

### 323. Molecular Polarisability. The Molar Kerr Constants of 2,2'-Bipyridyl and 1,10-Phenanthroline.

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The dipole moments and molar Kerr constants of 2,2'-bipyridyl and 1,10-phenanthroline are consistent with an equivalent conformation for the former molecule, as a solute in benzene or carbon tetrachloride, with the pyridyl rings twisted about the 4,4'-axis by 10—17° from the flat *trans*-arrangement reported to exist in the crystal.

GOETHALS,<sup>1</sup> Fielding and Le Fèvre,<sup>2</sup> Goethals and Wibaut,<sup>3</sup> and Cumper, Ginman, and Vogel<sup>4</sup> have reported the dipole moment in benzene of 2,2'-bipyridyl as small, consistently with a near-*trans*-conformation for this solute, and with expectations based on Cagle's X-ray analysis<sup>5</sup> of the crystalline substance. The actual values given for  $\mu_{\text{bipy}}$  have varied somewhat with the distortion polarisations assumed; the  $R_D$  now found (cf. Table 1) is 49.3 c.c., to be compared with 46.0 c.c. (ref. 2), 49.4 c.c. (ref. 4), or 49.1<sub>5</sub> c.c. (ref. 4). In carbon tetrachloride (Tables 1 and 2 below)  $\mu$  appears as 0.61 D, which is close to that (0.69 D) recorded by Vogel *et al.*<sup>4</sup> in benzene. Goethals and Wibaut's results suggest that  $\mu_{\text{bipy}}$  may increase slightly with rise of temperature. In contrast, the polarity of 1,10-phenanthroline (regarded as a rough model of the unknown *cis*-2,2'-bipyridyl) is<sup>2,4</sup> not below 3.6 D. By the argument of Fielding and Le Fèvre, who used the moment of pyridine,<sup>6,7</sup> a  $\mu_{\text{bipy}}$  of *ca.* 0.6 D should correspond to an azimuthal angle  $\chi^\circ$  (through which the C<sub>6</sub>H<sub>4</sub>N nuclei are twisted about the common axis) of 162—163°.

As the semi-axes of the polarisability ellipsoid for pyridine are now available, it is of interest to check the above conclusions by comparing the molar Kerr constants determined by experiment with those expected for different values of  $\chi$ . This is the main subject of the present paper. Methods of calculation have been explained previously,<sup>8-10</sup> a worked example being set out in ref. 10.

#### EXPERIMENTAL

*Solutes.*—2,2'-Bipyridyl, purified by sublimation at 0.25 mm., had m. p. 70—71° (Wibaut and Willink<sup>11</sup> give 70.5°); 1,10-phenanthroline monohydrate was heated to 80° in a phosphorus pentoxide-containing evacuated drying-pistol, then recrystallised from sodium-dried benzene and stored over sulphuric acid; the product had m. p. 116—117° (Beilstein's "Handbuch der organischen Chemie," Vol. XXIII, p. 227, cites 117° for the anhydrous base).

*Techniques, Apparatus, etc.*—Details have been as described in refs. 8*a*, p. 274, or 8*b*, p. 2462. Measurements and results are recorded in Tables 1 and 2, under the usual headings (cf. ref. 12 for a recent listing in this *Journal* of these and other symbols). Benzene and carbon tetrachloride as solvents were of "AnalaR" grade; after drying (Na and CaCl<sub>2</sub>, respectively) they

<sup>1</sup> Goethals, *Rec. Trav. chim.*, 1935, **54**, 299.

<sup>2</sup> Fielding and Le Fèvre, *J.*, 1951, 1813.

<sup>3</sup> Goethals and Wibaut, *Rec. Trav. chim.*, 1954, **73**, 35.

<sup>4</sup> Cumper, Ginman, and Vogel, *J.*, 1962, 1188.

<sup>5</sup> Cagle, *Acta Cryst.*, 1948, **1**, 158.

<sup>6</sup> Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

<sup>7</sup> Le Fèvre, Le Fèvre, Rao, and Smith, *J.*, 1959, 1188.

<sup>8</sup> Le Fèvre and Le Fèvre, (a) *Rev. Pure Appl. Chem.*, 1955, **5**, 261; (b) Chap. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ. Inc., New York, 3rd edn., Vol. I, p. 2459.

<sup>9</sup> Le Fèvre, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.

<sup>10</sup> Eckert and Le Fèvre, *J.*, 1962, 1081.

<sup>11</sup> Wibaut and Willink, *Rec. Trav. chim.*, 1931, **50**, 287.

<sup>12</sup> Le Fèvre and Sundaram, *J.*, 1962, 1494.

TABLE 1.

Increments in Kerr constant, refractive index, etc., for solutions in benzene or carbon tetrachloride containing weight fractions  $w_2$  of 2,2'-bipyridyl or 1,10-phenanthroline.

<i>Bipyridyl in benzene.*</i>										
$10^5 w_2$ .....	998	1065	1175	1266	1560	2026				
$10^4 \Delta n$ .....	10	10	11	12	15	20				
whence $\Sigma \Delta n / \Sigma w_2 = 0.096$ .										
<i>Bipyridyl in carbon tetrachloride.</i>										
$10^5 w_2$ .....	367	431	663	1035	1194	2336				
$10^{10} \Delta B$ .....	3	5	7	—	15	40				
$10^4 \Delta n$ .....	—	10	—	26	29	54				
$-10^4 \Delta d$ .....	—	—	—	58	67	131				
$10^4 \Delta \epsilon$ .....	—	—	—	126	148	290				
whence $10^7 \Delta B = 0.809w_2 + 39w$ , $\Sigma \Delta n / \Sigma w_2 = 0.239$ , $\Sigma \Delta d / \Sigma w_2 = -0.559$ , and $\Sigma \Delta \epsilon / \Sigma w_2 = 1.24$ .										
<i>Phenanthroline in benzene.</i>										
$10^6 w_2$ ...	3944	5646	6028	6266	7401	7885	9245	9694	10,827	11,187
$10^{10} \Delta B$ ...	75	94	110	102	129	130	169	167	195	201
$10^4 \Delta n$ ...	7	—	10	—	—	14	—	17	—	20
$10^6 w_2$ ...	4964	6166	8922							
$10^4 \Delta \epsilon$ ...	463	558	830							
whence $\Sigma \Delta B / \Sigma w_2 = 17.56$ ; $\Sigma \Delta n / \Sigma w_2 = 0.173$ ; and $\Sigma \Delta \epsilon / \Sigma w_2 = 9.23$ .										

\*  $\Delta B = ca. 0$  for  $w_2$ 's up to about 0.03.

TABLE 2.

Molar Kerr constants from data of Table 1 and ref. 2.

	Solvent	$\alpha \epsilon_1$	$\beta$	$\gamma$	$\delta$	$10^{12} \epsilon_{\infty} (mK_2)$
2,2'-Bipyridyl.....	$C_6H_6$	0.72 <sub>9</sub> *	0.221 *	0.064	ca. 0	4.3 <sub>3</sub>
„ .....	$CCl_4$ †	1.24 <sub>3</sub>	-0.353	0.164	11.2 <sub>4</sub>	13.8
1,10-Phenanthroline .....	$C_6H_6$	9.23 †	0.322 <sub>5</sub>	0.115 <sub>5</sub>	42.8 <sub>5</sub>	532.1

\* From ref. 2. †  $\infty P_2$  from the  $\alpha \epsilon_1$  and  $\beta$  shown is 59.3 c.c. With  $1.05R_D = {}_D P = 51.8$  c.c.,  $\mu = 0.61D$ . ‡ The re-measurement of  $\epsilon_{12}$  for phenanthroline solutions is reported because in ref. 2 the individual  $\alpha \epsilon_1$ 's are not constant. With  $\alpha \epsilon_1 = 9.23$ ,  $\infty P_2$  is 354.4<sub>5</sub> c.c. The refractions in Table 1 correspond to  $R_D = 58.7$  c.c., whence, with  ${}_D P = 1.05R_D$ ,  $\mu = 3.7_5D$ . Vogel *et al.*<sup>4</sup> quote  $R_D = 60.02$  c.c. and  $\mu = 3.64D$ .

TABLE 3.

Semi-axes of the molecular polarisability ellipsoid of 2,2'-bipyridyl and calculated molar Kerr constants in dependence on  $\chi$ .

Angle	Semi-axes	Direction cosines with			$\mu_{res}$	$10^{12} mK$ (calc.)
		<i>OX</i>	<i>OY</i>	<i>OZ</i>		
0°	$b_1 = 2.356$	1	0	0	$\mu_3 = 3.90$	+477
	$b_2 = 1.189$	0	0	1		
	$b_3 = 2.024$	0	1	0		
90°	$b_1 = 2.356$	0.9997	0.0173	0.0173	$\mu_3 = 2.76$	-286
	$b_2 = 1.606$	-0.0245	0.7069	0.7069		
	$b_3 = 1.606_5$	0	-0.7071	0.7071		
158°	$b_1 = 2.358$	0.9976	0.0686	0.0133	$\mu_3 = 0.74$	-7.7
	$b_2 = 1.992$	-0.0699	0.9792	0.1903		
	$b_3 = 1.219$	0	-0.1908	0.9816		
160°	$b_1 = 2.358$	0.9975	0.0700	0.0123	$\mu_3 = 0.68$	+2.5 <sub>5</sub>
	$b_2 = 1.997$	-0.0711	0.9823	0.1732		
	$b_3 = 1.214$	0	-0.1736 <sub>5</sub>	0.9848		
163°	$b_1 = 2.358$	0.9973 <sub>5</sub>	0.0720	0.0108	$\mu_3 = 0.58$	+16.4
	$b_2 = 2.004$	-0.0728	0.9864	0.1474		
	$b_3 = 1.207$	0	-0.1478	0.9890		
170°	$b_1 = 2.358$	0.9971	0.0755	0.0066	$\mu_3 = 0.34$	+40.9
	$b_2 = 2.016$	-0.0758	0.9933	0.0869		
	$b_3 = 1.195$	0	-0.0872	0.9962		
180°	$b_1 = 2.358$	0.9970	0.0775 <sub>5</sub>	0	$\mu_3 = 0$	+54.3
	$b_2 = 2.022$	-0.0775 <sub>5</sub>	0.9970	0		
	$b_3 = 1.189$	0	0	1		

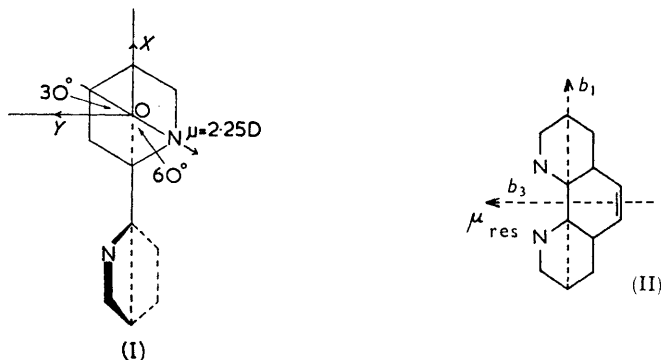
were fractionated, and stored over the desiccants named. When  $w_2 = 0$ , the following values apply at  $25^\circ$  (and, where appropriate, for sodium-D light):

	$10^7 B_D$	$n_D$	$\epsilon$	$d$	$H$	$J$	$10^{14} K_1$
$C_6H_6$ .....	0.410	1.4973	2.2725	0.8738	2.114	0.4681	7.56
$CCl_4$ .....	0.070	1.4575	2.2270	1.5845	2.060	0.4731	0.749

## DISCUSSION

*Conformation of 2,2'-Bipyridyl.*—From the measurements recorded by Le Fèvre, Le Fèvre, Rao, and Smith,<sup>7</sup> the principal polarisabilities\* of each pyridyl unit are  $b_1 = 1.006$ ,  $b_2 = 0.976$ , and  $b_3 = 0.581$ , with  $b_1$  along the 4,1-direction and  $b_3$  perpendicular to the  $C_5H_4N$  plane. By assuming all intervalency angles to be  $120^\circ$  (cf. Cagle<sup>5</sup>) and using normal C-C polarisabilities,<sup>8,9</sup> semi-axes of the molecular ellipsoid of 2,2'-bipyridyl can be calculated<sup>8-10</sup> for various values of  $\chi$  as in Table 3. If  $b_1 + b_2 + b_3 = 5.569$  (from  $\epsilon^P = 0.95R_D$ ), then a small exaltation,  $\Delta b = 5.569 - 2\Sigma b^{C,H,N} - \Sigma b^{C-C} = 0.29$ , is apparent; we apply this parallel to the 1,1'-bond (cf. analogy with biphenyl<sup>13</sup>).

Arbitrary axes  $OX$ ,  $OY$ , and  $OZ$  are located in one pyridyl ring as in (I) with the positive sense of  $OZ$  up from the plane of the paper. Since in the crystal the molecule



is *trans*, and in many co-ordination complexes is presumably *cis*, we include calculations to cover these extremes ( $\chi = 180^\circ$  or  $0^\circ$ , respectively) and their orthogonal intermediate ( $\chi = 90^\circ$ ).

From the two right-hand columns of Table 3 it is clear that single conformations with  $\chi$  between  $160^\circ$  and  $163^\circ$  would account for both the  $\mu$  observed and the  ${}_mK$  observed. In reality, however (remembering the evident ease of the *trans*  $\rightarrow$  *cis*-inversion which must occur during chelation of this base to metals), the bipyridyl molecules are probably in vibration about an unknown equilibrium configuration (so that part of the apparent polarity may be due to "vibration polarisation" as described for other cases by Coop and Sutton<sup>14</sup>). This configuration seems unlikely to be the flat *trans*-form because then  $\chi$ 's around  $180^\circ$  would be most preferred and  ${}_mK$ 's of  $40-50 \times 10^{-12}$  should follow. (Since the anisotropy term  $\theta_1$  for pyridine is *ca.* 1.2 times that for benzene, the  ${}_mK$  for bipyridyl with  $\chi = 180^\circ$  can reasonably be expected to exceed the  ${}_mK = 40.5 \times 10^{-12}$  measured<sup>13</sup> for biphenyl; the calculated value of  $+54.3 \times 10^{-12}$  in Table 3 is thus credible.) The  ${}_\infty({}_mK_2)$ 's recorded in Table 2 for bipyridyl being only  $4-14 \times 10^{-12}$ , the weighted mean  $\chi$  must be such as to produce a negative  $\theta_2$  term. [The solute species therefore behaves (cf. p. 294 of ref. 8a) as though it possessed a finite resultant dipole

\* Principal polarisabilities of molecules ( $b_1$ ,  $b_2$ , and  $b_3$ ) or of bonds ( $b_L$ ,  $b_T$ , and  $b_V$ ) are quoted throughout in  $10^{-23}$  c.c. units.

<sup>13</sup> Chau, Le Fèvre, and Le Fèvre, *J.*, 1959, 2666.

<sup>14</sup> Coop and Sutton, *J.*, 1938, 1269; cf. Sutton, *Ann. Reports*, 1940, **37**, 62.

moment.] Accordingly we propose (I) with  $\chi = 160\text{--}163^\circ$  as the "equivalent" conformation of dissolved 2,2'-bipyridyl, meaning thereby a specifiable single conformation from which observable quantities can be calculated *a priori* even if in fact these observables are drawn from an assemblage of conformations with  $\chi$ 's varying about an undetermined  $\chi_{\text{equilibrium}}$ .

*The Molar Constant of 1,10-Phenanthroline.*—The measurements on this solute were intended as checks of our predictions of  $\mu$  and  ${}_mK$  for the unknown *cis*-2,2'-bipyridyl. By using  $\mu_{\text{pyridine}}$  as before,  $\mu_{\text{resultant}}$  for (II) is calculated as 3.9 D, in satisfactory accord with 3.7<sub>8</sub> D from experiment. Tensorial additions of the anisotropic polarisabilities of two C-C bonds and one C=C bond<sup>8,15</sup> to the molecular semi-axes of bipyridyl with  $\chi = 0^\circ$ , yields for (II), if intervalency angles are all  $120^\circ$ ,  $b_1 = 2.436$ ,  $b_2 = 1.320$ , and  $b_3 = 2.259$ . These semi-axes produce an  ${}_mK$  calc. of  $655 \times 10^{-12}$ , and their sum corresponds to an electronic polarisation  ${}_E P$  of 50.58 c.c. (Tables 1 and 2); but when calculated (from  $R_D^{\text{pyridine}} = 24.07$  c.c.,  $R_D^{\text{C-C}} = 1.296$ ,  $R_D^{\text{C=C}} = 4.17$ , and  $R_D^{\text{C-H}} = 1.676$  c.c.)  ${}_E P$  is 52.85 c.c.; an exaltation  $\Delta R_D = 5.85$  c.c. is evidently present. On the basis that  ${}_E P = 0.95R_D$ , the polarisability exaltation,  $\Delta b$ , emerges as 0.661. This must be distributed between the  $b_1$ , and  $b_3$  just given for (II). When it is added wholly to  $b_1$ ,  ${}_mK$  calc. becomes  $201 \times 10^{-12}$  (which is too small); if added equally to  $b_1$  and  $b_3$  the  ${}_mK$  calc. becomes  $982 \times 10^{-12}$  (which is too great). By trial and error, division of  $\Delta b$  over  $b_1$  and  $b_3$  in the proportions of 3.5 : 1 produces  $b_1 = 2.950$ ,  $b_2 = 1.320$ ,  $b_3 = 2.406$ , and  ${}_mK$  calc. =  $531 \times 10^{-12}$  (cf.  ${}_mK$  observed =  $532 \times 10^{-12}$ ). This finding is qualitatively explicable since in structure (II) conjugation involving the -CH=CH- unit bridging the 1,10-positions must compete with the 4,1,1',4'-conjugation of bipyridyl; if the exaltation of polarisability is regarded as due to  $\pi$ -electron interactions from the two outer to the central ring, augmentation of  $b_3$  and  $b_1$  in a ratio near  $\sin^2 60^\circ : \cos^2 60^\circ$  is not unexpected.

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<sup>15</sup> Bramley, Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 1183.