that cannot undergo ring inversion. These hosts are described as being $g^+g^-g^+g^-g^+g^-$. (4) Finally, **5** contains an 18-membered ring which cannot invert nor can it attain as good a complexing conformation as the "ideal" one. This host has a $g^+g^-g^-g^+g^-g^+/g^-g^+g^+g^-g^+g^-$ structure which is a racemic modification. Inspection of the data in Tables I and II indicates that the magnitude of the $\Delta\Delta G$ values can be correlated qualitatively[15,22] with the above stereochemical classifications as follows:

$$g^+g^-g^-g^+g^-g^+/g^-g^+g^+g^-g^+g^- > g^+g^-g^+g^-g^+g^-$$
$$> g^+g^-g^+g^-g^+g^- \rightleftharpoons g^-g^+g^-g^+g^-g^+ > g^\pm g^\mp g^\pm g^\mp g^\pm g^\mp$$
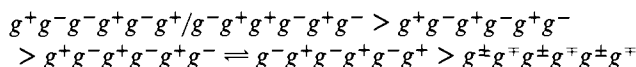
One feature emerges clearly from this analysis. The denial to **5** of binding sites which act simultaneously can provide an explanation as to why it forms weaker complexes than **4**. Recently, attention has been drawn[24] to the correspondence between the complexing ability of crown ethers—and their open-chain analogues—and the catalytic effect observed during their metal templated syntheses. There is also evidence, however, that the directional characteristics of noncovalent bonds can influence diastereoisomeric ratios in templated syntheses of crown ethers by cations. In the attempted synthesis of **4** and **5** by condensation of (±)-*trans*-2,2'-(1,2-cyclohexylidene)dioxyethanol (**9**) with its bistosylate (**10**) in benzene in the presence of *t*-BuOK, *only* **4** was isolated with a comment[25] about "the marked tendency for pairing of (+) with (−) in the cyclisation to give the *meso* form".

The fact that large $\Delta\Delta G$ values are observed for both metal and *t*-BuNH$_3^+$ ions suggests that the contributions from ion–dipole interactions,[26] as well as those from hydrogen bonding, are sensitive to small conformational differences in the hosts even though an all-gauche framework is available. By the same token, it should be possible to build more highly structured complexes by exercising control over synthetic host conformations. The ultimate in sophistication in synthetic host design will probably be realized by exercising configurational controls to locate constitutional features in particular conformational environments.[17] *It seems not only reasonable but logical that constitution, configuration, and conformation must define the structures of noncovalently bonded species in much the same way as they define the structures of covalently bonded species!*

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(13) Steric hindrance toward approach to one of the faces of **2** could be partly

(14) Available X-ray crystal structure data (M. R. Truter, *Struct. Bonding (Berlin)*, **16**, 71 (1973); J. D. Dunitz, M. Dobler, P. Seiler, and R. P. Phizackerley, *Acta Crystallogr., Sect. B*, **30**, 2733 (1974), and short structural papers immediately following; I. Goldberg, *ibid.*, **31**, 754, 2592 (1975)) indicate that complexes of 18-crown-6 and its derivatives in the solid state prefer, if possible, to assume conformations in which the oxygen atoms are displaced alternately above and below the mean plane of the ring. We shall refer to this general conformational type as an "*all-gauche*-OCH$_2$CH$_2$O" or "ideal" conformation. In most cases, this situation represents considerable conformational changes to the uncomplexed crowns in the solid state (see, for example, N. K. Dalley, J. S. Smith, S. B. Larson, J. J. Christensen, and R. M. Izatt, *J. Chem. Soc., Chem. Commun.*, 43 (1975); N. A. Bailey and S. Chidlow, unpublished results reported in ref 3; N. K. Dalley, D. E. Smith, R. M. Izatt, and J. J. Christensen, *J. Chem. Soc., Chem. Commun.*, 90 (1972); M. Mercer and M. R. Truter, *J. Chem. Soc., Dalton Trans.*, 2215 (1973)) in order that they can act efficiently as ligands. There is good evidence (J. Dale and P. O. Kristiansen, *Acta Chem. Scand.*, **26**, 1471 (1972); J. Dale, *Tetrahedron*, **30**, 1683 (1974); D. Live and S. I. Chan, *J. Am. Chem. Soc.*, **98**, 3769 (1976)) that the same phenomenon is characteristic of the conformations of complexed and uncomplexed crown ethers in solution.
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(20) The ^{1}H NMR spectrum of **1** in CHFCl$_2$ did not show any temperature dependence on cooling to −130 °C (J. Dale and P. O. Kristiansen, *Chem. Commun.*, 670 (1971)).
(21) The decomplexation of the *t*-BuNH$_3^+$PF$_6^-$ complex of **1** is a relatively slow process with an E_a of 20.4 kcal/mol reported in chloroform at 20 °C (F. de Jong, D. N. Reinhoudt, C. J. Smit, and R. Huis, *Tetrahedron Lett.*, 4783 (1976)). Alkaline earth metal cationic complexes—but not alkali metal ones—in the presence of excess of **1** showed (J. Dale, *Tetrahedron*, **30**, 1683 (1974)) separate signals for the ring protons in the ^{1}H NMR spectrum at room temperature.
(22) 1,2-Cis and 1,2-trans fusion of six-membered rings on to the 18-crown-6 constitution can be expected (C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.*, **4**, 39 (1969)) to cause small and different conformational perturbations to the macroring which in turn will influence the cooperativity of the noncovalent bonds in cationic complexes. In other words, the torsional angles associated with the bis(methylenedioxy) and substituted bis(methylenedioxy) units will vary in the "ideal" complexing conformations of **2**-α-D-**8**.
(23) The barrier to inversion of the 18-membered ring is expected to be of the order of 11 kcal/mol, i.e., that which has been observed (S. Wolfe and J. R. Campbell, *Chem. Commun.*, 874 (1967)) for cis-1,2-disubstituted cyclohexanes.
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(26) We recognize strong parallels between the highly directional characteristics of noncovalent bonds and the severe geometrical restrictions which govern the approach of reactant centers in, e.g., S$_N$2 displacements (L. Tenud, S. Farooq, J. Seibl, and A. Eschenmoser, *Helv. Chim. Acta*, **53**, 2059 (1970)), carbonyl additions (H. B. Burgi, J. D. Dunitz, J. M. Lehn, and G. Wipff, *Tetrahedron*, **30**, 1563 (1974)), and ring closures (J. E. Baldwin, *Ciba Found. Symp. 53*, (*new ser.*), 1978, 85 (1978)).

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Comment on the Communication "Photoionization by Green Light in Micellar Solution"

Sir:

A recent communication by Thomas and Piciulo[1] described and interpreted the dependence of the photoionization yield

of 3-aminoperylene on the intensity of 530-nm laser pulses. Plots of initial hydrated electron yield vs. the square of the laser intensity gave straight lines for aminoperylene in nonionic or cationic micelle solutions; yet in aqueous sodium dodecyl sulfate (SDS) the same electron yield was observed to vary linearly with laser intensity. These data were the basis for concluding that the photoionization of aminoperylene is biphotonic in nonpolar and cationic micelles and yet monophotonic in anionic micelles. The authors went on to mention that such a monophotonic ionization could be applied to the storage of solar energy. These conclusions should not be accepted uncritically, since a more thorough analysis of similar data from closely analogous systems indicates that the change from biphotonic to monophotonic may be apparent and not real.

Several studies of intensity effects in photoionization have noted that only at low excitation intensities should one expect strictly linear and quadratic dependence of ionization yield on intensity for monophotonic and biphotonic ionizations, respectively.[2-4] Clearly, at high enough intensities, saturation will occur. In the case of biphotonic ionization, an intermediate, quasi-linear region has been described[2] which depends critically on the relative magnitudes of the absorption coefficients of the ground state and the intermediate state involved in the photoionization. This quasi-linear region is most apparent when the two absorption coefficients differ considerably, and so the photoionization is limited by the weaker absorption at moderate intensities. Changes in the relative efficiency of the two photoexcitation steps could occur not only through changes in absorption coefficients, but also through changes in the processes competing with ionization, e.g., deactivation of the excited state and recombination of the ions.

It is commonly claimed that variation in ion-recombination probability is a major source of the medium dependence of photoionization efficiencies.[5-7] Highly efficient photoionization of aromatic solutes in SDS has been attributed to reduced ion recombination caused by the repulsion of the hydrated electron from the anionic micelle that contains the geminate cation.[8]

Recent results from our laboratory[9] using 347-nm laser photolysis of pyrene solutions offer a further example of the effects of ion recombination on the intensity dependence of photoionization in micellar solutions and in pure polar liquids. The apparatus and techniques have been described.[3] Figure 1a shows the dependence of the solvated electron yield on laser intensity in aqueous SDS and in methanol. At the lowest energies, methanolic pyrene shows the nonlinearity characteristic of a biphotonic process, while saturation is evident at higher intensities. In aqueous SDS, however, the hydrated electron yield increases linearly in the measured range of intensities. The intensity dependence of fluorescence is shown in Figure 1b for the same two systems. Fluorescence from methanolic pyrene increases toward saturation at laser intensities larger than 150 mJ/pulse, while the emission intensity from pyrene in aqueous SDS has a maximum near 50 mJ and decreases at higher intensities.

The interpretation that pyrene photoionization is biphotonic in methanol but monophotonic in aqueous SDS is not consistent with the fluorescence data. The fluorescent excited singlet state has been shown to be the intermediate state in the biphotonic ionization observed in methanol,[3] and so the fluorescence intensity is a measure of the concentration of intermediates at the end of the laser pulse. The shapes of the ion and excited-state formation curves in methanol are characteristic of a biphotonic ionization in which the excitation efficiencies of the two steps are similar.[2] The qualitatively different curves observed with aqueous SDS can still be associated with a biphotonic mechanism if the second step is considerably more efficient than the first. In this case, not only does the quasi-linear dependence of the ionization on excitation intensity
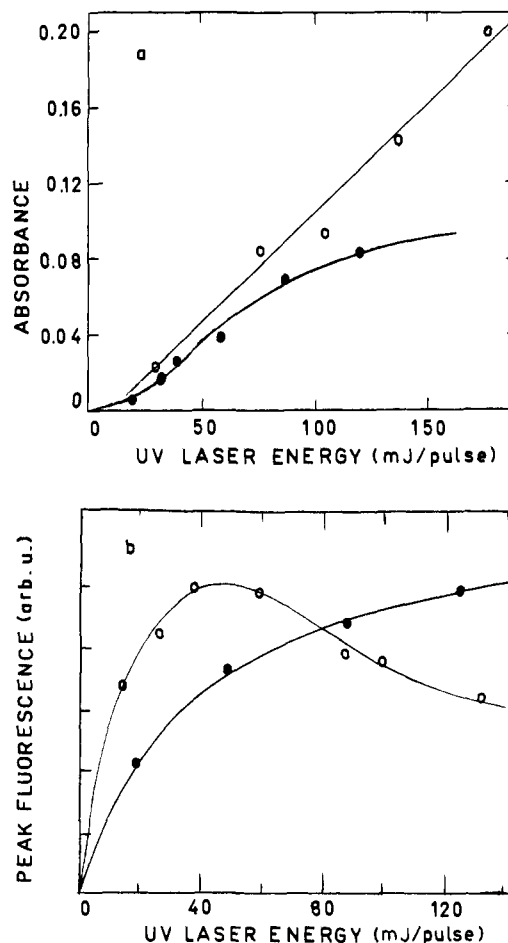

Figure 1. Plots of laser-intensity dependence of ion and excited-state yields from 5.7×10^{-5} M pyrene in methanol (●), and 3.3×10^{-5} M pyrene in 0.04 M SDS (○): (a) absorbance at 590 nm following 20-ns laser excitation measures the initial yield of solvated electrons in methanol, and hydrated electrons in aqueous SDS; (b) fluorescence intensity at 400 nm measures excited singlet yield at the end of laser excitation. Arbitrary units are not the same for methanol and SDS data.

occur, but the decline in the concentration of the intermediate is explained. During the later part of the excitation pulse, the previously formed excited-state molecules are ionized faster than they can be replaced by excitation of ground-state molecules. The reason for the increased efficiency of the second step in SDS may be either an increase in the excited-state absorption coefficient or a decrease in the ion-recombination probability; the latter is adequate to explain the data, although the available information is insufficient to preclude a contribution from the former.

Comparison of the photoionizations of pyrene and aminoperylene is warranted despite differences in the excited states involved and the wavelengths of excitation. Evidence from aminoperylene photolyses[1] has shown that in cationic and neutral micelles the n-π* state populated by monophotonic excitation can be ionized by a second green photon. Since a sequential biphotonic mechanism is operative in these solvent systems, the comparison with pyrene's yield/intensity relationships is not unreasonable.

In conclusion, the efficacy of anionic micelles in enhancing the photoionization efficiency of aromatic solutes can be explained by the inhibition of ion recombination, which can lead to an apparent change in the order of the photoionization from biphotonic to monophotonic. This interpretation seems not to have been considered by Thomas. The available evidence does not conclusively show the photoionization of aminoperylene in SDS to be monophotonic. More critical tests of the order of the photoionization include measurement of the dependence

of aminoperylene's fluorescence intensity on the pulsed excitation energy in the high-intensity region of 50-150 mJ/pulse; comparison of photoionization quantum efficiencies measured at high (laser) and low (sunlight) intensities; and determination of the intensity dependence of the photoionization yield at intensities considerably below those already studied. Until such results are available, the most cautious interpretation of the data is that the photoionization of aminoperylene at 530 nm is biphotonic.

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Proton, Deuterium, and Tritium Nuclear Magnetic Resonance of Intramolecular Hydrogen Bonds. Isotope Effects and the Shape of the Potential Energy Function

Sir:

The difference in chemical behavior of the three isotopes of hydrogen is mainly caused by the difference in their masses, which in turn influences the vibrational motions and the zero-point vibrational energies. Thus, from a measurement of an isotope effect in some property, one can make deductions about the shape of potential energy surfaces. This has been extensively exploited for elucidating chemical reaction paths from kinetic data.[1] Here we report the usefulness of ^{1}H, ^{2}H, and ^{3}H NMR as a means of studying the shape of the potential energy surface in the vicinity of the equilibrium position.

Primary isotope effects[2] of the NMR chemical shifts of ^{2}H and ^{3}H in organic compounds are usually very small, in the case of ^{3}H usually <0.03 ppm for tritium bound to sp^2- or sp^3-type carbons.[3,4] Exceptions to this general rule are systems with relatively strong hydrogen bonds, for which deuterium isotope effects, $\Delta\delta(^1H, {}^2H)$, as large as 0.6 ppm have been found.[5-7] We have previously reported the results of a systematic NMR study of the deuterium isotope effect, $\Delta\delta(^1H, {}^2H)$, in a series of systems all containing hydrogen bonds of the type O--H--O.[6] A correlation between the isotope effect and the value of the chemical shift, $\delta(^1H)$, was observed for the hydrogen-bonded nucleus.

The only conceivable source of isotope effects on chemical shifts within the Born–Oppenheimer approximation lies in the isotopes mass dependence of vibrational motion. The quantities that determine the magnitude are the vibrational wave functions, ψ, for the ground state (and possibly low-lying excited vibrational states) and the variation of the chemical shift, δ, with the nuclear configuration. Neglecting thermal averaging we have

$$\Delta\delta(^1H, {}^kH) = \int |\psi(^1H)|^2\delta \, d\tau$$
$$- \int |\psi(^kH)|^2\delta \, d\tau \ (k = 2 \text{ or } 3) \quad (1)$$
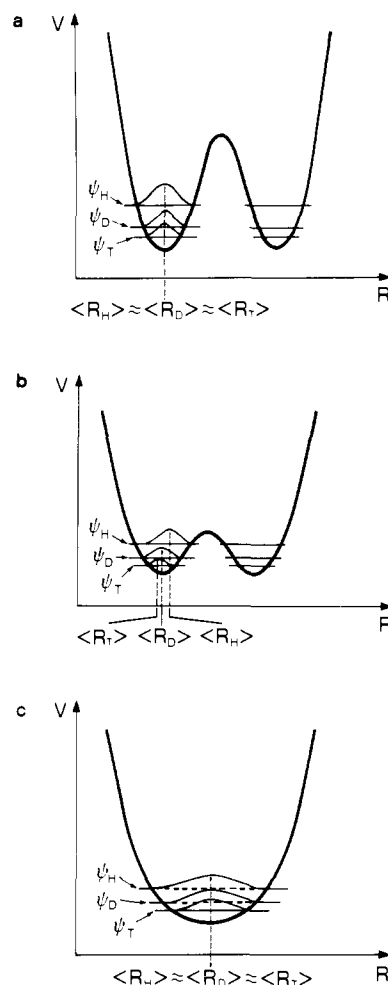

Figure 1. Schematic illustration of the position of the hydrogen isotopes, in the zero point vibrational levels, for different types of hydrogen bond potential functions: (a) a double minimum potential with a high central barrier and low anharmonicity at the potential minima; (b) a double minimum potential with a low central barrier and high anharmonicity at the potential minima; (c) a single minimum potential.

The variation of the proton chemical shift with nuclear distance in hydrogen-bonded systems is such that the proton is deshielded as the proton moves toward the midpoint between the heavy atoms (O, N, or F) of the bond.[8,9] This fact can be used to correlate the chemical shift with the shape of the hydrogen bond potential. In Figure 1 we have schematically illustrated three types of potentials that may be encountered in hydrogen-bonded systems.

In the case of weak hydrogen bonds (Figure 1a) the potential minima should be deep with a low anharmonicity approaching that of an ordinary covalent O-H bond. The effective equilibrium positions of the hydrogen isotopes, $\langle R \rangle$, will then be closely similar for ^{1}H, ^{2}H, and ^{3}H. In this case the isotope effect on the chemical shift is expected to be zero in the first approximation. Experimentally this situation should be encountered in, for example, water or alcohols. For stronger and shorter hydrogen bonds (Figure 1b) the potential minima draw closer together with an accompanying decrease of the central barrier and increase in the anharmonicity of the potential. The equilibrium positions will now be different—we expect $\langle R_H \rangle > \langle R_D \rangle > \langle R_T \rangle$ (assuming R to be measured from the nearest heavy atom of the hydrogen bond). In this case we will observe positive isotope effects in the chemical shift—larger for ^{3}H than for ^{2}H.

In the case of extremely strong and short hydrogen bonds we may encounter the situation shown in Figure 1c.[10] Here the potential is symmetrical and the equilibrium distances $\langle R_H \rangle$,