$$\frac{\partial E}{\partial C_{ip,i\alpha}} = \langle \chi_{ip} | F - \rho F | \tilde{\varphi}_{i\alpha} \rangle = 0 \qquad (3)$$

here F denotes the Fock matrix and ρ the one-particle density matrix.

Payne's equations[5] read

$$\langle \chi_{ip} | (1 - \rho + \rho_i) F (1 - \rho + \rho_i) | \varphi_{i\alpha} \rangle = \epsilon_{i\alpha} \langle \chi_{ip} | \varphi_{i\alpha} \rangle \qquad (4)$$

with

$$\rho_i = \sum_\alpha |\varphi_{i\alpha}\rangle \langle \varphi_{i\alpha}|$$

They are equivalent to

$$\langle \chi_{ip} | F - \rho F | \varphi_{i\alpha} \rangle = 0 \qquad (5)$$

The conditions of eq 3 and eq 5 lead to the same result only in two cases: (a) if orbitals from different subsystems are mutually orthogonal, or (b) if a common basis set is used for all subsystems. For nonorthogonal orbitals, expanded in different local basis sets, neither a nor b holds, so that Payne's equations[5] do not yield the determinant with the lowest energy, contrary to his assertion. The reason for this discrepancy is as follows. In the derivation of eq 4, Payne uses a Schmidt orthogonalization

$$|\varphi'_{j\beta}\rangle = \sum_{k\gamma} |\varphi_{k\gamma}\rangle W_{k\gamma,j\beta} \qquad (6)$$

which leaves $|\varphi_{i\alpha}\rangle$ invariant.

The $i\alpha$th column of W therefore has the structure $W_{j\beta,i\alpha} = \delta_{j\beta,i\alpha}$; clearly, this is also the case for the $i\alpha$th column of the inverse transformation W^{-1} and for the $i\alpha$th row of $(W^{-1})^T$. This structure is, in general, not the correct one, however, for the $i\alpha$th column of $(W^{-1})^T$, contrary to Payne's statement. Payne's statement holds for orthogonal transformations, where $(W^{-1})^T = W$, but the transformation in eq 6 from nonorthogonal to orthogonal orbitals is, of course, not orthogonal. The transformation eq 6 does not change the Slater determinant, nor the orbital $|\varphi_{i\alpha}\rangle$, but it does change the partial derivatives $\partial E / \partial C_{ip,i\alpha}$.

In order to illustrate these points we have done a calculation for CH_4 using a modified 4-31G basis set.[6] In Table I results from Payne's equations (eq 4) are compared with values from a steepest-descent method[7] which is based on eq 3. The total energy from Payne's method is, by ~7 kcal, higher than the lowest which can be obtained with the given local basis sets. It is open to question if the deviations from the lowest variational energies are the reason for the ill-behaved rotational barrier heights in Payne's paper.[5]

We want to conclude with a remark concerning the computational effort. With Payne's method no computational simplification is achieved with respect to the conventional HF–LCAO method. Actually, the diagonalization time is smaller, because the modified Fock matrix in eq 4 is block diagonal, but this is compensated for by an additional effort in constructing the modified matrix. The direct calculation of localized nonorthogonal orbitals in connection with the use of local basis sets leads to a considerable computational simplification, however, if approximations for interactions between different subsystems are introduced into the method[3,7]

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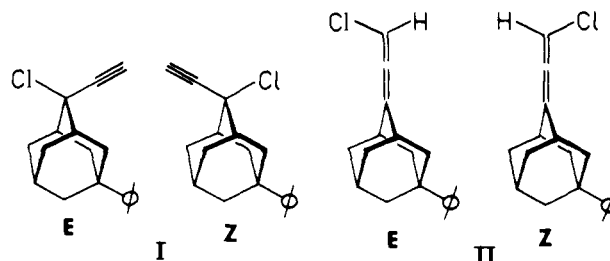
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Shape and Inversion of an Allenic Anion[1]

Sir:

We recently reported[2] the synthesis and configurational assignment of several epimeric pairs of 1,4- (or 2,5-) disubstituted adamantanes, among them the acetylenes I and the allenes II. It was noted that the availability of these pairs would
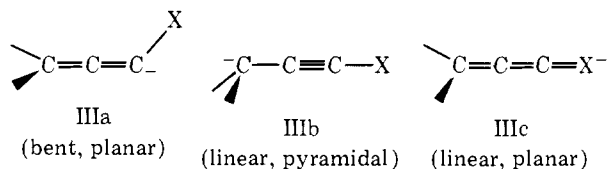

make possible a number of stereochemical studies, and we report here the first of these investigations, which is concerned with the shape of allenic anions. According to one published report,[3] α-haloallenic anions should be linear, but doubt was expressed in another.[4] Information on this point may become important since allenic anions have begun to play a role in synthesis.[5] The conclusion of the present work is that the anions of II are bent, and that the inversion barrier between them must be at least 22 kcal/mol.

Treatment of 0.3 M solutions of (Z)-I with catalytic amounts of t-BuOK in t-BuOD at 30 °C leads to complete exchange within seconds, as shown by ^{1}H NMR; under the same conditions, (E)-II exchanges its allenic proton with a half-life of 4 min. Similar data apply to the "norphenyl" parent compounds. Again under the same conditions, (E)- and (Z)-II do not interconvert significantly; thus, the (E)-II solution contains only 2% of the epimer after 4 h. Clearly, the anions of II must be bent, with a rate constant of epimerization ~2000 times slower than that of exchange, which fixes the free-energy barrier ~5 kcal/mol above that of the proton abstraction; the latter equals 21.5 kcal/mol. The very low degree of epimerization is not due to a lopsided equilibrium ratio as may be seen by the following experiment.

The slow epimerization is accompanied by base-promoted solvolysis (presumably by way of the corresponding carbene) which is several times faster. At 100 °C, if solutions 0.003 M in both substrate and base are allowed 30 min for reaction, the 35% (E)-II which remains unsolvolyzed has epimerized to the extent of 20%, and, similarly, the 45% (Z)-II that has not yet decomposed contains 13% (E)-II. From the approach to equilibrium, one can calculate[6] that K equals 1.08 in favor of the Z isomer. The time dependence of the epimerization processes, corrected for solvolysis, gives $\Delta G^\ddagger = 27$ kcal/mol.

The barriers calculated above are those in the energy profiles beginning from the substrates. In order to determine the epimerization barrier of the anion itself, the pK_a must be estimated; this can be done as follows. For acetylene, pK_a values ranging from 19 to 25 have been reported;[7] if the chlorine inductive effect (compare acetic acid, pK_a of 4.8, and chloroacetic acid, 2.8) is taken into account, this range for I would

be 17–23. The slower rate of D exchange of II means that its pK_a is in excess of that of the acetylene. The pK_a value of ethylene is 36.5; for II, the inductive effect of α-chlorine substitution (compare water, 16, and hypochlorous acid, 7.5) and the resonance effect of the cumulative double bond (compare ethane, 42, and propene, allylic H, 36) demand corrections that lead us to estimate its value as 22. Since *tert*-butyl alcohol has a pK_a of 19, the barrier to epimerization of the anions at 100 °C is 27–2.3 RT (22–19), or 22 kcal/mol. The precise pK_a values, even those of the analogues chosen, or, for that matter, the simple additivity assumed above, are still far from settled issues,[8] and hence an uncertainty of several kilocalories/mole in this barrier must be accepted. On the other hand, however, it should be emphasized that the mechanism for the epimerization is not known; it *may* occur via inversion of the bent anion, but alternatives—such as rotation, or even carbene

IIIa
(bent, planar)

IIIb
(linear, pyramidal)

IIIc
(linear, planar)

formation and return of the leaving group—are not ruled out. This means that the result of 22 kcal/mol is the *minimum barrier for inversion.*

It should be noted that, while our results are perhaps most conveniently discussed in terms of bent anions, strictly speaking the conclusion should be couched in terms of the anions' capability of maintaining configuration. Alternately, this capability could be due to some other unequal feature in the environment on the two sides of the molecule; the difference could involve a counterion, or a hydrogen-bonded solvent molecule, for example. The rather severe conditions, however, lead us to consider such possibilities less likely.

Another question that may be raised concerns the shape of unsubstituted allenic anions. Beside the allenic and acetylenic[9] structures (IIIa and IIIb, respectively), structure IIIc surely plays a role when X is chlorine; thus, Brower[10] has attributed the lack of electrostriction of the trichloromethide anion to delocalization of charge into the chlorine d orbitals. On the other hand, chlorine substitution surely increases the weight of structure IIIa over that of IIIb, and so conflicting arguments can be made for the effect of such substitution on the shape. Added to this must be some uncertainty about the effect of the chlorine atom on the hybridization of the unshared pair if it is largely localized as in IIIa. Our own inclination is that the barrier in the parent allenes will be lower; we tend to this conjecture primarily on the known effect of N-chlorine substitution on the barrier of inversion in aziridines.[11] However, we also feel that the barrier found in the present work is so large that the replacement of the chlorine atom by hydrogen or an alkyl group will certainly not reduce it to zero.

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Temperature Dependence of Rotational Correlation Times for an Inverse Temperature Transition. A Fundamental Characterization

Sir:

Inverse temperature transitions, for example of polypeptides in aqueous solutions, are commonly discussed in terms of entropy and the Second Law of Thermodynamics. By the Second Law the disorder of the total system, polypeptide plus water, must increase with increases in temperature. Where various physical methods argue for an increase in order of a polypeptide with an increase in temperature, i.e., for an inverse temperature transition, it is inferred that relatively ordered water surrounding exposed hydrophobic groups becomes less ordered bulk water concomitant with association of the hydrophobic side chains.[1–3]

Previous studies on the polytetrapeptide of tropoelastin, HCO-$(Val_1$-Pro_2-Gly_3-$Gly_4)_n$-Val-OMe, have led to the proposal that at 60 °C a specific additional intramolecular hydrogen bonding occurs.[4] Formation of this hydrogen bond structurally places the hydrophobic Val and Pro side chains in juxtaposition,[5] the implication being that this is the hydrophobic association attending the intramolecular inverse temperature transition. As a means of verifying this proposed association, proton–proton nuclear Overhauser enhancement studies were recently reported which show that the proximity of the Pro_2 δ-CH_2 protons and the Val_1 γ-CH_3 protons becomes dramatically increased at elevated temperature.[6] Thus the nuclear Overhauser effect provided direct experimental evidence for hydrophobic side-chain association attending an inverse temperature transition.

As the molecular expression of temperature is motion—vibrational, rotational, and translational—an increase in temperature means an increase in molecular motion. A corollary, therefore, of an inverse temperature transition would, in this fundamental sense, be a decrease in molecular motion with an increase in temperature. We report that spin-lattice relaxation studies on the polytetrapeptide of tropoelastin, the molecular structure referred to above, clearly demonstrate a decrease in mobility of the polytetrapeptide on going from 60 to 70 °C.

The ^{13}C spin-lattice relaxation times were measured on a JEOL FX-100 pulse Fourier transform NMR spectrometer using the inversion recovery method ($180°$–τ–$90°$ pulse sequence). A 44-μs pulse width was used for 180° tilt of the ^{13}C magnetization vector and a 22-μs pulse width for 90° tilt. Spectra were collected on the spectrometer using the deuterium signal from coaxial D_2O as an internal lock and broad band