</sup> A. Burawoy et alia, *J. Chem. Soc.* 3727 (1955).

*c. 4-Nitrothiobenzophenone*

Equal quantities (10 g) of 4-nitrobenzophenone, prepared from nitrobenzoylchloride by the methods of Adams and Jenkins<sup>40</sup> and Schroeter,<sup>41</sup> and POCl<sub>3</sub> were refluxed in benzene for 16 hr, H<sub>2</sub>S was passed through the solution which rapidly turned a deep blue colour. Spectroscopic determinations showed that the yield was about 12%. Any attempt to purify the thioketone caused almost instantaneous decomposition, the compound is only stable in solutions saturated with H<sub>2</sub>S and HCl. In consequence, only the R-Band of this compound could be determined.

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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.

<sup>41</sup> G. Schroeter, *Ber. Dtsch. Chem. Ges.* **42**, 3356 (1909).