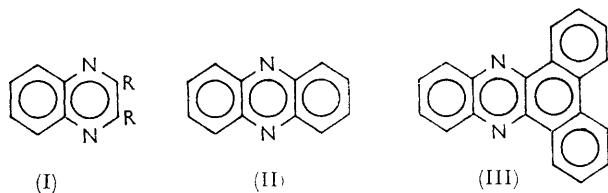


## Molecular Polarisability. Quinoxaline and Some of its Derivatives

By (Miss) J. Hurley and R. J. W. Le Fèvre, University of Sydney, Sydney, N.S.W., Australia

The anisotropies of polarisability of pyridine, quinoxaline, and phenazine are compared with those for benzene, naphthalene, and anthracene. Replacement of  $=CH-$  by  $=N-$  appears to reduce all principal molecular axes in each case, but no stereospecificity of this diminution can be discerned among the three structural pairs considered. For 2,3-diphenylquinoxaline present measurements indicate a conformation in which the two phenyl rings are rotated in the same sense by *ca.*  $39^\circ$  out of the heterocyclic plane.

MEASUREMENTS are here reported on quinoxaline (I;  $R = H$ ), its 2,3-dimethyl and 2,3-diphenyl derivatives



(I;  $R = Me$  or  $Ph$ ), phenazine (II), and 2,3,4,5-dibenzophenazine (III). No molar Kerr constants for

<sup>1</sup> J. L. Snoek, *Phys. Z.*, 1934, **35**, 196.

<sup>2</sup> E. D. Bergmann, L. Engel, and H. Meyer, *Ber.*, 1932, *B*, **65**, 446.

<sup>3</sup> I. G. M. Campbell, C. G. Le Fèvre, and E. E. Turner, *J. Chem. Soc.*, 1938, 404.

molecules of these types have been previously recorded. Dielectric polarisations have been examined hitherto only for 2,3-dimethylquinoxaline<sup>1</sup> and phenazine.<sup>2,3</sup> Although CH and a nitrogen atom are isoelectronic, it is known (from molecular refractions) that the mean polarisabilities of planar aromatic hydrocarbons slightly exceed those of their analogous N-containing heterocycles. Earlier attempts<sup>4a,5</sup> to recognise the sources of such differences partly suggested the present work.

<sup>4</sup> C. G. Le Fèvre and R. J. W. Le Fèvre, (a) *J. Chem. Soc.*, 1955, 2750; (b) ch. XXXVI in "Physical Methods of Organic Chemistry," ed. A. Weissberger, Interscience, New York and London, 3rd edn., 1960, vol. 1, p. 2459; (c) *J. Chem. Soc.*, 1955, 1641; (d) *Chem. and Ind.*, 1955, 1121.

<sup>5</sup> C. G. Le Fèvre, R. J. W. Le Fèvre, B. Purnachandra Rao, and M. R. Smith, *J. Chem. Soc.*, 1959, 1188.

## EXPERIMENTAL

**Solutes.**—The quinoxalines were prepared as described by Leonard and Mader.<sup>6</sup> Compound (I; R = H) was purified by distillation, b. p. 220–223°/760 mm., m. p. 27°; the dimethyl and diphenyl derivatives were recrystallised from water, m. p. 106°, and ethanol, m. p. 124°, respectively; (III) had m. p. 217° from benzene. Phenazine was a commercial specimen, m. p. 171°.

**Solvents, Apparatus, etc.**—Benzene or carbon tetrachloride as solvents were purified as in ref. 7a. Dielectric constants were determined with the apparatus noted by Buckingham *et al.*,<sup>8</sup> and electric birefringences with that of Le Fèvre and Ritchie.<sup>9</sup> Extrapolations, calculations, and other procedures have been standard;<sup>4b,7</sup> symbols used below are defined in the references just quoted (cf. also ref. 10a for a collected list).

**Measurements and Results.**—The increments from solvent to solution, caused by a weight fraction  $w_2$  of solute, in the dielectric constant  $\epsilon$ , density  $d$ , refractive index  $n$ , and Kerr constant  $B$ , at 25°, are indicated by the prefix  $\Delta$  in Table 1. When  $w_2 = 0$  the solvents have the following properties:

	$\epsilon$	$d_4^{25}$	$n_D^{25}$	$10^7 B_D^{25}$
Benzene .....	2.2725	0.87378	1.4973	0.410
Carbon tetrachloride	2.2270	1.58454	1.4575	0.070

TABLE 1

Observed increments of properties

$10^5 w_2$	$10^4 \Delta \epsilon$	$10^5 \Delta d$	$10^4 \Delta n$	$10^{11} \Delta B$
<i>Quinoxaline in benzene</i>				
1485	93	322	14	293
2278	131	491	—	446
2318	134	502	—	—
2629	166	586	30	515
2900	—	—	—	562
3399	197	752	36	696
4669	—	—	50	901

*2,3-Dimethylquinoxaline in benzene*

494	39	90	—	173
508	44	92	—	194
890	70	162	—	311
1087	86	193	—	379
1231	—	—	—	420
1242	98	226	—	433
1575	121	287	14	534
1607	—	—	14	—
1726	—	—	15	—

*2,3-Dimethylquinoxaline in carbon tetrachloride*

485	68	—340	10	235
530	71	—380	11	404
838	115	—	19	609
896	124	—	20	652
988	137	—660	22	—
1339	186	—900	31	671

*2,3-Diphenylquinoxaline in benzene*

454	35	103	6	146
665	47	150	—	—
767	66	173	13	224
933	73	196	—	—
993	77	223	16	341
1006	81	227	16	348
1121	83	256	—	—
1314	99	297	22	465

TABLE 1 (Continued)

*2,3:4,5-Dibenzophenazine in benzene*

228	15	62	2	—
251	17	68	4	—
302	20	81	5	—
311	21	84	5	—
374	—	—	—	241
381	—	—	—	269
397	27	103	6	—
404	—	—	6	269
416	—	—	—	287
427	—	—	7	290

*Phenazine in benzene*

$10^5 w_2$ .....	194	398	499	552	561	651
$10^{11} \Delta B$ .....	111	225	283	317	323	368

TABLE 2

Calculations from Table 1

Solute	{ R = H	(I) R = Me	(I) * R = Me	(I) R = Ph	(II)	(III)
$\alpha \epsilon_1$ .....	0.587	0.790	1.381	0.773	0.570†	0.672
$\beta$ .....	0.251	0.207	—0.430	0.256	0.288†	0.306
$\infty P_2$ (c.c.)	47.59	66.26	64.60	112.65	63.05†	101.64
$\gamma' n_1^2$ .....	0.320	0.263	0.650	0.483	0.570†	0.452
$R_D$ (c.c.) ...	40.61	49.97	50.36	96.40	62.59†	89.33
$\mu$ (D) ‡ ...	0.49	0.82	0.76	0.75	ca. 0†	0.62
$\gamma$ .....	0.071	0.059	0.153	0.107 <sub>5</sub>	0.127	0.100
$\delta$ .....	4.79 <sub>5</sub>	8.48 <sub>5</sub>	89.81	8.19 <sub>8</sub>	13.90	16.51
$10^{12} \infty (mK_2)$	51.0 <sub>8</sub>	105.7	107.1	180.6	193.5	355.4

\* Solvent: carbon tetrachloride. † From ref. 3. ‡ Calc. assuming  $1.05R_D$   $\delta$  distortion polarisation.

## DISCUSSION

**Polarisability Semi-axes for Quinoxaline.**—A knowledge of these is required for further discussion of quinoxaline derivations. If  $b_1$ ,  $b_2$ , and  $b_3$  (in  $10^{-24}$  c.c. units) are the principal polarisabilities of (I; R = H), then from the measurements by Brühl<sup>11</sup> we obtain (cf. ref. 7b, pp. 36 and 44)  $R_\infty = 38.183$  c.c. and

$$b_1 + b_2 + b_3 = 45.403 \quad (1)$$

Only one other equation based on experiment is available, namely (2),

$$\theta_1 + \theta_2 = 1214 \times 10^{-37} \quad (2)$$

(cf. ref. 7b, pp. 44 and 45 for expansions of  $\theta_1$  and  $\theta_2$ ); some assumption regarding one of the three unknowns in (1) is therefore unavoidable.

We note that the  $\infty(mK_2)$  of quinoxaline is near that ( $48.1 \times 10^{-12}$ ) recorded<sup>4c</sup> for naphthalene and for the  $\theta_1$ -containing component ( $49.0 \times 10^{-12}$ ) in the  $\infty(mK_2)$  of quinoline;<sup>5</sup>  $R_D$ 's are likewise close (quinoxaline, 40.6; naphthalene, 44.4; quinoline, 41.9 c.c.). As these molecules are similar in shape and planarity, and since

<sup>6</sup> N. J. Leonard and P. M. Mader, *J. Amer. Chem. Soc.*, 1950, **72**, 5388.

<sup>7</sup> R. J. W. Le Fèvre, (a) "Dipole Moments," Methuen, London, 3rd edn., 1953; (b) *Adv. Phys. Org. Chem.*, 1965, **3**, 1.

<sup>8</sup> A. D. Buckingham, J. Y. H. Chau, H. C. Freeman, R. J. W. Le Fèvre, D. A. A. S. Narayana Rao, and J. Tardif, *J. Chem. Soc.*, 1956, 1405.

<sup>9</sup> R. J. W. Le Fèvre and G. L. D. Ritchie, *J. Chem. Soc.*, 1963, 4933.

<sup>10</sup> R. J. W. Le Fèvre and K. M. S. Sundaram, (a) *J. Chem. Soc.*, 1962, 1494; (b) 1963, 4442.

<sup>11</sup> J. W. Brühl, *Z. phys. Chem.*, 1897, **22**, 390.

$b_1$  and  $b_2$  in quinoline and naphthalene do not differ greatly, a rough estimate may be made by supposing that  $b_1 = b_2$  in quinoxaline. Solution of (1) and (2) on this basis yields  $b_1 = b_2 = 18.09$  and  $b_3 = 9.23$ .

Alternatively, use may be made of the empirical fact that the "vertical" semi-axes of the polarisability ellipsoids of the C-C, C=C, and C≡C bonds,<sup>12,13</sup> are related to the carbon-carbon inter-centre distances  $r$  (in Å) by

$$b_V = 11.183 - 12.384r + 3.434r^2 \quad (3)$$

If the C-H link is isotropic<sup>4d,7b,12</sup> with  $b_V = 0.65$ , then, since  $r(\text{C} \cdots \text{C})$  in pyridine is  $1.3944$  Å and  $b_3$  (pyridine) is  $5.645$ , it follows that each CN bond in this heterocycle contributes a  $b_V$  of  $0.415$  to the polarisability perpendicular to the ring-plane. No bond lengths in quinoxalines seem yet to have been determined, but as the  $r(\text{C} \cdots \text{N})$ 's in pyridine, pyrazine, acridine, and phenazine are all<sup>14</sup> within the range  $1.334$ – $1.350$  Å we may reasonably take  $b_V(\text{CN})$  as the same throughout. Entry 167 s., in ref. 14, provides metrical details for phenazine; the mean  $r(\text{C} \cdots \text{C})$  is  $1.406$  Å. If  $r = 1.406$  Å is valid also for quinoxaline, the predicted  $b_3$  becomes  $9.48$  and  $b_1$  and  $b_2$  follow as  $18.72$  and  $17.21$ , respectively. The reported<sup>4a</sup> semi-axes for naphthalene are  $b_1 : b_2 : b_3 = 21.5 : 17.6 : 10.3$ ; each of these is slightly higher than the corresponding value for quinoxaline; benzene and pyridine are related in the same way ( $11.2 : 11.2 : 7.36$ ;  $10.7 : 10.4 : 6.45$ ).

**Polarisability Semi-axes for 2,3-Dimethylquinoxaline.**—Addition of  $b_V$ 's for two C-C and four C-H bonds to the  $b_3$  of quinoxaline gives  $12.60$  as the  $b_3$ (calc.) for the dimethyl derivative. The data in Table 2, with  $R_P = R_\infty = 0.944R_D$  (i.e., using the  $R_\infty/R_D$  ratio displayed by quinoxaline), yield  $b_1 : b_2 : b_3 = 23.9 : 19.6 : 12.6$  or  $24.5 : 19.4 : 12.6$  from the measurements in benzene or carbon tetrachloride, respectively. An assumption that  $b_1 = b_2$  leads to  $b_1 = b_2 = 22.5$  or  $22.7$  and  $b_3 = 11.0$  or  $11.1$  in these solvents. If, in 2,3-dimethylquinoxaline the two C-Me units are mutually inclined at  $60^\circ$  in the ring-plane and carry the usual<sup>12</sup> C-C and C-H polarisabilities, then computation from the semi-axes of quinoxaline requires  $b_1 = 22.9$ ,  $b_2 = 20.7$ , and  $b_3 = 12.6$ .

**Polarisability Semi-axes for Phenazine.**—The  $b_3$  for (II) should be near  $2 \times b_3(\text{benzene})$  plus  $4 \times b_V(\text{CN})$  minus  $4 \times b_V(\text{CH})$ , i.e., ca.  $13.8$ . However, the mean  $r(\text{CC})$  in phenazine is a little greater than in benzene.<sup>14</sup> Using  $r(\text{CC}) = 1.406$  Å in equation (3),  $b_3$ (phenazine) appears as  $13.57$ , whence (with other details from Table 2)  $b_1 = 35.9$  and  $b_2 = 20.8$ . These are different from the corresponding data (viz.,  $b_1 : b_2 : b_3 = 33.9 : 29.2 : 12.9$ ) for anthracene, deduced in ref. 10b under difficulties from low solubility, by the visual method of measuring electric birefringences. Currently,

repetitions<sup>15</sup> by the photometric technique<sup>9</sup> are indicating that the  $\infty(mK_2)$  recorded previously<sup>10b</sup> was probably too high; a more correct  $b_3$  for anthracene appears to be ca.  $16$  (as would be expected from the  $\text{C} \cdots \text{C}$  distances listed in ref. 14 for this hydrocarbon) with  $b_1$  and  $b_2$  being  $36$  and  $24$ , respectively.

**Polarisability Semi-axes for Dibenzophenazine (III).**—Noting that  $r(\text{CC})$  tends to increase with the size of the polynuclear hydrocarbon containing such bonds,<sup>14</sup> we may take  $1.41$  Å as a likely mean  $\text{C} \cdots \text{C}$  separation in (III); proceeding as above, therefore, the  $b_3$  expected for this molecule is  $21.56$ . Then, provided that  $R_P = 0.944R_D$ , the  $mK$  and  $\mu$  of Table 2 yield<sup>7b</sup>  $b_1 = 47.7_6$  and  $b_2 = 30.9_5$  ( $b_1$  being measured parallel to  $\mu_{\text{resultant}}$ ). A computation on the basis that  $b_1 = b_2$  leads to semi-axes of  $42$ ,  $42$ , and  $17$ . No data on the related dibenzanthracene are available for comparison. From the bond electronic polarisations of Le Fèvre and Steel,<sup>16</sup> the total  $b_1 + b_2 + b_3$  for (III) should exceed that for (II) by some  $38$  polarisability units; from observation, the excess is about  $30$ . An equation analogous to (3), but developed for longitudinal polarisabilities, suggests that an aromatic CC bond with  $r(\text{CC}) = 1.41$  Å should have  $b_L(\text{CC}) = 2.2$ ; since  $b_V(\text{CC})$  is ca.  $0.55$  for this length,  $b_T(\text{CC})$ , by difference from the total polarisability ( $3.027$ ) of the  $\text{C}_{\text{Ar}}\text{--C}_{\text{Ar}}$  link,<sup>16</sup> becomes  $0.29$ . Addition of ten CC and four CH bonds to (II) to produce (III) would (were all six-membered rings regular hexagons) cause increase in  $b_1$ ,  $b_2$ , and  $b_3$  of  $14$ ,  $16$ , and  $8$ , respectively. Present results indicate increments of  $12$ ,  $10$ , and  $8$ . We suspect, therefore, that some "negative exaltation" is occurring across the direction of action of  $\mu_{\text{resultant}}$ .

**The Conformation of 2,3-Diphenylquinoxaline.**—Let rectangular co-ordinates OX, OY, and OZ be located in (I;  $R = \text{Ph}$ ), as drawn, with the positive OX and OY directions running, respectively, to the right-hand side

TABLE 3  
Calculation of molar Kerr constants for 2,3-diphenylquinoxaline

$\phi^\circ$	$b_{xx}$	$b_{yy}$	$b_{zz}$	$b_{xx}$	$b_{yy}$	$10^{12} mK$ (calc.)
0	41.7	36.6	22.1	0	0	232
35 s. }	41.1	34.7	24.6 <sub>5</sub>	1.81	0	179
35 u. }				0	-3.13	189
40 s. }	40.9	34.2	25.3	1.90	0	167
40 u. }				0	-3.28	178
45 s. }	40.8	33.7	26.0	1.92 <sub>5</sub>	0	155
45 u. }				0	-3.33	167
90	39.8	30.8	29.8	0	0	104

and the top of the page. In the absence of structural information we assume that the two Ph-C bonds are mutually inclined at  $60^\circ$ . The phenyl groups may be twisted out of the OX,OY plane by  $\phi^\circ$  to produce

<sup>14</sup> "Interatomic Distances Supplement," ed. L. E. Sutton, *Chem. Soc. Spec. Publ.* No. 18, 1965.

<sup>15</sup> R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc. (B)*, 1967, 595.

<sup>16</sup> R. J. W. Le Fèvre and K. D. Steel, *Chem. and Ind.*, 1961, 670.

<sup>12</sup> R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, *J. Chem. Soc. (B)*, 1966, 273, 281.

<sup>13</sup> R. Bramley, C. G. Le Fèvre, R. J. W. Le Fèvre, and B. Purnachandra Rao, *J. Chem. Soc.*, 1959, 1183.

alternative conformations which are either (a) symmetrical or (b) unsymmetrical about the OZ,OX plane. Since each  $C_6H_5$  is attached next to an N atom, it seems unlikely that conjugative effects will act to twist one ring more than the other; accordingly, we consider only rotations of  $+\phi, -\phi$  and  $+\phi, +\phi$ . In terms of the polarisability tensor shown as equation 33 in ref. 7b, all non-diagonal elements will be zero when  $\phi = 0^\circ$  or  $90^\circ$ , but for intermediate values of this angle the  $b_{xy}$  ( $= b_{yx}$ ) in cases of type (a) and the  $b_{yz}$  ( $= b_{zy}$ ) in cases of type (b) will not vanish. Table 3 includes computations of molar Kerr constants for a few conformations (cf. ref. 7b, pp. 47, 53—55).

The observed value is  $181 \times 10^{-12}$ . Leybold models suggest that when  $\phi$  is *ca.*  $35^\circ$  the symmetrical form is sterically hindered while adoption of the unsym-

metrical version is unimpeded. Predicted  ${}_mK$ 's for unsymmetrical rotations can be summarised by

$${}_mK(\phi) = 104 + 128 \cos^2\phi$$

whence the measured  ${}_mK$  corresponds to  $\phi = 39^\circ$ , a credible result (cf. *o*-terphenyl<sup>17</sup>).

*Conclusion.*—Present results indicate that each of principal polarisabilities in pyridine, quinoxaline, or phenazine is less than the corresponding value for benzene, naphthalene, or anthracene, respectively. The differences show no regularities along the  $b_1$ ,  $b_2$ , and  $b_3$  directions of the related hydrocarbons and heterocycles; they appear unrelated to the sums  $b_1 + b_2 + b_3$  for the six molecules just named (27·55, 45·41, 70·3, 29·76, 49·4, and 76·2) or to the  $b_L + b_T + b_V$  totals expected<sup>16</sup> for  $(CHCH)_{Ar}$ ,  $CH=CH$ , and  $CH=N$  bonds.

<sup>17</sup> I. L. Karle and L. O. Brockway, *J. Amer. Chem. Soc.*, 1944, **66**, 1974.