

**610.** *Molecular Polarisability. Application of the N-H and N-C Link Polarisabilities to the Conformations of Tertiary Amines, Piperidine, and Morpholine.*

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The effective longitudinal and transverse polarisabilities of the N-H and N-C bonds are deduced from measurements on ammonia and trimethylamine. In conjunction with previous results for the C-H, C-C, and C-O links, these are applied to ascertain conformations for triethylamine, piperidine, *N*-methylpiperidine, and morpholine. The three heterocycles appear to be "chair" models with N-H bonds disposed axially rather than equatorially. *N*-Methylpiperidine shows evidence that its methyl group is attached axially and equatorially with about equal frequency. The volume requirement of a "lone" electron pair on a ring nitrogen atom exceeds that of a covalently bound hydrogen atom, and seems to approach in order of magnitude that of a methyl group. Some new dipole moments are reported.

THIS work was done to determine the anisotropic polarisabilities of the N-H and N-C links, and thus to supplement analogous data<sup>1</sup> for C-H, C-C, and various C-hal and C-oxygen bonds. Ammonia and trimethylamine were initially selected since the geometrical specifications of their structures appeared to be satisfactorily established,<sup>2</sup>

<sup>1</sup> Le Fèvre and Le Fèvre, (a) *Rev. Pure Appl. Chem.*, 1955, **5**, 261; (b) *J.*, 1954, 1577; (c) *Chem. and Ind.*, 1955, 506, 1121; 1956, 54; (d) *J.*, 1956, 3549; (e) Le Fèvre, Le Fèvre, and Oh, *Austral. J. Chem.*, 1957, **10**, 218.

<sup>2</sup> (a) Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, p. 439; (b) Brockway and Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036; (c) Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.

TABLE 1. *Kerr constants, dielectric polarisations, etc., of solutions in benzene at 25°.*

<i>Solute: Ammonia</i>										
$10^6 w_2$ .....	301	359	368	443	456	476	483	$10^6 w_2$ .....	485	497
$10^{10} \Delta B$ .....	10	12	14	16	16	17	17	$-10^4 \Delta n$ ...	19	19
Whence $10^7 \Delta B = 3.33w_2 + 47.9w_2^2$ ; $\Sigma \Delta n / \Sigma w_2 = -0.387$ .										
<i>Solute: Trimethylamine</i>										
$10^6 w_2$ .....	2706	5725	6202	7334	8334	9521	12,304	14,185	16,848	19,085
$-10^{10} \Delta B$ .....	10	21	26	25	34	34	43	52	—	71
$-10^4 \Delta n$ .....	—	—	135	—	154	—	—	243	285	—
Whence $10^7 \Delta B = -0.372w_2 + 0.021w_2^2$ ; $\Sigma \Delta n / \Sigma w_2 = -0.178_5$ .										
<i>Solute: Triethylamine</i>										
$10^6 w_2$ .....	2199	3972	6665	8913	9235	11,393	17,186	18,878		
$-10^{10} \Delta B$ .....	5	11	13	22	25	27	42	46		
Whence $10^7 \Delta B = -0.243w_2 - 0.009w_2^2$										
<i>Solute: Tri-n-propylamine</i>										
$10^6 w_2$ .....	867	2393	3022	3783	4178	6092	7813	9534		
$-10^{10} \Delta B$ .....	1	4	5	—	10	16	25	29		
$-10^4 \Delta n$ .....	—	—	—	41	44	-65	-82	-101		
Whence $10^7 \Delta B = -0.158w_2 - 1.69w_2^2$ ; $\Sigma \Delta n / \Sigma w_2 = -0.106$										
$10^6 w_2$ .....	867	2393	3022	3783	4178	6092	7813	9534		
$\epsilon^{25}$ .....	2.2734	2.2750	2.2756	—	2.2771	2.2787	—	2.2828		
$d_4^{25}$ .....	0.8725	0.8702	0.8693	0.8680	0.8676	0.8647	0.8625	0.8599		
Whence $\Sigma \Delta \epsilon / \Sigma w_2 = 0.105$ ; $\Sigma \Delta d / \Sigma w_2 = 0.149$										
<i>Solute: Tri-n-butylamine</i>										
$10^6 w_2$ .....	932	1725	2891	4136	6549	10,584				
$-10^{10} \Delta B$ .....	1	2	3	6	8	12				
$-10^4 \Delta n$ .....	—	—	25	37	—	89				
Whence $10^7 \Delta B = -0.134w_2 + 0.186w_2^2$ ; $\Sigma \Delta n / \Sigma w_2 = -0.086$										
$10^6 w_2$ .....	491	932	1725	2891	4136	5447	10,584			
$\epsilon^{25}$ .....	2.2730	2.2734	2.2742	2.2751	2.2768	2.2776	—			
$d_4^{25}$ .....	—	0.8727	0.8718	0.8704	0.8686	0.8673	0.8618			
Whence $\Sigma \Delta \epsilon / \Sigma w_2 = 0.097$ ; $\Sigma \Delta d / \Sigma w_2 = -0.135$										
<i>Solute: Tri-n-octylamine</i>										
$10^6 w_2$ .....	1634	2741	3903	4362	5248	5291				
$-10^4 \Delta n$ .....	11	18	26	28	34	34				
Whence $\Sigma \Delta n / \Sigma w_2 = -0.065$ ( $\Delta B = 0$ throughout)										
$10^6 w_2$ .....	782	1355	2094	2538	3549	3903	5248	5291		
$\epsilon^{25}$ .....	2.2729	2.2733	—	2.2738	—	2.2744	2.2747	2.2755		
$d_4^{25}$ .....	0.8730	0.8726	0.8719	0.8715	0.8707	0.8705	0.8690	0.8686		
Whence $\Sigma \Delta \epsilon / \Sigma w_2 = 0.051$ ; $\Sigma \Delta d / \Sigma w_2 = -0.090$										
<i>Solute: Tri-n-decylamine</i>										
$10^6 w_2$ .....	2269	2673	4958	6253						
$-10^4 \Delta n$ .....	14	16	30	38						
Whence $\Sigma \Delta n / \Sigma w_2 = -0.061$ ( $\Delta B = 0$ throughout)										
$10^6 w_2$ .....	1281	2067	2391	3654	3823	4754				
$d_4^{25}$ .....	0.8727	0.8720	0.8719	0.8710	0.8706	0.8701				
Whence $\Sigma \Delta d / \Sigma w_2 = -0.082$ ( $\Delta \epsilon = 0$ throughout)										
<i>Solute: Piperidine</i>										
$10^6 w_2$ .....	3592	6223	8828	13,565						
$-10^4 \Delta n$ .....	15	26	39	56						
Whence $\Sigma \Delta n / \Sigma w_2 = -0.0422$ ( $\Delta B = 0$ throughout)										
$10^6 w_2$ .....	1515	2679	3441	3550	5153	6649				
$\epsilon^{25}$ .....	2.2990	2.3200	—	2.3347	—	—				
$d_4^{25}$ .....	—	—	0.87361	—	0.87351	0.87347				
Whence $\Sigma \Delta \epsilon / \Sigma w_2 = 1.758$ ; $\Sigma \Delta d / \Sigma w_2 = -0.0054$										

TABLE 1. (Continued.)

Solute: <i>N-Methylpiperidine</i>								
$10^5 w_2$ .....	6519	6994	8079	8874	9656	11,467	13,224	
$-10^{10} \Delta B$ .....	29	30	35	38	41	47	58	
$-10^4 \Delta n$ .....	45	—	—	62	69	—	—	—95
Whence $10^7 \Delta B = -0.431w_2 - 0.0218w_2^2$ ; $\Sigma \Delta n / \Sigma w_2 = -0.070$								
$10^5 w_2$ .....	4617	6519	8079	8874	9656	13,224		
$\epsilon^{25}$ .....	2.3077	2.3237	2.3356	2.3404	2.3470	2.3744		
$d_4^{25}$ .....	0.87065	0.86940	0.86838	0.86776	0.86735	0.86513		
Whence $\Sigma \Delta \epsilon / \Sigma w_2 = 0.773$ ; $\Sigma \Delta d / \Sigma w_2 = -0.0673$								
Solute: <i>Morpholine</i>								
$10^5 w_2$ .....	785	1332	2325	2877	3829	3963	6305	6636
$-10^{10} \Delta B$ .....	10	16	31	39	49	48	71	86
$10^4 \Delta n$ .....	—	—	8	10	—	15	24	—
Whence $10^7 \Delta B = -1.32w_2 + 1.61w_2^2$ ; $\Sigma \Delta n / \Sigma w_2 = -0.0358$								
$10^5 w_2$ .....	1529	1726	2979	3714	3722	5392	6541	
$\epsilon^{25}$ .....	2.3158	—	—	2.3802	2.3807	2.4313	2.4669	
$d_4^{25}$ .....	0.87563	0.87575	0.87716	0.87831	0.87820	0.88022	0.88150	
Whence $\Sigma \Delta \epsilon / \Sigma w_2 = 2.91$ ; $\Sigma \Delta d / \Sigma w_2 = 0.118$								

and because (from symmetry) two semi-axes of the molecular polarisability ellipsoid in each case would be the same. Subsequently we examined six other tertiary amines, piperidine, and morpholine. Observations refer,<sup>3</sup> whenever possible, to the dissolved state. Results are in Table 2.

TABLE 2. *Polarisations, dipole moments, and molar Kerr constants (from observations on solutions in benzene at 25°).*

Solute	$\alpha \epsilon_1$	$\beta$	$\gamma$	$\delta$	$M_2$	$\infty P_2$ (c.c.)	${}_D P$ (c.c.)	$\mu$ (D)	$(\infty_m K_2)$ $\times 10^{12}$
NH <sub>3</sub> .....	11.4 <sup>a</sup>	-0.78 <sup>a</sup>	-0.26	8.12	17.03	46.8 <sub>5</sub>	5.90 <sup>b</sup>	1.41	6.24 <sub>5</sub>
NMe <sub>3</sub> .....	0.769 <sup>b</sup>	-0.334 <sup>b</sup>	-0.119	-0.907	59.12	35.4	20.2 <sup>b</sup>	0.86	0.89 <sub>4</sub>
NET <sub>3</sub> .....	0.447 <sup>c</sup>	-0.207 <sup>c</sup>	-0.085 <sup>c</sup>	-0.593	101.2	50.1	34.5 <sup>d</sup>	0.87	3.8 <sub>1</sub>
N(Pr <sup>n</sup> ) <sub>3</sub> .....	0.105	-0.171	-0.071	-0.385	143.3	59.9	48.7 <sup>d</sup>	0.74	8.8 <sub>4</sub>
N(Bu <sup>n</sup> ) <sub>3</sub> .....	0.097	-0.135	-0.057	-0.327	185.3	75.1	62.7 <sup>d</sup>	0.78	11.6
N( <i>n</i> -C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> .....	0.051	-0.103	-0.044	ca. 0	353.7	136.4	123.3 <sup>e</sup>	0.80	30.2
N( <i>n</i> -C <sub>10</sub> H <sub>21</sub> ) <sub>3</sub> .....	ca. 0	-0.094	-0.041	ca. 0	437.8	163.3	152.6 <sup>e</sup>	0.72	37.7
NH(CH <sub>2</sub> ) <sub>5</sub> .....	1.76	-0.006	-0.028	ca. 0	85.1	57.4	28.0 <sup>e</sup>	1.19	1.4
NMe(CH <sub>2</sub> ) <sub>5</sub> .....	0.773	-0.077	-0.047	-1.05	99.2	50.8	33.4 <sup>e</sup>	0.92	-2.1
NH(CH <sub>2</sub> ) <sub>4</sub> O .....	2.91	-0.135	-0.024	-3.23	87.1	73.4	24.6 <sup>e</sup>	1.54	-24.3

<sup>a</sup> Calc. from Kumler, *J. Amer. Chem. Soc.*, 1936, **58**, 1049. <sup>b</sup> Le Fèvre and Russell.<sup>4</sup> <sup>c</sup> Barclay, Le Fèvre, and Smythe, *Trans. Faraday Soc.*, 1950, **46**, 815. <sup>d</sup> Taken as  $R_G'$  from Vogel (*J.*, 1948, 1825) since no reliable measurement of  ${}_D P$  is available. <sup>e</sup> *I.e.*,  $1.05R_D$ . Refractions for the octyl and decyl compounds, calculated from  $R_G$  values for *n*-octane and *n*-decane (Vogel, *J.*, 1946, 133) together with appropriate bond refractions (Vogel, Cresswell, Jeffrey, and Leicester, *J.*, 1952, 514) are 119.5 and 148.0 c.c., whence  $\mu = 0.91$  and 0.87 D respectively.

*Experimental.*—The solvent was the remelted solid from partially frozen sodium-dried "thiophen-free benzene"; it was kept over clean sodium wire. Morpholine, piperidine, and the liquid trialkylamines (from L. Light and Co.) were dried (KOH pellets) and fractionated. Trimethylamine was prepared as in ref. 4. Ammonia was taken from a cylinder, *via* soda-lime and potassium hydroxide tubes, and directly dissolved in benzene. Solutions were made up by weight, except with ammonia: ammonia-benzene mixtures were analysed by shaking known weights with excess of standard hydrochloric acid and back-titrating with alkali (Methyl Orange). Dielectric constants were determined in the circuit noted in ref. 5; other details relating to dipole-moment estimations were as in ref. 6. Electric double refractions for sodium

<sup>3</sup> Ref. 1a, p. 298.<sup>4</sup> Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374.<sup>5</sup> Buckingham, Chau, Freeman, Le Fèvre, Narayana Rao, and Tardif, *J.*, 1956, 1405.<sup>6</sup> Le Fèvre, "Dipole Moments," Methuen, London, 3rd Edn., 1953.

light were measured as previously described.<sup>14,7</sup> Extrapolations and computations were as in ref. 1a, pp. 281—285.

Table 1 shows, for solutions of weight fractions  $w_2$ , the differences ( $\Delta B$  and  $\Delta n$ ) between the Kerr constants and refractive indexes of the solutions and the solvent, the dielectric constants ( $\epsilon$ ) and the densities ( $d$ ). Appropriate values for the pure solvent ( $w_2 = 0$ ) are:  $B_1 = 0.410 \times 10^{-7}$ ,  $(n_1)_{25}^{25} = 1.4973$ ,  $\epsilon_1^{25} = 2.2725$ , and  $(d_1)_{25}^{25} = 0.87380$ .

## DISCUSSION

(a) *Polarisability Ellipsoids of Ammonia and the Trialkylamines.*—The sums of the anisotropy and dipole terms,  $\theta_1 + \theta_2$ , are obtained<sup>1</sup> from the molar Kerr constants of Table 2 as  $\infty(mK_2)(9/2\pi N)$ . Using the dipole moments and other quantities listed in Tables 2 and 3, we can estimate the semi-axes  $b_1$ ,  $b_2$ , and  $b_3$  without recourse to further information, provided  $b_2 = b_3$  (cf. ref. 1a, p. 287). Such an assumption is valid for ammonia and trimethylamine, and seems reasonable for the higher members.

TABLE 3. *Polarisability semi-axes of ammonia and tertiary amines on the assumption that  $b_2 = b_3$ .*

Solute	$10^{25}(\theta_1 + \theta_2)$	$\epsilon P$ (c.c.)	$10^{23}(b_1 + 2b_2)$	$10^{23}b_1$	$10^{23}(b_2 = b_3)$
NH <sub>3</sub> .....	1.48 <sub>5</sub>	5.45 <sup>a</sup>	0.648	0.235	0.207
NMe <sub>3</sub> .....	0.212 <sub>4</sub>	19.34 <sup>b</sup>	2.299 <sub>5</sub>	0.774	0.763
NEt <sub>3</sub> .....	0.907 <sub>4</sub>	32.94 <sup>c</sup>	3.917	1.33 <sub>5</sub>	1.29 <sub>1</sub>
NPr <sub>3</sub> .....	2.10 <sub>2</sub>	46.51 <sup>c</sup>	5.530 <sub>5</sub>	1.93 <sub>2</sub>	1.79 <sub>9</sub>
NBu <sub>3</sub> .....	2.75 <sub>5</sub>	60.05 <sup>c</sup>	7.140 <sub>5</sub>	2.48 <sub>4</sub>	2.32 <sub>8</sub>
N( <i>n</i> -C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> .....	7.17 <sub>3</sub>	117.1 <sup>d</sup>	13.92	4.870 <sub>5</sub>	4.52 <sub>5</sub>
N( <i>n</i> -C <sub>10</sub> H <sub>21</sub> ) <sub>3</sub> .....	8.97 <sub>2</sub>	145.0 <sup>d</sup>	17.24	6.06 <sub>2</sub>	5.58 <sub>9</sub>

Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, A, 156, 144. <sup>b</sup> Extrapolated from  $R_G = 19.791$ ,  $R_G = 20.406$  (cf. Vogel *et al.*, J., 1952, 514. <sup>c</sup> Extrapolated from  $R_G$  and  $R_G$  (Vogel, J., 1948, 1825). <sup>d</sup> *I.e.*, 0.95(<sub>D</sub>P).

Apart from that of ammonia, the electric double refraction of none of these compounds has been examined before; dependable values exist for ammonia only as a gas.<sup>8,9</sup> Earlier determinations by Leiser and Hansen (quoted in ref. 1) were made relatively to carbon disulphide at unstated temperatures and wavelengths. Szivessy<sup>8</sup> reported the Kerr constant  $B$  as  $0.59 \times 10^{-10}$  for  $\lambda = 5890 \text{ \AA}$  at  $17.9^\circ$ , and Breazeale<sup>9</sup> gave  $0.623 \times 10^{-10}$  for  $\lambda = 6550 \text{ \AA}$  at  $0^\circ$  (both at 760 mm.); accordingly  $mK_{\text{gas}}$  is calculable as  $6.15 \times 10^{-12}$  and  $6.78 \times 10^{-12}$  respectively. These are in reasonable agreement with  $\infty(mK_2)$  now found ( $6.25 \times 10^{-12}$ ) when temperature differences are remembered; further, if  $\mu_{\text{gas}}$  for ammonia be taken<sup>4</sup> as 1.45 D, semi-axes can be deduced as  $b_1 = 0.233 \times 10^{-23}$ ,  $b_2 = b_3 = 0.208 \times 10^{-23}$  (from Szivessy's  $B$ ) and  $b_1 = 0.232 \times 10^{-23}$ ,  $b_2 = b_3 = 0.208 \times 10^{-23}$  (from Breazeale's  $B$ ), and concordance exists with the results (Table 3) obtained at infinite dilution in benzene.

(b) *Polarisability Ellipsoids of the N-H and N-C Bonds.*—In both ammonia and trimethylamine the molecular resultant dipole moment and the polarisability semi-axis  $b_1$  act through the nitrogen atom, along the three-fold axis of symmetry which is inclined at  $67^\circ 58'$  to the N-H links in ammonia<sup>2a</sup> and at  $69^\circ 4'$  to the N-C links in trimethylamine.<sup>2b</sup> If  $b_L^{N-H}$ ,  $b_T^{N-H}$ ,  $b_L^{C-N}$ , and  $b_T^{C-N}$  represent the longitudinal and transverse polarisabilities of the N-H and C-N bonds respectively, equations<sup>10</sup> can be set up for the (molecular) axes  $b_1$  and for the totals ( $b_L^{\text{bond}} + 2b_T^{\text{bond}}$ ). Thus for ammonia we have (Table 3):

$$0.235 \times 10^{-23} = 3(b_L^{N-H} \cos^2 67^\circ 58' + b_T^{N-H} \sin^2 67^\circ 58')$$

$$\text{and} \quad 0.648 \times 10^{-23} = 3(b_L^{N-H} + 2b_T^{N-H})$$

Solution yields  $b_L^{N-H} = 0.050 \times 10^{-23}$  and  $b_T^{N-H} = 0.083 \times 10^{-23}$  c.c.

<sup>7</sup> Le Fèvre and Le Fèvre, *J.*, 1953, 4041; Aroney and Le Fèvre, *J.*, 1956, 2775.

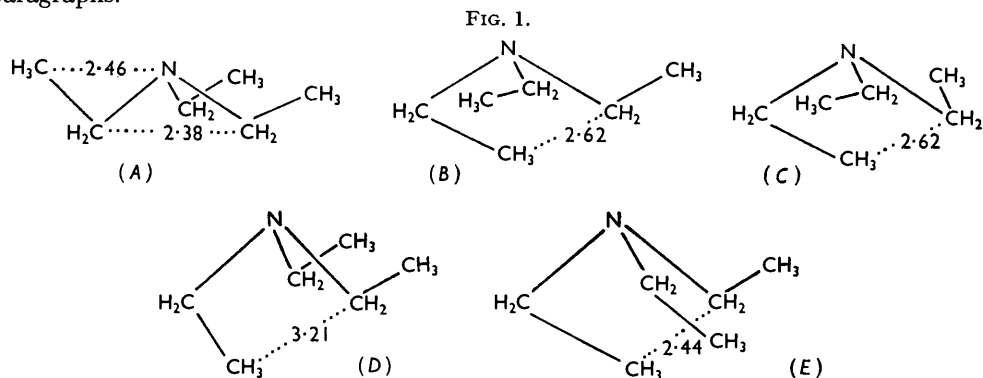
<sup>8</sup> Szivessy, *Z. Physik*, 1924, 26, 342.

<sup>9</sup> Breazeale, *Phys. Rev.*, 1935, 43, 237.

<sup>10</sup> Ref. 1, pp. 297—299.

Proceeding similarly for trimethylamine, and noting <sup>10,11</sup> that for the C-H bond  $b_L^{O-H} = b_T^{C-H} = b_V^{O-H} = 0.063_5 \times 10^{-23}$  c.c., we obtain values for the C-N bond:  $b_L^{O-N} = 0.057 \times 10^{-23}$  and  $b_T^{O-N} = 0.069 \times 10^{-23}$  c.c.

The N-H and C-N links are the first cases of singly-bound different atoms for which the  $b_T/b_L$  ratio exceeds unity (compare the following ratios, from ref. 1d: C-C 0.28, C-Cl 0.48, C-Br 0.51, C-I 0.52, C-O 0.48). Presumably, by the method of derivation, the polarisability of the "lone-pair" electrons is distributed over the three N-H or N-C bonds, so that these magnitudes do not relate entirely to the internuclear electrons. Nevertheless, such "apparent" link polarisabilities should be useful for conformational analysis of NR<sub>3</sub> groups containing structures in which the *s-p* hybridisation is likely to resemble that in ammonia and trimethylamine; examples of this kind are the subjects of the following paragraphs.



(c) *Triethylamine*.—Theoretically this base might assume an infinite number of conformations between two extremes, in both of which the three methylene and the three methyl carbon atoms are in parallel planes separated as far as permitted by the tetrahedral angles of the CH<sub>2</sub> groups. In one, *A* (Fig. 1), the "methyl plane" nearly includes the nitrogen atom; in the other, *F* (not shown in Fig. 1), it is most remote from it. Certain intermediate arrangements are also suggested in Fig. 1; in *C* the centres of the six carbon atoms are coplanar; in *B* five carbon atoms are coplanar but one methyl group is as in *A*; in *D* two methyl groups are as in *A* and one as in *F*; in *E* one of the methyl group is as in *A*, while the other two are located by rotating the ethyl groups containing them  $\pm 120^\circ$  respectively, about the C-N bonds, from position as in *A*. Forms *D* and *E* correspond to those suggested by Arbutov and Guzhovina <sup>11</sup> (from parachor measurements) and by Brown and Taylor <sup>12</sup> (from kinetic and stability studies, cf. ref. 13). Intercentre distances (Å), deduced by use of C-C and C-N bond lengths of 1.54 Å and 1.47 Å and C-C-N and C-N-C angles of 109° 28' and 108° respectively, are marked on Fig. 1, and further define the conformations. With the bond-polarisability ellipsoids given above, molecular semi-axes can be computed (Table 4) and, in turn, the molar Kerr constant to be expected for each form ( $\mu_{\text{resultant}}$  being taken as 0.87 D and acting along the  $b_1$  direction).

Measurement showed  $\infty(mK_2)$  to be  $3.8 \times 10^{-12}$ , a value suggesting that none of the above forms alone occurs. Scale (Catalin) models reveal considerable steric interference between the methyl groups in conformation *F* and varying degrees of interaction between hydrogen atoms in all the other arrangements *A-E*. Application of the principle that the six C-H bonds of the three methylene groups should be "staggered" requires model *A* to be modified (by rotating the -CH<sub>2</sub>·CH<sub>3</sub> units around the N-C bonds) towards model *C*. Whether triethylamine exists as a single form intermediate between *A* and *C*, or as a

<sup>11</sup> Arbutov and Guzhovina, *Doklady Akad. Nauk S.S.S.R.*, 1948, **61**, 63.

<sup>12</sup> Brown and Taylor, *J. Amer. Chem. Soc.*, 1947, **69**, 1332.

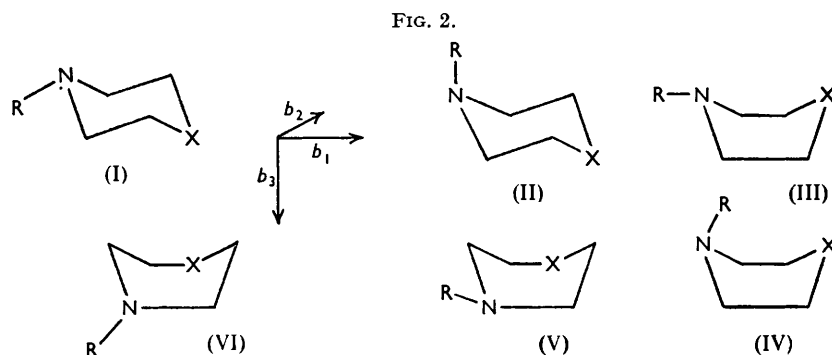
<sup>13</sup> Brown, *J.*, 1956, 1248.

mixture of *A* and *C*, or as a state in which *A* is one limit of a libration, cannot be decided; present data are harmonious with such possibilities.

TABLE 4. Polarisability semi-axes and molar Kerr constants calculated for conformations *A* to *F* of triethylamine.

Conformation	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10^{12}{}_mK_2$	Conformation	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10^{12}{}_mK_2$
<i>A</i>	1.361	1.271	1.271	8.6	<i>D</i>	1.391	1.264	1.249	13.1
<i>B</i>	1.278	1.354	1.271	-2.9	<i>E</i>	1.308	1.332	1.263	1.1
<i>C</i>	1.237	1.333	1.333	-8.4	<i>F</i>	1.450	1.227	1.227	22.6

In the higher homologues, the alkyl chains do not appear to be extended "zig-zags" since on such a hypothesis the calculated  $b_1$ 's fall short of those measured. If the radicals are taken as being isotropic, however, the predicted value agrees better with that observed (in parentheses) (all  $\times 10^{23}$ ): tri-*n*-butylamine 2.5 (2.5), tri-*n*-octylamine 4.8 (4.9), tri-*n*-decylamine 5.9 (6.1). The implication is therefore that, after triethylamine, no rotational isomer predominates, and that the larger alkyl groups are "crumpled," much as their parent hydrocarbons are thought to be.<sup>14</sup>



(d) *Piperidine and N-Methylpiperidine*.—Each of these bases, if the valencies of the nitrogen atom are disposed pyramidally as in trimethylamine and the C-C-C angles are tetrahedral, can exist without ring strain as six forms: one "chair" and two "boats," for each of which in turn there are two possible conformations of the N-H (or N-Me) link. The nomenclature used with *cyclohexanes* being used, the N-R bonds may be "equatorial" or "axial" in the chairs, and "pseudo-equatorial" or "pseudo-axial" in the boats (Fig. 2; X = CH<sub>2</sub>).

The polarisability semi-axes to be expected for the twelve structures have been computed from the bond values given above by methods detailed in ref. 1*d*. In order to pass from the  $b$ 's so estimated to the corresponding molar Kerr constants, the directions of action of the resultant dipole moments need to be known. In *N*-methylpiperidine this is taken as at 69° 4' to each N-C bond (*i.e.*, as in trimethylamine). In piperidine it should be nearer the H-N than to either C-N direction. From the dipole moments<sup>4</sup> of ammonia and trimethylamine and the geometry of these molecules  $\mu^{\text{H-N}}$  and  $\mu^{\text{Me-N}}$  appear as 1.29<sub>6</sub> and 0.80<sub>3</sub> D respectively—values which, applied in the case of dimethylamine, give the observed resultant an inclination of 45° 9' to the H-N link in the plane defined by the hydrogen and nitrogen atoms and the mid-point between the methyl groups; a similar situation is assumed to occur in piperidine. Table 5 summarises the calculations.

With piperidine, *positive* values of  ${}_mK$  are forecast for two axial conformations only, while with *N*-methylpiperidine, *negative* ones are predicted for three equatorial conformations only; the signs of the observed values show that axial N-H and equatorial N-Me links must be present to noticeable extents in the two cases. Indeed, if, as seems generally

<sup>14</sup> Ubbelohde and McCoubrey, *Discuss. Faraday Soc.*, 1951, 10, 94.

likely, and by analogy with cyclohexane<sup>1d</sup> and dioxan,<sup>15</sup> only *chair* structures need be considered, then piperidine contains 80% or more of the axial form, while its *N*-methyl derivative consists of the two conformations in roughly a 1 : 1 ratio.

TABLE 5. *Polarisability semi-axes and molar Kerr constants calculated for the various conformations of piperidine (R = H; X = CH<sub>2</sub>) and N-methylpiperidine (R = Me; X = CH<sub>2</sub>).*

Conformation	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10^{12}{}_mK_2$	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10^{12}{}_mK_2$
	Piperidine, $\infty({}_mK_2) = 1.4 \times 10^{-12}$				N-Methylpiperidine, $\infty({}_mK_2) = -2.1 \times 10^{-12}$			
(I) Chair, equatorial R ...	1.090	1.045	0.989 <sub>5</sub>	-8.1	1.285	1.221 <sub>5</sub>	1.169	-7.4
(II) ,, axial R .....	1.118	1.045	0.961	+1.9	1.295	1.221 <sub>5</sub>	1.159	+8.0
(III) Boat, $\psi$ -equatorial R	1.088	1.045	0.992	-0.9	1.286	1.221	1.168	-5.7
(IV) ,, $\psi$ -axial R .....	1.116 <sub>5</sub>	1.045	0.963	+12.8	1.296	1.221	1.158	+10.6
(V) ,, * $\psi$ -equatorial R	1.044	1.078	1.003	-5.0	1.222 <sub>5</sub>	1.269	1.184	-4.9
(VI) ,, * $\psi$ -axial R .....	1.044	1.100	0.981	-2.6	1.222 <sub>5</sub>	1.276	1.176	+3.6

\* Basal nitrogen atom.

(e) *Morpholine*.—Fig. 2 shows the six models expected ( $X = O$ ). The dipole moments expected for these, deduced from the N-H and N-C bond polarities used above, together with  $\mu_{\text{OH},\text{O}} = 1.05$  D and  $\angle\text{C-O-C} = 111^\circ$ , are given in Table 6. Since the moment as measured is 1.5<sub>4</sub> D, none of the four "boat" structures can be present alone. The likelihood that they occur as a mixture or equilibrium is also very small, since calculation reveals that  $\mu_{\text{resultant}}$  is, in each case, inclined towards  $b_1$  at an angle close to that<sup>16</sup> which makes  $\theta_2$  *ca.* zero, so that the corresponding  ${}_mK$  differs considerably from that observed. The details are in Table 6. Since  $\infty({}_mK_2)$  from experiment is  $-24.3 \times 10^{-12}$ , morpholine apparently exists almost wholly as the chair structure with the N-H link attached axially.

TABLE 6. *Polarisability semi-axes and molar Kerr constants calculated for the various conformations of morpholine (Fig. 2, R = H; X = O).*

Conformation	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10^{12}{}_mK_2$	$\mu(\text{D})$ (calc.)
(I) Chair, equatorial .....	0.973	0.902 <sub>5</sub>	0.879	+19.2	1.51
(II) ,, axial .....	1.002	0.902 <sub>5</sub>	0.851	-25.5	1.51
(III) Boat, $\psi$ -equatorial .....	0.978	0.902	0.875	-0.4	2.4
(IV) ,, $\psi$ -axial .....	1.006	0.902	0.846	+0.3	0.6
(V) ,, * $\psi$ -equatorial .....	0.908	0.955	0.892 <sub>5</sub>	-0.1	2.0
(VI) ,, * $\psi$ -axial .....	0.908	0.977	0.870 <sub>5</sub>	-0.9	0.7

\* Basal nitrogen atom.

The above results amplify the recognition<sup>17</sup> that the occurrence of *axial* N-H bonds in piperidine and morpholine was in accord with previous predictions, based on analogies with carbanions.<sup>18</sup> Although we<sup>17</sup> concluded that if ideas current in cyclohexane stereochemistry can be used with heterocycles, the volume requirement of a "lone" electron pair appears to exceed that of a covalently attached hydrogen atom, *N*-methylpiperidine indicates that it approaches, in order of magnitude, that of a methyl group.

*Previous Determinations of Dipole Moments*.—Of our seven determinations of dipole moments recorded  $\mu$  (D), four are repetitions of other work, the solvent being benzene: Tri-*n*-propylamine 0.74 (0.75<sup>19</sup>), piperidine 1.19 ( $1.17 \pm 0.02$ <sup>20</sup>), *N*-methylpiperidine 0.92 ( $0.91 \pm 0.01$ <sup>20</sup>), morpholine 1.54 (1.48,<sup>21</sup> 1.58,<sup>22</sup> 1.51<sup>23</sup>).

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<sup>15</sup> Armstrong, Le Fèvre, and Yates, *Austral. J. Chem.*, 1958, **11**, 147.

<sup>16</sup> Ref. 1a, p. 294.

<sup>17</sup> Aroney and Le Fèvre, *Proc. Chem. Soc.*, 1958, 82.

<sup>18</sup> Barton and Cookson, *Quart. Rev.*, 1956, **10**, 72.

<sup>19</sup> Cowley, *J.*, 1952, 3557.

<sup>20</sup> Rau and Narayanaswamy, *Z. phys. Chem.*, 1934, **B**, **26**, 23.

<sup>21</sup> Coomber and Partington, *Nature*, 1938, **141**, 918.

<sup>22</sup> Lewis and Smyth, *J. Amer. Chem. Soc.*, 1939, **61**, 3067.

<sup>23</sup> Maryott, Hobbs, and Gross, *ibid.*, 1940, **62**, 2320.