sulfanilic acid model but not with the aniline model.

Discussion

On the basis of the foregoing results it appears that the ^{13}C NMR methodology we have described here provides an experimentally simple yet reliable technique for precise determination of tautomer partitioning. While the method relies on chemical model systems as do earlier approaches, the criteria of internal consistency available with ^{13}C NMR analysis provides a level of reliability not previously available. This is a direct consequence of the essentially independent partitioning estimates provided by each carbon resonance and by independent modeling of functional groups. We note in this connection that the choice of chemical models seems to have little influence on the precision or reliability of partitioning coefficients based on carboxylic acid dissociation models. Thus, benzoate and hydroxybenzoate models provided adequate modeling for both *m*- and *p*-aminobenzoic acids. Apparently, resonance interaction of the electron-donating hydroxyl substituent with both the protonated ionized carboxyl substituents is not reflected in the ^{13}C NMR protonation displacements. However, it does seem likely that the converse effect, withdrawal of electron density from the ring by CO_2H and CO_2^- substituents, is responsible for the failure of aniline as a model for amine protonation in monoprotic *p*-aminobenzoic acid. In that case the electron-withdrawing properties of the sulfonate group in sulfanilic acid seemed to adequately model the NMR data. While it is difficult to generalize from these few examples, it does seem likely that large differences in resonance interactions rather than in electric field effects play a dominant role in ^{13}C protonation displacements of aniline derivatives.

Experimental Section

Stock solutions of commercial samples (Aldrich Chemical Co., 0.05 F) of anilinium chloride, *m*- and *p*-aminobenzoic acids, and 4-sufanilic acids were prepared by diluting weighed portions of the solid samples to 25 or 100 mL with 5% D_2O/H_2O (v/v). In a typical run, a 5-mL aliquot of the stock solution was pipetted into a 10-mm NMR sample tube and the ^{13}C NMR spectrum was recorded initially and following the addition of each of 2 half-equiv of 0.95 F NaOH or HCl solution (5% D_2O) with a 200-μL micropipet.

^{13}C NMR data were acquired at 30 ± 2 °C on a Bruker HX-270 spectrometer operating at 67.89 MHz for ^{13}C detection. Typical instrument settings were 7-μs pulse width ($\sim$30° tip angle), 14-kHz spectral width, 0.3-s acquisition time, 1.7-s pulse delay time, and 4–8K transients.

Registry No. *m*-Aminobenzoic acid, 99-05-8; *p*-aminobenzoic acid, 150-13-0.

Cyclic Imides. 13.[1] An Analysis of the Experimental Dipole Moments of Five-Membered Cyclic Imides in 1,4-Dioxane Solution[2]

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The dipole moments of six unsubstituted cyclic imides and three *N*-methylimides have been determined by the Guggenheim–Smith method for dioxane solution at 20 °C. The results have been compared with values derived from published data for the Halverstadt–Kumler method. The Guggenheim–Smith method gave lower values than the Halverstadt–Kumler method. The difference between the orientation polarizations, calculated by the two methods, is a measure of atomic polarization. The H–N bond moment is 0.6 D for measurements of the dipole moments taken in dioxane solution. This value, with standard bond and group moments, gives good estimates for the dipole moments of saturated and aromatic cyclic imides in dioxane solution but not for imides containing an olefinic double bond in the imide ring.

The solubilities of succinimide and of phthalimide in benzene are too low for measurements of the dipole moments of these compounds to be made with benzene solutions. Cowley and Partington[4] used 1,4-dioxane as the solvent for the earliest of these measurements. Most other cyclic imides are also insoluble in hydrocarbon solvents. Dioxane has served as solvent in all subsequent measurements of the dipole moments of cyclic imides. This use of dioxane in dipole moment measurements creates two problems. The first of these problems is experimental in nature. The second problem lies in the interpretation of the data in terms of molecular structure.

The experimental problem lies in the instability of dioxane toward atmospheric moisture and oxygen. It has been suggested that purified dioxane should be kept and used under an atmosphere of dry nitrogen.[5] There is no evidence, however, that this precaution has been taken in any of the studies of the dipole moments of imides.

Comparison of experimental results is complicated by the use of different experimental approaches by different authors. These are the Halverstadt–Kumler method[6] and

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(2) Financial support of this work was provided in part by Grant No. M-101 from the Robert A. Welch Foundation and in part by an institutional grant for organized research from the Texas Woman's University.
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the Guggenheim–Smith method.[7-9] Both methods involve the measurement of the dielectric constants of a solvent and a series of solutions but differ in other measurements taken. Review and comparisons of these methods have been published by Smith,[10] Thompson,[11] and Exner.[12] The degree of comparability of the results of the two methods is still open to discussion. Some values obtained for phthalimide derivatives by the Guggenheim–Smith method[13] differ widely from the values obtained for the same compounds by the Halverstadt–Kumler method.[14] It is not clear whether these differences derive from the difference in method, from a difference in solvent quality, or from some combination of these two factors.
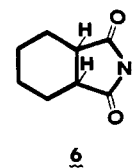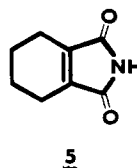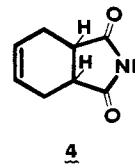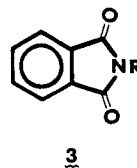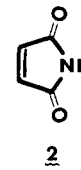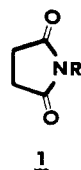
Structural interpretation of experimental dipole moments involves the discovery of a molecular geometry that will yield a calculated value for the dipole moment acceptably close to the experimental value. Calculation methods may be either quantum mechanical, or more often, the vectorial addition of bond and/or group moments. The calculations assume that the molecule is isolated in space, free from distortions in its electrical charge distribution that would be introduced by a neighboring polar molecule. This condition is approached in the measurements made with dilute solutions in nonpolar hydrocarbon solvents. 1,4-Dioxane, however, is a nonpolar solvent by virtue of balancing of equal and opposite dipoles. A solute molecule can interact with one of these dipoles to alter the experimental dipole moment.[15,16] According to Lutskii and his co-workers,[17,18] this "dioxane effect" can be interpreted, depending on the nature of the solute, in terms of hydrogen-bond donation from the solute to one of the dioxane oxygens and/or in terms of weak n,π donor–acceptor interactions from a nonbonding orbital on a dioxane oxygen to a π system in the solute.

Hydrogen bonding must be assumed to exist between dioxane and imides with N protons. Infrared studies by LeGall and co-workers[19] have given estimates of the complexation constants of succinimide, maleimide, and phthalimide with dioxane in carbon tetrachloride solution. Maleimide was found to be self-associated in the absence of dioxane. Crystallographic studies have shown that succinimide,[20] phthalimide,[21] and to tetrahydrophthalimides[22,23] are intermolecularly hydrogen bonded in the solid state. This self-association is the reason for the poor solubilities of these compounds in the solvents that are most suitable for dipole moment studies.

The complication introduced into dipole moment studies by hydrogen bonding between solute and solvent has not been closely examined. A study relevant to the problem was that of Bates and Hobbs,[24] who dealt with the dipole moments of formamide, propionamide, and isobutyramide in benzene and in dioxane. The results showed that clusters of self-associated amide molecules in benzene solution dissociate as the solution is diluted, whereas there is no self-association in the dioxane solutions. Within the concentration range used, a concentration-independent association with dioxane molecules existed instead. Similar situations should exist with dilute solutions of imides.

The only study to deal with the problem of H bonding to dioxane in the structural interpretation of the dipole moment of a cyclic imide is the study of 3-ethyl-3-methylglutarimide by Popov and Holm,[25] who found that they could not match their experimental dipole moment with a moment calculated by vectorial addition of bond moments for any reasonable structure of this molecule. This result was attributed to the use of the accepted value of 1.3 D for the H–N bond. This value had been derived[26] from a compound, methylamine, with a pyramidal nitrogen under non-hydrogen-bonding conditions, and its applicability to an imide, with a trigonal nitrogen, under H-bonding conditions, was questioned. The results suggested that the H–N bond moment should be 0.7 D.

We have undertaken a study of the problems that are suggested in this review by measuring the dipole moments of a selected group of model compounds and interpreting the results with the assistance of the structural studies of other workers. Since the dipole moments of the imides cannot be measured in non-hydrogen-bonding solvents, the next best approach is to compare the moments of the imides with those of N-substituted imides. Accordingly, the compounds we selected were succinimide (1, R = H),

N-methylsuccinimide (1, R = CH₃), maleimide (2, R = H), *N*-methylmaleimide (2, R = CH₃), phthalimide (3, R = H), and *N*-methylphthalimide (3, R = CH₃). To give greater range to the work, measurements have also been made with cis-1,2,3,6-tetrahydrophthalimide (4), 3,4,5,6-tetrahydro-

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Table I. Dipole Moments of Cyclic Imides in Dioxane Solution

compd	method[a]	temp, °C	ϵ_1	slopes	polarizations, mL	μ, D
1, R = H	GS	20	2.2165	$\alpha = 3.920$, $\gamma = 0.2022$	$P_0 = 60.1$	1.70
1, R = H	H[b]	20	2.244	$\alpha' = 3.8018$, $\beta' = -0.2610$	$P_2 = 75.4$	1.55
					$R_D = 25.6$	
1, R = H	HK[c]	30	2.20700	$\alpha = 2.8413$, $\beta = -0.3031$	$P_2 = 65.6$	1.47
					R_D 22.0[d]	
1, R = CH$_3$	GS	20	2.2169	$\alpha = 4.05$, $\gamma = 0.209$	$P_0 = 70.5$	1.84
1, R = CH$_3$	HK[e]	25	f	$\alpha = 3.34$, $\beta = -0.162$	$P_2 = 88.0$	1.71
					$R_D = 28.5$[d]	
1, R = CH$_3$	HK[c]	30	2.20700	$\alpha = 2.9933$, $\beta = -0.2305$	$P_2 = 80.1$	1.60
					$R_D = 28.9$[d]	
2, R = H	GS	20	2.2121	$\alpha = 2.203$, $\gamma = 0.2424$	$P_0 = 30.8$	1.22
2, R = CH$_3$	GS	20	2.2160	$\alpha = 2.512$, $\gamma = 0.201$	$P_0 = 41.6$	1.41
3, R = H	GS[g]	20	2.2131	$\alpha = 4.490$, $\gamma = 0.4258$	$P_0 = 96.8$	2.16
3, R = H	H[b]	20	2.243	$\alpha' = 7.232$, $\beta' = -0.3598$	$P_2 = 135.3$	2.14
					$R_D = 40.4$	
3, R = H	HK[h]	20	2.2212	$\alpha = 4.3458$, $\beta = -0.2313$	$P_2 = 135.4$	2.14
					$R_D = 40.6$	
3, R = H	HK[i]	30	2.20935	$\alpha = 7.124$, $\beta = -0.1523$	$P_2 = 207.6$	2.91
					$R_D = 37.3$[d]	
3, R = CH$_3$	GS	20	2.21515	$\alpha = 4.986$, $\gamma = 0.3577$	$P_0 = 120.9$	2.41
3, R = CH$_3$	HK[h]	20	2.2212	$\alpha = 4.2955$, $\beta = -0.16421$	$P_2 = 150.2$	2.26
					$R_D = 44.5$[d]	
4	GS	20	2.2155	$\alpha = 2.847$, $\gamma = 0.2869$	$P_0 = 63.2$	1.74
5	GS	20	2.2318	$\alpha = 3.78$, $\gamma = 0.298$	$P_0 = 84.6$	2.02
6	GS	20	2.2192	$\alpha = 3.1426$, $\gamma = 0.2317$	$P_0 = 72.1$	1.86
6	HK[c]	30	2.20160	$\alpha = 2.4994$, $\beta = -0.16732$	$P_2 = 99.2$	1.74
					$R_D = 38.5$[d]	

[a] GS = Guggenheim–Smith; H = Hedestrand; HK = Halverstadt–Kumler. [b] Reference 4. [c] Reference 28. [d] Calculated. [e] Reference 27. [f] Not given. [g] Reference 13. [h] Reference 14. [i] Reference 29.

phthalimide (5), and cis-hexahydrophthalimide (6). The Guggenheim–Smith method was used.

Results and Discussion

Treatment of Data. In the Guggenheim–Smith treatment, the dipole moment is calcuated from the slopes α and γ of eq 1 and 2. In these equations ϵ is dielectric

$$\Delta \epsilon = \epsilon_{12} - \epsilon_1 = \alpha w_2 \qquad (1)$$

$$\Delta n^2 = n_{12}^2 - n_1^2 = \gamma w_2 \qquad (2)$$

constant, n is refractive index, w is weight fraction, and the subscripts 1, 2, and 12 refer respectively to solvent, solute, and solution. The orientation polarization P_0 of the solute molecule is related to these slopes, and to the dipole moment μ, by the relationships[12]

$$P_0 = \frac{4\pi N}{9kT} \mu^2 = \frac{3M_2}{d_1} \left[\frac{\alpha}{(\epsilon_1 + 2)^2} - \frac{\gamma}{(n_1^2 + 2)^2} \right] \qquad (3)$$

in which M is molecular weight, d is density, N is Avogardro's number, k is the Boltzmann constant, T is the absolute temperature, and the subscripts have the meanings already noted.

Plots of $\Delta \epsilon$ vs. w_2 and Δn^2 vs. w_2 were prepared in accord with eq 1 and 2. A data point was discarded if it lay significantly off the straight line defined by the other points. Data sets displaying significant curvature or containing more than two questionable points were discarded entirely and the measurements were repeated with fresh materials. The slopes α and γ were evaluated by the method of least squares. Data sets whose least-squares slopes gave plots that failed to go through the origin were also discarded. When satisfactory values for α and γ were obtained, eq 3 was used to calculate the dipole moment. The value used for d_1 in this equation was that of Hess and Frahm,[5] 1.03375 g mL^{-1}. Table I summarizes the results of these measurements.

Comparison of Measurements. Table I also includes the results of the dipole moment measurements of Lum-

broso and his co-workers[14,27] and of Lee and Kumler.[28,29] The Halverstadt–Kumler method, which was used by these workers, is based on the relationships[12]

$$P_2 = \frac{3\alpha M_2}{d_1(\epsilon_1 + 2)^2} + M_2 \frac{\epsilon_1 - 1}{\epsilon_1 + 2}(v_1 + \beta) =$$

$$P_E + P_A + \frac{4\pi N}{9kT}\mu^2 \qquad (4)$$

where P_2 is total solute polarization, P_E is electronic polarization, P_A is atomic polarization, α has the same meaning as in eq 3, and β is defined by

$$\Delta v = v_{12} - v_1 = \beta w_2 \qquad (5)$$

where v is specific volume, or d^{-1}. In the studies that are reviewed in Table I, the quantity $(P_E + P_A)$ was approximated by the molar refraction of the solute for NaD light, R_D. For cases in which the data were given in the original papers, the dipole moments were recalculated according to the statistical standards used in our work. The data of Cowley and Partington[4] for succinimide and phthalimide were recalculated according to the method of Hedestrand,[30] in which the slopes α' and β' are obtained from plots of $\Delta \epsilon$ and Δv vs. mole fraction.

Each slope in Table I is carried only to the number of significant figures allowed by the error limits calculated as the product of the standard deviation and the t factor at the 95% confidence level for the appropriate number of degrees of freedom. The average error limits of our values of α and γ were ±0.2% and ±0.3%, respectively.

Since densitites can be measured more accurately and precisely than refractive indices, it has been suggested[10,11] that the Halverstadt–Kumler method may give more accurate values of dipole moments than the Guggenheim–Smith method. The average error limits for the values of

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Table II. Estimation of Atomic Polarizations of Cyclic Imides in Dioxane Solution at 20 °C

| compd | ref | Halverstadt–Kumler | | Guggenheim–Smith | | | |
		P_o, mL	μ, D	P_o, mL	μ, D	P_A, mL	$100P_A/R_D$
phthalimide	13[a]	98.6	2.18	96.8	2.16	1.8	4.4
phthalimide	14	94.9	2.14	92.9	2.11	2.0	4.9
N-methylphthalimide		124.1	2.44	120.9	2.41	3.2	7.2
N-methylphthalimide	14	105.7	2.26	102.4	2.22	3.3	7.4
3-chlorophthalimide	13[a]	124.1	2.44	119.1	2.39	5.0	11.0
3-chlorophthalimide	14	106.9	2.27	101.8	2.21	5.1	11.2
4-nitrophthalimide	13[a]	185.4	3.04	180.5	2.95	4.9	10.4
4-nitrophthalimide	14	136.6	2.61	134.2	2.54	2.4	5.1

[a] Calculated from unpublished data upon which the results in ref 13 were based.

β in Table I are ±0.05%, which is indeed significantly less than the ±0.3% for our values of γ. The source of largest error in our measurements, however, was in the dielectric constant values. The values of α are an order of magnitude larger than those of γ, but the devisors of these quantitites in eq 3 are nearly equal. As a result, the error in α determines the error of the dipole moments. The compound with the largest error in γ is 3,4,5,6-tetrahydrophthalimide, with $\alpha = 3.78 \pm 0.01$ (±0.3%) and $\gamma = 0.298 \pm 0.002$ (±0.7%). These numbers yield a variation of only ±0.004 D. The largest error in α is given by N-methylsuccinimide, with $\alpha = 4.05 \pm 0.02$ (±0.5%) and $\gamma = 0.209 \pm 0.001$ (±0.5%), giving ±0.005 D.

The absolute error in the dielectric constant measurements is larger than is suggested by the precision of α. Our values, based on measurements using a commercial instrument, are less precise than those reported in other studies, which have an average precision of ±0.05%. The accuracy as well as the precision of the dielectric constant measurements is a function of the measuring device and the accuracy of its calibration, as well as of solvent purity and, as we have shown elsewhere,[13] length of working time.

The values reported in Table I for our measurements of the dipole moments of succinimide (1, R = H), N-methylmaleimide (2, R = CH₃), and N-methylphthalimide (3, R = CH₃) are the results of combining the data from two sets of measurements. The dipole moments individually calculated from these sets were, respectively, 1.75 and 1.66 D; 1.38 and 1.42 D; and 2.39 and 2.41 D. These results suggest that the maximum error limits for our dipole moment measurements should be ±0.05 D. Limits of ±0.02 D were claimed for most of the measurements made by others.

A test of comparability of the Guggenheim–Smith and Halverstadt–Kumler methods would be to determine the dipole moment by both methods for the same compound with the same set of solutions, same temperature, and same equipment. In the few cases where this has been done,[31–33] the results are within ±0.05 or less for a variety of compounds. Thompson and co-workers[34] have suggested that the two methods will give comparable results if the same values for ϵ_1 and α are used in both methods, provided all measurements have been made at the same temperature. We tested this idea with the data for N-methylphthalimide (3, R = CH₃). Insertion of the values of ϵ_1 and α from the data of Lumbroso and Dabard[14] into the Guggenheim–Smith equation with our values for γ and n_1^2 gave 2.22 D, in good agreement with their value of 2.26 D. Insertion of our values for ϵ_1 and α into the Halverstadt–Kumler

calculation along with their values for v_1, β, and R_D gave 2.44 D, in good agreement with our value of 2.41 D. These results are summarized in the fourth and sixth columns of Table II, along with the results of comparable calculations for three other imides.

These results agree with the conclusion[34] that the Guggenheim–Smith calculation gives slightly lower results than the Halverstadt–Kumler method, where both calculations are based on the same dielectric constant data. The difference between the two results may be explained by the treatment of atomic polarizaton in the derivation of the Guggenheim–Smith equation. Guggenheim[7] used an atomic polarization term $P_A - P_A'$ where P_A is the total atomic polarization of the solute and P_A' is an atomic polarization of the solute according to which the polarizabilities of the solute and solvent would be in ratio of their molar volumes V:

$$P_A' = \left[\frac{\epsilon_1 - 1}{\epsilon_1 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} \right] \left(\frac{V_{12}}{V_1} \right) \left(\frac{3}{4\pi N} \right)$$

For rigid molecules, which certainly include the cyclic imides, $P_A \simeq P_A'$, and the atomic polarization term is negligible. The difference between the orientation polarizations P_o calculated by the two methods should then be an estimate of P_A. The difference between the values of the dipole moments calculated by the two methods falls within the 0.05–D range estimated by Exner[12] to be the error introduced by ignoring P_A in measuring dipole moments in the 2–3 D range.

Table II summarizes the results of calculations suggested by these ideas. For three of the four listed compounds, the two data sets yield effectively the same values for P_A. The lack of agreement for 4-nitrophthalimide is the result of a difference in the concentration ranges in the two sets of measurements.[13] The last column in Table II gives the values of P_A as a percent of the molar refractions, R_D, used by Lumbroso and Dabard. These values are within, or close to, the range of 5–15% of R_D which may be used to estimate P_A.[11,12]

Structural Evaluations. The following assumptions are made to aid in evaluating μ_{HN} for measurements made in dioxane solutions. First, it is assumed that all bond and group moments, except those for H-donor systems, that have been evaluated for measurements on benzene solutions[35] are also applicable to measurements with dioxane solutions. Second, it is assumed that the cyclic imide moiety is planar with a C_2 axis and that the dipole moment vector of the imide coincides with this axis. Crystallographic data[20–23] show that this is a reasonable approximation for unsubstituted imides. We will assume that the CH₃–N bond of N-methylimides also coincides with the axis of the imide moiety.

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Table III. Calculated Dipole Moments for Unsubstituted Imides in Dioxane Solution

| compd | angles, deg | | | ref | μ_{calcd}, D | μ_{exptl}, D |
	A	B	C			
1, R = H	30.8	135.1	112.6	20	1.8	1.70
2, R = H	37.6	140.9	110.5	a	1.6	1.22
2, R = H	40	142.5	115	b	1.5	1.22
3, R = H	36	138	112.2	21	2.2	2.16
4	29.6	135.5	113.5	23	1.8	1.74
5	37.6	140.9	110.5	22	1.6	2.02
6	29.6	135.5	113.5	c	1.8	1.86

[a] Angles assumed to be the same as in 5.   [b] Angles estimated from a model.   [c] Angles assumed to be the same as in 4.
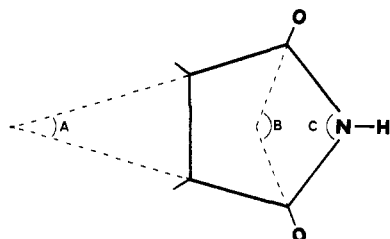

Figure 1. Angles used in estimating the dipole moments of the cyclic imide moiety.

The differences between the dipole moments of N-methylimides and unsubstituted imides measured in the same laboratory are for the succinimide system, 0.14 D from our data and 0.13 D from the data of Lee and Kumler;[28] for the maleimide system, 0.19 D; and for the phthalimide system, 0.25 D from our data and 0.12 D from the data of Lumbroso and Dabard.[14] The average of these five values is 0.17 D. The estimated value of μ_{HN} is then given by

$$\mu_{HN} = \mu_{H_3CN} - 0.17 = \mu_{HC_{al}} + \mu_{CN} - 0.17 = 0.6 \text{ D}$$

This result agrees well with the value of 0.7 D obtained by Popov and Holm[25] from their measurement on a six-membered imide.

Figure 1 provides a diagram for the calculation of the dipole moment of the imide moiety from bond moments. The angles A, B, and C can be calculated from crystallographic data, if it is available, or estimated from models. The resultant will then be

$$2\mu_{CC} \cos \frac{A}{2} + 2\mu_{C=O} \cos \frac{B}{2} + 2\mu_{CN} \cos \frac{C}{2} - \mu_{HN}$$

To this quantity must be vectorially added the dipole moment increments of groups on the back of the molecule. Table III gives the results of such computations with the six unsubstituted imides of the present study, using the bond and group moments given by Exner[35] and our value for μ_{HN}.

Comparison of these calculated values with the experimental dipole moments in Table I shows that agreement is excellent for phthalimide (3, R = H), cis-1,2,3,6-tetrahydrophthalimide (4), and cis-hexahydrophthalimide (6). Poor agreement is observed only for the two imides with an olefinic double bond in the imide ring, maleimide (2) and 3,4,5,6-tetrahydrophthalimide (5). The lack of agreement in the latter two cases cannot be attributed to different hydrogen-bonding abilities by these compounds, since there is no significant difference between the abilities of succinimide, maleimide, and phthalimide to H bond to dioxane.[19] It may be that the π system of the maleimide ring can function as an acceptor in an n,π interaction with dioxane.

The calculated μ_{HN} is valid only for hydrogen-bonding solvents, perhaps only for dioxane. Solute–solvent hydrogen bonding causes an increase in the apparent dipole moment of the solute. With cyclic imides, the H–N moment is in opposite direction from the molecular dipole moment so that a decrease in the apparent H–N bond moment results in going from a non-hydrogen-bonding solvent to a H bonding one.

Experimental Section

Materials. Imides were obtained from commercial sources (Aldrich, EK, or Frinton) and were each recrystallized at least once for alcohol and at least once from benzene. They were stored in a vacuum desiccator between purification and use. Both Aldrich Gold Label and Burdick and Jackson Distilled in Glass 1,4-dioxane were used. The dioxane was purified by refluxing with sodium metal, under the exclusion of atmospheric moisture, until the floating globules of molten sodium coalesced into a single sphere with a mirror surface. The dioxane was then distilled through an 18-in. Vigreux column. Two-thirds of the pot volume was distilled, and the second half of the distillate was used as the solvent in the dipole moment measurements. Calibration liquids were spectrophotometric grades of cyclohexane, carbon tetrachloride, benzene, and di-n-butyl ether, such as Aldrich Gold Label, Burdick and Jackson Distilled in Glass, and MCB Omnisolv. The first three calibration liquids were dried at least 1 week prior to use over type 4A molecular sieves. The di-n-butyl ether gave good calibration only if used immediately after receipt.

Apparatus. Dielectric constants were measured with a WTW type DMO1 Dipolmeter, using a type DFL1 sample holding cell. The dipolmeter was calibrated according to the procedure and dielectric constant values in the manual supplied with the instrument.[36] Refractive indices were measured with a Bellingham & Stanley high-precision refractometer, which yields measurements to one more decimal place than the conventional Abbé refractometer. The temperature in the sample holding cell and the refractometer was maintained during all measurements at 20.0 ± 0.2 °C by means of a circulating thermostat.

Measurements. In each set of measurements, six samples of approximately 50-mL volume were prepared, with weight fractions of solute, w_2, ranging from 0.002 to 0.02. When a sample had come to temperature, approximately 2 mL of it was transferred to the refractometer and the refractive index was measured immediately. The remainder of the sample was transferred to the dipolmeter cell, part of it being used to rinse the cell and the rest to fill the cell. Repeated readings of the dipolmeter were taken until the same value was obtained for five consecutive readings. Both the refractometer and the dipolmeter cell were thoroughly rinsed with absolute methanol between samples and dried with a stream of dry nitrogen.

(36) Oehme, F.; Wirth, H. "The Determination of the Molecular Electrical Dipole Moment"; Kahl Scientific Instrument Corp.: El Cajon, CA, 1960.