o-*Mercapto-azo-compounds. Part VI.* Preparation and Structure of Azobenzene-2-sulphenyl Derivatives.*

By A. Burawoy, F. Liversedge, and C. E. Vellins.
(*With an Appendix by* G. W. R. Bartindale *and* G. Farrow.)

[Reprint Order No. 5597.]

Azobenzene-2-sulphenyl bromide (Part V) is converted into the cyanide, chloride, iodide, thiocyanate, and perchlorate. The equivalent conductivities in water of the chloride, bromide, and perchlorate, the molecular weights in water and bromoform of the chloride and bromide, and the electronic spectra of all derivatives in various solvents have been determined. They show that with exception of the non-ionic cyanide all azobenzene-2-sulphenyl derivatives exist in water and ethyl alcohol as true salts involving a 2-phenylbenzo-1-thia-2 : 3-diazolium ion (IV) and in benzene and chloroform as equilibria between the ionic isomers (IV) and the non-ionic isomers (as I). The ionic structure of the crystalline azobenzene-2-sulphenyl chloride is established by *X*-ray analysis.

AZOBENZENE-2-SULPHENYL BROMIDE (I) is a very stable substance, which undergoes the characteristic reactions of sulphenyl halides such as the disproportionation by sodium hydroxide to disulphide and sulphinate and condensation with bases (Part V *). It is also converted into the disulphide on treatment with zinc in boiling benzene, a similar reaction being known with benzenesulphenyl chloride (Lecher and Holschneider, *Ber.*, 1924, **57**, 755). However, in contrast to other sulphenyl halides which are practically insoluble in water and generally react quantitatively with water or ethyl alcohol to yield a variety of products (cf. Kharasch, Potempa, and Wehrmeister, *Chem. Reviews*, 1946, **39**, 269), azobenzene-2-sulphenyl bromide is soluble in water and crystallises from water and ethyl alcohol in spite of some solvolysis (cf. below).

We have now found that azobenzene-2-sulphenyl chloride, thiocyanate, and iodide, which are formed from the bromide by double decomposition reactions, are also obtained analytically pure by crystallisation from water or alcohol. Previous attempts to isolate crystalline sulphenyl iodides have been unsuccessful (cf. Fries and Schürmann, *Ber.*, 1914, **47**, 1195). Kharasch and Buess (*J. Amer. Chem. Soc.*, 1949, **71**, 2724) and Kharasch and Orr (*ibid.*, 1953, **75**, 6031) used the liberation of iodine on addition of potassium iodide to a solution of a sulphenyl halide to follow the kinetics of various reactions. Rheinboldt and Motzkus (*Ber.*, 1939, **72**, 657) observed that 1 : 1-dimethylethanesulphenyl iodide is stable in ether for a few hours at —20° but slowly yields the disulphide and iodine. Messer (U.S.P. 2,257,974/1942) reported the preparation of benzothiazole-2-sulphenyl iodide by treating di(benzothiazol-2-yl) disulphide with iodine in anhydrous solvents, but as sole evidence gave a rather indefinite m. p. 105—125° (decomp.).

The red-orange crystalline azobenzene-2-sulphenyl iodide dissolves in water with a pale greenish-yellow, but in benzene and chloroform with a blue and violet-red colour respectively. This is similar to the behaviour of other organic iodides such as the methiodides of pyridine and quinoline which are almost colourless in water, but yellow in solvents such as chloroform, the colour being due to the appearance of new characteristic absorption bands in the visible spectrum. It has been attributed to the presence of these iodides in non-ionic forms, in which the iodine participates in a covalent linkage (cf. Hantzsch, *Ber.*, 1911, **44**, 1783; 1919, **52**, 1544; Hantzsch and Burawoy, *ibid.*, 1932, **65**, 1059). This observation and the exceptional stability and solubility of the azobenzene-2-sulphenyl halides in water suggested that, in contrast to other sulphenyl halides, they might exist in the crystalline state and at least in aqueous and ethanolic solutions as true (ionic) salts. This is confirmed by the existence of a very stable, water-soluble perchlorate, prepared by addition of potassium perchlorate to an aqueous solution of azobenzene-2-sulphenyl bromide, for which a covalent structure is most unlikely; this is the first sulphenyl

---

* Parts IV and V, *J.*, 1954, **82**, 90.

perchlorate to be recorded. On the other hand, azobenzene-2-sulphenyl cyanide, prepared by the addition of potassium cyanide to the aqueous bromide solution, should be non-ionic and is, indeed, insoluble in water.

Determinations of the electrical conductivities in aqueous solution of the chloride, bromide, and perchlorate establish their presence as strong electrolytes. The equivalent conductivities for M/100-, M/1000-, and M/10,000-solutions are shown in Table 1, together with those of the corresponding potassium salts. The pH of these solutions have also been determined, in order to ensure that the electrical conductivity is not due to acid formed by hydrolysis. When the (least favourable) simplifying assumption is made that all hydrogen ions are due to the mineral acid formed by hydrolysis, *i.e.*, when any contribution from the carbon dioxide present is ignored, these determinations show that the degree of hydrolysis in M/100- and M/1000-solutions is definitely less than 1% and in M/10,000-solutions less than 4% (Table 1).

TABLE 1. *Equivalent conductivities of azobenzene-2-sulphenyl derivatives* (ArSX) *in water at* 18°.

	M/100			M/1000			M/10,000		
Substance	Λ	pH	Hydrolysis (%)	Λ	pH	Hydrolysis (%)	Λ	pH	Hydrolysis (%)
ArSCl	86·6	4·75	0·18	96·0	4·98	1·0	123·7	5·58	2·6
KCl[a]	122·2	—	—	127·1	—	—	129·4	—	—
ArSBr	88·5	4·92	0·12	96·6	5·32	0·47	120·7	5·45	3·4
KBr[a]	124·1	—	—	129·1	—	—	130·9	—	—
$ArSClO_4$	—	—	—	91·5	5·2	0·62	117·1	5·43	3·6
$KClO_4$[a]	—	—	—	118·8	—	—	121·6	—	—

[a] Intern. Crit. Tables, 1929, Vol. VI, p. 229.

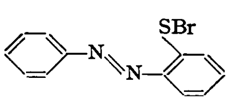
The solubilities and stabilities allowed molecular weight determinations of the chloride and bromide in water and bromoform (Table 2). Although an appreciable experimental error is to be expected, these determinations confirm that in water both halides are dissociated. The molecular weights in bromoform are normal; but this fact cannot be unambiguously interpreted, since in solvents such as bromoform and chloroform electrolytes such as ammonium salts are strongly associated, to a degree which depends on both the halide anion and the size of the cation (cf. Turner, *J.*, 1912, 1923; Hantzsch and Hofmann, *Ber.*, 1911, **44**, 117; Wedekind and Paschke, *Ber.*, 1911, **44**, 3072; 1912, **45**, 1449). Since it is difficult to predict the behaviour of the (ionic) azobenzene-2-sulphenyl halides, the presence, at least in part, of these halides as true salts cannot be excluded.

TABLE 2. *Molecular weights of azobenzene-2-sulphenyl halides.*

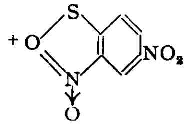
Substance	Wt. (g.)	Solvent	Wt. (g.)	Method *	Δ	Mol. wt.†	" *i* " factor
RCl	0·1984	H_2O	39·9	C	0·069°	135	1·8
	0·2968	H_2O	39·9	C	0·102	136	1·8
	1·300	H_2O	30·7	E	0·141	156	1·6
	1·287	H_2O	30·7	E	0·147	148	1·7
	0·197	$CHBr_3$	115·6	C	0·091	271	0·9
RBr	1·205	H_2O	29·8	E	0·097	224	1·3
	1·256	H_2O	26·0	E	0·120	209	1·4
	0·100	$CHBr_3$	45·0	C	0·114	281	1·0
	0·200	$CHBr_3$	45·0	C	0·240	300	1·0

* C = cryoscopic, E = ebullioscopic. † Calc. for RCl, 248·5. Calc. for RBr, 293.

The intermediate formation of sulphenyl ions $R{\cdot}S^+$ was postulated in reactions of sulphenyl halides and thiocyanates (cf. Kharasch and Assony, *J. Amer. Chem. Soc.*, 1953, **75**, 1081), but Orr and Kharasch (*ibid.*, p. 6030) showed that the addition of 2 : 4-dinitrobenzenesulphenyl chloride to styrene is not initiated by the ionisation of the S–Cl linkage. Lecher and Simon (*Ber.*, 1921, **54**, 632) found that *o*-nitrobenzenesulphenyl thiocyanate is a non-conductor in liquid sulphur dioxide, and Kharasch and Buess (*J. Amer. Chem. Soc.*, 1949, **71**, 2724) observed that 2 : 4-dinitrobenzenesulphenyl chloride in benzene has a normal molecular weight. On the other hand, Kharasch, Buess, and King (*ibid.*, 1953, **75**, 6035) attributed the red colour of 2 : 4-dinitrobenzenesulphenyl chloride in concentrated sulphuric acid to the presence of a dinitrobenzenesulphenyl cation, in which the sulphur atom and the oxygen atom of the *o*-nitro-group interact, producing the ring structure (II).

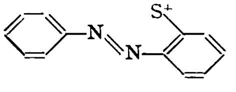


(I)

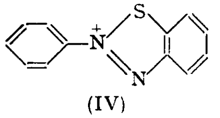


(II)

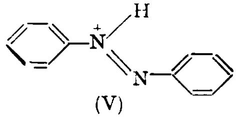
The azobenzene-2-sulphenyl derivatives investigated by us are the first isolated stable salts of this series, but it is unlikely that the cation involved has structure (III), *i.e.*, a true azobenzene-2-sulphenyl cation, since this would not easily account for its exceptional stability. Structure (IV), representing a 2-phenylbenzo-1-thia-2 : 3-diazolium ion formed by ring-closure, is more likely and is supported by the electronic spectra of the azobenzene-2-sulphenyl derivatives.



(III)



(IV)



(V)

The spectrum of azobenzene shows two absorption bands above 2000 Å : a low-intensity *R*-band at longer wave-lengths due to an electronic transition essentially localised in the azo-group; and a high-intensity *K*-band at shorter wave-lengths resulting from an electronic transition along the conjugated system. *R*-Bands, in contrast to *K*-bands, are displaced to shorter wave-lengths and generally become more intense as the dielectric constant of the solvent is increased, though the effect is small for the non-polar azobenzene. *R*-Bands also disappear on salt formation, *e.g.*, the addition of a proton to the azo-group in the salts of azobenzene (see V) (Burawoy, *Ber.*, 1930, **63**, 3155; 1931, **64**, 464; 1932, **65**, 941; *J.*, 1937, 1865; 1939, 1177; *Discuss. Faraday Soc.*, 1950, **9**, 70; cf. Gillam and Stern, " Electronic Absorption Spectroscopy in Organic Chemistry," Arnold, London, 1954, p. 111). Thus, the *R*-band should be absent in the spectrum of a cation (IV), but should be shown by a cation (III).

Table 3 summarises the maxima and molecular extinction coefficients of the *R*- and the *K*-bands, for our sulphenyl derivatives, and gives also molecular extinction coefficients at 4500 and 5000 Å to serve as a measure of the intensity of the inflexions. The spectrum of azobenzene-2-sulphenyl cyanide (2-thiocyanatoazobenzene) (Fig. 2) is very similar to that of azobenzene. The positions of the two absorption bands show only slight variations in carbon tetrachloride, alcohol, chloroform, and benzene. Since water would be expected to be responsible for a greater shift of the *R*-band towards the violet, its effect has also been investigated. The insolubility of the cyanide precluded its examination, but the spectra of azobenzene itself in alcohol–water (1 : 9) and of sodium azobenzene-2-sulphinate (Fig. 1) in water show that the *R*-band is still present in the aqueous solutions, though somewhat displaced to shorter wave-lengths and more intense. This is similar to the known effect of water on the *R*-band of the carbonyl group of acetone, mesityl oxide, and phorone (Scheibe, Rössler, and Backenköhler, *Ber.*, 1925, **58**, 586).

The almost identical spectra of azobenzene-2-sulphenyl perchlorate (Fig. 2) in water, alcohol, chloroform, and benzene show only a high-intensity *K*-band at 3500—3600 Å. Moreover, the spectra of the three halides and of the thiocyanate in water (Fig. 3—6) and those of the chloride and bromide in alcohol are almost identical with those of the perchlorate. In all cases, the *R*-band characteristic for the azo-group is absent. Thus the same absorbing entity is present in each case and this should be the cation (IV). The absence of the *R*-band definitely excludes structure (III).

In contrast to the spectra of the perchlorate in chloroform and benzene (Fig. 2), those of the halides and thiocyanate in these solvents show at longer wave-lengths a band or an inflexion of varying intensity indicating the presence of the *R*-band (Figs. 3—6). This long-wave-length absorption is more pronounced in benzene and, as shown by the spectrum of the chloride, still more so in benzene–hexane (the other derivatives were not sufficiently soluble to allow examination in the latter solvent mixture or in hexane). These observations indicate the existence of equilibria between the ionic and non-ionic isomers (IV) and (I), the concentration of the latter increasing in the order chloroform < benzene < hexane.

The perchlorate and the cyanide represent extremes, since they exist in all investigated solvents almost exclusively as the ionic and the non-ionic isomer respectively. The long-wave-length inflexions become more pronounced in the order R·S·Cl < R·S·Br < R·S·SCN and finally appear as bands in R·S·I. This may indicate that the tendency of the S–Hal linkages to ionise increases in the order I < Br < Cl, *i.e.*, the reverse of the order known for C–Hal bonds. However, the intensity and position of the inflexions may not necessarily be a quantitative measure of amount of the non-ionic isomer present. The increasing absorption at longer wave-lengths will be partly due to a displacement of the *R*-bands of the individual sulphenyl derivatives to longer wave-lengths with the increasing polarisability of the halogen atom and possibly, particularly with the iodide, to an independent contribution of the group SX. This and other aspects are being further investigated.

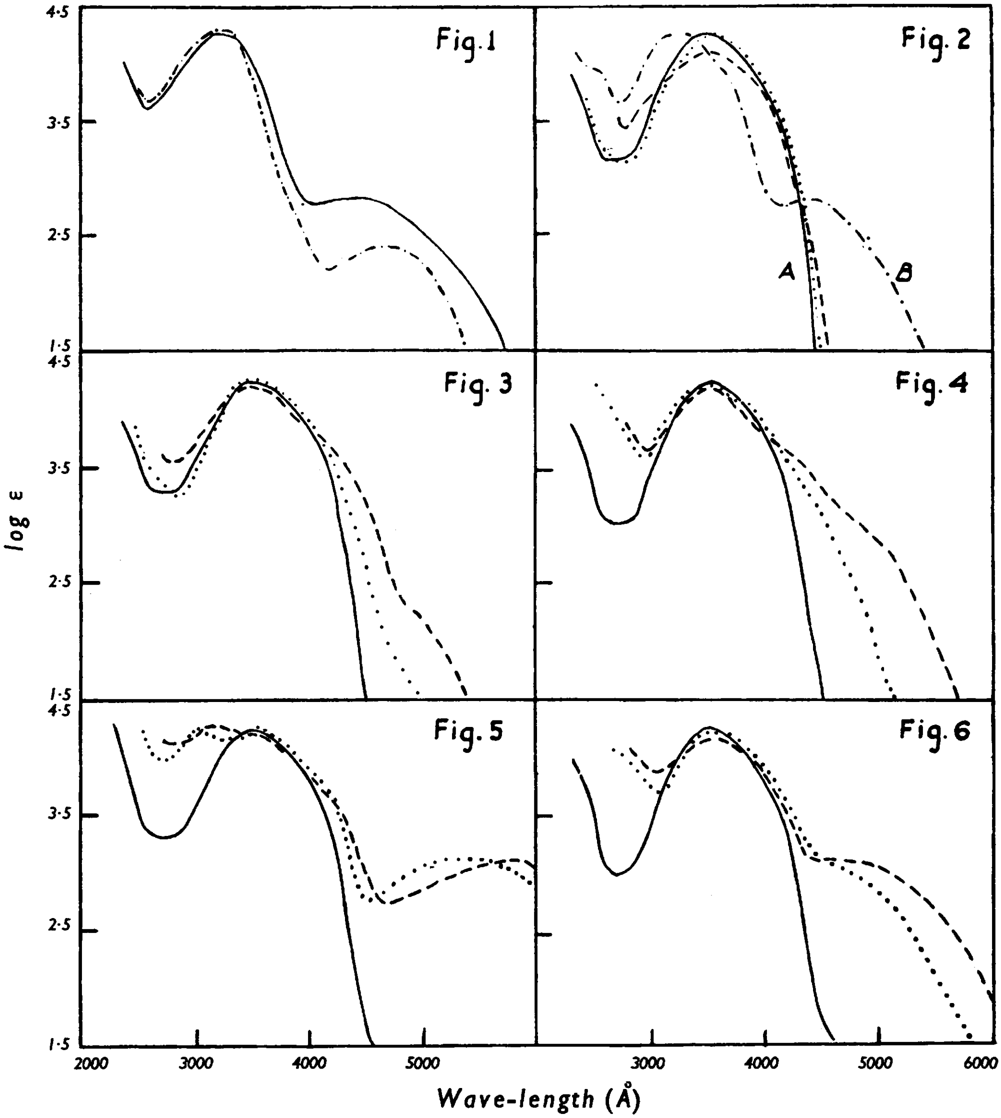
TABLE 3. *Absorption spectra of substances* $2\text{-X}\cdot C_6H_4\cdot N{:}NPh$.[a]

		R-Band				*K*-Band		
X	Solvent	$\lambda_{max.}$ (Å)	ε	ε_{4500}	ε_{5000}	$\lambda_{max.}$ (Å)	ε	Fig.
H	EtOH	4425	490	482	170	3175	17,500	—
	EtOH–H_2O (1 : 9)	4230	837	615	122	3200	21,600	—
SO_2Na ...	EtOH	4675	267	240	183	3225	20,800	1
	H_2O	4400	687	675	350	3250	19,200	1
SCN	CCl_4	4450 *	590 *	580 *	234 *	3300	19,800	—
	EtOH	4400 *	600 *	586 *	200 *	3290	19,000	2
	C_6H_6	4400 *	600 *	588 *	220 *	3310	17,800	—
	$CHCl_3$	4425 *	685 *	678 *	248 *	3300	17,200	—
$SClO_4$ ...	H_2O	—	—	28 *	4 *	3500	19,100	2
	EtOH	—	—	5 *	1 *	3550	17,000	—
	$CHCl_3$	—	—	46 *	5 *	3590	17,200	2
	C_6H_6	—	—	—	—	3500 †	12,500	2
SCl	H_2O	—	—	31 *	7 *	3500	17,800	3
	EtOH	—	—	56 *	10 *	3520	18,100	—
	$CHCl_3$	—	—	372 *	28 *	3520	18,100	3
	C_6H_6	—	—	1500	133 *	3500	16,800	3
	C_6H_6–C_6H_{14} (1 : 4)	—	—	1760	212	3450	12,800	—
SBr	H_2O	—	—	45	10	3525	17,500	4
	EtOH	—	—	320 *	23 *	3550	17,200	—
	$CHCl_3$	—	—	1340	92	3525	17,000	4
				1380 *	118 *			
	C_6H_6	—	—	2082	752	3550	15,200	4
				2206 *	788 *			
SI	H_2O	—	—	45	10	3550	17,900	5
	$CHCl_3$	5350	1340	583	1123	3050	17,000	5
						3550	17,800	
	C_6H_6	5825	1285	1063	720	3165	19,200	5
						3450 ‡	17,800	
S·SCN ...	H_2O	—	—	59 *	25 *	3530	17,500	6
	$CHCl_3$	—	—	1310	617	3550	16,000	6
				1366 *	770 *			
	C_6H_6	—	—	1295	1052	3550	14,500	6

* 0·001M. † 0·000,02M. ‡ Inflexion. [a] 0·0001M unless otherwise stated.

The facts discussed do not throw light on the structure of the crystalline azobenzene-2-sulphenyl derivatives, but the perchlorate and cyanide can be safely assumed to be ionic and non-ionic respectively, and *X*-ray analysis of the chloride, as yet incomplete, carried out by Bartindale and Farrow has already established its ionic structure (cf. Appendix). On the other hand, the colour of the crystalline substances changes from greenish-yellow for the perchlorate to light-yellow for the chloride and bromide, orange-yellow for the cyanide, orange for the thiocyanate, and red-orange for the iodide. The possibility of a non-ionic structure of the thiocyanate and iodide cannot, therefore, be excluded.

Alternatively, the colour changes may indicate the presence of at least some non-ionic molecules in the crystalline state.



Solvents : —— *Water.* —·—·— *Ethanol.* .... *Chloroform.* ---- *Benzene.*

Substances (Ph·N:N·C_6H_4R-2).

Fig.	1	2*A*	2*B*	3	4	5	6
R	·SO_2Na	·S·ClO_4	·S·CN	·SCl	·SBr	·SI	·S·SCN

APPENDIX

Crystals of azobenzene-2-sulphenyl chloride have been examined by optical and *X*-ray methods. The crystals are orthorhombic prisms {011} terminated by {100}, and under the polarising microscope are seen to be slightly pleochroic. By Farquhar and Lipson's method (*Proc. Phys. Soc.*, 1946, **58**, 200) it was found that the unit-cell dimensions are $a = 7{\cdot}591 \pm 0{\cdot}004$ Å, $b = 20{\cdot}32 \pm 0{\cdot}01$ Å, $c = 7{\cdot}582 \pm 0{\cdot}004$ Å. There are four molecules per unit cell (*d*, 1·43; calc., 1·41). Absent spectra are $0kl$ for $k + l$ odd, $h0l$ for h odd, showing that the space group is either $D_{2h}^{16} - Pnma$ or $C_{2v}^{9} - Pna2_1$. The first of these is ruled out since it would require the molecule to lie in a plane of symmetry and intensity relations show that this is not the case.

The space group $Pna2_1$ has no centre of symmetry but the projection on (001) has a centre of symmetry due to the two-fold screw axis. A Patterson–Fourier projection on (001) showed clearly the positions of the chlorine and the sulphur atoms and these were confirmed by a Fourier F-synthesis. It was found that the smallest projected S–Cl distance is 2·7 Å. This is so large that it at once excludes the possibility of a covalent link between sulphur and chlorine, the length of which would be 2·0 Å (cf. Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360; Stevenson and Beach, *ibid.*, p. 2872).

A complete structure determination is in progress, by the methods of Hanson, Lipson, and Taylor (*Proc. Roy. Soc.*, 1953, *A*, **218**, 371).

EXPERIMENTAL

Action of Zinc on Azobenzene-2-sulphenyl Bromide.—A solution of azobenzene-2-sulphenyl bromide (0·4 g.) in benzene (30 c.c.) was refluxed for 30 min. with zinc dust (3 g.), then filtered hot, and concentrated. Almost pure di-(*o*-phenylazophenyl) disulphide (0·2 g., 68%) separated. It crystallised from light petroleum (b. p. 60—80°) as orange needles, m. p. 141—142°, identical with the product obtained by Burawoy and Vellins (Part V, *loc. cit.*).

Azobenzene-2-sulphenyl Chloride.—Concentrated hydrochloric acid (40 c.c.) was added to a solution of azobenzene-2-sulphenyl bromide (0·45 g.) in water (50 c.c.) at 45°. Extraction with chloroform yielded almost pure *azobenzene-2-sulphenyl chloride* (0·35 g., 92%), yellow prisms, m. p. 227—228°, from water or benzene (Found: C, 57·7; H, 3·5; N, 11·3. $C_{12}H_9N_2SCl$ requires C, 57·9; H, 3·6; N, 11·3%).

Azobenzene-2-sulphenyl Iodide.—A solution of potassium iodide (1 g.) in water (10 c.c.) was added to azobenzene-2-sulphenyl bromide (0·3 g.) in water (40 c.c.) at 45°. The precipitate of almost pure *azobenzene-2-sulphenyl iodide* (0·35 g., 94%) crystallised from ethyl alcohol as red-orange prisms, m. p. 192—193° (Found: C, 42·0; H, 2·5; N, 8·0. $C_{12}H_9N_2SI$ requires C, 42·4; H, 2·6; N, 8·2%).

Azobenzene-2-sulphenyl Thiocyanate.—A solution of sodium thiocyanate (0·5 g.) in water (10 c.c.) was added to azobenzene-2-sulphenyl bromide (0·3 g.) in water (40 c.c.) at 45°. The precipitate of almost pure *azobenzene-2-sulphenyl thiocyanate* (0·25 g., 90%) crystallised from benzene as orange prisms, m. p. 147—148° (Found: C, 57·7; H, 3·7; N, 15·4. $C_{13}H_9N_3S_2$ requires C, 57·6; H, 3·3; N, 15·5%).

Azobenzene-2-sulphenyl Perchlorate.—A solution of sodium perchlorate (1 g.) in water (20 c.c.) was added to azobenzene-2-sulphenyl bromide (0·5 g.) in water (40 c.c.) at 45°. The precipitate of almost pure *azobenzene-2-sulphenyl perchlorate* (0·5 g., 93%) recrystallised from ethyl alcohol as greenish-yellow needles, m. p. 214—216° (decomp.) (Found: C, 46·0; H, 2·9; N, 8·7. $C_{12}H_9O_4N_2SCl$ requires C, 46·1; H, 2·9; N, 9·0%).

Azobenzene-2-sulphenyl Cyanide (*2-Thiocyanatoazobenzene*).—A solution of potassium cyanide (0·5 g.) in water (10 c.c.) was added to azobenzene-2-sulphenyl bromide (0·45 g.) in water (60 c.c.). The precipitated *product* (0·4 g.) crystallised from light petroleum (b. p. 40—60°) as orange-yellow needles, m. p. 99—100° (Found: C, 64·8; H, 3·6; N, 16·8. $C_{13}H_9N_3S$ requires C, 65·3; H, 3·8; N, 17·6%).

Spectra were determined with a Hilger Uvispek Photoelectric Spectrophotometer. The chloroform used was purified according to Hantzsch (*Ber.*, 1919, **52**, 1546) and dried over potassium carbonate. The spectra of all solutions were unchanged after 4 days in the dark. The spectra of the azobenzene-2-sulphenyl chloride, bromide, and perchlorate in ethyl alcohol were determined in presence of 10 mols. of the corresponding acid in order to inhibit the otherwise appreciable solvolysis, but no similar allowance was made for the spectra in water, in which hydrolysis is negligible. Beer's law was tested in a few cases in the long-wave-length region; small deviations showing a slight increase of the intensity of the inflexions at higher concentrations were observed (cf. Table 3).

This investigation has been carried out with the help of a maintenance allowance from the Department of Scientific and Industrial Research (to C. E. V.) which is gratefully acknowledged.

COLLEGE OF TECHNOLOGY, UNIVERSITY OF MANCHESTER. [*Received, July 28th,* 1954.]