Dipole Moments of Some *N*-Phenyl-substituted Derivatives of Pyrrolidine, Piperidine, Morpholine, and Thiomorpholine

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Apparent dipole moments in benzene of various *p*-substituted *N*-phenyl derivatives of pyrrolidine, piperidine, morpholine, and thiomorpholine and of some analogous *NN*-diethylanilines have been determined. Vector moments along the bisector of angle $CH_2\hat{N}CH_2$ and also in the direction of the major axis of the aromatic ring have been calculated for the parent compounds. The order of magnitude of the latter is *N*-phenylpyrrolidine > *NN*-diethylaniline > *N*-phenylpiperidine > *N*-phenylmorpholine > *N*-phenylthiomorpholine. The nature of the heterocycle does not greatly affect the additional moment, μ(add.), along the major axis of the aromatic ring, required to account for the moments of the *p*-substituted compounds. In each series of compounds, μ(add.) parallels the Hammett substituent constant, σ.

In connection with a study of dyes containing cyclic terminal groups, the electric dipole moments of various *p*-substituted *N*-phenyl derivatives of pyrrolidine, piperidine, morpholine, and thiomorpholine have been measured. Comparative data for some related *p*-substituted *NN*-diethylanilines are also included. The discussion focuses on the change in aromatic ring–nitrogen resonance interaction as the saturated hetereocycle is varied. Appropriate data are provided by calculation of vector moments in the direction of the major axis of the aromatic ring and along the bisector of the $CH_2\hat{N}CH_2$ angle, which are necessary to account for the dipole moments of the parent compounds. Previous relevant work includes n.m.r. studies [1] in which the ^1H n.m.r. chemical shifts of protons *ortho* to NR_2 groups in benzene derivatives are in the sequence pyrrolidinyl > NMe_2 > piperidino > morpholino. Dipole moment measurements [2] of 4-diethylaminoazobenzenes and pyrrolidinylazobenzenes indicate improved conjugation in the latter compounds. Also, pK_a values [3] measured in 50% aqueous ethanol indicate decreasing acidity in the order pyrrolidinyl > NMe_2 > piperazinyl > NEt_2; the anomalously high value for *NN*-diethylaniline has been attributed to loss of solvation as a result of the congested situation obtaining in the vicinity of the nitrogen atom which destabilises the base relative to the ammonium ion.[4]

Experimental

The apparent dipole moments were calculated as described previously [5] from experimental measurements at 298 K of permittivity, specific volume, and refractive index to Na-D radiation [listed in Supplementary Publication No. 23780 (24 pp.†)] of a series of dilute solutions of graded concentrations of each solute in benzene. The slopes α, β, and ν, respectively, of the linear graphs of permittivity, specific volume, and refractive index squared against weight fraction, together with polarisation data, in which the symbols have their usual significance, and the computed dipole moments, are given in Table 1.

Materials.—Benzene was purified as previously.[6] The solutes, which gave satisfactory microanalytical data and n.m.r. spectra, were purified immediately prior to use; purity was confirmed by g.l.c. *N*-Phenylpyrrolidine, b.p. 106 °C at 2 mmHg,[7] *N*-(4-methylphenyl)pyrrolidine, b.p. 112 °C at 2 mmHg,[8] and *N*-(4-bromophenyl)pyrrolidine, m.p. 103 °C,[9] were prepared from the appropriately substituted aniline and 1,4-dichlorobutane.[8] The use of 1,5-dichloropentane led to *N*-phenylpiperidine, b.p. 106 °C, at 2 mmHg,[10] and *N*-(4-bromophenyl)piperidine, m.p. 76 °C,[11] whilst *N*-phenylmorpholine, m.p. 53 °C,[12] (which became commercially available during this work), *N*-(4-methylphenyl)morpholine, m.p. 56 °C,[13] and *N*-(4-bromophenyl)morpholine, m.p. 115—116 °C,[14] resulted from similar reactions involving bis-(2-chloroethyl) ether.[15] The above bromo-compounds were also obtained by reaction of the *N*-phenylheterocycle with bromine in acetic acid or with 2,4,4,6-tetrabromocyclohexa-2,5-dienone.[16]

Two approaches were used to synthesize *N*-(phenyl)thiomorpholine. Aniline and ethylene sulphide afforded 2-mercapto-*N*-phenylethylamine, b.p. 122 °C at 1 mmHg,[17] which reacted with 1,2-dibromoethane in the presence of sodium acetate and sodium carbonate to give the heterocycle. The 4-methyl derivative was obtained in an analogous manner from the related ethylamine, b.p. 133 °C at 2 mmHg.[18] The preferred route involved conversion of *NN*-bis-(2-hydroxyethyl)aniline into *NN*-bis-(2-chloroethyl)aniline, m.p. 42—44 °C,[19] with phosphorus pentachloride in chloroform. Subsequent reaction with sodium sulphide in ethanol gave *N*-(phenyl)thiomorpholine, m.p. 31—32 °C.[19] Treatment of *N*-(4-bromophenyl)thiomorpholine with n-butyl-lithium followed by reaction with iodomethane gave, after chromatography [silica, light petroleum (b.p. 40—60 °C)] and repeated crystallisations from ethanol and from light petroleum (b.p. 40—60 °C), *N*-(4-methylphenyl)thiomorpholine, m.p. 30—31 °C.[20]

N-(4-Nitrophenyl)pyrrolidine, m.p. 168 °C,[21] *N*-(4-nitrophenyl)-piperidine, m.p. 103 °C,[21] and *N*-(4-nitrophenyl)-morpholine, m.p. 150 °C,[22] were obtained from 4-chloronitrobenzene and the appropriate amine. *N*-(4-Cyanophenyl)-piperidine, m.p. 55 °C,[23] and *N*-(4-cyanophenyl)morpholine, m.p. 85 °C,[24] were similarly prepared from 4-chlorobenzonitrile in the presence of dimethylformamide. The nitriles were also obtained from the corresponding bromo-compound by reaction with copper(I) cyanide in dimethylformamide.[25]

N-(4-*Cyanophenyl*)*pyrrolidine* (59%), m.p. 81 °C, as plates

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† For details of the Supplementary Publication Scheme see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.

Table 1. Polarisation data and dipole moments, μ, at 298 K for solutions in benzene of *p*-substituted *N*-phenyl saturated heterocycles and of *NN*-diethylaniline

Substituent	α	β	ν	$P_{2,\infty}$/cm^3	$_EP_2$/cm^3	μ/D	Lit. values
In *NN*-diethylaniline							
4-Br	6.171	−0.390	0.174	336.57	78.05	3.56 ± 0.01	3.62 [a]
4-CN	27.999	−0.161	0.219	968.71	57.44	6.68 ± 0.04	
4-NO_2	28.873	−0.283	0.411	1 104.86	64.21	7.13 ± 0.02	7.16 [a]
In *N*-phenylpyrrolidine							
H	3.186	−0.187	0.207	130.25	47.11	2.02 ± 0.01	2.04 [a]
4-Me	2.091	−0.169	0.212	110.33	52.65	1.68 ± 0.01	
4-Br	7.072	−0.433	0.259	349.04	58.28	3.77 ± 0.02	3.76 [a]
4-CN	29.644	−0.307	0.359	1 003.42	54.05	6.81 ± 0.03	
4-NO_2	30.528	−0.359	0.529	1 149.41	63.63	7.29 ± 0.01	7.23 [a]
In *N*-phenylpiperidine							
H	1.496	−0.155	0.176	92.90	52.16	1.41 ± 0.02	1.48,[a] 1.74 [b]
3,5-Me_2	0.834	−0.113	0.143	87.83	62.37	1.12 ± 0.01	
4-Br	4.507	−0.424	0.233	255.22	61.36	3.08 ± 0.02	3.10 [a]
4-CN	24.308	−0.170	0.291	906.69	63.26	6.42 ± 0.01	
4-NO_2	24.410	−0.323	0.484	997.91	68.69	6.74 ± 0.01	6.69,[a] 6.80 [b]
In *N*-phenylmorpholine							
H	0.383	−0.237	0.184	55.93	49.14	0.58 ± 0.01	
4-Me	0.543	−0.207	0.162	67.57	54.19	0.81 ± 0.01	
4-Br	1.421	−0.459	0.187	114.14	57.30	1.67 ± 0.02	
4-CN	12.765	−0.321	0.334	498.22	57.36	4.64 ± 0.03	
4-NO_2	13.650	−0.403	0.456	580.83	63.35	5.03 ± 0.01	
In *N*-(phenyl)thiomorpholine							
H	0.664	−0.274	0.303	68.87	56.11	0.79 ± 0.01	
4-Me	0.880	−0.250	0.306	83.52	61.97	1.03 ± 0.01	
4-Br	1.273	−0.485	0.299	112.57	64.62	1.53 ± 0.03	
4-CN	11.947	−0.323	0.390	509.53	64.30	4.67 ± 0.02	
4-NO_2	13.185	−0.431	0.515	604.20	68.93	5.12 ± 0.02	

[a] Ref. 32. [b] Ref. 28.

from ethanol, was obtained by boiling 4-chlorobenzonitrile (0.2 mol), pyrrolidine (0.4 mol), and dimethylformamide (15 cm^3) for 4 h (Found: C, 76.5; H, 6.9; N, 16.1. $C_{11}H_{12}N_2$ requires C, 76.7; H, 7.0; N, 16.3%).

N-(3,5-*Dimethylphenyl)piperidine* (51%), b.p. 117 °C at 2.0 mmHg, was prepared by boiling 3,5-dimethylaniline (0.1 mol) and 1,5-dibromopentane (0.1 mol) with anhydrous sodium carbonate (0.1 mol) in toluene (50 cm^3) for 24 h (Found: C, 82.4; H, 9.9; N, 7.4. $C_{13}H_{19}N$ requires C, 82.5; H, 10.1; N, 7.4%).

N-(4-*Nitrophenyl)thiomorpholine* (73%), m.p. 140—142 °C, was prepared from 4-chloronitrobenzene (0.025 mol) and thiomorpholine (0.062 mol) in butan-1-ol as dark green leaflets from ethanol (Found: C, 53.5; H, 5.2; N, 12.6; S, 14.2. $C_{10}H_{12}N_2O_2S$ requires C, 53.6; H, 5.4; N, 12.5; S, 14.3%).

N-(4-*Cyanophenyl)thiomorpholine* (67%), m.p. 94—95 °C, was obtained by boiling thiomorpholine (0.11 mol) and 4-fluorobenzonitrile (0.044 mol) in butan-1-ol (20 cm^3) for 10 days. Chromatography (silica, toluene) followed by crystallisations from ethanol and from toluene gave colourless crystals (Found: C, 64.5; H, 6.0; N, 14.0; S, 15.5. $C_{11}H_{12}N_2S$ requires C, 64.7; H, 5.9; N, 13.7; S, 15.7%).

N-(4-*Bromophenyl)thiomorpholine* (81%), m.p. 96—97 °C, off-white crystals from methanol, resulted from the reaction of *N*-(phenyl)thiomorpholine with bromine in acetic acid at room temperature (Found: C, 46.7; H, 4.7; Br, 31.0; N, 5.5; S, 12.1. $C_{10}H_{12}BrNS$ requires C, 46.5; H, 4.7; Br, 31.0; N, 5.4; S, 12.4%).

Discussion

The extent of overlap of the nitrogen lone-pair electrons with the π-electrons of the aromatic ring in *N*-phenyl-substituted saturated heterocycles may depend upon the molecular conformation, the nature of the heterocycle, the angle of rotation of the aromatic ring about the N–C(phenyl) bond, and any *p*-substituent present. In order to assess the influence of the various heterocyclic residues on the extent of conjugation, component moments, *x*, along the major axis of the aromatic ring, which are necessary to account for the dipole moments of the parent compounds, have been calculated.

A first requirement in this procedure is the evaluation of the angles, γ, which the resultant moments of the parent *N*-phenylheterocycles make with the major axis of the aromatic ring. These values of γ, recorded in Table 2, are obtained by combining vectorially the moments of the parent *N*-phenyl heterocycle, the 4-methyl- or the 3,5-dimethyl-substituted derivative and that of toluene (0.37 D). It is assumed that the methyl groups do not perturb the electron distribution in the vicinity of the nitrogen atom. Various approaches have then been made to complete the calculations of *x*; each method involves different assumptions regarding the geometry of the C(phenyl)–N–$(CH_2)_2$ moiety and gives rise to slightly different values of *x*. The trend in *x* remains the same however, and the values are recorded in Table 2. The method which we have chosen to report involves the assumption that δ, the $\widehat{CNC}$(phenyl) angle, remains constant throughout. A reasonable value of δ has been selected as follows. From the dipole

Table 2. Vector moments along the major axis of the aromatic ring (x), and along the bisector of the CH_2NCH_2 angle (y), and angle, γ, which the observed resultant moments make with the major axis of the ring

Compound	x/D	y/D	γ (°)
(1) *N*-Phenylpyrrolidine	1.44	0.85	21.0
(2) *NN*-Diethylaniline	0.97	1.07	29.5
(3) *N*-Phenylpiperidine	0.61	0.96	33.5
(4) *N*-Phenylmorpholine	0.15	0.89	115.0
(5) *N*-(Phenyl)thiomorpholine	−0.13	0.99	121.0

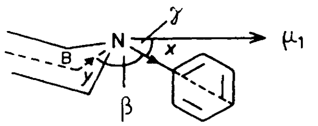
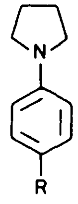
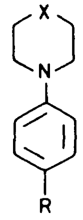


Figure 1. *NN*-Diethylaniline: μ_1 = 1.80 D, β = 124.0°, γ = 29.5° (31°, ref. 32). *N*-Phenylpiperidine: μ_1 = 1.41 D, β = 126.0°, γ = 33.5°. *N*-Phenylpyrrolidine: μ_1 = 2.02 D, β = 121.5°, γ = 21.0°



(I)



(II)

Table 3. Additional moments, μ(add.) in the direction of the N–C(phenyl) bond, and necessary to account for the observed dipole moments of the *p*-substituted compounds

p-Substituent	Heterocyclic moiety				
	$(CH_2)_4$	$(C_2H_5)_2$	$(CH_2)_5$	$(CH_2)_4O$	$(CH_2)_4S$
Br	0.25	0.32	0.24	0.27	0.22
CN	0.86	1.03	1.17	0.83	1.00
NO_2	1.36	1.50	1.51	1.24	1.47

moment of trimethylamine[26] (0.86 D) and a $\widehat{CNC}$ bond angle[27] of 110°, the $\overset{+}{C}$–$\overset{-}{N}$ bond moment is calculated to be 0.88 D. Aroney and Le Fèvre,[26] using an angle of 108°, calculated a corresponding moment of 0.80 D. Using a value of γ of 33.5° for *N*-phenylpiperidine (*cf.* Aroney and Le Fèvre's value[28] of 36°) and a moment along BN, the bisector of angle $\widehat{CNC}$, of 0.96 D (2 × 0.88 × cos57°), β, the angle which this bisector makes with the N–C(phenyl) bond is calculated to be 126° (Figure 1). From this value of β, and taking the angle $\widehat{CNC}$ (ρ) to be 114°,[29] the $\widehat{CNC}$(phenyl) angle, δ, is found directly to be 108.5° on applying $\cos\delta = \cos\beta \cdot \sin\frac{1}{2}(180 - \rho)$, a formula derived from tetrahedral geometry.

In our subsequent calculations, the values of ρ used are those determined by *X*-ray crystallography and selected from data of appropriate saturated heterocyclic derivatives;[29] they are pyrrolidine 105°, piperidine 114°, morpholine 107.4°, thiomorpholine 111.5°, and *NN*-diethylaniline 110°.

(a) p-*Substituted Derivatives of* N-*Phenylpyrrolidine* (I), N-*Phenylpiperidine* (II; X = CH_2), *and* NN-*Diethylaniline*.—Although only the geometry of the C(phenyl)–N–$(CH_2)_2$ moiety has been taken into account in the vector calculations, it is instructive to note that the piperidine ring exists in a chair conformation. This is indicated by electron diffraction and n.m.r. results for cyclohexanes and piperazines.[30] In a comprehensive discussion, Jones *et al.*[31] deduced that an unhindered hydrogen on the heteroatom prefers the equatorial conformation. Thus, for *N*-phenylpiperidine, the large *N*-substituent will be attached equatorially. Supporting evidence is provided by the results of measurements of Kerr constants carried out by Aroney and Le Fèvre.[28] This evidence is, however, based on a dipole moment of 1.74 D for *N*-phenylpiperidine and this value compares unfavourably with the present authors' figure of 1.41 D and also that of 1.48 D measured by Mazet *et al.*[32] In the case of pyrrolidine, the non-planar half-chair conformation is considered to be the most reasonable. However, several overlapping bands appear in the infrared first overtone region, suggesting a possible mixture of several conformers of comparable energy.[33] Using the vector diagram and the parameters quoted (Figure 1), the values of the component moments x and y in the direction of the N–C(phenyl) bond and along the bisector BN of angle $\widehat{CNC}$, respectively, have been calculated by resolving moments along and perpendicular to the N–C(phenyl) bond. These values of x and y are recorded in Table 2. In the case of *NN*-diethylaniline, the angle γ, which the resultant moment makes with the major axis of the ring, is calculated from the moments of the parent compound (1.80 D) and its *p*-methyl derivative (1.49 D) previously determined.[34]

The additional moments, μ(add.), acting along the major axis of the aromatic ring and necessary to account for the observed moments of the *p*-substituted derivatives, μ(R), are calculated from equation (1) where μ_1 is the moment of the

$$\mu^2(R) = \mu_1^2 + \mu_3^2 + 2\mu_1\mu_3\cos\gamma \qquad (1)$$

parent *N*-phenylheterocycle, μ_3 = μ(add.) + μ(X), and μ(X) = moment of the correspondingly substituted benzene (Br = 1.56, CN = 4.03, NO_2 = 4.01 D). Values of μ(add.) are recorded in Table 3.

(b) p-*Substituted Derivatives of* N-*Phenylmorpholine* (II; X = O) *and* N-*(Phenyl)thiomorpholine* (II; X = S).—In the case of morpholine, dipole moments and molar Kerr constant measurements were interpreted by Aroney and Le Fèvre[26] in terms of a chair conformation. A similar conclusion was reached by Ansell and Finnegan[35] from an *X*-ray analysis of a silver iodide–morpholine complex. That the N–H equatorial conformer predominates was concluded by Baldock and Katritzky[33] from i.r. spectroscopic studies. In the case of *N*-phenylmorpholine, it is expected that the phenyl group is disposed equatorially. We have therefore assumed a chair conformation for both *N*-phenylmorpholine and *N*-(phenyl)-thiomorpholine. Recognising that the dipole moments of these compounds contain a contribution from the polar C–O–C and C–S–C moieties, respectively, it becomes necessary to calculate the angles θ, which the ring plane (atoms 1,2,6) makes with the ring plane (atoms 3,4,5). Combining vectorially the moments of tetrahydropyran[36] (1.55 D) and tetrahydrothiopyran[36] (1.71 D) separately with that of *N*-phenylpiperidine (1.41 D), it is found that the observed moments of *N*-phenylmorpholine and *N*-(phenyl)thiomorpholine are accounted for if the angles between the component moments are 158.0° and 153.0°, respectively. Knowing β, θ becomes 2.0°

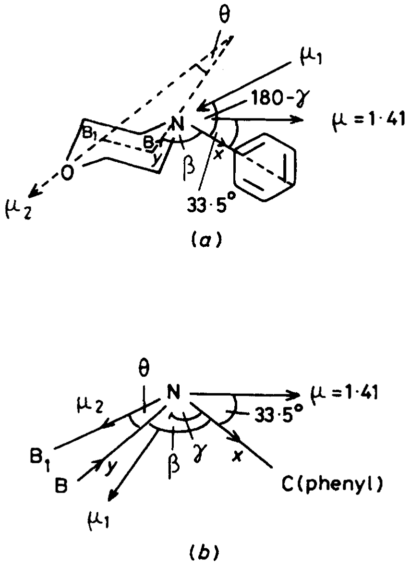


Figure 2. (*a*) *N*-Phenylmorpholine: $\mu_1 = 0.59$ D, $\mu_2 = 1.55$ D, $\beta = 122.5°$, $\gamma = 115.0°$, $\theta = 2.0°$. (*b*) *N*-Phenylmorpholine vector diagram

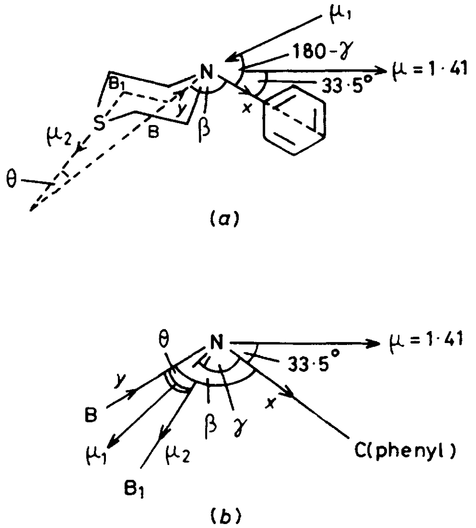


Figure 3. (*a*) *N*-(Phenyl)thiomorpholine: $\mu_1 = 0.79$ D, $\mu_2 = 1.71$ D, $\beta = 124.5°$, $\gamma = 121.0°$, $\theta = 5.0°$. (*b*) *N*-(Phenyl)thiomorpholine vector diagram

and 5.0°, respectively (Figures 2 and 3). In the vector diagrams, μ_2 is the moment of tetrahydropyran or tetrahydrothiopyran acting along the bisector of angle C–O–C or C–S–C, and μ_1 the moment of *N*-phenylmorpholine or *N*-(phenyl)thiomorpholine disposed at the angle γ to the N–C(phenyl) bond. Values of x, y, and μ(add.) are calculated as before and are recorded in Tables 2 and 3.

Considering the data in Table 2, it is interesting to observe that the values of y are similar, whereas the values of x decrease in the order of compound (1) > (2) > (3) > (4) > (5). From the y values, corresponding $\overset{+}{C}-\overset{-}{N}$ bond moments of 0.70, 0.93, 0.88, 0.75, and 0.88 D, respectively, are calculated. These values imply that the presence of polar moieties, C–O–C or C–S–C in compounds (4) and (5), does not significantly affect the $\overset{+}{C}-\overset{-}{N}$ bond moment. In trimethylamine, overall polarity depends upon the moments of the N–Me bonds, each of which includes a contribution from the nitrogen lone pair. Replacing an N–Me moiety by N–Ph changes the $\overset{+}{N}-\overset{-}{C}$ bond moment from −0.88 D to −0.13, 0.15, 0.61, 0.97, and 1.44 D for compounds (5)—(1), respectively. The authors consider it likely that these bond-moment changes reflect the extent of overlap of the nitrogen lone-pair electrons with the π-electrons of the ring, giving rise to a delocalisation moment in the direction $\overset{+}{N}-\overset{-}{C}$(phenyl). Variations in extent of overlap may be explained by changes in the geometry of the $(CH_2)_2$–N–C(phenyl) moiety and also by rotation of the aromatic ring around the N–C(phenyl) bond, the latter diminishing the conjugation of the nitrogen lone pair with the ring. From the results in Table 3, it suffices to comment that the nature of the heterocyclic component seems to have little effect on μ(add.). This parameter directly measures the influence of a *p*-substituent on the electron density distribution in the ring, and increases as the Hammett substituent constant, σ, increases.

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