

Evidence from UV Spectra for *d*-Orbital Utilization by Sulphur

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The spectral changes caused in the 1L_a bands of aniline and *N,N*-dimethylaniline by the introduction of $-SCh_3$ and $-SC_6H_5$ substituents in the *para* position suggest the ability of sulphur to expand its valence shell. The UV spectra of some substituted 4-amino- and 4-dimethylaminodiphenyl sulphides and their oxygen analogues have also been studied. An estimate of the oscillator strengths of the absorption bands shows that the presence of a Cl, Br or I atom in the 4'-position of 4-amino- or 4-dimethylaminodiphenyl sulphide increases the oscillator strength significantly. This suggests a possibility of conjugative interaction of the amino groups with Cl, Br and I atoms through the intervening sulphur. The spectral behaviour of the oxygen analogues does not indicate any such conjugative interaction.

THE various electronic effects due to divalent sulphur in organic compounds have been discussed¹ on the basis of many physical methods of study, especially, IR²⁻⁴, NMR^{5,6}, ESR⁷, PMR⁸ and electronic spectroscopy⁹⁻²³. The interpretations given by different workers differ in respect of the ability of sulphur to utilize its vacant *d*-orbitals. The present study was undertaken with a view to obtaining spectral data on some aromatic sulphides where sulphur could utilize its vacant *d*-orbitals. Since a study of this type would be more fruitful by comparing the behaviour of the sulphur compounds with that of their oxygen analogues, the spectral characteristics of their oxygen analogues have also been studied.

Materials and Methods

4-Amino-, 4-amino-4'-fluoro-, 4-amino-4'-chloro-, 4-amino-4'-bromo-, 4-amino-4'-iodo-, 4-amino-4'-methyl-, 4-dimethylamino-, 4-dimethylamino-4'-fluoro-, 4-chloro-4'-dimethylamino-, 4-bromo-4'-dimethylamino-, 4-dimethylamino-4'-iodo-, 4-dimethylamino-4'-methyldiphenyl sulphide, and 4-amino-, 4-amino-4'-fluoro-, 4-amino-4'-chloro-, 4-amino-4'-bromo-, 4-amino-4'-methyl-, 4-dimethylamino-4'-fluoro-, 4-chloro-4'-dimethylamino-, 4-bromo-4'-dimethylamino-, 4-dimethylamino-4'-methyldiphenyl ether were prepared as described earlier²⁴.

The spectra were determined with a Hilger and Watts Uvispek photoelectric spectrometer, model H 700.308 equipped with a silica prism. The solvent used was 95% ethanol, purified by distillation after treatment with lead acetate and sodium hydroxide.

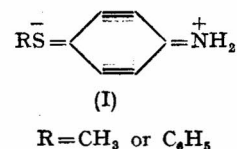
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Results and Discussion

When a charge-transfer takes place from the π -system to sulphur, the lower the ionization potential of the π -system, the higher will be the electron affinity of the vacant orbital on sulphur. The degree of overlapping of the vacant orbital of sulphur with π -charge cloud is an important factor to be considered. Thus, strong donor substituents like $-NH_2$ and $-N(CH_3)_2$, in the phenyl ring, will favour valence shell expansion by decreasing the ionization potential of the π -system.

The spectral data (Table 1) show how the 1L_a band of aniline (λ_{max} , 234 nm; ϵ_{max} , 11500) is affected by the *para* substituents, CH_3S- and C_6H_5S- . There is a bathochromic shift of about 20-30 nm with an increase in intensity indicating the existence of conjugation between the electron-donating amino group and the sulphur atom as shown in structure (I). The 1L_a band of *p*-anisidine or



4-aminodiphenyl ether does not undergo any significant red shift (compared with that of aniline) and the intensity of the band also remains practically the same.

The same is the case with *N,N*-dimethylanilines. The 1L_a band of *N,N*-dimethylaniline is affected by *para*-substitution with methylthio or phenylthio group (Table 1). The contrast that the oxygen compounds offer is also apparent.

Instead of analysing the spectral data with reference to λ_{max} and ϵ_{max} , it is often preferable to consider the oscillator strength (*f*) on theoretical grounds.

TABLE 1 — UV SPECTRAL CHARACTERISTICS OF SOME ANILINES AND N,N-DIMETHYLANILINES

Compound	¹ L _a band			¹ L _b band	
	λ _{max} (nm)	ε _{max}	Δλ	λ _{max} (nm)	ε _{max}
Aniline ²⁵	234	11,500	—	284.5	1,700
<i>p</i> -Aminophenyl methyl sulphide ¹⁹	264	13,800	30	294.0	1,700
<i>p</i> -Anisidine ²⁵	236	7,900	2	299.0	1,600
4-Aminodiphenyl sulphide*	256	17,400	22	—	—
4-Aminodiphenyl ether*	242	11,800	8	296.0	1,900
N,N-Dimethylaniline ²⁵	250	12,600	—	297.0	1,600
<i>p</i> -Dimethylaminophenyl methyl sulphide ²¹	271	20,400	21	303.0	2,500
<i>p</i> -Methoxy-N,N-dimethylaniline ²⁵	247	10,000	3	307.0	2,000
4-Dimethylaminodiphenyl sulphide*	278	24,300	28	—	—
4-Dimethylaminodiphenyl ether*	256	15,500	6	—	—

*Present work.

TABLE 2 — SPECTRAL DATA FOR
4-AMINODIPHENYL SULPHIDES,
4-DIMETHYLAMINODIPHENYL SULPHIDES,
4-AMINODIPHENYL ETHERS AND
4-DIMETHYLAMINODIPHENYL ETHERS

Compound	λ _{max} (nm)	ε _{max}	<i>f</i>
DIPHENYL SULPHIDES			
4-Amino	256	17,400	0.560
4-Amino-4'-fluoro	255	15,600	0.498
4-Amino-4'-chloro	263	19,400	0.600
4-Amino-4'-bromo	266	20,700	0.643
4-Amino-4'-iodo	266	23,300	0.664
4-Amino-4'-methyl	257	18,000	0.545
4-Dimethylamino	278	24,300	0.662
4-Dimethylamino-4'-fluoro	278	23,600	0.629
4-Dimethylamino-4'-chloro	278	25,900	0.740
4-Dimethylamino-4'-bromo	279	26,900	0.775
4-Dimethylamino-4'-iodo	278	29,300	0.875
4-Dimethylamino-4'-methyl	278	23,000	0.671
DIPHENYL ETHERS			
4-Amino	242	11,800	0.313
4-Amino-4'-fluoro	241	15,900	0.320
4-Amino-4'-chloro	241	13,400	0.329
4-Amino-4'-bromo	242	13,100	0.332
4-Amino-4'-methyl	243	13,200	0.332
4-Dimethylamino	256	15,500	0.360
4-Dimethylamino-4'-fluoro	258	14,300	0.309
4-Dimethylamino-4'-chloro	257	16,100	0.358
4-Dimethylamino-4'-bromo	258	16,600	0.379
4-Dimethylamino-4'-methyl	255	15,500	0.329

In the present study an estimate of the oscillator strengths has also been made for some compounds. The *f* values were computed from the integrated areas under the curves by use of the equation:

$$f = 4.32 \times 10^{-9} \int \epsilon d\nu$$

where ϵ is the molar extinction coefficient and ν is the wave-number in cm^{-1} . For a given band the area was measured under the two minima on each side of the band.

When Cl, Br or I is the substituent in the 4'-position of 4-aminodiphenyl sulphide, there is a bathochromic shift of the band at 256 nm with an

increase in the intensity. In a more quantitative way, the substituent effects are seen in the oscillator strengths. The high intensities of the bands occurring in the spectra of 4-amino-4'-chloro-, 4-amino-4'-bromo- and 4-amino-4'-iododiphenyl sulphides suggest the possibility of interaction of the *d*-orbitals of chlorine, bromine or iodine with the π -orbitals of the ring. The presence of a Cl, Br or I atom in the 4'-position of 4-aminodiphenyl sulphide raises the oscillator strength of 4-aminodiphenyl sulphide by 7, 15 and 18.5% respectively (Table 2). On the other hand, a F atom present in the same position decreases the oscillator strength by 11%.

A similar trend is observed in 4-dimethylaminodiphenyl sulphides. In fact, in these cases the introduction of a Cl, Br or I atom at the 4'-position of 4-dimethylaminodiphenyl sulphide causes a greater increase in the oscillator strength, viz. 12, 17, and 32% respectively (Table 2). A fluorine atom decreases the value by 5%. These facts indicate conjugative interaction between the amino groups and Cl, Br and I atoms through the intervening sulphur. An examination of the spectral characteristics of 4-amino-4'-halogenodiphenyl ethers and 4-dimethylamino-4'-halogenodiphenyl ethers lends additional support to the above view. There is no significant increase in the oscillator strengths of the substituted diphenyl ethers in comparison with the parent compound (Table 2).

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