989. *Physical Properties and Chemical Constitution. Part XLIII.* The Electric Dipole Moments of Azobenzene, Azopyridines, and Azoquinolines*

By D. J. W. BULLOCK, C. W. N. CUMPER, and A. I. VOGEL

The electric dipole moments of *cis*- and *trans*-azobenzene, two *cis*- and three *trans*-azopyridines, and of five azoquinolines have been calculated from measurements of the dielectric constants, specific volumes, and refractive indices of their solutions in pure benzene at 25·00°. Of the azoquinolines, only the 6,6′-isomer showed any change in its dipole moment after exposure to ultraviolet light. The conformations of the various molecules in solution are discussed.

THE electric dipole moments of azobenzene [1] and of the azopyridines [2] have been measured previously. That reported [2] for 4,4′-azopyridine (2·0 D) seems exceptionally high, and merits further investigation, but in any case the results have only been employed in discussing *cis–trans* isomerism. Equally interesting are the conformations of these molecules, as it is unlikely that either the *cis*- or the *trans*-forms are planar in solution. The dipole moments of five azoquinolines have also been measured. Only with the 6,6′-isomer did irradiation with ultraviolet (u.v.) light change the dipole moment, indicating a very small conversion of the stable *trans*- into the less stable *cis*-form. The u.v. spectra of the compounds in pure ethanol were measured and agreed with published results.[3]

EXPERIMENTAL AND RESULTS

Preparation and Purification of the Azo-compounds.—The dipole moment of each compound was measured immediately it had been purified.

Azobenzene. Purified nitrobenzene in methanol was reduced by refluxing with sodium hydroxide and powdered zinc for 12 hr. The mixture was neutralised, filtered, most of the methanol distilled off, and the compound allowed to crystallise. It was then filtered off, washed well with water, and warmed with dilute hydrochloric acid to remove occluded zinc salts. The *trans*-azobenzene was washed, dried, and recrystallised from ethanol to constant m. p. (69°).

trans-Azobenzene was converted [4] into the *cis*-isomer by irradiation in glacial acetic acid solution with u.v. light for 6 hr. A Hanovia mercury vapour lamp, placed 25 cm. from the solution, was used. Most of the residual *trans*-isomer was precipitated with water and filtered off. The remaining azobenzene was extracted with cold chloroform, washed rapidly with

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* Part XLII, preceding Paper.

[1] G. S. Hartley and R. J. W. Le Fèvre, 1939, 531.

[2] N. Campbell, A. W. Henderson, and D. Taylor, *J.*, 1953, 1281.

[3] G. M. Badger and R. G. Buttery, *J.*, 1953, 2156.

[4] G. S. Hartley, *J.*, 1938, 633; A. H. Cook, *J.*, 1938, 876.

water, dried, and the solvent removed under reduced pressure. The residue was dissolved in light petroleum (b. p. 40—60°), the solution applied to an alumina column, and the chromatogram developed with further solvent. The more strongly adsorbed *cis*-isomer was extracted with light petroleum containing 1% of methanol. The solvent was removed *in vacuo*, and the red *cis*-azobenzene recrystallised from light petroleum (b. p. 40—60°) to constant m. p. (71°). All the operations were performed in subdued light, and the recrystallisations were performed at low temperature.

2,2'-*Azopyridines*. An aqueous solution of 2-aminopyridine was stirred with sodium hypochlorite solution at 5° for 3 hr.[5] The azopyridine was extracted with ether and recrystallised from light petroleum (b. p. 60—80°) to constant m. p. (85°). Further purification was effected by chromatography [2] on silica gel, the *trans*-2,2'-azopyridine being eluted with ether (80%)–ethanol (20%) and recrystallised from light petroleum to constant m. p. (86°).

The *trans*-isomer, dissolved in dry benzene–light petroleum (b. p. 60—80°), was irradiated with u.v. light for 12 hr., and the *cis*-isomer separated by chromatography [2] on a silica gel column. The water-soluble *trans*-isomer was strongly adsorbed at the top of the column, whilst the *cis*-isomer was eluted with benzene–light petroleum. The solvents were distilled off and the *cis*-2,2'-azopyridine crystallised from light petroleum (b. p. 40—60°) to constant m. p. (87°).

3,3'-*Azopyridines*. The *trans*-isomer was prepared from 3-aminopyridine as described for 2,2'-azopyridine and recrystallised from dry benzene–light petroleum (b. p. 60—80°) to constant m. p. (140°).

This isomer was irradiated and applied to a silica gel column as described above. The unconverted *trans*-isomer was eluted with benzene–light petroleum which had been saturated with water, and the *cis*- isomer was then removed with dry benzene containing 2% of methanol. The solvent was removed at 3-mm. pressure, and the *cis*-3,3'-azopyridine recrystallised at low temperature from light petroleum (b. p. 60—80°) to constant m. p. (81°). These operations were conducted in subdued light.

4,4'-*Azopyridine*. (i) *trans*-4,4'-Azopyridine was prepared from 4-aminopyridine as described above. The product was crystallised from light petroleum (b. p. 60—80°) to constant m. p. (106°).

(ii) 4,4'-Azopyridine 1,1'-dioxide, prepared by reducing 4-nitropyridine *N*-oxide [6] with hydrogen, using 10% palladium–barium sulphate as catalyst, was deoxygenated by refluxing for 2 hr. with phosphorus trichloride in chloroform solution. The reaction mixture was neutralised with sodium carbonate, the product extracted with benzene, washed with water, dried, and the solvent removed. It was recrystallised from light petroleum to constant m. p. (107°).

Attempts to isolate the *cis*-isomer were unsuccessful, and the physical properties of benzene solutions of the *trans*-isomer were unchanged after irradiation with u.v. light for 24 hr.

Azoquinolines. The 3,3'- and 8,8'-azoquinolines are unknown and attempts to prepare them were unsuccessful. The other symmetrical isomers were made by the methods described by Badger and Buttery.[3] Only the *trans*-isomers were isolated.

2,2'-*Azoquinoline*. 2-Chloroquinoline was refluxed with hydrazine for 4 hr. at 140°; the resulting solid was washed with water, and dissolved in 50% acetic acid. Nitrogen oxides were passed through this solution for ½ hr., the solution neutralised with aqueous ammonia, and the solid collected and washed with water. It was recrystallised from dry benzene to constant m. p. (233°).

4,4'-*Azoquinoline*. 4-Chloroquinoline, obtained as described previously,[7] was heated with hydrazine hydrate in a sealed glass tube at 140° for 2 hr. The product was dissolved in 50% acetic acid, and nitrogen oxides passed through the solution until it became dark red. After concentrating under reduced pressure, the 4,4'-azoquinoline was precipitated with cold water, filtered off, dried, and recrystallised from dry benzene–light petroleum (b. p. 60—80°) to constant m. p. (202°).

5,5'-*Azoquinoline*. 5-Aminoquinoline, prepared as described previously,[8] was diazotised in dilute sulphuric acid solution and the solution set aside for ½ hr. Sodium acetate and then

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[5] A. Kirpal and E. Reiter, *Ber.*, 1927, **60**, 664.
[6] E. Ochiai, *J. Org. Chem.*, 1953, 534.
[7] C. W. N. Cumper, D. G. Redford, and A. I. Vogel, *J.*, 1962, 1183.
[8] C. W. N. Cumper, R. F. A. Ginman, D. G. Redford, and A. I. Vogel, *J.*, 1963, 1731.

sodium sulphate solutions were added. The mixture was heated for 15 min., and the red solid filtered off, washed with water, dried, and recrystallised from xylene to constant m. p. (257°).

6,6′-*Azoquinoline* was prepared from 6-aminoquinoline[8] in a similar manner to the 5,5′-isomer. The product was crystallised to constant m. p. (248°) from xylene.

TABLE 1

$100\,w_2$	ε_{12}	v_{12}	n_{12}	$100\,w_2$	ε_{12}	v_{12}	n_{12}
	cis-*Azobenzene*				trans-*Azobenzene*		
0·2234	2·2875	1·14387	1·49767	0·3714	2·2762	1·14355	1·49873
0·2856	2·2914	1·14372	1·49777	0·8480	2·2790	1·14249	1·49899
0·5059	2·3050	1·14311	1·49793	1·3344	2·2823	1·14135	1·49969
0·7302	2·3189	1·14256	1·49829	1·9132	2·2849	1·14125	1·50061
0·9009	2·3281	1·14213	1·49852	1·9511	2·2884	1·13991	1·50065
1·1869	2·3457	1·14140	1·49886	2·3001	2·2881	1·13908	1·50113
				3·0534	2·2917	1·13751	1·50228
	trans-4,4′-*Azopyridine*						
0·1782	2·2749	1·14381	1·49773				
0·2280	2·2752	1·14372	1·49776				
0·3190	2·2757	1·14337	1·49786				
0·6253	2·2769	1·14245	1·49820				
0·8975	2·2786	1·14128	1·49864				
1·0638	2·2788	1·14090	1·49886				
1·1676	2·2794	1·14062	1·49894				
	cis-3,3′-*Azopyridine*				trans-3,3′-*Azopyridine*		
0·1021	2·2886	1·14405	1·49759	0·1106	2·2783	1·14403	1·49761
0·1803	2·2825	1·14375	1·49773	0·1321	2·2794	1·14394	1·49783
0·3511	2·2905	1·14306	1·49798	0·1975	2·2823	1·14379	1·49790
0·4298	2·2958	1·14294	1·49808	0·3433	2·2879	1·14325	1·49793
0·5652	2·3022	1·14248	1·49829	0·5304	2·2952	1·14260	1·49823
0·6998	2·3098	1·14098	1·49849	1·0791	2·3160	1·14076	1·49902
				1·2266	2·3222	1·14017	1·49929
	cis-2,2′-*Azopyridine*				trans-2,2′-*Azopyridine*		
0·0568	2·2796	1·14419	1·49751	0·0701	2·2787	1·14419	1·49351
0·1404	2·2880	1·14395	1·49765	0·1437	2·2805	1·14386	1·49771
0·2597	2·3001	1·14353	1·49777	0·3046	2·2831	1·14339	1·49776
0·3226	2·3062	1·14326	1·49785	0·3807	2·2852	1·14307	1·49793
0·5007	2·3243	1·14239	1·49810	0·9758	2·2980	1·14116	1·49863
0·7001	2·3443	1·14170	1·49845	1·1949	2·3034	1·14026	1·49894
				1·4741	2·3104	1·13841	1·49934
	2,2′-*Azoquinoline*				2,2′-*Azoquinoline* *		
0·0134	2·2742	1·14440	1·49775	0·0592	2·2758	1·14423	1·49813
0·0431	2·2746	1·14428	1·49776	0·1415	2·2761	1·14393	1·49833
0·0647	2·2748	1·14420	1·49779	0·1713	2·2768	1·14384	1·49838
0·0943	2·2751	1·14407	1·49783	0·2078	2·2775	1·14366	1·49845
0·1574	2·2758	1·14383	1·49801	0·3002	2·2783	1·14329	1·49865
0·2044	2·2764	1·14358	1·49811	0·3512	2·2786	1·14317	1·49878
0·2561	2·2768	1·14341	1·49820	0·4324	2·2800	1·14268	1·49892
	4,4′-*Azoquinoline*				4,4′-*Azoquinoline* *		
0·1019	2·2747	1·14408	1·49820	0·0500	2·2740	1·14425	1·49810
0·1499	2·2751	1·14387	1·49831	0·0992	2·2747	1·14407	1·49821
0·2103	2·2754	1·14366	1·49842	0·1749	2·2752	1·14380	1·49836
0·2518	2·2756	1·14350	1·49851	0·2301	2·2755	1·14358	1·49847
0·3140	2·2759	1·14332	1·49863	0·2741	2·2757	1·14342	1·49856
0·3250	2·2761	1·14323	1·49866	0·3019	2·2759	1·14332	1·49861
				0·3536	2·2763	1·14315	1·49871
	5,5′-*Azoquinoline*				5,5′-*Azoquinoline* *		
0·0552	2·2747	1·14427	1·49812	0·0511	2·2745	1·14427	1·49810
0·0761	2·2750	1·14415	1·49817	0·0641	2·2747	1·14422	1·49815
0·1220	2·2753	1·14399	1·49826	0·1128	2·2749	1·14409	1·49825
0·1842	2·2762	1·14372	1·49834	0·1498	2·2754	1·14385	1·49832
0·2673	2·2765	1·14341	1·49854	0·1745	2·2758	1·14379	1·49832
0·2717	2·2765	1·14340	1·49855	0·2253	2·2761	1·14361	1·49847
0·3200	2·2772	1·14323	1·49865	0·2751	2·2767	1·14344	1·49855

TABLE 1 (*Continued*)

100 w_2	ε_{12}	v_{12}	n_{12}	100 w_2	ε_{12}	v_{12}	n_{12}
	6,6′-*Azoquinoline*				6,6′-*Azoquinoline* *		
0·0303	2·2754	1·14419	1·49753	0·0201	2·2749	1·14428	1·49549
0·0311	2·2756	1·14418	1·49755	0·0443	2·2756	1·14406	1·49560
0·0450	2·2759	1·14409	1·49760	0·0501	2·2759	1·14402	1·49563
0·0553	2·2764	1·14407	1·49766	0·0657	2·2765	1·14388	1·49571
0·0664	2·2767	1·14386	1·49772	0·0763	2·2769	1·14380	1·49576
0·0721	2·2768	1·14365	1·49774	0·0906	2·2775	1·14359	1·49584
	7,7′-*Azoquinoline*				7,7′-*Azoquinoline* *		
0·0159	2·2744	1·14434	1·49779	0·0521	2·2751	1·14411	1·49782
0·0315	2·2747	1·14417	1·49786	0·0901	2·2761	1·14372	1·49794
0·0361	2·2750	1·14417	1·49787	0·1314	2·2773	1·14360	1·49810
0·0614	2·2754	1·14402	1·49791	0·1711	2·2778	1·14317	1·49815
0·0992	2·2763	1·14377	1·49805	0·1994	2·2787	1·14298	1·49823
0·1299	2·2769	1·14352	1·49808	0·2357	2·2790	1·14268	1·49832
0·1491	2·2774	1·14328	1·49818	0·3357	2·2817	1·14189	1·49858
0·1724	2·2778	1·14285	1·49823				

* After irradiation with ultraviolet light.

TABLE 2

Compound	α	β	$_\infty P_2$ (cm.^{3})	R_D (cm.^{3})	$_0P$ (cm.^{3})	μ (D)	Previous values for C_6H_6 solns.
cis-Azobenzene	6·02$_3$	−0·256$_1$	254·6	60·37	194·2	3·08	3·0 [a]
trans-Azobenzene	0·57$_7$	−0·226$_2$	69·65	64·19	5·46	0·52	0, 0·4 [a]
trans-4,4′-Azopyridine	0·44$_1$	−0·328$_2$	60·09	57·39	2·70	0·36	2·0 [b]
cis-3,3′-Azopyridine ...	5·25$_2$	−0·340$_5$	225·9	59·01	166·9	2·85	2·85 [b]
trans-3,3′-Azopyridine	3·90$_0$	−0·343$_7$	178·5	58·90	119·6	2·42	2·40 [b]
cis-2,2′-Azopyridine ...	10·0$_6$	−0·401$_5$	389·0	55·06	333·9	4·04	4·0 [b]
trans-2,2′-Azopyridine	2·18$_4$	−0·341$_5$	119·1	54·29	64·85	1·78	1·77,[b] 1·8 [c]
2,2′-Azoquinoline	1·11	−0·414	121·0	95·4	25·6	1·12	
2,2′-Azoquinoline * ...	1·13	−0·405	122·0	96·0	26·0	1·13 *	
4,4′-Azoquinoline	0·59$_6$	−0·365	97·9	97·8	0·1	0·09	
4,4′-Azoquinoline * ...	0·60$_0$	−0·366	98·0	97·3	0·7	0·19 *	
5,5′-Azoquinoline	0·86$_5$	−0·391	110·1	94·8	15·3	0·87	
5,5′-Azoquinoline * ...	0·85$_3$	−0·379	110·5	95·5	15·0	0·86 *	
6,6′-Azoquinoline	3·36	−1·107	182·6	†	86·6	2·06	
6,6′-Azoquinoline * ...	3·72	−0·949	215·0	†	119·0	2·42 *	
7,7′-Azoquinoline	2·24	−0·751	153·9	†	57·9	1·68	
7,7′-Azoquinoline * ...	2·32	−0·766	155·3	†	59·3	1·70 *	

* After irradiation with ultraviolet light. † Assumed to be 96·0 cm.^{3}.

[a] G. S. Hartley and R. J. W. Le Fèvre, *J.*, 1939, 531. The zero dipole moment was obtained in the absence of daylight, and the value of 0·4 without special precautions. [b] N. Campbell, A. W. Henderson, and D. Taylor, *J.*, 1953, 1281. [c] R. J. W. Le Fèvre and C. V. Worth, *J.*, 1951, 1814.

7,7′-*Azoquinoline* was prepared from 7-aminoquinoline as for the two previous isomers. Purification was by crystallisation from benzene to constant m. p. (246°).

Benzene solutions of the azoquinolines in a quartz vessel were irradiated for about 24 hr. with a Hanovia mercury-vapour lamp placed about 25 cm. away, and the dipole moment of the solute was determined immediately to see whether partial conversion into the *cis*-isomer could be detected. This procedure increased the dipole moment of *trans*-2,2′-azopyridine by >1 D.

The apparatus, experimental technique, and method of calculation and presentation of the results are as described in previous Parts [9] of this Series. The measured properties of the benzene solutions at 25·00° are presented in Table 1, and the slopes of the linear graphs of their dielectric constants (α) and specific volumes (β) against weight fraction, together with the polarisation data and dipole moments (μ), are collected in Table 2. Two azoquinolines, 6,6′- and 7,7′-, absorbed Na$_D$ light; the R_D value was assumed to be that found for the other isomers.

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[9] C. W. N. Cumper, A. A. Foxton, J. Read, and A. I. Vogel, *J.*, 1964, 430.

Discussion

The angle [10] between the planes containing the two rings in biphenyl is 41·6°, and in 4,4′-bipyridyl it is 37·2°; the angles are probably similar in solution.[11] The nitrogen atoms in 2,2′-bipyridyl [12] are *trans* to one another and the smaller steric interactions between a hydrogen atom in one ring and the lone-pair electrons on the nitrogen atom of the other enables the molecules to be more nearly planar, and the electron conjugation between the rings to be greater. Electron-diffraction results [10] for scattering between the N and C′-3 atoms in 2,2′-bipyridyl indicates that the angle between the planes of the rings is $>20°$, but the other distances, which are less reliable, correspond more closely to a planar molecule. The dipole moments [12] of 2,2′-bipyridyl and of 2,2′-biquinolyl indicate that in both cases the average value of this angle is 18°. In the crystalline state 2,2′- and 4,4′-bipyridyl are planar.[13]

Steric interactions in *trans*-azobenzene should be very similar to those in 2,2′-bipyridyl; in the solid state,[14] half the *trans*-azobenzene molecules are nearly planar and half have the rings rotated through 5° about their C–N bonds. It is unlikely that the molecules in solution are planar. The situation in the *trans*-forms of 3,3′- and 4,4′-azopyridine and in 6,6′- and 7,7′-azoquinoline is probably similar. In the 2,2′-isomers, however, the steric interactions are between the lone-pair electrons of all the nitrogen atoms; this also produces greater dipole–dipole interactions. Consequently, the angle through which the plane of each ring is twisted might differ somewhat in these isomers.

cis-Azobenzene cannot be planar. In the solid state [15] each ring is twisted through an angle $\phi = 56°$ about the C–N bond from a planar structure. Also, the C–N bond emerging from the benzene ring is bent about 4° from its normal direction. The conformation is probably similar in solution and in the *cis*-azopyridines.

Azobenzenes. *trans*-Azobenzene has an apparent dipole moment of 0·52 D; in fact the molecule has a centre of symmetry, so its dipole moment must be zero. The discrepancy could arise in either or both of the following ways. Firstly, the allowance for the distortion polarisation could be inadequate. Hartley and Le Fèvre [1] assumed that the distortion polarisation was equal to the measured total polarisation; in our case the distortion polarisation was taken as the R_D value (64·19 cm.^{3}) which differs appreciably from the measured total polarisation (69·65 cm.^{3}). Secondly, a small quantity of azobenzene could have been converted into the *cis*-isomer; this change occurs readily in the presence of light.[1]

The dipole moment of *cis*-azobenzene is 3·08 D. Hartley and Le Fèvre resolved it into two C_6H_5–N component moments [1] inclined at 80°; crystallographic analysis shows that the $\widehat{\mathrm{CNN}}$ angle is 121°, so that if the C_6H_5–N group moments lie along the C–N bond direction they are actually inclined at an angle of 62°, corresponding to an effective group moment of 1·80 D. The lone-pair electrons of the nitrogen atom make a major contribution to this group moment, and determine its direction; this direction is confirmed by the 1·6 D increase in the dipole moment when the compound is converted into *cis*-azoxy benzene.[16]

trans-*Azopyridines*. With 4,4′-azopyridine only the *trans*-isomer had been isolated. The dipole moment reported for this molecule [2] (2·0 D) must be in error, since that of the *trans*-isomer should be zero, and the *cis*-form should only have a moment of about 0·71 D. The values found in this investigation for two independent samples of 4,4′-azopyridine were 0·36 and 0·46 D, the apparently finite value being due to an inadequate allowance

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[10] A. Almenningen and O. Bastiansen, *Kgl. Norske Videnskab. Selskabs Skrifter*, 1958, no. 4.

[11] Cf. O. Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408; 1950, **4**, 926; 1952, **6**, 205.

[12] C. W. N. Cumper, R. F. A. Ginman, and A. I. Vogel, *J.*, 1962, 1188.

[13] J. Dahr, *Indian J. Phys.*, 1932, **7**, 43; D. H. Saunder, *Proc. Roy. Soc.*, 1946, *A*, **188**, 31; J. N. Nickerk and D. H. Saunder, *Acta Cryst.*, 1948, **1**, 44.

[14] J. J. de Lange, J. M. Robertson, and I. Woodward, *Proc. Roy. Soc.*, 1939, *A*, **171**, 398.

[15] G. C. Hampson and J. M. Robertson, *J.*, 1941, 409.

[16] K. A. Gehrckens and E. Muller, *Annalen* 1933, **500**, 296.

for atom polarisation, which would be particularly great, since the molecule possesses large opposing component moments.

There are three possible conformations for *trans*-3,3′-azopyridine with the pyridine nitrogen atoms, Figure 1, at the positions labelled (1) cc′, (2) ee′, and (3) ce′. For a planar molecule the first two are non-polar and the third conformation has a calculated dipole moment of 3·91 D (assuming the component moments to be that of pyridine,[17] 2·21 D, the rings to have the conformation of isolated pyridine molecules,[18] and the $\widehat{CNN}$ angle to be 120°). If, on the other hand, the rings are twisted through 18° about the $C-N_{(azo)}$ bonds (cf. conformation of 2,2′-bipyridyl, above), conformations (1) and (2) each have calculated moments of 0 or 1·21 D, and conformation (3) 3·91 or 3·72 D, depending upon whether the two rings are twisted in the opposite or the same direction. The experimental moment of 2·42 D indicates that a mixture of conformations exist in solution. Any interaction between the heterocyclic nitrogen atoms, and between them and the azo-nitrogens must be small, so that no single conformation is preferred. Interchange between the different conformations can occur readily. For an equal molecular distribution between the above possibilities the calculated dipole moment is 2·31 D.

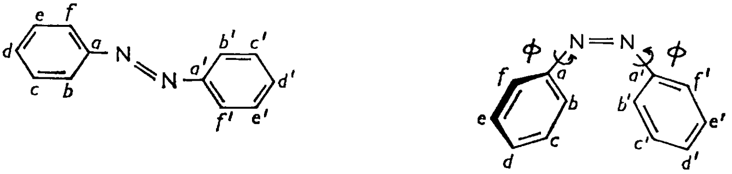

FIGURE 1. Position of ring nitrogen atoms

	(1)	(2)	(3)
2,2′-Azopyridine	*bb′*	*ff′*	*bf′*
3,3′-Azopyridine	*cc′*	*ee′*	*ce′*

Analogous conformations are possible in *trans*-2,2′-azopyridine (Figure 1). The steric interactions will be different, and there will be significant dipole and exchange interactions between the azo- and heterocyclic-nitrogen atoms which would favour structure (1). If all the molecules had this conformation, however, the rings would have to be twisted 28° about the $C-N_{(azo)}$ bonds for the calculated and experimental dipole moments to agree. This angle seems rather excessive, in which case the molecules must spend a small fraction of their time with conformation (3).

cis-*Azopyridines*. The *cis*-form of 4,4′-azopyridine could not be isolated; its calculated moment of 0·71 D is in the opposite direction to that of the azo-group. (This conclusion is based upon the dipole moments of pyridine and *cis*-azobenzene.)

cis-3,3′-Azopyridine also has three conformational positions for its nitrogen atoms (Figure 1). Their calculated dipole moments, expressed as a function of the angle of twist ϕ about the $C-N_{(azo)}$ bonds, measured from the planar structure, are in Figure 2. The experimental dipole moment of 2·86 D corresponds to conformation (2) with $\phi \sim 40°$. This conformation minimises the interactions between the four nitrogen atoms. Conformation (3) would be the next most stable, and if the molecules did spend a small fraction of their time in this conformation, then the angle ϕ would have to be a little greater for the calculated dipole moment to agree with the experimental value.

The calculated dipole moments of the three conformations of *cis*-2,2′-azopyridine are also shown in Figure 2. The experimental dipole moment (4·04 D) shows that there is only one real possibility *viz.*, conformation (1) with $\phi \sim 56°$. This is the angle found[15] in crystalline *cis*-azobenzene. In this conformation the dipole interaction between the lone

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[17] C. W. N. Cumper, A. I. Vogel, and S. Walker, *J.*, 1956, 3621.

[18] B. Bak, L. Hansen-Nygaard, and J. Rastrup-Anderson, *Mol. Spectroscopy*, 1958, **2**, 361.

pair electrons of the heterocyclic nitrogen atoms is most favourable; in (3) this stabilising factor would have been replaced by a repulsion between heterocyclic and azo-nitrogen atoms.

It is interesting to note that in *mm'*-disubstituted diphenyl sulphides,[19] the conformation of the phenyl group is similar to that in *cis*-3,3'-azopyridine. The same conformation is also the preferred one for *oo'*-disubstituted diphenyl sulphides, but in the corresponding sulphones the conformation similar to that suggested for 2,2'-azopyridine is favoured.

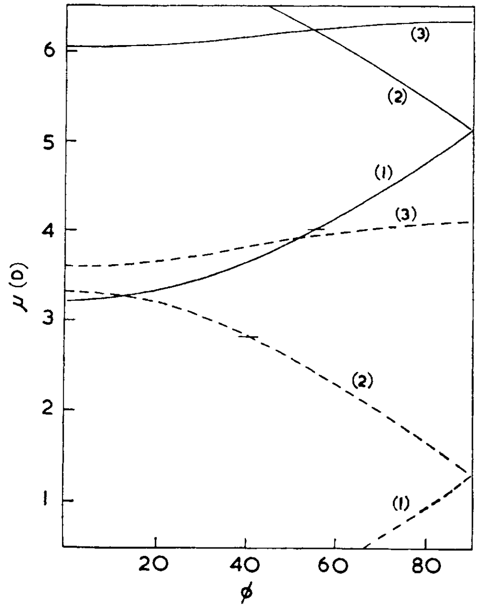

FIGURE 2. Variation of dipole moment with the angle between the rings, φ
(——) *cis*-2,2'-Azopyridine.
(– – – –) *cis*-3,3'-Azopyridine.

Azoquinolines. Azoquinolines are not readily soluble in benzene, so the precision of the experimental values for their dipole moments is not as high as is normally achieved. Of the five isomers studied only 6,6'-azoquinoline showed any change in dipole moment after prolonged exposure of its solutions to u.v. light. The *cis*-isomer could not be isolated, and the u.v. spectra of the solutions before and after irradiation did not reveal its presence. The dipole moments of the stable *trans*-isomers are discussed below.

The apparent orientation polarisation of 4,4'-azoquinoline is very small, and its dipole moment is obviously zero, as expected for a molecule with a centre of symmetry.

A zero dipole moment might also be expected for *trans*-5,5'-azoquinoline. The experimental value of 0·87 D may be high, because of inadequate allowance for atom polarisation, but the compound seems to have a finite dipole moment. This probably arises because the component moments are not quite parallel with the $C_{(5)}$–$N_{(azo)}$ bonds, and hence any conformation of the 5,5'-azoquinoline molecule in which the quinoline residues were rotated in opposite directions about their $C_{(5)}$–$N_{(azo)}$ bonds would have a finite dipole moment.

The situation in 2,2'-azoquinoline should be similar to that in the corresponding *trans*-azopyridine. Its dipole moment is 0·6 D less. If the molecules had conformation (1) (see Figure 1), the planes of the quinoline residues would have to be rotated 19° about the $C_{(2)}$–$N_{(azo)}$ bonds, assuming the group moment of each of the quinoline residues is that of quinoline[20] (2·15 D). This angle is less than for the azopyridine; this could arise from the greater delocalisation energy possible with the larger ring system tending to stabilise a more planar molecule.

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[19] C. W. N. Cumper, J. Read, and A. I. Vogel, unpublished work.
[20] C. W. N. Cumper, D. G. Redford, and A. I. Vogel, *J.*, 1962, 1176.

7,7′-Azoquinoline could have several conformations, but if the molecule is non-planar its dipole moment of 1·68 D suggests that in the predominant conformation the quinoline-group moments oppose one another. A single conformation in which the quinoline residues were rotated through 28° about the $C_{(7)}-N_{(azo)}$ bonds would explain the observed dipole moment.

Finally the conformation of 6,6′-azoquinoline should be similar to that of the 7,7′-isomer; its dipole moment (2·06 D) is greater by 0·38 D. The group moments of substituents in the 6- and 7-positions of quinoline are known to differ significantly.[7,12,20]

No allowance has been made for the effect of the benzene solvent upon the experimental dipole moments nor upon those of the group moments of pyridine and quinoline employed in the above discussion.

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