343. *The Suggested Identification of* cis-*Azobenzene with an Equimolecular Mixture of Hydrazobenzene and Azoxybenzene.*

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The mixture named in the title has been examined at 25° in benzene solution. It differs from *cis*-azobenzene in two important respects: (*a*) polarity measurements lead to an apparent moment of about 1·6 D. (in contrast to 3·0 D. for *cis*-azobenzene) and (*b*) illumination (daylight) causes only a very slight *increase* of dielectric constant (in contrast to the marked decrease already recorded for *cis*-azobenzene).

Hydrazobenzene and azoxybenzene do not appear to interact mutually under the conditions stated. The apparent moment observed for a mixture is of the order to be expected from that of each solute separately.

During the last few years Hodgson has several times indicated generally that he questions the existence of *cis*-azobenzene (cf. *J. Proc. R.I.C.*, 1947, 248; *Chem. and Ind.*, 1947, 774; 1948, 270, 428, 588). Recently a fuller exposition of his views has appeared (*J.*, 1948, 1097). Under the sub-title " A Critical Discussion of Some of the Properties of the Alleged *cis*-Azobenzene," he says (p. 1102) " . . . that a double compound of azoxybenzene and hydrazobenzene exhibits far more convincingly many of the reactions given by *cis*-[azobenzene]." This statement is the basis for the remainder of Hodgson's considerations.

The correctness of the underlying suggestion seems to us *a priori* unlikely. Among other measured physical properties, " *cis*-azobenzene " has a dipole moment in benzene solution of 3·0 D. units (Hartley and Le Fèvre, *J.*, 1939, 531). This is notably higher than the values for (ordinary) azoxybenzene (1·57 D., Calderbank and Le Fèvre, *J.*, 1948, 1949) or hydrazobenzene (1·79 D., present work) separately in the same solvent. Unless molecular compound formation takes place, therefore, it should be impossible for these two solutes together to simulate the *cis*-azobenzene with which we are familiar.

To investigate the last eventuality we have examined the dielectric constants and densities of two solutions containing equivalent quantities of azoxybenzene and hydrazobenzene.

Experimental.

These solutions had the following compositions: (*A*), 0·1527, 0·1678, and 92·023$_5$ g.; (*B*) 0·2982, 0·3256, and 83·857$_5$ g., of hydrazobenzene, azoxybenzene, and benzene respectively in each case. They were prepared, with exclusion of daylight, in brown glass bottles, from pure solutes and solvent which had been stored over sodium wire. Measurements were commenced forthwith. Apparatus and technique were as noted in *J.*, 1948, 1949. Table I displays the results (determined relatively to benzene, see Table II).

TABLE I.

	$\varepsilon_{25°}$ (before exposure).	$\varepsilon_{25°}$ (calc.).	$\varepsilon_{25°}$ (after exposure).	$d_{4°}^{25°}$ (before exposure).	$d_{4°}^{25°}$ (calc.).	$d_{4°}^{25°}$ (after exposure).
Soln. (*A*)	2·2792	2·2795	2·2805	$0·8745_4$	0·8745	$0·8744_9$
Soln. (*B*)	2·2873	2·2873	2·2887	$0·8754_8$	0·8753	$0·8754_3$

Discussion.—Densities and dielectric constants of dilute solutions of graded dilution can frequently be represented by the equations: $d_{12} = d_2(1 + \beta w_1)$ and $\varepsilon_{12} = \varepsilon_2(1 + \alpha w_1)$, where w_1 is the weight fraction of the solute in the total mixture and α and β are constants (cf. Le Fèvre, " Dipole Moments," 2nd Edn., Methuen, 1948, pp. 39—41). From Le Fèvre and Calderbank's observations on azoxybenzene, and our own on hydrazobenzene, values for α and β appropriate to the present problem are available. By taking first one solute and then the other with the benzene, weight fractions may be ascribed to each of the three components in (*A*) or (*B*), and ε_{12} or d_{12} expressed as $\varepsilon_2(1 + \alpha w_1 + \alpha' w'_1)$ or $d_2(1 + \beta w_1 + \beta' w'_1)$ respectively (see Table I).

The closeness of the figures so obtained (cols. 3 and 6) to those from experiment (cols. 2 and 5) indicates that each solute has contributed independently. A direct test of Hodgson's suggestion may be made by treating our data as a determination of the dipole moment of " *cis*-azobenzene." Then w_1 would be the fraction: total solute/total solution. Table II shows our measurements set out in conventional form.

TABLE II.

$10^6 w_1$	0	3471	7384	Mean $\alpha\varepsilon_2$ = 1·97
$\varepsilon_{25°}$	2·2725	2·2792	2·2873	Mean β = 0·257
$d_{4°}^{25°}$	0·87378	0·87454	0·87548	$_\infty P_1$ = 113·6 c.c.

whence, if $[R_L]_D$ = 59·2 c.c. (Auwers, *Ber.*, 1938, **71**, 611), $\mu = 1·6_2$ D.

These results should be contrasted with those of Hartley and Le Fèvre (*loc. cit.*), *viz.*,

	$\alpha\varepsilon_2$.	β.	$_\infty P_1$ c.c.	μ, D.
cis-Azobenzene	6·05	0·221	255·3	3·0
trans- ,, ...	0·51	0·192	67·4	*ca.* 0

It is quite evident therefore that, in polar properties, the mixture of azoxy- and hydrazo-benzene does not resemble *either cis-* or *trans*-azobenzene.

An important characteristic of solutions of both the forms of azobenzene (Hartley and Le Fèvre, *loc. cit.*) is the action on them of daylight. Thus in sodium-dried benzene, the *same* equilibrium mixture can be produced from solutions initially containing only one of the separate varieties. Further, if a photo-equilibrated mixture is kept in the dark, it slowly becomes wholly of *trans*-content. Re-illumination can reproduce the equilibrium, etc. Because of the substantial differences (just quoted) in $\alpha\varepsilon_2$ for the *cis*- and *trans*-isomers, the processes can be detected easily and followed kinetically *via* the dielectric constants of the solutions. The same phenomena occur in solvents other than benzene (*e.g.*, " sodium-dry " ligroin, compare Hodgson, *loc. cit.*, p. 1102). For these reasons, therefore, we have submitted (*A*) and (*B*) to the test of exposure for 1 hour to sunlight, transferring them to clear glass flasks for the purpose. (At this stage it was obvious for the first time that the mixture was a pale yellow—quite unlike an azobenzene solution.) Redetermination then gave the figures in cols. 4 and 7 of Table I. The solutions became permanently deeper in colour. It will be seen that the dielectric constants *did not fall* as they should have done had the solute been authentic *cis*-azobenzene.

Two explanations are possible for the very slight increases actually obtained. The first is that some loss of benzene during the handling of the solutions from brown bottle to flask, through exposure, to condenser, etc., is unavoidable. The second is that we have found azoxybenzene of m. p. 38°, dissolved in dry benzene, itself to show a small increment of ε_{12} under parallel treatment. Thus a solution of w_1 = 0·0504 had $\varepsilon_{25°}$ = 2·2774 before, and 2·2925 after, irradiation by direct sunlight. The increment—as with our mixtures of hydrazo- and azoxy-benzene—did not decay in the dark and was accompanied by a visible reddening. As to the latter, the literature records that ultra-violet light can bring about the formation from azoxybenzene of *o*-hydroxyazobenzene (Knipscheer, *Rec. Trav. chim.*, 1903, **22**, 1; cf. Cumming and Ferrier, *J.*, 1925, **127**, 2374, who report it also in benzene solution).

Melting Points of Mixtures of Hydrazo- and Azoxy-benzene.—An attempt to record a fusion point curve was abandoned when it became evident that approximately 50 : 50 mixtures became fluid at room temperatures. We therefore rubbed together accurately weighed equimolecular proportions and observed liquefaction to be complete at *ca.* 20° with considerable softening from 15° onward. Since the m. p.s concerned are hydrazobenzene, 131°, azoxybenzene, 35°, *cis*-azobenzene, 71°, and *trans*-azobenzene, 68°, the non-identity of Hodgson's " double compound " with *cis*-azobenzene is clear.

Dipole Moment of Hydrazobenzene.—This has been given by Audrieth, Nespital, and Ulich (*J. Amer. Chem. Soc.*, 1933, **55**, 673) as 1·53 D., and by Cowley and Partington (*J.*, 1933, 1252) as 1·66 D. We have made a re-determination in order to secure α and β values on a weight fraction basis for use in this paper:

$10^6 w_1$	0	3288·7	5753·5	12439
$\varepsilon_{25°}$	2·2725	2·2803	2·2864	2·2982
$d_{4°}^{25°}$	0·87378	0·87448	0·87504	0·87646

whence mean $\alpha\varepsilon_2$ = 2·28, mean β = 0·247, and $_\infty P_1$ = 126·3 c.c. If $[R_L]_D$ = 60 c.c., then μ = 1·79 D.

This moment is higher than either of the two previously recorded values, but since (*a*) we have merely assumed the refractivity of hydrazobenzene to be 2 × R_{aniline} minus 2 × R_{H}, and (*b*) our solutions were only about one-tenth of the concentration of those of the other authors, we do not think the difference is significant at this stage; in any case it does not affect the main contention of this paper.

General Note.—Water would presumably be necessary to produce Hodgson's mixture from *trans*-azobenzene. We do not think it can enter seriously during our experiments. These always start with benzene standing over dry sodium. We have examined successfully, by the same technique, solutions of such solutes as carbon suboxide (*J.*, 1935, 1696) and diphenylketen (unpublished) which absorb water avidly. Further, if *cis*-azobenzene were as Hodgson suggests, during the (dark) reversion to the *trans*-form, water would be produced. Now the dielectric constant of the latter is *ca.* 80 and its effect on benzene is known (Williams, *J. Amer. Chem. Soc.*, 1930, **52**, 1831). Yet the final dielectric constants observed during the *cis*- to *trans*-transformation are equal to the ε values of freshly prepared *trans*-azobenzene solutions, and are evidently correct since they lead to polarisations close to the expected refraction figures (Hartley and Le Fèvre, *loc. cit.*). If, in fact, a half equivalent of water were present, the apparent polarisations would notably exceed the calculated molecular refractions. Further, we note that the literature mentions the reaction $Ph{\cdot}N_2O{\cdot}Ph + Ph{\cdot}NH{\cdot}NHPh = 2Ph{\cdot}N{:}NPh + H_2O$ as only occurring in the presence of reagents (such as alcoholic potash, Freundler, *Bull. Soc. chim.*, 1094, **31**, 459), not spontaneously in anhydrous media at ordinary temperatures. Effects of ultra-violet light may, of course, enter, but that the situation might not then be uncomplicated is suggested, *e.g.*, by the photolysis of azobenzene in aqueous alcohol mixtures (Fukushima, Horio, and Ohmori, *J. Soc. Chem. Ind. Japan*, 1932, **35**, 398) which, in the presence of zinc oxide and the absence of oxygen, produce hydrazobenzene quantitatively, but which, if oxygen is admitted, show no detectable change.

Finally, we mention that our views on other aspects of –N=N– stereochemistry raised by Hodgson's " reaffirmation " paper have been put forward in *Chemistry and Industry*, 1948, 158, 543, 732, 782, and in recent papers with Northcott (this vol., pp. 333, 944) and Wilson (*ibid.*, p. 1106).

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