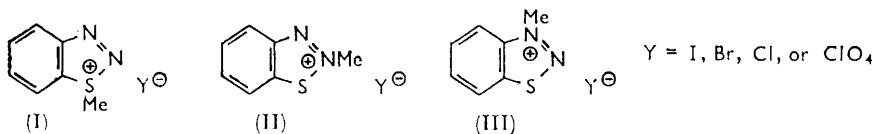


1034. 1,2,3-Benzothiadiazolium Salts. Part I. The Structure of Jacobson's Benzothiadiazolium Salts.

By W. H. POESCHE.

Jacobson's methylbenzothiadiazolium salts, obtained by quaternisation of 1,2,3-benzothiadiazole with methyl iodide and subsequent conversions, and hitherto believed to be 1-methylbenzothiadiazolium salts, are shown to be the 3-isomers. The colour changes of the iodide in different solvents, thought by Hodgson and Dodgson to indicate the structure, arise from charge-transfer transitions. Similar colour changes of 2-aryl-1,2,3-benzo- and naphthothiadiazole can be explained similarly better than by assuming an equilibrium with an un-ionised form.

IN 1893, Jacobson and Janssen¹ obtained a number of 1,2,3-benzothiadiazolium salts, among them methyl-1,2,3-benzothiadiazolium iodide by quaternisation of 1,2,3-benzothiadiazole with methyl iodide. Of the three possible structures (I—III), they considered

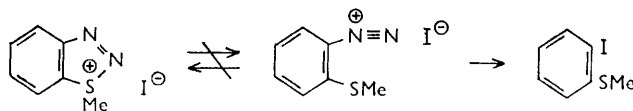


structure (I) the most likely, since "up to now there exists no observation, which indicates the possibility of quaternisation of azo-compounds," but they emphasised that a decision could not be reached from the available facts.

Hantzsch,² 15 years later, observed a number of remarkable colour changes of methyl-1,2,3-benzothiadiazolium iodide. It was almost colourless in aqueous, yellow in alcoholic, and bright red in pyridine and chloroform solution.

Still later, Hodgson and Dodgson³ argued that these colour changes support the structure (I) originally proposed, as "in aqueous solution the ionisation of the salt will account for the absence of colour, since the colourless benzthiadiazole is now subjected to still greater strain by the positively charged sulphur atom, whereas in less polar solvents repression of ionisation will enable the sulphur grouping to relax its strain on the azo-group, with development of yellow and red colours according to the extent of the relaxation, which will also be facilitated by the dissolution of the aromatic sextet."

Two facts seemed not in agreement with this picture. First, since Jacobson's work the quaternisation of azo-linkages has been achieved,⁴ while no example for a sulphonium salt in which the sulphur is incorporated in an aromatic five-membered ring is known hitherto. This makes the original assignment unlikely. Secondly, methyl-1,2,3-benzothiadiazolium iodide is stable in aqueous solution,¹ and therefore not in equilibrium with the ring-opened form (diazonium salt) which would decompose immediately to give *o*-iodothioanisole:



This means that the methyl-1,2,3-benzothiadiazolium salt would have to be much more stable than its valency tautomer, and one would therefore expect that the *o*-diazoniathioanisole ion, when formed, would immediately close the ring to yield the former. This is

¹ Jacobson and Janssen, *Annalen*, 1893, **277**, 227.

² Hantzsch, *Ber.*, 1909, **42**, 81.

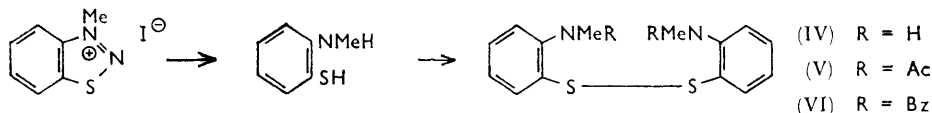
³ Hodgson and Dodgson, *J. Soc. Dyers and Colourists*, 1948, **64**, 65; Sherman, in "Heterocyclic Compounds," ed. Elderfield, Wiley, New York, 1961, Vol. VII, pp. 556—557.

⁴ Kehrman and van der Laar, *Ber.*, 1922, **55**, 511.

not what is observed. Diazotised *o*-aminothiophenol gives the usual reactions of the diazonium group,⁵ in particular displacement by iodine on addition of potassium iodide.^{5a} We conclude that the methyl group in the methylbenzothiadiazolium ion cannot be attached to the sulphur.

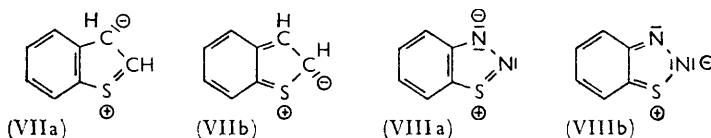
Although these facts were known long before Hodgson and Dodgson's Paper, their bearing on the methylbenzothiadiazolium problem has never been recognised.

We have now shown, by reduction with zinc in acetic acid, that the methyl group occupies the 3-position. The reduction product, *o*-(methylamino)thiophenol, was converted into its known⁶ disulphide (IV), and the latter identified by analysis, m. p., and m. p.s of the (also known⁷) acetyl (V) and benzoyl (VI) derivatives. Non-production of the 2-



methyl-1,2,3-benzothiadiazolium ion (II) was shown by our failure to find any di(*o*-aminophenyl) disulphide in the zinc reduction experiment, carried out on both the recrystallised product and the mother-liquor residue (after it had been freed from 1,2,3-benzothiadiazole). Its absence from the recrystallised product was also evident from the absence of another methyl peak in the nuclear magnetic resonance (n.m.r.) spectrum (in acetonitrile).

Preferred attack at the 3- rather than at the 2-position is reminiscent of the behaviour of benzothiophen towards electrophiles⁸ and may well have the same cause, namely, that the basicity of the 3-position is enhanced by the conjugative effect of the sulphur atom (VIIa, VIIIa), while this is not so for the 2-position where conjugation within the benzene ring would have to be disturbed⁸ (VIIb, VIIIb).



The colour changes in various solvents, thought by Hodgson and Dodgson to be indicative of the structure, have now been shown to be due to charge-transfer complexes ($n' + v^*$ in Mulliken's terminology⁹) rather than to a type of strain the origin of which the present author finds difficult to visualise. This interpretation is supported by the following facts: (i) The long-wavelength absorption band of the iodide in solution is very broad and without fine structure. Its intensity is similar to that of 1-ethyl-4-methoxycarbonylpyridinium iodide in the same solvents.^{10a} (ii) A straight line is obtained when the wave numbers of the long-wavelength maxima of the iodide are plotted against Kosower's *Z* values^{10c} for the corresponding solvents. (iii) In a given solvent, Beer's law is not obeyed.^{10a} The deviation is towards higher intensity at higher concentrations. (iv) A smooth curve is obtained when the wave numbers of the long-wavelength maxima of the iodide, bromide, and chloride are plotted against those of the corresponding sodium halides in the gas phase;¹¹ these are known¹² to arise from charge-transfer transitions. A straight line could not be expected, since our values for the maxima of the bromide and the chloride may be slightly in error, being obtained by taking the difference between their spectra and that of the perchlorate, and since the coulombic energy would be expected to differ by a small amount.

⁵ (a) Zincke and Siebert, *Ber.*, 1915, **48**, 1243; (b) Burawoy and Turner, *J.*, 1950, 471.

⁶ Harries and Löwenstein, *Ber.*, 1894, **27**, 867.

⁷ Clark, *J.*, 1925, **127**, 974.

⁸ Eaborn and Sperry, *J.*, 1961, 4922.

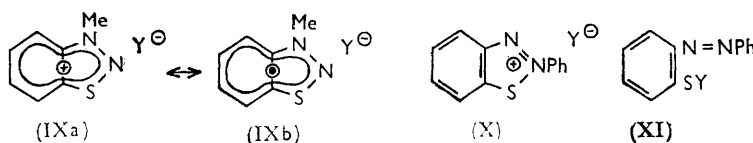
⁹ Mulliken, *J. Phys. Chem.*, 1952, **56**, 814, 815.

¹⁰ (a) Kosower, *J. Amer. Chem. Soc.*, 1955, **77**, 3883; (b) Kosower and Klinedinst, *ibid.*, 1956, **78**, 3493; (c) Kosower, *ibid.*, 1958, **80**, 3253.

¹¹ Müller, *Ann. Phys.*, 1927, **82**, 63.

¹² Franck, Kuhn, and Rollefson, *Z. Phys.*, 1927, **43**, 155.

These complexes may be depicted as (IX), (IXa), and (IXb), being the principal contributing structures in the ground state and the excited state, respectively.



A number of 2-aryl-substituted 1,2,3-benzo- and naphthothiadiazolium salts have been prepared by Burawoy and his co-workers.¹³ They also show colour changes in solution, when passed from one solvent to another; ^{13a} the colour of the solid salts depends similarly on the (otherwise colourless) anions,¹³ and their solutions do not obey Beer's law.^{13a}

The ultraviolet spectra of some 2-phenyl-1,2,3-benzothiadiazolium salts (X) have been published.^{13a} The halides show a long-wavelength band or inflexion, which Burawoy considers to be an *R*-band (a band due to an electronic transition localised in the azo-group), since it is displaced to shorter wavelengths and becomes more intense as the dielectric constant of the solvent is increased. Such bands normally disappear when the azo-group is converted into its salt, and Burawoy therefore takes its presence to mean that the ionic form (X) is in equilibrium with its non-ionic isomer (XI). The facts that such a band is absent from the spectrum of the perchlorate, and it is "more pronounced" for benzene-hexane than for chloroform solutions, were taken to indicate that the tendency of the S-Y linkages to ionise increases in the order $I < Br < Cl < ClO_4$. However, sulphenyl iodides are known to disproportionate into disulphide and iodine,¹⁴ while 2-phenyl-1,2,3-benzothiadiazolium iodide is stable in all solvents tried. This, in our view, rules out the presence of form (XI; Y = I), and we believe that the observed bands and inflexions also arise from charge-transfer transitions.

EXPERIMENTAL

3-Methyl-1,2,3-benzothiadiazolium Iodide.—A solution of 1,2,3-benzothiadiazole (15 g.) in methyl iodide (60 ml.) was heated in a sealed tube to 100° for 10 hr. The solid which had been formed was filtered off and recrystallised from ethanol (250 ml.; refrigerator) (yield 10.1 g., 32%). A sample, recrystallised twice from ethanol and dried at 80° *in vacuo*, formed yellow-orange needles, m. p. 196° (decomp.) [Jacobson¹ gives the colour as deep red, Hantzsch² as golden-yellow; Jacobson¹ gives no m. p., Hantzsch² one of 163° (decomp.)]. The salt became red when heated (not brown as stated by Hantzsch²) (Found: C, 30.2; H, 2.7; I, 45.8. Calc. for C₇H₇IN₂S: C, 30.2; H, 2.5; I, 45.6%). The n.m.r. spectrum in acetonitrile, taken with a 100 Mc./sec. instrument, showed only one signal due to *N*-methyl, at 5.145 τ.

3-Methyl-1,2,3-benzothiadiazolium Bromide.—A solution of the above iodide (1.4 g.) in water (50 ml.) was passed through an ion-exchange column (Amberlite IRA-400 CP; bromide form). The first 500 ml. eluate (eluent, water) was evaporated to dryness at 80° on a rotatory evaporator, and the residue recrystallised from ethanol (refrigerator) (yield, 0.81 g., 70%). The bromide, recrystallised once more from ethanol and dried at 80° *in vacuo*, formed a yellow powder, m. p. 227—228° (decomp.) (Found: C, 36.3; H, 3.1; Br, 34.6. C₇H₇BrN₂S requires C, 36.4; H, 3.05; Br, 34.6%).

3-Methyl-1,2,3-benzothiadiazolium Chloride.—This was prepared by ion-exchange as described above. The evaporation residue was dissolved in hot propan-1-ol (6 ml.), hot dioxan (6 ml.) was added, and the solution was kept in the refrigerator. The salt (0.56 g., 60%) was washed with dioxan. Recrystallised once more in the same way and dried at 80° *in vacuo*, it formed a yellowish-white powder, m. p. 218—221° (decomp.) (Jacobson¹ gives no m. p.) (Found: C, 44.9; H, 3.85; Cl, 18.9. Calc. for C₇H₇ClN₂S: C, 45.0; H, 3.8; Cl, 19.0%).

3-Methyl-1,2,3-benzothiadiazolium perchlorate was prepared by ion-exchange as described above. The evaporation residue was recrystallised from much ethanol (refrigerator) and dried

¹³ (a) Burawoy, Liversedge, and Vellins, *J.*, 1954, 4481; (b) Burawoy, Chaudhuri, and Vellins, *J.*, 1955, 3798; Burawoy, Chaudhuri, and Vellins, *J.*, 1956, 90; Burawoy, Chaudhuri, and Hyslop, *J.*, 1956, 96; Burawoy and Mistry, *J.*, 1959, 3877.

¹⁴ See ref. 11a for references.

at 80° *in vacuo* (yield, 0.80 g., 65%). A sample, recrystallised once more from ethanol and dried at 80° *in vacuo*, formed pure white crystals, m. p. 129.5–131° (decomp.) (Found: Cl, 14.1. C₇H₇ClN₂O₄S requires Cl, 14.15%. C and H could not be determined since the compound exploded).

The above four salts are not hygroscopic.

Orientation of the N-Methyl Group.—Zinc dust (2 g.) was added in 5 hr. to methyl-1,2,3-benzothiadiazolium iodide (1 g., once crystallised) in 50% acetic acid (10 ml.) at 100°. After being heated overnight, the mixture was taken to dryness. The residue was dissolved in concentrated aqueous ammonia plus benzene, air was passed through this solution for 1 hr., and the organic matter was extracted with benzene. The dried (Na₂SO₄) extract was taken to dryness, and the residue was dissolved in light petroleum (b. p. 65–70°) and divided into halves. To the second half was added di-(*o*-aminophenyl) disulphide (0.05 g.), prepared from di-(*o*-nitrophenyl) disulphide by reduction with hydrazine hydrate.¹⁵ Both solutions were chromatographed on 60 × 1.5 cm. aluminium oxide (BDH)-light petroleum columns under identical conditions. Benzene-light petroleum (1 : 3) eluted di-(*o*-methylaminophenyl) disulphide (0.225 g.), m. p. [after recrystallisation from light petroleum (b. p. 65–70°)] 67–68° (lit., 67–68°) (Found: N, 9.8. Calc. for C₁₄H₁₆N₂S₂: N, 10.1%) [acetyl, m. p. 173–173.5° (lit., 171°) and benzoyl derivative, m. p. 164.5–165° (lit., 164°)]. After elution of two other yellow bands (0.13 g.) with benzene, which were not further investigated, a further yellow band was seen only on the second column. Elution with benzene-ethyl acetate (8 : 1) gave back the di-(*o*-aminophenyl) disulphide (0.048 g.) originally added. No compound was eluted from the first column at this point.

The mother-liquor after crystallisation of the benzothiadiazolium salt was evaporated, and the residue extracted with light petroleum to remove benzothiadiazole. Reduction by zinc and chromatography were carried out with this material as described above. No di-(*o*-aminophenyl) disulphide was found on the first column.

TABLE 1.

Dependence of the charge-transfer maximum on solvent
(3-methyl-1,2,3-benzothiadiazolium iodide in 1.6 × 10⁻³M-solution).

| Solvent | Colour of soln. | Z-value | $\lambda_{\max.}$ (m μ) | $\tilde{\nu}_{\max.}$ (kK) | Cell (cm.) | Opt. density | $\epsilon_{\text{app.}}$ | 10 ² Osc. strength |
|---------------------------------|-----------------|---------|---------------------------------|-------------------------------|---------------|-----------------|--------------------------|----------------------------------|
| C ₆ H ₆ N | Wine-red | 64.6 * | 497 | 20.12 | 1.0 | 0.840 | 525 | 1.03 |
| CHCl ₃ (0.14M-EtOH) | Rubin-red | 66.0 * | 490 | 20.41 | 0.5 | 1.090 | 1363 | 2.86 |
| COMe ₂ | Red | 65.7 | 483 | 20.70 | 1.0 | 0.792 | 495 | 1.00 |
| Me ₂ N·CHO | Beige | 68.5 | 463 | 21.60 | 10.0 | 0.396 | 25 | 0.05 |
| MeCN | Ochra | 71.3 | 449 | 22.27 | 5.0 | 0.620 | 78 | 0.17 |
| PrOH | Deep yellow | 76.3 | 407 | 24.57 | 2.0 | 0.885 | 277 | 0.88 |

* Corr. for electrolyte concn. from data in ref. 13.

TABLE 2.

Dependence of the charge-transfer maxima of the 3-methyl-1,2,3-benzothiadiazolium halides, in CHCl₃ (0.14M-EtOH), 1.6 × 10⁻³M solution, on those of the corresponding sodium halides (in the gas phase).

| Anion | $\tilde{\nu}_{\max.}$ (NaX) (kK) | Colour of soln. | $\lambda_{\max.}$ (m μ) | $\tilde{\nu}_{\max.}$ (kK) | Cell (cm.) | Opt. density | $\epsilon_{\text{app.}}$ |
|-------|-------------------------------------|-----------------|---------------------------------|-------------------------------|---------------|-----------------|--------------------------|
| I | 30.85 | Ruby red | 490 | 20.41 | 0.5 | 1.090 | 1363 |
| Br | 36.50 | Yellow | 383 | 26.11 | 0.1 | 0.27 | 1688 |
| Cl | 41.19 | Buff | 345 | 28.99 | 0.1 | 0.31 | 1938 |

TABLE 3.

Dependence of extinction coefficient on concentration (3-methyl-1,2,3-benzothiadiazolium iodide in MeCN).

| Concn. (10 ⁻³ mole/l.) | Cell (cm.) | Opt. density | $\epsilon_{\text{app.}}$ | $\lambda_{\max.}$ (m μ) |
|-----------------------------------|------------|--------------|--------------------------|------------------------------|
| 1.6 | 5.0 | 0.620 | 77.5 | 449 |
| 4.0 | 1.0 | 0.640 | 169 | 450 |

Ultraviolet Spectra.—These were determined with a Cary model 14M recording spectrophotometer in commercial Spectro-grade solvents. For comparable results, the concentration was

¹⁵ Möhlau, Beyschlag, and Köhres, *Ber.*, 1912, **45**, 134.

kept constant for the first and the second series as the absorption maxima of charge-transfer bands are somewhat sensitive to the ionic strength of the solution. In the first series the length of the quartz absorption cells was, as far as possible, chosen so as to give an optical density of the charge-transfer peak between 0.7 and 1.0. In the second series the charge-transfer bands of the bromide and the chloride overlapped with the spectrum of the 3-methylbenzothiazolium cation to such an extent that their peaks could not be observed directly. They were obtained by taking the difference between their spectra and that of the perchlorate; perchlorates show only the spectrum of the cation.^{13b} Here the length of the quartz cells was chosen so that the optical density never exceeded 1.0 over the whole range. The details are in Tables 1—3.

UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA.

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