Nuclear magnetic resonance study of intramolecular electronic effects in diphenyl sulfides, sulfoxides, and sulfones[1]

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A nuclear magnetic resonance (n.m.r.) method has been applied to the study of variations in electron density in the aromatic rings of *para*-disubstituted diphenyl sulfides, sulfoxides and sulfones. The n.m.r. response of the aromatic ring protons has been determined as a function of the nature of the *para* substituents and particularly as a function of the nature of the bridging group between the rings. Certain diphenyl ethers and diphenyl methanes have been investigated for comparison purposes. The results establish that a transmission mechanism is operative through sulfur in diphenyl sulfides that is not effective when the bridging function is sulfoxide or sulfone. The extent to which transmission is operative even in the sulfides is dependent on the precise nature of the *para* substituents, in particular whether they are donors or acceptors and the manner in which they interact with the remainder of the molecule.

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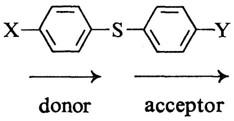
Introduction

Many experimental techniques have been applied to the study of transmission of electronic effects through a sulfur bridge. In any bridged system we may expect σ-conduction which rapidly diminishes with distance. The potentially much stronger transmission of effects through a system of delocalized π-bonds in particular has attracted much attention; for instance the question of whether a bridging sulfur atom linking two π-bonded systems, one a potential electron donor, the other a potential acceptor, permits "leakage" of electron density from one ring to the other:



In general the state of hybridization of the bridging atom is fundamental to the question of transmission across a bridging atom or group located between potential donor and acceptor functions in a molecule. When the energy differences between the various possible states of hybridization of the bridging function become small, as is the case in sulfur compared with oxygen, it also becomes increasingly difficult to establish whether there exists sufficient "incentive" for the molecule to promote electrons from lower lying orbital energy levels to slightly higher ones, i.e. undergo rehybridization. The possibility of expansion of the sulfur valence shell has been discussed by many workers and reviews covering this topic up to a recent date have been published (2, 3).

Mangini and co-workers, studying the ultraviolet spectra of a large variety of aromatic sulfides found no evidence for transmission of electronic effects (4–6). Szmant and McIntosh (7) have, on the basis of similar studies, come to the conclusion that there was indeed evidence for this type of transmission when there was sufficient driving force in the form of both a powerful electron donating and an electron accepting potential within the molecule. The conclusion that interaction through the sulfur atom in various diphenyl sulfides was very limited was reached by other workers as a result of infrared and polarographic studies (8, 9). The effect of various ring substituents on the acid strengths of β-phenylthio, β-phenylsulfinyl, and β-phenylsulfonyl acrylic acids led Hogeveen (10) to the conclusion that the effects were more efficiently transmitted through the sulfide *S*-bridge than through the sulfinyl or sulfonyl bridges. Litvinenko and co-workers (11–14) studied the reactivity of the primary amino group in di-*para*-substituted compounds of the type Y—C_6H_4—X—C_6H_4—NH_2, where X = S, Se or NH. These authors suggested that the ability to transmit electronic effects decreases in the order —NH—>—S—>—Se—>—O—.

In any experimental investigation of the possible transmission of electronic effects through a bridging sulfur atom the question as to whether

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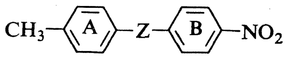
[1] Preliminary results were presented at the Princeton University Conference on "The Chemistry of Sulfides", June 1966 (1).

TABLE I

Average chemical shift* of the aromatic protons† of some diphenyl compounds ("whole molecules") and of the corresponding *para*-substituted "half molecules"‡



	A ring		B ring	
Z = S	Half molecule	429.3	Half molecule	461.8
	Whole molecule	440.9	Whole molecule	455.1
	Change§	−11.6	Change	+6.7
Z = SO	Half molecule	444.3	Half molecule	486.5
	Whole molecule	445.2	Whole molecule	484.0
	Change§	−0.9	Change	+2.5
Z = SO_2	Half molecule	455.3	Half molecule	497.5
	Whole molecule	456.1	Whole molecule	493.8
	Change§	−0.8	Change	+3.7

*All figures in c.p.s. from tetramethylsilane internal standard in $CDCl_3$, calibrated on singlet peak of residual $CHCl_3$ at 435 c.p.s.

†The shift of the center of the aromatic multiplet was taken.

‡For explanation see text.

§A negative change indicates a downfield shift, the protons being less shielded in the diphenyl compound.

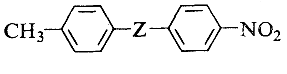
excited states are involved in the study must be clearly established. Transmission mechanisms operative in excited states may not be important in the ground state. Any evidence obtained from the study of ultraviolet spectra and reactivity differences must be considered to be in a different class from that obtained in studies where ground states are involved, such as dipole moment, infrared, and nuclear magnetic resonance studies. In a recent paper Wehry (15) discussed the results of his measurement of acid dissociation constants of various phenols with sulfur-containing substituents in the ground state, the lowest triplet and the first excited singlet state. He obtained good evidence for both $3p_\pi$ donor and $3d_\pi$ acceptor conjugation of sulfide sulfur in the ground state.

Because the nature of the transmission process is subtle and may be energetically of minor magnitude, the proper choice of the experimental tool to be applied would seem to be important. It is therefore not surprising that in recent times nuclear magnetic resonance techniques have been increasingly used in studies of sulfur bonding (6, 16–18). We also chose to use this tool to study the transmission of electronic effects in di-*para*-substituted diphenyl compounds of the sulfide, sulfoxide, sulfone, ether and methylene types.

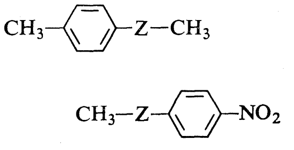
Methods and Results

The specific aim of our study was to investigate changes in the electron density of the aromatic rings of disubstituted diphenyl systems by measuring the chemical shifts associated with the protons of each aromatic ring. Almost all compounds contained unsymmetrically *para*-disubstituted rings only and the splitting pattern associated with the n.m.r. response of each set of four ring protons, although strictly of the A_2B_2 type, may be considered as two superimposed identical AB patterns, yielding a typical AB quartet. The average n.m.r. shift associated with the four ring protons was obtained by measuring the position of the center of the multiplet. The value of this shift was then taken as a measure of the relative electron density in each aromatic ring in the various compounds studied. The further approach chosen to find an answer to the basic question of whether a bridging function Z acts as an insulator or a transmitter of electronic effects will be illustrated by reference to a specific set of compounds.

The average n.m.r. shifts observed for the aromatic protons in the "whole molecule" were compared with those of the corresponding "half molecules", where Z = S, SO, or SO_2:



"whole molecule"



"half molecules"

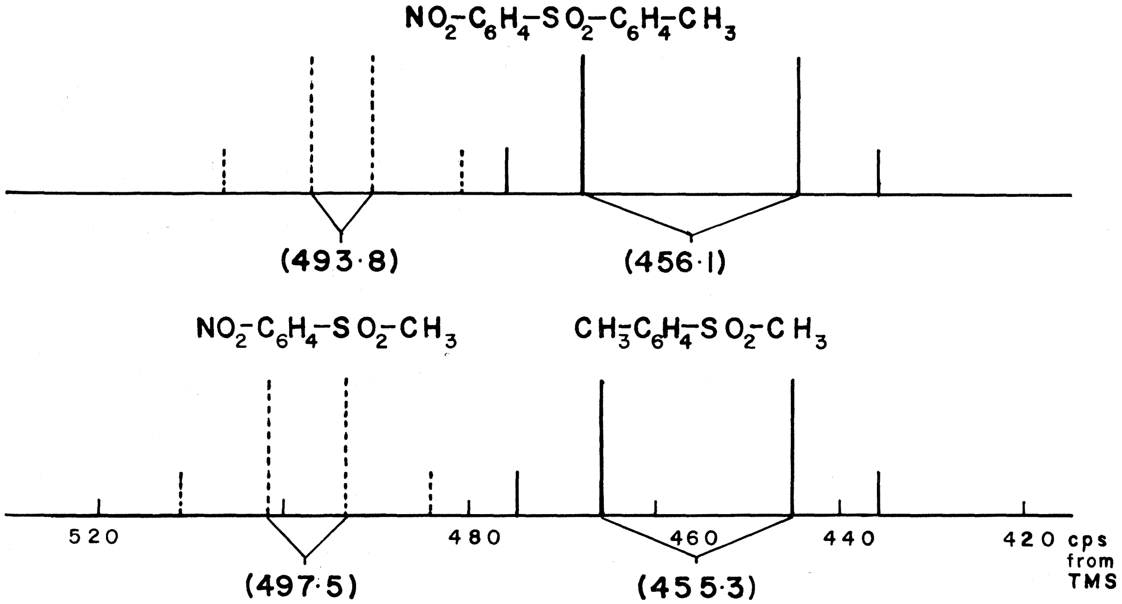


FIG. 1. Diagrammatic representation of the nuclear magnetic resonance spectra for 4-(*p*-nitrophenylsulfonyl)-toluene.

If the sum of the n.m.r. ring spectra of the "half molecules" shows no significant difference from that of the "whole molecule", it must be concluded that the Z-function bridge acts as an insulator between the two phenyl rings. Even if there is no transmission across the Z-function, it is to be expected that strict additivity will not be observed, since replacing the terminal methyl group in the "half molecules" by a substituted phenyl ring, as in the "whole molecule", must lead to minor changes in electron density due to inductive effects (σ-conduction). The shifts observed for the three sets of compounds under consideration are presented in Table I. The sign convention used for the differences is indicated in this Table.

In these three systems it was found that in the sulfone and sulfoxide cases ($Z = SO_2$ or SO) there was little difference between the ring proton shifts in the "half molecules" compared with the "whole molecule" as manifest in the small value of the "change". Such was not the case where $Z = S$ (Figs. 1, 2, and 3). In the diphenyl sulfide ($Z = S$) the electron density of the methyl-carrying ring was significantly decreased, while that of the nitro-substituted ring was increased when compared with the n.m.r. data obtained for the "half molecules".

Based on the initial analysis described above the study was extended to cover a wider range of *para*-substituents and the corresponding oxygen- and methylene-bridged compounds. The complete n.m.r. data are presented in Tables II and III. In Table IV the differences in chemical shifts for the aromatic protons, calculated in exactly the same way as the "change" entry in Table I, are tabulated.

Discussion

The n.m.r. results for 4-(*p*-nitrophenylthio)-toluene (Table I, $Z = S$) are in agreement with transmission through the sulfur bridge, the electron density in the methyl-substituted ring having decreased, that in the nitro-substituted ring having increased in the "whole molecule" compared with two "half molecules". This can only arise if the molecule is polarized along its entire length, permitting electron density to leak from the donor ring to the acceptor ring. In the case of the corresponding sulfoxide and sulfone (Table I, $Z = SO$ or SO_2) the changes in shift are comparatively minor and may be due to inductive effects. These results clearly established the fact that a transmission effect is operative in the sulfide that is not operative in the sulfoxide or sulfone. This trend is also evident from the data

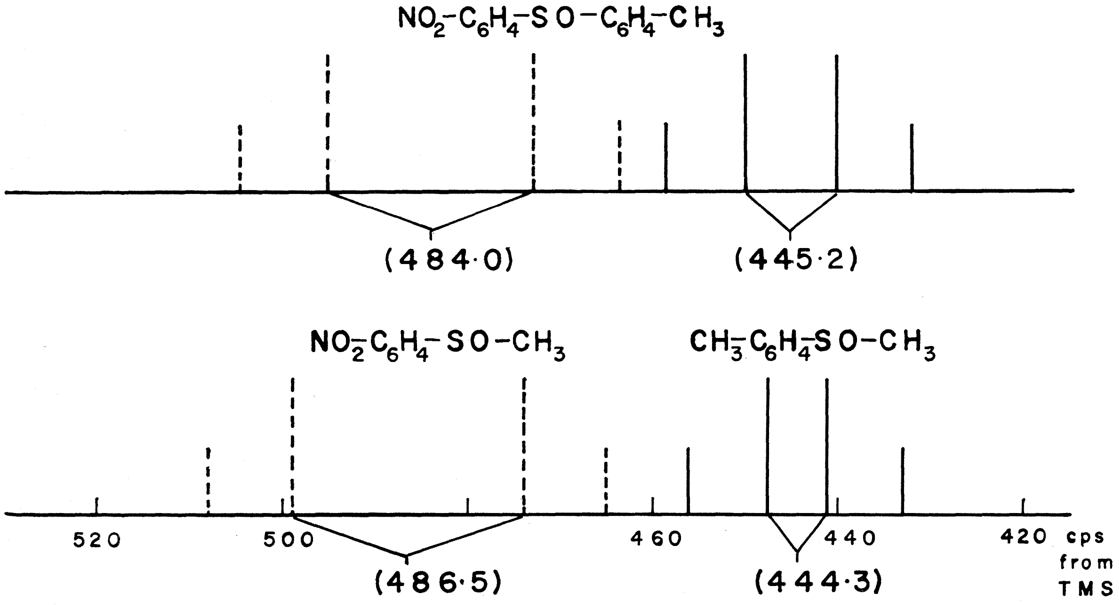


FIG. 2. Diagrammatic representation of the nuclear magnetic resonance spectra for 4-(*p*-nitrophenylsulfinyl)-toluene.

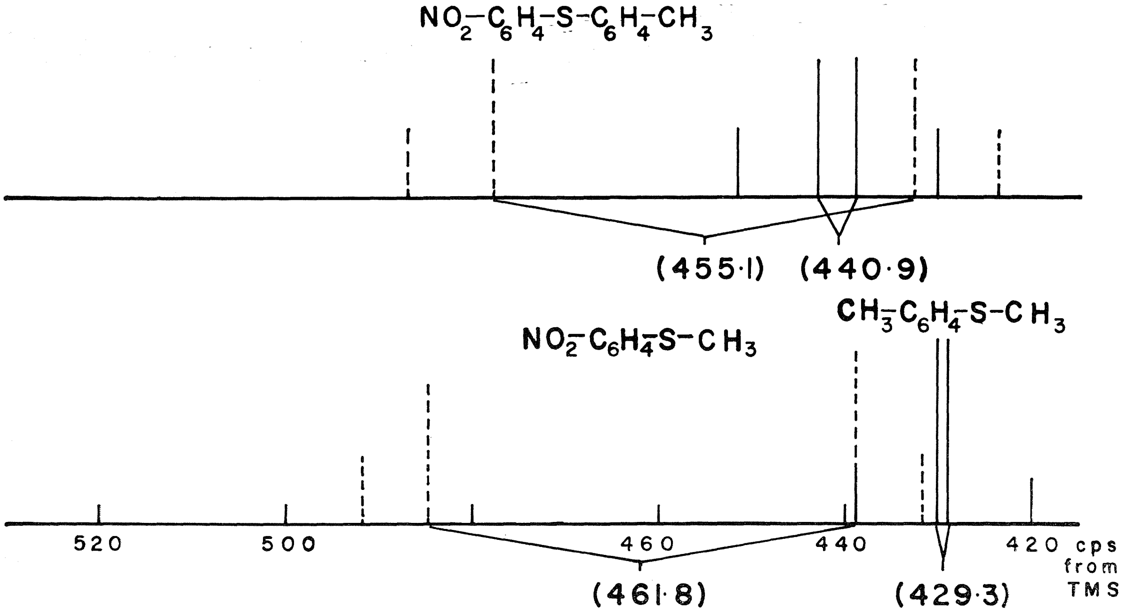
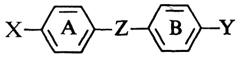


FIG. 3. Diagrammatic representation of the nuclear magnetic resonance spectra for 4-(*p*-nitrophenylthio)toluene.

TABLE II

Chemical shift of the aromatic multiplet of diphenyl compounds ("whole molecules")



Compound	Z	Substituents X	Substituents Y	Chemical shift in c.p.s.* of center of AB quartet Ring A	Chemical shift in c.p.s.* of center of AB quartet Ring B
1	S	CH_3O	NO_2	433.4	454.0
2	S	NH_2	NO_2	421.2	454.2
3	S	CH_3O	CH_3	427.0	427.0
4	S	CH_3	NO_2	440.9	455.1
5	S	CH_3	H	433.9	436.0
6	S	H	NO_2	449.0	457.0
7	S	$(CH_3)_2N$	NO_2	423.4	453.2
8	S	NH_2	CH_3	417.8	424.2
9	S	Cl	NO_2	445.9	458.1
10	S	CH_3	Br	433.4	433.8
11	S	CH_3	Cl	433.5	432.2
12	SO	CH_3O	NO_2	435.4	482.2
13	SO	NH_2	NO_2	421.2	481.0
14	SO	CH_3O	CH_3	434.2	441.6
15	SO	CH_3	NO_2	445.2	484.0
16	SO_2	CH_3O	NO_2	446.1	492.4
17	SO_2	NH_2	NO_2	431.2	490.0
18	SO_2	CH_3O	CH_3	443.5	451.7
19	SO_2	CH_3	NO_2	456.1	493.8
20	O	CH_3O	NO_2	418.2	454.5
21	O	NH_2	NO_2	407.1	452.5
22	O	CH_3O	CH_3	414.2	417.7
23	O	CH_3	NO_2	425.5	455.7
24	CH_2	CH_3O	NO_2	417.5	463.5
25	CH_2	NH_2	NO_2	407.2	462.8
26	CH_2	CH_3O	CH_3	417.8	425.1

*All figures in c.p.s. from tetramethylsilane internal standard in $CDCl_3$ solution (2.5% W/W), calibrated on singlet peak of residual $CHCl_3$ at 435 c.p.s.

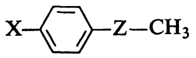
collected for the three other diphenyl sulfides whose sulfoxides and sulfones were used in this study together with their corresponding ethers and methylenes (see Table IV, first four lines). There are some notable exceptions, however.

In general the changes in the shifts are largest for the sulfide-bridged molecules with the exception of the 4-methoxy-4′-methyl-disubstituted sulfide; here the behavior is more comparable with the shift changes observed for the sulfoxides and sulfones. This may be a reflection of the fact that both substituents are electron donors, working against each other. The necessary ''incentive'' for the bridging sulfur to transmit may therefore be missing in this case, as was suggested by Szmant and McIntosh (7) in their study of the ultraviolet spectra of some other diphenyl sulfides.

The methylene-bridged compounds were included in this study because it was not expected that they would transmit by other than an inductive mechanism, and therefore would serve as a useful reference. Indeed, all changes in the shifts for both rings in the substituted diphenylmethane compounds are positive. This strongly suggests that these changes arise from a diamagnetic anisotropy effect resulting from the replacement of the terminal methyl group in the ''half molecule'' by the aromatic ring in the ''whole molecule''. Since this shift effect is extraneous to the transmission effect, these data serve to establish the fact that changes in shift of the order of 2 c.p.s. can not be considered as meaningful as far as the study of transmission is concerned. This would conveniently account for many of the minor shift variations listed in Table IV but it does not account for the very sizeable negative variations (decreased electron density) in the shifts observed in the X-substituted ring of the oxygen-bridged compounds (see Table IV). There is no corresponding positive variation

TABLE III

Chemical shift of the aromatic multiplet of *para*-disubstituted benzenes ("half molecules")



Compound	Z	X	Chemical shift in c.p.s.* of center of AB quartet
27	S	CH_3	429.3
28	S	CH_3O	423.5
29	S	NH_2	413.2
30	S	NO_2	461.8
31	S	H	435.4
32	S	$(CH_3)_2N$	418.8
33	S	Br	434.8
34	S	Cl	432.6
35	SO	CH_3	444.3
36	SO	CH_3O	436.2
37	SO	NH_2	423.6
38	SO	NO_2	486.5
39	SO_2	CH_3	455.3
40	SO_2	CH_3O	445.0
41	SO_2	NH_2	430.6
42	SO_2	NO_2	497.5
43	O	CH_3	416.4
44	O	CH_3O	408.9
45	O	NH_2	399.8
46	O	NO_2	454.7
47	CH_2	CH_3	426.9
48	CH_2	CH_3O	418.3
49	CH_2	NH_2	408.4
50	CH_2	NO_2	464.9

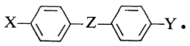
*All figures in c.p.s. from tetramethylsilane internal standard in $CDCl_3$ solution (2.5% W/W), calibrated on singlet peak of residual $CHCl_3$ at 435 c.p.s.

TABLE IV

Changes in chemical shifts (in c.p.s.)* associated with the center of aromatic multiplets, calculated as in Table I ("whole molecule" compared with "half molecule")†

		Z									
		S		SO		SO_2		O		CH_2	
X	Y	X-C_6H_4-	Y-C_6H_4-	X-C_6H_4-	Y-C_6H_4-	X-C_6H_4-	Y-C_6H_4-	X-C_6H_4-	Y-C_6H_4-	X-C_6H_4-	Y-C_6H_4-
CH_3	NO_2	−11.6	+6.7	−0.9	+2.5	−0.8	+3.7	−9.1	−1.0		
CH_3O	NO_2	− 9.9	+7.8	+0.8	+4.3	−1.1	+5.1	−9.3	+0.2	+0.8	+1.4
NH_2	NO_2	− 8.0	+7.6	+2.4	+5.5	−0.6	+7.5	−7.3	+2.2	+1.2	+2.1
CH_3O	CH_3	− 3.5	+2.3	+2.0	+2.7	+1.5	+3.6	−5.3	−1.3	+0.5	+1.8
CH_3	H	− 4.6	−0.6								
H	NO_2	−13.6	+4.8								
$(CH_3)_2N$	NO_2	− 4.6	+8.6								
NH_2	CH_3	− 4.6	+5.1								
Cl	NO_2	−13.3	+3.7								
CH_3	Br	− 4.1	+1.0								
CH_3	Cl	− 4.2	+0.4								

*A negative change indicates a downfield shift, i.e., the protons in the diphenyl compound are less shielded than in the corresponding ring in the "half molecule".

†Compounds of structure .

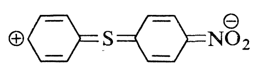
(increase in electron density) observed in the Y-substituted ring as is the case in the sulfides.

At first sight it is hardly conceivable that the flow of electron density from the donor ring of the oxygen-bridged compounds would find its way on to the oxygen without being subsequently transmitted to the acceptor ring by some mechanism. The findings of Marcus *et al.* (18) are of interest in this regard. These authors concluded on the basis of results of their own n.m.r. study as well as of the work of others that in conjugative roles sulfur is a better transmitter than oxygen when acting as an acceptor or acceptor–donor of negative charge, but that the situation is reversed when only conjugative donation by the bridging atom is called for. When this conclusion is accepted it is clear that the relative order of the sulfur and oxygen bridge-effects may depend to a great extent on the role these atoms are called upon to play by the specific relative nature of the two *para*-substituents on the aromatic rings. Indeed, it is possible using these conclusions by Marcus *et al.* to account qualitatively for the marked differences in the shift changes (Table IV) obtained for sulfur and oxygen-bridged compounds where strong donor and acceptor groups are present as substituents, i.e. in the case of the combinations of CH_3O— with NO_2—, and of NH_2— with NO_2—. In the other two cases where comparison is possible between O and S as a bridging atom, i.e. in the case of the combinations of CH_3— with NO_2—, and of CH_3O— with CH_3— as *para*-substituents, the predictions on the basis of the same conclusions of Marcus *et al.* (18) do not always agree with the changes in the shift.

There are probably many interesting facts relevant to the problem hidden within the many minor changes in shift as tabulated in Table IV. However, there are also a number of minor perturbing factors at work which are not directly related to the transmission problem. We are obliged therefore to restrict our attention to *the more salient features of the data* and accordingly limit our conclusion to the fact that there is evidence for the existence of a transmission mechanism across the sulfide bridge that is absent in the cases of the sulfoxide, sulfone and methylene bridges. There does not appear to be a similar transmission mechanism operative in the oxygen bridge but some type of deshielding of the donor ring protons takes place when oxygen is flanked by two π-electron systems.

In the case of the sulfides, where transmission appears to be operative, the study was extended to cover a wider range of substituents (see Table IV). In all but one of these compounds the donor ring is deshielded and the acceptor ring shows increased shielding. The exception is the case where CH_3— and H— are the substituents; conjugative interaction would be expected to be weaker.

The deshielding of the donor ring in the *p*-nitro-substituted diphenyl sulfide coupled with the increase in shielding in the nitro-substituted acceptor ring provides evidence for a transmission process and is in contrast with the conclusion reached by Szmant and McIntosh (7). On the basis of their ultraviolet studies, there is no evidence for involvement of the resonance structure:



Wehry (15) found that when donor–acceptor type conjugation is present in the ground state of sulfides it must be expected to increase upon excitation, unless electron releasing p_π conjugation is sterically inhibited.

The data obtained for the 4-chloro-4′-nitro-substituted diphenyl sulfide (see Table IV) indicate that in the presence of the powerful electron withdrawing nitro group the chloro substituent is also forced to act as a donor.

Conclusion

The n.m.r. evidence presented supports the conclusion that intramolecular transmission of electronic effects between a donor and acceptor moiety occurs more readily across a sulfide bridge than across sulfoxide, sulfone, ether or methylene bridges. The extent to which such transmission occurs, however, is strongly dependent upon the nature of the donor and acceptor functions and the availability of a mechanism for establishing a sufficient degree of polarization across the bridging function to provide sufficient "incentive" for the bridging function to act as a conductor as opposed to an insulator.

Experimental

Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer. The concentration of the solutions was 2.5% (W/W) in $CDCl_3$, with tetramethylsilane as an internal reference. All spectra were run at a sweep width of 500 c.p.s., but the aromatic multiplets were always re-run at sweep widths of 100 or 50 c.p.s. In this region the residual $CHCl_3$ in the solvent served as a convenient standard for calibration (at 435 c.p.s. from tetramethylsilane).

Microanalyses were carried out by Mrs. S. Bagley, and the nuclear magnetic resonance spectra were recorded by Mrs. V. Boon, both of the Department of Chemistry, The University of Calgary.

Most of the compounds used in this study had been reported previously and several were commercially available. The data for those prepared follow. Melting points are not corrected. Numbers given to compounds refer to the listing in Tables II and III.

Preparation of Sulfides

(a) Methyl Phenyl Sulfides

Most of the methyl phenyl sulfides were prepared by methylation of the corresponding thiols, using the procedure of Gilman and Beaber (19): 1-bromo-4-(methylthio)benzene (**33**), m.p. 38–39° from aqueous methanol (lit. m.p. 38° (20)); 1-chloro-4-(methylthio)-benzene (**34**), b.p. 87° at 5 mm (lit. b.p. 170° (21)); 4-(methylthio)toluene (**27**), b.p. 82° at 6 mm (lit. 104–105° at 20 mm (19)); 1-(methylthio)-4-nitrobenzene (**30**), m.p. 71–72° from methanol (lit. m.p. 72° (22)); 4-(methylthio)-anisole (**28**), b.p. 100° at 5 mm (lit. b.p. 99° at 4 mm (23)); *N*,*N*-dimethyl-4-(methylthio)aniline (**32**), b.p. 74–77° at 0.13–0.20 mm (lit. b.p. 140° at 3 mm (5)).

4-(Methylthio)aniline (**29**) was prepared as reported (24), b.p. 74° at 0.15 mm (lit. b.p. 155° at 23 mm (24)).

(b) Diphenyl Sulfides

The procedure given by Gilman and Broadbent (25) was used for the preparation of the following sufides: 4-(*p*-nitrophenylthio)anisole (**1**), m.p. 67–68° from ethanol (lit. m.p. 67–68° (26)); 4-(*p*-nitrophenylthio)-toluene (**4**), m.p. 80–82° from ethanol (lit. m.p. 80–81° (25)); (*p*-nitrophenylthio)benzene (**6**), m.p. 55–56° from ethanol (lit. m.p. 55° (25)); *N*,*N*-dimethyl-4-(*p*-nitrophenylthio)aniline (**7**), m.p. 181.5–183° from ethanol–chloroform (lit. m.p. 181° (4)); 1-chloro-4-(*p*-nitrophenylthio)benzene (**9**), m.p. 85–87° from ethanol (lit. m.p. 83–84° (25), 88° (27)).

Diazotization of *p*-anisidine, *p*-bromoaniline, and *p*-chloraniline, followed by reaction with a solution of the appropriate sodium thiolate (28, 29) gave the following sulfides respectively: 4-(*p*-tolylthio)anisole (**3**), b.p. 145–149° at 0.8 mm, m.p. 43–45° from 95% ethanol (lit. b.p. 181–182° at 4 mm, m.p. 45–46° (28)); 4-(*p*-bromophenylthio)toluene (**10**), m.p. 82.5–83.5° from methanol (lit. m.p. 82.5° (30)); 4-(*p*-chlorophenylthio)toluene (**11**), m.p. 72–74° from methanol (lit. m.p. 72–73° (31)).

The method described by Campbell (32) was used for the preparation of *p*-(phenylthio)toluene (**5**), b.p. 137–140° at 3.2 mm (lit. 169° at 13 mm (29)).

4-(*p*-Nitrophenylthio)aniline (**2**) was prepared from *p*-chloronitrobenzene (33), m.p. 144–145.5° from ethanol (lit. m.p. 145° (33)). Acetylation of this amine gave 4′-(*p*-nitrophenylthio)acetanilide, m.p. 196.5–198° from methanol (lit. m.p. 198° (33)).

4-(*p*-Tolylthio)aniline (**8**) was prepared by reduction of the corresponding nitro compound with stannous chloride (34), m.p. 72.5–73.5° from 50% ethanol, as reported (35).

Preparation of Sulfoxides

A variety of oxidation methods was used for the preparation from the corresponding sulfides.

(a) Methyl Phenyl Sulfoxides

4-(Methylsulfinyl)toluene (**35**) was prepared by oxidation with sodium periodate (36), m.p. 42–44° (lit. m.p. 42–43° (37)). 1-(Methylsulfinyl)-4-nitrobenzene (**38**) was prepared by oxidation with H_2O_2 in glacial acetic acid (38), m.p. 147–149° after repeated crystallizations from benzene (lit. m.p. 151–152° from benzene (38)).

4-(Methylsulfinyl)anisole (**36**) was prepared by oxidation with H_2O_2 in acetone as described by Ghersetti and Palotti (39), b.p. 110–115° at 0.1 mm, m.p. 44–45° from low-boiling petroleum ether (lit. m.p. 43°, b.p. 153–154° at 5 mm (37)). This oxidation method was also used for the preparation of 4-(methylsulfinyl)aniline (**37**). In this case it was found to be advantageous to keep the reaction mixture in the dark for 2–4 days. It was necessary to purify the crude sulfoxide by chromatography on an alumina column as described by Ghersetti and Palotti (39) for some other sulfoxides. Using the eluents benzene, benzene–chloroform (1:1), chloroform and finally ethanol, the sulfoxide was isolated from the ethanol fraction, m.p. 96–96.5° from chloroform – petroleum ether (1:1); lit. m.p. 95–96° (39).

(b) Diphenyl Sulfoxides

Most required diphenyl sulfoxides were prepared using the same procedure: the sulfide and the theoretically required quantity of hydrogen peroxide (30% aqueous solution) were mixed, and glacial acetic acid was added until the mixture had become homogeneous after thorough mixing. The mixture was left standing for 4–7 days at about 20°. Water was added and the mixture was extracted with chloroform, from which the sulfoxide was isolated. The following sulfoxides were prepared by this method.

4-(*p*-Nitrophenylsulfinyl)toluene (**15**), m.p. 125.5–126.5° after crystallization from methanol (2 times) and petroleum ether.

Anal. Calcd. for $C_{13}H_{11}NO_3S$: C, 59.76; H, 4.24; N, 5.36. Found: C, 59.92; H, 3.93; N, 5.05.

4-(*p*-Tolylsulfinyl)anisole (**14**), m.p. 69–70° after crystallization from aqueous methanol and petroleum ether.

Anal. Calcd. for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73. Found: C, 67.98; H, 5.69.

4-(*p*-Nitrophenylsulfinyl)anisole (**12**), m.p. 122° from petroleum ether.

Anal. Calcd. for $C_{13}H_{11}NO_4S$: C, 56.31; H, 4.00; N, 5.05. Found: C, 56.01; H, 3.90; N, 4.93.

Deacetylation of crude 4′-(*p*-nitrophenylsulfinyl)-acetanilide with m.p. 194–196°, prepared according to Gabel and Grinberg (40), gave 4-(*p*-nitrophenylsulfinyl)-aniline (**13**), m.p. 130–131° from water, as reported (7).

Preparation of Sulfones

All sulfones, except where indicated, were prepared by oxidation of the corresponding sulfides with hydrogen peroxide in refluxing glacial acetic acid.

(a) Methyl Phenyl Sulfones

4-(Methylsulfonyl)toluene (**39**), m.p. 88–89° from ethanol, as reported (41); 4-(methylsulfonyl)anisole

(**40**), m.p. 120–121° from water (lit. m.p. 121° (42)); 1-(methylsulfonyl)-4-nitrobenzene (**42**), m.p. 142–143° from methanol (lit. m.p. 142.5° (43)). Low pressure hydrogenation of the latter compound using Raney nickel catalyst as described by Gilman and Broadbent (25) gave an 80% yield of 4-(methylsulfonyl)aniline (**41**), m.p. 136.5–137.5° from water (lit. m.p. 134–135° (44)).

(b) Diphenyl Sulfones

4-(*p*-Nitrophenylsulfonyl)toluene (**19**), m.p. 171–172.5° from ethanol, as reported (25); 4-(*p*-tolylsulfonyl)-anisole (**18**), m.p. 102.5–104° from petroleum ether containing 5% *p*-dioxane (lit. m.p. 103–104.5° (45)); 4′-(*p*-nitrophenylsulfonyl)acetanilide, m.p. 227–229° from tetrahydrofuran (lit. m.p. 229–230° (33)). Deacetylation of this compound (46) gave 4-(*p*-nitrophenylsulfonyl)-aniline (**17**), m.p. 170–171° from methanol (lit. m.p. 168–169° (46)).

4-(*p*-Nitrophenylsulfonyl)anisole (**16**), a compound not yet reported to our knowledge, was also prepared by oxidation of the corresponding sulfide. After crystallization from ethanol m.p. 162–163.5°.

Anal. Calcd. for $C_{13}H_{11}NO_5S$: C, 54.16; H, 3.85; N, 4.86. Found: C, 53.93; H, 4.01; N, 4.84.

Preparation of Diphenyl Ethers

4-(*p*-Nitrophenoxy)aniline (**21**) was prepared from 4′-hydroxyacetanilide and 1-bromo-4-nitrobenzene according to Ikawa (47), m.p. 134° from ethanol (lit. m.p. 133° (47)). The same method was used for the preparation of 1-methoxy-4-(*p*-nitrophenoxy)benzene (**20**), m.p. 111° from methanol, as reported (48), and for the preparation of 1-methoxy-4-(*p*-tolyloxy)benzene (**22**). Even after many recrystallizations the m.p. 52–53° reported by Tomita and Ikawa (49) for the last compound could not be duplicated, but remained at 46–47° (from petroleum ether), in agreement with the m.p. 47–48° reported by Harrington (50). 4-(*p*-Nitrophenoxy)toluene (**23**) was prepared as reported (51), m.p. 67° (sharp) from petroleum ether. Tomita and Ikawa (52) report a m.p. 82°. This could not be duplicated, but our m.p. is in better agreement with another reported value, m.p. 69° (53).

Preparation of Diphenyl Methanes

α-(*p*-Nitrophenyl)*p*-toluidine (**25**) was prepared by nitration of *p*-benzylaniline (54, 55), m.p. 98–99° from ethanol (lit. 97.5–98.5° (54)). The required *p*-benzylaniline was prepared by reduction of the corresponding nitro compound with iron powder in aqueous acetic acid (56) and isolated as its *N*-acetyl derivative, m.p. 120° for the crude product (lit. m.p. 125–126° (57)). 4-(*p*-Methylbenzyl)anisole (**26**), prepared as reported by Pratt *et al.* (58) was found to be impure and contaminated with what seemed to be 2-(*p*-methylbenzyl)anisole, on the basis of the n.m.r. spectrum of the distilled product. An attempt to separate the two isomers on an alumina column failed. The compound was finally prepared by a method described by Houston (59). In this preparation a mixture of the two isomers was obtained again, but the pure *para* isomer could be obtained after careful distillation:

To a well stirred mixture of 30.5 g (0.25 mole) of *p*-methylbenzyl alcohol, and 39 g (0.36 mole) of anisole in 100 ml of low-boiling petroleum ether were added 18.8 g (0.14 mole) of aluminium trichloride in small portions over a period of 30 min. The temperature was kept at 15–25°. After standing overnight, ice, water and hydrochloric acid were added, as well as ether. After work-up and distillation of the products (a fore-run of anisole was collected) two main fractions were collected. The first fraction, weighing 19.75 g, collected at 99–101° (0.13–0.15 mm), n_D^{25} 1.5696 contained again a mixture of the *ortho* and *para* isomers. The second fraction, weighing 5.80 g, distilling at 103–109° (0.08–0.15 mm), n_D^{25} 1.5691, was the desired 4-(*p*-methylbenzyl)anisole (lit. b.p. 140–145° at 2.7 mm, n_D^{25} 1.5671 (58)).

4-(*p*-Nitrobenzyl)anisole (**24**) was prepared according to Blackwell and Hickinbottom (60). The crude product, a yellow oil, was purified by chromatography on aluminium oxide, and the compound was isolated from the first eluent fraction (petroleum ether – benzene 5:1). After recrystallization from methanol m.p. 70–71° (lit. m.p. 61° (60)).

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