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Influence of *Ortho* Substituents on UV Spectra of Aryl Methyl Sulphoxides

V BALIAH*† & R VARADACHARI
Department of Chemistry, Annamalai University, Annamalainagar 608 002

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The UV spectra of some *ortho* substituted aryl methyl sulphoxides are recorded and analysed. A comparison of the steric effects of *ortho* substituents on conjugation of CH_3S-, CH_3SO- and CH_3SO_2- groups with the *para* substituents in the benzene ring has been made. The *ortho* substituents do not inhibit conjugation in the case of sulphones while they cause a marked inhibition in the case of sulphides and sulphoxides. The inhibition of conjugation of the CH_3SO- group under the influence of *ortho* substituents is observed when the CH_3SO- group acts both as an electron donor and as an electron acceptor. An explanation is offered for the observed steric effects.

Though the UV spectra of sulphides[1-5] and sulphones[6-12] have been extensively studied, available spectral data on sulphoxides[13-17] are not much. The sulphoxide group can be compared with either the sulphonyl or the sulphide group. Price and Hydock[13] as well as Bordwell and Boutan[14] found that methyl phenyl sulphoxide behaves more like methyl phenyl sulphide, the sulphinyl group entering into electron-donor type of conjugation. The possibility of the sulphoxide group, when present *para* to a hydroxyl group, entering into electron-acceptor type of conjugation, was also suggested by Bordwell and Boutan[14]. The main objective of the present study is to know whether bulky *ortho* substituents inhibit the conjugation of the CH_3SO- group with benzene nucleus.

Materials and Methods

UV spectra were recorded in purified ethanol (95%), cyclohexane and dioxane on a Beckmann spectrophotometer, model DU.

Methyl 2,6-dimethyl-4-nitrophenyl sulphoxide was prepared by the H_2O_2 oxidation of methyl 2,6-dimethyl-4-nitrophenyl sulphide[19]. It was recrystallised from methanol, m.p. 165-66° (Found: C, 50.4; H, 5.1. $C_9H_{11}O_3NS$ requires C, 50.7; H, 5.2%).

Methyl 4-amino-2,6-dimethylphenyl sulphide was prepared by the Sn(IV)/HCl reduction of methyl 2,6-dimethyl-4-nitrophenyl sulphide under H_2S atmosphere. The desired compound, which separated out as an oil, solidified after keeping for two days in the refrigerator. It was crystallised from methanol, m.p. 68-69° (Found: C, 64.5; H, 7.9. $C_9H_{13}NS$ requires C, 64.6; H, 7.8%).

Methyl 4-acetamido-2,6-dimethylphenyl sulphide was prepared by the acetylation (acetyl chloride/pyridine; 1 hr) of the corresponding amino derivative. It was recrystallised from ethanol-water, m.p. 149-50° (Found: C, 63.0; H, 7.0. $C_{11}H_{15}ONS$ requires C, 63.2; H, 7.2%).

Methyl 4-acetamido-2,6-dimethylphenyl sulphoxide was prepared by the H_2O_2 oxidation of the above sulphide and recrystallised from benzene, m.p. 69-70° (Found: C, 58.4; H, 6.7. $C_{11}H_{15}O_2NS$ requires C, 58.7; H, 6.7%).

Methyl 2,6-dibromo-4-nitrophenyl sulphide was prepared as follows: A solution of 2,6-dibromo-4-nitroaniline (23.4 g) in hot glacial acetic acid (270 ml) was rapidly cooled to room temperature and gradually added to a solution of sodium nitrite (5.5g) in conc. sulphuric acid (40 ml), keeping the temperature at 20°. The temperature was raised to 70° until the nitrite dissolved, the solution cooled to room temperature, filtered and added to a paste of cuprous cyanate (21.6g) and potassium thiocyanate (10g). The mixture was stirred for 6 hr and heated on a water-bath for 30 min. After cooling, it was diluted with water, the separated solid filtered off (7g), treated with a solution of potassium hydroxide (7g) in water (15 ml) and dimethyl sulphate (18g) and refluxed for 1 hr. The excess of dimethyl sulphate was destroyed by adding aq. sodium hydroxide and the mixture poured into water. An oil separated, which solidified after cooling in ice; yield 5.5g. It was crystallised from ethanol, m.p. 85-86° (Found: C, 25.9; H, 1.6. $C_7H_5O_2NSBr_2$ requires C, 25.7; H, 1.5%).

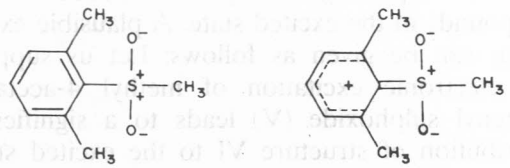
Methyl 2,6-dibromo-4-nitrophenyl sulphoxide was prepared by the H_2O_2 oxidation of the above sulphide and crystallised from methanol, m.p. 128-29° (Found: C, 24.7; H, 1.4. $C_7H_5O_3NSBr_2$ requires C, 24.5; H, 1.5%).

†Present address: 79, 3rd Cross Road, Venkatanagar, Pondicherry 605 011

Methyl 2,6-dibromo-4-nitrophenyl sulphone was prepared by oxidising the above sulphoxide with excess of H_2O_2. It was recrystallised from ethanol, m.p. 118-19° (Found: C, 23.7; H, 1.6. $C_7H_5O_4NSBr_2$ requires C, 23.4; H 1.4%).

Results and Discussion

The UV spectra of methyl phenyl, methyl *o*-tolyl, methyl *o*-*t*-butylphenyl and methyl 2,6-dimethylphenylsulphones in ethanol exhibit maximum absorptions (only most intense band is given) at 217 (ε_{max}, 7100), 219(7200), 222(7200) and 219 nm(7400), respectively. The data indicate that no steric inhibition of resonance is observable with the sulphonyl group. Even in a compound like methyl 2,6-dimethylphenyl sulphone, the *ortho* methyl groups do not sterically inhibit the conjugation of the sulphonyl group with the benzene nucleus. Structure I chiefly

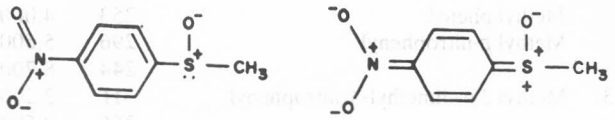


I II

contributes to the ground state of the molecule. The four valence bonds of sulphur in I result from $3s3p^3$, i.e. from sp^3 hybridisation and they may be taken as essentially tetrahedral. Structure II makes a contribution to the excited state. The four σ-bonds of sulphur in II are still tetrahedral. The electron that moves from the benzene ring to the sulphur atom goes into one of the vacant *d*-orbitals of sulphur and the double bond is formed by the overlapping of 2*p*-orbital of carbon with the 3*d*-orbital of sulphur, i.e. it is a *pπ-dπ* bond. In that case planarity of the atoms of the sulphonyl group with the benzene ring is not necessary for conjugation. So there is no steric inhibition of resonance in the exicited state of methyl 2,6-dimethylphenyl sulphone.

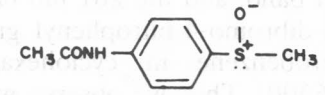
When we consider steric inhibition of resonance in sulphoxides, we will have to examine two different cases: (i) when the sulphoxide group behaves as an electron donor and (ii) when it behaves as an electron acceptor. Methyl *p*-nitrophenyl sulphoxide (III) is an example of the former type. If there is to be effective conjugation between the CH_3SO- and $-NO_2$ groups (as in structure IV) the atoms C, S and O of the CH_3SO- group should be in the plane of the benzene ring. So bulky substituents *ortho* to the CH_3SO- group are expected to cause steric inhibition of resonance.

Methyl *p*-acetamidophenyl sulphoxide (V) provides an example in which the sulphoxide group acts as an electron acceptor.

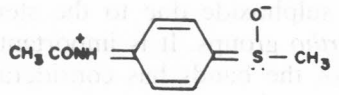


III IV

If in structure VI one of the vacant 3*d*-orbitals of sulphur is filled and is used in π-bond formation, bulky substituents *ortho* to the CH_3SO- group should not inhibit conjugation.



V



VI

With a view to testing the above predictions, several sulphoxides with the requisite substituents were prepared and their spectra were recorded. The data are given in Table 1. When the -SO- group is electron releasing, its conjugation is inhibited by bulky *ortho* substituents. In order to see clearly the steric influence on the specra, it is necessary to know first the electronic origin of the various bands observed. Comparing the spectra of methyl phenyl sulphoxide and methyl *p*-nitrophenyl sulphoxide, it is seen that the 296 nm band arises from conjugation between -SO- and $-NO_2$ groups. The band at 244 nm is due to the $-C_6H_4.NO_2$ partial chromophore (for nitrobenzene in cyclohexane[18]; λ_{max} 253 nm; ε_{max} 9,900). By the same consideration the 311 nm band of methyl 2,6-dimethyl-4-nitrophenyl sulphoxide must be due to conjugation between -SO- and $-NO_2$ groups through the benzene nucleus and the 256 nm band must be due to 2,6-dimethyl-4-nitrophenyl chromophore. This view gains support from an examination of the spectrum of 3,5-dimethylnitrobenzene in cyclohexane (λ_{max} 264 nm; ε_{max} 7,700).

The 319 nm band of methyl 2,6-dibromo-4-nitrophenyl sulphoxide is weaker than the 296 nm band of methyl 4-nitrophenyl sulphoxide. It is

Table 1 — UV Spectra of Sulphoxides

[Spectra in cyclohexane for Nos.1-4 and in dioxane for Nos.5 and 6]

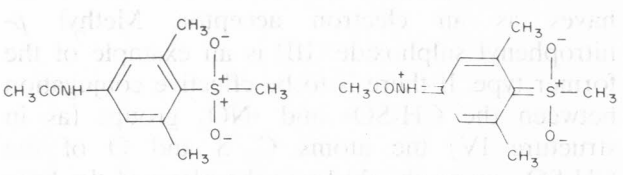
No.	Sulphoxide	λ_{max} (nm)	ε_{max}
1.	Methyl phenyl	253	4,000
2.	Methyl *p*-nitrophenyl	296	5,600
		244	8,700
3.	Methyl 2,6-dimethyl-4-nitrophenyl	311	2,200
		256	9,600
4.	Methyl 2,6-dibromo-4-nitrophenyl	319	2,800
		261	6,400
5.	Methyl 4-acetamidophenyl	263	18,500
6.	Methyl 2,6-dimethyl-4-acetamidophenyl	256	12,600
		275(sh)	11,000

the conjugation band, and the 261 nm band must be due to 2,6-dibromo-4-nitrophenyl group (for 3,5-dibromonitrobenzene in cyclohexane: λ_{max} 260 nm; ε_{max} 6300). Thus we observe weakening of the conjugation band in methyl 2,6-dimethyl-4-nitrophenyl sulphoxide and methyl 2,6-dibromo-4-nitrophenyl sulphoxide due to the steric influence of the *ortho* groups. It is important to note that the ε_{max} of the bands has considerably decreased, though there is some bathochromic shift of the absorption maxima. A considerable decrease in ε_{max} is the true index of steric inhibition of resonance. The UV spectra (not given) clearly reveal the steric influence. Hence there seems to be no doubt that the sulphinyl-aryl conjugation undergoes steric inhibition. In this respect the sulphoxide function is comparable to the sulphide function. The UV spectral data of sulphides in cyclohexane support this view: Methyl phenyl, methyl *p*-nitrophenyl, methyl 2,6-dimethyl and methyl 2,6-dibromo-4-nitrophenyl sulphides exhibit UV λ_{max} (ε_{max} values in parentheses) at 255 (6900); 326 (16000); 320 (4700), 265 (8000); and 340 (2800), 268 nm (7400) respectively.

The influence of substituents *ortho* to the sulphoxide group, when they are electron attracting, may be seen by comparing the spectra of methyl 4-acetamidophenyl sulphoxide and methyl 4-acetamido-2,6-dimethylphenyl sulphoxide. The former exhibits λ_{max} at 263 nm (ε_{max}, 18500). Relative to the spectra of methyl phenyl sulphoxide (λ_{max} 249 nm; ε_{max} 3500 in dioxane) and acetanilide (λ_{max} 242 nm; ε_{max} 14400), there is a bathochromic shift of absorption maximum and a considerable increase in ε_{max}. This is to be expected if there is conjugation between CH_3CONH- and $-SOCH_3$ groups through benzene nucleus. The two methyl groups in methyl 4-acetamido-2,6-dimethylphenyl sulphoxide have very much affected the 263 nm band, the ε_{max} being significantly reduced (which is the criterion for steric inhibition of resonance); only a shoulder appears at 275 nm (ε_{max} 11,000). There is an absorption maximum at 256 nm (ε_{max} 12,600) which is presumably due to the partial 4-acetamido-2,6-dimethylphenyl chromophore. Such a view gets support from the spectrum of 3,5-dimethylacetanilide (λ_{max} 248 nm; ε_{max} 13,200 in dioxane). The behaviour of 4-acetamido-2,6-dimethylphenyl sulphoxide is in contrast to that of methyl 4-acetamido-2,6-dimethylphenyl sulphone (λ_{max} 263 nm; ε_{max} 24,000 in dioxane) in which no steric inhibition of conjugation is observable.

The lack of steric effect in sulphones was explained[11] as due to *d*-orbital π-bonding which does not demand coplanarity of the atoms. The fact that there is steric effect in sulphoxides (when the -SO- group is electron withdrawing) indicates a different type of geometry of the bonds in these compounds in the excited state. A plausible explanation can be given as follows: Let us suppose that electronic excitation of methyl 4-acetamidophenyl sulphoxide (V) leads to a significsant contribution of structure VI to the excited state. In V, $3p^3$ electrons of sulphur are involved in bond formation, the bonds being pyramidal. In VI, if the excited electron occupies 4*s*-orbital and not the 3*d*-orbital of sulphur, there will be four valence electrons available for bond formation. These are $3p^34s$ electrons. Of these one *p* electron will be involved in π-bond formation with the carbon atom of the benzene ring. The remaining three electrons ($3p^24s$) hybridize to give three equivalent sp^2 hybridized orbitals for the formation of σ-bonds; sp^2 hybridization leads to planarity of the atoms and they cannot be coplanar with the benzene ring having two *ortho* methyl groups. Thus the observed steric effect of the *ortho* methyl groups becomes understandable.

Why should the excited electron enter the 3*d*-orbital in the case of sulphones and 4*s*-orbital in the case of sulphoxides? This question can be answered if we take into account the valence electrons in sulphones. As in the previous examples, we can consider the structures of sulphones VII and VIII. In VII the valence electrons of sulphur



VII VIII

which are involved in bond formation are $3s3p_x3p_y3p_z$. They are hybridized to give four equivalent orbitals. The bonds are therefore tetrahedral. In VIII if the excited electron enters the 4*s*-orbital of sulphur, the electrons available for bond formation are $3s3p_x3p_y3p_z4s$. Of these one of the *p*-electrons must be used for π-bond formation. The electrons left for the four σ-bonds are $3s3p^24s$. This means s^2p^2 hybridization which is not possible for bond arrangement[20]. Hence in the case of sulphones, the excited electron enters the 3*d*-orbital and this itself may be involved in π-bond formation. The σ-bonds still retain their tetrahedral character and no planarity of the atoms is required for conjugation with the benzene ring.

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