XXXIV.—*The Miscibility of Azobenzene and Azoxybenzene in the Solid State and the Supposed Existence of a Stereoisomeride of Azobenzene.*

By Harold Hartley and John McArthur Stuart.

In the preparation of azobenzene by the electrolytic reduction of nitrobenzene in aqueous alcohol containing sodium acetate with a nickel cathode a small quantity of a deep red liquid was occasionally obtained, which crystallised on keeping, giving radiating masses of orange, acicular crystals melting at 25°. It appeared to be identical with the substance obtained by C. V. and R. A. Gortner (*J. Amer. Chem. Soc.*, 1910, **32**, 1294) as a by-product in the preparation of azobenzene by the distillation of azoxybenzene with iron filings. The authors describe the by-product of this reaction as forming orange-red, stellate groups of needles, readily soluble in ether, light petroleum, alcohol, acetone, or methyl alcohol, and melting at 25° to a deep red liquid. Analysis gave N=15·35, azobenzene requiring N=15·38 per cent. They say, further: "It will not crystallise when seeded with the 68° substance (ordinary azobenzene), but in two instances we have succeeded in quantitatively transforming the 25° substance into the 68° substance, once by boiling with dilute hydrochloric acid, and in the other instance the cause of conversion is unknown to us. We can give no method which will always ensure conversion, nor have we been able to transform the 68° substance into the 25° modification. According to Holleman, the *syn*-modifications are the least stable, so it seems probable that the new compound is *syn*-azobenzene."

Attempts to discover the conditions which favoured the production of the substance of low melting point in place of ordinary azobenzene by the electrolytic method failed, as little of it was obtained. It was then found that carefully dried azoxybenzene when distilled with iron filings gave, as a rule, nothing but ordinary azobenzene; however, on moistening the azoxybenzene with alcohol, or, better still, with aniline, a considerable quantity of the product of low melting point was obtained. If aniline was used, the solution of the distillate in light petroleum was well washed with dilute hydrochloric acid before crystallisation. Various specimens gave melting points varying from 25·2° to 26°, and two nitrogen estimations gave 14·95 and 14·84 per cent. respectively, showing that the substance is not pure azobenzene, which contains 15·38 per cent. of nitrogen. The resemblance of the crystalline form to that of azoxybenzene, and the fact that the drops of the supercooled liquid crystallised if seeded with crystals of azoxybenzene, suggested that the orange crystals melting at 25° might be a solid solution of azobenzene in azoxybenzene. The results of determinations of the freezing-point and melting-point curves of mixtures of those two substances confirmed this conjecture. The freezing-point curve was determined in a Beckmann apparatus in the usual way, and the melting-point curve by allowing mixtures of known composition to crystallise slowly, and then finding the temperature at which melting begins when a thin-walled tube containing the mixture is slowly heated. The melting-point curve determined in this way is necessarily rough, and gives only an approximate estimate of the composition of the solid phase. The horizontal portion of the curve must pass through the eutectic point, but it will be noticed that the experimental points lie from 1° to 3° above it owing to the difficulty of deciding when melting has really begun to take place.

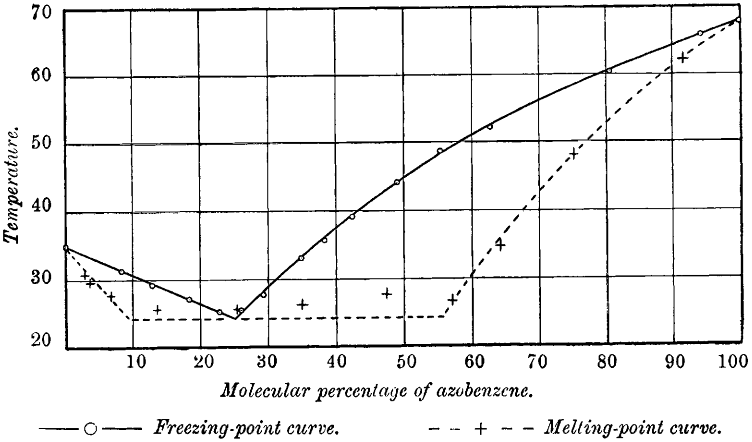
The experimental results are given below:

Molecular percentage of azobenzene.	Freezing point.	Molecular percentage of azobenzene.	Melting point.
0	35·0	0	35·3
8·3	31·3	2·9	30·9
12·9	29·3	3·6	29·6
18·2	27·1	6·9	27·8
22·6	25·3	13·5	25·6
25·9	25·5	25·2	25·7
29·1	27·8	34·8	26·4
34·8	33·1	47·3	27·7
38·1	35·8	56·9	26·8
42·4	39·2	64·0	34·6
48·9	44·1	75·0	48·0
55·1	47·7	91·5	62·1
62·6	52·2		
80·5	60·4		
94·1	65·8		
100·0	67·9		

The form of the diagram shows that the substances give two sets of mixed crystals with an eutectic temperature of 24·5°; at this temperature crystals of azoxybenzene can dissolve about 10 per cent. of azobenzene molecules, whilst those of the azobenzene dissolve about 45 per cent. of molecules of azoxybenzene.

The crystalline form of azoxybenzene has not been fully investigated. Bodewig (*Zeitsch. Kryst. Min.*, 1879, **3**, 411) measured the prism angle of the needles (87°32′), and from their optical properties described them as orthorhombic. The crystalline form of azobenzene has been examined by Calderon (*Zeitsch. Kryst. Min.*, 1880, **4**, 234), and by Boeris (*ibid.*, 1901, **34**, 301), who describes it as monoclinic with a prism angle of 55°3′, and axial ratios: $a:b:c=2\cdot1076:1:1\cdot3312$; $\beta=114^\circ26'$. The evidence is thus insufficient to decide whether there is any relationship between the normal crystalline structures of the two substances. Their miscibility in the crystalline state is probably similar to a number of instances noticed by Jaeger (*Zeitsch. Kryst. Min.*, 1907, **42**, 236), where the miscibility seems to depend, not on a relationship of crystalline form, but on the similar spacial structure of two molecules, for example, the miscibility of azobenzene and benzylaniline (Miss Isaac, *Proc. Roy. Soc.*, 1911, *A*, **84**, 344). Crystals produced by the crystallisation of mixtures of azobenzene and azoxybenzene from light petroleum appeared identical in every respect with the product of low melting point obtained by the electrolytic reduction of nitrobenzene or by distilling azoxybenzene with iron filings, and it seems certain that the substance obtained by C. V. and R. A. Gortner, and described by them as a new stereoisomeride of azobenzene, was a mixed crystal of azobenzene and azoxybenzene. Their analysis gave N = 15·35, the theoretical content for azobenzene being N = 15·38 per cent.; the specimens analysed above gave N = 14·95 and 14·84; the eutectic mixture would contain about 14·4 per cent. of nitrogen, so that the substance analysed probably contained some azobenzene.

The production of the mixed crystals, owing to the contamination of azobenzene by azoxybenzene, is easily explained in both processes where they have been obtained. In the distillation of azoxybenzene with iron filings the product of low melting point was only obtained in quantity when some volatile substance was present which carried over the azoxybenzene at a temperature below that at which it decomposes. In the electrolytic reduction, since azoxybenzene is a product of the reduction of nitrobenzene in alkaline solution, some will be present if the current is passed for an insufficient time to reduce it further. In the unsuccessful attempts to prepare the substance of low melting point by electrolytic reduction, on the assumption that it was a stereoisomeride of azobenzene, the current was always continued until reduction was complete.



Physical Chemistry Laboratory,
Balliol College and Trinity College, Oxford.