650. *The Polarities and Ultra-violet Spectra of Phenyl* p-*Tolyl Azoxysulphone and its Dialkylamino-derivatives.*

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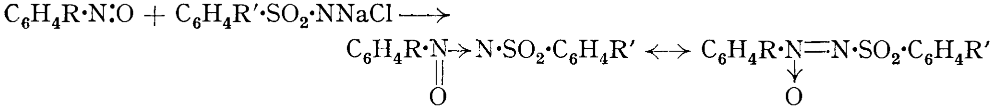
The moment of phenyl *p*-tolyl azoxysulphone is found to be 6·0 D. This is increased to 8·5 D in the *p*-dimethylamino- and to 8·9 D in the *p*-diethylamino-derivative. These polarity changes can be explained by mesomerism. The spectra between 2300 and 4700 Å of all three substances in alcohol are recorded. With the dialkylamino-azoxysulphones two bands are found, that at longer wave-length being the more intense. The spectrum of phenyl *p*-tolyl azoxysulphone resembles that of azoxybenzene in the 300-mμ region. No indications of *cis-trans*-isomerism have been detected by the usual tests.

The experiments described in the preceding paper suggested an exploratory examination of the azoxysulphones. These substances, unknown to Hantzsch, were discovered fairly recently by Farrar and Gulland (*J.*, 1944, 368) through the interaction of nitrosoaryls with chloramine-T or -B in pyridine solution :



$$C_6H_4R{\cdot}N{:}O + C_6H_4R'{\cdot}SO_2{\cdot}NNaCl \longrightarrow C_6H_4R{\cdot}\underset{\underset{O}{\|}}{N}{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4R' \longleftrightarrow C_6H_4R{\cdot}\underset{\underset{O}{\downarrow}}{N}{=}N{\cdot}SO_2{\cdot}C_6H_4R'$$

When R and R′ were both hydrocarbon radicals the azoxysulphones produced were pale yellow and readily soluble in non-polar liquids; when however R was NR_2 the colours were greatly deepened and the solubilities diminished.

For the present purposes we have taken phenyl *p*-tolyl azoxysulphone (R = H, R′ = Me) as an example of the former and *p*-dimethylamino- and -diethylamino-phenyl *p*-tolyl azoxysulphones (R = NMe_2 or NEt_2, R′ = Me) as examples of the latter type. In appearance, m. p., etc., each sample agreed with the description given by Farrer and Gulland. Before we determined their apparent dipole moments (in benzene) and ultra-violet absorption spectra (in alcohol), preliminary tests were made on the effects of sunlight on such solutions. These revealed no changes of dielectric constant or transmission. The precautions against illumination (cf. previous paper) usually adopted by us when handling azo-derivatives were therefore not necessary in these cases.

Polarisations.—Table 1 presents the dielectric constant, density, and concentration data necessary for the calculations of the moments shown in Table 2. Owing to their small solubility, the dialkylamino-azoxysulphones were conveniently dissolved in benzene at *ca.* 60° and the solutions then cooled to 30° for measurement. Recrystallisation was seldom observed, nor—to judge from the constancy of the $\alpha\varepsilon_2$ figures—did this treatment cause decomposition.

TABLE 1. *Densities and dielectric constants * of three azoxysulphones in benzene at* 30°.

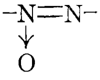
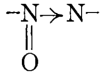
	Phenyl p-*tolyl azoxysulphone.*				
$10^6 w_2$	7742	16,128	24,893	33,093	44,180
ε^{30}	2·3709	2·4873	2·6150	2·7281	2·8853
d_4^{30}	0·86954	0·87199	0·87484	0·87748	0·88086
	p-*Dimethylaminophenyl* p-*tolyl azoxysulphone.*				
$10^6 w_2$	1342	2098	2173	3690	6388
ε^{30}	2·2954	2·3145	2·3153	2·3521	2·4132
d_4^{30}	0·86754	0·86785	0·86784	0·86834	0·86907
	p-*Diethylaminophenyl* p-*tolyl azoxysulphone.*				
$10^6 w_2$	1431	2115	2515	3139	
ε^{30}	2·2982	2·3142	2·3238	2·3391	
d_4^{30}	0·86757	0·86790	0·86797	0·86819	

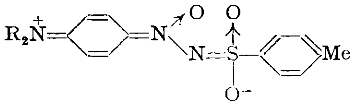
* For $10^6 w_2 = 0$, $\varepsilon^{30} = 2·2628$ and $d_4^{30} = 0·86718$.

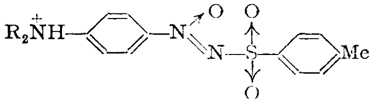
TABLE 2. *Polarisations and dipole moments.*

Azoxysulphone	M_2	Mean $\alpha\varepsilon_2$	Mean β	${}_{\infty}P_2$ (c.c.)	$[R_L]_D$ * (c.c.)	μ (D)
Phenyl *p*-tolyl	276·3	14·1	0·355	803	76	$6·0_1$
p-Dimethylaminophenyl *p*-tolyl-	319·4	24·0	0·348	1531	91	$8·4_6$
p-Diethylaminophenyl *p*-tolyl-	347·4	24·4	0·365	1689	100	$8·8_9$

* Estimated from observed $[R_L]_D$ for *trans*-azoxybenzene (63·6 c.c.; von Auwers, *Annalen*, 1932, **499**, 131), together with R_{SO_2} = 7·8 c.c. and other constants as listed by Vogel (*J.*, 1948, 1842).

Discussion.—In the preceding paper the moment of $Ph\cdot N{:}N\cdot SO_2\cdot Ph$ has been recorded as 4·2 D, *i.e.*, some 1·8 D less than the corresponding value for phenyl *p*-tolyl azoxysulphone (6·0 D). Between *trans*-azoxybenzene and *trans*-azobenzene there is a similar difference (Calderbank and Le Fèvre, *J.*, 1948, 1949), which suggests that the real structures of the pale yellow azoxysulphones should be formulated with the  $-\underset{\underset{O}{\downarrow}}{N}{=}N-$ unit as in azoxybenzene, and that the contribution from the alternative,  $-\underset{\underset{O}{\|}}{N}\rightarrow N-$, offered by Farrar and Gulland, is small. The increases of polarity following the introduction of *p*-NR_2 groups are parallel to those observed with the nitrosobenzenes (PhNO, 3·1 D; *p*-$Me_2N\cdot C_6H_4\cdot NO$, 6·9 D; *p*-$Et_2N\cdot C_6H_4\cdot NO$, 7·2 D; Le Fèvre and Smith, *J.*, 1932, 2239) and like them are obviously due to mesomerism, since in the absence of extended resonance a NR_2 group should not alter a molecular resultant by much more than 1·6 D, *i.e.*, the moment of a dialkylaniline (Marsden and Sutton, *J.*, 1936, 599; Barclay, Le Fèvre, and Smythe, *Trans. Faraday Soc.*, 1951, **47**, 357). Our present results thus support the opinion of Farrar and Gulland that the polar natures of the amino-azoxysulphones arise from quinonoid forms such as (I); the formation, in strong acids, of colourless salts is consistent with this since a cation of structure (II) will be unable to mesomerise towards (I) and should therefore not have more colour than if the NR_2 group were absent.

(I) 

 (II)

Absorption Spectra.—The absorptions between 2200 and 5500 Å of alcoholic solutions of the azoxysulphones are shown in Figs. 1 and 2. They, as well as the curves shown in

FIG. 1. FIG. 2.

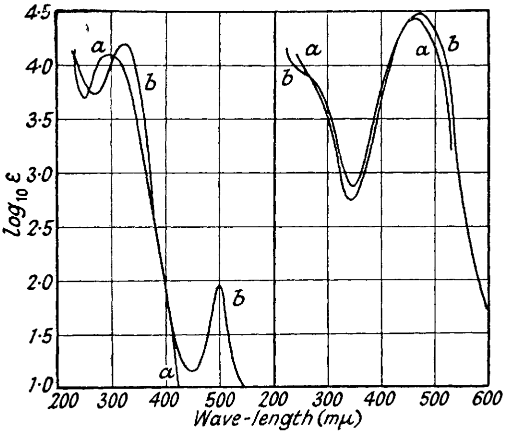


FIG. 1.
a, $C_6H_5{\cdot}NO{:}N{\cdot}SO_2{\cdot}C_6H_4Me$.
b, $C_6H_5{\cdot}NO{:}N{\cdot}C_6H_5$.

FIG. 2.
a, *p*-$Me_2N{\cdot}C_6H_4{\cdot}NO{:}N{\cdot}SO_2{\cdot}C_6H_4Me$.
b, *p*-$Et_2N{\cdot}C_6H_4{\cdot}NO{:}N{\cdot}SO_2{\cdot}C_6H_4Me$.

FIG. 3. FIG. 4. FIG. 5.

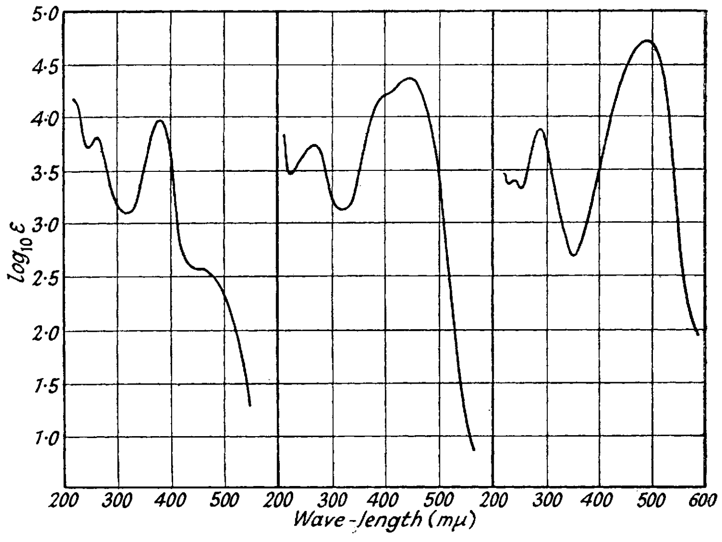


FIG. 3.
p-$Et_2N{\cdot}C_6H_4{\cdot}N_2{\cdot}SO_2{\cdot}C_6H_5$.

FIG. 4.
p-$Et_2N{\cdot}C_6H_4{\cdot}N_2{\cdot}SO_3Na$.

FIG. 5.
p-$Et_2N{\cdot}C_6H_4{\cdot}N_2{\cdot}CN$.

Figs. 3—5, were determined with the Beckman Photoelectric Spectrophotometer, model D.U. Details of the maxima recorded are included in Table 3.

Two observations are notable: (*a*) the general similarity of the spectrum of phenyl *p*-tolyl azoxysulphone with that of *trans*-azoxybenzene (cf. Fig. 1), and (*b*) the particularly strong absorption shown by both of the dialkylamino-derivatives in the visible region, and the apparently reduced wave-lengths of their other absorptions.

The first point is not unexpected, since many aromatic azo- and azoxy-containing molecules possess certain common spectral features. These usually consist of: (i) a band

TABLE 3. *Alterations of* $\lambda_{\text{max.}}$ (mμ) *and* $\log_{10} \varepsilon$ (*in parentheses*) *due to* p-*dialkylamination.*

Compound	*E*-Bands		*K*-Bands		*R*-Bands		Solvent	Refs.
A, Ph·CH=CH·Ph	200 (4·4)	226 (4·2)	295 (4·4)	305 * (4·4)		—	EtOH	Calvin and Alter, *J. Chem. Phys.*, 1951, **19**, 765
p-$Me_2N \cdot C_6H_4 \cdot$CH=CH·Ph		238 (4·1)	346 (4·5)			—	EtOH	Haddow *et al.*, *Phil. Trans.*, 1948, **241**, *A*, 146
B, Ph·N=N·Ph		—	320 (4·2)		450 (2·5)		EtOH	Le Fèvre and Wilson, *J.*, 1951, 1814
p-$H_2N \cdot C_6H_4 \cdot$N=N·Ph		—	362 (4·4)			—	EtOH	Burawoy, *J.*, 1937, 1865
C, Ph·NO=N·Ph		—	320 (4·2)			—	EtOH	Present work
p-$H_2N \cdot C_6H_4 \cdot$NO=N·Ph		250 (4·2)	420 (4·5)			—	EtOH	Szegö, *Ber.*, 1928, **61**, 2087; 1929, **62**, 736
D, *p*-$Cl \cdot C_6H_4 \cdot N_2 \cdot CN$		235 (3·9)	338 (4·3)		438 (2·5)		Et_2O	Le Fèvre and Wilson, *J.*, 1950, 1106.
p-$Et_2N \cdot C_6H_4 \cdot N_2 \cdot CN$	241 (3·4)	285 (3·9)	492 (4·7)			—	EtOH	Present work
E, $Ph \cdot N_2 \cdot SO_3Na$		—	278 *		417		H_2O	Hantzsch and Lifschitz, *Ber.*, 1912, **45**, 3011
o-$Cl \cdot C_6H_4 \cdot N_2 \cdot SO_3Na$		228 * (3·8)	292 (3·9)		423 (2·3)		H_2O	Freeman and Le Fèvre, *J.*, 1951, 415
p-$Et_2N \cdot C_6H_4 \cdot N_2 \cdot SO_3Na$		266 (3·7)	395 * (4·2)	445 (4·4)		—	H_2O	Present work
F, $Ph \cdot N_2 \cdot SO_2 \cdot Ph$		—	295 (4·1)		425 (2·3)		EtOH	Preceding paper
p-$Cl \cdot C_6H_4 \cdot N_2 \cdot SO_2 \cdot Ph$		—	295 (4·4)		415 (3·1)	533 (2·3)	EtOH	Preceding paper
p-$Et_2N \cdot C_6H_4 \cdot N_2 \cdot SO_2 \cdot Ph$		261 (3·8)	380 (4·0)		460 (2·6)		EtOH	Present work
G, Ph·NO=N·$SO_2 \cdot C_6H_4Me$		—	290 (4·1)		500 (2·0)		EtOH	Present work
p-$Et_2N \cdot C_6H_4 \cdot$NO=N·$SO_2 \cdot C_6H_4Me$		247 * (4·0)	465 (4·5)			—	EtOH	Present work

* Denotes an inflexion.

near 220—250 mμ with intensity corresponding to $\varepsilon = ca.\ 10^4$; (ii) a second high-intensity band with $\varepsilon = ca.\ 10^4$ near 300 mμ; and (iii) a band near 450 mμ with $\varepsilon = ca.\ 10^2$. Feature (i) appears to be characteristic of the aromatic system, thus being a benzene—" E "—band (Braude, *Ann. Reports*, 1945, **42**, 105). Such bands are typically affected by auxochromic substituents in a manner similar to ethylenic bands in aliphatic compounds, maximum displacements to longer wave-length being caused by groups with lone-pair electrons, *viz.*, $-NH_2$ and $-SH$ (compare $CH_2{:}CH{\cdot}CH{:}CH_2$, $\lambda_{max.} = 217$ mμ, with $CH_2{:}CH{\cdot}CH{:}CHNEt_2$, $\lambda_{max.} = 281$ mμ, in hexane).

Feature (ii), the second intense absorption, is due (Braude, *loc. cit.*) to conjugation between aromatic nuclei and substituents. That the 320-mμ band of azobenzene is of the class " K " is inferred from the following comparison : $Ph{\cdot}CH{:}CH_2$, $\lambda_{max.} = 244$ mμ ($\varepsilon = 1{\cdot}2 \times 10^4$); *trans*-$Ph{\cdot}CH{:}CH{\cdot}Ph$, 295 mμ ($2{\cdot}7 \times 10^4$); *trans*-$Ph{\cdot}N{:}N{\cdot}Ph$, 320 mμ ($1{\cdot}6 \times 10^4$). This band is not altered greatly either by substituents in the aromatic ring or in *cis*-isomers, although in the latter as well as in some *ortho*-substituted compounds non-planarity due to steric hindrance is shown by smaller intensities of absorption (cf., *e.g.*, preceding paper).

Feature (iii) for the azo-series is usually ascribed to the $-N{=}N-$ linkage itself (Burawoy, *J.*, 1937, 1865; Cook, Jones, and Polya, *J.*, 1939, 1315).

The question now arises, to which class the 465-mμ bands of the *p*-dialkylaminobenzene *p'*-tolyl azoxysulphones belong. At first sight these correspond to the R-bands occurring at comparable wave-lengths with other azo-compounds, in which event the K-absorption found at 290 mμ for the parent azoxysulphone would be represented by the weaker band at 240—250 mμ. It seems doubly unlikely that this assignment is correct : first, in view of the high intensity ($\log \varepsilon = 4$—5) of the longer-wave band in comparison with the usual intensity of R-bands ($\log_{10} \varepsilon\ ca.\ 3$), and secondly, since a lowering of the absorption wave-length by a *p*-dialkylamino-substituent would be unexpected.

Alternatively, we may regard the spectral features of the two NR_2-compounds as displaced E- and K-bands. The expected intensification, due to extended resonance, for the K-bands would then be realised. While a shift after *p*-dialkylamination of 175 mμ (13,000 cm.$^{-1}$) is unusually large, there are at least some known similar cases, designated *A*—*C* in Table 3. Stilbene has been included to illustrate the analogy between the series containing $-CH{=}CH-$ and $-N{=}N-$; and it is to be noted that the effect of replacing H by NR_2 in azoxybenzene (100 mμ) is much greater than that in azobenzene (43 mμ). To provide further confirmation, the absorptions of *p*-diethylaminobenzene-diazocyanide, -diazosulphonate, and -diazosulphone have been measured (Figs. 3—5). The results, with those for the azoxysulphones, are also shown in Table 3, *D*—*G*, in which the values for the NR_2-derivatives are juxtaposed with those for the parent compound and/or a halogen derivative. The three new NEt_2-compounds show, respectively, K-band shifts of 154, 165, and 85 mμ (9300, 3500, 7600 cm.$^{-1}$). From these figures, as well as from the general parallelism of the spectral characteristics of " ordinary " azo-compounds on the one hand and their *p*-NR_2-derivatives on the other, the conclusion that the 465-mμ bands of *p*-$NR_2{\cdot}Ph{\cdot}NO{:}N{\cdot}SO_2{\cdot}C_6H_4Me$ are abnormally displaced K-bands seems inescapable.

EXPERIMENTAL

p-Diethylaminobenzenediazocyanide, m. p. 111·5° (Found : N, 28·8. $C_{11}H_{14}N_4$ requires N, 27·7%), *sodium* p-*diethylaminobenzenediazosulphonate* (Found : N, 14·2. $C_{10}H_{14}O_3N_3SNa,H_2O$ requires N, 14·1%), and p-*diethylaminobenzenediazosulphone*, m. p. 127° (Found: N, 14·3. $C_{16}H_{19}O_2N_3S$ requires N, 14·3%), were prepared from an alcoholic diazonium solution obtained as follows (cf. Koenigs and Ruppelt, *Annalen*, 1934, **509**, 149) : Freshly distilled *p*-diethylaminoaniline (1 ml.) was dissolved in a mixture of absolute ethanol (7·5 ml.) and 10N-hydrochloric acid (1 ml.). Amyl nitrite (1·5 ml. ; freshly distilled) in ethanol (1·5 ml.), then added slowly at 5°, gave a green solution from which the solid diazonium salt was, however, not obtained on the addition of ether (such treatment merely yielded a yellow oil). The green solution produced the above derivatives on addition, respectively, to a concentrated solution of potassium cyanide (0·6 g.), a solution of crystalline sodium sulphite (2 g.) and sodium carbonate (3 g.) in water (25 ml.), and a solution of sodium benzenesulphinate (1 g.) in water (5 ml.) acidified with acetic acid. The diazocyanide gave deep-red leaflets by recrystallisation from alcohol, the diazosulphonate yellow plates from water (in which it was extremely soluble), and the diazosulphone bright red needles from alcohol. The analysis reported above for the diethylaminodiazocyanide, although unsatisfactory, was obtained again after further crystallisation. From the preparative route followed, and from the recorded experience of Hantzsch, it is possible that our specimen contained a small amount of the HCN addition product, $C_{12}H_{15}N_5$ (Calc.: N, 30·6%).

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