

MOLECULAR SPECTRA OF SOME ORGANIC SULPHUR COMPOUNDS

A. MANGINI

Istituto di Chimica Industriale, Viale Risorgimento 4, Bologna, Italia

INTRODUCTION

In aromatic sulphides or heteroaromatic compounds of divalent sulphur, the carbon π -system is coupled to sulphur orbitals of the same symmetry.

If the sulphur atom is taken to be in its normal valence state (s^2p^4), then in the mesomeric systems—besides covalent structures—others arise such as (1) and (2) in *Figure 1*; the latter involves a participation of sulphur $3d$ orbitals (possibly $4s$, $4p$), while the double bond —S=C is not necessarily formed, since the difference in size of the orbitals involved is large and thus the overlapping negligible.

By exciting one valence electron of sulphur to one of these higher lying orbitals (*e.g.* to give the configuration s^2p^3d) the possibility (3) arises, representing the formal analogy between —S— and a —C=C— double bond.

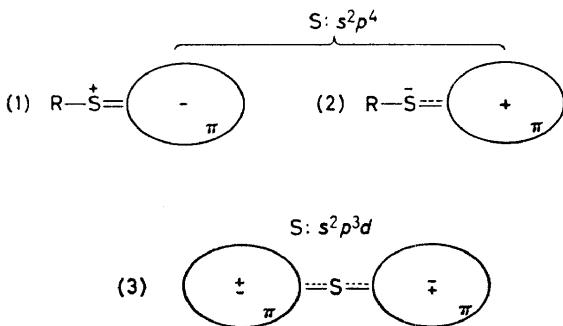


Figure 1. Charge transfer structures in aromatic sulphides: (1) S: electron donor, (2) S: electron acceptor, (3) S: conductor of conjugation

The relative importance of (1), (2) and (3) depend for their energies and overlapping on the remaining structures in the mesomeric systems.

In general, however, from the energetics of the problem it can be inferred that (1) ought to be the most important, while it is doubtful whether (2) and (3), in that order, can significantly affect the molecular properties, also taking into account the interatomic perturbation* on the diffuse vacant

* In the free atom the dimension of the $3d$ orbitals is of the order of magnitude of 7.8–8.0 a.u. while the promotion energy for the process $s^2p^4 \rightarrow s^2p^3d$ is 8.4 e.v. When the sulphur atom is bonded to two carbon atoms, Craig and Zauli, using an electrostatic type of treatment, have found¹ that the relevant $3d$ orbital contracts by about 1 a.u. while the promotion energy, neglecting exchange, is not significantly affected.

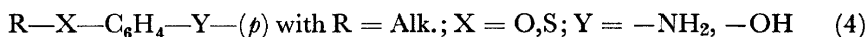
orbitals of sulphur by the environment. This problem can be investigated with the help of various spectroscopic techniques, namely i.r., P.M.R., X-ray transitions (together with dipole moments, reduction potentials, *etc.*) for the ground state, and with electronic spectra for the excited states.

GROUND STATE

Infrared and P.M.R. spectra

Infra-red data of characteristic frequencies and band intensities of suitable groups may give useful information on the local charge distribution, and thus on the perturbing power of substituents; P.M.R. chemical shifts can also be used with advantage to characterize the electronic effects of substituting groups.

Set (4) has been studied with both techniques²:



The relevant data are collected in *Table 1*, and diagrammatically represented

Table 1

X	X—C ₆ H ₄ —NH ₂			X—C ₆ H ₄ —OH	
	ν^*_a	ν^*_s	Δ^\dagger	ν^*	Δ^\ddagger
H	3479	3391	6.55	3612	5.64
<i>m</i> -OCH ₃	3483	3393	6.47	3613	5.60
<i>m</i> -SCH ₃	3484	3393	6.51	3611	5.62
<i>m</i> -OC ₂ H ₅	3482	3392	6.52	3613	5.70
<i>m</i> -SC ₂ H ₅	3484	3394	6.50	3611	5.66
<i>p</i> -OCH ₃	3457	3377	6.84	3619	6.00
<i>p</i> -SCH ₃	3482	3393	6.50	3610	5.67
<i>p</i> -OC ₂ H ₅	3459	3377	6.84	3619	6.01
<i>p</i> -SC ₂ H ₅	3484	3395	6.46	3610	5.63

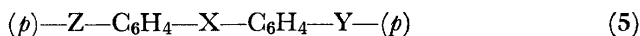
* Solvent CCl₄, concentration 5·10⁻³ mole l., cell length 3 cm; reproducibility ± 1 cm⁻¹.

† Chemical shift: Solvent CCl₄—Reference (CH₃)₄Si; estimated error ± 0.05.

‡ Extrapolated at infinite dilution.

in *Figure 2*. The data on the *sym/asym* stretching frequencies and proton chemical shifts of Y, show that a strong correlation exists between the perturbative effects of X on the local charge distribution of the NH₂— and OH—group respectively: moreover, while the *p*-OR substitution has quite an effect on the charge distribution of—NH₂ and —OH, *m*-O-alk., *p*- and *m*-S-alk have roughly the same small perturbing effect, which can be explained on inductive basis.

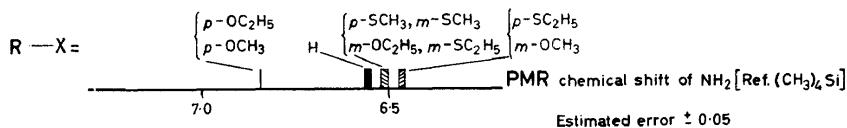
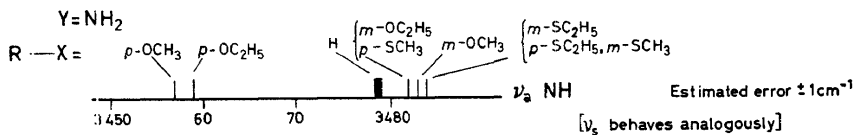
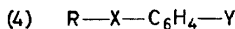
The results on the stretching frequencies and band intensities of group Z in set (5)² led to the same conclusions.



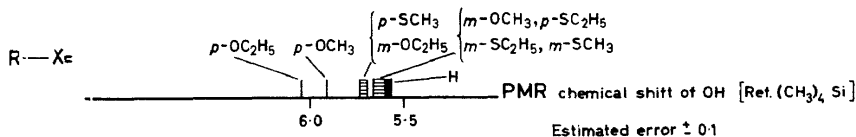
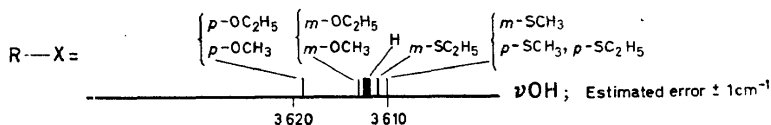
Y being an electron donor group; X=O, S; Z=NO₂, COCH₃.

The relevant data are reported in *Table 2* and show that even in the case

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Y = OH



Solvent: Carbon tetrachloride

Figure 2. Stretching frequencies and chemical shifts of group Y in compounds (4)

where Y = N(CH₃)₂, one of the strongest electron-releasing groups, there is no appreciable transmission of effects, as one would expect if (2) and (3) were operating.

Table 2. Stretching frequencies and intensities of group Z in compounds (5)

Y	X	Z—C ₆ H ₄ —X—C ₆ H ₄ —Y Z = NO ₂			Z = —CO—CH ₃ B = $\epsilon\Delta\nu_{1/2} 10^{-4}$	
		$\nu_{\text{NO}_2}^{\text{S}}$	$\nu_{\text{NO}_2}^{\text{A}}$	q^*	ν_{CO}	B
H	O	1353	1528	1.85	1689	0.81
NH ₂	O	1351.5	1520	1.3	1689	0.86
N(CH ₃) ₂	O	1351	1524	1.1	1689	0.87
H	S	1346	1526	2.4	1690	0.81
OCH ₃	S	1346	1522	2.1	1688	0.86
NH ₂	S	1345	1521	2.1	1689	0.91
N(CH ₃) ₂	S	1345	1522	1.7	1686	0.98

* $q = \epsilon^{\text{S}}/\epsilon^{\text{A}}$; estimated error $\pm 10\%$.

X-ray transitions

Faessler³ has shown that a correlation exists between the valence state of sulphur and the frequency of the K_{α} -doublet. Coulson and Zauli⁴ have theoretically correlated the shift with the net charge on sulphur. For the compounds shown in *Figure 3*, net charges of -0.11 to $-0.17e$ have been computed from the experimental shifts.

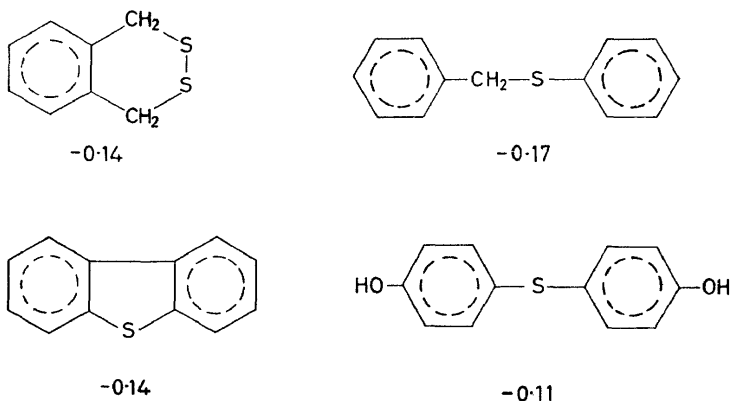


Figure 3. Sulphur charges in some aromatic sulphides from X-ray data

Thus, within the errors involved, the data support the idea that sulphur in the ground state does not couple appreciably with the neighbouring π -system, neither as a donor nor as an acceptor.

EXCITED STATES

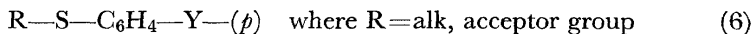
For the situation existing in the excited states we must rely on information given by u.v. absorption.

The problem when the sulphur is in a side chain will be dealt with first.

It may be expected that when energy is fed to the molecule to reach an excited state the participation of structures (1) to (3) will increase: thus, if (2) and (3) are effective, the spectral properties of appropriate sets of compounds will at least show a qualitative evidence of $3d$ -orbital participation.

Many such sets have been studied by us: however, we shall limit ourselves to the most significant examples and refer the reader to our previous publications for a more thorough and systematic approach⁵.

One of the most obvious sets is that of benzene derivatives (6)

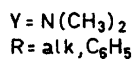
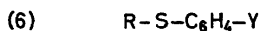


Since we are looking for evidence of sulphur exhibiting acceptor properties we limit the choice of Y to $-N(CH_3)_2$, one of the strongest donor groups.

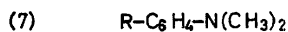
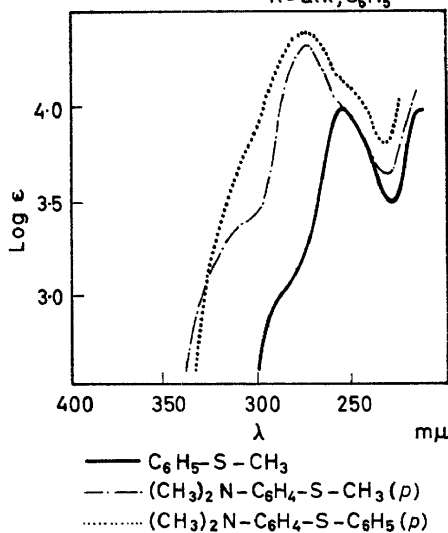
The reference compound, thioanisole, shows in solution two overlapping bands at lower frequencies, due to two distinct transitions of the $\pi-\pi$ type (see *Figure 4*). Without going into details of their assignment, it is to be expected that the electron charge fed into the benzene ring—by the donor

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group—will enhance the probability of an acceptor mechanism by sulphur in respect of mechanism (1), particularly when R is an acceptor group. This is easily seen, since a positivization of the sulphur atom will on the one hand increase the electron-affinity of the empty $3d$ orbital, and on the other cause a contraction of these orbitals allowing a better overlapping with the benzene π -system.



R	$\Delta\nu$	$\Delta\nu'$
CH ₃	+25	+27
C ₆ H ₅	+29	+29



R	$\Delta\nu$	$\Delta\nu'$
$-CH_2S-CH_3$	+18	+6
$-S-CH_3$	+30	+14
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	$\Delta\Delta 12$	8

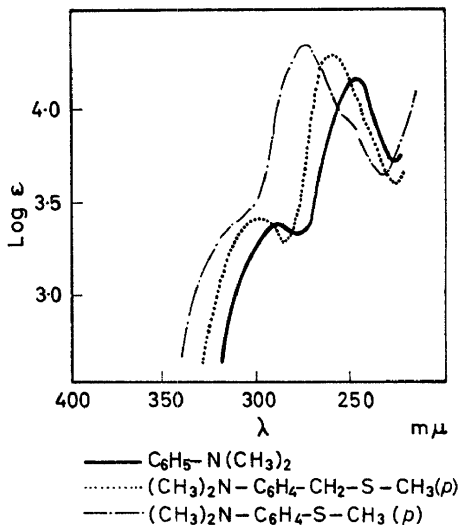


Figure 4. Ultraviolet absorption spectra and band shifts for compounds (6) and (7)

The shifts $\Delta\nu$ and $\Delta\nu'$ (10^{-2} cm^{-1} units)* in respect of the first two bands of thioanisole for compounds (6), are given in *Figure 4*.

These shifts, although in the correct direction for an extended conjugation, have, nonetheless, little significance for the following reasons:

(i) Extended conjugation usually produces greater shifts, as can be seen in the case $\text{Y}=\text{NO}_2$ (*p*-nitrothioanisole (6)), where the character of the sulphur atom described by (1) can play its rôle fully: the shifts are in fact for $\text{R}=\text{CH}_3$, $\Delta\nu \sim 43\text{--}51$; $\text{R}=\text{C}_6\text{H}_5$, $\Delta\nu \sim 54$, and are accompanied by a great increase in intensity.

(ii) The shifts observed in the series (7) $\text{R}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)_2$ in respect of dimethylaniline are also reported in *Figure 4*, and indicate that the significant part of the shifts ($\Delta\Delta$) is of the same order of magnitude as the zero-point vibration correction and solvent effects.

(iii) For *p*-disubstitution in (7) with two donor substituents, such as $-\text{N}(\text{CH}_3)_2$ ($\text{R}=\text{N}(\text{CH}_3)_2$) shifts of +21 and +33 are observed in respect of the bands of the monosubstituted compounds: these shifts cannot represent extended conjugation but only the perturbation induced by the donors on the benzene π -system.

On the other hand, a further increase of the accepting power of R in (6) does not show the expected modifications: a comparison between the spectra of *p*-dimethylamino-*p'*-nitro-diphenylsulphide and the correspondent phenylbenzyl-sulphide (*Figure 5*) does not show evidence⁵ of extended conjugation.

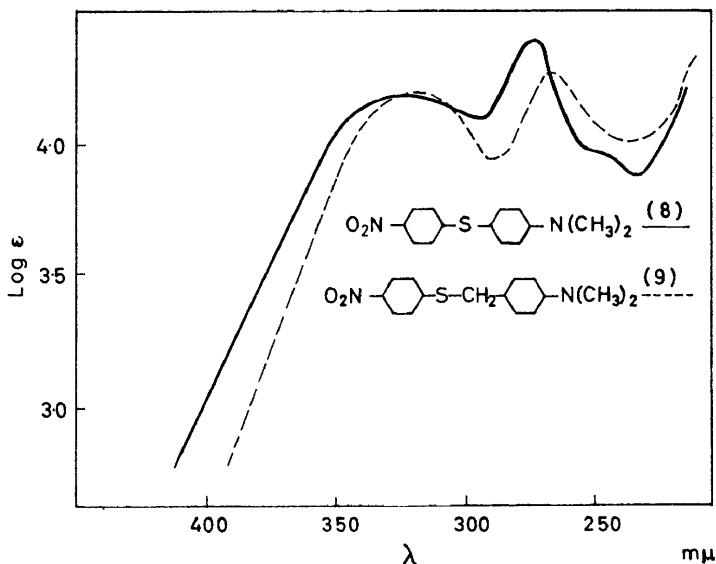


Figure 5

* These shifts refer to maxima or inflexions of the spectra measured in solution, and not to the effective differences in energy of the electronic transitions, since it is not possible to locate band origins; it may be supposed, however, that molecular dimensions in the excited states are roughly comparable. The uncertainties on solvent correction and zero-point vibration energy remain: their order of magnitude is difficult to estimate, but is at least hundreds of cm^{-1} .

It is noteworthy that the twisting of the two rings in the former compound ought not to matter for structures (2) and (3) since an appropriate combination of d orbitals, which can interact with the π -system of benzene, always exists. In fact an investigation⁵ on the dibenzothiophene series—where the planarity of the aromatic system is ensured—shows that the situation appears to be identical with the previous one: since in this series the sulphur atom is a part of the aromatic system it could be concluded that a heteroaromatic sulphur atom behaves substantially as the sulphur atom of diphenyl sulphides.

However a distinction has to be made for thiophene (and its derivatives), where sulphur participates actively to the π -charge delocalization already in the ground state⁶: thus it cannot be excluded that in the excited state of this compound the strong positive charge on sulphur will stabilize the $3d$ orbitals enough to draw back some charge from the ring. It is, however, difficult to see how this possibility can be tested experimentally.

CONCLUSIONS

Within experimental error, the spectroscopic evidence indicates that in the ground state $3d$ -orbital participation, if existing, does not modify appreciably the molecular properties involved. This conclusion is substantiated by other experimental data, such as dipole moments and polarographic reduction^{2, 7}.

As far as the first few excited states of aromatic molecules are concerned, the spectral modifications observed are not self-contained evidence for the participation of $3d$ orbitals.

Only in the case of thiophene do theoretical reasons exist which point to the possibility of such a participation.

References

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- ³ R. Faessler and R. Mecke. *Z. Elektrochem.* **64**, 587 (1960).
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- ⁵ See literature cited by A. Mangini. *Boll. Sci. Fac. Chim. Ind. Bologna* **16**, 67 (1958); *Boll. Sci. Fac. Chim. Ind. Bologna* **18**, 191 (1960); *J. Chem. Phys.* **1959**, 240.
- ⁶ B. Bak. *Bol. Sci. Fac. Chim. Ind. Bologna* **21**, 8 (1963).
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- ⁷ H. Lumbroso and R. Passerini. *Bull. Soc. Chim. France* **1957**, 311;
M. Rolla, G. Leandri *et al.* *Ann. Chim. (Paris)* **45**, 1106 (1955); *Boll. Sci. Fac. Chim. Ind. Bologna* **13**, 56 (1955).