7. *Studies in the Diphenyl Series. Part IV. The Preparation and Properties of Substituted Diaminodiphenyls.*

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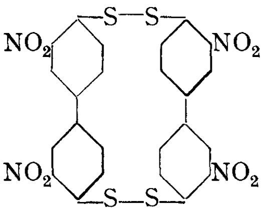
The chlorine atoms in 4 : 4′-dichloro-3 : 3′-dinitrodiphenyl (Hodgson and Walker, J., 1933, 1620) resist attack by sodium methoxide or ethoxide, but readily react with sodium disulphide, a very sparingly soluble *polysulphide* being formed, the molecular weight of which could not be determined; its analysis and properties, however, indicate the probable formula (I). The polysulphide was reduced readily to the dimercaptan, which was easily methylated to give 3 : 3′-*dinitro*-4 : 4′-*dimethylthioldiphenyl*, the reduction of which produced 3 : 3′-*diamino*-4 : 4′-*dimethylthioldiphenyl*. The latter compound and its 4 : 4′-*dimethoxy*-analogue gave rise to a series of bisazo-dyes with Schäffer, H-, and J-acids which exhibited definite but greatly reduced substantivity for cotton as compared with the isomeric 3 : 3′-disubstituted 4 : 4′-bisazo-compounds.



The isomeric 4 : 4′-*dichloro*-3 : 3′-, -2 : 3′-, and -2 : 2′-*diaminodiphenyls* likewise afforded substantive bisazo-dyes with the above intermediates, the affinity being in the above order, the 2 : 2′-disazo-compounds possessing only slight substantivity. Whereas the presence of azo-groups in the 4 : 4′-positions is therefore not essential for substantivity, they appear to promote it far more powerfully than when elsewhere in the molecule.

The melting point of 4 : 4′-*dimethylthioldiphenylene*-3 : 3′-*bisazo*-β-*naphthol* is 16° lower than that of its *dimethoxy*-analogue and indicates that chelation between the ortho-groups is strongest for the dimethylthiol derivative (cf. Hodgson and Handley, J., 1926, 542).

Experimental.

The Action of Sodium Disulphide on 4 : 4′-*Dichloro*-3 : 3′-*dinitrodiphenyl*.—The diphenyl (15 g.), boiled for 30 minutes under reflux with a mixture of alcohol (200 c.c.) and sodium disulphide (14·8 g.) dissolved in the minimum amount of water, afforded an insoluble yellow *polysulphide*, which did not melt at 340° but decomposed suddenly if rapidly heated to this temperature (cf. Blanksma, *Rec. trav. chim.*, 1901, **20**, 141, for the similar behaviour of 4 : 4′-dinitrodiphenyl disulphide). Prior to analysis it was extracted thoroughly with hot solvents in the following sequence : water, alcohol, benzene, carbon disulphide, and alcohol [Found : S, 21·0. $(C_{12}H_6O_4N_2S_2)_n$ requires S, 20·9%].

3 : 3′-*Dinitro*-4 : 4′-*dimethylthioldiphenyl*.—The polysulphide, suspended in alcohol (600 c.c.), was boiled under reflux for 5 minutes with sodium (4·6 g.) and the solution was filtered as rapidly as possible and shaken immediately with excess of methyl sulphate; 3 : 3′-*dinitro*-4 : 4′-*dimethylthioldiphenyl*, precipitated as a bright yellow solid, crystallised from glacial acetic acid in yellow clusters, m. p. 262° (Found : S, 19·2. $C_{14}H_{12}O_4N_2S_2$ requires S, 19·0), only slightly soluble in alcohol.

3 : 3′-*Diamino*-4 : 4′-*dimethylthioldiphenyl*.—(*a*) Reduction of the above nitro-compound with tin and concentrated hydrochloric acid afforded pale yellow crystals of the *stannichloride* of the base, m. p. 242° after recrystallisation from hot hydrochloric acid (Found : S, 10·6. $C_{14}H_{18}N_2S_2,SnCl_6$ requires S, 10·4%). (*b*) Reduction of the above nitro-compound with iron and aqueous acetic acid afforded a product, which was dried and extracted with benzene.

3 : 3′-*Diamino*-4 : 4′-*dimethylthioldiphenyl dihydrochloride*, precipitated from the extract by hydrogen chloride and recrystallised from hydrochloric acid, formed colourless needles, m. p. 228° (Found : Cl, 20·8. $C_{14}H_{16}N_2S_2,2HCl$ requires Cl, 20·4%). The *base* could not be crystallised from alcohol, benzene or glacial acetic acid, and its solubility in the hot and the cold liquids appeared to be the same, since only a white opalescence was discerned when saturated solutions were cooled to 0°; it was purified by repeated dissolution in dilute hydrochloric acid and fractional precipitation by aqueous ammonia until the m. p. 71° remained constant (Found : S, 23·4. $C_{14}H_{16}N_2S_2$ requires S, 23·2%). The base was readily tetrazotised and then coupled with alkaline β-naphthol to give 4 : 4′-*dimethylthioldiphenylene*-3 : 3′-*bisazo*-β-*naphthol*, which separated from glacial acetic acid in red micro-crystals, m. p. 318° (Found : S, 11·2. $C_{34}H_{26}O_2N_4S_2$ requires S, 10·9%).

3 : 3′-*Dinitro*-4 : 4′-*dimethoxydiphenyl*.—3 : 3′-Dinitro-4 : 4′-dihydroxydiphenyl (4 g.), prepared by Kunze's method (*Ber.*, 1888, **21**, 3331), was mixed with potassium carbonate (5 g.) and sufficient water to form a paste and heated on the water-bath with methyl sulphate (10 c.c.) until the red colour of the potassium salt had disappeared; repeated additions of potassium carbonate and methyl sulphate alternately were made until the mass was permanently yellow; it was then extracted with hot dilute sodium hydroxide solution and with hot water, dried (4 g.), and crystallised from glacial acetic acid; m. p. 214° (Found : N, 9·4. $C_{14}H_{12}O_6N_2$ requires N, 9·2%).

3 : 3′-*Diamino*-4 : 4′-*dimethoxydiphenyl*.—The above dinitro-compound (11 g.) was boiled under reflux for 4 hours with glacial acetic acid (33 c.c.) and water (33 c.c.), excess of iron powder being added gradually, the mixture made alkaline with ammonia, and the dried solids extracted with benzene. The procedure described for the isolation of the dimethylthiol analogue then gave 3 : 3′-*diamino*-4 : 4′-*dimethoxydiphenyl dihydrochloride* in colourless needles, m. p. 262° (Found : Cl, 22·1. $C_{14}H_{16}O_2N_2,2HCl$ requires Cl, 22·4%). The *base* had m. p. 195° (Found : N, 11·7. $C_{14}H_{16}O_2N_2$ requires N, 11·5%), its *diacetyl* derivative formed colourless crystals, m. p. 330°, from glacial acetic acid (Found : N, 8·6. $C_{18}H_{20}O_4N_2$ requires N, 8·5%), and 4 : 4′-*dimethoxydiphenylene*-3 : 3′-*bisazo*-β-*naphthol* formed red micro-crystals, m. p. 334° (Found : N, 10·3. $C_{34}H_{26}O_4N_4$ requires N, 10·1%).

4 : 4′-*Dichloro*-3 : 3′-*diaminodiphenyl*, prepared by refluxing 4 : 4′-dichloro-3 : 3′-dinitrodiphenyl (5 g.) for 2 hours with iron filings (7 g.) and 50% aqueous acetic acid (30 c.c.), the mixture being worked up as described above, crystallised from alcohol in colourless plates, m. p. 133·5° (Found : Cl, 28·0. $C_{12}H_{10}N_2Cl_2$ requires Cl, 28·1%).

4 : 4′-*Dichloro*-2 : 3′-*diaminodiphenyl*, similarly obtained from 4 : 4′-dichloro-2 : 3′-dinitrodiphenyl (Dennett and Turner, J., 1926, 477), crystallised from 30% aqueous acetic acid in colourless needles, m. p. 83° (Found : Cl, 28·2. $C_{12}H_{10}N_2Cl_2$ requires Cl, 28·1%). The *diacetyl* derivative crystallised from glacial acetic acid in colourless needles, m. p. 90° (Found : Cl, 21·0. $C_{16}H_{14}O_2N_2Cl_2$ requires Cl, 21·1%).

4 : 4′-*Dichloro*-2 : 2′-*diaminodiphenyl*.—2 : 2′-Dinitrobenzidine was prepared by Täuber's method (*Ber.*, 1890, **23**, 795) and converted into 4 : 4′-dichloro-2 : 2′-dinitrodiphenyl by the method of Hodgson and Walker (J., 1933, 1620). This on reduction gave the *diamine*, which formed faint brown micro-crystals, m. p. 87° (Found : Cl, 28·0. $C_{12}H_{10}N_2Cl_2$ requires Cl, 28·1%).

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