damantane (**2**) were calculated by the extended Hückel method,[10] and the symmetries and energy ordering of the highest occupied levels matched the ab initio results obtained for 1,3,5,7-tetramethylenecyclooctane (**3**).

Table I summarizes the ab initio results for the HOMOs and the LUMO. The orbital energy splittings of the four occupied olefinic π bonds due to through-space interactions in the first model (four ethylene units) are 0.06 au (1.6 eV). The magnitude of this energy splitting indicates[11] that the perturbing effect of one ethylenic π system on the other is significant. The lowest unoccupied molecular orbital is ϕ_{b_2} (π^*). The outstanding feature of this orbital is that besides the internal π^* antibonding nature of each olefin unit, a given carbon atom p_π atomic orbital overlaps (bonding) two different neighboring p_π atomic orbitals on adjacent double bonds, thus creating double-concentric overlapping systems of the inner-ring and outer-ring p_π orbitals (Figure 2a). Consequently, the energy of the $\pi \rightarrow \pi^*$ excited state in which this group π^* orbital is occupied is expected to be lowered, leading to a long-wavelength electronic transition in the olefinic chromophore.

Still, the picture is incomplete because the predicted lowest energy transition from Table I, $a_2 \rightarrow b_2$ (B_1), is symmetry forbidden in the D_{2d} point group. In order to study the possible through-bond interactions, four methylene groups were placed at a single carbon–carbon bond distance between adjacent ethylene units to create the 1,3,5,7-tetramethylenecyclooctane **3**. The four $>CH_2$ units form group orbitals made up of the $C-H_2$ σ orbitals, all of which belong to the a_1, b_2, and e symmetry representations in D_{2d}. The new group orbitals of e symmetry interact with the ϕ_e (π) orbital (Figure 2b), and this interaction is sufficient to cause a splitting in the ϕ_e (π) energy level so that it becomes the highest occupied molecular orbital (see Table I). The lowest unoccupied molecular orbital is still the ϕ_{b_2} (π^*) discussed before, and the HOMO → LUMO transition, $e \rightarrow b_2$, is now symmetry allowed.

Recently, Paquette[12,13] et al. studied structures like hexaquinacene, which also constitute a cyclic arrangement of nonconjugated double bonds. Analogous to what was found here, an inversion of the energy ordering of highest occupied levels was also observed, apparently due to an interaction between the olefinic π system with the σ frame. However, a cyclic overlapping p_π orbital system cannot be formed in this case because of the odd number of olefinic double bonds. Therefore, as observed, the UV spectrum of hexaquinacene shows the normal olefinic double-bond wavelength absorption (192 nm).

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Chelation of the Sodium Cation by Polyamines: A Novel Approach to Preferential Solvation, and to the Understanding of Sodium-23 Chemical Shifts and Quadrupolar Coupling Constants

Sir:

Important technological processes such as electrolysis, and liquid–liquid extraction, depend critically upon the influence of dissolved salts on phase equilibria.[1-3] Much effort is applied to obtain a better understanding of the preferential solvation of ions in solvent mixtures.[4,5] NMR methods are especially well-suited for such investigations.[5-10] We report here the marked changes undergone by the ^{23}Na chemical shifts for $NaClO_4$ with the composition of binary solvent mixtures of THF with amines.[11] These changes are analyzed in a novel application of the Hill formalism.[12] With unidentate amines (pyridine, piperidine, pyrrolidine, aniline, propylamine, and isopropylamine), there is equality of the intrinsic equilibrium constants k for the successive steps upon displacement of THF from sodium coordination by one of these ligands.[13] The results, which are entirely consistent with tetracoordination of the sodium cation by these solvents,[13] also indicate proportionality of the k values to the amine chemical shifts. With bidentate amines (ethylenediamine, diethylenetriamine, 1,3-diaminopropane, and cadaverin), entries of the first and second diamine molecules into the sodium coordination shell are independent and equiprobable steps:[14,15] $k_1 = k_3$ and $k_2 = k_4$. This also affords a direct intramolecular measurement of the chelate effect[14] from the molar ratio of the two solvates α_2/α_1 (Scheme I). The apparent equilibrium constants K_i are related to the *intrinsic* equilibrium constants k_i (i = 1–4) through the statistical factors appearing in Scheme I.

Scheme I

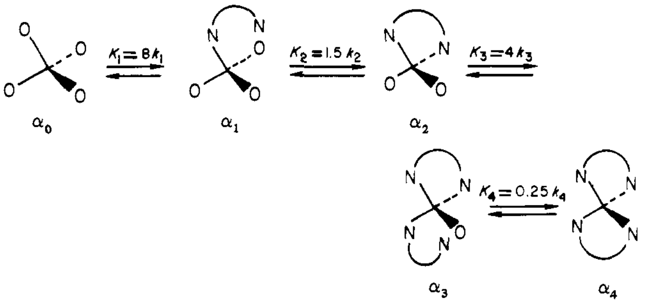

Table I. Values of the Intrinsic Equilibrium Constants (k) for the Successive Replacement of THF Molecules by Amine Solvents[a]

solvent	k_1	k_1k_2	k_3	k_3k_4
cdv	0.9	20	1.1	43
dap	0.4	38	0.5	35
eda	1.5	110	1.1	95

[a] Cadaverin (cdv), 1,3-diaminopropane (dap), and ethylenediamine (eda).

A Hill plot is a representation of ln ($Y/1 - Y$) as a function

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[15] The k values were derived from simultaneous optimization, using the Simplex procedure,[16] of the calculated changes in chemical shifts and in line widths (corrected for the viscosity) with composition of the binary solvent mixture. The full procedure is described in another article.[14]

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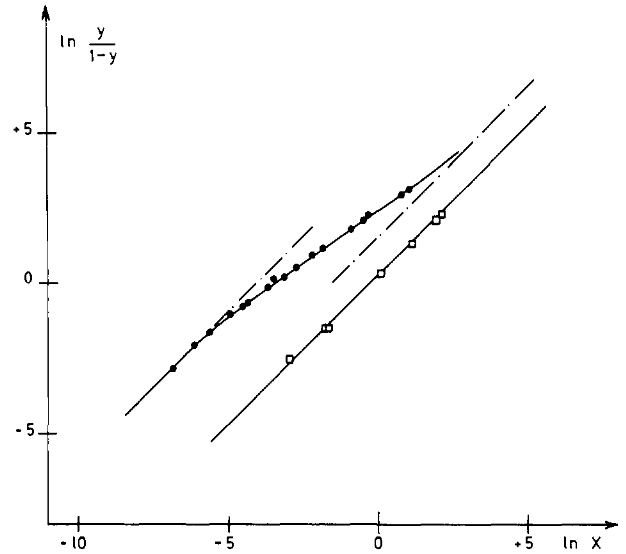

Figure 1. Hill plots of ln $Y/(1-Y)$ vs. ln $[L_A][L_B]$ for $NaClO_4$ (10^{-2} M) in binary mixtures of pyridine/THF (□) and ethylenediamine/THF (●). The theoretical tangents of unit slope are shown for the ethylenediamine/THF system in order to better visualize the curvature of the Hill plot.

of ln $[L_A]/[L_B]$, Y being the fraction of sites on the Na^+ cation occupied by an amine ligand, and L_A and L_B being the THF reference solvent. *In a formal sense*, the fixation of a ligand on the sodium cation is indeed equivalent to the determination of the cooperativity in the binding of a ligand to a biomolecule with four subunits, such as the binding of O_2 to hemoglobin. For *unidentate* ligands,

$$Y = \sum_{i=1}^{4} \frac{i\alpha_i}{4} = \sum_{i=1}^{4} \frac{i\beta_i X^i}{4D} \qquad (1)$$

with $X = [L_A]/[L_B]$; $\beta_i = K_1.K_2...K_i$; $D = \sum_{i=0}{}^4 \beta_i X^i$. For bidentate ligands, the saturation fraction Y is given by eq 2, where R_A and R_B are the molar volumes of the constituents L_A and L_B.

$$Y = \{\beta_1 X + 2\beta_2 X(R_A X + R_B) + 3\beta_3 X^2(R_A X + R_B) + 4\beta_4 X^2(R_A X + R_B)^2\}/\{4[1 + \beta_1 X + \beta_2 X(R_A X + R_B) + \beta_3 X^2(R_A X + R_B) + \beta_4 X^2(R_A X + R_B)^2]\} \qquad (2)$$

A typical linear unit slope Hill plot, as obtained for *each* of the unidentate amines studied,[13] is shown in Figure 1. This finding demonstrates[17] the equality of the intrinsic constants $k_1 = k_2 = k_3 = k_4$, i.e., the absence of cooperativity with such ligands. Conversely, the Hill plots for bidentate ligands[14] (see Figure 1 for a representative example) *deviate strongly from linearity with a unit slope*. For each of these bidentate ligands, analysis of these Hill plots[14,17] shows that, within an uncertainty of ca. 20%, $k_1 = k_3$ and $k_2 = k_4$ (Table I). The successive binding of the first and second amine *molecules* onto Na^+ are independent and equal steps. However, pronounced positive cooperativity occurs in the binding of the first and second nitrogen *atoms* from the same bidentate ligand: measuring this chelate effect by the α_2/α_1 ratio, we find values of 4.5 (cadaverin), 8.0 (1,3-diaminopropane), and 12.0 (ethylenediamine).

This new definition of the chelate effect bypasses the traditional snags, which have made it a controversial topic,[18] i.e., the choice of concentration units,[19-21] and of the appropriate standard states,[22,23] when comparing the equilibrium constants for a unidentate and for the corresponding bidentate ligand.

Our approach bypasses both these problems completely. Since all the results are obtained relative to one and the same reference solvent (THF), we isolate the chelate effect with no ambiguity from data obtained solely on the bidentate ligands. Instead of an *inter*molecular comparison between bidentate and unidentate ligands, we make the more appropriate *intra*molecular comparison between unity and the second *intrinsic* binding constants for a bidentate ligand, corrected for the presence of the reference solvent (K_2R_B).

Two other features of our results[13,14] deserve mention here. With the *unidentate* amines, we find that intrinsic equilibrium constants k are simply proportional to the ^{23}Na chemical shifts measured for Na^+ in the pure amine solvents. It may appear surprising that a thermodynamic quantity (k) is related to a chemical shift, i.e., to an electronic distribution. However, there is precedence for such an observation: the ^{23}Na chemical shifts are also linearly correlated to another thermodynamic quantity, the Gutmann donicity of the solvent, when a salt such as $NaBPh_4$ is dissolved in a series of oxygen- and nitrogen-donor solvents.[24] The strength of the (predominantly electrostatic) chemical bond between Na^+ and nitrogen increases with nitrogen basicity, which is measured indirectly by the ^{23}Na chemical shift, and obeys the sequence aniline < pyridine < quinoline < pyrrolidine < benzylamine < propylamine < isopropylamine.

Furthermore, four clean straight lines arise when plotting the square root of the line widths reduced to unit viscosity $(\nu_i^*)^{1/2}$ against the chemical shift δ_i for each of the four solvates (i = 1-4).[25] Such a linearity is that predicted from the Deverell approach,[26] in which the quadrupolar coupling constant $\chi = e^2qQ/\hbar$ is proportional to the paramagnetic part of the shielding constant σ_p, as already observed experimentally for ^{23}Na in sodium cryptates.[27] These four $(\nu_i^*)^{1/2}$ vs. δ_i lines converge to a single focal point, corresponding to the *diamagnetic* part of the shielding constant σ_d. This amounts to a direct experimental determination of σ_d for Na^+ ions dissolved in mixtures of THF and amines: it differs by ca. −11 ppm from that for the hexaquo ion.

Thus, one may characterize fully, using the Hill procedure, each distinct solvate from its position in the ^{23}Na (δ,ν^*) configuration space. This mapping reduces into a single axis because chemical shifts and (line widths)$^{1/2}$ are proportional to one another. In this manner, an abundant array of hitherto poorly understood facts begins to be put into satisfying order.

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Mediated Photochemical Oxidative Dimerization

Sir:

Despite the efficiency of electron ejection as a primary photoprocess in carbanion photochemistry,[1] a variety of anions resist

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