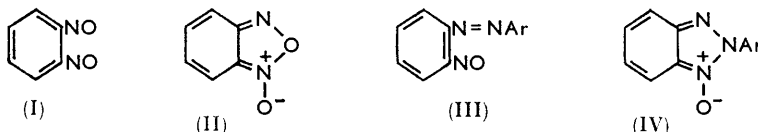


## 148. *N*-Oxides and Related Compounds. Part XXIV.<sup>1</sup> The Structure of *ortho*-Bisazo-compounds.

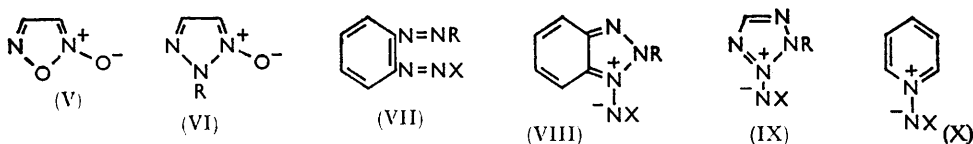
By H. BAUER, G. R. BEDFORD, and A. R. KATRITZKY.

*ortho*-Bisazo-compounds in which an electron-withdrawing group is attached to one of the azo-groups exist as the cyclised products, benzotriazole 1-imides.

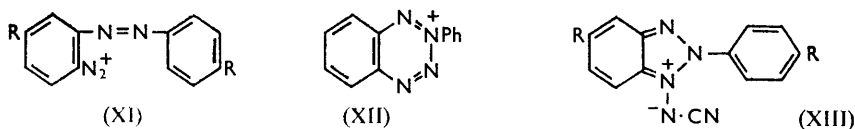
It has been shown,<sup>2</sup> in our laboratory and elsewhere, that *o*-dinitroso-compounds (cf. I) exist as the cyclised products 2,1,3-benzoxadiazole 1-oxides (cf. II). It has been accepted for many years that *o*-nitrosoazo-compounds (III) exist as benzotriazole 1-oxides (IV).<sup>3</sup> Monocyclic analogues [furoxans (V); triazole *N*-oxides<sup>4</sup> (VI)] are well authenticated.



For *ortho*-bisazo-compounds (VII), structures of type (VIII) therefore merit attention, together with the monocyclic type (IX). No one appears to have considered such structures except Curtin, Crawford, and Wedegaertner<sup>5</sup> who state that they "have no known prototype and little to recommend them." However, pyridine 1-imides (X; X = Ph or *p*-NHAc·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>) are well known,<sup>6a</sup> and structures of types (VIII) and (IX) in which R and X form part of a ring have recently been described.<sup>6b,c</sup> We have found much to recommend structures of types (VIII) and (IX); in this Paper we present evidence that certain *ortho*-bisazo-compounds exist in the cyclised form (VIII); a later communication will deal with the monocyclic analogues (IX).



Azo-compounds have characteristic ultraviolet absorption spectra; *e.g.*, azobenzene absorbs at 228, 318, and 442 m $\mu$  (log  $\epsilon$  4.15, 4.34, and 2.73). *o*-Bisphenylazobenzene (VII; R = X = Ph) absorbs at 225, 304, and 445 m $\mu$  [log  $\epsilon$  4.19, 4.45, and 2.99 (alcohol)] [cf. *p*-bisphenylazobenzene: 228, 359, and 445 m $\mu$ ; log  $\epsilon$  4.24, 4.64, and 3.48 (alcohol)],<sup>7</sup> which shows that it cannot exist in the cyclised form (VIII; R = X = Ph) to more than a minor extent.



<sup>1</sup> Part XXIII, Bedford, Katritzky, and Wuest, *J.*, 1963, 4600.

<sup>2</sup> Katritzky, Øksne, and Harris, *Chem. and Ind.*, 1961, 990; Harris, Katritzky, and Øksne, *J.*, 1963, 197.

<sup>3</sup> Cf., *e.g.*, Boyer in Elderfield's "Heterocyclic Compounds," Wiley, New York, Vol. VII, 1961, p. 397.

<sup>4</sup> Ponzio, *J. prakt. Chem.*, 1898, **57**, 160; *Gazzetta*, 1899, **29**, 283.

<sup>5</sup> Curtin, Crawford, and Wedegaertner, *J. Org. Chem.*, 1962, **27**, 4300.

<sup>6</sup> (a) Sisler, Omietanski, and Rudner, *Chem. Rev.*, 1957, **57**, 1021; (b) Carboni and Castle, *J. Amer. Chem. Soc.*, 1962, **84**, 2453; (c) Pflieger, Garthe, and Rauer, *Chem. Ber.*, 1963, **96**, 1827.

<sup>7</sup> Dahn and Castelmur, *Helv. Chim. Acta*, 1953, **36**, 640.

A strongly electron-attracting group X should stabilise the adjacent negative charge and facilitate cyclisation of a bisazo-compound (VII) to (VIII). We therefore prepared the cyano-derivative (VII; R = Ph, X = CN) and its dimethyl analogue through the diazonium ions (XI; R = H and Me).<sup>\*</sup> The properties of the cyano-derivative and its dimethyl analogue showed that they exist in the cyclised cyanoimide forms (XIII; R = H and Me). No azo-peak at *ca.* 440 m $\mu$  is shown in the ultraviolet spectrum (Fig. 1 and Table). Reduction with stannous chloride in hydrochloric acid gives the corresponding 2-arylbenzotriazole (XIV), which argues against the compound's existing in the form (XV). The cyanoimides dissolve in strong hydrochloric acid (presumably as XVI) and are precipitated therefrom unchanged by sodium hydroxide. Reaction of the cyanoimide (XIII; R = H) with benzenesulphonic acid yields a product tentatively formulated as (XVII) since its ultraviolet spectrum was similar to that of the cyanoimide (XIII; R = H). The dimethyl analogue behaved similarly.

## Ultraviolet spectral maxima.

Compound	$\lambda$ (m $\mu$ )	$10^{-3}\epsilon$	$\lambda$ (m $\mu$ )	$10^{-3}\epsilon$	$\lambda$ (m $\mu$ )	$10^{-3}\epsilon$
XIII; R = H .....	219	20.0	303	14.6	375	5.7
XIII; R = Me .....	227	24.8	312	15.6	367	5.8
XIX .....	226	12.7	341	16.4	354,* 448	14.5, 2.1
XX; R = H .....	213 *	25.1	301	14.3	—	—
XX; R = Me .....	220	27.4	306	14.4	—	—
Phenyl <i>p</i> -phenylazobenzene-diazosulphone .....	217	21.0	347	28.7	445 *	1.6
XVII .....	220	24.4	317	13.1	382	6.5

\* Infection.

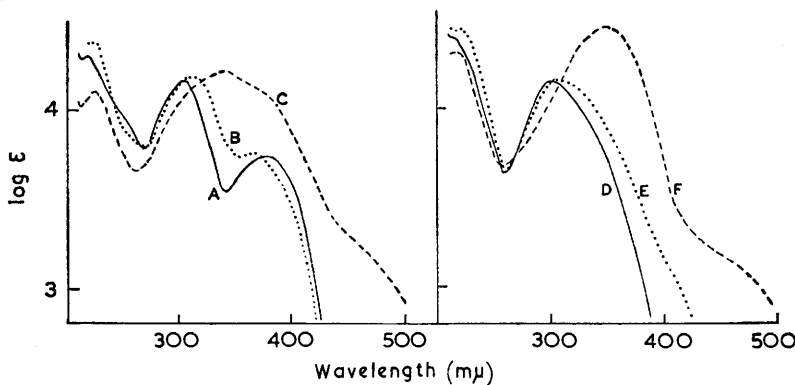


FIG. 1.

FIG. 2.

Figs. 1 and 2. Electronic spectra of ethanol solution.

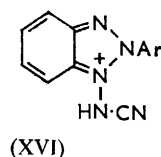
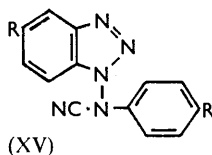
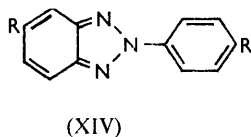
- (A) 2-Phenylbenzotriazole 1-cyanoimide (XIII; R = H). (B) 5-Methyl-2-*p*-tolylbenzotriazole 1-cyanoimide (XIII; R = Me). (C) *anti-p*-Phenylazobenzenediazocyanide (XIX).  
 (D) 2-Phenylbenzotriazole 1-benzenesulphonylimide (XX; R = H). (E) 5-Methyl-2-*p*-tolylbenzotriazole 1-benzenesulphonylimide (XX; R = Me). (F) Phenyl azobenzenediazosulphone.

Further evidence for the cyanoimide structures is provided by a comparison of the infrared spectra with those of the *syn*- (XVIII) and *anti-p*-phenylazobenzenediazocyanide (XIX). As with other diazocyanides,<sup>9</sup> the *syn*-isomer is formed initially and changes

\* Strong  $\nu_{\text{N}\equiv\text{N}}$  at 2300 and 2270  $\text{cm}^{-1}$  (in Nujol), respectively, in the infrared spectrum of the diazonium tetrafluoroborate are evidence against this ion's existing as (XII) (cf. ref. 8).

<sup>8</sup> Bunnett, Buncel, and Nahabedian, *J. Amer. Chem. Soc.*, 1962, **84**, 4139.

<sup>9</sup> Le Fèvre and Vine, *J.*, 1938, 431.

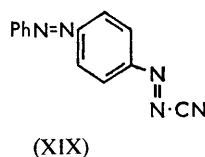
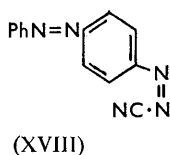
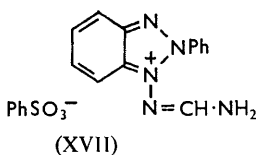


spontaneously to the *anti*-isomer. The frequency ( $\text{cm}^{-1}$ ) and intensity of the cyano-stretching vibration in these compounds (in chloroform) are:

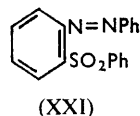
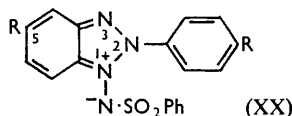
	XIII; R = H	XIII; R = Me	XVIII	XIX
$\nu_{\text{C}\equiv\text{N}}$ .....	2150	2155	2200	2195
$\epsilon_{\text{A}\text{C}\equiv\text{N}}$ .....	400	480	15	72

It is well known<sup>10</sup> that the intensity of  $\nu_{\text{C}\equiv\text{N}}$  increases with the electron-donor ability of the group to which the cyano-group is attached. This indicated that in compounds (XIII; R = H or Me) the cyano-group is not attached to the weakly electron donating  $-\text{N}=\text{N}-$  group. Of the diazocyanides, the *syn*-isomer shows the lower intensity, probably because of steric inhibition of resonance.

*p*- and *o*-Aminoazobenzene and 2-amino-5,4'-dimethylazobenzene were diazotised and treated with benzenesulphonic acid. Whereas the *para*-compound yielded the diazo-sulphone as expected,<sup>11</sup> the *ortho*-derivatives formed cyclised products of type (XX) as indicated by the ultraviolet spectra (see Table): there was no appreciable absorption above 400  $\text{m}\mu$ , in contrast to the *para*-analogue. The fact that *ortho*-compounds of the cyano-series show peaks in the 370—380  $\text{m}\mu$  region presumably reflects the greater



conjugating ability of a cyano than a sulphonyl group. The reduction of the sulphonylimide (XX; R = Me) by zinc and acetic acid gave the 2-arylbenzotriazole (XIV; R = Me), as expected.



However, the cyclised form probably exists in equilibrium with a small quantity of the diazosulphone because, when heated, compound (XX; R = H) yielded what is probably the azosulphone (XXI).

#### EXPERIMENTAL

*o*-(Phenylazo)benzenediazonium Tetrafluoroborate.—2-Aminoazobenzene (0.5 g.) in 6*N*-hydrochloric acid (2 c.c.) at 5° was treated with sodium nitrite (0.25 g.) in water (1 c.c.) followed by sodium tetrafluoroborate (1.4 g.) in water (2 c.c.). The precipitate (0.7 g., 93%) was washed with ethanol and ether and crystallised from ethanol (some nitrogen was evolved) to give the *diazonium salt* as brown-orange needles, m. p. 143° (decomp.) (Found: N, 17.9.  $\text{C}_{12}\text{H}_9\text{N}_4\text{BF}_4$  requires N, 18.9%).

<sup>10</sup> Sensi and Gallo, *Gazzetta*, 1955, **85**, 224, 235.

<sup>11</sup> Hantzsch and Singer, *Ber.*, 1897, **30**, 314; Freeman, Le Fèvre, Northcott, and Youhotsky, *J.*, 1952, 3381.

4-Methyl-2-(*p*-tolylazo)benzenediazonium Tetrafluoroborate (XI; R = Me).—2-Amino-5,4'-dimethylazobenzene<sup>12</sup> (2 g.) in ethanol (20 c.c.) and concentrated hydrochloric acid (4 c.c.) was treated with sodium nitrite and tetrafluoroborate as above. The *diazonium tetrafluoroborate* (2.9 g., 97%) crystallised from methanol as orange needles, m. p. 151° (decomp.) (Found: N, 17.6%. C<sub>14</sub>H<sub>13</sub>N<sub>4</sub>BF<sub>4</sub> requires N, 17.3%).

2-Phenylbenzotriazole 1-Cyanoimide.—To 2-aminoazobenzene (0.5 g.) in aqueous 6*N*-hydrochloric acid (2 c.c.) at 0° was gradually added sodium nitrite (0.25 g.) in water (1 c.c.), followed by sodium acetate (*ca.* 2.5 g.), and then potassium cyanide (0.5 g.) in water (1 c.c.). The yellow precipitate was washed with water and crystallised from ethanol, yielding the *cyanoimide* (0.4 g., 67%), as yellow needles, m. p. 165° (decomp.) (Found: C, 66.2; H, 3.7; N, 30.1. C<sub>13</sub>H<sub>9</sub>N<sub>5</sub> requires C, 66.4; H, 3.9; N, 29.8%).

The cyanoimide (0.12 g.), in 12*N*-hydrochloric acid (3 c.c.), and stannous chloride (0.7 g.) were heated at 100° for 25 min. After cooling and dilution with water (9 c.c.), a precipitate was formed which crystallised from aqueous ethanol to give 2-phenylbenzotriazole as needles, m. p. 110° (lit.,<sup>13</sup> 109.5°) (Found: N, 21.1. C<sub>12</sub>H<sub>9</sub>N<sub>3</sub> requires N, 21.5%), λ<sub>max.</sub> 306 mμ (log ε 4.32 in MeOH) [lit.,<sup>14</sup> λ<sub>max.</sub> 310 mμ (log ε 4.48)].

1-Formamidino-2-phenylbenzotriazolium Benzenesulphonate (XVII).—To the cyanoimide (0.1 g.) in ethanol was added benzenesulphonic acid (0.2 g.). Evaporation, and recrystallisation of the residue from ethanol gave the *formamidine* (0.05 g., 30%) as orange prisms, m. p. 149—150° (decomp.) (Found: C, 57.9; H, 4.3; N, 17.7. C<sub>19</sub>H<sub>17</sub>N<sub>5</sub>O<sub>3</sub>S requires C, 57.7; H, 4.3; N, 17.7%).

5-Methyl-2-*p*-tolylbenzotriazole 1-Cyanoimide (XIII; R = Me).—A diazonium solution, prepared from 2-amino-5,4'-dimethylazobenzene (2 g.) as described above, was treated with sodium acetate (10 g.) and potassium cyanide (2 g.) in water (10 c.c.). The resulting precipitate was crystallised from ethanol to yield the *cyanoimide* (1.93 g., 82%) as yellow needles, m. p. 177° (decomp.) (Found: C, 67.9; H, 5.1; N, 26.6. C<sub>15</sub>H<sub>13</sub>N<sub>5</sub> requires C, 68.4; H, 5.0; N, 26.6%).

Reduction of the cyanoimide (0.6 g.), as described for 2-phenylbenzotriazole 1-cyanoimide, gave 5-methyl-2-*p*-tolylbenzotriazole (0.17 g.), plates (from ethanol), m. p. 125—126° (lit.,<sup>15</sup> 125—126°). The ultraviolet absorption (λ<sub>max.</sub> 313 mμ; log ε 4.14) is similar to that of 2-phenylbenzotriazole.

*syn*- (XVIII) and anti-*p*-Phenylazobenzenediazocyanide (XIX).—4-Aminoazobenzene (4 g.) in 6*N*-hydrochloric acid (16 c.c.) was treated with sodium nitrite (1.5 g.) in water (10 c.c.) at 5°. Ethanol (20 c.c.) was added and then, to the filtered solution, sodium acetate (4 g.) and potassium cyanide (3 g.) in water (10 c.c.). After 15 min., the precipitate was washed, and then recrystallised from ethyl acetate by brief warming followed by strong cooling. The *syn-cyanide* (2.5 g., 52%) formed yellow-brown needles, double m. p. 82—83° and 154—156° (decomp.) (Found: C, 66.4; H, 4.0; N, 30.1. C<sub>13</sub>H<sub>9</sub>N<sub>5</sub> requires C, 66.4; H, 3.9; N, 29.8%). On storage for some days the *syn*- is converted into the anti-*cyanide*, m. p. 154.5—156° (decomp.) (Found: C, 66.4; H, 3.8; N, 29.9%).

Phenyl *p*-(Phenylazo)benzenediazosulphone.—4-Aminoazobenzene (4 g.) in 6*N*-hydrochloric acid (16 c.c.) was treated with sodium nitrite (1.5 g.) in water (10 c.c.) at 5°, followed by ethanol (20 c.c.). The filtered solution was treated with benzenesulphonic acid (5.5 g.) and sodium acetate (4 g.) in water (20 c.c.). Crystallisation of the resulting precipitate from ethanol gave the *sulphone* (4.6 g., 65%), orange plates, m. p. 123° (decomp.) (Found: C, 62.0; H, 4.2; N, 16.5. C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>S requires C, 61.7; H, 4.0; N, 16.0%).

2-Phenylbenzotriazole 1-Benzenesulphonylimide.—2-Aminoazobenzene (0.27 g.), in ethanol (5 c.c.) and 12*N*-hydrochloric acid (0.7 c.c.), was diazotised with sodium nitrite (0.15 g.) in water (1 c.c.) at 5°. The solution was added dropwise to benzenesulphonic acid (0.3 g.) and sodium acetate (2.5 g.) in water (4 c.c.) at -10°. The resulting precipitate was collected and recrystallised rapidly from methanol, to give the *benzenesulphonylimide* (0.15 g., 31%) as yellow prisms, m. p. 84—85° (decomp.) (Found: C, 61.8; H, 4.1; N, 16.1. C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>S requires C, 61.7; H, 4.0; N, 16.0%).

<sup>12</sup> Ruggli and Cortin, *Helv. Chim. Acta*, 1932, **15**, 90.

<sup>13</sup> Witt, *Ber.*, 1912, **45**, 2381.

<sup>14</sup> Krollpfeiffer, Pötz, and Rosenberg, *Ber.*, 1938, **71**, 596.

<sup>15</sup> Zincke, *Ber.*, 1885, **18**, 3142.

When this was heated in ethanol for 5 min., nitrogen was evolved. On cooling, 2-(*phenylsulphonyl*)azobenzene (XXI) separated as red needles, m. p. 160—161° (Found: C, 67·2; H, 3·9; N, 8·5.  $C_{18}H_{14}N_2O_2S$  requires C, 67·1; H, 4·4; N, 8·7%).

5-Methyl-2-p-tolylbenzotriazole 1-Benzenesulphonylimide.—A diazonium solution from 2-amino-5,4'-dimethylazobenzene was treated with benzenesulphonic acid as described above. The *sulphonylimide* (95%) crystallised from methanol as yellow prisms, m. p. 102° (decomp.) (Found: C, 62·8; H, 4·7; N, 14·7.  $C_{20}H_{18}N_4O_2S$  requires C, 63·5; H, 4·8; N, 14·8%).

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