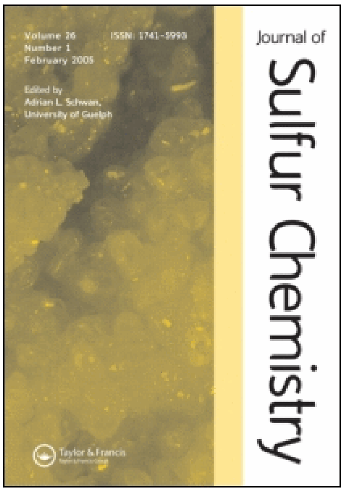

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Summary of Some of My Research on Organo Sulphur Compounds

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SUMMARY OF SOME OF MY RESEARCH ON ORGANO SULPHUR COMPOUNDS

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Sulfur Reports takes great pride in featuring another personal account of a grand old man in sulfur chemistry, this time by the eminent physical organic chemist Professor Angelo Mangini. Apart from the straightforward and lucid presentation of his personal ideas in theoretical sulfur chemistry, the author shares with us the excitement and thrill of the explosive development of theoretical organic chemistry from the early postwar period to the present.

Key words: Furans, A. Mangini, sulfides, sulfones, sulfoxides, thiophens.

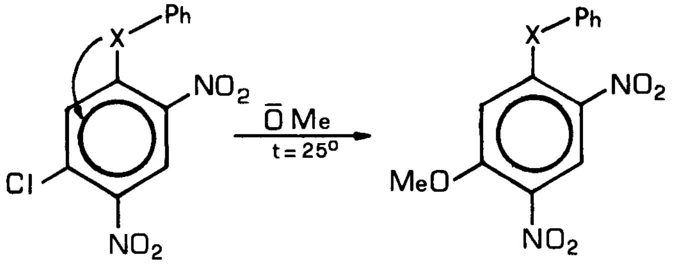
I would like to point out that my first encounter with organic sulphur took place towards the end of the thirties when I decided to study furfural thionation in order to obtain sulphurated dyes.[1] Despite their encouraging results, these studies were abandoned and it was only about ten years later that I undertook a systematic research of the UV spectra of sulphur-containing compounds, with the aim of determining the modifications induced on the spectrum of benzene by sulphur-containing substituents.[2] I was then necessarily involved in the problem of the so-called expansion of the valence shell of divalent dicoordinate sulphur: according to this hypothesis sulphur, as for example in sulphides R–S–R (where R is an unsaturated or aromatic group), besides acting as an electron donor, may also act as an electron acceptor, and in some instances as an acceptor-donor group. This induced a change in the scope of the original studies and suggested the use of different experimental techniques: thus, in addition to polarographic, diffractometric and kinetic research a systematic IR investigation was carried out as well as studies which took advantage of spectroscopic techniques which only in those days began to be exploited in organic chemistry, i.e. magnetic resonance spectroscopies (NMR and ESR) and photoelectron spectroscopies (ESCA and PES). In the early sixties, in collaboration with Professor C. Zauli, the first theoretical studies on thiophen and furan were carried out by means of the VB method, and more recently, i.e. in the mid seventies, together with Professor F. Bernardi, I began investigating by the MO method the interaction between –SR and –OR substitutents and unsaturated residues. I should like to point out here that as a corollary to my work more specific chemical research was carried out by some of my young collaborators, including G. Leandri (sulphides, disulphides, and sulphones), F. Montanari (sulphoxides), G. Modena (sulphur oxidation), A. Tundo (sulphides, sulfones, and thiophen derivatives), J. Degani (sulphur-containing heterocycles), and, more recently, G. Maccagnani (sulphines and small sulphur heterocycles).

Because of the vastness and heterogeneity of the matter it does not seem advisable to give here a survey however short of all my research: I shall therefore only summarize the results on sulphides and their oxygenated analogues in their ground and photoexcited states, on the UV spectra of sulphoxides, sulphones and some dibenzothiophene derivatives, and on calculations carried out with the VB and MO methods. For the sake of readability and of conciseness in the following discussion reference will be made to some of the results of my collaborators as well as to a paper of mine published by the Accademia Nazionale dei Lincei.[3] Moreover, the discussion will not follow a chronological order, but will proceed topic by topic (for example the ground state of sulphides will be dealt with completely before turning to the excited state). More common chemical compounds will be indicated in the test and figures with their acronyms, A standing for anisole, TA for thioanisole, DPhS for diphenyl sulphide, DPhE for diphenyl ether, DMA for *N,N*-dimethylaniline, DBT and $DBTSO_2$ for dibenzothiophene and dibenzothiophene sulphone, respectively.

As a necessary preamble I would like to recall that C. K. Ingold in elaborating his theory (1926) assumed, on the basis of chemical evidence such as electrophilic substitutions and transpositions, that in planar or quasiplanar molecules (R–X–R, where R = aromatic or unsaturated residue and X = O, S) the sulphur, as well as the oxygen, behaves as an electron donor: this assumption found additional support by physical data (such as dipole moments, interaction moments, conjugation energies, etc.); Ingold further postulated that the donor effect of oxygen in the ground state was greater than that of sulphur: also this second hypothesis was experimentally proven to be essentially correct. However, we will encounter cases in which substituents –SR and –OR may, under particular conditions, behave as electron accepting groups, and we shall see that sometimes the donor power of the sulfurated substituent –SR is greater than that of the oxygenated one –OR.

1. AROMATIC SULPHIDES: NEUTRAL AND RADICAL SPECIES

1-1. In the nucleophilic reaction indicated in Eq. 1 (X = NH, O, or S)[4] the rate of substitution of the chlorine atom is expected to increase with decreasing charge transfer from X to the aromatic ring. Actually the experimental substitution rates increase in the order k(NH): k(O):k(S) = 100:851:1431, the rate being greatest with the sulphide, where the sulfurated substituent has the least donating ability.



(1)

1-2. Diffractometric analysis of *p*-nitro-, *p*-dimethylamino- and *p*-dimethylamino-*p'*-nitro-DPhS[5] afforded the following results: i) the aromatic rings in the first two sulphides occupy planes with a dihedral angle slightly smaller than 90° while in the dimethylamino-nitro derivative the angle is reduced to 68°; the valence angle of the two sulphur bonds is 104–105°, and the plane containing the dimethylamino group is twisted approximately 4° with respect to the plane containing the contiguous phenyl ring; ii) the

S–C(Ph) bond lengths are 1.77–1.78 Å in all three compounds (a single C–S bond is 1.81 Å long); iii) the Me_2N–Ph bonds in the nitro and dimethylamino derivatives are 1.38 and 1.35 Å long, respectively (the length of the single C–NMe_2 bond is 1.47 Å); iv) the C–N(NO_2) bond is 1.45 Å long. From these results the following conclusions can be derived: a) there is an alternate interaction between both aromatic rings, independent of the nature of the para and para-para′ substituents: b) the NMe_2 group strongly interacts with the phenyl ring, but this dative interaction does not involve the sulphur atom; c) the extent of conjugation between phenyl and the nitro group is very modest and does not involve the sulphur atom.

1-3. The polarographic research[6] involves DPhS bearing *p*- and *p*′-acceptor and -donor substituents, respectively, and, for comparative purposes, the corresponding DPhE and diphenylamino derivatives

$$\underbrace{p\text{---}Z}_{O_2N,\ COMe}\text{---}C_6H_4\text{---}\underbrace{X}_{S,\ O,\ NH}\text{---}C_6H_4\text{---}\underbrace{Y\text{---}p'}_{H,\ OMe,\ NH_2,\ N(Me)_2} \tag{2}$$

The results are shown in Fig. 1 and indicate that the variations of the half-wave potentials of the polarographic reduction with the nature of Y are negligible compared to those of the monosubstituted compounds (Y = H), whatever the nature of X (S, O,

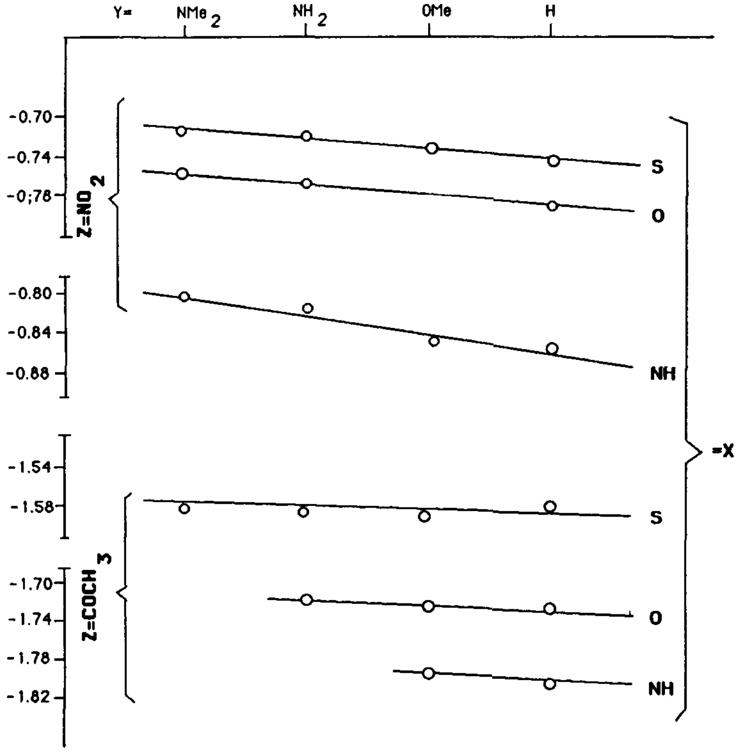
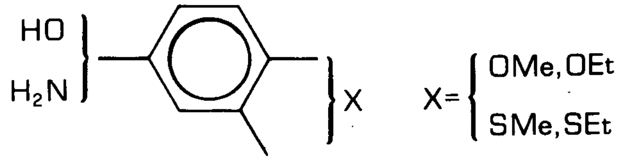


Figure 1 Polarographic half wave $E_{1/2}$ (V) of the compounds p–Z–C_6H_4–X–C_6H_4–Y–p (calomel electrode: pH = 9.2, accuracy ± 0.01 V).

NH). It can therefore be stated that there is no transmission of effect from the donor to the acceptor substituent and that, just as O and NH, sulphur acts as insulator for the electronic effects.

1-4. The same conclusion can be derived by IR spectroscopy: in fact the stretching frequencies of the nitro (ν_s, ν_{as}) and the carbonyl group are practically unaffected by the substituent Y.[6]

In the combined IR and NMR studies[7] *m*- and *p*-alkoxy- and *m*- and *p*-alkyl thiophenols and -anilines (Form. 3) were examined; it should be noted that in the para derivatives the alkylthio group is in a position formally conjugable with the electron



(3)

donor OH and NH_2 groups. The results indicate that the NH_2 frequencies (ν_s and ν_{as}) correlate linearly with the chemical shifts (τ) of the phenolic hydroxyl group, but the most important result is that the effect of a *p*-alkoxy substituent on the H(OH) chemical shift and on the frequencies of the amino group is much stronger than that of a *m*-alkoxy or of a *p*- or *m*-alkylthio group (Fig. 2; only values for NH_2 are shown, ν_{as} exhibiting a

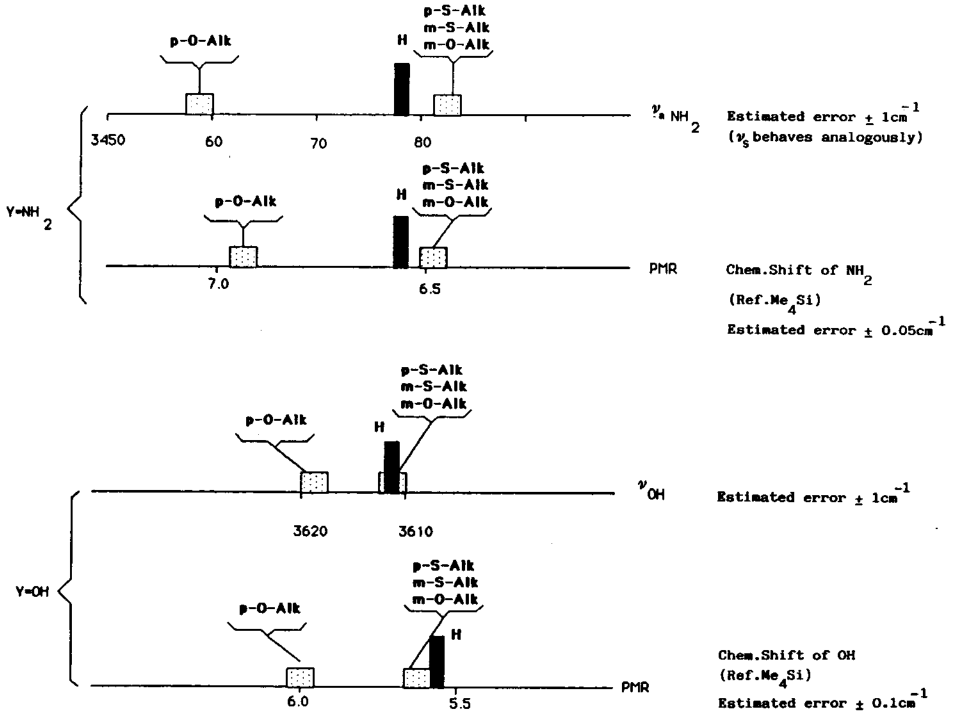


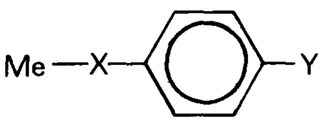
Figure 2

similar trend). This indicates that in the last three cases the substituents exert only an inductive effect. On the other hand the effect of the *p*-alkoxy group is hard to explain unless some sort of para effect is conceived.

1-5. ESR spectroscopy has been applied to the study of a variety of radical species,[8] either neutral or ionic (anions and cations), and the results were checked against spin density calculations performed with both the p and the d model within the MO method. In most cases the former model led to good agreement with experiment, the spin density distributions being at least qualitatively respected, whereas the d model led to distributions at odds with those derived from experimental data; yet, this was not always the case, and in a few instances the p model proved inadequate.

1-6-1. A different approach to the problem of the expansion of the sulphur valence shell was attempted by making use of ESCA spectroscopy,[9] the compounds investigated being *m*- and *p*-amino- and -dimethylamino-TA and -DPhS, *m*- and *p*-nitro-TA and -DPhS. The results are expressed in terms of B.E. (= binding energy) differences (eV) between N_{1s} of the NX_2 group (X = H, Me) and the thiolic $S_{2p_{3/2}}$ in the amino and dimethylamino derivatives, and between N_{1s} of NO_2 and the same thiolic $S_{2p_{3/2}}$ in the nitro derivatives (these differences can be measured directly from the distance of the peaks in the spectra, with an accuracy better than 0.2 eV). Because the B.E. on the N_{1s} electrons is lower than that of the $S_{2p_{3/2}}$ electrons one can easily show that in nitro-TA and in nitro-DPhS the difference ΔB.E. is in favour of the meta derivatives (where the nitro group is not conjugated); it can also be proven that if in the amino and dimethylamino substituted compounds sulphur actually acted as an electron acceptor (conjugated sulphur) one should have a different trend, with ΔB.E. in favour of *p*-substituted with respect to *m*-substituted derivatives (unconjugated sulphur). Similar to what was previously found for nitroanilines, the experimental data indicate that the ΔB.E. are in favour of the meta derivatives for nitro-TA (0.5 eV) and nitro-DPhS (0.6 eV). The data are almost the same also for *p*- and *m*-amino- and -dimethylamino-TA, but slightly in favour of the *p*-dimethylamino-DPhS (0.2 eV) with respect to the *m*-derivative, although the value is within the experimental error. As a consequence, an acceptor ability of thiolic sulfur (NX_2 being the donor) could not be derived from the ESCA results.

1-6-2. PES spectroscopy has been applied to the *p*-substituted anisoles and thioanisoles indicated in Form. 4,[10] and the results have been discussed on the basis of CNDO/2 combined with a PMO analysis. As far as the expansion of the sulphur valence shell is concerned it should be pointed out that the HOMO of A has mainly ring character (70.7%) while the HOMO in TA has essentially sulphur character (78.3%), thus confirming that in the case of TA the interaction with the ring is very small (21.7%), and anyway smaller than that of oxygen in A (29.3%). As a consequence the participation of 3 d sulphur orbitals seems unlikely.



$$Y=\begin{cases} H, Me, OMe, SMe \\ NH_2, NMe_2, NO_2 \end{cases}$$

(4)

2. ELECTRONIC PROPERTIES OF —SR AND —OR SUBSTITUENTS

We summarize here the results of ab-initio MO computations dealing with the electronic properties of –SR and –OR substituents in various types of molecular species, such as neutral unsaturated species, methyl cations and anions, aromatic radical anions and amino derivatives.

2-1. The donor or acceptor effects we have been considering so far refer to planar or quasi-planar molecules (Fig. 3a). It is usually assumed that the conjugative interaction between –XR and the adjacent π system takes place through the π-type lone pair of the heteroatom, implying a charge transfer to the unsaturated system: this is the electron donating effect. The conjugative interaction may alternatively occur at the expense of the π system with a charge transfer to the heteroatom, this being the electron-accepting effect. On the other hand, when the –XR group adopts a nonplanar conformation (orthogonal in the limiting situation) conjugative interactions may in principle occur between the π system and the orbitals of the XR group. In Fig. 4 the planar and nonplanar conformations are shown for an –XR substituent.

Figure 3

For planar or quasi-planar molecules the donating effect consists in the interaction of the doubly occupied orbital (n_{π^*}) of the heteroatom with an empty orbital of the R_π residue, π_{R^*} (Fig. 4:a). Conversely, in the electron-accepting effect a doubly occupied orbital of the residue R interacts with a vacant orbital of X, for example a 3d or higher orbital (Fig. 4:b). These latter interactions usually involve a modest electronic effect.

In nonplanar molecules the situation is generally more complex, involving π orbitals of the residue R_π and of the XR group. The case of the simpler substituent –XH will be analyzed. The more noteworthy interactions are those between a σ lone pair (n_x) and the vacant π orbital of the unsaturated fragment R_π, which therefore imply a donor mechanism (Fig. 4:c). With R_π fragments characterized by a high efficiency, as is the case with negatively charged groups (carbanions), the dominant interaction is the one between a π electron and the empty orbital σ^*_{XH} (Fig. 4:d); that is a π–σ^* accepting mechanism. It can be seen that in this last case the –XH (–XR) substituent is involved as a whole, and not only the X heteroatom.

According to the OEMO (One-Electron Molecular Orbital) model the amount of the net charge transfer (Q) resulting from the interaction of the two orbitals Φ_1 and Φ_2 can

$$Q=(n_1-n_2)\left[H_{\Phi_1\Phi_2}/\Delta\varepsilon_{\Phi_1\Phi_2}\right]^2 \tag{5}$$

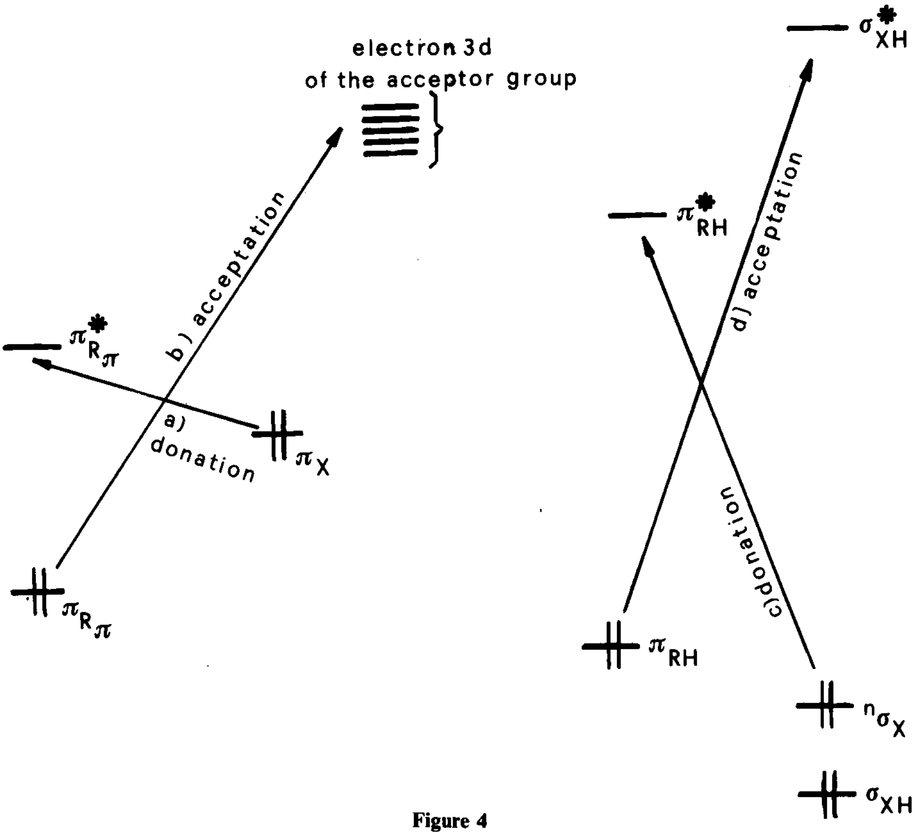


Figure 4

be calculated by means of Eq. 5, where n_1 and n_2 represent the number of electrons on F_1 and Φ_2, respectively, **H** is the matrix element between Φ_1 and Φ_2, $\Delta\varepsilon_{\Phi_1\Phi_2}$ is the energy gap between the two interacting orbitals Φ_1 and Φ_2.

2-2. In the following Table 1 are collected for the substituents –SH and –OH the charge transfers (expressed in electrons) calculated by applying eq. 5 to planar or quasi-planar

Table 1. Donor effect (in electrons) of the substituents OH and SH with respect to some unsaturated systems

X	C_6H_5	$H_2C{=}CH$	$HC{\equiv}C$
SH	0.06	0.06	0.06
OH	0.09	0.09	0.08

Donor Effect OH > SH

(5) $H_2\overset{+}{C}-X-H \leftrightarrow H_2C=\overset{+}{X}-H$
X = SH 0.53 (*) OH 0.38 (*)

Donor Effect SH > OH

system[11] and to carbocations (starred values have been obtained with 4-31G calculations, unstarred values with STO-3G calculations).

These calculations confirm that in the ground state the donating ability of oxygen is greater than that of sulphur, but the new feature is that in the cations sulphur is a better donor than oxygen; it should also be pointed out that the donating effect in neutral compounds is small (ca. 10%) compared to that in the methyl cations (50–60%) and it may be anticipated here that the greater donor effect shown by sulphur with respect to oxygen in carbocations becomes a general trend in the excited state.

An inversion of the order of the donating effects (*i.e.* S > O) similar to that observed above is also exhibited by the halogenated series R–Hlg (Hlg = F, Cl)[12]. Indeed in neutral systems fluorine acts as a better donor than chlorine, but in the halogenated methyl cations the situation is reversed. Again in neutral R–Hlg compounds the electronic effects are very small (even smaller than in R–XH), while with the methyl cation it is large again.

2-3. The effect exerted by –XH (X = O, S) substituents has also been studied for the oxy and thio carbanions $H_2C–XH$.[13] An investigation carried out with extended basis sets, inclusive of diffuse functions and 3d orbitals, indicated that: i) the rotation-inversion surface of $H_2C–XH$ (X = O, S) has two minima corresponding to the conformers W and Y (Fig. 5); for X = OH conformer Y is more stable than W (3 kcal/mol), while for X = SH W becomes more stable (1.3 kcal/mol); ii) in both carbanions the carbanionic centre is markedly pyramidal; iii) the bond distance C–X increases when going from $H_3C–XH$ to $H_2\bar{C}–XH$ for X = O while the reverse is true when X = S; iv) the carbanionic centre is stabilized to a greater extent by SH than by OH; v) 3d orbitals in sulphur have a marked effect on the structural properties of the carbanion (C–S bond length, degree of pyramidalization of the carbanionic centre, barrier to inversion), but not on the stabilizing effect of the SH group.

Figure 5 (X = OH, SH)

On the basis of what was said in Section 2-1, a π–σ^* type conjugative interaction should be operative in the carbanions and mainly responsible for the conformational preferences.

A similar study was dedicated to hydroxylamine $H_2N–OH$ and thiohydroxylamine $H_2N–SH$[14] which are isoelectronic with $H_2C–XH$ (X = O, S, respectively); the rotation-inversion surface was again characterized by two minima corresponding to the conformers W and Y. At the STO-3G level Y has a greater stability (7 kcal/mol) than W in H_2N–OH, while in H_2N–SH the two conformers have similar stabilities (STO-3G*). It can be safely assumed that also in thiohydroxylamine a π–σ^* conjugative interaction operates.

2-4. The INDO treatment has been applied to a number of substituted phenyl radical anions[15] with rather satisfactory results.

In radical anions (Form. 6) the X–R bond may lie either

$$[C_6H_5\text{–X–R}]^{\dot{-}} \qquad (6)$$

in the plane of the phenyl ring (planar conformation), or out of it (nonplanar conformation). These two situations are related to the electronic configuration which may be symmetric (S) or antisymmetric (A). The mathematical treatment has indicated that there is donation from the –XR substituent in the planar or quasi-planar (P) conformation for both (S) and (A) configurations, as well as in the nonplanar conformation with the (A) configuration. On the other hand in the nonplanar conformation with the (S) configuration the –XR substituent becomes the acceptor. In the following Table 2 are collected the charge transfer values expressed in electrons (the limiting orthogonal conformation has been assumed in the calculations for the nonplanar conformations). The energetic balance as a function of the angle between the X–R bond and the plane of the aromatic ring indicates that alkoxy substituted radical anions, with either planar or orthogonal conformations, should be assigned an (A) configuration. In alkylthio substituted radicals the (A) configuration is still slightly favoured for angles deviating only slightly from planarity (12° for SH and 20° for SMe), while in all other cases the preferred configuration is the symmetric one.

Another feature to emerge from the values collected in the table is that typical electron donor substituents such as OH, OMe, SH, and SMe can behave as electron acceptors in radical anions.

It must, however, be stressed that the above conclusions, particularly those concerning the electron-withdrawing ability of sulphur-containing substituents, refer to the substituent –XR as a whole, and are not related in any way to the problem of the expansion of the valence shell of divalent dicoordinate sulphur.

Table 2. Donor and acceptor effects (in electrons) of some substituents in substituted phenyl radical anions

Configuration	Conformation	Effect	OH	SH	OMe	SMe
A	P	donor	0.050	0.024	0.054	0.023
A	O	donor	0.031	0.001	0.034	0.005
S	P	donor	0.032	0.013	0.029	0.012
S	O	acceptor	0.013	0.018	0.006	0.037

Donor power: OH $\gtrless$ OMe < SH < SMe
Acceptor power: SH > SMe > OH > OMe

3. ARYL SULPHIDES, PHOTOEXCITED STATE

The UV spectra of a variety of substituted aryl sulphides (H, Me, Hlg, OH, OMe, NH_2, NMe_2, NO_2, etc.) have been recorded either in the gas phase or in solution, but the discussion will be limited to alkyl phenyl sulphides, since in DPhS the second aromatic ring makes the interpretation of the spectra more difficult; DPhS will nevertheless be considered in some instances for comparative purposes.

3-1. The gas phase UV spectra of benzene derivatives bearing an –SR substituent[16] show, in the low-frequency region, an absorption which obeys the same linear correlation exhibited by benzene derivatives substituted with other electron donor groups such as NH_2 or NMe_2: these absorptions belong to the modified B_{2u} band which in benzene occurs in the region 220–270 nm and, being symmetry forbidden, is characterized by a low intensity ($\log \varepsilon = 2.15$ at the peak 225 nm). The linear correlation mentioned above shows that the spectroscopic effect of the substituent Y follows the order: $NMe_2 > NH_2 > SMe > SH > OH > OMe > Hlg$. It is assumed that the donor effect follows the same trend.

In benzene the absorption preceding the B_{2u} band, that is the central part of the spectrum, is of intermediate intensity, and occurs at approximately 200 nm; in monosubstituted benzene derivatives it usually begins in the 220 nm region ($\log \varepsilon \sim 4$).

3-2. The gas phase absorption spectra of A and TA[16] are shown in Figs 6 and 7 and it should be noticed that the sulphurated substituent has the stronger spectroscopic effect.

TA shows in solution[17] two absorption regions (Fig. 8) characterized by different intensities: one at 254 nm (as compared with 250 nm in DPhS) with $\log \varepsilon \sim 4$, and a series of low-intensity shoulders in the region 270–290 nm (modified B_{2u} band) which correspond to the maximum at 227 nm in the spectrum of DPhS[18] (Fig. 8). The lower-wavelength absorption, also observed for other sulphides in a number of solvents, is

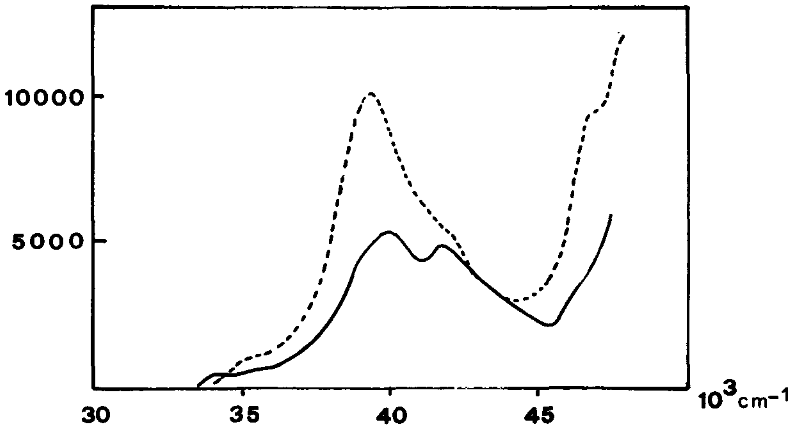


Figure 6 Spectrum of TA:(——) vapour phase (----) solution of 2-2-4-trimethylpentane.

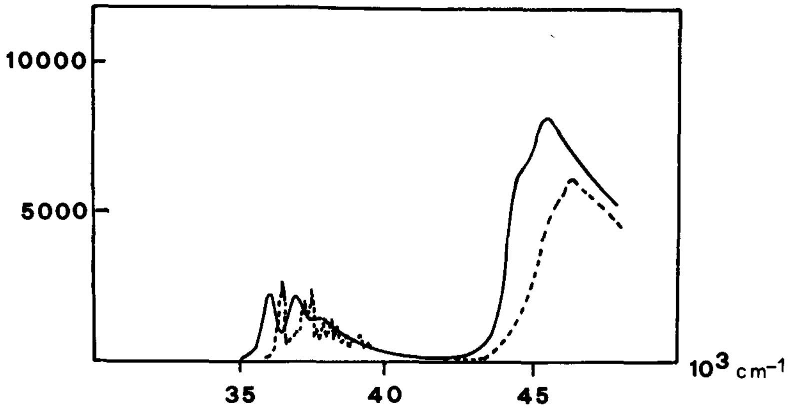


Figure 7 Spectrum of A: (——) solution of 2,2,4-trimethylpentane; (----) vapour.

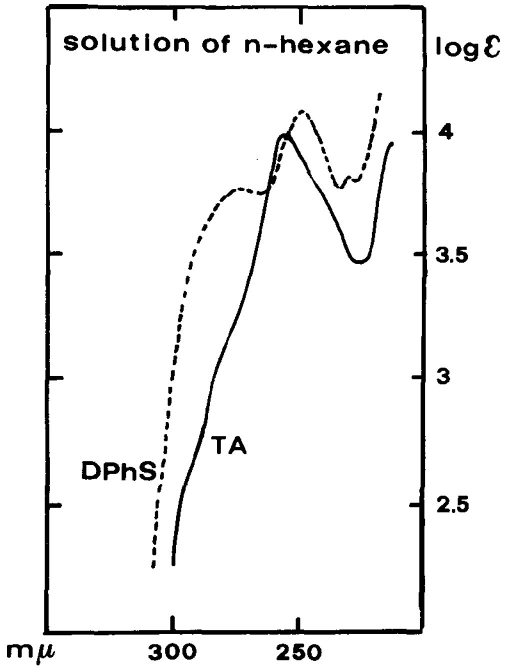


Figure 8

attributed to charge transfer from the heteroatom to the aromatic ring which leads the conjugated chromophore phenylthio, $C_6\overbrace{H_5\text{–}S\text{–}Me}$.[19]

In solution[20], anisole shows (Fig. 9) a high-intensity absorption (log ε ~ 3.90) in the region 220–230 nm attributed to the charge transfer O→Ph; this is followed by the modified B_{2u} band with a partially resolved vibrational structure, extending to 280 nm. DPhE[19] gives a very similar, although more intense (Fig. 9), absorption spectrum.

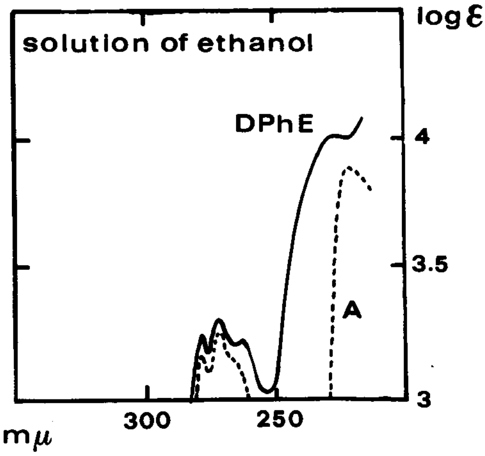


Figure 9

3-3. In nitro-TA[20] the absorption is located on the red side corresponding to the conjugate chromophore p–$O_2N–C_6H_4$–X–Me (X = S) at 335–340 nm, and can be compared to that of nitro-A (X = O) which is centred at 300 nm; the analogous bands in *p*-nitro-DPhS[18] and *p*-nitro-DPhE[19] appear at 350 nm (X = S) and 300 nm (X = 0).

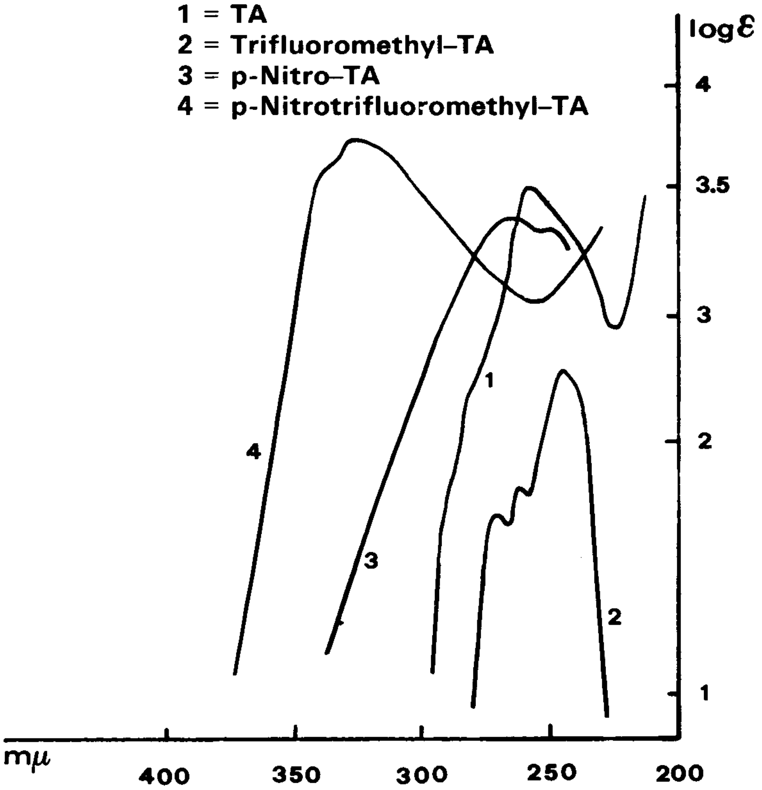


Figure 10

3-4. Substitution of a SCF_3 for a SCH_3 group in TA leads to a dramatic spectroscopic effect[21] (Fig. 10): in fact the extreme positivization of the sulphur atom induced by the trifluoromethyl group makes it impossible for the lone pair to transfer part of its charge to the aromatic ring and wipes out the donating effect of the SR group.

3-5. The greater electron donating ability of sulphur in the photoexcited state of aryl sulphides relative to that of oxygen in aryl ethers appears to be a general feature: thus, the relative donor effects in the ground and excited states of ethers and sulphides are reversed (ground state: OR > SR, photo-excited state: SR > OR).

3-6. With regard to the problem of the expansion of the sulphur valence shell, we have taken into consideration *p*-amino- and *p*-dimethylamino-DPhS.[18] Unfortunately, the absorption spectra do not provide useful information since it is not possible to recognize the bands of the individual chromophores, presumably due to a mixing of $\overbrace{-S-C_6H_5}$ with some higher states of $\overbrace{H_2N-C_6H_4}$. The spectra of *p,p'*-diamino- and *p,p'*-dimethylamino-DPhS are more complex.[18]

A valid approach to the problem is possible by starting with the spectra of *p*-methoxy-, *p*-amino-, and *o*- and *p*-dimethylamino-TA[22] which can be easily interpreted, bearing in mind that the main absorptions in anisole, aniline, and *N,N*-dimethylaniline occur at 220–230, 220–230, and 250 nm, respectively. In the *p*-methoxy-[22] and *p*-amino-TA[22] (Fig. 11) three different absorption systems can be distinguished, where the band more shifted

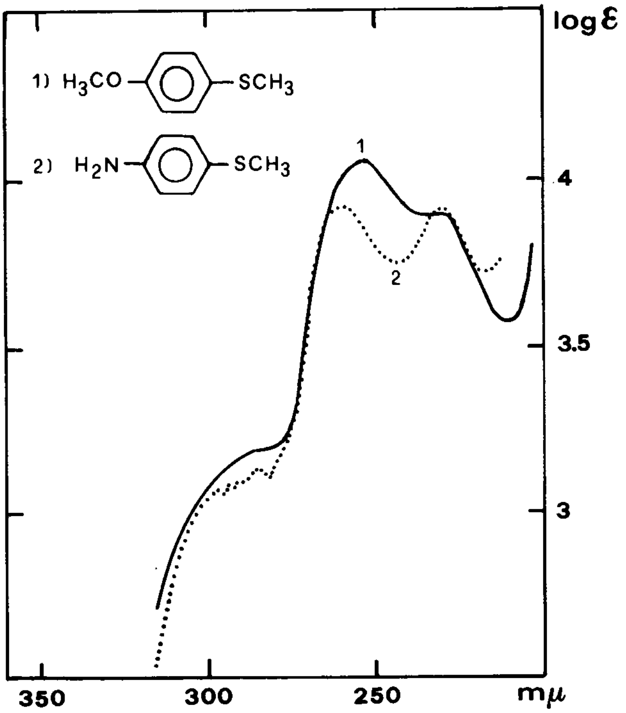


Figure 11

to the red is the usual modified B_{2u} band. In methoxy-TA the central-region band occurring at 250 nm is the one originally present in TA, while the one at higher frequencies (*ca.* 225 nm) is certainly to be attributed to the methoxyanisole moiety of the molecule. In *p*-amino-TA the aniline moiety can be discerned (225 nm) together with the thioanisole moiety which is shifted to 264 nm due to inductive effects.

In *p*-amino-(trifluoromethylthio)-TA[23] the band is shifted back to 256 nm: if sulphur really acted as an acceptor, its effect should be enhanced by the positivization induced by the CF_3 group and the 264 nm absorption should undergo a bathochromic rather than a hypsochromic shift.

Coming to the dimethylamino-TA it will be convenient to start with the ortho derivative:[22] indeed due to steric interactions between NMe_2 and SMe groups its absorption spectrum (shown in Fig. 12) is fairly simple. Thus one can distinguish the B_{2u} band at longer wavelengths, then the thioanisole band (as an inflexion) and the band of DMA shifted from 250 to 230–240 nm because of steric effects. In HCl this last absorption disappears and is replaced by the normal band of TA at 250 nm.

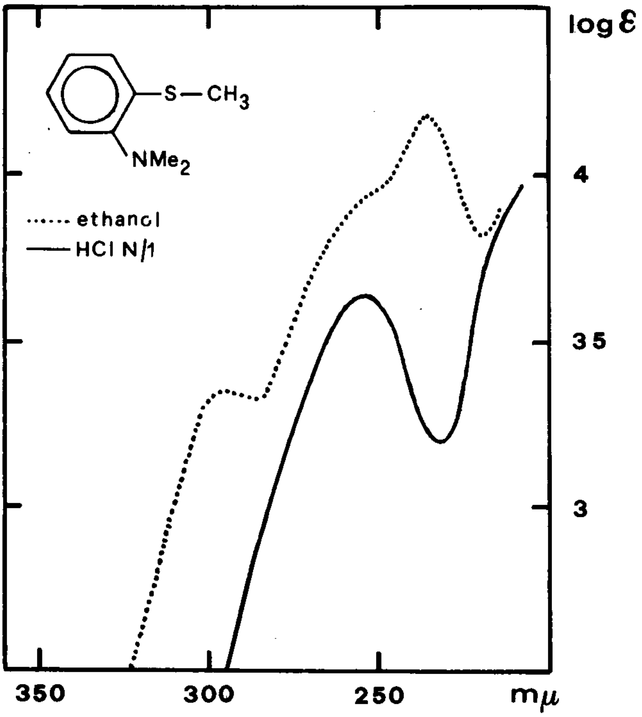


Figure 12

The spectrum of *p*-dimethylamino-TA[22] is shown in Fig. 13. Beside the modified benzenoid B_{2u} band which now extends beyond 300 nm it exhibits a broad asymmetric band at 272 nm which we attributed to DMA and a pronounced inflexion in the 250 nm region which is to be assigned to the thioanisole moiety of the molecule. These last two features, even though coalescing, represent two different absorption systems: in fact by developing the inflexion the usual TA band can be observed.

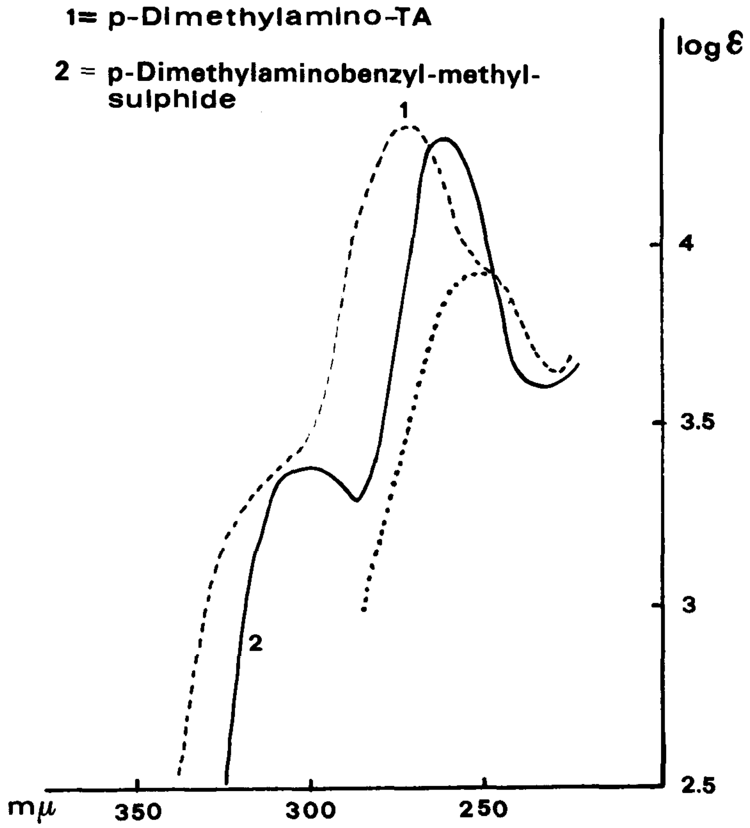
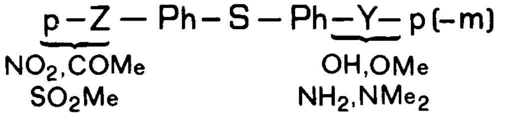


Figure 13

The bathochromic shift of the DMA band is of inductive origin as emerges from a comparison with the spectra of some DMA substituted with nonconjugated groups, where bathochromic shifts of similar magnitude are observed.[24] On the other hand, in *p*-dimethylamino-phenyl benzyl sulfide,[25] where the methylene group acts as a conjugation insulator, the principal band occurs at 262 nm, but it is rather sharp and does not show any inflexion in the 250 nm region.

3-7. In diaryl sulphides (Form. 7) the effect of the donor substituent Y on the absorption band toward the red corresponding to photoexcitation of the group *p*–Z–Ph–S (Z being an electron accepting substituent) is very small and comparable to that observed when the donating substituent is in a meta position. In the excited state, as was the case in the ground state, the sulphur bridge is inefficient for the transmission of the effect of the Y substituent.[26]



$$p-\underbrace{Z}_{\substack{NO_2,COMe\\SO_2Me}} - Ph-S-Ph-\underbrace{Y}_{\substack{OH,OMe\\NH_2,NMe_2}}-p(-m) \qquad (7)$$

3-8. From the complete picture of these results it can be safely concluded that the UV spectra, photoexcited state, do not support the hypothetical expansion of the sulphur valence shell.

4. SULPHOXIDES AND SULPHONES

4-1. The SO group is a rather strong chromophore, and indeed saturated sulphoxides absorb in the region 220–230 nm[27,28] (sulphoxides will be simply abbreviated with the acronym SO).

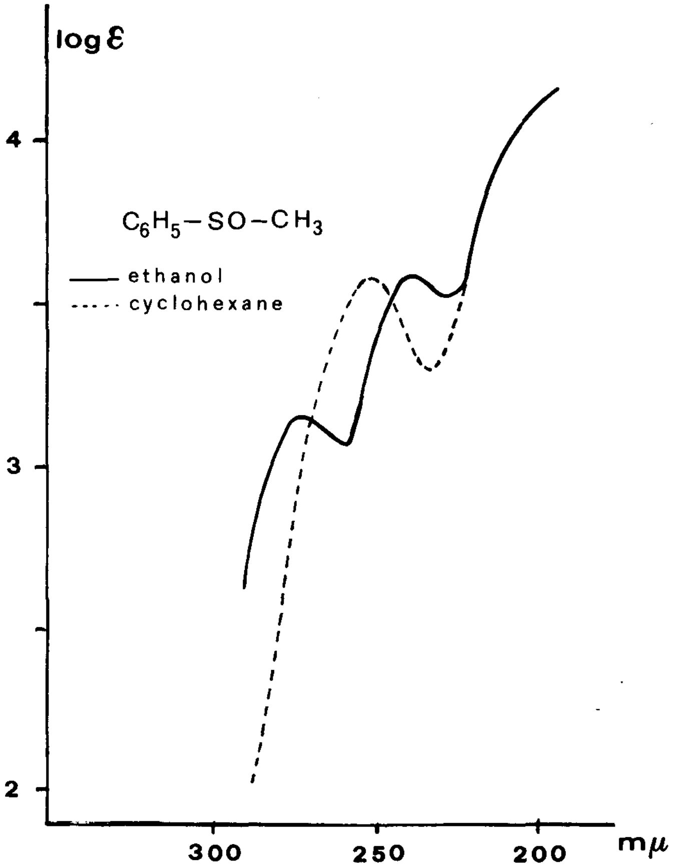


Figure 14

The spectrum of MePhSO in cyclohexane[27,28] (Fig. 14) is dominated by a medium-intensity band in the proximity of 250 nm while in ethanol two absorption systems are observed at 236 m (log ε = 3.60) and at 260–290 nm, the latter being attributable to the modified benzenoid B_{2u} band; in tolyl sulphoxides[28] these two absorption systems are also present in cyclohexane. The band close to 236 mμ should result from the coupling of the SO group with the benzene ring, with a weak charge transfer toward the phenyl

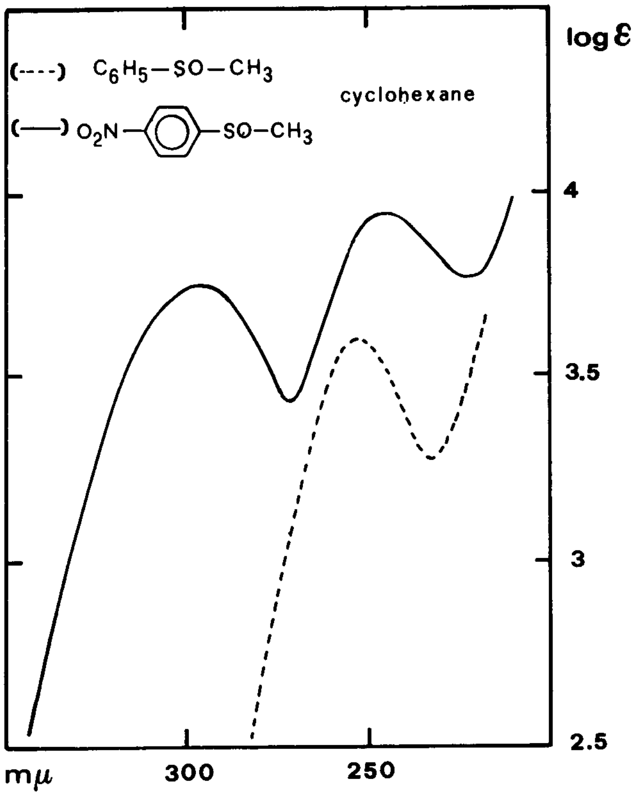


Figure 15

group. Accordingly, in the spectrum of *p*-nitrophenyl methyl sulphoxide (Fig. 15) the band at longer wavelength (300 nm, log ε = 3.75) indicates a weak conjugation of the nitro group with the phenyl sulphoxide moiety (cf. ref. 29 for the orienting effect of SO).

DiphenylSO[30] in cyclohexane (Fig. 16) shows again two absorption systems which become more evident in ethanol, *i.e.* a high-intensity maximum in the region 220–230 nm and a medium-intensity shoulder at 270–280 nm; *p*-nitro diphenylSO[30] shows a spectrum similar to that of *p*-nitro-PhMeSO.

4-2. Unlike the sulphoxides, saturated sulphones are transparent down to the low-wavelength limit accessible to the spectrophotometer;[27] yet $MePhSO_2$[31] shows an absorption system with partially resolved vibrational structure in the region 250–280 nm (see Fig. 17). $DPhSO_2$,[31] beside the absorption at 250–280 nm, shows an additional high-intensity band (log ε = 4) at 235 nm; in dimesitylSO_2 the band occurs at 241 nm[31] and is even more intense. In our opinion the absorption system present at higher frequencies in $DPhSO_2$, and not detected for $MePhSO_2$, should be attributed to the conjugation of the two benzene rings through the sulphur 3d orbitals. The strong involvement of the aromatic rings if further demonstrated by the fact that *p*-nitrophenylphenylSO_2[31] and *p,p'*-dinitro-$DPhSO_2$[31] absorb in the 260 nm region which is typical of nitrobenzene. On this basis it is understandable why para substitution of one of the phenyl groups with

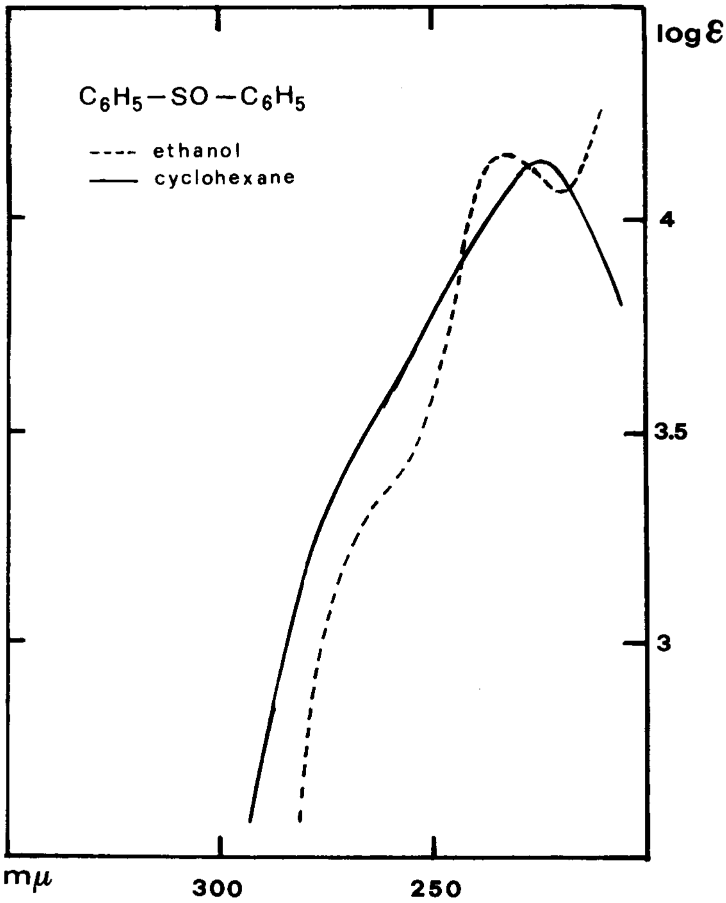
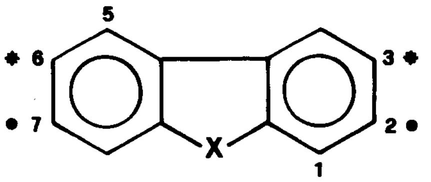


Figure 16

an electron donating group (NH_2, NMe_2) induces a significant shift of the main band at 239 nm of $DPhSO_2$.

5. DIBENZOTHIOPHENE AND DIBENZOTHIOPHENE SULPHONE

Our investigations have been extended to the cyclic analogue of DPhS, the planar dibenzothiophene (DBT)[32], and to $DBTSO_2$[32] (Form. 8).



X = S : DBT
X = SO_2 : $DBTSO_2$ (8)

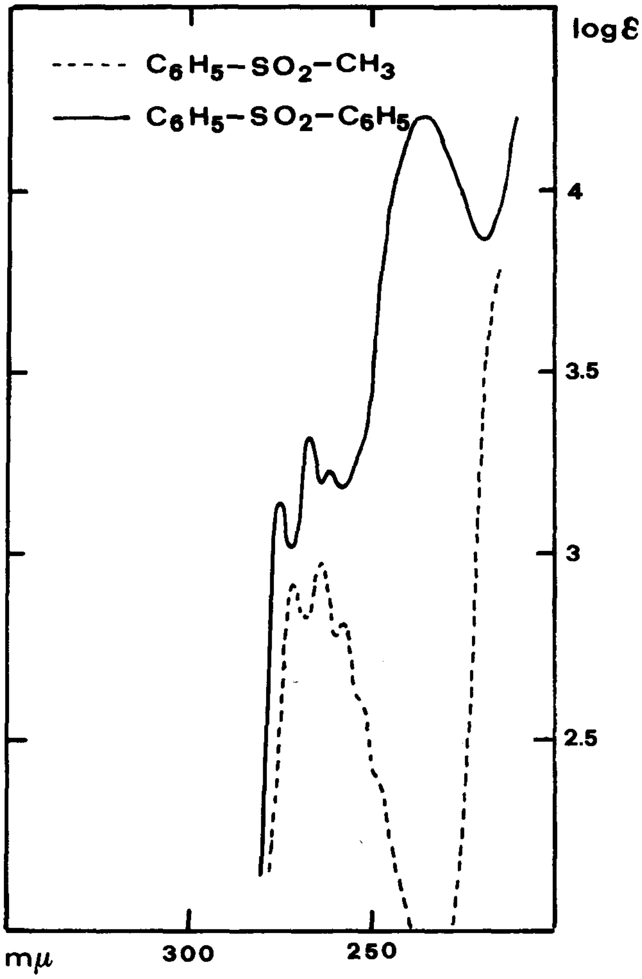


Figure 17

The spectra of these compounds, reported in the same period also by other authors, are very similar and show three absorption systems extending from 210–220 nm up to 320–330 nm. For the sake of conciseness we will not give here a description of these spectra, but will confine our discussion to some nitro and amino nitro derivatives.

It is easily noticeable that in planar DBT (Form. 8, X = S) there are two pairs of formally conjugable positions: positions 3 and 6 *via* sulphur, and positions 2 and 7 *via* C-9/C-10. In 3-amino-6-nitro-DBT the band at long wavelength is very close to that of 6-nitro- (or 3-nitro-)-DBT (*i.e.* in the 330 nm region): this means that despite the planar nature of the molecule there are no conjugative interactions between the amino and the nitro group. Consequently, the absence of donor-acceptor interaction in substituted DPhS (Form. 7) is not to be attributed to nonplanarity of the molecule, but to the failure of sulphur to transmit conjugation. In 2-amino-7-nitro-DBT the long-wavelength band occurs at 417 nm (log ε = 4.03), thus indicating a strong NH_2–NO_2 conjugative interaction *via* C-9/C-10.

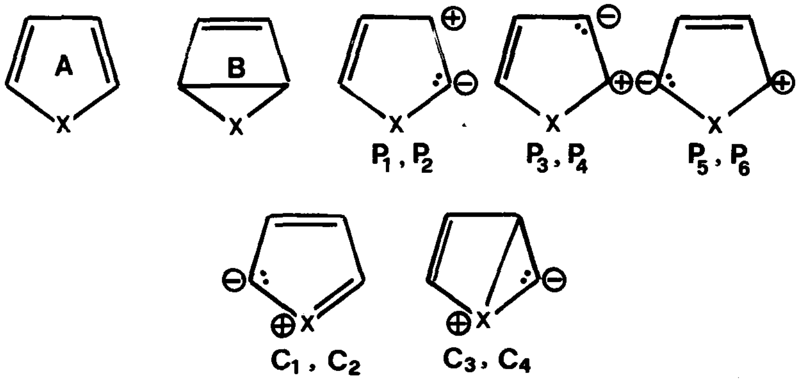
In 2-nitro-$DBTSO_2$ the band located toward the red shows a high-intensity maximum at 316 nm, but in the 3-nitro and 3,6-dinitro derivatives the band has low intensity (log ε = 3.20), indicating that nitro groups in positions 3 and 6 are scarcely conjugated. 2-Amino-7-nitro-$DBTSO_2$, in turn, has a high-intensity absorption at 417 nm which is also characteristic of the corresponding amino-nitro-DBT.

6. OTHER SULPHUR-CONTAINING COMPOUNDS

Studies have also been carried out on pyridyl sulphides,[33] thienyl ketones,[34] thiophene chromium tricarbonyl,[35] *N*-sulfinylamines,[36] tetrahydrothiophene as compared to other five-membered heterocycles,[37] protonated thiophen as compared to protonated furan,[38] and on several other sulphurated derivatives.

7. THIOPHEN AND FURAN, GROUND AND EXCITED STATES[39]

These two compounds have been studied in the late fifties by the VB method in the π approximation. To describe the singlet state of these two compounds the following structures (Form. 9) were taken into consideration, only the structure correlated to the rotation about the C_2 axis of the C_{2v} symmetry group being shown.



(9)

The following transition energies were computed from the molecular symmetry functions A and B (in parentheses are quoted literature values):

Transition	Furan	Thiophen
A_I–A_I^*	7.2	5.9
A_I–B_I	7.4 (4.8)	6.9 (6.1)

The results reproduce properly the direction of the shift observed when passing from furan to thiophen, and indicate that it reflects the order of the ionization potentials of oxygen and sulfur, respectively. The approximate weights of the different structures in the ground and first excited states were also determined (see Table 3).

Table 3. Weight % of the various structures of furan and thiophen in the ground state (A_1) and in the first photoexcited state (B_1)

Structure	Covalent		Polar		Conjugated	
Symmetry	A_1	B_1	A_1	B_1	A_1	B_1
Furan	58	0	7	78	35	22
Thiophen	32	0	15	25	53	75

In the ground state conjugate structures are much more important in thiophen than in furan which indicates a greater perturbation of the dienic system in thiophen and hence its higher aromaticity with respect to furan. In the first excited state the difference is more evident, consistent with the dienic character observed for the first transition in furan and not in thiophen.

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