120. *Dielectric Polarisation Data for the Allegedly Isomeric 4 : 4'-Dihydroxyazobenzenes of Willstätter and Benz.*

By I. DOSTROVSKY and R. J. W. LE FÈVRE

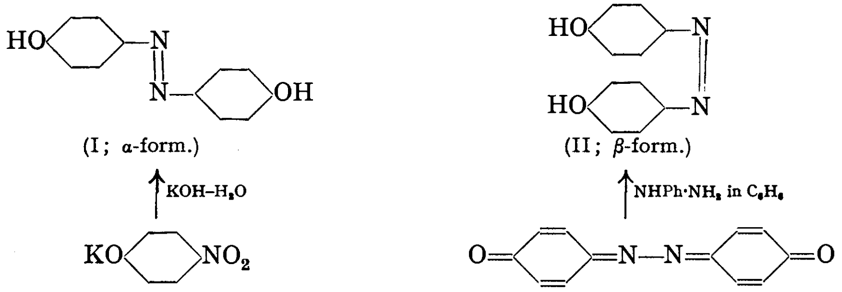
Willstätter and Benz (1906—1907) found that the *p*-azophenol obtained by reducing *p*-nitrophenol or by coupling *p*-hydroxydiazobenzene salts with phenol was different from the isomeride formed by reduction of benzoquinoneazine. Hantzsch (1910) suggested that these varieties were homochromoisomerides for which a *cis-trans* relationship was fundamentally responsible.

It is now shown that the dipole moments of these forms are almost identical in dioxan solution, a result which makes such an explanation seem less likely to be correct. No definite conclusion can be stated, however, because, owing to the natures of the dipolar groups involved, an accidental coincidence of moment values between *cis-* and *trans*-azophenols would not appear to be impossible.

p-AZOPHENOL exists in two forms, termed α and β, having many distinct properties, such as colour and solubility in common solvents (Willstätter and Benz, *Ber.*, 1906, **39**, 3492; 1907, **40**, 1578). They are prepared respectively (i) by direct coupling or by fusing *p*-nitrophenol with potassium hydroxide and a little water, and (ii) by the reduction of benzoquinoneazine, by means of sulphur dioxide or phenylhydrazine in benzene solution. They crystallise unchanged from a number of solvents and are recoverable nearly quantitatively from aqueous solutions of their potassium or sodium salts. For such reasons Hantzsch (*Ber.*, 1910, **43**, 2512) concluded that they were not chromoisomers (like the yellow and red nitroanilines, whose differences disappear in the dissolved state) but examples of homochromoisomerism in which some stereochemical relationship is involved. He found that their absorption spectra in alcohol or ether were the same, a fact which was consistent with his explanation, since—in the visible regions at least—geometrical isomers have similar spectra (Hantzsch, *Ber.*, 1910, **43**, 1662; Le Fèvre and Vine, J., 1935, 431). Willstätter and Benz (*loc. cit.*) originally gave the m. p.'s as α, m. p. 215°, and β, m. p. 212°, with a transition from β ⟶ α at the latter temperature. Robertson (J., 1913, **103**, 1472, 1475) states that both melt at 216—218° and records two chemical contrasts : (*a*) that they show different results on nitration under identical conditions (the α-azophenol giving a tetranitro-, and the β only a dinitro-, derivative), and (*b*) that they give, by direct halogenation, two tetrabromoazophenols, m. p. 252° and 271°, respectively.

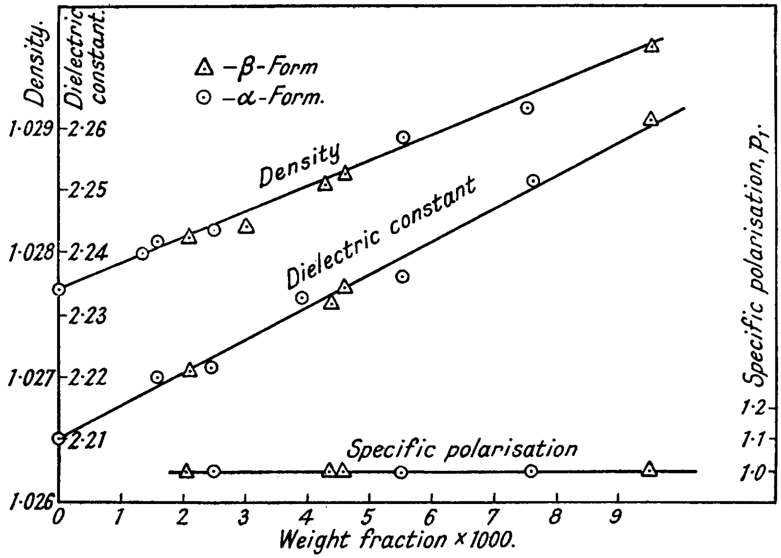
Hantzsch (*loc. cit.*) had allocated to the α-form a *trans-* (I) and to the β- a *cis*-configuration (II). These substances formed the only possible case of genuinely geometrically isomeric azobenzene derivatives prior to the discovery of a second variety of azobenzene itself by Hartley (*Nature*, 1937, **140**, 281; J., 1938, 633); earlier claims had been made—*e.g.*, by Janovsky (*Monatsch*, 1889, **10**, 583) for two trinitroazotoluenes, and by Gortner and Gortner (*J. Amer. Chem. Soc.*, 1910, **32**, 1294) for two azobenzenes, m. p.'s 68° and 25°—but these were explained (Hartley and Stewart, J., 1914, **105**, 309) as complications arising from the occurrence of position isomerides in the first case and of mixed crystals of azo- and azoxy-benzenes in the second.

We therefore thought it of interest to examine the dipole moments of these two forms, since—if they are geometrically isomeric—their polarities *might* differ sensibly. The results have been inconclusive, however, for the apparent moments in dioxan solutions (the only non-polar solvent which sufficiently dissolves both forms) appear to be practically identical, and both of the order to be expected for the *trans*-modification. In this connexion it should be noted that a precise forecast of the moments of both the *cis*- and the *trans*-structures is made difficult by the presence of the hydroxyl groups, which have an angular configuration and consequently a resultant moment which is *not* coincident with the N—Ar bond direction. The occurrence of intramolecular rotation of such groups thus makes possible an infinitude of relative orientations corresponding to molecular resultant moments lying between some high maximum (? *ca.* 3 D.) and zero.


(I; α-form.)

(II; β-form.)

p Azophenol-Dioxan.



Experiment affords an average value; this—since μ is zero for both *trans*-azobenzene and benzene—can be anticipated as of the same order of magnitude as that of quinol (*viz.*, 2·5 D.) in which there are similarly two opposed hydroxyls. Our measurements confirm this. The case of *cis*-azophenol is less certain; for although the moments of catechol and *cis*-azobenzene are known (2·2 and 3·0 respectively), no information exists as to the effective direction of action of the resultant in the former molecule. Hence all that can be said is that *cis*-azophenol will have a moment within the range 3 ± 2 D.

Although the closeness of our final moment values, therefore, *cannot eliminate* the possibility that these preparations are geometrically isomeric, yet we would draw attention to the underlying experimental quantities. These are illustrated in the figure, which shows densities and dielectric constants for both preparations plotted against concentrations. It is seen that the appropriate curves are superposed; this, if the solutes *are* different, is an unprecedented coincidence among dipole-moment studies of geometrical isomerism.

EXPERIMENTAL.

Measurements.—These were made in dioxan solution at 25° and are recorded under the headings: w_1 (weight fraction) × 1000, ε (dielectric constant), d (density $^{25^\circ}_{4^\circ}$), and p_{12} (specific polarisation of the solution). From the last quantity the specific polarisations of the solutes have been evaluated by the mixture rule, $p_1 = p_2 + (p_{12} - p_2)/w_1$, and are shown graphically in the figure.

α-Form (green).

$1000w_1$	0	1·594	2·4745	3·912	5·5016	7·628
ϵ	2·2106	—	2·2218	2·2331	2·2365	2·2470
d	1·02772	1·02810	1·02819	—	1·02895	1·02913
p_{12}	0·27976	—	0·28146	—	0·28364	0·28528

β-Form (red).

$1000w_1$	2·0735	3·0124	4·357	4·5626	9·514
ϵ	2·2212	—	2·2321	2·2349	2·2572
d	1·02813	1·02820	1·02854	1·0286	1·02967
p_{12}	0·28138	—	0·28305	0·28347	0·28680

From these data the factors $\Sigma(p_{12} - p_2)/\Sigma w_1$ are: 0·71 for the α-form and 0·76 for the β; the total molecular polarisations are therefore 212 and 222 c.c. respectively. If a distortion polarisation of 72 c.c. be assumed (from azobenzene, 68 c.c.; hydroxylic oxygen, *ca.* 1·5 c.c.) the apparent moments become: α-azophenol, μ = 2·60 D.; β-azophenol, μ = 2·69 D.

Materials.—The α- and β-azophenols were prepared exactly as by Willstätter and Benz (*loc. cit.*). Analytically they were not absolutely identical, the α-variety affording lower data for C and H than the β-; our results are given below, together with the only C and H analysis reported by the German authors:

	Found (D. and Le F.).		Found (W. and B.).		Calc.	
	C, %.	H, %.	C, %.	H, %.	C, %.	H, %.
α-Azophenol	67·0	4·64	—	—	67·2	4·70
β-Azophenol	67·6	4·81	67·6	4·82		

Various properties described in the literature have been checked. In particular, we are indebted to Dr. G. S. Hartley for examining the *relative* extinction coefficients of the two forms in dilute solution in methyl alcohol and acetone. They were approximately the same in both solvents for violet, blue, and green light, with the β-form showing a slightly greater coefficient in the green. In the blue, both substances absorb about 14 times as strongly as azobenzene. It is thus likely that the absorption spectra of both varieties in these solvents are similar, as was found to be the case (Hantzsch, *loc. cit.*, 1910) for solutions in ethyl alcohol or ether.

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

[*Received, January 25th,* 1939.]