119. *The Dipole Moments of* cis- *and* trans-*Azobenzenes and of Some Related Compounds.*

By G. S. HARTLEY and R. J. W. LE FÈVRE.

The measurements recorded in this paper show: (1) that *cis*- and *trans*-azobenzenes have moments of 3·0 D. and zero respectively, and that from either form in benzene solution at ordinary temperatures an equilibrium, containing 22% of the *cis*-modification, is produced by illumination with sunlight; (2) that the known *p*-azotoluene is the *trans*-form, which—similarly to azobenzene—is partly converted into its *cis*-variety in sunlight; and (3) that, under the conditions which suffice to isomerise azobenzene and azotoluene, benzene- and toluene-azo-β-naphthols are unchanged.

These conclusions, drawn from dielectric-polarisation data, are in agreement with those previously reported by Hartley (J., 1938, 633), obtained by using other methods.

THE dielectric polarisation measurements recorded in the following three sections have been made in benzene solution at 25°, the apparatus and method detailed in "Dipole Moments" (Methuen, 1938, pp. 29—35) being used. They are tabulated below, together with brief descriptions of the conditions under which they were obtained.

The symbols used denote the following quantities: w_1 the weight fraction of the solute in a solution, ε the dielectric constant of the solution at a frequency *ca.* 1200 kc., d the density of the solution compared with water at 4°, p the specific polarisation of the solution, and ${}_{\mathrm{T}}P_{\infty}$ the total polarisation of the solute at infinite dilution. The results are worked out on the assumption that the densities and dielectric constants of a series of solutions have rectilinear dependence upon the concentration, *i.e.* (subscripts 1 and 2 being used to denote solute and solvent respectively), $d = d_2(1 + \beta w_1)$ and $\varepsilon = \varepsilon_2(1 + \alpha w_1)$. In the present cases this treatment is justified by the constancy of the products $\alpha\varepsilon_2$ and βd_2. The specific polarisation of a substance at infinite dilution is then obtained from the equation $p_{\infty} = p_2(1 - \beta) + C\alpha\varepsilon_2$, where $p_2 = (\varepsilon_2 - 1)/(\varepsilon_2 + 2)d_2$ and $C = 3/d_2(\varepsilon_2 + 2)^2$. The observations which follow were made at various times during the last 18 months, and in consequence slightly different samples of benzene have been used. For convenience in presentation, the data have been adjusted to correspond with a specimen of solvent for which $p_2 = 0{\cdot}34086$ c.c., $C = 0{\cdot}18809$, $\varepsilon = 2{\cdot}2725$, and $d = 0{\cdot}87378$. Where M is the molecular weight of the solute, the total molecular polarisation at infinite dilution is given by ${}_{\mathrm{T}}P_{\infty} = Mp$ c.c.

TABLE I.

Dielectric-polarisation Data for the Azobenzenes.

$100w_1$.	ϵ.	d.	$\alpha\epsilon_2$.	βd_2.	$100w_1$.	ϵ.	d.	$\alpha\epsilon_2$.	βd_2.
(A) Solutions of the pure *trans*-form were made up in opaque or brown glass bottles and examined as far as possible in the absence of daylight.									
0·9086	2·2771	0·87531	0·506	0·1684	1·1160	2·2782	0·87566	0·506	0·1681
1·1054	2·2781	0·87564	0·505	0·1679					
(B) Solutions of the pure *trans*-form were made up in ordinary glass flasks and the measurements conducted at once without any special precautions or departures from the normal routine for light-insensitive substances.									
0·3942	2·2749	0·87445	0·609	0·1700	1·5974	2·2837	0·87654	0·701	0·1728
1·5644	2·2828	0·87647	0·658	0·1720					
(C) Solutions of the pure *cis*-form were examined as in (A).									
0·80945	2·3222	0·87536	6·140	0·1952	1·1047	2·3401	0·87592	6·124	0·1940
1·0390	2·3346	0·87576	5·977	0·1906					
(D) The following observations relate to the above solutions after they had been exposed to bright sunlight for several hours in plain, white-glass flasks.									
0·9086	2·2888	0·87540	1·794	0·1782	0·3942	2·2798	0·87447	(1·8518)	0·1750
1·1054	2·2918	0·87570	1·748	0·1736	1·5644	2·2996	0·87649	1·738	0·1732
1·1160	2·2920	0·87573	1·749	0·1745	1·5974	2·3006	0·87656	1·759	0·1740
0·8095	2·2864	0·87521	1·721	0·1765	1·1047	2·2913	0·87574	1·702	0·1774
1·0390	2·2898	0·87562	1·670	0·1771					

1. cis- *and* trans-*Azobenzenes and their Photochemical Equilibrium in Benzene Solution.*—The measurements in this section were made with specimens of *cis-* and *trans*-azobenzene prepared by one of us (Hartley, *Nature*, 1937, **140**, 281; J., 1938, 633). For details and m. p.'s, the second reference may be consulted.

It is of interest that the earlier dipole-moment determinations for azobenzene, made, before the *cis*-isomeride was discovered, by Bergmann, Engel, and Sandor (*Ber.*, 1930, **63**, 2572), agree well with the measurements set out in (A), notwithstanding that these authors do not mention any precautions against light. Our work under ordinary laboratory conditions has always led to results of which the three in (B) are samples. This point has been the subject of previous comment (*Chem. and Ind.*, 1938, **57**, 255).

In Table II are given the apparent dipole-moment values indicated by the figures of paragraphs (A)—(D), combined with an estimate of 67 c.c. for the distortion polarisation of both forms of azobenzene. This figure is taken from the total polarisations obtained in the first set of measurements above, and should therefore include a fuller correction for atomic polarisation than would the Na-*D* line refraction—the recorded values for which are all lower : Duval (*Compt. rend.*, 1911, **153**, 875) gives $[R_L]$ for the Li line, $\lambda = 670{\cdot}5$, as 62·28 c.c.; Auwers and Heimke (*Ber.*, 1928, **61**, 1030) give $d_{4^\circ}^{78\cdot1^\circ}$ 1·0362 and $n_{\alpha}^{78\cdot1^\circ}$ 1·62662, whence $[R_L]_{\alpha}$ is 62·22 c.c.; recently, Auwers (*Ber.*, 1938, **71**, 611) has reported for solutions of *cis-* and *trans*-azobenzenes in quinoline and α-methylnaphthalene $[R_L]_{\mathrm{D}}$ 59—60 c.c. and 63—64 c.c. respectively. The refraction calculated from the sum of the appropriate atomic and constitutive refractions is of the order 57 c.c. (Auwers, *loc. cit.*, 1938). If a distortion polarisation of 63 c.c.—instead of 67 c.c.—is taken for *cis*-azobenzene, μ is raised from 3·02 to 3·05.

TABLE II.

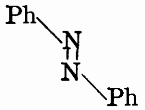
The Apparent Dipole Moments calculated from the Above Data.

	Mean $\alpha\epsilon_2$.	Mean β.	p_∞.	$_{\mathrm{T}}P_\infty$, c.c.	μ, D.
(A)	0·506	0·1924	0·3704	67·4	0
(B)	0·656	0·1964	0·3973	72·3	0·4
(C)	6·047	0·2212	1·4029	255·3	3·0
(D)	1·735	0·2008	0·5987	109·0	1·4

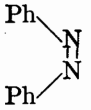
Hartley (*loc. cit.*) has already referred to the significance of the final μ values, which entirely justify his allotment of configurations between the two forms; further confirmation may be found in the density measurements of this paper : generally, the density of a *trans*-isomer is less than that of a *cis*-, and this is true even for solutions under comparable conditions of concentration and temperature (cf. examples among the aromatic diazocyanides, J., 1938, 431); for the two azobenzenes we find mean β values of 0·1924 and 0·2212 (Table II), *i.e.*, these are the *trans*- and the *cis*-variety respectively.

The case of azobenzene has an interesting resemblance to that of azoxybenzene, interconvertible labile (m. p. 81°) and stable (m. p. 36°) forms of which have been known for some years (cf. Reissert, *Ber.*, 1909, **42**, 1367), and whose configurations have recently been demonstrated by their dipole moments (Gehrckens and Müller, *Annalen*, 1933, **500**, 296), *viz.*, 4·67 and 1·70 D respectively. The former is therefore the *cis*-isomeride, and these moments—differing by roughly the same amount as do the corresponding values for the two azobenzenes—show clearly the similarities between the spatial configurations of the Ar–N=N–Ar skeletons in the appropriately related pairs of azo- and azoxy-substances (I) and (II).

(I.)

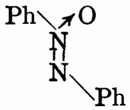


M.p. = 68°; $\mu = 0.$

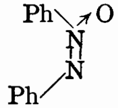


M.p. = 71°; $\mu = 3{\cdot}0.$

(II.)

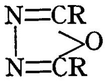


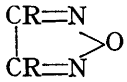
M.p. = 36°; $\mu = 1{\cdot}7.$



M.p. = 81°; $\mu = 4{\cdot}7.$

These differences of *ca.* 3 D. seem large but would be explicable if the C_6H_5–N system were to have an effective moment of 2·0 D. (*i.e.*, if in *cis*-azobenzene the two C_6H_5–N axes are mutually inclined at 80°; cf. Le Fèvre and Vine, J., 1938, 431). Unfortunately, data from which carbon–nitrogen link moments can be calculated are few. By analogy with carbon–oxygen links, raising the multiplicity should increase the link moment, and this seems to be the case from Milone's results (*Gazzetta*, 1935, **65**, 152) for a number of 1 : 3 : 4- (III) and 1 : 2 : 5-oxadiazoles (IV) which were found to have the high values indicated.


(III; μ = 3·3—3·9 D.)


(IV; μ = 4·0—4·7 D.)

The Photochemical Equilibrium between the two Azobenzenes.—The data in line (D) of Table II are the average of those obtained from solutions, initially containing pure *cis*- or pure *trans*-azobenzene, which were allowed to attain equilibrium by exposure to daylight. This process has been discussed by Hartley (*loc. cit.*), who showed that, at ordinary temperatures and light intensities, the position of equilibrium is determined almost entirely by the relative velocities of the two photochemical reactions, *cis* $\longrightarrow$ *trans* and *trans* $\longrightarrow$ *cis*, and scarcely at all by the (slow) thermal *cis* $\longrightarrow$ *trans* inversion.

From the figures of Table II a calculation of the equilibrium concentrations in benzene can be made. In a solution containing two solutes, a mixture rule can often be applied to the measured orientation polarisations, or—what amounts to the same thing—to the squares of the respective dipole moments. Thus, from the apparent moment of the equilibrated solution, the zero moment of the *trans*-component and the large moment of the *cis*-component, the composition at equilibrium is found to 22% *cis*- and 78% *trans*-. Hartley (*loc. cit.*), using a photometric method (the absorption band of azobenzene in the blue end of the visible spectrum being about 2½ times more intense in the *cis*-form), found 25% of *cis*-form in acetone and 24% in glacial acetic acid. A greater variation than this, however, is found if a wider solvent range is examined; *e.g.*, the *cis*-contents in 25% acetone–water and heavy paraffin respectively are 40% and 15% (Hartley, unpublished data).

2. p-*Azotoluene.*—For the following experiments a sample, m. p. 144—145° (after recrystallisation successively from acetone and petrol in a darkened room) was used. The results are in Table III.

TABLE III.

Dielectric Polarisation Data for p-*Azotoluene.*

$100w_1$.	ϵ.	d.	$d\epsilon_2$.	βd_2.	$100w_1$.	ϵ.	d.	$d\epsilon_2$.	βd_2.
(E) Solutions were made up as in (A) (Table I).									
2·6510	2·2866	0·87806	0·532	0·161	3·8015	2·2927	0·87992	0·531	0·161
3·7832	2·2927	0·87988	0·534	0·161					
(F) The above solutions were exposed to sunlight for 2 hrs. in plain glass flasks and re-examined forthwith.									
2·6510	2·2962	0·87807	0·899	0·162	3·8015	2·3070	0·88001	0·908	0·164
3·7832	2·3064	0·87990	0·896	0·162					

A direct measurement on the strongest solution of set (E) showed $[R_L]_D$ = 77—78 c.c.; this compared satisfactorily with the corresponding datum for azobenzene, so 78 c.c. was used in calculating the moments given in Table IV. The differences caused by illumination are less in this case than with *trans*-azobenzene; this is unexpected, for by analogy the effect of the two $CH_3 \longrightarrow C$ vectors in the 4 : 4′-positions should be to raise the resultant moment of the *cis*-modification above that of *cis*-azobenzene by perhaps 0·5 D. The above data, however, clearly show that *p*-azotoluene has a moment approach-

TABLE IV.

Apparent Dipole Moments calculated from the Data of Table III.

	Mean $\alpha\epsilon_2$.	Mean β.	p_∞.	${}_TP_\infty$.	μ, D.		Mean $\alpha\epsilon_2$.	Mean β.	p_∞.	${}_TP_\infty$.	μ, D.
(E)	0·532	0·1843	0·378	79·4	*ca.* 0	(F)	0·901	0·1865	0·447	93·9	0·9

ing zero, which increases when sunlight acts upon the substance. The known *p*-azotoluene is therefore the *trans*-form, which must be non-polar from symmetry considerations.

In the absence of knowledge of the moment of the pure *cis*-form no estimate of the equilibrium proportions can be made with certainty, but if the reasonable figure for μ_{cis} of 3·5 D. be assumed, then since μ_{trans} is 0 D., and $\mu_{\text{equil.}}$ is 0·9 D., the equilibrium *cis* : *trans* ratio is 7 : 93—notably different from the analogous results for the azobenzenes. That this result is of the correct order has been shown by solubility determinations : toluene at 0°, shaken with *p*-azotoluene in the dark until saturated, was found to contain 0·0167 g. per g. of solution, whereas the corresponding value with fresh solvent in daylight was 0·0188 g. Hence, the *cis*-form constitutes 11·2% of the equilibrium mixture.

3. *Benzene- and Toluene-azo-β-naphthols.*—Hartley (*loc. cit.*) found a number of derivatives of azobenzene to behave qualitatively like their parent when exposed to light in various solvents, but in all cases the rates of *cis* ⟶ *trans* thermal reversion were very much higher, most notably so with the 4-hydroxy-derivative. An explanation was advanced attributing this to the existence in non-ionising solvents of the uncharged molecules of these substances in a mesomeric state for which contributing structures can be formulated having in common the feature of a single link between the two azo-nitrogen atoms, the net result of which is to diminish, in the real form, the resistance of the molecule to internal rotation about the N–N axis.

The measurements in Table V refer to benzene- and toluene-azo-β-naphthols; those taken after illumination are not shown because in no case has any evidence of change of benzene solutions been detected dielectrically. This means that *if* a photochemical inversion occurs the thermal inversion at 25° is complete within about 1½—2 minutes, *i.e.*, the minimum time required to make a dielectric-constant reading on a solution which at zero time is at some distance from the apparatus.

The materials were prepared by direct coupling of the necessary components and recrystallised from hot acetic acid; m. p. 133—134° and 134—135° respectively.

Table V.

Dielectric Polarisation Data for Benzene- and Toluene-azo-β-naphthols.

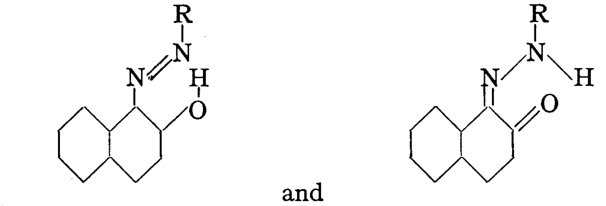
(G) *Benzeneazo-β-naphthol.*					(H) p-*Tolueneazo-β-naphthol.*				
$100w_1$.	ϵ.	*d*.	$\alpha\epsilon_2$.	βd_2.	$100w_1$.	ϵ.	*d*.	$\alpha\epsilon_2$.	βd_2.
0·2434	2·2762	0·87441	1·54	0·260	0·3449	2·2781	0·87469	1·64	0·264
0·3106	2·2772	0·87457	1·52	0·255	0·4906	2·2797	0·87500	1·45	0·249
0·3228	2·2774	0·87460	1·53	0·254	0·5010	2·2805	0·87508	1·60	0·259

The distortion polarisations of these solutes were estimated from the following figures for Na line refractions : Benzene, 26·2 c.c.; toluene, 31·1 c.c.; α-naphthol, 46·3 c.c.; hydrogen, 1·1 c.c.; nitrogen, 2·21 c.c.; increment for the diazo-linkage, 3·13 c.c.. The dipole moments calculated therewith are shown below.

Dipole Moments of Benzene- and Toluene-azo-β-Naphthols.

	Mean $\alpha\epsilon_2$.	Mean β.	p_∞.	${}_{\text{T}}P_\infty$.	μ, D.		Mean $\alpha\epsilon_2$.	Mean β.	p_∞.	${}_{\text{T}}P_\infty$.	μ, D.
(G)	1·53	0·293	0·529	131	1·60	(H)	1·56	0·294	0·534	140	1·66

Incidentally, these measurements tend to support Auwers's opinion (*Annalen*, 1908, **360**, 18) that azo-dyes of these types, although sometimes easily prepared from quinones and arylhydrazines, are, in fact, better formulated as azo-compounds than as quinone-



Real form

phenylhydrazones (cf., *e.g.*, Zincke and Bindewald, *Ber.*, 1884, **17**, 3032), since the dipole moment values found are much more nearly of the order to be expected for a simple phenol than for a molecule in which two relatively large group moments ($\mu_{C=N}$ and $\mu_{C=O}$) are compounded in the same sense in the resultant. A likely possibility already cited, however, would seem to be that these compounds are mesomerides, towards which the quinone-hydrazone structure makes normally but a small contribution; such an explanation would require the groups at the ends of the doubly-linked nitrogen atoms to be in the more stable *trans*-relation to one another. This is an arrangement which is strongly indicated also by the evident relation with the *o*-hydroxyazo-mordant dyes (Pfeiffer, *J. pr. Chem.*, 1930, **126**, 108; Sidgwick, " The Electronic Theory of Valency," p. 234).

THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON.

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