436. *Molecular Polarisability. The Conformations of Various* N-*Substituted Anilines, Piperidines, and Piperazines.*

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The following conclusions regarding solute species in benzene are reached by the application of polarity, polarisability, and steric considerations to the measurements reported in Tables 1—3: aniline has a pyramidal conformation in which the H–H line is parallel to the C_6H_5 plane; *NN*-dimethylaniline conforms to the aniline model, as also do the $Ar{\cdot}N(CH_2{\cdot})_2$ portions of *NN*-diethylaniline, 1-phenylpiperidine, and the 1,4-diarylpiperazines; 1-phenylpiperidine is a "chair" structure with the C_6H_5 group attached equatorially; with piperazine and its disubstituted derivatives both "boat" and "chair" forms occur, the N–H and N–Me bonds being sometimes equatorial and sometimes axial, and the N–Ar bonds always equatorial.

THE primary objective of the present work is to examine the conformations of 1-phenylpiperidine and of certain 1,4-disubstituted piperazines by using polarisability information recently established[1,2] for the various linkages involved. Measurements of the dipole

TABLE 1. *Depolarisation factors for light scattered by solutions of* (a) *aniline and* (b) *dimethylaniline in n-hexane.*

(a) Solute: Aniline

10^5f_2 *	1854	2137	2478	2736
$\Delta\Delta_{12}$	0·013	0·015	0·016	0·019

whence $\Delta\Delta_{12} = 0{\cdot}726f_2 - 1{\cdot}80f_2^2$

10^5f_2 *	984	1292	1447	1786
d_4^{25}	0·67553	0·67625	0·67660	0·67738

whence $\sum\Delta d/\sum f_2 = 0{\cdot}230$, and $_\infty\delta_2^2 = 0{\cdot}054$

(b) Solute: Dimethylaniline

10^5f_2 *	1020	1866	3393	5171	6147
$\Delta\Delta_{12}$	0·005	0·010	0·020	0·030	0·035
d_4^{25}	—	—	0·68293	0·68810	0·69040

whence $\Delta\Delta_{12} = 0{\cdot}576_5f_2 - 0{\cdot}188f_2^2$, $\sum\Delta d/\sum f_2 = 0{\cdot}283$, and $_\infty\delta_2^2 = 0{\cdot}043$.

* For $f_2 = 0$, $\Delta_1 = 0{\cdot}0973$, $d_4^{25} = 0{\cdot}67327$ (f_2 = molar fraction of solute, cf. ref. 3).

TABLE 2. *Incremental Kerr effects, refractive indexes, dielectric constants, and densities for solutions in benzene * at 25°.*

Solute: 1-Phenylpiperidine

10^5w_2	539	623	949	1045	1205	1462	1834
$10^7\Delta B$	0·044	0·049	0·081	0·092	0·106	0·132	0·170

whence $10^7\Delta B = 7{\cdot}71_4w_2 + 87{\cdot}6w_2^2$

10^5w_2	1893	3547	4442	5614	7520	8522
Δn	0·0011	0·0020	0·0024	0·0032	0·0042	0·0046

whence $\sum\Delta n/\sum w_2 = 0{\cdot}056$

10^5w_2	1459	1893	3547	4019	8552	10,328	14,069
ε^{25}	2·3076	2·3175	2·3542	2·3667	2·4602	2·4994	2·5777
d_4^{25}	—	0·87589	0·87790	0·87849	0·88768	0·88588	0·89037

whence $\sum\Delta\varepsilon/\sum w_2 = 2{\cdot}29$; $\sum\Delta d/\sum w_2 = 0{\cdot}116$

Solute: 1-*p*-Nitrophenylpiperidine

10^5w_2	115	193	224	352	430	569	833
$10^7\Delta B$	0·37	0·63	0·68	1·18	1·46	1·79	2·60

whence $10^7\Delta B = 338w_2 - 3027w_2^2$

10^5w_2	1866	2763	3197	3735
Δn	0·0028	0·0043	0·0049	0·0057

whence $\sum\Delta n/\sum w_2 = 0{\cdot}154$

10^5w_2	224	430	569	833	1382	2351	3622
ε^{25}	2·3304	2·3818	2·4141	2·4779	2·6173	2·8581	3·1757
d_4^{25}	0·87427	0·87486	—	0·87578	0·87731	0·87975	0·88298

whence $\sum\Delta\varepsilon/\sum w_2 = 25{\cdot}1$, $\sum\Delta d/\sum w_2 = 0{\cdot}246$

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[1] Aroney and Le Fèvre, *Proc. Chem. Soc.*, 1958, 82; *J.*, 1958, 3002.

[2] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261; *J.*, 1954, 1577; *Chem. and Ind.*, 1955, 506, 1121; 1956, 54; *J.*, 1956, 3549.

[3] Le Fèvre and Purnachandra Rao, *J.*, 1957, 3644; 1958, 1465; 1960, 119.

TABLE 2. (*Continued.*)

Solute: Piperazine

10^5w_2	619	697	817	870	968	1159	1350	1365
$10^7\Delta B$	−0·004	−0·005	−0·005	−0·006	−0·005	−0·007	−0·009	−0·009

whence $10^7\Delta B = -0{\cdot}605w_2 - 2{\cdot}87w_2^2$

10^5w_2	446	533	697
Δn	0·0001	0·0002	0·0002

whence $\sum\Delta n/\sum w_2 = 0{\cdot}026$

10^5w_2	534	606	703	845	916	1159	1365
ε^{25}	2·2880	2·2892	2·2917	2·2971	2·2989	2·3055	2·3121

whence $\sum\Delta\varepsilon/\sum w_2 = 2{\cdot}85$

10^5w_2	307	446	534	697	703	769
d_4^{25}	0·87411	0·87428	0·87435	0·87450	0·87441	0·87458

whence $\sum\Delta d/\sum w_2 = 0{\cdot}104$

Solute: 1,4-Dinitrosopiperazine

10^5w_2	187	219	339	415	488
$10^7\Delta B$	−0·006	−0·007	−0·013	−0·015	−0·018
Δn	—	—	—	—	0·0001

whence $10^7\Delta B = -3{\cdot}15w_2 - 121w_2^2$, $\Delta n/w_2 = 0{\cdot}02$

10^5w_2	187	219	292	339	415	488
ε^{25}	2·2790	2·2800	2·2825	2·2838	2·2863	2·2889
d_4^{25}	0·87435	0·87447	0·87470	0·87487	0·87520	0·87536

whence $\sum\Delta\varepsilon/\sum w_2 = 3{\cdot}39$, $\sum\Delta d/\sum w_2 = 0{\cdot}321$

Solute: 1,4-Dimethylpiperazine

10^5w_2	1730	3275	5874	6498	7463
$10^7\Delta B$	−0·006	−0·009	−0·012	−0·014	−0·018
Δn	—	—	−0·0029	−0·0032	−0·0039

whence $10^7\Delta B = -0{\cdot}284w_2 + 0{\cdot}851w_2^2$, $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}050$

10^5w_2	1730	3275	5874	6498	7463
ε^{25}	2·2742	2·2752	2·2770	2·2784	2·2784
d_4^{25}	0·87338	0·87301	0·87240	0·87229	0·87205

whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}085$, $\sum\Delta d/\sum w_2 = -0{\cdot}0233$

Solute: 1,4-Diphenylpiperazine

10^5w_2	267	343	462	605	617	708	938
$10^7\Delta B$	0·005	0·008	0·011	0·014	0·015	0·017	0·020

whence $10^7\Delta B = 2{\cdot}51w_2 - 32{\cdot}5w_2^2$

10^5w_2	576	605	617	963
Δn	0·0005	0·0006	0·0007	0·0010

whence $\sum\Delta n/\sum w_2 = 0{\cdot}101$

10^5w_2	558	603	605	617	637	670
ε^{25}	2·2755	2·2756	2·2756	2·2757	2·2759	2·2761
d_4^{25}	0·87481	0·87489	0·87488	0·87491	0·87497	0·87505

whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}526$, $\sum\Delta d/\sum w_2 = 0{\cdot}185$

Solute: 1,4-Di-*p*-tolylpiperazine

10^5w_2	193	219	377	559	752	974	1063	1150
$10^7\Delta B$	0·004	0·006	0·011	0·015	0·019	0·024	0·028	0·030

whence $10^7\Delta B = 2{\cdot}64w_2 - 6{\cdot}04w_2^2$

10^5w_2	711	752	848	974	1150
Δn	0·0007	0·0007	0·0008	0·0010	0·0011

whence $\sum\Delta n/\sum w_2 = 0{\cdot}097$

10^5w_2	558	652	711	752	848	974
ε^{25}	2·2753	2·2757	2·2761	2·2761	2·2766	2·2769

whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}486$

10^5w_2	382	494	558	652	711	848	974	1150
d_4^{25}	0·87436	0·87456	0·87463	0·87479	0·87490	0·87514	0·87532	0·87555

whence $\sum\Delta d/\sum w_2 = 0{\cdot}156$

Solute: *NN'*-Di-*p*-nitrophenylpiperazine

10^6w_2	98	104	134
ε^{25}	2·2737	2·2737	2·2740
d_4^{25}	0·87381	0·87381	0·87382

whence $\sum\Delta\varepsilon/\sum w_2 = 11{\cdot}6$; $\sum\Delta d/\sum w_2 = 0{\cdot}298$

* For $w_2 = 0$, $\varepsilon^{25} = 2{\cdot}2725$, $d_4^{25} = 0{\cdot}87378$, $n_1 = 1{\cdot}4973$, $B_1 = 0{\cdot}410 \times 10^{-7}$.

moments and molar Kerr constants in benzene have therefore been made, as listed in Tables 2 and 3; to assist their interpretation, knowledge of the molecular anisotropies of aniline and dimethylaniline as solutes became necessary, and these—determined[3] in n-hexane—are given in Table 1.

EXPERIMENTAL

Apparatus and Procedures.—These have been as described in refs. 1—3; ref. 3 deals particularly with the observation of depolarisation factors for scattered light. Computational methods and symbols here used are as explained in a review;[2] a full list of symbols with definitions also appears in ref. 4.

Materials.—Solutes were obtained or purified as follow: 1-phenylpiperidine, b. p. 255—260°, from bromobenzene, piperidine, and sodamide;[5] 1-*p*-nitrophenylpiperidine, m. p. 102—103° (from alcohol), from *p*-chloronitrobenzene and piperidine;[6] piperazine, b. p. 142°, from the hydrate by twice distilling it over solid sodium hydroxide followed by once over sodium metal with exclusion of moist air; dinitrosopiperazine, m. p. 156° (from hot water), from the base;[7] 1,4-dimethylpiperazine, b. p. 130—131°, from piperazine, formic acid, and formaldehyde;[8] 1,4-diphenylpiperazine, m. p. 164° (from benzene), from ethylene dibromide and aniline;[9] 1,4-di-*p*-tolylpiperazine, m. p. 189° (from benzene), from *p*-toluidine as in ref. 9; 1,4-di-*p*-nitrophenylpiperazine, m. p. 261° (decomp.) after three crystallisations from nitrobenzene, extraction with boiling alcohol, and drying at 100° (Found: C, 58·5; H, 5·0. Calc. for $C_{16}H_{16}O_4N_4$: C, 58·5; H, 4·9%), from *p*-chloronitrobenzene and piperazine hexahydrate at 150° for 3 hr. [cf. Schmidt and Withmann,[10] who gave m. p. 248° (decomp.)].

DISCUSSION

Previous Work Relevant to Table 3.—Each of the seven molar Kerr constants is here reported for the first time; that for 1-*p*-nitrophenylpiperidine is remarkable as the largest so far recorded, considerably exceeding the $_\infty({}_mK_2)$ values for nitrobenzene[11] (*ca.* 1100×10^{-12}) or 4-nitrodiphenyl[12] (*ca.* 3260×10^{-12}).

Of the dipole moments listed in Table 3, the literature contains information only for piperazine and its 1,4-dimethyl and -diphenyl derivatives.[13,14] The following points may be noted: The moment of 1-phenylpiperidine ($1{\cdot}7_4$ D) is close to that ($1{\cdot}7_8$ D) obtained for *NN*-diethylaniline when the data of Barclay, Le Fèvre, and Smythe[15] are recalculated on the basis that $_DP = 1{\cdot}05R_D$; the high polarity of 1-*p*-nitrophenylpiperidine recalls Marsden and Sutton's value[16] for *p*-nitrodimethylaniline ($6{\cdot}8_7$ D). Our estimate for piperazine is identical with that ($1{\cdot}4_7$ D) given by Martin,[13] but for the 1,4-diphenyl derivative, our moment is $0{\cdot}2_6$ D lower. For 1,4-dimethylpiperazine we obtain the same value for $_\infty P_2$ as George and Wright,[14] but use of $_DP = 37{\cdot}8$ c.c. leads to the smaller moment of $0{\cdot}4_4$ D.

Conformations of Aniline, Dimethylaniline, and Diethylaniline.—Consideration of these three molecules must precede discussion of others named in Table 3. Aroney and

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[4] Le Fèvre, Le Fèvre, and Oh, *Austral. J. Chem.*, 1957, **10**, 218.

[5] Brotherton and Bunnett, *Chem. and Ind.*, 1957, 80.

[6] Le Fèvre and Turner, *J.*, 1927, 1113.

[7] Ladenburg, *Ber.*, 1891, **24**, 2400.

[8] Eschweiler and Clarke, " Organic Reactions," Wiley, New York, Vol. 5, p. 323.

[9] Pratt and Young, *J. Amer. Chem. Soc.*, 1918, **40**, 1429.

[10] Schmidt and Withmann, *Ber.*, 1891, **24**, 3240.

[11] Le Fèvre and Le Fèvre, *J.*, 1953, 4041.

[12] Chau, Le Fèvre, and Le Fèvre, *J.*, 1959, 2666.

[13] Martin, Thesis, London, 1936, pp. 134, 180 (quoted by Partington, " An Advanced Treatise on Physical Chemistry," Vol. 5, Longmans, Green & Co., London, 1954, p. 538).

[14] George and Wright, *Canad. J. Res.*, 1958, **36**, 189.

[15] Barclay, Le Fèvre, and Smythe, *Trans. Faraday Soc.*, 1951, **47**, 357.

[16] Marsden and Sutton, *J.*, 1936, 599.

TABLE 3. *Polarisations, dipole moments, and molar Kerr constants deduced from benzene solutions at 25°.*

	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ(D)	$_\infty(_mK_2) \times 10^{12}$
1-Phenylpiperidine	2·29	0·133	0·037	18·81	117·1	52·0	1·7$_4$	226
1-*p*-Nitrophenylpiperidine	25·1	0·282	0·103	824	1024	67·7	6·8$_0$	12,670
Piperazine	2·85	0·119	0·017	−1·47$_6$	72·0	26·7	1·4$_7$	−12·7
1,4-Dinitrosopiperazine ...	3·39	0·367	0·013	−7·68	123·0	32·2	2·1$_0$	−94
1,4-Dimethylpiperazine ...	0·085	−0·027	−0·033	−0·693	41·8	36·0	0·44	2·9
1,4-Diphenylpiperazine ...	0·526	0·212	0·067	6·12$_2$	87·6	76·7	0·59	119
1,4-Di-*p*-tolylpiperazine ...	0·486	0·179	0·065	6·43$_9$	98·9	88·1	0·56	140
1,4-Di-*p*-nitrophenylpiperazine	11·6	0·341	—	—	790	108·4	*ca.* 6	—

* Calculated by assuming the distortion polarisation to be 1·05R_D.

Le Fèvre[17] have recorded the following values for $10^{12}\,_\infty(_mK_2)$: Aniline, 22·4; dimethylaniline, 134·2; diethylaniline, 190·6.

For aniline, $\mu_{\text{resultant}} = 1{\cdot}50$ D,[18] $R_\infty = 29{\cdot}1$ c.c. (calc. from refractions by Vogel[19]), and $_\infty\delta_2{}^2 = 0{\cdot}054$ (present work). If now, following Marsden and Sutton,[16] $\mu_{\text{resultant}}$ is taken as acting at 43° to the C–N bond and in the plane defined by the C–N longitudinal axis and the bisector of the HNH angle, we have, since $b_1 + b_2 + b_3 = 3{\cdot}460 \times 10^{-23}$,

$$\theta_1 = 3{\cdot}49 \times 10^{-35} \text{ and } \theta_2 = 1{\cdot}83 \times 10^{-35}$$

which lead to alternative solutions:

$$\left.\begin{array}{l} 10^{23}b_1 = 1{\cdot}49 \\ 10^{23}b_2 = 1{\cdot}14 \\ 10^{23}b_3 = 0{\cdot}83 \end{array}\right\} \text{ or } \left\{\begin{array}{l} 0{\cdot}87 \\ 1{\cdot}08 \\ 1{\cdot}51 \end{array}\right.$$

(It is assumed that b_1 lies along the C–N axis, and that b_3 is at 90° to the C–N bond and in the plane just mentioned.) By tensor addition (using the anisotropic C–N and N–H polarisabilities of ref. 1 together with related data[3] for the phenyl group) semi-axes and molar Kerr constants are calculable for the two extreme models: (*a*) in which the line joining the amino-hydrogen atoms is parallel to the plane of the C_6H_5 ring, or (*b*) in which it is perpendicular. (The CNH and HNH inter-bond angles are taken as tetrahedral; cf. refs. 20 and 21.) Results appear as follows:

	Conformation (*a*)	Conformation (*b*)
$10^{23}b_1$	1·27	1·27
$10^{23}b_2$	1·24	0·86
$10^{23}b_3$	0·89	1·27

Evidently, therefore, of the two experimental sets of semi-axes, that in which $b_1 = 1{\cdot}49 \times 10^{-23}$ is the more appropriate. No account has so far been taken of resonance interaction; this (cf. second ref. under 3) should cause a positive exaltation of polarisability along the b_1 direction; in fact, comparison of the semi-axes predicted above for (*a*) with those from experiment shows that exaltations of $\Delta b_1 = +0{\cdot}22$, $\Delta n_2 = -0{\cdot}10$, and $\Delta b_3 = -0{\cdot}06$ (all $\times\ 10^{-23}$ c.c.) will satisfactorily explain the present measurements.

In passing, it is relevant to the conclusions of ref. 17 that if, in the analysis of our observations, b_1 were taken along the direction of $\mu_{\text{resultant}}$, b_1 would emerge as $1{\cdot}17 \times 10^{-23}$—a figure smaller than any of the predicted values. Moreover, were aniline

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[17] Aroney and Le Fèvre, *J.*, 1956, 2775.

[18] Le Fèvre, Roberts, and Smythe, *J.*, 1949, 902.

[19] Vogel, *J.*, 1948, 1825.

[20] Brockway and Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036.

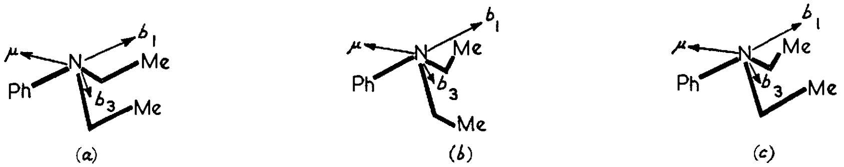
[21] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945.

to be a completely flat structure, b_1, b_2, and b_3 would be (exaltations being neglected) respectively 1·26, 1·24, and 0·90 ($\times 10^{-23}$ c.c.), corresponding to a molar Kerr constant of $+52 \times 10^{-12}$, against the ${}_{\mathrm{m}}K_{\mathrm{obs.}}$ of $22{\cdot}4 \times 10^{-12}$; the ${}_{\mathrm{m}}K_{\mathrm{calc.}}$ would be increased if exaltations were considered. Aniline as a solute in benzene is thus clearly non-planar; for it, conformation (*a*) above is suggested as most reasonably meeting the requirements of available evidence.

For dimethylaniline we have $b_1 + b_2 + b_3 = 4{\cdot}608 \times 10^{-23}$ c.c. (from ref. 19) and ${}_{\infty}\delta_2{}^2 = 0{\cdot}043$ (Table 1); θ_1 is therefore $5{\cdot}15 \times 10^{-35}$. From Table 3, $\theta_1 + \theta_2$ is $31{\cdot}9 \times 10^{-35}$, whence $\theta_2 = 26{\cdot}76 \times 10^{-35}$. Extraction of the molecular semi-axes of polarisability requires knowledge of the disposition of $\mu_{\mathrm{resultant}}$ (1·61 D, cf. ref. 15) in relation to the directions of b_1, b_2, and b_3. In the absence of other information we make two assumptions: (*a*) following Wepster,[22] that the Me • • • Me line lies parallel to the plane of the C_6H_5 ring, and (*b*) following Marsden and Sutton,[16] that $\mu_{\mathrm{resultant}}$ acts at 38° to the C_{Ar}–N bond and in the plane perpendicular to the Ar ring. Without modification these do not permit the mathematical solution desired, probably because of small errors in our observational equations. Accordingly, rather than altering either (*a*) or (*b*), we prefer to reduce the unknown semi-axes to two by estimating that b_i which is certain to be the least, namely b_3. This may be done by using the bond and group semi-axes [1-3] for N–C, C_6H_5–, and C–H, in a model in which the three angles at the nitrogen atom are tetrahedral, and by correcting the value so obtained by adding the exaltation already noted for aniline; alternatively, the b_3 quoted above for aniline may be changed by withdrawal of data for the N–H links and substitution of those for two N–CH_3 units. By the first route $10^{23}b_3$ emerges as $1{\cdot}25 - 0{\cdot}06 = 1{\cdot}19$; by the second, directly as 1·19. Insertion of $b_3 = 1{\cdot}19 \times 10^{-23}$ into the expressions for the total polarisability and for θ_2 now yields $10^{23}b_1$ and $10^{23}b_2$ as 2·16 and 1·26, respectively. From these, by subtractions corresponding to two C–H links, may be drawn the semi-axes (2·03, 1·13, and 1·06) appropriate for that fragment, namely $C_6H_5{\cdot}N(CH_2{\cdot})_2$, which is basic to several of the molecules to be discussed later.

As a test the new data are applied to diethylaniline, for which [15] $\mu_{\mathrm{resultant}}$ (= 1·81 D) is taken as acting as in dimethylaniline.[16] Three conformations are depicted in Fig. 1 (*a*), (*b*), and (*c*); the calculated semi-axes, and the expected ${}_{\mathrm{m}}K$'s being given below. Inspection of models shows 1(*a*) to be less stable than (*b*) or (*c*) in which the methyl groups are more separated. The molar Kerr constant by experiment is 191×10^{-12}, in good agreement with that forecast for (*c*), a conformation intermediate between (*a*) and (*b*).

FIG. 1.



(*a*) Calc. $b = b_1 = 2{\cdot}62 \times 10^{-23}$
$b_2 = 1{\cdot}57$,,
$b_3 = 1{\cdot}50$,,
Calc. ${}_{\mathrm{m}}K = 218 \times 10^{-12}$

(*b*) Calc. $b = b_1 = 2{\cdot}48 \times 10^{-23}$
$b_2 = 1{\cdot}64$,,
$b_3 = 1{\cdot}57$,,
Calc. ${}_{\mathrm{m}}K = 166 \times 10^{-12}$

(*c*) Calc. $b = b_1 = 2{\cdot}55 \times 10^{-23}$
$b_2 = 1{\cdot}61$,,
$b_3 = 1{\cdot}54$,,
Calc. ${}_{\mathrm{m}}K = 190 \times 10^{-12}$

Conformation of N-*Phenylpiperidine*.—By analogy with the stereochemistry of cyclohexane and from the evidence put forward by us recently,[1] *N*-phenylpiperidine should contain the piperidino-ring as a " chair " to which a phenyl group, being large, would be attached by an "equatorial" bond (see Fig. 2). The observed ${}_{\infty}({}_{\mathrm{m}}K_2)$ of 226×10^{-12} agrees with this: if b_1 is along the C–N direction and b_3 is perpendicular to b_1 and in the plane of C–N and the bisector of the angle $CH_2{\cdot}N{\cdot}CH_2$, the semi-axes ($\times 10^{23}$) predicted are $b_1 = 2{\cdot}70$, $b_2 = 1{\cdot}70$, and $b_3 = 1{\cdot}60$, from which (with $\mu_{\mathrm{resultant}} = 1{\cdot}74$ D, cf. Table 3)

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[22] Wepster, *Rec. Trav. chim.*, 1957, **76**, 335, 357.

an ${}_{\mathrm{m}}K$ of 202×10^{-12} is calculable if $\mu_{\text{resultant}}$ is at 38° to b_1; were the angle only 3° less, ${}_{\mathrm{m}}K_{\text{calc.}}$ is 229×10^{-12}; the correct angle thus appears to be *ca.* 36°. The corresponding ${}_{\mathrm{m}}K$'s computed for the conformation in which the phenyl group is attached axially are 179×10^{-12} if the angle between b_1 and $\mu_{\text{resultant}}$ is 35° or 157×10^{-12} if it is 38°. The measured ${}_{\mathrm{m}}K$ (226×10^{-12}) is thus in agreement with expectations noted at the beginning of this paragraph.

Conformations of Piperazine and its 1,4-*Disubstituted Derivatives*.—For the base itself we have considered nine conformations produced by taking NCC and CCC angles as tetrahedral, and the HNC angle as already quoted; these possibilities are indicated as 4*a*—4*i* in Table 4 and Fig. 3. Bond polarisability data give expected semi-axes as shown below the formulæ; in these calculations b_1 is computed in a left-to-right direction for each diagram while b_3 is in, and b_2 perpendicular to, the plane of the paper. The molar Kerr constants and resultant moments corresponding to structures 4*a* to 4*i* are also included in Table 4.

FIG. 2.

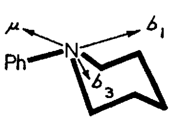

FIG. 3.

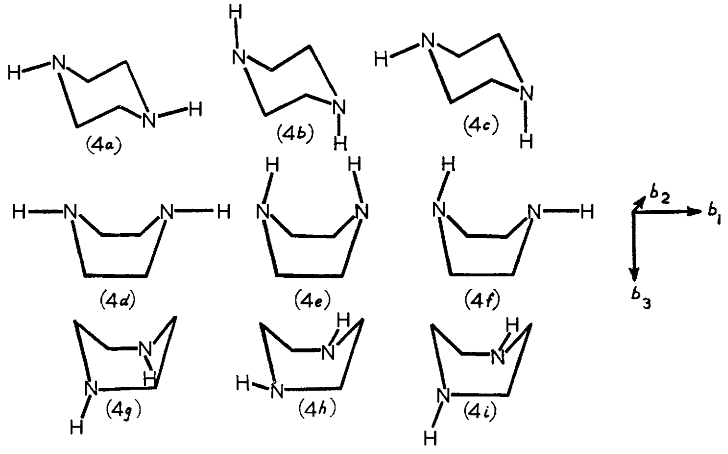

TABLE 4. *Polarisability semi-axes* ($\times 10^{23}$), *molar Kerr constants* ($\times 10^{12}$), *and resultant dipole moments* (D) *expected for nine possible conformations of piperazine.*

Conformation (see Fig. 3)	Dispositions of N–H bonds	Semi-axes (calc.) †	${}_{\mathrm{m}}K$ (calc.)	$\mu_{\text{res.}}$ (calc.)
4*a*	eq, eq	1·062, 0·974, 1·007	+0·3	0
4*b*	ax, ax	$1{\cdot}120_5$, 0·974, 0·949	+1·2	0
4*c*	eq, ax	1·091, 0·974, 0·978	+1·7	2·1
4*d*	ψeq, ψeq	1·075, 0·974, 0·994	−9·0	1·7
4*e*	ψax, ψax	1·134, 0·974, 0·935	−11·5	1·0
4*f*	ψeq, ψax	1·105, 0·974, 0·964	+53	1·9
4*g*	ψax, ψax	0·987, 1·084, 0·972	−20	1·7
4*h*	ψeq, ψeq	0·987, 1·040, 1·016	+1·2	2·0
4*i*	ψeq, ψax	0·987, 1·062, 0·994	+9·1	1·1

* Indicated as equatorial or axial in " chair " forms, or as pseudo-equatorial or pseudo-axial in " boat " forms.

† Reported in descending order as b_1, b_2, and b_3.

The observed ${}_{\mathrm{m}}K$ and μ are respectively $-12{\cdot}7 \times 10^{-12}$ and $1{\cdot}4_7$ D. No single conformation fits both these properties simultaneously. Since the volume requirement of the nitrogen lone-pair orbital exceeds that of an N–H bond,[1] the arguments used in cyclohexane stereochemistry suggest that the three " boat " conformations 4*d*, 4*e*, and 4*f* are unlikely to be present in significant amounts, and that 4*b* is more probable than 4*a* or 4*c*. Since the molar Kerr constant as measured is negative, form 4*b* must be admixed with a form whose

$_{\mathrm{m}}K$ is itself negative: this criterion is satisfied only by *4g*. Accordingly, we suggest that piperazine in benzene solution contains the conformations *4b* and *4g* in roughly the ratio 1 : 2; for such a mixture $10^{12}{}_{\mathrm{m}}K$ and $\mu_{\mathrm{resultant}}$ would be −13 and 1·4 D, in good agreement with the values found.

Table 5 summarises an attempt to analyse our observations with 1,4-dimethylpiperazine. The situation is less clear than with the parent base but, after examining models and bearing in mind our earlier findings[1] with 1-methylpiperidine, we suggest that 1,4-dimethylpiperazine in solution contains the species *5a, 5b, 5c, 5g, 5h,* and *5i,* with the last in rather greater proportion than the other five.

FIG. 4.

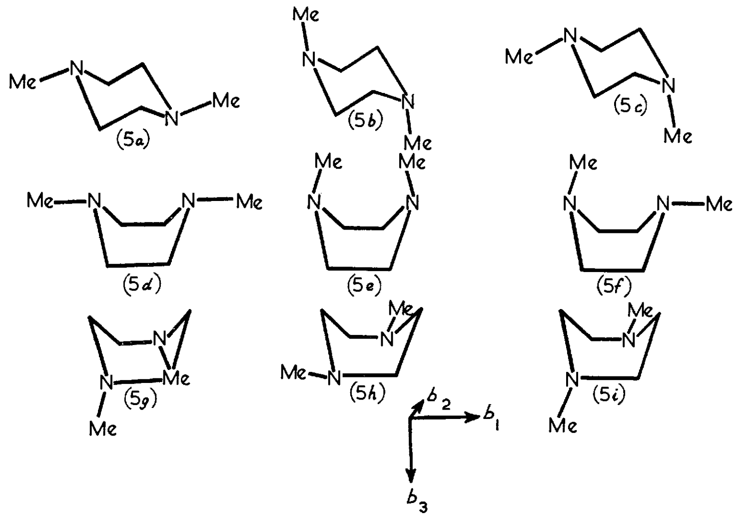

TABLE 5. *Predictions for nine possible conformations of* 1,4-*dimethylpiperazine.*

Conformation (see Fig. 4)	Dispositions of N–Me bonds	Semi-axes (calc.)	$_{\mathrm{m}}K$ (calc.)	$\mu_{\mathrm{res.}}$ (calc.)
5a	eq, eq	1·453, 1·326, 1·365	+0·6	0
5b	ax, ax	1·473, 1·326, 1·344$_5$	+0·9	0
5c	eq, ax	1·463, 1·326, 1·355	+3·5	1·3
5d	ψeq, ψeq	1·471, 1·326, 1·346$_5$	−16·4	1·7
5e	ψax, ψax	1·491, 1·326, 1·326	+1·3	0
5f	ψeq, ψax	1·481, 1·326, 1·336	+21·4	1·5
5g	ψax, ψax	1·345, 1·436, 1·363	−2·0	0·8$_7$
5h	ψeq, ψeq	1·345, 1·421, 1·378	−1·4	1·7
5i	ψeq, ψax	1·345, 1·429, 1·370$_5$	+4·4	0·8^7

Such a conclusion is harmonious with proton magnetic resonance determinations reported by George and Wright[14] (which indicated that a " chair " conformation alone was inadequate, and that flexible structures should be postulated) and also with details of diquaternary salt formation with alkylene dibromides published by Mann and Senior[23] (which can be readily understood if " boat " forms participate in the equilibrium; presumably, for reasons originally given by Wightman,[24] " boat " structures such as *5g, 5h,* and *5i* should be readily interconvertible; steric hindrances involving the methyl groups and/or the lone-pair orbitals are likely to depress the generation of structures *5d*—*5f*).

George and Wright[14] give the dipole moment of 1,4-dichloropiperazine in benzene as

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[23] Mann and Senior, *J.*, 1954, 4476.

[24] Wightman, *J.*, 1925, **127**, 1421.

0·71 D. Since the van der Waals radius of chlorine (1·8 Å) is not far short of that (2·0 Å) of methyl,[25] considerations just outlined for dimethylpiperazine should apply to the dichloro-analogue. For conformations corresponding to 5*a*—5*i*, but with chlorine replacing methyl, moments are calculable (μ_{N-Cl} being taken as 0·3D) respectively as follows: 0,0, $0{\cdot}4_9$, 1·61, 2·16, 1·93, 1·31, 0·50, $0{\cdot}9_4$. The molecule therefore cannot be merely a mixture of " chair " forms because $\mu_{obs.}$ is too great; if instead, as a solute, it is a mixture of the first three and the last three forms, the apparent moment by measurement can be explained.

FIG. 5.

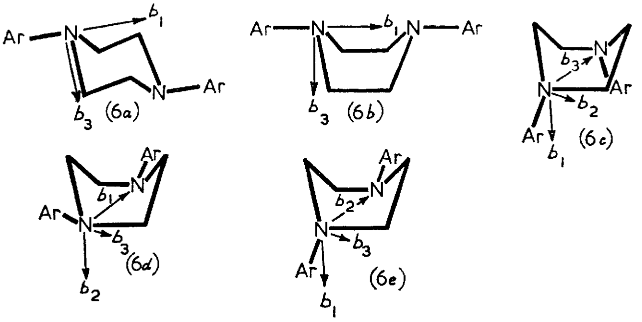

TABLE 6. *Predictions for five possible conformations of* N,N′-*diphenyl- and -di-*p-*tolyl-piperazines.*

Conformation (see Fig. 5)	Dispositions N–Ar bonds	$\mu_{res.}$ calc. for both substances	Semi-axes (calc.) for diphenylpiperazine	Semi-axes (calc.) for ditolylpiperazine	${}_{m}K_{calc.}$ for diphenylpiperazine	${}_{m}K_{calc.}$ for ditolylpiperazine
6*a*	eq, eq	0	4·27, 2·32, 2·18	4·72, 2·62, 2·48	195	225
6*b*	*p*eq, *p*eq	2·0	4·27, 2·32, 2·18	4·72, 2·62, 2·48	−290	−392
6*c*	*p*ax, *p*ax	2·4	4·08, 2·45, 2·22	4·52, 2·77, 2·53	1260	1360
6*d*	*p*eq, *p*eq	0·4	3·75, 2·66, 2·34	4·17, 3·01, 2·65	73	85
6*e*	*p*eq, *p*ax	1·6	3·37, 2·99, 2·40	3·76, 3·35, 2·71	182	200

The axis of maximum polarisability is denoted by b_1, and of the least by b_3 in each case.

The situation with 1,4-diphenyl- and 1,4-di-*p*-tolyl-piperazine is partly summarised in Table 6, where calculations for five conformations are listed. We retain the assumption that the $Ar{\cdot}N(CH_2{\cdot})_2$ units are as in *NN*-dimethylaniline. Inspection of Leybold models shows that other possibilities can be rejected on steric grounds. That the diequatorial chair form does not exist alone is clear from dielectric polarisation evidence: neither the diphenyl nor the ditolyl compound is non-polar, although the moments are small and therefore difficult to assess with accuracy. Moreover, both the ${}_{m}K$'s from experiment are much below those calculated for 6*a*. Any considerable participation of 6*b*, 6*c*, or 6*e* is also counter-indicated on polarity and/or polarisability grounds.

Accordingly, we suggest that these diarylpiperazines are present in solution as mixtures of types 6*a* and 6*d*, with the latter predominating; a small amount of 6*e* could also occur without invalidating our numerical results. The fact (Table 3) that di-*p*-nitrophenylpiperazine has a high moment (around 6 D, sparing solubility prevents this being more than an estimate) is reconcilable with this conclusion, since the values of $\mu_{calc.}$ for the five structures 6*a*—*e* are 0, *ca.* 2, *ca.* 13, *ca.* 6, and *ca.* 6·5 D, respectively.

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[25] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 2nd edn., 1945, p. 189.