

### 396. *The Configuration of 2 : 2'-Dipyridyl.*

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Comparison of the dipole moments of 2 : 2'-dipyridyl and *o*(or 1 : 10)-phenanthroline indicates that the former molecule is approximately planar, with the two nitrogen atoms in a *trans*-disposition about the 1 : 1'-bond. Ultra-violet spectra suggest that there is less inter-nuclear conjugation in the dipyridyls than in diphenyl.

THE *cis*-configuration required by 2 : 2'-dipyridyl during its co-ordination with metals evidently cannot be difficult to achieve since qualitatively this base and *o*-phenanthroline seem to react equally easily. It therefore became of interest to check the earlier conclusions of Goethals (*Rec. Trav. chim.*, 1935, **54**, 299) and Cagle (*Acta Cryst.*, 1948, **1**, 158) that the two nitrogen atoms are normally arranged in the dipyridyl molecule *trans* to one another.

#### EXPERIMENTAL.

We are indebted to Dr. F. P. Dwyer for gifts of the two compounds just mentioned. The 2 : 2'-dipyridyl was sublimed at 0.1 mm. pressure, and then had m. p. 69.5°. *o*-Phenanthroline monohydrate, dehydrated at 105° and then recrystallised from dry benzene, had m. p. 99—100°. After the dielectric-constant observations, during which solutions were in contact with slightly tarnished brass electrodes, the recovered material showed a green tinge. This was removed by redissolving the compound in benzene and adding a few drops of water, thus precipitating the monohydrate, which was collected and dehydrated as before. Sublimation at 10<sup>-3</sup> mm. then afforded a white specimen which was used for the spectra.

Procedures, symbols, and calculation methods were as noted before (*e.g.*, *J.*, 1948, 1949; 1949, 333). Measurements and results are given in Table I.

TABLE I.

$10^6 w_1$	$\epsilon^{25}$	$d_4^{25}$	$\alpha\epsilon_2$	$\beta d_2$	$10^6 w_1$	$\epsilon^{25}$	$d_4^{25}$	$\alpha\epsilon_2$	$\beta d_2$
0	2.2725	0.87378	—	—					
2 : 2'-Dipyridyl.									
9,030	2.2783	0.87559	0.642	0.200	15,602	2.2809	0.87706	0.538	0.210
12,435	2.2799	0.87634	0.595	0.203	20,257	2.2831	0.87801	0.525	0.209
whence $(\alpha\epsilon_2)_{w_1} = 0.729 - 11w_1$ , and $(\beta d_2)_{w_1} = 0.193 + 0.88w_1$ .									
o-Phenanthroline.									
5,220	2.3211	0.87518	9.31	0.268	10,220	2.3624	0.87638	8.79	0.254
6,680	2.3437	0.87558	10.66	0.269	10,620	2.3622	0.87675	8.44	0.263
8,180	2.3538	0.87591	9.31	0.260	15,870	2.4146	0.87769	8.95	0.246
8,780	2.3661	0.87614	10.65	0.269					
whence $(\alpha\epsilon_2)_{w_1} = 10.5_4 - 117w_1$ , and $(\beta d_2)_{w_1} = 0.282 - 2.2w_1$ .									
		$M_1$	$(\alpha\epsilon_2)_{w_1} - 0$	$(\beta)_{w_1} - 0$	$\infty P_T$ , c.c.	$[R_L]_D$ , c.c.	$\mu$ , D.		
2 : 2'-Dipyridyl	.....	156.2	0.729	0.221	62.9	46.0 *	0.91		
o-Phenanthroline	.....	180.2	10.54	0.322 <sub>g</sub>	398.9	52.5 †	4.11		
					* <i>I.e.</i> , $2 \times (R_{\text{pyridine}} \text{ minus } R_{\text{H}})$ .				
					† <i>I.e.</i> , $R_{\text{Dipyridyl}} + 2R_C + R_{\text{double bond}}$ .				

The moment of 2 : 2'-dipyridyl has been recorded as "less than 0.68 D." by Goethals (*loc. cit.*). His material had  $m. p. 70.5^\circ$ , but on the last page of his paper he formulates the molecule as 3 : 3'-dipyridyl, the  $m. p.$  of which is  $68^\circ$  (as against the literature value for the 2 : 2'-isomer of  $69.5^\circ$ ; cf. Beilstein, "Handbuch," XXII, pp. 199, 200). Moreover, the only polarisation tabulated (that for  $17^\circ$ ) is 49.4 c.c., whilst the molecular refraction is entered thrice as 59.2, 59.3, and 59.5 c.c. In view of these (probably clerical) errors we felt repetition to be justified.

## DISCUSSION.

Qualitatively, it is obvious that 2 : 2'-dipyridyl exists in solution as a near-*trans* form—a conclusion already drawn by Goethals (*loc. cit.*) from his own measurements. Further, we may note that the moment of pyridine is about 2.2 D. (Lange, *Z. Physik*, 1925, 33, 169; Bergmann, Engel, and Meyer, *Ber.*, 1932, 65, 446; Rau and Narayanaswamy, *Z. physikal. Chem.*, 1935, B, 26, 23; Goethals, *loc. cit.*; Middleton and Partington, *Nature*, 1938, 141, 516; Leis and Curran, *J. Amer. Chem. Soc.*, 1945, 67, 79), and assume that this resultant acts in the direction  $4 \rightarrow 1$  (*i.e.*, from the  $\gamma$ -carbon to the nitrogen atom, with the negative pole toward the nitrogen). Since the  $C_5N$  ring system of pyridine itself is almost a regular hexagon (cf. the list by Allen and Sutton, *Acta Cryst.*, 1950, 3, 46), we may infer that this shape is retained in 2 : 2'-dipyridyl, in which therefore the pair of component "pyridine" moments can each be taken as inclined to the 5 : 2 : 2' : 5' line at approximately  $60^\circ$ , with their actual relative directions being set by the azimuthal angle,  $\chi$ , through which the  $C_5H_4N$  nuclei are twisted about the common axis. Completely *cis*- or *trans*-configurations should therefore show moments of *ca.* 3.8 D. and *ca.* 0 D., respectively, the unlikely condition of "free rotation" requiring a moment of 2.7 D.

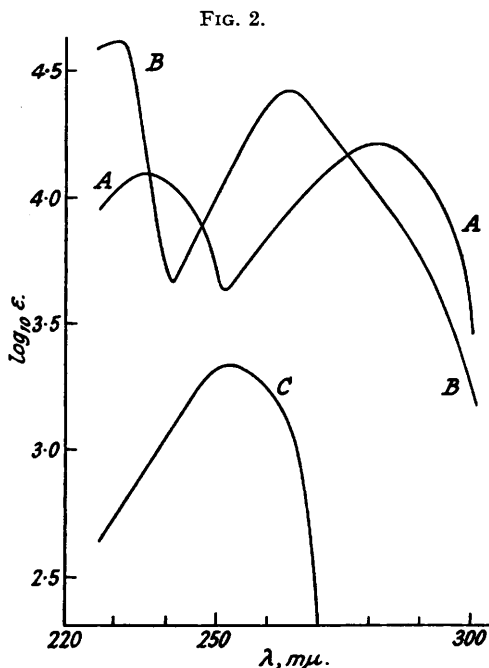
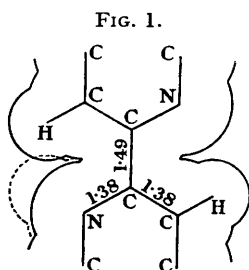
The resultant in fact found (0.91 D.) corresponds to  $\chi = 152\text{--}153^\circ$ . (This calculation is not particularly sensitive to the value adopted for the "pyridine" component; *e.g.*, 2.0 D. leads to  $\chi = 150\text{--}151^\circ$ , or 2.3 D. to  $\chi = 153\text{--}154^\circ$ .) Our measurements therefore indicate an angle (about  $28^\circ$ ) between the ring planes which is smaller than those reported (*via* spectroscopic data) for diphenyl ( $45^\circ$ ) and 3 : 3'-dibromodiphenyl ( $54^\circ$ ; cf. Allen and Sutton, *loc. cit.*). As a comparison, it is of interest that, from the dipole moments of a number of 2 : 2'-dinitro- and -dicarboxy-diphenyl derivatives,  $\chi$  figures of *ca.*  $90^\circ$  have been deduced (Le Fèvre and Vine, *J.*, 1938, 967).

From elementary considerations it seems credible that, of the above cases, 2 : 2'-dipyridyl should be the most nearly flat. A scale drawing (Fig. 1), based on the known dimensions of pyridine and diphenyl (Allen and Sutton, *loc. cit.*) and including the "Wirkungsradien" of Stuart (*Z. physikal. Chem.*, 1935, 27, 350), shows there to be no interference, at the positions adjacent to the central bond, in the *trans*-configuration of 2 : 2'-dipyridyl, while with the corresponding *cis*-form, as also for diphenyl when flat, hydrogen atoms are at least in contact, and in such molecules as the 2 : 2'-disubstituted diphenyls mentioned above the overlapping is considerable in both the *cis*- and the *trans*-arrangement.

Factors (cf. Weissberger, Sängewald, and Hampson, *Trans. Faraday Soc.*, 1934, 30, 884) of an electrical nature which may enter the problem as the two halves rotate are (*a*) van der Waals attractions, and (*b*) dipolar forces, which may be attractive or repulsive. Although it might be

possible to examine (a) by estimating binding energies *via* Slater and Kirkwood's empirical formula (*Physical Rev.*, 1931, **37**, 682), yet we have not attempted this because, although it is clear that attractions will be greatest when  $\chi = 0^\circ$  or  $180^\circ$ , yet in the similar example of diphenyl such attractions are not sufficient to enforce co-planarity of the molecule. As to (b), we have applied the methods used earlier for benzil (*J.*, 1939, 1614) to calculate the variations in reciprocal energies of two dipoles, each of 2 D., situated on the nitrogen atoms, when  $\chi = 0^\circ$ ,  $20^\circ$ ,  $40^\circ$ , etc., to  $180^\circ$ . The results again suggest that preferred configurations are of the *trans*-type, although a twisting out of the common plane by  $20$ – $30^\circ$  should be easily accomplished.

Finally, with regard to our own measurements, we may note that, because the allowance for atomic polarisation is most probably inadequate (cf. especially Coop and Sutton, *J.*, 1938, 1269), a polarity of 0.91 D. for 2 : 2'-dipyridyl must be a maximum estimate: the lower its value, of course, the smaller is  $\chi$ . Our conclusions are, therefore, in general accord with those of Cagle (*loc. cit.*) drawn from an X-ray study of crystalline 2 : 2'-dipyridyl.



A. 2 : 2'-Dipyridyl. B. *o*-Phenanthroline. C. Pyridine.

*The Moment of o-Phenanthroline.*—Earlier in this paper we assumed certain directions of action for the main components in 2 : 2'-dipyridyl. The moment of *o*-phenanthroline has therefore been determined to check this point. The value found (4.1 D.) is of the order expected (3.8 D.) for *cis*-dipyridyl on the basis indicated.

*Ultra-violet Spectra.*—Cagle's analysis (*loc. cit.*) of 2 : 2'-dipyridyl, being as yet incomplete, and thus not providing a figure for the internuclear separation of the 1 : 1'-carbon atoms, does not allow an inference—from the % double-bond character of this link—concerning the degree of mesomerism of dipyridyl. In the case of diphenyl, the related dimension is 1.48 Å. (Dhar, *Indian J. Physics*, 1932, **7**, 43), corresponding to a double-bond order of about 10% (cf. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, 1945, p. 174). With diphenyl, also, conjugation between the nuclei is indicated by the higher intensity, compared with benzene, of absorption of ultra-violet light of wave-length *ca.* 2500 Å. ( $\log_{10} \epsilon = 4.3$  and  $2.3$ , respectively).

Using the Beckman photoelectric spectrophotometer, we now find (in alcohol) a less marked contrast between 2 : 2'-dipyridyl and pyridine (see Fig. 2). Our results are very close to those of other authors using heptane as solvent (see Table II), who also showed that the spectrum of 3 : 3'-dipyridyl was less different from that of pyridine than was that of the 2 : 2'-isomer. The indications are, therefore, that internuclear conjugation is not so great in the dipyridyls as in diphenyl.

In view of the *trans*-structure of 2:2'-dipyridyl we have also recorded the spectrum of *o*-phenanthroline. It bears an obvious relationship to that of 2:2'-dipyridyl (Fig. 2). The same cannot be said for diphenyl and phenanthrene (see Table II). A minor point concerning

TABLE II.

	$\lambda_{\max.}$ (m $\mu$ ).	$\log_{10} \epsilon_{\max.}$		$\lambda_{\max.}$ (m $\mu$ ).	$\log_{10} \epsilon_{\max.}$
Pyridine .....	Below 200 <sup>1</sup>	Above 3.75 <sup>1</sup>	Benzene <sup>4</sup> .....	200	3.65
	250 <sup>1</sup>	3.3 <sup>1</sup>		255	2.35
	251 <sup>5</sup>	3.32 <sup>5</sup>			
2:2'-Dipyridyl .....	239 <sup>5</sup>	4.04 <sup>5</sup> (4.12) <sup>2</sup>	Diphenyl <sup>4</sup> .....	246	4.3
	283 <sup>5</sup>	4.16 <sup>5</sup> (4.14) <sup>2</sup>			
3:3'-Dipyridyl .....	266 <sup>3</sup>	3.95 <sup>3</sup>			
<i>o</i> -Phenanthroline ...	230 <sup>5</sup>	4.61 <sup>5</sup>	Phenanthrene <sup>4</sup> .....	210	4.5
	264 <sup>5</sup>	4.43 <sup>5</sup>		250	4.7
				295	4.1
				330	2.9

<sup>1</sup> In heptane, Fischer and Steiner (*Compt. rend.*, 1922, **175**, 882); in heptane, Spiers and Wibaut (*Rec. Trav. chim.*, 1937, **56**, 573). <sup>2,3</sup> In heptane, Spiers and Wibaut (*loc. cit.*). <sup>4</sup> Cf. Review by Braude (*Ann. Reports*, 1945, **42**, 105). <sup>5</sup> In alcohol, present work.

the spectrum of pyridine is that Fischer and Steiner (*loc. cit.*), working with heptane solutions, reported five subsidiary absorption peaks, with diminishing  $\log \epsilon$  values, between 2500 and 3000 A.; accordingly, a number of alcoholic solutions have been carefully examined by us over this interval several times. On each occasion the final curve has agreed with that in Fig. 2.

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