Organic and Biological Chemistry

Magnetic Nonequivalence in Derivatives of α-Hydroxy Acids

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The n.m.r. spectra of a series of isopropyl esters of α-hydroxy acids and their derivatives have been observed. It has been found that when the acid contains an asymmetric α-carbon atom and also an aromatic group, the isopropyl methyl protons are magnetically nonequivalent. If there is no aromatic function present, nonequivalence may be induced by acylation of the hydroxyl group. Similarly the methylene protons in propyl and isobutyl esters of tartartic acid were shown to differ in chemical shift. Both effects were found to be temperature dependent, and an effort is made to correlate this behavior in terms of conformational requirements impressed by the carboxyl groups.

Introduction

In the absence of restricted rotation, geminal groups will be magnetically nonequivalent if the molecule can assume more than one conformation and if the magnetic environment of the groups in question is different in these conformations. Thus the methyl protons of an isopropyl group situated in a molecule which also contains an asymmetric center may display such magnetic nonequivalence and give rise to a pair of doublets in the nuclear magnetic resonance spectrum; similar compounds containing a methylene rather than an isopropyl group may show an AB-type splitting pattern. Although the earliest examples[3,4] of such cases were for molecules in which the center of asymmetry was directly bonded to the carbon attached to the magnetically nonequivalent atoms, it has been subsequently demonstrated that in compounds such as sulfites,[5] sulfinates,[6] ketones,[7] acetals,[6] esters,[8] ethers,[9,10] and organophosphorus esters,[11] magnetic nonequivalence may also exist even though the interacting sites are two or more bonds removed.

Unequal populations of the various conformers in such molecules is normally accepted as the cause of nonequivalence,[4,12] although Waugh and Cotton[6]

(1) National Science Foundation College Teacher Research Participant, 1964.

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(10) G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 2628 (1964).

(11) T. H. Siddall, III, and C. H. Prohaska, *ibid.*, **84**, 3467 (1962).

(12) J. A. Pople, *Mol. Phys.*, **1**, 3 (1958).

have pointed out that this is not a necessary requisite and Gutowsky[13] has evaluated an asymmetric effect for $CF_2BrCFBrCl$. However, a temperature dependence of the difference in chemical shift is indicative of a changing population,[12] and where no such dependence has been observed,[9] this behavior has been interpreted in terms of favored conformations which persist through the temperature range investigated.

The origin of preferred conformations has been explicitly investigated in only a few cases. Roberts, Nagarajan,[9,14] and co-workers have shown the splitting pattern of the methylene hydrogens in cyclopropylmethylcarbinyl ethyl ether to be compatible with conformational requirements which disappear when the smaller deuterium atom is substituted for the methyl group in the ethyl moiety. Siddall and Prohaska[11,15] have proposed that a consideration of steric factors can account for unequal conformer populations and yields results consistent with their data, while Whitesides, Holtz, and Roberts[10] in a study of benzyl ethers have shown that their results cannot be fully explained in terms of conformations derived from a simple consideration of steric factors alone.

We have found the isopropyl methyl groups in diisopropyl tartrate diacetate give rise to resonance doubling, and it is the purpose of this investigation to study the generality of this effect. Since the diisopropyl ester of tartaric acid itself does not display magnetically nonequivalent methyl groups, a series of esters of α-hydroxy acids and their derivatives were prepared in order to ascertain whether it was possible to correlate this nonequivalence with factors such as the extent of long-range shielding, the size of groups bonded to the asymmetric center, and the site of nonequivalence.

Results

From the data given in Tables I and II, several observations may be made. In the compounds studied, only those esters of structure I in which there is a highly anisotropic function, such as a carbonyl or aromatic group located in R or R' (or both), display magnetic nonequivalence. This and the absolute values observed for the chemical shift of the methyl signals are suggestive of a preferred orientation of the isopropyl group relative to the asymmetric center in which one of the methyl groups lies in the shielding cone of the aromatic ring or carbonyl group. That

(13) H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962).

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Table I. Chemical Shifts of Methyl Protons in Alcohol Moiety of Esters of α-Hydroxy Acids[a]

| Compd.	Temp., °C. 39[b]	180[c]
Isopropyl lactate	1.267	
Diisopropyl tartrate	1.288	1.281
Isopropyl mandelate	1.233, 1.061	1.151, 1.036
Isopropyl benzilate	1.160	
Diisobutyl tartrate	0.958	0.948
(Diisopropyl succinate)	(1.214)	

[a] All chemical shifts reported are in p.p.m. from TMS. [b] All low-temperature spectra are for 10 mole % solutions in carbon tetrachloride unless otherwise noted. [c] All high-temperature spectra were obtained on the undiluted esters.

Table II. Chemical Shifts of Methyl Protons in Alcohol Moiety of Esters of Tartaric Acid

Compd.	Temp., °C. 39	180
Diisopropyl tartrate	1.288	1.281
Diisopropyl tartrate, diacetate	1.272, 1.197	1.252, 1.206
Diisopropyl tartrate, dibenzoate	1.230, 1.080[a]	1.209, 1.151
Diisopropyl tartrate, di-α-naphthoate	1.198, 1.114[a]	
Diisobutyl tartrate	0.958	0.948
Diisobutyl tartrate, dibenzoate	0.821	0.834

[a] Deuteriochloroform solvent.

Table III. Chemical Shifts of Isopropyl Methyl Protons in Esters of Lactic Acid

Compd.	Temp., °C. 39	180
Isopropyl lactate	1.267	
Isopropyl lactate, acetate	1.256, 1.228	1.220
Isopropyl lactate, cyclohexylcarboxylate	1.251, 1.222	1.217
Isopropyl lactate, benzoate	1.256, 1.218	1.200

**Table IV.** Chemical Shifts of Methylene Protons in Esters of Structure II

Compd.	Temp., °C. 39	180
Diethyl tartrate	4.280	
Diethyl tartrate, dibenzoate	4.190	
Dipropyl tartrate	4.202, 4.122[a]	
Dipropyl tartrate, dibenzoate	4.115, 4.060[b]	
Diisobutyl tartrate	4.074, 3.919[c]	4.062
Diisobutyl tartrate, dibenzoate	3.949, 3.877[d]	4.028

[a] Obtained from analysis of ABX₂ system: J_{AB} = 10.8 c.p.s., J_{AX} = 7.0 c.p.s., J_{BX} = 6.2 c.p.s., $\nu_A - \nu_B$ = 4.8 c.p.s. Signs of coupling constants on these and subsequent spectra were not determined. [b] Obtained from analysis of ABX₂ system: J_{AB} = 10.7 c.p.s., J_{AX} = 7.4 c.p.s., J_{BX} = 5.7 c.p.s., $\nu_A - \nu_B$ = 3.3 c.p.s. [c] Obtained from analysis of ABX system: J_{AB} = 10.5 c.p.s., J_{AX} = 6.7 c.p.s., J_{BX} = 6.4 c.p.s., $\nu_A - \nu_B$ = 9.3 c.p.s. [d] Obtained from analysis of ABX system: J_{AB} = 10.6 c.p.s., J_{AX} = 6.8 c.p.s., J_{BX} = 6.0 c.p.s., $\nu_A - \nu_B$ = 4.3 c.p.s.

such is likely to be the case is supported by the greater difference in chemical shifts observed for the benzoate compared to the acetate, and the temperature dependence of these differences.
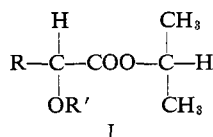
In the isopropyl esters investigated, all methyl proton resonances are subject to dilution shifts to lower fields. This is particularly noticeable in those molecules containing an aromatic function, and is reflected in the values recorded for the high-temperature spectra which were obtained on the undiluted esters. Because of this dilution effect, the chemical shifts recorded for a compound at high and low temperature are not strictly comparable. However, the difference between the chemical shifts of magnetically nonequivalent groups obtained at low temperature may be compared with the difference obtained at high temperature. This comparison shows that increasing the temperature decreases the degree of magnetic nonequivalence as indicated by the smaller separation of signals found at 180°.

While dilution studies were not carried out on the majority of compounds, dilution effects of several representative esters were investigated, and the results show that the chemical shifts of the methyl groups obtained at concentrations of 10 mole % do not differ by more than 0.07 p.p.m. from those found by extrapolation to infinite dilution; in those esters which do not contain an aromatic nucleus, the value is considerably less than 0.07 p.p.m. At the same time, the difference in chemical shifts between the nonequivalent groups

remains essentially unchanged on further dilution. Therefore while it is difficult to state positively whether the differences observed between the low field methyl signals of diisopropyl tartrate, its acetate, benzoate, and naphthoate are due to intra- or intermolecular effects, it seems likely that both methyl resonances of the α-naphthoate are displaced to higher fields relative to diisopropyl tartrate itself. This is compatible with the larger area of the naphthoate ring which could shield both methyl groups, but unequally, and would in turn account for the smaller chemical shift difference observed for the methyl protons of the α-naphthoate as contrasted to the benzoate.

Table III lends support to the conclusion that ring current rather than steric factors is primarily responsible for the larger chemical shift differences displayed by the benzoates compared to the acetates. In Table III, the cyclohexylcarboxylate shows the same difference in chemical shift as that observed for the acetate. In addition another aspect of the problem is suggested by the data contained in the first three tables, namely that in esters of structure I, the nature of R is of consequence both in determining the extent of nonequivalence and the tendency for nonequivalence to persist at higher temperatures.

It was pointed out above that diisobutyl tartrate, an ester of structure II, does not display nonequivalent methyl groups. The values in Table IV show that in
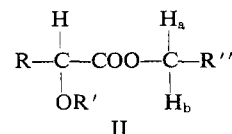
certain cases the a and b methylene protons in such esters, however, may be nonequivalent. For diethyl tartrate, these protons appear as a simple quartet expected from an A_2X_3 system. In the case of the diisobutyl and dipropyl tartrates, this region of the spectrum showed multiplicities to be expected from the AB portion of ABX and ABX_2 systems. The spectra were explicitly analyzed, and the values obtained for each ester showed the same trend; namely that benzoylation moves both nonequivalent proton resonances to higher fields, but unequally, so that the difference in chemical shifts between these protons is decreased.

Discussion

It is evident that the esters studied offer another example of the growing list of compounds which display magnetic nonequivalence because of the presence of a center of asymmetry rather far removed from the site of nonequivalence. It is reasonable to suppose, particularly in view of the temperature dependence of the spectra, that this is basically a result of differences in the populations of conformations rather than an effect due to intrinsic asymmetry. In the compounds investigated, nonequivalence is displayed only by protons or methyl groups directly bonded to the carbon atom attached to the carboxyl oxygen, and is highly dependent on the nature of the substituents at the asymmetric center.

The origin of this behavior is complex in that changes in the molecule as far as seven atoms removed affect the magnetic nonequivalence. There are therefore vast numbers of possible conformations, and on the basis of the data gathered, it seems impossible to make a simple correlation between the degree of magnetic nonequivalence and any single parameter. The values obtained, however, do suggest that certain structural features may be more important than others.

As was noted earlier, the behavior of the isopropyl esters could be explained if the isopropyl group is oriented relative to the asymmetric center in such a fashion that the two methyl groups are unequally shielded by R or R' as shown for instance in structure III. A number of other conformations will be populated, but will also be characterized by different stereochemical environments of the two methyl groups.

There is ample evidence[16] that esters of α-hydroxy acids are intramolecularly hydrogen bonded. This obviously impresses a highly preferred arrangement of the asymmetric center relative to the carbonyl group as indicated in structure III (R' = H). In molecules
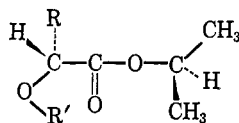
III

where R' is some group other than hydrogen, it again seems likely that the substituents on the asymmetric carbon atom will possess a preferred conformation relative to the carbonyl oxygen as a result of either the steric or electrostatic nature of R or R'. This has been

shown to be the case for certain aldehydes, ketones, and acid chlorides.[17] In addition, the large number of additions to carbonyl groups which follow Cram's[18] or Prelog's[19] rules indicates that such is the case at least in the transition state, and it seems reasonable to extend a preferred conformation to the ground state as well. At the same time the isopropyl group may also assume a preferred conformation relative to the carbonyl oxygen. There is evidence for the existence of this type of preferred conformation in undiluted esters.[20,21] Whitesides and co-workers[10] have interpreted their data in terms of the orientation of two groups relative to each other as a consequence of being bonded through an ethereal oxygen. Finally Prelog's rule[19] demands that the substituents on the carbon bonded to oxygen in certain esters assume a definite conformation with respect to the carbonyl group. Thus as a consequence of the intervening carboxyl group, the molecule will probably preferentially populate one conformation in which the asymmetric center and isopropyl group adopt a certain orientation with respect to each other, even though there be negligible direct steric or electrostatic interaction between them.

This interpretation is consistent with several experimental observations. Since the degree of nonequivalence is controlled by rotations about both the asymmetric carbon-to-carbonyl bond and the two oxygen-to-carbon bonds, the smaller difference in chemical shift observed for the lactates as compared to the tartrates can be rationalized in terms of less highly favored conformations in the former as a consequence of the smaller R group. The contrast between the lactates and tartrates is more evident at 180° as would be expected from a greater population leveling at higher temperatures because of lesser steric interactions in the lactates. Likewise since the methyl groups in the diisobutyl tartrates are not directly attached to the carbon bonded to oxygen, their nonequivalence is expected to be considerably less that that observed for the isopropyl derivatives, and in practice no difference could be detected within the limits of resolution.

While this view is then in qualitative agreement with the experimental observations, it does not account quantitatively for all the features noted. Thus the chemical shift given in Table I for isopropyl benzilate shows the value to lie midway between those observed for the two methyl resonances of isopropyl mandelate. Table V indicates that acylation and benzoylation have little effect on the chemical shifts of the methyl protons when compared to isopropyl mandelate itself. The methyl ether on the other hand shows a marked decrease in the degree of nonequivalence between the two groups. On the basis of the data gathered, it is impossible to say whether these results are a consequence of gross alterations in conformational preference, or may be attributed to more subtle causes such as changes in the dihedral angle between the planes of the aromatic and carbonyl groups as a result of rotation about the phenyl-to-carbon bond.

(16) See N. Mori, S. Omura, O. Yamamoto, T. Suzuki, and Y. Tsuzuki, *Bull. Chem. Soc. Japan*, **36**, 1401 (1963), for recent n.m.r. studies dealing with hydrogen bonding in esters of α-hydroxy acids as well as for a compilation of earlier references involving similar conclusions from optical rotation and infrared investigations.

(17) See R. J. Abraham and J. A. Pople, *Mol. Phys.*, **3**, 609 (1960), and references cited therein.
(18) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 5828 (1952).
(19) V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953).
(20) M. Kashima, *Bull. Chem. Soc. Japan*, **25**, 79 (1952).
(21) M. Bailey, *Acta Cryst.*, **2**, 120 (1949).

Compd.	Temp., °C.	
	39	180
Isopropyl mandelate	1.233, 1.061	1.151, 1.036
Isopropyl mandelate, acetate	1.229, 1.077	1.172, 1.075
Isopropyl mandelate, benzoate	1.238, 1.079	1.193, 1.076
Isopropyl mandelate, methyl ether	1.197, 1.115	1.147, 1.088

Finally the origin of nonequivalence in esters of type IV cannot arise from the same, long-range shielding proposed for the isopropyl groups since the unacylated tartrates themselves show nonequivalent methylene protons. In this case there is no carbonyl or aromatic group present in R' which may shield the geminal hydrogens unequally. Unlike the similar isopropyl esters, nonequivalence in esters of structure IV ($R' = H$) is decreased by benzoylation and does not persist at high temperature. These data are not incompatible with the explanation proposed for the isopropyl esters. One can again imagine a structure such as IV in which there is a preferred orientation of the two tetrahedral carbon atoms as a consequence of the intervening carboxyl group. It is not unreasonable to

IV
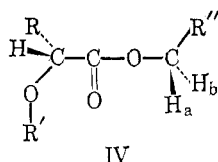
suppose that conformational requirements about the O-methylene bond would be dependent on R'' and account for the observation that the separation between H_a and H_b shifts follows the sequence $R'' = CH_3 < R'' = C_2H_5 < R'' = i\text{-}C_3H_7$. At the same time, because of the smaller number of alkyl groups attached to the carbon bonded to the carboxyl oxygen, these compounds might be expected to display less rigid conformational preference, and consequently to show more highly temperature-dependent spectra. The origin of unequal shielding of these two protons can only be speculated on. It may arise from different proximity or angles of the carbonyl group to the two methylene protons, or be the consequence of more distant effects.

Experimental Section

All spectra were taken on a Varian A-60 spectrometer. The calibration of the instrument was checked frequently, and spectra of identical samples were recorded periodically to verify reproducibility. In general the signals arising from methyl groups were sharp lines, and chemical shifts were recorded to the nearest 0.1 c.p.s. These data were converted to p.p.m., and are believed to be accurate to within 0.01 p.p.m.

The difference in chemical shifts arising from magnetically nonequivalent geminal groups in the same molecule is of the order of magnitude normally encountered for coupling constants. It is therefore possible to determine this difference with a greater accuracy than the chemical shifts themselves. The error in these differences is believed to be no greater than 0.003 p.p.m. This limit was established by periodically comparing

the coupling constant obtained for acetaldehyde with the accepted value of 2.84 c.p.s.

All low-temperature spectra were determined for solutions of 10 mole %. Carbon tetrachloride was employed as the solvent with the exception of the dinaphthoate and dibenzoate of diisopropyl tartrate for which deuteriochloroform was used. High-temperature spectra were obtained on the undiluted esters.

d,l-Isopropyl Mandelate. This compound was prepared in 90% yield by the direct esterification of mandelic acid with isopropyl alcohol in the presence of sulfuric acid catalyst. Benzene was employed as a solvent, and water was removed azeotropically through a Dean–Stark trap as formed. Final distillation yielded the ester of b.p. 125° (2 mm.), n^{28}D 1.4977.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.01; H, 7.27. Found: C, 68.18; H, 7.09.

Isopropyl Benzilate. This compound was prepared in a similar manner in 57% yield, b.p. 186–188° (3 mm.). Further distillation yielded a product of b.p. 149–150° (1 mm.), n^{26}D 1.5453.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.71; H, 6.59.

Acyl and aroyl derivatives of esters of α-hydroxy acids were prepared from the appropriate acid chlorides and α-hydroxy esters by the method given below. One preparation is described in detail, and only yields, physical constants, analyses, and modifications of the procedure are given for those compounds not previously reported.

Diisopropyl L-Tartrate, Dibenzoate. To a solution of 25.0 g. of diisopropyl L-tartrate in 175 ml. of anhydrous pyridine, 45 ml. of benzoyl chloride was added slowly with stirring. After heating for 45 min. on a steam bath, the reaction mixture was poured slowly into 10% sodium carbonate solution. The oily layer was taken up in ether, and the ether extracts were washed successively with water, 10% sulfuric acid, water, concentrated calcium chloride solution, and finally with water. After drying over anhydrous magnesium sulfate and removing the solvent, crystallization was induced in the glassy residue by the addition of carbon tetrachloride. The crude material was then recrystallized once from ethanol–water and twice from ethanol to yield 26.8 g. of product melting at 74.0–74.5°, $[\alpha]^{25}$D −67.8° (c 9.90, chloroform).

Anal. Calcd. for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92. Found: C, 65.01, 64.88; H, 5.62, 5.80.

d,l-Isopropyl Lactate, Benzoate. This compound was obtained in 85% yield, b.p. 161–166° (17 mm.), n^{28}D 1.4840. A portion of this was subjected to two additional distillations giving a product of b.p. 164° (17 mm.), n^{27}D 1.4838.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.10; H, 7.05.

d,l-Isopropyl lactate, cyclohexylcarboxylate was obtained in 84% yield, b.p. 150–160° (24 mm.), n^{26}D 1.4428. Redistillation of a portion of this fraction gave a product of b.p. 153–154° (21 mm.), n^{27}D 1.4410.

Anal. Calcd. for $C_{13}H_{22}O_4$: C, 64.43; H, 9.15. Found: C, 64.27; H, 8.88.

d,l-Isopropyl mandelate, benzoate was obtained in 67% yield as white crystals, m.p. 79.3–79.9° after two recrystallizations from ethanol.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.60; H, 6.23.

Diisopropyl L-*Tartrate, Di-α-naphthoate.* This compound was obtained in 59% yield after five recrystallizations from ethanol, m.p. 109.0–109.5°, $[α]^{25}D$ −53.1° (*c* 19.2, chloroform).

Anal. Calcd. for $C_{32}H_{30}O_8$: C, 70.83; H, 5.57. Found: C, 70.60, 70.82; H, 5.45, 5.61.

d,l-Isopropyl mandelate, acetate was obtained in 68% yield as a liquid, b.p. 128–129° (1 mm.), $n^{24}D$ 1.4859.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 65.94; H, 6.69.

d,l-Isopropyl Mandelate, Methyl Ether. A mixture of 25 g. of isopropyl mandelate and 109.5 g. of methyl iodide was cooled in an ice bath, and 89.5 g. of freshly prepared silver oxide was added portionwise with stirring. The reaction mixture was slowly warmed to room temperature and refluxed for 3 hr. After cooling, an additional 55 g. of methyl iodide and 45 g. of silver oxide were added, and the reaction mixture was refluxed for 3 hr. The inorganic residue was removed by filtration and washed with ether, and the combined filtrate and washings were dried over magnesium sulfate. After removal of the solvent, the product was obtained in 89% yield, b.p. 108° (1 mm.), $n^{24}D$ 1.4882.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.10; H, 7.76.

The Influence of Hydration on Base Strength.
I. General Theory for Amines

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Contribution from the Department of Chemistry, The City College of the City University of New York, New York, New York. Received March 27, 1965

The theory that preferential hydration of ammonium ions is an important factor influencing the base strengths of amines in aqueous solution is supplemented by considerations based on the general theory of substituent effects on reaction rates and equilibria. Possible effects on the base strength resulting from hydration of the amine as well as the ammonium ion are considered, and a general equation is proposed relating hydration effects to the number and nature of the substituents attached to nitrogen in the amine. On the theory that the hydration energy of an ammonium ion is larger than that of an amine solely because of the electrostatic potential between a positive charge on nitrogen and the dipole of a water molecule, the difference for the first water molecule is estimated as 4–8 pK units for values of the "internal" dielectric constant between 2 and 1. The effect is expected to diminish with increasing number of water molecules because of charge dispersal and repulsions between the dipoles of two or more water molecules.

The past 15 years have seen a growing realization of the importance of hydration effects on the base strengths of amines in aqueous solution, as measured by pK_a, the negative logarithm of the thermodynamic equilibrium constant for the dissociation

$$R_1R_2R_3NH^+ + H_2O \rightleftharpoons R_1R_2R_3N + H_3O^+ \qquad (1)$$

where one or more of the R_i's may be H. Trotman-Dickenson[1] expressed the ideas that hydration of the ammonium ion would be more important than that of the amine; that it would tend to stabilize the ion and thereby increase base strength; and that the amount of hydration would be directly related to the number of hydrogens attached to nitrogen in the ammonium ion. In this way he was able to account qualitatively for the well-known irregularities in the base strengths of the methylamines[2] and for a lack of correspondence between the pK_a values and catalytic constants for the decomposition of nitramide, when comparison was made between aromatic amines of different classes. Pearson came to the same conclusion from a study of amine-catalyzed ionization of nitroethane.[3]

Steric hindrance to hydration of ammonium ions has been invoked to explain the decreased base strength of certain aliphatic amines with bulky substituents[4] and of anilines with bulky *ortho* substituents.[1,5,6]

Hall[4] found that the base strengths of 77 aliphatic amines were well correlated by means of the substituent constants, $σ^*$, devised by Taft,[7] but that each class of amine fell on a different straight line plot of pK_a against a sum of substituent constants, one for each of the substituents attached to nitrogen. Folkers and Runquist found that a series of N-substituted anilines behaved similarly.[8] These findings were interpreted as favorable to the hydration theory and in opposition to alternative theories involving steric strain[2] or "polarstriction" effects.[9] None of these authors, however, took into consideration the statistical factor, which becomes significant (up to 0.60 pK_a unit) when one is comparing the

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(4) H. K. Hall, Jr., *ibid.*, **79**, 5441 (1957).
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(8) E. Folkers and O. Runquist, *J. Org. Chem.*, **29**, 830 (1964).
(9) S. R. Palit, *J. Phys. Colloid Chem.*, **51**, 1028 (1947).