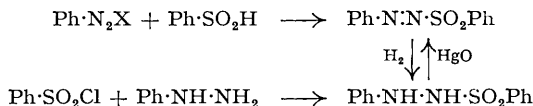


649. *The Possible Occurrence of Geometrical Isomerism Among the Diazosulphones.*

By H. C. FREEMAN, R. J. W. LE FÈVRE, (MISS) J. NORTHCOTT,  
and (MISS) I. YOUHOTSKY.

The dipole moments and spectra of  $C_6H_5 \cdot N \cdot N \cdot SO_2 \cdot C_6H_5$  and five of its derivatives have been examined. The azo-group appears to be *trans* in the known forms, although irradiation of their solutions in benzene or alcohol provides signs that beneath an irreversible photo-decomposition some reversible change may be occurring.

DESPITE the fact that all diazo-compounds of the general formula  $Ar \cdot N \cdot N \cdot X$  should—on Hantzsch's configurational view of the  $-N \cdot N-$  group—be capable of existence in *cis*- and *trans*-forms, many are recorded in the literature which have never been so separated. Accordingly, examples where  $X = CO \cdot NH_2$  and  $NMe_2$  were recently reinvestigated and observations were noted (Freeman, Le Fèvre, and Wilson, *J.*, 1951, 1977; Le Fèvre and Liddicoet, *J.*, 1951, 2743) of a kind reconcilable with classical prediction (cf. *Ber.*, 1894, 27, 1702). The present paper continues this programme with the diazosulphones  $R \cdot N \cdot N \cdot SO_2 \cdot R'$ . These substances, although formed directly from sulphinic acids and diazonium salts, were recognised by their discoverer, Koenigs (*Ber.*, 1877, 10, 1531), as sulphones, and not sulphinates  $R \cdot N \cdot N \cdot O \cdot SO \cdot R$ , by the reaction :



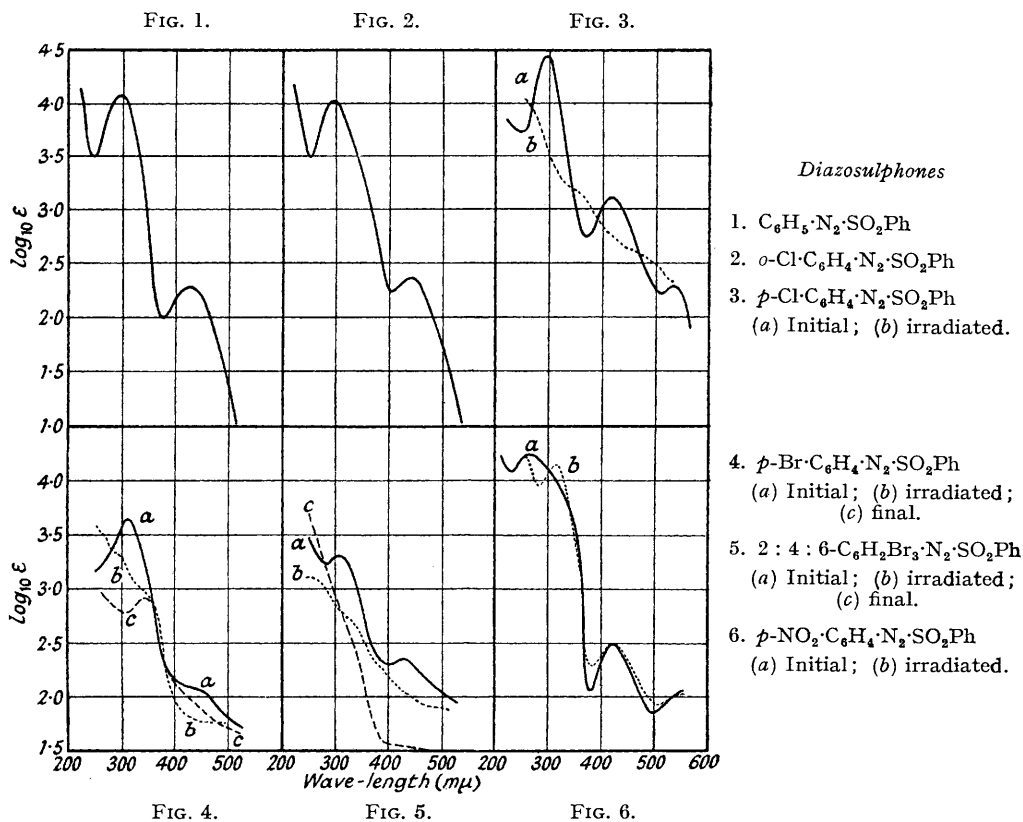
Unsuccessful searches among the diazosulphones for geometrical isomerism have been reported by von Pechmann (*Ber.*, 1895, 28, 861) and Hantzsch and Singer (*ibid.*, 1897, 30, 312), while Hantzsch and Glogauer (*ibid.*, p. 2557) found that certain pairs of "*n*-" and "*iso*-"diazocyanides were chemically transformable into *single* diazosulphones. It should be mentioned, for completeness, that Claasz (*ibid.*, 1911, 44, 1415) has claimed the isolation of an authentic diazonium sulphinate, having salt-like properties and differing in other respects from the diazosulphones handled by us.

*Present Work.*—This concerns six phenyldiazosulphones, prepared by methods described by Hantzsch or von Pechmann in the following papers: *Ber.*, 1895, **28**, 862; 1897, **30**, 312; 1898, **31**, 641. The m. p.s and appearances of the specimens used are listed :

R in R·N <sub>2</sub> ·SO <sub>2</sub> ·C <sub>6</sub> H <sub>5</sub>		M. p.
C <sub>6</sub> H <sub>5</sub> .....	Orange rhombs from EtOH	78° (lit., 78°)
<i>o</i> -Cl·C <sub>6</sub> H <sub>4</sub> * .....	Orange flakes from EtOH	98° (new)
<i>p</i> -Cl·C <sub>6</sub> H <sub>4</sub> .....	Yellow needles from EtOH	107° (lit., 106°)
<i>p</i> -Br·C <sub>6</sub> H <sub>4</sub> .....	Bronze needles from EtOH	115° (lit., 116°)
<i>p</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> .....	Red prisms from CHCl <sub>3</sub>	136° lit., 136°)
2 : 4 : 6-C <sub>6</sub> H <sub>2</sub> Br <sub>3</sub>	Yellow-orange powder, pptd. from Et <sub>2</sub> O by absolute EtOH	121° (decomp.)

\* Found : N, 9.9. C<sub>12</sub>H<sub>9</sub>N<sub>2</sub>O<sub>2</sub>SCl requires N, 10.0%.

These (with one exception) have been examined by applying to them procedures previously used by Le Fèvre *et al.* on other azo- (*J.*, 1939, 531, 1595; *J.*, 1951, 1814) and diazo-derivatives (*J.*, 1949, 33, 1106; 1950, 3128; 1951, 415, and *loc. cit.*): solutions, made



up in the absence of daylight in opaque flasks, were submitted to dielectric-constant, density, and spectrographic-absorption measurements, benzene being the solvent for the first two observations, and alcohol for the third. Next, the same solutions were transferred to clear-glass containers and exposed to direct sunlight for 1—2 hours, and the measurements at once repeated. Finally, the solutions were stored in the dark for two days, after which measurements were made a third time.

Apparatus and techniques have been described in the references just quoted (cf. also Calderbank and Le Fèvre, *J.*, 1948, 1949); symbols are as defined by Le Fèvre \* (*Trans.*

\* Except that subscripts 1 and 2 are now used to denote solvent and solute respectively (cf. Buckingham and Le Fèvre, *J.*, 1952, 1932).

*Faraday Soc.*, 1950, **46**, 1). The spectra were recorded on a Beckman photoelectric spectrophotometer, Model D.U.; they are reproduced as in the figures. Table 1 contains the dielectric-constant and density data from which the apparent dipole moments of the solutes before irradiation can be estimated. This is done in Table 2, the polarisations ( ${}_{\infty}P_2$ ) at infinite dilution being derived *via* the equation  ${}_{\infty}P_2 = M_2[\rho_1(1 - \beta) + C\alpha\epsilon_1]$ , where  $\rho_1 = 0.34086$  or  $0.34161$  c.c. and  $C = 0.18809$  or  $0.19039$  for benzene at  $25^\circ$  or  $30^\circ$ , respectively. The mean quantities  $\alpha\epsilon_1$  and  $\beta d_1$  have been obtained as  $\Sigma(\epsilon_{12} - \epsilon_1)/\Sigma w_1$  and  $\Sigma(\bar{d}_{12} - \bar{d}_1)/\Sigma w_2$ . The refractivities under  $[R_L]_D$  have been calculated by assuming that  $R_{N_2} = 9$  c.c. (Anderson, Le Fèvre, and Wilson, *J.*, 1949, 2082) and  $R_{C_6H_6} = 25.4$ ,  $R_{SO_2} = 7.8$  (as in sulphates),  $R_{Cl} = 5.8$ ,  $R_{Br} = 8.9$ , and  $R_{NO_2} = 6.71$  (Vogel, *J.*, 1948, 1833). The following actual determination on the *p*-chloro-compound in benzene was made as a check :

$10^6 w_2$	$d_4^{25}$	$n_D^{25}$	$[R_L]_D$ , c.c.	$10^6 w_2$	$d_4^{25}$	$n_D^{25}$	$[R_L]_D$ , c.c.
0	0.87378	1.4972	—	20,680	0.87962	1.4984	72.9

Table 3 summarises the details of the curves shown in Figs. 1—6.

TABLE 1.\*

Benzenediazophenylsulphone at $25^\circ$					<i>p</i> -Chlorobenzenediazophenylsulphone at $25^\circ$				
$10^6 w_2$	2276	2281	3681	4059	$10^6 w_2$	5064	8341	9637	10,941
$\epsilon^{25}$	2.2916	2.2910	2.3019 <sub>5</sub>	2.3054	$\epsilon^{25}$ (Inl.)	2.3100	2.3335	2.3452	2.3540
$d_4^{25}$	0.87448	0.87447 <sub>5</sub>	0.87492	0.87503	$d_4^{25}$ (Inl.)	0.87517	0.87611	0.87642	0.87680
<i>p</i> -Chlorobenzenediazophenylsulphone at $30^\circ$ †					<i>p</i> -Bromobenzenediazophenylsulphone at $30^\circ$				
$10^6 w_2$	842	1717	2820	4796	$10^6 w_2$	263	378	962	
$\epsilon^{30}$ (Inl.)	2.2691	2.2774	2.2825	—	$\epsilon^{30}$ (Inl.)	2.2639	2.2650	2.2700	
$\epsilon^{30}$ (Irr.)	2.286	2.293	2.299	—	$\epsilon^{30}$ (Irr.)	—	2.278	2.288	
$\epsilon^{30}$ (Fin.)	Decomposition evident				$\epsilon^{30}$ (Fin.)	—	2.272	2.274	
$d_4^{30}$ (Inl.)	0.86739	0.86780	—	0.86892	$d_4^{30}$ (Inl.)	0.86728	0.86739	0.86751	
<i>p</i> -Nitrobenzenediazophenylsulphone at $25^\circ$					2 : 4 : 6-Tribromobenzenediazophenylsulphone at $30^\circ$				
$10^6 w_2$	868	2211	3519	4685	$10^6 w_2$	2159	4199	8260	
$\epsilon^{25}$ (Inl.)	2.2815	2.2918	2.3031	2.3132	$\epsilon^{30}$ (Inl.)	2.2726	2.2864	2.3033	
$\epsilon^{25}$ (Irr.)	2.279 <sub>5</sub>	—	2.292 <sub>5</sub>	2.303	$\epsilon^{30}$ (Irr.)	2.289	2.325	2.365	
$\epsilon^{25}$ (Fin.)	2.280	—	2.302	2.313	$\epsilon^{30}$ (Fin.)	2.273	2.284	2.313	
$d_4^{25}$ (Inl.)	0.87409	0.87450	0.87549	0.87547	$d_4^{30}$ (Inl.)	0.86813	0.87008	0.87217	

\* Solvent = benzene. For  $10^6 w_2 = 0$ ,  $\epsilon^{25} = 2.2725$ ,  $\epsilon^{30} = 2.2628$ ,  $d_4^{25} = 0.87378$ ,  $d_4^{30} = 0.86718$ .  
 † Inl. = initial; Irr. = irradiated; Fin. = final.

TABLE 2.

Solute	$M_2$	Mean $\alpha\epsilon_1$	Mean $\beta$	${}_{\infty}P_1$ , c.c.	$[R_L]_D$ , c.c.	$\mu,^* D$
Ph·N <sub>2</sub> ·SO <sub>2</sub> Ph	246	8.12	0.352	430	68	4.2 <sub>0</sub>
<i>p</i> -Cl·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·SO <sub>2</sub> Ph	281	{ 7.55 7.44	{ 0.403 0.316	{ 461 459	73	{ 4.3 <sub>9</sub> 4.3 <sub>1</sub>
<i>p</i> -Br·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·SO <sub>2</sub> Ph	325	6.55	0.460	465	76	4.4 <sub>0</sub>
<i>p</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·SO <sub>2</sub> Ph	291	8.83	0.449	538	74	4.7 <sub>6</sub>
2 : 4 : 6-C <sub>6</sub> H <sub>2</sub> Br <sub>3</sub> ·N <sub>2</sub> ·SO <sub>2</sub> Ph	483	5.05	0.697	514	91	4.5 <sub>9</sub>

\* Evaluated as  $k({}_{\infty}P_2 - R_L)^{0.5}$ , where  $k = 0.221$  at  $25^\circ$  and  $0.223$  at  $30^\circ$ .

TABLE 3. Absorptions of diazosulphones.

R in R·N <sub>2</sub> ·SO <sub>2</sub> Ph	$\lambda_{max}$ . (log <sub>10</sub> $\epsilon$ )	$\lambda_{max}$ . (log <sub>10</sub> $\epsilon$ )	R in R·N <sub>2</sub> ·SO <sub>2</sub> Ph	$\lambda_{max}$ . (log <sub>10</sub> $\epsilon$ )	$\lambda_{max}$ . (log <sub>10</sub> $\epsilon$ )
C <sub>6</sub> H <sub>5</sub>	295 (4.1)	425 (2.3)	<i>p</i> -Br·C <sub>6</sub> H <sub>4</sub>	280 (4.1)	450 (2.6)
<i>o</i> -Cl·C <sub>6</sub> H <sub>4</sub>	296 (4.0)	435 (2.35)	<i>p</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub>	260 (4.8)	410 (3.0)
<i>p</i> -Cl·C <sub>6</sub> H <sub>4</sub>	295 (4.4)	415 (3.1)	2 : 4 : 6-C <sub>6</sub> H <sub>2</sub> Br <sub>3</sub>	260 (3.8)	445 (2.8)

*Discussion.*—The spectra of the unilluminated solutions show absorptions around 300 and 420 m $\mu$  with intensities corresponding to log<sub>10</sub>  $\epsilon$  between 4 and 5 and *ca.* 3, respectively. These are features common to most diazo-compounds (Le Fèvre and Wilson, *J.*, 1949, 1106; Freeman and Le Fèvre, *J.*, 1951, 415). The curves for the *o*- and the *p*-chloro-compound are almost identical, except for the uniformly lower absorptions of the former; this difference of intensity may be due to slight steric interference between the substituent and the azo-group.

By the action of sunlight the absorption, particularly that in the 300 m $\mu$  region, was changed. Very little evidence of reversal on storage of an irradiated solution in the dark could be noted. Decomposition and formation of tar was clearly visible with the *p*-chloro- and the *p*-nitro-derivative, and similar behaviour was therefore inferred with the other substances. In these respects the situation is reminiscent more of the triazens (Le Fèvre and Liddicoet, *loc. cit.*) than of the alkali diazosulphonates (*J.*, 1951, 415).

The dielectric constants give clearer signs of reversibility. Reference to Table 1 shows that in all cases illumination alters  $\epsilon_{12}$  (usually causing an increase). Although darkness does not completely restore the initial value, nevertheless our observations on the last three compounds are compatible with (reversible) photo-productions of new species—possibly the *cis*-isomers—accompanied by considerable (irreversible) photo-decompositions.

The reliable *a priori* estimation of the relative magnitudes of the moments of *cis*- and *trans*-diazosulphones is made difficult by the possibility of intra-molecular rotation about the N-S link. Some stabilisation of the molecule in a planar configuration may result from conjugation across the sulphone group (Koch and Moffitt, *Trans. Faraday Soc.*, 1951, 47, 7). We note, however, that the polarity now reported for *p*-chlorobenzenediazophenylsulphone (4.3—4.4 D) is close to that of 4-chlorodiphenylsulphone (given as 4.42 D by Bergmann and Tschudnowsky, *Ber.*, 1932, 65, 446). Evidently the vectors associated with the C-Cl and SO<sub>2</sub> groups interact similarly in both molecules, a fact which is most reconcilable with a *trans*-configuration of the N:N unit.

Finally, it may be mentioned that the steric considerations set out by Freeman and Le Fèvre (*loc. cit.*) for the *cis*-diazosulphonates should apply *a fortiori* to the (unknown) *cis*-diazosulphones, for which we would therefore predict a high degree of instability, a forecast in line with their non-isolation.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA.

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