820.   *Molecular Polarisability.   The Molecular Conformations of Morpholine and of* N-*Methylmorpholine in Non-polar Media.*

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Dipole moments and molar Kerr constants are reported for morpholine and *N*-methylmorpholine as solutes in cyclohexane and in benzene. The electric birefringence data are interpreted in terms of a chair-shaped heterocyclic ring with the N–R group (R = H or Me) disposed in the following equatorial/axial ratios: morpholine in cyclohexane (37/63); *N*-methylmorpholine in cyclohexane (57/43); morpholine in benzene (13/87); *N*-methylmorpholine in benzene (98/2). In an " inert " solvent the 1,3-(axial/axial) interactions for these molecules, though weak, appear to increase in the order: N–H < N–lone-pair < N–Me. The differences between the molar Kerr constants observed for morpholine and *N*-methylmorpholine as solutes in benzene and cyclohexane are attributed to solvent–solute interactions in the former medium. Infrared and n.m.r. evidence seems to favour such an association.

IT was recently inferred,[1] from a study of the stereochemistry of the monomethylquinolizidines, that the volume requirement of the nitrogen lone-pair electrons is less than that of a covalently bound hydrogen atom. Such a conclusion appears at variance with a comment made by Aroney and Le Fèvre [2] after interpreting the electric birefringences displayed by morpholine and by piperidine, as solutes in benzene, in terms of chair models having the N–H bonds disposed axially. In this Paper we examine the dipole moments, electric birefringences, infrared spectra, and nuclear magnetic resonance spectra of morpholine and *N*-methylmorpholine in various (non-polar) media. The electric birefringence data are analysed using a more refined computational procedure than that of ref. 2.

EXPERIMENTAL

Materials, Apparatus, Etc.—The solutes were commercial samples which were purified immediately before use, to give: morpholine, b. p. 127—128°; *N*-methylmorpholine, b. p. 114—115°. Measurements of dipole moments and of electric birefringences have been described before.[3-5] The quantities $\Delta\varepsilon$, Δd, Δn, and ΔB are the differences found between the dielectric constants, densities, refractive indexes, and Kerr constants, respectively, of the solvent and of solutions containing weight fractions w_2 of solute. The following data apply at 25°:

	ε_1	d_1	$(n_1)_D$	$10^7 B_1$	$10^{12} K_1$
Benzene	2·2725	0·87378	1·4973	0·410	0·0756
Cyclohexane	2·0199	0·77389	1·4235	0·059	0·0147
Carbon tetrachloride	2·2270	1·58454	1·4575	0·070	0·00749

The infrared spectra recorded for this work were measured with a Perkin-Elmer 221 spectrometer with grating prism and matching cells. The n.m.r. spectra were taken on a Varian A-60 spectrometer operating at 60 Mc./sec.

DISCUSSION

Because of the similarity in C–C, C–N, and C–O bond lengths, and in the bond angles C–C–C, C–N–C, and C–O–C, the heterocyclic ring in morpholine, like that of cyclohexane,

[1] Moynehan, Schofield, Jones, and Katritzky, *J.*, 1962, 2637.
[2] Aroney and Le Fèvre, *J.*, 1958, 3002.
[3] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953; Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.
[4] Le Fèvre and Le Fèvre, (*a*) *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 261; (*b*) *J.*, 1953, 4041; (*c*) *J.*, 1954, 1577; (*d*) Chap. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience, New York and London, 3rd edn., Vol. 1, p. 2459.
[5] Le Fèvre, Pierens, and Steel, *Austral. J. Chem.*, in the press.

exists in the chair configurations (ref. 6, p. 72). Ring inversion as well as the rapid inversion of nitrogen could distribute the imino hydrogen between the axial and equational positions to produce the pairs of conformers shown. In the absence of environmental influences, the disposition of the nitrogen-bound substituent group R (R = H for morpholine; R = Me for *N*-methylmorpholine) is thought to be determined mainly by the relative interactions of R, and of the nitrogen lone-pair electrons, with the axial 3-hydrogens. In this work we interpret the physical measurements recorded in Tables 1 and 2 in terms of an equilibrium
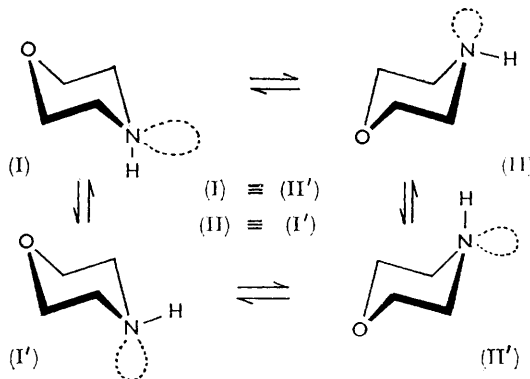

$$(I) \equiv (II')$$
$$(II) \equiv (I')$$

TABLE 1.

Incremental Kerr effects, refractive indices, dielectric constants, and densities for solutions at 25°.

Morpholine in benzene.

$10^5 w_2$	961	1370	1870	3201
$10^7 \Delta B$	−0·0126	−0·0172	−0·0234	−0·0409

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -1 \cdot 27$.

Morpholine in cyclohexane.

$10^5 w_2$	1136	1673	2197	2908	2945	3506	4151	4795	5097	5692
$10^7 \Delta B$	−0·005	−0·007	—	—	−0·013	−0·016	−0·017	−0·021	−0·023	—
$10^4 \Delta n$	—	1	—	3	—	—	3	—	5	6
ε^{25}	—	—	2·0722	2·0914	2·0927	2·1051	—	2·1376	2·1467	2·1651
$d_4{}^{25}$	—	0·77632	—	0·77818	—	0·77898	0·77999	—	0·78124	0·78235

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -0 \cdot 43_8$; $\Sigma \Delta n / \Sigma w_2 = 0 \cdot 010$; $\Sigma \Delta \varepsilon / \Sigma w_2 = 2 \cdot 47$; $\Sigma \Delta d / \Sigma w_2 = 0 \cdot 146$.

N-Methylmorpholine in benzene.

$10^5 w_2$	7698	8935	9144	10,319	10,555	13,012
$10^7 \Delta B$	0·057	0·063	0·063	0·077	0·079	0·099

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = 0 \cdot 73_4$.

$10^5 w_2$	2531	3421	4252	7631	7766	8935	10,555	13,012
ε^{25}	2·3143	2·3298	2·3433	2·3994	—	2·4211	—	2·4868
$d_4{}^{25}$	—	0·87517	0·87544	0·87671	0·87680	—	0·87778	0·87876
$10^4 \Delta n$	—	−20	−27	−45	—	−53	−64	−76

whence $\Sigma \Delta \varepsilon / \Sigma w_2 = 1 \cdot 66$; $\Sigma \Delta d / \Sigma w_2 = 0 \cdot 039$; $\Sigma \Delta n / \Sigma w_2 = - 0 \cdot 060$.

N-Methylmorpholine in cyclohexane.

$10^5 w_2$	1142	2793	3294	5284	5540	7594	12,851
$10^7 \Delta B$	—	0·003	—	—	0·007	0·009	0·015
ε^{25}	2·0369	2·0624	2·0704	2·1009	2·1046	2·1356	—
$d_4{}^{25}$	0·77500	0·77664	0·77721	0·77921	0·77944	0·78147	—

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = 0 \cdot 11_8$; $\Sigma \Delta \varepsilon / \Sigma w_2 = 1 \cdot 53$; $\Sigma \Delta d / \Sigma w_2 = 0 \cdot 100$; $\Delta n = 0$ for concentrations up to $10^5 w_2 = 12{,}851$.

mixture of conformational isomers having axial $R(R_a)$ or equatorial $R(R_e)$ attached to a chair-shaped heterocyclic ring. Alternatively, the ratio $[R_a]/[R_e]$ may be regarded as the

[6] Barton and Cookson, *Quart. Rev.*, 1956, **10**, 44.

relative probability distribution of the substituent R between the two energetically favoured locations.

Our approach is to calculate, by addition of component bond polarity and polarisability data, the theoretical dipole moment and molar Kerr constant for each molecular model

TABLE 2.

Polarisations, dipole moments, and molar Kerr constants (from observations on solutions at 25°).

Solute: Morpholine.

Solvent	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D) ¶	$10^{12} _\infty(_mK_2)$
Benzene	2·91 *	0·135 *	−0·024 *	−3·10 §	73·4 *	23·4 *	1·54 *	−23·5
Cyclohexane	2·47	0·189	0·007	−7·42	74·8	23·9	1·56 †	−10·0

Solute: N-Methylmorpholine.

Benzene	1·66	0·044	−0·040	1·79	64·5	28·9	1·29 †	+15·4
Cyclohexane	1·53	0·129	0	2·00	66·0	29·0	1·32 †	+3·1
Carbon tetrachloride	3·48 ‡	−0·675 ‡	−0·002 ‡	1·47 ‡	68·3	29·0	1·36 †	+1·1

    * From ref. 2.   † Calculated assuming $_DP = 1·05R_D$.   ‡ Morpholine is very unstable in carbon tetrachloride; N-methylmorpholine–carbon tetrachloride mixtures slowly become cloudy. The results recorded here were derived from measurements made very rapidly on a small number of freshly prepared solutions.   § Measurements by Mr. R. K. Pierens using the photometric technique described in ref. 5.   ¶ Other dipole moment determinations for morpholine are listed in ref. 2; the dipole moment of N-methylmorpholine does not appear to have been previously measured.

considered, and to compare the values so obtained with those from experiment. Bond polarisability semi-axes * used in the calculations are:

	C–H	C–C	C–N	H–N	C–O
b_L	0·064	0·099	0·057	0·050	0·089
$b_T = b_V$	0·064	0·027	0·069	0·083	0·046
Ref.	4a	7	2	2	8

From the dipole moments [9,10] of ammonia, trimethylamine, and dimethyl ether, and the geometry of these molecules,[11,12] $\mu(H \dashrightarrow N)$, $\mu(Me \dashrightarrow N)$, and $\mu(Me \dashrightarrow O)$ appear as 1·30, 0·80, and 1·17 D, respectively. If $\mu(C \dashrightarrow H) = 0·30$ D,[13] then it follows that $\mu(C \dashrightarrow N) = 1·10$ and $\mu(C \dashrightarrow O) = 1·47$ D. The method of derivation of the polarity and polarisability data listed above is such as to include the lone-pair electron contributions in the case of bonds or groups involving nitrogen or oxygen atoms.

Morpholine and N-*Methylmorpholine as Solutes in Benzene.*—Aroney and Le Fèvre in 1958 measured the Kerr effect of morpholine–benzene mixtures for concentrations of morpholine up to $w_2 = 6636 \times 10^{-5}$. The experimental results, when fitted to a regression equation and extrapolated to infinite dilution, yielded an $_\infty(_mK_2)$ value for morpholine of $−24·3 \times 10^{-12}$ (cf. $−23·5 \times 10^{-12}$ in Table 2). The present study was restricted to a low concentration range to avoid possible solute–solute association.

Specification of the polarisability tensor for each molecular model considered was made with reference to the co-ordinate system of axes $OXYZ$ in Fig. 1. In the present work we redetermine the theoretical dipole moments and molar Kerr constants of the two chair forms of morpholine, using (a) a more sophisticated computational procedure as outlined in ref. 4d, pp. 2483—2486, (b) the following geometrical parameters to determine, by the

    * Polarisability semi-axes of bonds, b_L, b_T, or b_V, or of molecules, b_1, b_2, or b_3, are quoted throughout in 10^{-23} c.c. units.

   [7] Le Fèvre and Le Fèvre, *J.*, 1956, 3549.
   [8] Le Fèvre, Sundaram, and Pierens, *J.*, 1963, 479.
   [9] Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374.
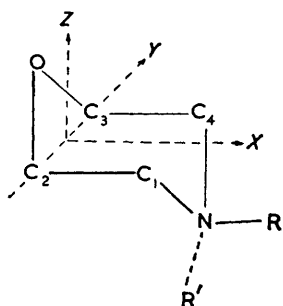   [10] Aroney, Le Fèvre, and Saxby, *J.*, 1962, 2886.
   [11] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, p. 439.
   [12] Sutton, " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.* No. 11, 1958.
   [13] Cumper and Vogel, *J.*, 1959, 3521.

method of Corey and Sneen,[14] the atomic co-ordinates and thence the direction cosines of all component bond semi-axes within the reference system $OXYZ$: $\angle C-O-C = 111°$; $\angle C-N-C = 108°$; $\angle C-N-H = 107°$; $\angle C-C-C = 109.5°$; $C-O = 1.43$ Å; $C-N = 1.47$ Å; $C-C = 1.54$ Å; $N-H = 1.01$ Å (Aroney and Le Fèvre [2] had assumed tetrahedral angles

Fig. 1.

C_1 (1·540, −1·189, 0)   N (2·038, 0, −0·707)
C_2 (0, −1·178, 0)   R (=H) (3·046, 0, −0·646)
C_3 (O, 1·178, 0)   R′ (=H) (1·641, 0, −1·636)
C_4 (1·540, 1·189, 0)   R (=C) (3·505, 0, −0·618)
O (−0·468, 0, 0·662)   R′ (=C) (1·460, 0, −2·059)

throughout), and (c) more recent estimates of the C–O bond polarisabilities (cf. $b_L{}^{C-O}/b_T{}^{C-O} = 0.081/0.039$ in ref. 2). The calculations are summarised in Table 3. The numbers in parentheses refer to the values calculated if the C–O bond moment were taken as 1·68 D, as derived from μ(tetrahydropyran) $= 1.56$ D,[15] $\mu^{C-\!|\!\rightarrow H} = 0.30$ D, and $\angle C-O-C = 111°$.

TABLE 3.

Calculated polarisability semi-axes, dipole moments, and molar Kerr constants.

Compound	b_i (calc.)	Direction cosines with			μ (calc.) (D)	$10^{12}{}_M K$ (calc.)
		X	Y	Z		
Morpholine (eq. H)	$b_1 = 0.998$	+0·995	0	−0·104		
	$b_2 = 0.922$	0	+1	0	1·53 (1·70)	+24·0 (+28·7)
	$b_3 = 0.891$	+0·104	0	+0·995		
,, (ax. H)	$b_1 = 1.027$	+0·992	0	−0·128		
	$b_2 = 0.922$	0	+1	0	1·53 (1·70)	−27·9 (−35·1)
	$b_3 = 0.861$	+0·128	0	+0·992		
N-Methylmorpholine (eq. Me)	$b_1 = 1.196$	+0·997	0	−0·078		
	$b_2 = 1.100$	0	+1	0	1·05 (1·24)	+13·5 (+16·8)
	$b_3 = 1.069$	+0·078	0	+0·997		
,, (ax. Me)	$b_1 = 1.207$	+0·996	0	−0·091		
	$b_2 = 1.100$	0	+1	0	1·05 (1·24)	−10·6 (−14·6)
	$b_3 = 1.058$	+0·091	0	+0·996		

The observed dipole moments and molar Kerr constants are, respectively, 1·54 D and −23·5 × 10⁻¹² (for morpholine) and 1·29 D and +15·4 × 10⁻¹² (for N-methylmorpholine). The dipole moments calculated for the rival space-formulæ are, in each case, identical and cannot be used to differentiate between the isomers. However, comparison of the calculated molar Kerr constants of Table 3 with those observed suggests that, in benzene solution, morpholine exists 87 ± 6% in the axial and 13 ± 6% in the equatorial form, and N-methylmorpholine 2 ± 5% in the axial and 98 ± 5% in the equatorial form [the axial conformation is (I) and the equatorial (II)]. The estimated error arises mainly from the uncertainty in the C–O bond moment utilized in the calculations. Small changes in the value taken for μ(C–H) or in the molecular geometry do not significantly affect the conclusions.

Morpholine and N-*Methylmorpholine as Solutes in Cyclohexane.*—Analogous measurements made in cyclohexane show that the molar Kerr constants (at infinite dilution), unlike the dipole moments, are appreciably solvent-dependent. The observed values are 1·56 D and −10·0 × 10⁻¹² (for morpholine) and 1·32 D and +3·1 × 10⁻¹² (for N-methylmorpholine), from which we infer that morpholine in an " inert " solvent exists preferentially as the axial isomer (ax H/eq H $\approx$ 3/2) and N-methylmorpholine as the equatorial

[14] Corey and Sneen, *J. Amer. Chem. Soc.*, 1955, 2505.
[15] Le Fèvre *et al.*, unpublished work.

form (ax Me/eq Me $\approx 2/3$). In cyclohexane, the values are: morpholine, $63 \pm 4\%$ axial and $37 \pm 4\%$ equatorial; N-methylmorpholine, $43 \pm 4\%$ axial and $57 \pm 4\%$ equatorial. For N-methylmorpholine dissolved in carbon tetrachloride, $\mu = ca.\ 1\cdot36$ D and $_\infty(_mK_2) = ca.\ 1\cdot1 \times 10^{-12}$, consistent with a roughly equal contribution of axial and equatorial isomers.

Infrared and Nuclear Magnetic Resonance Spectra.—From our analysis of the electric birefringence data we infer that for morpholine and for N-methylmorpholine in an " inert " environment, the 1,3-(axial) interactions, though weak, appear to increase gradually in the
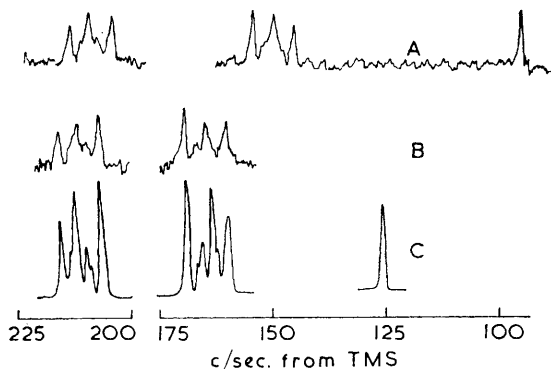
FIG. 2. The n.m.r. spectra of morpholine, using tetramethylsilane (TMS) ($\tau = 10$) as internal standard.

A, in benzene; $w_2 = 721 \times 10^{-5}$.
B, in cyclohexane; $w_2 = 872 \times 10^{-5}$.
C, as the pure liquid.

The high-field band in A is 15 c./sec. upfield and the low-field band 3 c./sec. upfield relative, in each case, to the corresponding absorptions in B and C.
The imino hydrogen signal in B is obscured by the solvent absorption.
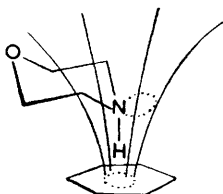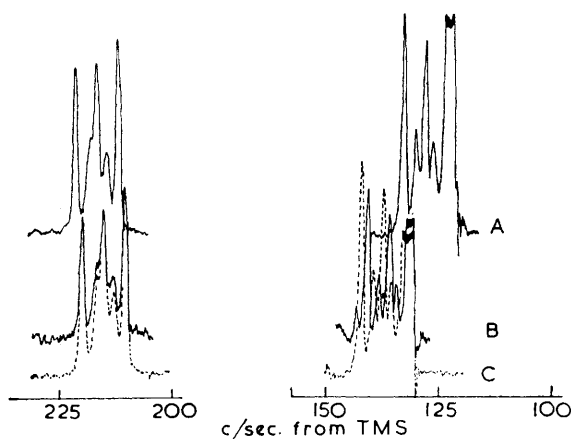

FIG. 4. The n.m.r. spectra of N-methylmorpholine, using tetramethylsilane (TMS) ($\tau = 10$) as internal standard.

A, in benzene; $w_2 \sim 8000 \times 10^{-5}$.
B, in cyclohexane; $w_2 \sim 3000 \times 10^{-5}$.
C, in carbon tetrachloride; $w_2 \sim 5000 \times 10^{-5}$.

In A, the methyl peak and the high-field band are 9·5 c./sec. upfield relative to the corresponding absorptions in B and C.
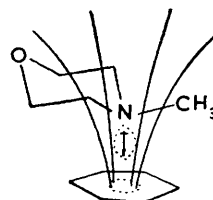

FIG. 3. π-Bonded complex of morpholine in benzene.

FIG. 5. Solvent–solute complex of N-methylmorpholine.

order N–H $<$ N–lone-pair $<$ N–Me. This result is, in part, contrary to the conclusions of Katritzky and his co-workers.[1] However, it should be noted that the problems are not completely analogous; the mobility of the N–lone-pair electrons as well as the molecular environment they encounter are quite different in the quinolizidines.

Examination of the infrared spectra of morpholine solutions in cyclohexane shows that solute–solute association is not appreciable at concentrations lower than $w_2 \approx 4000 \times 10^{-5}$. For solutions in benzene, however, the presence of hydrogen-bonded species can be detected even at high dilutions ($w_2 \approx 600 \times 10^{-5}$; the resolution of our spectrometer does not allow an accurate detection below this concentration). The ratio of the relative areas for the absorption peaks of the monomer (N–H stretching, 3345 cm.$^{-1}$) and of the bonded species

(N−H stretching, 3309 cm.$^{-1}$) appears to be independent of concentration over the range examined; $w_2 = (600—4000) \times 10^{-5}$. It seems reasonable to attribute this to bonding of the imino hydrogen with the benzene π-electrons (cf. also refs. 16 and 17). Further support for such an assignment comes from the nuclear magnetic resonance spectra of morpholine solutions in benzene. The chemical shift of the imino hydrogen is virtually constant in the range $(288—4000) \times 10^{-5}$, consistent with the presence of π-hydrogen bonding rather than solute–solute association. In Fig. 2 we reproduce nuclear magnetic resonance spectra of morpholine. If we assume that weak hydrogen bonding does not cause significant perturbation of the molecular polarisabilities, the molar Kerr constant observed for morpholine in benzene would seem to indicate that, in the π-bonded complex, the imino hydrogen is predominantly axial, as shown in Fig. 3. The nuclear magnetic resonance spectra of *N*-methylmorpholine appear also to be solvent-dependent (see Fig. 4) and suggestive of an interaction of the solute and benzene. The electric birefringence measurements indicate that, in the solvent–solute complex, the methyl group is mostly equatorial, a conclusion which can be correlated with an inductive association [18] of the type shown in Fig. 5.

[16] Pimentel and McClellan, " The Hydrogen Bond," Freeman, San Francisco and London, 1960, p. 202.
[17] Giessner-Prettri, *Compt. rend.*, 1961, **252**, 3238.
[18] Schneider, *J. Phys. Chem.*, 1962, **66**, 2653.