[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Electric Moments, Association and Structure of Some N-Monosubstituted Amides[1a]

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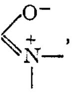
The electric moments of N-ethyl, N-β-chloroethyl, N-phenyl and N-*p*-chlorophenylbenzamide and of N-ethyl, N-phenyl, N-*p*-chlorophenyl and N-β-(*p*-chlorobenzoxy)-ethyl-*p*-chlorobenzamide were determined in dilute benzene solution. The results of the measurements when compared to calculated moments indicate that the amide group is planar and that the remaining N–H bond of the N-monosubstituted amides is *trans* to the carbonyl group. The data indicated that the N-monosubstituted amides associate to form linear complexes in contrast to the ring complexes formed by the unsubstituted amides. A large contribution to the ground state of the amide group from the highly polar resonance form,  $-\mathrm{C}\begin{smallmatrix}\diagup\mathrm{O}^-\\ \diagdown\!\!\diagdown\overset{+}{\mathrm{N}}-\\ |\end{smallmatrix}$, appears to be inconsistent with the electric moment values obtained.

Introduction

In a previous paper[2] the electric moments of a series of unsubstituted acid amides were reported. It was found that the observed electric moments were consistent with those calculated by simple vector addition of the component bond moments for the planar configuration of the amide group deduced from the crystal structure[3] of acetamide. The planar structure of the amide group is also consistent with the calculations carried out by Richards[4] in connection with observations of the infrared absorption spectra of a number of amides. The present paper deals with the electric moments of a number of N-monosubstituted amides as determined in dilute benzene solutions and it is shown that the results are consistent with the bond moment vector addition principles used for the unsubstituted amides.[2] The preferred orientation of the remaining N–H bond and the type of association of the N-monosubstituted amides are discussed.

Experimental

Benzene.—Thiophene-free reagent grade benzene obtained from the Jones and Laughlin Steel Company was refluxed over sodium wire and distilled through a 180-cm. Dufton column immediately before use. The middle fraction, distilling over a range of 0.015° or less, was collected with precautions to exclude atmospheric moisture; b.p. (cor.), 80.083 ± 0.015°, d^{30}_4 0.86814 ± 0.00002 g./ml.

N-Ethylbenzamide.—This compound was prepared by the Schotten–Baumann reaction from Eastman Kodak Co. white label ethylamine and benzoyl chloride. After four recrystallizations with cyclohexane the material was dried in a vacuum oven for 10 hours; f.p. 69.35 ± 0.05°, m.p. (capillary) 71.5°.

Benzanilide.—Eastman Kodak Co. white label product was extracted with 70–90° ligroin in a Soxhlet extractor. The recrystallized benzanilide was then oven dried overnight at 120°; f.p. 160.84 ± 0.05°, m.p. (capillary) 163.4–164.0°.

N-Ethyl-*p*-chlorobenzamide.—This material, furnished by the University of Illinois, was dissolved in chloroform, washed with 10% solutions of NaOH, HCl and Na_2CO_3, precipitated by addition of ligroin and then recrystallized three times from cyclohexane. The product was then oven dried at 90° and stored in a vacuum desiccator; f.p. 109.18 ± 0.05°, m.p. (capillary) 110.5–110.9°.

N-β-Chloroethylbenzamide.—This compound was prepared by the Schotten–Baumann reaction from benzoyl chloride and β-chloroethylamine, the latter having been prepared by chlorination of 2-ethanolamine with thionyl chloride. The amide was extracted with 70–90° ligroin in a Soxhlet extractor and the recrystallized product dried overnight in a vacuum oven. *Anal.* Calcd. Cl, 19.31, found 19.15; f.p. 103.01 ± 0.05°, m.p. (capillary) 106.7–107.1°.

N-Phenyl-*p*-chlorobenzamide, N-*p*-Chlorophenylbenzamide and N-*p*-Chlorophenyl-*p*-chlorobenzamide.—All of these substances were prepared by the Schotten–Baumann reaction using the appropriate amine and benzoyl chloride. Purification was effected by extraction with benzene in a Soxhlet extractor, recrystallization and drying in a vacuum oven. N-Phenyl-*p*-chlorobenzamide: *Anal.* Calcd. Cl, 15.31, found 15.18; f.p. 196.31 ± 0.05°, m.p. (capillary) 196.6–197.2°. N-*p*-Chlorophenylbenzamide: f.p. 189.81 ± 0.05°, m.p. 192.2–192.4°. N-*p*-Chlorophenyl-*p*-chlorobenzamide: *Anal.* Calcd. Cl, 26.65, found 26.74; f.p. 209.53 ± 0.05°, m.p. 212.5–213.2°.

N-β-(*p*-Chlorobenzoxy)-ethyl-*p*-chlorobenzamide.—In an attempt to prepare N-β-chloroethyl-*p*-chlorobenzamide repeated preparations gave a product with a f.p. of 140.4° having a chlorine analysis of 20.6 and a molecular weight greater than 300 as determined by freezing point depression measurements. The compound $ClC_6H_4CONH-C_2H_4-OCOC_6H_4Cl$ has a calculated chlorine content of 20.97% and a molecular weight of 338.2 and was suggested to us by Professor C. K. Bradsher as a possible product of the reaction mixtures involved. The compound obtained in the preparations was not definitively identified as N-β-(*p*-chlorobenzoxy)-ethyl-*p*-chlorobenzamide but the analysis and, as will be indicated later, the electric moment of the prepared material is consistent with the proposed structure; f.p. 140.42 ± 0.05°, m.p. (capillary) 144.6–145.2°.

All solutes were stored in desiccators until used. The m.p. reported above were obtained using capillaries and a Hershberg device. The freezing points were determined from cooling curves using calibrated thermometers. The uncertainty of ±0.05° given for the freezing points is estimated from probable calibration errors and the reproducibility of the freezing temperatures. One new compound, N-*p*-chlorophenyl-*p*-chlorobenzamide, is reported and another partially identified is recorded.

The procedure and equipment used in making the necessary measurements have been described previously.[5,6]

Results

The molar polarization of the solute at infinite dilution was calculated from the Hedestrand equation[7] given below.

$$P_{2\infty} = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{1}{d_1}\left[M_2 - \frac{M_1}{d_1}\frac{\Delta d}{f_2}\right] + \frac{3M_1}{(\epsilon_1 + 2)^2} \cdot \frac{1}{d_1}\left(\frac{\Delta\epsilon}{f_2}\right)_\infty$$

Here $P_{2\infty}$ is the molar polarization of the solute at infinite dilution, ϵ is the dielectric constant, M is the molecular weight, d the density and f the

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(1) (a) Taken in part from a thesis submitted by James E. Worsham, Jr., in partial fulfillment of the requirements for the Ph.D. degree in Chemistry at Duke University. (b) Monsanto Chemical Company Fellow, Duke University, 1952–1953.

(2) W. W. Bates and M. E. Hobbs, THIS JOURNAL, **73**, 2151 (1951).

(3) F. Senti and D. Harker, *ibid.*, **62**, 2008 (1940).

(4) R. E. Richards, *Trans. Faraday Soc.*, **44**, 40 (1948).

(5) A. J. Weith, Jr., M. E. Hobbs and P. M. Gross, THIS JOURNAL, **70**, 805 (1948).

(6) A. A. Maryott, M. E. Hobbs and P. M. Gross, *ibid.*, **62**, 2320 (1940).

(7) G. Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

mole fraction. The subscripts 1 and 2 refer to the solvent and solute, respectively, and Δd and $\Delta\epsilon$ are the differences in density and dielectric constant of the solution and the solvent. The value of $\Delta d/f_2$ was taken as the average of the measured values for the several solutions of a particular solute while $(\Delta\epsilon/f_2)_\infty$ was taken as the intercept of the graph of $\Delta\epsilon/f_2$ *vs.* f_2 at $f_2 = 0$. The data are shown graphically in Fig. 1. All graphs of $\Delta\epsilon$ *vs.* f_2 had zero–zero intercepts within the experimental error of the measurements.

The electric moments, μ_D, expressed in debye units were calculated from the relation

$$\mu_D = 0.2231\,(P_{2\infty} - R_D)^{1/2}$$

where R_D is the molar refraction for the sodium D lines as obtained from the refraction equivalents for the atoms involved. The data and results are summarized in Table I in which the listed values of μ_D are estimated to be in error by about 1.5% or less. All results are for measurements carried out at 30.00 ± 0.02°.

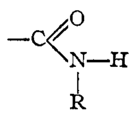
TABLE I

SUMMARY OF DATA AND RESULTS

Substances, benzamide	$(\Delta\epsilon/f_2)_\infty$	$(\Delta d/f_2)_{av}$	R_D	$P_{2\infty}$	μ_D
N-Ethyl-	18.2	0.36 ± 0.01	43.6	304	3.60
N-Ethyl-*p*-chloro-	16.8	.73 ± .07	48.4	284	3.42
N-β-Chloroethyl-	13.1	.59 ± .01	48.4	186	3.04
Benzanilide	17.6	.67 ± .02	58.4	302	3.38
N-Phenyl-*p*-chloro-	15.3	1.1 ± .1	63.3	264	3.17
N-*p*-Chlorophenyl-	27.3	1.06 ± .01	63.3	443	4.35
N-*p*-Chlorophenyl-*p*-chloro-	15.9	1.3 ± .1	68.2	282	3.26
N-β-(*p*-Chlorobenzoxy)-ethyl-*p*-chloro-	16.2	1.43 ± .01	83.7	299	3.28

Discussion

Since it has been shown[2] that the observed electric moments of the unsubstituted amides were, without recourse to a highly polar resonance form, consistent with the simple vector addition of the component bond moments of the planar structure found by Senti and Harker,[3] it seems desirable to extend such considerations to the N-monosubstituted benzamides reported here. With angles of approximately 120° in the assumed planar structure of the amido group three possibilities are apparent: (1) the N–H bond is *cis* to the carbonyl bond I, (2) the N–H bond is *trans* to the carbonyl bond II and (3) there is free rotation about the carbon–nitrogen bond.



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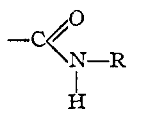

II

Moments were calculated for the N–H *cis* and *trans* configurations for each of the substances studied by vector addition of the component bond moments using the structure and angles found by Senti and Harker.[3] The bond moments, expressed in debyes, used in the calculation were: C=O, 2.4; C–H, 0.4; C–N, 0.4; φ-Cl, 1.5; N–H, 1.3, C–O, 0.7. The results of the calculation are compared with the observed values in Table II. Free rotation about the C–N bond gives values intermediate between the *cis* and *trans* configurations. It is apparent that the calculated values for the N–H *trans*, case II, are generally in good agreement with the observed values. The excellent correspondence in some cases is certainly somewhat fortuitous. A recently reported[8] infrared absorption investigation on some simple and substituted amides corroborates the findings of the *trans* configuration for the N-monosubstituted structure. The reason for the preference of the *trans* configuration is not clear but the evidence seems rather unambiguous.

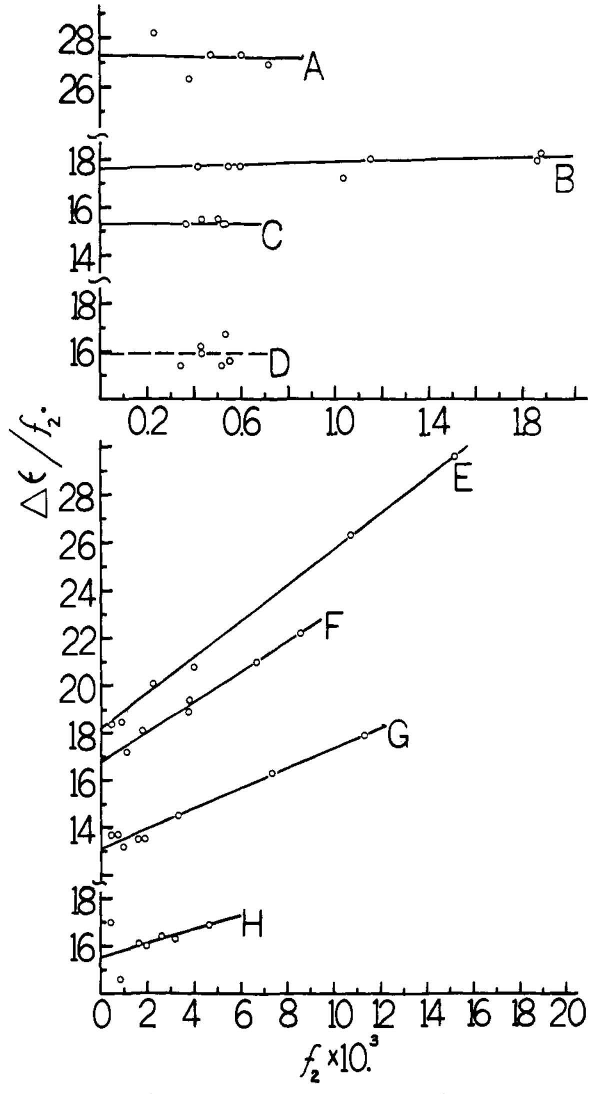

Fig. 1.—Ratio of the increment in dielectric constant, $\Delta\epsilon$, to mole fraction, f_2, as a function of f_2 for several N-monosubstituted amides in benzene solution: A, N-*p*-chlorophenylbenzamide; B, benzanilide; C, N-phenyl-*p*-chlorobenzamide; D, N-*p*-chlorophenyl-*p*-chlorobenzamide; E, N-ethylbenzamide; F, N-ethyl-*p*-chlorobenzamide; G, N-β-chloroethylbenzamide; H, N-β-(*p*-chlorobenzoxy)-ethyl-*p*-chlorobenzamide.

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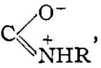
[8] R. M. Badger and H. Rubalcava, *Science*, **117**, 465 (1953); also private communication.

TABLE II

CALCULATED AND OBSERVED ELECTRIC MOMENTS IN DEBYE UNITS

Substance, benzamide	N–H *cis*	N–H *trans*	Observed
N-Ethyl-	1.8	3.6	3.60
N-Ethyl-*p*-chloro-	2.2	3.2	3.42
N-*β*-Chloroethyl-	2.1	3.3	3.04
Benzanilide	2.1	3.3	3.38
N-Phenyl-*p*-chloro-	2.6	2.8	3.17
N-*p*-Chlorophenyl-	0.8	4.3	4.35
N-*p*-Chlorophenyl-*p*-chloro-	2.3	3.3	3.26
N-*β*-(*p*-Chlorobenzoxy)-ethyl-*p*-chloro-	4.0	3.3	3.28

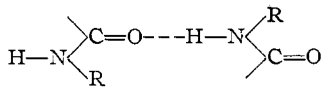
In the case of N-*β*-(*p*-chlorobenzoxy)-ethyl-*p*-chlorobenzamide the structure used in the calculation of the moment assumes a configuration involving an internal hydrogen bonding between the carbonyl oxygen of the *p*-chlorobenzoxy group and the amido hydrogen. This possibility was suggested by use of Fisher–Hirschfelder models.

It may be noted that contributions of the order of 30–40% from the highly polar form,  $—C\genfrac{}{}{0pt}{}{\diagup O^-}{\diagdown\!\!\diagdown \overset{+}{N}HR}$, as has been suggested[9] in other connections, would lead to calculated moments much larger than those observed. In view of this, it appears that here, as in the case of the unsubstituted amides, contributions from this structure to the ground state of the amide group are small, absent or compensated. Recently Nagakura[10] has given a molecular orbital treatment of the amide group and finds π moments considerably in excess of the observed values.

It is of interest in connection with this discussion of the planarity of the amide group and of the *trans* configuration of the remaining N–H in the N-monosubstituted amides that Carpenter and Donahue[11] found that planar structure and *trans* configuration for this group in the crystal of acetylglycine. Also Pauling, Corey and Branson[12] have postulated the *trans* configuration in their model of the associated peptide chains.

The possibility of accounting for the planar structure of amides in terms of sp^2 hybrid bonding orbitals in the nitrogen of the amide group is apparent from the geometry of such orbitals. Richards[4] has considered this hybridization problem in some detail in order to explain the observed[13] force constants for the N–H stretching vibration in amide structures. The calculated and observed force constants are brought into reasonable agreement by the assumption of increased s character of the nitrogen bonding orbitals in the amides as compared to ammonia. The increased overlap[14,15] in the sp^2 orbitals over that for pure *p* orbitals would probably account in large measure for the decreased C–N distance[9] in the amides as compared to the sum of the covalent radii and in addition would make the very small increase, ~0.02 Å., in the carbon–oxygen distance in the amides somewhat more understandable than does the postulate of large contributions from the highly polar resonance form.

Figure 1 shows that, for those substances which could be studied above 1×10^{-3} mole fraction, the value of $\Delta\epsilon/f_2$ increases with concentration. The precision of the measuring apparatus was such that the limited solubility of several of the substances prohibited determination of trends in $\Delta\epsilon/f_2$ being established in the range of concentration accessible to measurement. The increase of $\Delta\epsilon/f_2$ with f_2 corresponds to an increase of total polarization with concentration and is taken to indicate that the solute molecules are associating in such a fashion that the electric moment of the associated complex, or complexes, is greater than that of the monomer. This situation is to be expected if the N–H bond is *trans* to the carbonyl group and the associated complex can probably be represented somewhat as shown in the diagram below.



Examination of a model in which the N–H bond is *cis* to the carbonyl group reveals that the molecules, in the initial stages of complexing, would likely associate into a ring with two hydrogen bonds per ring such as is found[8,16] for the unsubstituted amides. Such an association would lead to an observed decrease in total polarization with increasing concentration[17–20] and this was not observed in the present series of measurements. Thus the inference from the association seems again to confirm the *trans* configuration.

In an attempt to further establish the structure of the amide group a limited series of measurements of Kerr constants of some of the N-monosubstituted amides in benzene were carried out. Because of low solubility and limited precision of the apparatus available only a few cases could be studied satisfactorily. The results obtained are more consistent with the *trans* than with the *cis* configuration.

It is of interest to note that by using methods previously employed[2] it was found that the simple aliphatic or aromatic N-monosubstituted amide group moment makes an angle of approximately 70° with the phenyl carbon–carbonyl carbon axis and this is in good agreement with the angle of 69° found for the unsubstituted amide group moment. It thus appears that aliphatic or aromatic substitution of the amido group has no large effect on either the magnitude or direction of the amide group moment.

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[9] L. Pauling, "The Nature of the Chemical Bond," 2nd edition, Cornell University Press, Ithaca, N. Y., 1945, p. 127.

[10] S. Nagakura, *Bull. Chem. Soc. Japan*, **25**, 164 (1952).

[11] G. B. Carpenter and J. Donahue, THIS JOURNAL, **72**, 2899 (1950).

[12] L. Pauling, R. B. Corey and H. R. Branson, *Proc. Natl. Acad. Sci. U. S.*, **37**, 205 (1951).

[13] R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1248 (1947).

[14] A. Maccoll, *Trans. Faraday Soc.*, **46**, 369 (1950).

[15] C. A. Coulson, "Valence," Oxford University Press, Oxford, 1952, p. 198.

[16] M. E. Hobbs and W. W. Bates, THIS JOURNAL, **74**, 746 (1952).

[17] G. R. Leader and J. F. Gormley, *ibid.*, **73**, 5731 (1951).

[18] M. Tsuboi, *Bull. Chem. Soc. Japan*, **22**, 215 (1949).

[19] S. Nagakura and A. Kubayama, *Reports Tokyo Inst. Sci. Technol.*, **5**, 27 (1951).

[20] H. A. Pohl, M. E. Hobbs and P. M. Gross, *Ann. N. Y. Acad. Sci.*, **40**, 389 (1940).