TABLE V

ERROR IN VISCOSITY DUE TO IMPURITIES

Compound	Assumed impurity, %	Δm	t, °C.	Error in η, %
Heptadecane	0.2 $C_{15}H_{32}$	−0.06	22	−0.04
Octacosane	5 $C_{24}H_{50}$	−2.8	62	−1.0
Hexatriacontane	5 $C_{32}H_{66}$	−2.8	100	−0.7
Tetrahexacontane	10 $C_{60}H_{122}$	−5.6	110	−0.9

The maximum probable error in each viscosity measurement (listed in Table III under "Accuracy, %") was calculated on the basis of the foregoing considerations, and it is felt almost certain that the correct values lie within the region of the assigned error. It should be noted that the assigned error values are many times the degree of precision (reproducibility) obtainable with the apparatus. In several cases values were redetermined later using repurified samples and measuring the temperatures with the standard platinum resistance thermometer. The new values in these cases checked the original ones to ±0.1–0.2%.

A discussion of the results of these measurements will be published elsewhere.

S. CHARLESTON 3, W. VA. RECEIVED SEPTEMBER 15, 1950

[CONTRIBUTION FROM CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

The Dipole Moments of Some Acid Amides and the Structure of the Amide Group[1]

BY W. W. BATES[2] AND MARCUS E. HOBBS

The structure, association and direction of the group moment of acid amides have been studied by means of dipole moment measurements on a series of aliphatic and aromatic amides in dilute benzene and dioxane solutions. The group moment is found to be directed at an angle of about 70° to the C–C axis in the aromatic compounds. Association of amide molecules is found to occur in quite dilute benzene solutions and seems to be influenced quite significantly by the nature of the hydrocarbon fraction of the molecule. The structure of the amide group, as determined from dipole moment measurements, seems consistent with the keto form and does not require significant contributions from the highly polar resonance form usually associated with this group.

A knowledge of the details of the structure of the amide group is of considerable importance because of the role this group plays in many physiologically active compounds and in fibers. The information that might be made available on this problem through the measurement of the dipole moments of the amides has been limited to only a few studies.[3] In view of this the systematic investigation of the dipole moments of a series of quite pure aliphatic and aromatic acid amides was undertaken in the attempt (1) to establish the magnitude and direction of the amide group moment, (2) to study the relation of association of the amides in dilute solutions to the geometry of the molecule and (3) to furnish data for a critical examination of the possible relations between the electric moment values and the structure of the amide group. The particular compounds investigated in dilute benzene and dilute dioxane solutions were formamide, acetamide, propionamide, *n*-butyramide, isobutyramide, benzamide, *m*- and *p*-chlorobenzamide and *m*- and *p*-bromobenzamide. In addition approximate values of the dipole moments of oxamide and malonamide were determined from measurements in very dilute dioxane solutions.

Experimental

Materials and Methods.—Jones and Laughlin reagent grade benzene was dried over sodium wire for several days, refluxed over fresh sodium wire and finally distilled from fresh sodium through a 180 cm. Dufton column. The middle fraction was then redistilled in the same manner before use. Some benzene was recovered from measurements and used again. The recovery consisted in a simple distillation, followed by refluxing with 20% potassium hydroxide solution, drying with potassium hydroxide and finally refluxing over sodium wire. Two subsequent distillations over sodium yielded a product indistinguishable, by means of the dielectric constant, from the best benzene. The average b.p. and density of all benzene used is given in Table I. The benzene used in a particular measurement boiled over an average range 0.01°. The dioxane used was obtained from the Carbide and Carbon Chemical Corp. The purification procedure followed was storage over pellets of potassium hydroxide for several weeks, followed by siphoning off of the clear liquid. Three liters of this product was then mixed with 300 ml. of 1.0 *N* sulfuric acid and refluxed 12 hours with air bubbling through the liquid. The product so obtained was distilled from potassium hydroxide pellets and then refluxed with fresh sodium wire until the sodium remained bright. This refluxing was followed by distillation from sodium wire through a 180 cm. Dufton column. The middle fraction was stored and distilled over sodium just prior to use. Dioxane was recovered from measurements by refluxing over sodium until corrosion ceased, then carrying out a simple distillation. This recovered product was then treated in the same manner as the middle fractions of the originally purified material. Physical constants for the average of all samples of dioxane used are given in Table I. The average range in boiling point of any particular sample of dioxane used in a measurement was 0.03°.

The freezing points of all solutes are collected in Table I along with literature reference values. The freezing points were determined with calibrated thermometers by the cooling curve method and generally were constant for one-half frozen to better than 0.02°, or the product was further purified. The temperature limits shown in Table I are an estimate of the accuracy of the freezing temperature. When fractional freezing was used in the purifications, procedures, apparatus and technique similar to those of the cylindrical tube method of Schwab and Wichers[4] were employed.

Formamide.—Eastman Kodak Co. best grade of formamide was dried over anhydrous sodium sulfate and then vacuum distilled. The middle fraction from the distillation was then fractionally crystallized three times in the absence of moisture. Essentially one-half of the product was discarded in each crystallization.

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[1] Part of the thesis of W. W. Bates submitted in partial fulfillment of the requirements of the Ph.D. degree in chemistry at Duke University.

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[3] (a) C. T. Zahn, *Physik. Z.*, **33**, 515 (1933); (b) G. Devoto, *Gazz. chim. ital.*, **63**, 495 (1933); (c) Kumler and Porter, THIS JOURNAL, **56**, 2549 (1934); (d) Davis, Bridge and Svirbely, *ibid.*, **65**, 857 (1943).

[4] Schwab and Wichers, *J. Research Natl. Bur. Standards*, **32**, 253 (1944).

TABLE I

THE PHYSICAL CONSTANTS OF THE SOLVENTS AND SOLUTES

	Present investigation			Literature		
Solvents	B.p., °C.	Density, g./ml. 30.00°	Dielectric contant 30,00°	B.p., °C.	Density, g./ml. 30.00°	Ref.
Benzene	80.053 ± 0.017	0.86829 ± 0.00002	2.2629[a] ± 0.0003	80.094	0.86818 .86835 .86844	b,c,d,e
Dioxane	101.357 ± 0.014	1.02181 ± 0.00015	2.0005 ± 0.0005	101.320	1.02212 1.02179	b,f,g

Solutes	Freezing point, °C.	Melting point, °C.	Reference
Formamide	2.50 ± 0.06	2.55	i
Acetamide	80.16 ± 0.06	81.5; 80.0–80.1	j,k
Propionamide	80.94 ± 0.06	81.3; 79.5	j,l
n-Butyramide	114.96 ± 0.06	114.8–115.0	j
Isobutyramide	128.35 ± 0.06	127.5	h
Benzamide	127.22 ± 0.06	130	g
m-Chlorobenzamide	134.00 ± 0.06	134.5	n
p-Chlorobenzamide	178.55 ± 0.06	178.3	o
m-Bromobenzamide	156.40 ± 0.06	155.3	o
p-Bromobenzamide	191.80 ± 0.06	189.5	o
Malonamide (m.p.)	169.0–169.5	170	p

[a] This value is the average of the measured value of ϵ using an original calibration with benzene for which the value of ϵ at 30.0° was taken at 2.2628 from the work of Hartshorn and Oliver, *Proc. Roy. Soc.* (*London*), **A123**, 664 (1929). [b] E. L. Lind, M.A. Thesis, Duke University (1948). [c] M. Wojciechowski, *J. Research Natl. Bur. Standards*, **19**, 347 (1937). [d] Pohl, Hobbs and Gross, *Ann. N. Y. Acad. Sci.*, **40**, 389 (1940). [e] Timmermans and Martin, *J. chim. phys.*, **23**, 733 (1926). [f] Smith and Wojciechowski, *J. Research Natl. Bur. Standards*, **18**, 461 (1937). [g] Davis, Bridge and Svirbely, THIS JOURNAL, **65**, 857 (1943). [h] Meldrum and Turner, *J. Chem. Soc.*, **97**, 1605 (1910). [i] G. F. Smith, *ibid.*, 3257 (1910). [j] Mitchell and Reid, THIS JOURNAL, **53**, 1879 (1931). [k] Kumler and Porter, *ibid.*, **56**, 2549 (1934). [l] Taylor and Davis, *J. Phys. Chem.*, **32**, 1469 (1928). [n] M. P. J. Montagne, *Rec. trav. chim.*, **19**, 59 (1900). [o] Remsen and Reid, *Am. Chem. J.*, **21**, 299 (1899). Kahovec and Wagner, *Z. physik. Chem.*, **B49**, 156 (1941).

Acetamide.—Merck and Co., Inc., reagent grade acetamide was recrystallized from methyl acetate, an equal volume mixture of ethyl acetate and benzene and finally from benzene. This product was then sublimed and stored over phosphorus pentoxide for two weeks. The very dry product was found rather difficult to transfer for weighings because of the accumulation of considerable charge on the substance.

Propionamide, *n*-Butyramide and Isobutyramide.—Eastman Kodak Co. best grade products were recrystallized three times from acetone, once from benzene and were then dried in a vacuum desiccator containing 99% sulfuric acid.

Benzamide.—Merck and Co., Inc., reagent grade product was recrystallized from dilute aqueous ammonia, water, acetone and then from benzene by using a soxhlet extractor. All of the aromatic amides were recrystallized from benzene by using about 200 cc. of refluxing benzene in a soxhlet extractor with the sample in a fresh thimble. The extractions were run for 6–24 hours depending on the solubility of the amide. The final recrystallization from a non-polar solvent was considered quite desirable in view of the projected end use of the products in dielectric measurements. The benzamide from the benzene recrystallization was ground in an agate mortar, dried in an oven at 110° for 8 hours and stored in a desiccator over 99% sulfuric acid.

***m*-Chlorobenzamide.**—Eastman Kodak Co. best grade of *m*-chlorobenzoic acid was converted to the acid chloride by thionyl chloride and this reaction mixture poured into cold (approximately 0°) concentrated aqueous ammonia to prepare the amide. The amide thus prepared was recrystallized from methyl alcohol, two times from benzene, once from acetone and finally once again from benzene. This recrystallized product was subjected to a slow fractional freezing in which approximately one-third of the product was discarded.

***m*-Bromobenzamide.**—Eastman Kodak Co. best grade of *m*-bromobenzoyl bromide was converted to the amide by treatment with cold concentrated aqueous ammonia solution. The amide was then recrystallized twice from acetone, once from benzene and was further purified by a slow fractional freezing in which approximately one-half of the compound was discarded.

***p*-Bromobenzamide.**—Eastman Kodak Co. best grade of *p*-bromobenzoic acid was converted to the acid chloride with thionyl chloride and the reaction product converted to the amide by pouring the reaction mixture into cold concentrated aqueous ammonia solution. The amide was then recrystallized twice from methyl alcohol, once from acetone, once from benzene and finally subjected to a fractional freezing in which approximately one-third of the product was discarded. An odor (nitrile like) developed in the material during the fractional freezing so the product from the fractional freezing was recrystallized from purified benzene. The odor was thus eliminated, presumably by removal of the decomposition product that was formed during the long heating period involved in the fractional freezing process.

Oxamide.—Eastman Kodak Co. best grade product was recrystallized three times from water, ground in an agate mortar and dried in an oven at 150° before being stored in a desiccator.

Malonamide.—Eastman Kodak Co. best grade product was recrystallized twice from water, ground in an agate mortar and stored in a desiccator over 99% sulfuric acid.

The oscillator equipment has been described elsewhere[5] as have the liquid measuring cell and procedure for carrying out the measurements.[6] In the present work precautions were taken to minimize contact between the compounds used and moisture of the atmosphere by making transfers in a dry-box.[7]

The limited solubility of all the amides in benzene and of the aromatic and diamides in dioxane restricted the concentration range examined. The precision of the measuring equipment was satisfactory for all compounds except the oxamide and malonamide. In these cases the dielectric constant data was of such uncertainty as to yield only approximate values of the dipole moments.

Data.—The data are presented in abbreviated form in Table II. The symbols have the following meaning: R_D is the molar refraction of the solute obtained by addition of the atomic refractions for the D lines of sodium, $\Delta\epsilon$ is the increment of the dielectric constant of the solution over that of the solvent, f_2 is the mole fraction of the solute, Δd is the difference in density of the solution and solvent, $P_{2\infty}$ is the molar polarization of the solute at infinite dilution calculated by the Hedestrand[8] equation and μ_D is the dipole moment in debyes obtained from $\mu_D = 0.2231\sqrt{P_{2\infty} - R_D}$.

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(5) Weith, Hobbs and Gross, THIS JOURNAL, **70**, 805 (1948).

(6) Maryott, Hobbs and Gross, *ibid.*, **62**, 2320 (1940).

(7) See Table 1, reference *d*.

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

TABLE II

DATA FROM MEASUREMENTS (30.0°)

Substance	Solvent	R_D	$\Delta\epsilon/f_2$	$\Delta d/f_2$	$P_{2\infty}$	μ_D
Formamide	Benzene	10.3	15.3	0.132	238	3.37
	Dioxane		20.5 ± 0.1	.064	310	3.86[a]
Acetamide	Benzene	14.9	15.9	.124	253	3.44
	Dioxane		20.93 ± 0.03	.030	322.2	3.90[b,c]
Propionamide	Benzene	19.5	14.5	.102	237	3.30
	Dioxane		20.22 ± 0.02	− .015	317.1	3.85
n-Butyramide	Benzene	24.1	16.5	.149	268	3.48
	Dioxane		20.40 ± 0.05	− .052	324.7	3.86
Isobutyramide	Benzene	24.1	16.0	.072	266	3.46
	Dioxane		20.51 ± 0.05	− .066	326.7	3.88
Benzamide	Benzene	34.2	18.3	.391	301	3.65
	Dioxane		20.6 ± 0.1	.217	330	3.84[b,d]
m-Chlorobenzamide	Benzene	39.1	18.2	.603	305	3.64
	Dioxane		18.8 ± 0.2	.446	308	3.67
p-Chlorobenzamide	Benzene	39.1	15.9	.663	269	3.38
	Dioxane		19.5 ± 0.1	.462	318	3.73
m-Bromobenzamide	Benzene	42.0	15.9	1.095	274	3.40
	Dioxane		18.9 ± 0.1	0.926	311	3.66
p-Bromobenzamide	Benzene	42.0	14.1	1.11	243	3.16
	Dioxane		19.5 ± 0.2	0.927	320	3.68
Oxamide	Dioxane	18.3	29	1	1800	9
Malonamide	Dioxane	22.9	17.4 ± 0.4	0.21	280	3.5

[a] C. T. Zahn, *Physik. Z.*, **33**, 515 (1932), gives 3.22 for the gas value. [b] G. Devoto, *Gazz. chim. ital.*, **63**, 495 (1933), reports 3.6 for each of these compounds. [c] Kumler and Porter, THIS JOURNAL, **56**, 2549 (1934), give 3.72. [d] Davis, Bridge and Svirbely, *ibid.*, **65**, 857 (1943), report 3.72 but recalculation of their data using the Hedestrand equation gives 3.86.

The average error of the value of $\Delta\epsilon/f_2$ for the dioxane solutions is shown as the uncertainty for this value. The special nature of the value of $\Delta\epsilon/f_2$ for benzene solutions recorded in Table II is considered in the first paragraphs of the **Discussion**. Generally the uncertainty in $\Delta d/f_2$ was about 1% or less when three significant figures are given and about 2% or greater when two significant figures are shown. The mole fractions used in the measurements ranged from 2×10^{-4} to 2×10^{-2}, the lower limit being reached only with the most insoluble compounds.

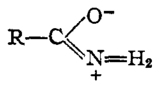
Discussion

The electric moment values given in Table II for benzene as a solvent are rather uncertain because of association of the amides. The values were obtained by taking the slope of the $\Delta\epsilon$ *vs.* f_2 curve at such a low value of f_2 that the plot was essentially linear in that region. Using these values of the slope in the Hedestrand equation gave the values of μ_D as recorded. The values of the moments obtained using dioxane as a solvent are quite well determined as is shown by the low dispersion in values of $\Delta\epsilon/f_2$ for this solvent. A consideration of the results for the dioxane solutions shows that, except for oxamide and malonamide, the error should be less than 2% and the precision better than 1%.

The deviation between Kumler and Porter's value for acetamide and ours led us to attempt a re-evaluation of the moment from their data. The three solutions from which Kumler and Porter obtained the moment value scattered so widely that no satisfactory graph of $\Delta\epsilon$ *vs.* f_2 could be drawn. In view of this we do not regard the disagreement as serious and accept our value of 3.90 as the more correct one. The graph of Davis, Bridge and Svirbely's data on a $\Delta\epsilon$ *vs.* f_2 plot for benzamide gave a straight line with a negative extrapolated intercept on the $\Delta\epsilon$ axis. Their method of calculation would lead to a low value of the moment since they used values of P_2 calculated at each concentration and then extrapolated to zero mole fraction to obtain a value of $P_{2\infty}$. As noted in Table II we obtain excellent agreement with our value for benzamide when their data are calculated from the slope of the $\Delta\epsilon$ *vs.* f_2 plot. It seems that Devoto's values for both acetamide and benzamide are low. Zahn's value of 3.22 debyes for formamide in the gas state indicates that, even in benzene, the amide shows a positive solvent effect and in dioxane the effect is quite large. This point will be considered later in some detail.

The compounds oxamide and malonamide were of such low solubility that only approximate values of μ_D could be obtained with the equipment at hand. The data do indicate that the moments in the two acid amide groups of oxamide are probably parallel or nearly so and that they are at some intermediate configuration for malonamide. The substances succinamide, glutaramide and adipamide were investigated but were of such low solubility in dioxane, as well as in benzene, that no satisfactory data could be obtained.

The rather large value of about 3.4 debyes for the amide group moment has usually been considered[9] as arising from large contributions (est. 30–40%) from the highly polar resonance form, *viz.*



$$R{-}C\begin{matrix}\diagup O^- \\ \diagdown \overset{+}{N}{=}H_2\end{matrix}$$

It is of some interest to investigate how necessary the above resonance form is to an understanding of the magnitude of the moment.

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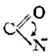
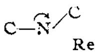
(9) (a) Reference 3c; (b) L. Pauling, "The Nature of the Chemical Bond," 2nd edition, Cornell University Press, Ithaca, N. Y., 1945, p. 127.

Recent infrared[10] and X-ray[11] data seem to point quite clearly to the existence of the amide group in the keto form, *viz.*, $RCONH_2$, rather than in a tautomeric equilibrium with the enolic form. By considering only this form one can readily calculate an expected moment for the amide group from a proper vectorial addition of the component bond moments. The angular and distance relations within the amide group as taken from the literature are summarized in Table III.

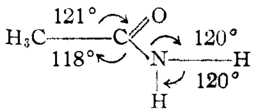
TABLE III

BOND DISTANCES AND ANGLES

Compound	C=O, Å.	C–N, Å.			Ref.
Acetamide	1.28	1.38	122°	..	[a]
N-Acetylglycine	1.24	1.32	121°	120°	[b]
Diketopiperizine	1.25	1.33	120°	120°	[c]
β-Glycylglycine	1.23	1.39(?)	125°	122°	[d]
Urea	1.25	1.37	..	..	[e]

[a] Senti and Harker, ref. 11a. [b] Carpenter and Donahue, ref. 11b. [c] R. B. Corey, THIS JOURNAL, **60**, 1598 (1938). [d] Hughes and Moore, *ibid.*, **71**, 2618 (1949). [e] Wyckoff and Corey, *Z. Krist.*, **89**, 462 (1934).

In view of the data of Table III and information from the appropriate references we have assumed a planar geometry of the acetamide molecule with angles

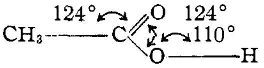


The bond moments used to calculate a resultant moment have been taken as 2.4, 0.4, 1.3 and 0.4 for the C=O, C–N, N–H and $C–CH_3$ bonds, respectively. With these values and the indicated geometry one calculates a resultant moment of 3.1 debyes which resultant makes an angle of 68° with the C–C axis. If we accept the value of 3.4–3.5 debyes for the gas value of this molecule it is apparent that a small intramolecular induction effect would account for the difference between the gas value and the calculated value of 3.1 debyes.

It may be noted here that the calculated electric moments of a number of substituted amides are in reasonable agreement with the values reported in the literature. The calculations were made using the geometry and bond moments set out for the acetamide case. Space does not permit the details of these calculations to be presented.

On the basis of the above calculations and the lack of necessity to call on a highly polar resonance structure to explain the magnitude of the moments it is of some interest to see if other evidence can be found which tends to support the postulate that—*either because of its absence or of contributions from a compensating polar structure, the usual polar resonance form written for the amides makes a very small or negligible contribution to the structure of the amide group.*

Significant evidence in favor of this postulate may be derived from a consideration of the electric moment values of the carboxylic acids in which substances a quite similar polar resonance form is supposed to make a considerable contribution to the ground state of the molecule. The calculated moment of acetic acid, using bond moments of 1.5, 0.9, 2.4 and 0.4 for the O–H, C–O, C=O and C–H bonds, respectively, and the geometry shown below, is 1.2 debyes with the resultant making an angle of 63° with the C–C axis. The measured value[12] in dioxane solution is 1.74 debyes and allowing for a solvent effect estimated as +0.1 we see that no large contribution from a highly polar resonance structure seems to be necessary.



The magnitude of the expected contributions from the polar resonance form is based on bond distance changes and on assigned "resonance energies." For the case of the acids and amides the resonance energies are given[13] as 28 and 21 kcal. per mole, respectively, and the relative changes of bond distances are greater[14] in the acids than in the amides. In view of this evidence it seems that the polar structure would be expected to contribute more to the acid moment than to the amide moment and, further, one would expect the polar structure to be a quite important factor in each case as both bond distances, as they are interpreted with the resonance picture, and resonance energies support this expectation. The evidence of the dipole moments speaks rather strongly against the general principles of considering resonance structures with large charge separation as important contributors to the ground states of the molecules concerned and is thus taken as supporting the previously stated postulate.

The force constants, evaluated from infrared data,[15] for the N–H bonds in amides seem to add further support to the above postulate in that only slight differences are indicated between these bonds and those in NH_3 where the nitrogen is not regarded as participating appreciably in a resonance form which gives it a positive charge. The small differences observed between the N–H in an amide and in NH_3 may be explicable in terms of the perturbation by the adjacent C=O group and even so the perturbations are quite small when compared to the differences between NH in NH_3 and in NH_4^+. This line of evidence, therefore, seems to point to the absence of a significant change in the charge distribution on the nitrogen in amides and that found in amines and ammonia and thus it seems to disfavor the supposed large contribution from the polar resonance structure in amides.

We have suggested the absence, or compensation of significant polar contributions to the amide structure by the usual polar resonance form and if such is the case the usual explanation offered[16] for the low basicity of the amido group would no

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(10) (a) Randall, Fowler, Fuson and Dangl, "Infrared Determination of Organic Structure," D. Van Nostrand Co., New York, N. Y., 1949, p. 10; (b) Richards and Thompson, *J. Chem. Soc.*, 1248 (1947).

(11) (a) Senti and Harker, THIS JOURNAL, **62**, 2008 (1940); (b) Carpenter and Donahue, *ibid.*, **72**, 2315 (1950); (c) Corey and Donahue, *ibid.*, **72**, 2899 (1950).

(12) Wilson and Wenzke, *J. Chem. Phys.*, **2**, 546 (1934).

(13) Reference 9b, p. 138.

(14) Reference 9b, pp. 202, *et seq.*

(15) W. Linnett, *Trans. Far. Soc.*, **41**, 223 (1945).

(16) Reference 9b, p. 208.

longer be applicable. It seems reasonable from qualitative considerations to suggest that the low basicity of the amido group may well be dependent on the proximity of the large carbonyl dipole, the net result of which is to establish a relative positive potential at the amido nitrogen. Resonance may play a part, of course, but it does not seem to be an essential one in this case.

The strongest evidence for the magnitude of the contribution from the polar resonance form is derived from the bond distances in that there is considerable shortening of the C–N bond and an apparent slight lengthening of the C=O bond in the amides as compared to the normal values. It seems reasonable to suggest that, in the amide and acid groups the effects on the bond lengths may originate, in part, from the increased electrostatic interaction of the bonded atoms. For instance, the nitrogen atom in simple amines is attached to carbon atoms with no great charge whereas in the amides the nitrogen atom is attached to the carbon atom which forms one end of the C=O group dipole. An entirely consistent system of accounting for bond length changes in terms of differences in electrostatic interaction is not suggested, nor is it seriously proposed as the reason for all changes. The electrostatic interaction does, however, justify mention as it seems to be neglected in present day literature. Referring to this point the resonance picture, as usually presented, has not offered, to the authors' knowledge, a reasonable explanation of the observation that the C=O bond length in acids is usually 1.19 Å., whereas in acetaldehyde it is 1.22 Å. and in the amides it is generally about 1.25 Å.

In the previous paragraphs the direction of the resultant amide group moment has been calculated as about 68° with respect to the C–C axis in acetamide when no contribution from the polar resonance form is considered. The data on benzamide, *p*-chloro- and *p*-bromobenzamides can be used to evaluate experimentally the direction of the resultant amide moment by means of the respective chlorobenzene and bromobenzene moments of 1.61 and 1.58 debyes in dioxane and of 1.58 and 1.53 debyes in benzene. The results of these calculations, using the cosine law, are given in Table IV. The angle referred to is shown below.

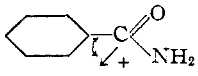

TABLE IV

Substance	Angle of resultant, degrees
p-Chlorobenzamide (benzene)	67.5
p-Bromobenzamide (benzene)	59.5
p-Chlorobenzamide (dioxane)	74.0
p-Bromobenzamide (dioxane)	73.5
Average	69

The lack of consistency in the values of the angle is, in part, caused by the uncertainty in the value of the single amide molecule moment in benzene. The good agreement between the dioxane solution values gives the angle with reasonable precision but it is undoubtedly complicated by significant solvent effects. A calculation of the expected moments of the *m*-compounds using the average angle and assuming free rotation of the amide group, or the presence of a 50–50 mixture of *cis* and *trans* molecules, leads to moment values about 0.2 debye higher than the observed ones. The reason for this discrepancy is not known but may be related to group interactions which give rise to compensating induced electric moments or to a favoring of a particular geometry of the *m*-compounds. In general, we have reason to believe, both from the experimental and calculated values, that the resultant moment of the amide group probably makes an angle of about 70° with the C–C axis. The reason for choosing the 70° in preference to 74° is set forth in the next paragraphs where solvent effects are considered.

The solvent effect on the measured values of the dipole moment of the amides have been mentioned briefly in the previous discussion. A somewhat more detailed consideration of this effect seems warranted; in particular, it is of some consequence to try to explain the difference between the very large effect of dioxane on the amides as compared to the rather small effect on the carboxylic acids.

In Table II the data[3a] on formamide in the gas phase and our values for benzene and dioxane solutions show that the benzene solvent effect amounts to about +0.15 whereas the dioxane effect is about +0.6. The solvent effects for the higher homologs will probably be lower than these values but they are, as seen in Table II, still quite significant.

Wilson and Wenzke[12] have found that, with the apparent exception of formic acid, the carboxylic acids have about the same moment in dioxane as Zahn[17] finds in the gas state. The reason for this marked difference between the acids and amides probably is to be found in the fact that, in the amides, one of the hydrogen bonds formed with dioxane is nearly in line with the direction of the resultant amide group moment. The acids, on the other hand, form a hydrogen bond which is probably nearly perpendicular to the direction of the resultant group moment and thus any effect on the resultant of the moment created by the hydrogen bonding is considerably minimized. This same situation holds for one of the hydrogen bonds of the amide group. It has been assumed in the above discussion that the primary effect on the O–H or N–H bond when it forms a hydrogen bond with dioxane is to increase the ionic character of the OH and NH bonds. With this in mind the chief effect on the resultant moments of the acids and amides, when the hydrogen bond is nearly parallel to the C–C axis of the amide or acid, is a change in the direction of the resultant moment and not a large change in its magnitude. This effect, as here set out, would tend to increase the observed angle of the resultant group moment with respect to the C–C axis. For this reason the value of about 70° rather than 74° was chosen in the previous discussion as the angle the amide group moment makes with the C–C-axis.

The dielectric constant evidence shows that

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(17) C. T. Zahn, *Phys. Rev.*, **37**, 1516 (1931).

formamide and propionamide are probably unassociated below a mole fraction of 3×10^{-3} in benzene, whereas the data for isobutyramide indicate association at mole fractions of less than 1×10^{-3} in benzene. Figure 1 shows the values of $\Delta\epsilon$, the dielectric constant increment, plotted against f_2 the mole fraction for each of the above cases in benzene and dioxane solution. No solute association is expected or observed in the dioxane solutions in the range of concentrations covered and the dielectric evidence bears this out. Undoubtedly the reason[18] for the association of the amides is the formation of hydrogen bonds between two or more molecules. It may be noted that the highest mole fraction point plotted for formamide in benzene in Fig. IA is rather uncertain because of the low solubility of the compound. As shown in Fig. IB, the solubility of propionamide in benzene allowed measurements being made at rather higher mole fractions than was the case for formamide. In this compound, by analogy with the lower acid strength and high association of the corresponding acid, one may expect higher association than was found for formamide. The chief factor responsible for the more pronounced association is presumed to be the electrostatic interaction. In the case of isobutyramide the association is markedly greater than for the propionamide, yet the acid strengths of the two corresponding acids are essentially the same. In the aromatic series of amides definitive evidence of association was established only for the case of benzamide. There are indications of association for the substituted benzamides but the low solubility of these substances in benzene and the precision of our present measurements made it impractical to investigate the compounds over a larger concentration range.

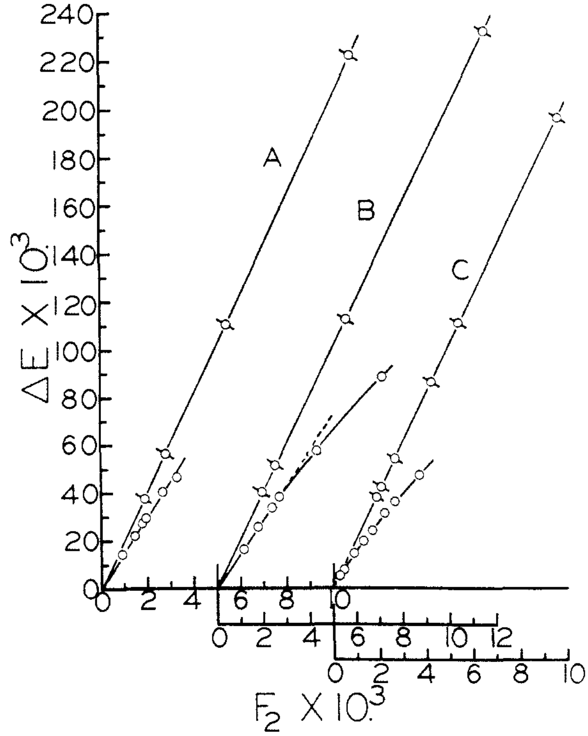

Fig. 1.—The dielectric constant increment, $\Delta\epsilon$, as a function of the mole fraction of solute, f_2 for solutions in benzene, O—O, and in dioxane, ϕ—ϕ. A is formamide, B propionamide and C isobutyramide. The benzene solutions of A and B show little evidence of association below 3×10^{-3} mole fraction, whereas C exhibits association down to the lowest measured concentration.

A detailed consideration of the association constants and of the factors influencing association, similar to those given for some other substances by Pohl, Hobbs and Gross[19] and Maryott,[20] will be reported for several of the amides at a later date.

Durham, N. C. Received November 20, 1950

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[18] (a) Chapin and Hunter, *J. Chem. Soc.*, 1114 (1937); (b) Copley, Zellhoffer and Marvel, This Journal, **60**, 133 (1938); (c) E. N. Lassettre, *Chem. Revs.*, **20**, 259 (1937).

[19] Pohl, Hobbs and Gross, *J. Chem. Phys.*, **9**, 408 (1941).

[20] A. A. Maryott, *J. Research Natl. Bur. Standards*, **41**, 1, 7 (1948).