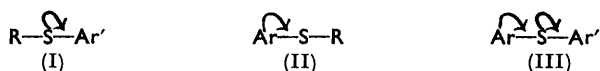


962. *Search for Spectral Evidence of Expansion of the Valency Shell of Sulphur in Aromatic Sulphides.*

By A. MANGINI and R. PASSERINI.

The possibility of spectral changes through the occurrence of a type of conjugation in which sulphur is the electron acceptor in systems $p\text{-X}\cdot\text{C}_6\text{H}_4\cdot\text{SR}$, where $\text{X} = \text{O}^-$, OH , NH_2 , or NMe_2 , has been examined. For this purpose the near-ultraviolet absorption spectra of some 30 aromatic sulphides or (for comparison) ethers have been traced, often in more than one solvent, and, in some cases in which acid or basic groups were present, at more than one pH. It is concluded that none of the observed spectral effects can be assigned with certainty to conjugation of the type considered. These results, together with parallel work on the dipole moments of aromatic sulphides, indicate that this form of conjugation, if operating, is not important in these systems.

WE have for some time been studying the spectral evidence of sulphur conjugation in aromatic sulphides. There are two basic types of possible conjugation. The best understood (I) involves inclusion of sulphur $3p$ electrons in an aryl π shell: evidence concerning it comes from the study of chemical equilibrium,¹ dipole moments,² and spectra.³ The other type (II) depends on incorporation of aryl π electrons into $3d$ sulphur orbitals, and we began our spectral study of this possible effect by considering its expected consequence that a combination of processes (I) and (II) in a diaryl sulphide should, as shown in (III), lead to conjugation between one aromatic ring and the other. The main



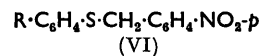
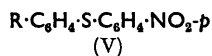
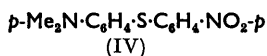
result of this study was to show that process (III) is spectrally unimportant in structures such as (IV), which should provide for it a maximum of opportunity: for a variety of substituents, R, with and without unshared electrons, in the *para*-position in (V), and for purposes of control, in the *meta*-position, and also in the homologous structure (VI),

¹ Baker, Barrett, and Tweed, *J.*, 1952, 2831.

² Chierici, Lumbroso, and Passerini, *Bull. Soc. chim.*, 1955, 686.

³ Mangini and Passerini, *J.*, 1952, 1168; Leandri *et al.*, *Gazzetta*, 1954, **84**, 3, 73; Mangini *et al. ibid.*, p. 47.

did not affect the long-wave band assigned to the chromophore $S \cdot C_6H_4 \cdot NO_2$, except for small modifications attributable to the inductive effect :



Although this was clearly a negative result as regards through-conjugation of the form (III), one could not accept it as excluding the component process (II) in general, because steric twisting in diaryl sulphides might have broken an otherwise effective conjugation. We therefore sought spectral evidence of the octet-enlarging aryl-sulphur conjugation (II) in a more direct way, and, in part, in simpler systems.

The main numerical results (wavelengths and extinction coefficients of band maxima) are in Tables 1—3, and a few of the more significant spectra are illustrated in Figs. 1—3. The following is a summary of the main conclusions.

Starting with methyl phenyl sulphide, benzyl phenyl sulphide, or diphenyl sulphide, a bathochromic shift of a few $m\mu$ and intensification of the band near 250 $m\mu$ is the general result of introducing the substituents O^- or NH_2 into the *para*-position of the *S*-phenyl group. The red shifts produced by the dimethylamino-group are considerably larger (about 23 $m\mu$) than by the other groups, and therefore the spectral effect of this substituent in other positions, and in other parent compounds, has been studied with some care. It may be noted first that the red shift largely disappears when the dimethylamino-group is introduced into the *meta*-position in methyl phenyl sulphide or diphenyl sulphide, where the formal conjugation between nitrogen and sulphur is removed, and also when the dimethylamino-group is introduced into the *para*-position in methyl phenyl ether and diphenyl ether, where octet expansion is impossible.

These results alone might have suggested that a spectral effect of the conjugative process (II) was under observation in the *p*-dimethylaminophenyl sulphides : but, because of the somewhat small magnitude of the effect, and our inability always to interpret small differences in the spectra of such complex molecules, more extensive control experiments seemed necessary. A series of such controls is included in the record. Two illustrations of their general effect may first be given. These are that a dimethylamino-group, if introduced into the *para*-position of dimethylaniline, or into the *para*-position of the benzyl group of benzyl phenyl sulphide, induces red-shifts of at least half as much as those found in *p*-dimethylaminophenyl sulphides.

In more detail, the following results show how the long-wave band of dimethylaniline, λ_{max} , 250 $m\mu$, $\log \epsilon$ 4.15, is affected by a series of sulphur-containing *para*-substituents. The figures represent the bathochromic shift $\Delta\lambda$ in $m\mu$, and (in parentheses) the intensity $\log \epsilon$ of the shifted band :

$S \cdot CH_3$ +22 (4.31)	$S \cdot C_6H_5$ +24 (4.39)	$S \cdot C_6H_4 \cdot NO_2 \cdot p$ +25 (4.41)	$S \cdot CH_2 \cdot C_6H_4 \cdot NO_2 \cdot p$ +22 (4.48)
$CH_2 \cdot S \cdot CH_3$ +12 (4.27)	$CH_2 \cdot S \cdot C_6H_5$ +14 (4.39)	$CH_2 \cdot S \cdot C_6H_4 \cdot NO_2 \cdot p$ +16 (4.24)	

We see that the excess of the shift when nitrogen-sulphur conjugation of type (II) is formally permitted, over the shift obtaining when it is excluded, is only of the order of magnitude of the latter shift and is therefore not large enough to allow us to conclude that aryl-sulphur conjugation involving octet expansion produces the spectral consequences which have been observed.

Moreover, the original bands at 255 $m\mu$ in *p*-aminodiphenyl sulphide and 274 $m\mu$ in *p*-dimethylaminodiphenyl sulphide are only very little enhanced by *para*-substitution with NX_2 , OR, and O^- (see Table 3).

These results confirm our former provisional conclusion.⁴ Sanesi and Leandri recently found no evidence of conjugation of type II in their dipole-moment measurements on aromatic sulphides.⁵ It would appear therefore that this form of sulphur conjugation is unimportant in aryl sulphides.

⁴ Mangini and Passerini, *loc. cit.*, ref. 3; *J. Phys. Radium*, 1954, **15**, 625; *Gazzetta*, 1954, **84**, 606; *Experientia*, 1956, **12**, 49.

⁵ Sanesi and Leandri, *Boll. Sci. Fac. chim. ind. (Bologna)*, 1955, **13**, 56; *Ann. Chim. appl.*, 1955, **45**, 1106.

TABLE I. Amino- and hydroxy-substituted sulphides.

Substituent	Thioanisoles			Benzyl phenyl sulphides*			Diphenyl sulphides		
	No.	λ (m μ)	log ϵ	No.	λ (m μ)	log ϵ	No.	λ (m μ)	log ϵ
H	(1) B. p. 82°/16 mm.	(225 254 280)	(3.05 3.99 3.00 (a))	(2) M. p. 42—43°	(242 255)	(3.62 3.83)	(3) B. p. 176—177°/10 mm.	(232 251 265 277)	(3.76 4.09 3.70 3.76)
<i>p</i> -NH ₂	(4) B. p. 140°/15 mm.	(220 242 246 264 296)	(3.54 3.90 (b) 3.97 4.03 3.14 (c))	(5) M. p. 74—75°	(227 248 255 290)	(3.86 4.09 4.25 (b) 3.45 (d))	(6) M. p. 96°	(224 240 255 275)	(3.79 4.07 (e) 4.27 3.96 (d))
<i>p</i> -O-	(7) M. p. 84—85°	(224 259 295)	(3.64 4.17 3.35 (d))			not ex.	(8) M. p. 50.1°	(228 260)	(3.92 4.29)
<i>p</i> -NMe ₂	(9) B. p. 140°/3 mm.	(230 250 272 305)	(3.63 3.93 (e) 4.31 3.39 (d))			not ex.	(10) M. p. 66—67°	(228 274)	(3.78 4.39 (f))
<i>m</i> -NMe ₂	(11) B. p. 165—168°/16 mm.	(238 248 270 281 308)	(4.28 (b) 4.25 (d) 3.63 (a) 2.99 3.45)			not ex.	(12) B. p. 180°/5 mm.	(228 254 285 311)	(4.03 4.31 (g) 3.68 (e) 3.53)

* Substituents in benzyl nucleus.

(a) Weak inflexion. (b) Ill-defined max. (c) Inflexion followed by ill-defined max. (d) Inflexion. (e) Slight shoulder. (f) Max. preceded by very weak shoulder at 250 and 268 m μ . (g) Broad band.(1) *Ber.*, 1887, 20, 2026; spectrum in *n*-hexane: Mangini *et al.*, *Gazzetta*, 1954, 84, 3; in EtOH, *idem*, *ibid.*; Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, 71, 84. (2) *Ber.*, 1907, 40, 4194; spectrum in EtOH, Fehnel and Carmack, *loc. cit.* (3) Prepared and purified by method (c) referred to by Mangini *et al.*, ref. (1); spectrum in EtOH, Fehnel and Carmack, *loc. cit.*; in *n*-hexane: Mangini *et al.*, *loc. cit.*; in ethanol, *idem*, *ibid.*, and *J.*, 1952, 1168; Fehnel and Carmack, *loc. cit.*; Koch, *J.*, 1949, 387; see also, Robertson and Matsen, *J. Amer. Chem. Soc.*, 1950, 72, 5250. (4) *Annalen*, 1912, 388, 232; spectrum registered in *n*-hexane; in EtOH, Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1923, 45, 2399. (5) *J. Amer. Chem. Soc.*, 1923, 45, 2399. (6) *Rec. Trav. chim.*, 1912, 31, 30; spectrum registered in *n*-hexane; in EtOH (envelope (*Bologna*), 1956, 14, 9. (7) *Ber.*, 1914, 47, 1100; spectrum in 0.1*n*-NaOH; λ_{max} 256, log ϵ 4.28. Mangini *et al.*, *Gazzetta*, 1954, 84, 47; in cyclohexane, Tundo and Ruzzier, *loc. cit.* (8) *J. Amer. Chem. Soc.*, 1929, 51, 1530; spectrum in 0.1*n*-NaOH; in EtOH-NaOEt, Fehnel and Carmack, *loc. cit.*, ref. 4. (9) *Ber.*, 1909, 42, 3374; spectral results of Tundo and Ruzzier, *loc. cit.* (10) Sanesi and Leandri, *Boll. sci. Fac. chim. ind. (Bologna)*, 1955, 13, 56; *Ann. chimica*, 1955, 45, 1106; spectrum registered in *n*-hexane; in EtOH, Mangini *et al.*, *J.*, 1952, 1168 and *loc. cit.* in (6). (11), (12) See Experimental.

TABLE 2. *p*-Substituted dimethylamines.

No.	NMe ₂ ·C ₆ H ₄ X(p)	λ (mμ)	log ε	No.	NMe ₂ ·C ₆ H ₄ X(p)	λ (mμ)	log ε
(13)	X = H (M. p. 192—193°)	(>225) 250 (274 295	— 4·15 3·80 3·35	(14)	X = OMe (M. p. 48°)	(222 250 285 314	3·62 4·13 3·20 3·41
(16)	X = O ⁻	(~230) 245 (282 309	— 4·06 2·94 3·27	(17)	X = NH ₂ (M. p. 41°)	(225 256 297 323	3·60 4·08 3·10 3·35
(19)	X = CH ₂ Ph (M. p. 31°)	(227 259 (283 303	3·58 4·23 3·07 3·32	(20)	X = CH ₂ OPh (M. p. 119—120°)	(234 261 (284 301	3·68 4·36 3·21 (b) 3·39
(22)	X = NMe ₂ (M. p. 51°)	(228 264 (304 327	3·67 4·21 3·27 3·39	(23)	X = CH ₂ ·SMe (B. p. 123°/5 mm.)	(230 262 (286 300	3·59 4·27 3·25 3·38
(25)	X = S·C ₆ H ₄ ·NO ₂ (p) (M. p. 180—181°)	(236 252 275 324	3·88 4·00 (a) 4·41 4·15	(26)	X = CH ₂ ·S·C ₆ H ₄ ·NO ₂ (p) (M. p. 136—137°)	(240 266	3·99 4·24

(a) Inflection. (b) Min preceded by weak inflexion at 282 mμ, log ε = 3·63. For the compounds 25—27 we report only our results for <300 mμ region; for the region >300 mμ see *Experientia*, 1956, **12**, 49.

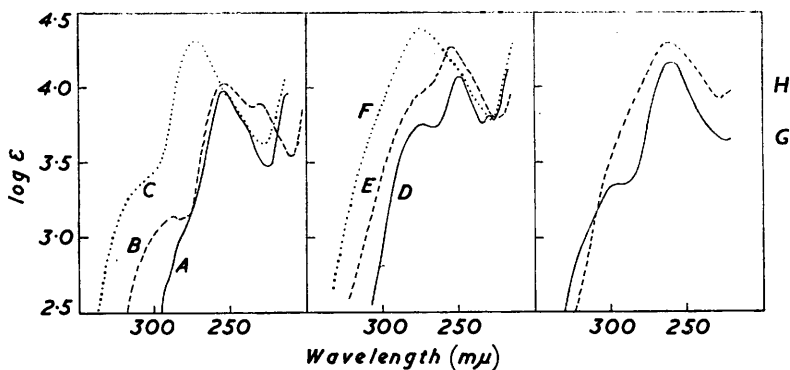
(13) Spectrum in *n*-heptane; results of Klevens and Platt, *J. Amer. Chem. Soc.*, 1949, **71**, 1714. (14), (18), (20), (23), (24), (26), (27) See Experimental. (15) *Ber.*, 1899, **32**, 3681. (16) Spectrum in *n*-NaOH. (17) *Ber.*, 1875, **8**, 619. (19) *Ann. Chim.*, 1918, **10**, 243. (21) *Chem. Ztg.*, 1900, **24**, 564. (22) *Ber.*, 1903, **36**, 2979; the spectrum is practically coincident with that recorded by Albrecht and Simpson, *J. Amer. Chem. Soc.*, 1955, **77**, 4454. (25) *Boll. sci. Fac. chim. ind. (Bologna)*, 1955, **13**, 56; *Ann. Chimica*, 1954, **45**, 1106; spectrum in EtOH, Mangini and Passerini, *J.*, 1952, 1168.

TABLE 3. *pp'*-Disubstituted diphenyl sulphides.

No.	λ (mμ)	log ε	No.	λ (mμ)	log ε
(28)	<i>p</i> -NH ₂ ·C ₆ H ₄ ·S·C ₆ H ₄ ·NH ₂ - <i>p'</i> M. p. 108°	(227 250 261 285	(31)	<i>p</i> -NH ₂ ·C ₆ H ₄ ·S·C ₆ H ₄ ·O ⁻ - <i>p'</i> M. p. 130°	(225) 263 282
(29)	<i>p</i> -NH ₂ ·C ₆ H ₄ ·S·C ₆ H ₄ ·OMe- <i>p'</i> M. p. 94—95°	(220 237 258 280	(32)	<i>p</i> -NMe ₂ ·C ₆ H ₄ ·S·C ₆ H ₄ ·NH ₂ - <i>p'</i> M. p. 130°	(225) 250 272 295
(30)	<i>p</i> -NH ₂ ·C ₆ H ₄ ·S·C ₆ H ₄ ·OH- <i>p'</i> M. p. 151—152°	(220 233 258 280			

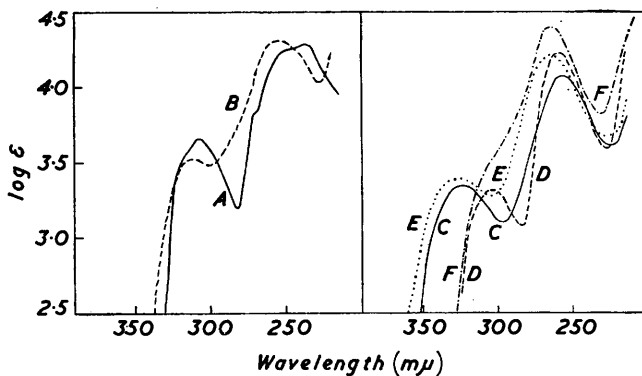
(a) Inflection. (b) Weak inflection. (c) Flat region 235—240 mμ
(28) *Ber.*, 1894, **27**, 3262; spectrum in EtOH, Mangini *et al.*, *J.*, 1952, 1168; *Gazzetta*, 1954, **84**, 47. (29) *J. Amer. Chem. Soc.*, 1930, **52**, 1146; spectrum in EtOH, Mangini *et al.*, *Gazzetta*, *loc. cit.* (30) *J. Amer. Chem. Soc.*, 1934, **56**, 1978. (31) Spectrum in *n*-NaOH. (32) Mangini *et al.*, *loc. cit.*; spectrum registered in *n*-hexane; in EtOH, Mangini *et al.*, *loc. cit.*

FIG. 1.



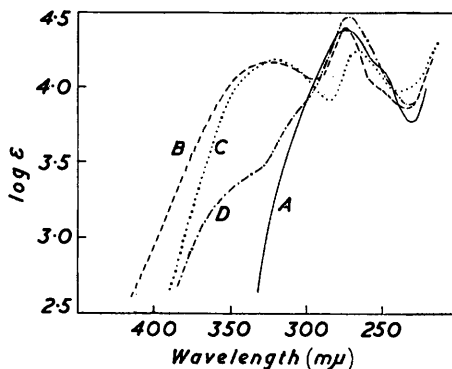
- A, $\text{Ph}\cdot\text{S}\cdot\text{CH}_3$ in hexane. D, $\text{Ph}\cdot\text{S}\cdot\text{Ph}$ in hexane. G, $\text{p}\text{-}\overline{\text{O}}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_3$.
 B, $\text{p}\text{-}\text{H}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_3$ in hexane. E, $\text{p}\text{-}\text{H}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{Ph}$ in hexane. H, $\text{p}\text{-}\overline{\text{O}}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{Ph}$.
 C, $\text{p}\text{-}(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_3$ in cyclohexane. F, $\text{p}\text{-}(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{Ph}$ in hexane.

FIG. 2.



- A, $\text{m}\text{-}(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_3$ in cyclohexane. C, $\text{p}\text{-}\text{H}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_3)_2$ in cyclohexane.
 B, $\text{m}\text{-}(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{Ph}$ in cyclohexane. D, $\text{p}\text{-}(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Ph}$ in cyclohexane.
 E, $\text{p}\text{-}(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_3)_2$ in cyclohexane.
 F, $\text{p}\text{-}\text{Ph}\cdot\text{S}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_3)_2$ in cyclohexane.

FIG. 3.



- A, $\text{p}\text{-}(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{Ph}$ in cyclohexane.
 B, $\text{p}\text{-}\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_3)_2\text{-p}$ in hexane.
 C, $\text{p}\text{-}\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_3)_2\text{-p}$ in cyclohexane.
 D, $\text{p}\text{-}\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_3)_2\text{-p}$ in cyclohexane.

EXPERIMENTAL

Spectra were determined with a Hilger Uvispek photoelectric spectrophotometer. The concentrations used were $10^{-5}M$. The compounds were measured in *cyclohexane* (or in *n*-hexane, as indicated in the Tables) in order to reduce the solvent effect. The results are reported in Tables 1—3, where the wavelengths of maxima and minima are given as $m\mu$, and extinction values as $\log \epsilon$: minima are indicated in parentheses.

References are given in the Tables to the methods used in the preparation of the compounds, and also references to spectra already recorded by other authors and in other solvents. The absorption curves are reproduced in Figs. 1—3.

The following descriptions relate to the preparation of new compounds or of known compounds by modified methods.

m-Dimethylaminodiphenyl sulphide was prepared as follows. *m*-Aminodiphenyl sulphide⁶ (10 g.) was suspended in water (100 c.c.), and sodium hydrogen carbonate (13 g.) and then dimethyl sulphate (16 g.) were added with constant stirring. The mixture was kept at 30° until evolution of carbon dioxide had ceased, and then at 50—60° for 30—60 min. On cooling, an oil separated (together with a small amount of a crystalline product which was neglected) and was extracted with ether. Distillation of the dried ether extract afforded an oil, b. p. 180—181°/5 mm. (Found: N, 6.1. $C_{14}H_{15}NS$ requires N, 6.1%).

m-Dimethylamino(thioanisole) was obtained in better yield and more easily by methylation of *m*-amino(thioanisole) as above than by distillation of the quaternary iodide. The product had b. p. 165—166°/16 mm. *p*-Methoxydimethylaniline, obtained by methylation of *p*-anisidine as indicated above, crystallised from water in plates, m. p. 48° (in agreement with Griess,⁸ who obtained it by distillation of the quaternary iodide). *NN*-Dimethyl-*p*-phenoxyaniline was prepared similarly from *p*-aminodiphenyl ether, as an oil, b. p. 193°/16 mm. (Found: N, 6.7. $C_{14}H_{15}ON$ requires N, 6.6%).

p-Dimethylaminobenzyl phenyl ether. A solution of *p*-dimethylaminobenzyl alcohol (5 g.) in concentrated hydrochloric acid (25 c.c.) was heated for 2 hr. in a sealed tube⁹ at 100°, and to the cooled reaction mixture, which contained *p*-dimethylaminobenzyl chloride, was added aqueous-ethanolic sodium phenoxide (2.5 g. of phenol in 50 c.c. of ethyl alcohol and 60 c.c. of aqueous 20% NaOH). The mixture was refluxed for 15 min.; after cooling, a white product was separated. Crystallization from ligroin gave the ether as needles, m. p. 119—120° (Found: N, 6.2. $C_{15}H_{17}ON$ requires N, 6.2%).

p-Dimethylaminobenzyl methyl sulphide was prepared as was the preceding ether, except that the *p*-dimethylaminobenzyl chloride was condensed with sodium thiomethoxide in a sealed tube. Extraction of the solution with ether yielded an oil, which on distillation had b. p. 123°/5 mm. (Found: N, 7.9. $C_{10}H_{13}NS$ requires N, 7.7%). *p*-Dimethylaminobenzyl phenyl sulphide was prepared similarly from *p*-dimethylaminobenzyl chloride and sodium thiophenoxide. It separated in plates, m. p. 106—107°, from ethanol (Found: N, 5.9. $C_{15}H_{17}NS$ requires N, 5.75%). *p*-Dimethylaminobenzyl *p*-nitrophenyl sulphide, prepared from *p*-dimethylaminobenzyl chloride and sodium *p*-nitrothiophenoxide, crystallized from *isopropyl* alcohol in orange-yellow plates, m. p. 136—137° (Found: N, 9.7. $C_{15}H_{16}O_2N_2S$ requires N, 9.7%). *p*-Dimethylaminophenyl *p*-nitrobenzyl sulphide was prepared from a solution of dimethylaminothiophenol (10 g.) in aqueous sodium hydroxide (3 g. in 30 c.c.) and an ethanolic solution (150 c.c.) of *p*-nitrobenzyl bromide (15 g.). After the mixture had been refluxed for 15 min. a red crystalline product separated on cooling, and crystallized from ligroin in prisms, m. p. 102—103° (Found: N, 9.72. $C_{15}H_{16}O_2N_2S$ requires N, 9.79%).

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⁶ Hünig, *Chem. Ber.*, 1952, **85**, 1056.

⁷ Zincke and Muller, *ibid.*, 1913, **46**, 781.

⁸ Griess, *ibid.*, 1880, **13**, 249.

⁹ As described by Barun and Kruber, *Ber.*, 1912, **45**, 2992.