to design a suitable host system for this aim. No reasonable account can be offered at this point for the effect of substitution on the guest aryl group on the resolution. In conclusion, it appears that the spatial relationships that affect optical resolution in the above described *coordination-assisted clathrates* are similar to those characterizing some optically resolved *molecular complexes*.[19] This should encourage additional applications of the lattice inclusion phenomena to problems of chiral recognition.

Registry No. **1a**:(+)-**2b**, 111469-58-0; **1a**:(+)-**2c**, 111469-47-7; **1a**:(+)-**2d**, 111469-60-4; **1a**:(+)-**5a**, 111555-51-2; **1a**:(+)-**5c**, 111469-62-6; **1b**:(−)-**2a**, 111469-63-7; **1b**:(−)-**2b**, 111469-65-9; **1b**:(−)-**2c**, 111469-67-1; **1b**:(−)-**2d**, 111469-69-3; **1b**:(−)-**5a**, 111555-52-3; **1b**:(−)-**5c**, 111469-71-7; (±)-**2a**, 90458-69-8; (+)-**2a**, 34647-07-9; (−)-**2a**, 34647-06-8; (±)-**2b**, 111469-72-8; (+)-**2b**, 111469-57-9; (−)-**2b**, 111469-64-8; (±)-**2c**, 111469-73-9; (+)-**2c**, 111469-79-5; (−)-**2c**, 111469-66-0; (±)-**2d**, 111469-74-0; (+)-**2d**, 111469-59-1; (−)-**3d**, 111469-68-2; (±)-**4a**, 111469-75-1; (±)-**4b**, 111611-87-1; (±)-**5a**, 99396-67-5; (+)-**5a**, 17045-47-5; (−)-**5a**, 26515-05-9; (±)-**5b**, 111469-76-2; (±)-**5c**, 111469-77-3; (+)-**5c**, 111469-61-5; (−)-**5c**, 111469-70-6; (±)-**5d**, 111469-78-4; I, 111469-56-8; II, 111469-80-8.

Supplementary Material Available: Tables of atomic coordinates, lists of anisotropic thermal parameters, hydrogen atom coordinates, bond lengths, bond angles, melting points, and results of chemical analyses, and Figure 3 (10 pages). Ordering information is given on any current masthead page.

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Solvent Effects on the Basicity of Alkyl-Substituted Dimethylamines

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The basicity of alkyl-substituted dimethylamines in various solvents is dictated largely by specific solvation of the ammonium ion. Solvent attenuation factors, which reflect the extent to which solvents solvate ions, are directly proportional to the solvent's hydrogen bond acceptor ability, β. Substituent polarizability attenuation factors indicate that charge-induced stabilization varies in different solvents.

Solvents play an important role in the equilibrium position of various proton-transfer reactions.[2,3] The position of equilibrium 1, where X represents any substituent, G some rigid framework, and B is the protonation site, can be altered depending on the solvent.[4-7] Solvation of ions offers stability not available in the gas phase. A comparison of proton-transfer reactions in the gas phase and various solutions demonstrates this fact. Various methods have been developed that attempt to define and quantify parameters that determine how solvents alter various equilibria.[8-11]

$$\mathrm{X{-}G{-}B} + \mathrm{H{-}G{-}BH^+} \rightleftharpoons \mathrm{X{-}G{-}BH^+} + \mathrm{H{-}G{-}B} \quad (1)$$

Equilibrium 1 can also be altered by changing the substituent X. Brauman and Blair[12] observed that the basicities of amines, alcohols, and ethers increased with branching alkyl substituents. Mercaptans[13] and phenols[14] show a similar behavior. Substituents that do not form chelates with the reaction site may affect equilibrium 1 by any combination of three generalized kinds of inherent substituent effects: resonance, field/inductive, or polarizability effect.[15]

Table I. Relative Basicity of Alkyl-Substituted Dimethylamines in Various Media at 298 K, $\delta\Delta G^\circ_{298}$ in kcal mol^{-1}

X	$\delta\Delta G^\circ$-(gas)[26]	$\delta\Delta G^\circ$-(H_2O)[31,32]	$\delta\Delta G^\circ$-(DMSO)	$\delta\Delta G^\circ$-(AN)
CH_3	0.0	0.0	0.0	0.0
C_2H_5	−2.3	−0.6	−0.3	−0.6
n-C_3H_7	−3.0	−0.6	−0.4	−0.7
n-C_4H_9	−4.4	−0.6	−0.5	−1.1
i-C_3H_7	−4.7	−1.0	−0.6	−1.2
sec-C_4H_9	−5.9	−1.1	−0.6	−1.4[a]
t-C_4H_9	−6.5	−1.4	−0.8	−1.5
c-C_6H_{11}	−7.3	−1.6	−0.9	−1.8
t-C_5H_{11}	−7.9	−1.8	−0.9	−1.9[a]

[a] Calculated with eq 4.

Experimental Section

Dimethyl sulfoxide (DMSO)[16] and acetonitrile (AN)[17] were purified as described elsewhere.

Potentiometry. Potentiometric titrations of DMSO and AN solutions of dimethylamines were carried out at 25 °C in a glovebox under a dry nitrogen atmosphere with CF_3SO_3H in DMSO and AN, respectively. Constant ionic strength was maintained with 0.100 M Et_4NI. The electrodes used were an

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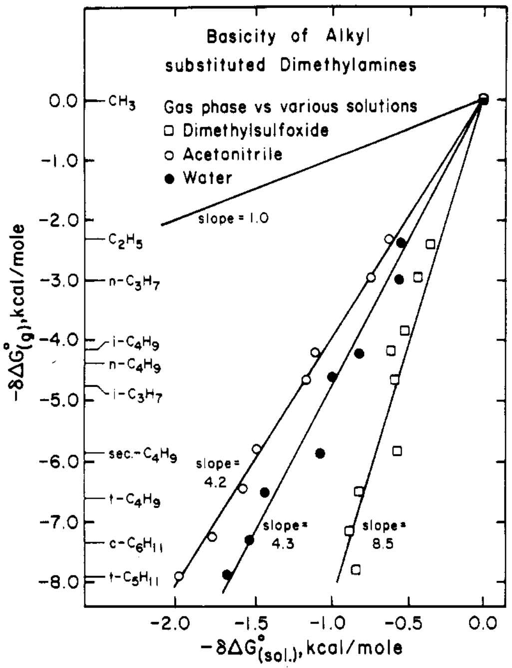

Figure 1. Relative basicities of alkyl-substituted dimethylamines: gas vs dimethyl sulfoxide, acetonitrile, and water. Ordinant: $-\delta\Delta G°$(g), kcal/mol. Abscissa: $-\delta\Delta G°$(sol), kcal/mol.

Orion glass electrode and an I^-/I_3^- reference electrode with a connecting junction of Et_4NClO_4 in DMSO or AN. Stable readings were obtained within 1 min on a Beckman 404 pH meter. The glass electrode was calibrated with a series of CF_3SO_3H solutions in DMSO or AN in 0.100 M Et_4NI. pK_a values in aqueous medium[18] were determined potentiomerically with 0.1 M HCl.

Results

Free Energy. Equilibrium constants were determined for reaction 2, where X represents an alkyl substituent, in DMSO and AN from potentiomeric curves obtained from neutralization of each amine by trifluoromethanesulfonic acid. The slopes of the least-squares plots of the EMF

$$X\text{-}N(CH_3)_2 + (CH_3)_3NH^+ \rightleftharpoons X\text{-}N(CH_3)_2H^+ + (CH_3)_3N \tag{2}$$

of the glass electrode against log of activity of BH^+/B (where BH^+ and B represent the protonated and free amine, respectively) varied between 59.0 and 60.0 mV, depending on the amine. The activity coefficients were calculated from the following relationships: $-\log f_i = 1.12\sqrt{\mu}/(1 + 3.9 \times 10^{-7}a\sqrt{\mu})$ for DMSO[19] and AN[20] $-\log f_i = 1.64\sqrt{\mu}/(1 + 0.48 \times 10^{-7}a\sqrt{\mu})$, where μ is the ionic strength in mol dm^{-3} and $a = 6$ Å. The changes in standard Gibbs free energies, shown in Table I, were determined from the relationship, $\Delta G° = -RT(\ln K)$.

Discussion

Solvent Effect. Solvent attenuation factors (SAF) are used to evaluate the overall solvent effect on reactions relative to the gas phase and are determined from the slope of a suitable plot of $\delta\Delta G°$ (gas) vs. $\delta\Delta G°$ (sol). The effects that solvents have on reactions may be described by the solvatochromic parameters:[21] (a) polarity/polarizability, which describe the solvent's ability to stabilize a charge or a dipole by virture of its dielectric effects, (b) hydrogen bond donor ability from solvent to solute, and (c) hydrogen bond acceptor ability from solvent to solute. For each solvent, the extent of these solvent–solute interactions are different and result in solvent attenuation factors, for a particular reaction, that vary for different solvents.

Table II. Solvent Attenuation Factors (SAF), Polarizability Attenuation Factors (PAF) for the Basicities of Alkyl-Substituted Dimethylamines in Various Solvents, and Solvent's Hydrogen Bond Acceptor Ability

solvent	SAF	PAF	β
(gas phase)	1.0	1.0	
dimethyl sulfoxide	8.5	8.7	0.76
acetonitrile	4.2	4.2	0.40
water	4.3	4.5	0.45

Figure 1 shows a plot of the relative basicities of alkyl-substituted dimethylamines in the gas phase vs various solvents. Due to the linearity of the correlations, there seems to be a consistent pattern of solvation. A solvent attenuation factor (slope) of unity indicates negligible solvation whereas a large factor suggests a highly solvated system. The effectiveness of DMSO to create a highly solvated ammonium ion is reflected in the large value of its SAF (8.5).

A solvent's ability to solvate alkylammonium ions seems to be largely dictated by the solvent's hydrogen acceptor ability, β, as indicated from Table II. Solvent attenuation factors are directly proportional to β. Thus, solvent effectiveness in the solvation of alkylammonium ions should obey the following trend: DMSO > H_2O > AN, which is consistent with the observed trend in Figure 1.

Substituent Effect. Table I reveals that for alkyl-substituted dimethylamines bulky substituents attached directly to nitrogen lead to increased basicity in each solvent when compared to the methyl substituent. Alkyl substituents offer no stabilization by field/inductive effect.[22,23] There is also no contribution from resonance effect that is of statistical significance.[24] Stabilization comes primarily from the substituent polarizability effect. Polarizability potential measures this polarizability effect.[25] A single-parameter $\rho\sigma$ treatment[26] considering only polarizability effect in the gas phase and various solvents is shown in eq 3–6. Equations 3–6 show a linear dependence

$$\delta\Delta G(\text{gas}) = (16.5 \pm 0.4)\sigma_\alpha + 5.8 \pm 0.3 \tag{3}$$

$$n = 9,\ r = 0.998\ \text{SD} = 0.2$$

$$\delta\Delta G(\text{AN}) = (3.9 \pm 0.2)\sigma_\alpha + 1.3 \pm 0.2 \tag{4}$$

$$n = 9\ r = 0.989\ \text{SD}\ 0.1$$

$$\delta\Delta G(\text{aq}) = (3.7 \pm 0.3)\sigma_\alpha + 0.1 \pm 0.2 \tag{5}$$

$$n = 9\ r = 0.975\ \text{SD} = 0.1$$

$$\delta\Delta G(\text{DMSO}) = (1.9 \pm 0.1)\sigma_\alpha + 0.6 \pm 0.1 \tag{6}$$

$$n = 9\ r = 0.992\ \text{SD} = 0.04$$

of the basicities with polarizability potentials, σ_α. ρ values show the dependence of substituent polarizability on the

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basicities in the gas phase and various solutions.

Polarizability attenuation factors (PAF)[27] are used to evaluate the overall substituent polarization effect on a particular system in various solvents relative to the gas phase. PAF is defined as $\rho_\alpha(\text{gas})/\rho_\alpha(\text{sol})$, where ρ_α is the sensitivity of a reaction to substituent charge-induced stabilization. The closer this ratio is to unity means that stabilization of the ion is increasingly gained inherently and not from the solvent. A value of unity has been attained for large, stable, dispersed ions in water and DMSO.[28] For the more localized ions, such as ammonium ions, this value is greater than unity as a result of stability gained from solvation. For primary alkylammonium ions in aqueous medium, which are solvated primarily by three hydrogen bonds to water, it was observed that the substituent polarizability effect (ρ_α) is essentially zero.[29] This implies that stabilization by solvation overwhelms any inherent charged-induced stability.

For tertiary ammonium ion, with only the availability of one hydrogen bond to the solvent, stabilization by the solvent is much less reduced when compared to primary alkylammonium ions. Thus, of the solvents studied, the PAF value of 4.2 (Table II) for AN suggests that, in this solvent, the substituents of dimethylammonium ion have the greatest ability to exert their effect in an inherent stabilization by the polarizability effect, whereas DMSO (PAF = 8.5) shows the least.

The difference in polarizability attenuation factors in various solvents can be explained in terms of the energy involved in charge-induced stabilization given by eq 7,

$$E = -\alpha q^2/2Dr^4 \qquad (7)$$

where D is the dielectric constant on the medium, r is the distance from charge, and q is the distance to the center of material of polarizability, α. The energy is directly proportional to the square of the charge; therefore, due to the changes of relative residual charge, which results primarily from differences in specific solvation in different solvents, the energy will be larger in solvents with low hydrogen bond acceptor ability and vice versa.

The possibility of changes in basicities due to steric effects can be ruled out since there is a poor correlation between $\Delta G°$ and steric substituent constants, E_s.[30] Also, if steric hindrance to protonation or strain of the ion were fully operational, then as the alkyl substituent gets bulkier the basicities should decrease, but instead, the reverse is observed in all cases of solvents studied.

Alkyl-substituted dimethylammonium ions are solvated primarily by hydrogen bonds to the ion from the solvent, which serve to disperse the charge on the ion into the solvent offering some degree of stability to the ion. The ion also gains stability inherently from substituents via charge-induced stabilization. However, this stabilization is dictated by the extent of solvation of the ion. Acetonitrile and water interact the least with the ion, which results in a smaller solvent attenuation factor when compared to DMSO for which the large factor shows a strong interaction.

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Registry No. NMe_3, 75-50-3; $EtNMe_2$, 598-56-1; $PrNMe_2$, 926-63-6; $BuNMe_2$, 927-62-8; *i*-$PrNMe_2$, 996-35-0; *sec*-$BuNMe_2$, 921-04-0; *t*-$BuNMe_2$, 918-02-5; c-$C_6H_{11}NMe_2$, 98-94-2; *t*-$C_5H_{11}NMe_2$, 57757-60-5.

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Columnar Homoconjugation

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Homoconjugative orbital interactions in "columnar" cyclic arrays of π bonds are analyzed through a simple perturbation approach and through ab initio calculations. These interactions lead to Hückel arrays of bonding and antibonding orbitals and should have a net destabilizing effect. Specific compounds (**1**–**3**) which engender columnar homoconjugation consist of n ($n \geq 3$) 1,4-cyclohexadiene units which are connected in a cyclic structure of D_{nh} symmetry. These have been previously referred to as "beltenes". Optimized geometries (STO-2G, RHF) are reported for compounds with n = 3–5. Single point 3-21G calculations have been performed at optimized geometries. The double bonds in these columnar structures are predicted to be significantly pyramidalized. Orbital interactions and estimates for the potential stability of columnar structures are discussed.

Introduction

The concept of homoconjugation has proved fundamental to our understanding of the electronic structure and energetics of neutral and charged organic molecules and transition states.[1] This reflects the recognition that formally nonconjugated portions of molecules can undergo physically and chemically significant interactions. Homoconjugation occurs either through direct "through-

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