The Dipole Moments, Molar Kerr Constants, and Solution-state Conformations of Some Substituted Benzamides

By **Raymond K. Pierens** * and **Alan J. Williams**, School of Chemistry, University of Sydney, Sydney, N.S.W. 2006, Australia.

The dipole moments and molar Kerr constants are reported for 24 substituted benzamides as solutes in dioxan. These data are analysed to indicate the preferred solution conformations. Our results indicate that for a given ring substituent the dihedral angle between the planar amide group and the benzene ring is similar for both the 3- and 4-substituted benzamides but less than that for the 2-substituted isomer. For the 3-substituted benzamides both ' *cis*- ' and ' *trans*- '-conformers contribute to the observed dipole moment and molar Kerr constant whereas for the 2-substituted species only that conformer with the C=O bond of the amide group remote from the *ortho*-substituent is proposed.

PREVIOUS studies of benzamide in the solid state [1] and as a solute in dioxan [2] have indicated that the planar amide group is not coplanar with the benzene ring plane. There appears to be no similar conformational studies for substituted benzamides. This work is concerned with the application of polarity and polarisability considerations to the investigation of some substituted benzamides as solutes in dioxan. Because of severe solubility problems in solvents such as carbon tetrachloride and benzene, we are restricted to the use of dioxan as solvent even though dioxan is a known hydrogen-bonding solvent.[3] McClellan [4] indicates that, for those benzamides that have been measured previously (see Experimental section), there is a small increment in the measured dipole moment as the solvent changes from benzene to dioxan. However benzene cannot be regarded as a non-interacting solvent. Further, the dioxan molecule is almost isotropically polarisable. Because of these considerations, we have omitted solute–solvent interactions from our discussions.

EXPERIMENTAL

Materials, Apparatus, etc.—The solutes were obtained from commercial sources and were recrystallised to give m.p.s in accord with literature values. Analytical reagent grade dioxan was purified by passing through a neutral alumina column and stored over molecular sieves (0.4 nm, 30 g for 2 l). The apparatus, techniques, and symbols used, the solvent constants, and the computational procedures for obtaining infinite-dilution dipole moments, molar refractions, and molar Kerr constants have been reported before.[5-7]

Previous Measurements.—McClellan [4] lists dipole moments only for benzamide and its 3- and 4-bromo-, 3- and 4-chloro-, 4-nitro-, and 4-amino derivatives. These previous determinations of the dipole moments (μ), expressed in S.I. units as $10^{30}\,\mu$/C m together with the solvents used are as follows: benzamide 12.5(dioxan),[2] 12.0(dioxan),[8] 12.4 (dioxan),[9] 12.2(benzene),[10] 12.8(dioxan),[10] 11.8(benzene),[11] 12.9(dioxan),[12] 12.6(benzene),[12] 11.4(benzene); [13] 3-bromobenzamide 11.3(benzene),[10] 12.2(dioxan); [10] 4-bromobenzamide 10.5(benzene),[10] 12.3(dioxan),[10] 10.8(benzene); [11] 3-chlorobenzamide 12.1(benzene),[10] 12.2(dioxan),[10] 11.9(benzene); [11] 4-chlorobenzamide 11.3(benzene),[10] 12.4(dioxan),[10] 11.6(benzene); [11] 4-nitrobenzamide 16.3(dioxan),[8] 15.3-(benzene),[14] 16.1(dioxan); [14] 4-aminobenzamide 15.7(dioxan),[8] 15.5(benzene),[14] 16.6(dioxan).[14] Except for benzamide (see Discussion), the molar Kerr constant for the solutes investigated have not been reported previously.

Present Measurements.—The results of our measurements are summarised in Table 1. Because of space considerations, error estimates have been given only for the infinite-dilution molar refractions (R_D) and molar Kerr constant $_\infty({}_mK_2)$ entries. The uncertainty in any electric dipole value is $< \pm 1\%$. For all other listings in Table 1, the number of significant figures gives an indication of the reliability. S.I. Units have been used throughout; the conversion factors from the electrostatic (c.g.s., e.s.u.) system are respectively: $1 \text{ C m} = 0.299\,8 \times 10^{30}$ D, $1 \text{ m}^5 \text{ V}^{-2} \text{ mol}^{-1} = 0.898\,8 \times 10^{15}$ e.s.u. mol^{-1}.

DISCUSSION

The procedure used in this investigation involves the use of polarity data together with bond or group polarisability anisotropies extracted from structurally suitable molecules in a vectorial and tensorial analysis [7,15] to yield molar Kerr constants (${}_mK$) expected for a particular stereostructure. Comparison between calculated and observed ${}_mK$ values allows choice to be made between candidate conformations. The necessary polarisability parameters are listed in Table 2. To determine the direction of action of the observed dipole moments for the substituted benzamides, it is necessary first to determine the line of action of the molecular dipole moment of benzamide itself. We do this by considering the polarity data for 4-X·C_6H_4·$CONH_2$ † of Table 1.

Observed electric dipole moments of these species can be considered to be the resultant of the moment of C_6H_5X (X = F, 4.94×10^{-30}; [16] X = Cl, 5.30×10^{-30}; [17] X = Br, 5.04×10^{-30}; [18] X = NO_2, 13.2×10^{-30}; [17] X = CF_3, 8.41×10^{-30} [19]) and that of benzamide (12.9×10^{-30}, Table 1). Using this simple vectoral treatment a mean value of $\theta = 106 \pm 3°$ for the angle between the direction of the benzamide dipole moment and the 1,4-axis of the benzene ring is obtained (see Figure 1a).

We are aware that the simple analysis ignores interaction moments arising from electromeric interactions of the substituent groups and the benzene ring. Because the angle so calculated varies little with the changing

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† Although dipole moments and molar Kerr constants for 2-, 3-, and 4-aminobenzamide are reported in Table 1, no polarity or polarisability analyses have been attempted because of the complication due to the non-planarity of the C_{Ar}–NH_2 group.

nature of the substituent, it is our belief that such interaction moments are small. Further, it will be shown later that small variations in θ have negligible effect in subsequent calculations.

TABLE 1

Molar polarisations and refractions, dipole moments, and molar Kerr constants (from observations on dioxan solutions at 25°)

Compound	Concentration range $10^5 w_2$	$\alpha\varepsilon_1$ *	β *	γ *	δ *	$_\infty P_2$/cm³	R_D/cm³	$10^{30}\mu$/C m †	$10^{27}{}_\infty(_mK_2)$/m⁵ V⁻² mol⁻¹ ‡
Benzamide	102—626	15.77	0.159	0.110	166	343	34.7 ± 1.7	12.9	249 ± 7
4-Fluorobenzamide	195—3185	12.36	0.238	0.083	141	313	34.6 ± 0.8	12.3	244 ± 2
3-Fluorobenzamide	244—1073	13.74	0.228	0.073	150	345	33.6 ± 1.3	13.0	259 ± 3
2-Fluorobenzamide	164—1309	9.61	0.219	0.074	67	251	34.1 ± 0.4	10.8	114 ± 1
4-Trifluoromethylbenzamide	170—1023	9.34	0.251	0.040	133	331	40.3 ± 1.0	12.5	316 ± 12
3-Trifluoromethylbenzamide	178—956	8.10	0.267	0.038	96	291	39.5 ± 0.6	11.6	226 ± 2
2,3,4,5,6-Pentafluorobenzamide	136—719	9.71	0.380	0.010	−135	374	34.0 ± 0.6	13.5	−378 ± 6
4-Chlorobenzamide	81—3021	11.78	0.242	0.105	24	335	41.0 ± 0.6	12.6	38 ± 4
3-Chlorobenzamide	156—3622	11.42	0.247	0.102	168	326	40.4 ± 0.5	12.4	327 ± 7
2-Chlorobenzamide	124—3027	13.84	0.259	0.103	−137	387	40.0 ± 0.4	13.7	−287 ± 4
2,6-Dichlorobenzamide	110—609	13.74	0.323	0.081	−364	466	42.7 ± 1.5	15.2	−908 ± 7
2,4-Dichlorobenzamide	112—618	10.16	0.315	0.090	−229	354	44.6 ± 2.2	12.9	−573 ± 25
4-Bromobenzamide	99—2488	9.03	0.405	0.093	−24	331	42.8 ± 1.3	12.4	−71 ± 11
3-Bromobenzamide	159—787	8.53	0.400	0.085	133	315	42.2 ± 1.1	12.1	333 ± 18
2-Bromobenzamide	203—1137	11.24	0.408	0.092	−127	404	42.4 ± 1.0	14.0	−339 ± 8
2-Iodobenzamide	203—886	8.15	0.498	0.091	−93	366	46.5 ± 1.5	13.1	306 ± 8
2,4,6-Trimethylbenzamide	92—625	12.68	0.062	0.088	−339	384	48.2 ± 0.9	13.4	−726 ± 15
4-Nitrobenzamide	110—990	17.35	0.314	0.106	504	507	40.9 ± 0.9	15.9	1 065 ± 42
3-Nitrobenzamide	103—546	11.31	0.303	0.101	221	342	41.1 ± 1.8	12.7	464 ± 7
2-Nitrobenzamide	187—718	25.8	0.293	0.102	181	739	41.1 ± 1.0	19.5	363 ± 8
3,5-Dinitrobenzamide	180—956	12.49	0.404	0.094	557	470	45.0 ± 1.9	15.1	1 505 ± 11
4-Chloro-3,5-dinitrobenzamide	170—957	11.51	0.406	0.090	451	506	52.0 ± 5.4	15.7	1 416 ± 10
4-Aminobenzamide	181—544	23.02	0.243	0.125	615	545	38.2 ± 0.9	16.6	1 063 ± 3
3-Aminobenzamide	182—931	15.38	0.234	0.118	166	374	37.3 ± 1.4	13.5	280 ± 6
2-Aminobenzamide	129—673	6.12	0.225	0.131	40	167	38.7 ± 1.6	8.3	67 ± 1

* Incremental changes in the relative permittivities, densities, refractive indices, and Kerr constants (Δε, Δd, Δn, and ΔB, respectively) were measured for solutions having solute weight fractions w_2. The coefficients, $\alpha\varepsilon_1$, β, γ, and δ were derived from the relations: $\alpha\varepsilon_1 = \Sigma\Delta\varepsilon/\Sigma w_2$; $\beta = \Sigma\Delta d/d_1\Sigma w_2$; $\gamma = \Sigma\Delta n/n_1\Sigma w_2$; $\delta = \Sigma\Delta B/B_1\Sigma w_2$. † Calculated on the basis that $_DP = 1.05R_D$. ‡ The term $_\infty(_mK_2)$ refers to the solute molar Kerr constant at infinite dilution.

The error in θ due to uncertainties in the dipole moments used in the derivation has been estimated by using the extreme moment values of the range given for C_6H_5X in McClellan.[4] In the case of 4-chlorobenzamide this procedure yields a maximum error of ±1°. Hence the realistic value of θ of 106 ± 4° has been used to obtain the necessary polarity parameters for the $_mK$ calculations.

TABLE 2

Anisotropic polarisabilities of bonds and groups (expressed as $10^{40}b$/C m² V⁻¹)

	b_L	b_T	b_V	Ref
C–H	0.72	0.72	0.72	20
$H_2NCO{\cdot}C$	† 4.98	† 3.25	† 3.25	
C_6H_5	11.69	11.69	7.56	21
$F{\cdot}C_6H_4$	12.01	11.51	7.22	16
$CF_3{\cdot}C_6H_4$	13.86	13.74	9.28	19
C_6F_5	11.66	12.43	5.89	16
$2,4,6\text{-}(CH_3)_3{\cdot}C_6H_2$	18.35	18.35	13.00	22
$Cl{\cdot}C_6H_4$	15.73	13.24	8.41	23
$Br{\cdot}C_6H_4$	17.97	13.75	9.28	24
$I{\cdot}C_6H_4$	21.20	16.97	10.51	24
$NO_2{\cdot}C_6H_4$	16.57	13.86	8.29	25

† Derived from ref. 2 using C–H data from ref. 16.

4-*Substituted Benzamides*.—First, we shall consider the conformation of the benzamide molecule. An *X*-ray crystal structure study[1] has indicated that, in the solid state, the benzamide molecule can be described as a planar benzene ring and a planar amide group twisted about the connecting C–C bond such that the resulting dihedral angle (ϕ) is 26°. For all solutes considered in this work we have assumed the amide group to be planar. An earlier molecular polarisability study[2] of benzamide as a solute in dioxan yielded ϕ = 37 ± 5°. By means of equations listed in ref. 7 and using the experimental data for benzamide given in Table 1, the appropriate bond and group polarisability anisotropies of Table 2, together with the previously calculated resultant dipole moment direction (θ), molar Kerr constants can be calculated for various values of ϕ. Agreement between calculated and observed Kerr constants occurs when ϕ = 39 ± 2°. The error estimate for ϕ, has been deduced from a consideration of the known reliabilities of $_\infty(_mK_2)$ and θ; no allowance has been made for uncertainties in the bond and group polarisability parameters. Further it should be noted that for all solutes examined in this work the contribution of the uncertainty in θ to the error estimate for ϕ, is always <1°

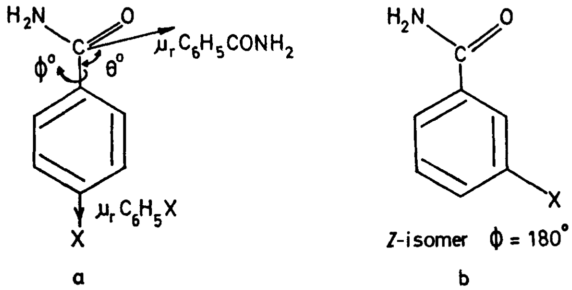

FIGURE 1

An analogous procedure applied to the data for the 4-substituted benzamides of Table 1 yield the values for ϕ listed in Table 3. In the case of 4-nitrobenzamide, $_{\infty}({}_{\mathrm{m}}K_2)$ is appreciably greater than the maximum calculated value (corresponding to that conformation where the planes containing the benzene ring and the amide grouping are coplanar) and this may be attributed to a very marked degree of conjugative interaction of the amide and nitro groups through the benzene ring.

TABLE 3

Solute	ϕ (°)
Benzamide	39 ± 2
4-Fluorobenzamide	33 ± 1
4-Trifluoromethylbenzamide	32 ± 1
4-Chlorobenzamide	37 ± 1
4-Bromobenzamide	36 ± 1
4-Nitrobenzamide	*ca.* 0

3-*Substituted Benzamides*.—A discussion of *meta*-substituted benzamides (see Figure 1b) is complicated by the possible existence of E- and Z-isomers corresponding to the carbonyl bond of the amide group being either '*trans*' or '*cis*' to the *meta*-substituent. Hence the magnitude of the observed dipole moments and molar Kerr constants for the various 3-substituted benzamides listed in Table 1 are dependent on the proportions of the two isomers present. The expected dipole moments and Kerr constants for a particular 3-substituted benzamide as ϕ is varied over the range 0—180° can be readily calculated by procedures outlined earlier. Figure 2 shows the variation of $_{\mathrm{m}}K_{\mathrm{calc.}}$ for 3-chlorobenzamide over the range $\phi = 0°$ (the E-isomer) to $\phi = 180°$ (the Z-isomer). The contours of the curves for the other 3-substituted benzamides are very similar. The isomer abundances for a given ϕ that yields agreement between observed and calculated parameters are now obtainable. Table 4 summarises the results of these calculations. The percentages of the *trans*-conformer from the dipole moment data being more accurate than those calculated from Kerr constant measurements, are listed in the Table. In estimating errors in the isomer abundances we have assumed a maximum error of 1% in any dipole moment measured in this present work while for those values taken from McClellan [4] an uncertainty of 2% has been assumed. However, in the case of $_{\mathrm{m}}K_{cis}$ and $_{\mathrm{m}}K_{trans}$, error estimates are difficult to deduce hence we have treated these quantities as being experimentally measured. A consequent ±3% error has been attached to these quantities. Comparison of the isomer abundances calculated for the various 3-substituted benzamides from μ and $_{\mathrm{m}}K$ data yields the uncertainties in ϕ listed in Table 4. It can be seen that, except for 3-nitrobenzamide, there is agreement between the ϕ values obtained for the *meta*-substituted benzamides and those for the corresponding *para*-species (Table 3). For 3-nitrobenzamide the plane of the amide group is no longer coplanar with the benzene ring; however the dihedral angle ϕ is still much less than that for benzamide. It should be noted that for each of the *meta*-substituted benzamides listed in Table 4, no single conformer has both $\mu_{\mathrm{calc.}}$ and $_{\mathrm{m}}K_{\mathrm{calc.}}$ in accord with the observed quantities.

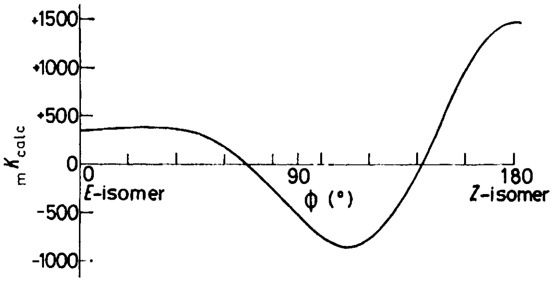

FIGURE 2 Variation of $_{\mathrm{m}}K_{\mathrm{calc.}}$ with ϕ for 3-chlorobenzamide

TABLE 4

Solute	% *trans* from μ	ϕ (°) from μ and $_{\mathrm{m}}K_2$
3-Fluorobenzamide	53 ± 5	34 ± 2
3-Trifluoromethylbenzamide	73 ± 3	29 ± 1
3-Chlorobenzamide	62 ± 5	34 ± 2
3-Bromobenzamide	66 ± 4	38 ± 2
3-Nitrobenzamide	75 ± 2	20 ± 1

2-*Substituted Benzamides*.—In this section we shall include in our discussion 2,4-dichlorobenzamide. Using procedures already described, dipole moments and molar Kerr constants can be readily calculated for each of these species as the dihedral angle ϕ varies from 0 to 180°. Agreement between the observed and calculated dipole moments occurs for a single value of ϕ and these calculations are summarised in Table 5. Our results do not indicate the existence of E- and Z-type isomer mixtures.

TABLE 5

Solute	ϕ (°) from μ	ϕ (°) from $_{\mathrm{m}}K_2$
2-Fluorobenzamide	32 ± 2	65 ± 2
2-Chlorobenzamide	76 ± 3	79 ± 2
2,4-Dichlorobenzamide	85 ± 3	80 ± 2
2-Bromobenzamide	81 ± 3	76 ± 2
2-Iodobenzamide	71 ± 3	71 ± 2
2-Nitrobenzamide	88 ± 3	74 ± 2

Except for the case of 2-nitrobenzamide (see below), Table 5 indicates that the C=O bond of the amide group is remote from the *ortho*-substituent *i.e.* $0° < \phi < 90°$. The polarity and spatial requirements of the various *ortho*-substituents are sufficient to account for these observations. For 2-nitrobenzamide, molecular models suggest that the NO_2 group may not be coplanar with the benzene ring in which case the use of the dipole moment of nitromethane (10.5×10^{-30} C m) [26] in the calculation of $\mu_{\mathrm{res.}}$ with varying ϕ would be more applicable than that for nitrobenzene. The ϕ value so obtained (107 ± 3°) is clearly inconsistent with the other entries of Table 5 and hence the nitrobenzene polarity and polarisability parameters have been used in these and later calculations. Table 5 also lists the values of ϕ that yield agreement between $_{\mathrm{m}}K_{\mathrm{obs.}}$ and $_{\mathrm{m}}K_{\mathrm{calc.}}$. Agreement is obtained between the dihedral angles calculated from the dipole moment and Kerr constant data except for 2-fluoro- and 2-nitro-benzamide. A g.l.c. analysis of 2-fluorobenzamide showed the presence of an unidentified impurity (<1%) which may account for the discrepancy. In the case of 2-nitrobenzamide, small but unknown rotations of the nitro group relative to the benzene ring would affect $_mK$ considerations but not those involving dipole moments.

3,5-*Dinitro-*, 4-*Chloro*-3,5-*dinitro-*, 2,6-*Dichloro-*, 2,4,6-*Trimethyl-*, *and Pentafluoro-benzamide.*—In our calculations, no allowance has been made for mutual inductive interactions and, because such effects are maximised in these compounds, our conclusions are therefore limited by the simplifications used in the calculation of resultant dipole moments discussed earlier. Further, molecular models of 4-chloro-3,5-dinitrobenzamide imply that the two nitro groups are no longer coplanar with the benzene ring. Accordingly, we record only generalised conclusions. Our results indicate that the dihedral angle ϕ for the two dinitro compounds is *ca.* 0° while for the remaining three solutes ϕ = *ca.* 90°.

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REFERENCES

[1] B. R. Penfold and J. C. B. White, *Acta Cryst.*, 1959, **12**, 130.

[2] M. J. Aroney, R. J. W. Le Fèvre, and A. N. Singh, *J. Chem. Soc.*, 1965, 3179.

[3] A. E. Lutskii and V. V. Prezhdo, *Russ. J. Phys. Chem.*, 1971, **45**, 723.

[4] A. L. McClellan, ' Tables of Experimental Dipole Moments,' Freeman, San Francisco, 1963; Rahara, California, 1974.

[5] R. J. W. Le Fèvre and D. J. Millar, *Chem. and Ind.*, 1971, 399.

[6] R. J. W. Le Fèvre and S. C. Solomons, *Austral. J. Chem.*, 1968, **21**, 1703.

[7] C. G. Le Fèvre and R. J. W. Le Fèvre, ' The Kerr Effect,' in ' Techniques of Chemistry,' eds. A. Weissberger and B. Rossiter, Wiley–Interscience, New York, 1972.

[8] G. Devoto, *Gazzetta*, 1933, **63**, 495.

[9] R. Davis, H. S. Bridge, and W. J. Svirbely, *J. Amer. Chem. Soc.*, 1943, **65**, 857.

[10] M. E. Hobbs and W. W. Bates, *J. Amer. Chem. Soc.*, 1951, **73**, 2751.

[11] M. E. Hobbs and W. W. Bates, *J. Amer. Chem. Soc.*, 1952, **74**, 746.

[12] G. K. Estok and S. P. Sood, *J. Phys. Chem.*, 1957, **61**, 1445.

[13] W. P. Purcell and J. A. Singer, *J. Phys. Chem.*, 1967, **71**, 4316.

[14] G. K. Estok, S. P. Sood, and C. H. Stembridge, *J. Phys. Chem.*, 1958, **62**, 1464.

[15] M. J. Aroney, *Angew. Chem. Internat. Edn.*, 1977, **16**, 663.

[16] M. J. Aroney, G. Cleaver, R. K. Pierens, and R. J. W. Le Fèvre, *J.C.S. Perkin II*, 1974, 3.

[17] C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1953, 4041.

[18] C. G. Le Fèvre and R. J. W. Le Fèvre, *Austral. J. Chem.*, 1954, **7**, 33.

[19] K. E. Calderbank and R. K. Pierens, *J.C.S. Perkin II*, 1972, 293.

[20] C. L. Cheng, I. G. John, G. L. D. Ritchie, and P. H. Gore, *J.C.S. Perkin II*, 1974, 1318.

[21] R. J. W. Le Fèvre and L. Radom, *J. Chem. Soc.* (*B*), 1967, 1295.

[22] P. H. Gore, J. A. Hoskins, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1969, 485.

[23] C. L. Cheng, P. A. Goodman, P. H. Gore, R. J. W. Le Fèvre, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1971, 1198.

[24] R. J. W. Le Fèvre and B. P. Rao, *J. Chem. Soc.*, 1958, 1465.

[25] K. E. Calderbank, R. J. W. Le Fèvre, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1968, 503.

[26] C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1954, 1577.