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SCF CALCULATIONS OF ACIDITIES OF DISTORTED METHANES

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The kinetic acidities of cycloalkanes have been shown to vary systematically with ring size and to correlate with measures of s-character of the C-H bond.[1] As a theoretical model of this effect suitable for ab initio calculation we studied the deprotonation of distorted methanes in which one HCH bond angle was varied and the other HCH was retained at the tetrahedral value. The corresponding carbanion was obtained by removing a proton from the unperturbed methylene group. By constraining one HCH bond angle to be the same in hydrocarbon and conjugate base, we provide a model for the bond angle constraint in ionization of a cycloalkane. Indeed, this model is the simplest possible SCF-MO model of a physical organic concept that is normally couched in terms of hybrid components of isolated 2-center bonds. In keeping with these deliberate constraints of simplicity, the ab initio SCF calculations were performed at the minimum basis STO-4G level[2] using an isotropic sp basis set (Iso/sp)[3] with the C(1s), C(2s,2p), H(1s) exponents and the C-H bond distance taken, respectively, for methane as 5.67, 1.76, 1.17, 1.089 Å, and for methyl anion as 5.67, 1.547, 1.078 and 1.189 Å.[4]

The results of the calculations are summarized in Table I and Fig. 1. As expected, all distorted methanes are less stable than tetrahedral methane but the optimum HCH angle for methyl anion is less than tetrahedral.[3] The changes are such that pinching a HCH angle in methane from 113.5° to 90.4° results in a monotonic increase in acidity (decrease in the calculated proton affinity of the corresponding methyl anion).

The usual interpretation of this effect, as given in terms of the increasing s-character of the exocyclic C-H bond with decreasing ring size, is also reflected

TABLE I. Energies of Distorted Methane and Methyl Anion

HCH angle	Methane energy, Hartree	Methyl anion, energy Hartree	Proton affinity of methyl anion Kcal/mole
90.4°	-39.9669	-39.2084	475.9
97.2°	-39.9922	-39.2123	489.3
103.4°	-40.0068	-39.2082	501.0
108.9°	-40.0121	-39.1987	510.3
113.5°	-40.0089	-39.1865	515.9

TABLE II. s-Character of Distorted Methane C-H Bonds

	% s-Character of distorted C-H		% s-Character of undistorted C-H	
HCH angle	Overlap Population	Localization	Overlap Population	Localization
90.4°	23.85	23.67	37.49	39.72
97.2°	25.17	24.90	34.53	36.73
103.4°	26.38	26.23	31.42	32.61
108.9°	27.56	27.69	28.06	28.35
113.5°	28.75	29.32	24.40	23.31

in C-H wave functions of the distorted methanes. One definition of the fraction of s-character of a C-H bond is given as the ratio of s-overlap population from carbon to the total s+p overlap population:[3]

$$S(C/C\text{-}H) = \sum_{\substack{i=s \text{ on } C \\ j=s \text{ on } H}} P_{ij} \Big/ \sum_{\substack{i=s,p \text{ on } C \\ j=s \text{ on } H}} P_{ij}$$

Table II shows a monotonic change of the calculated s-character of an undistorted C-H as expected when the other HCH angle is varied. Correspondingly, the p-character of a distorted C-H bond increases as the HCH bond angle decreases.

Alternatively, s and p character can be determined directly from localized C-H bonds. Table II also contains results obtained by applying the localization criterion of Boys.[5] These results were obtained by localizing the STO-4G Iso/sp eigen functions of the distorted methanes using a computer program written by Dr. J. Hashmall. The results of this approach parallel the results obtained by the population analysis definition.

Despite the known limitations of minimum basis sets and of Hartree-Fock calculations of anions, the present simple system provides an effective model of a well-known physical-organic phenomenon and provides a quantum mechanical interpretation. As one bond angle of a tetravalent carbon is reduced an exocyclic C-H bond gains s-character and becomes more acidic.

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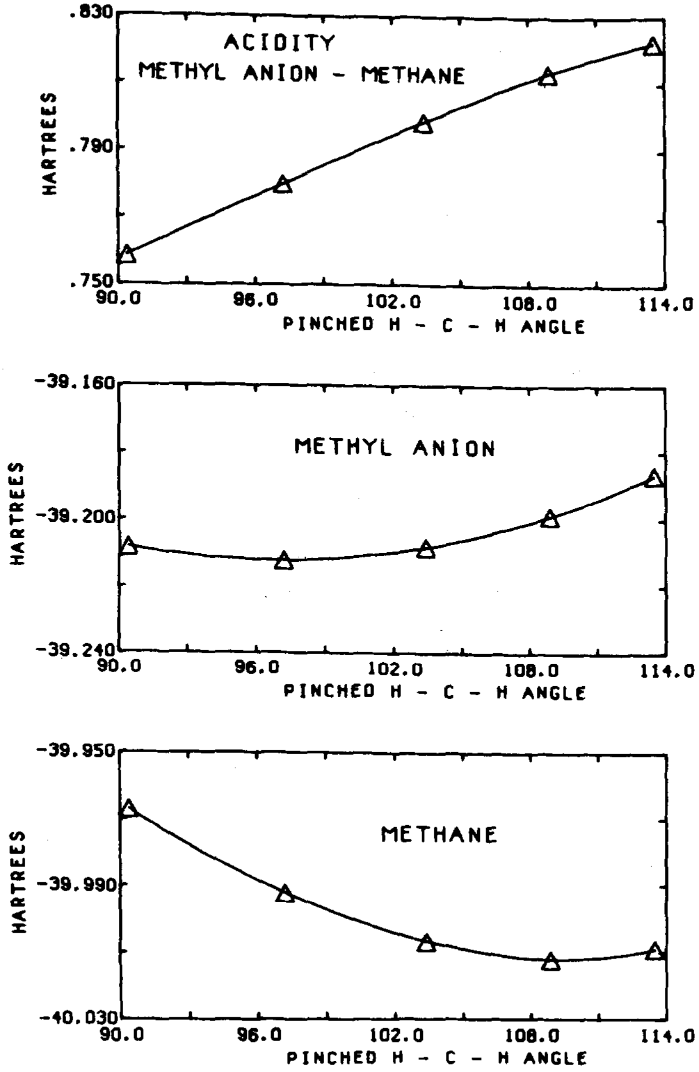

Fig. 1. Energies of methane and methyl anion with variation of one HCH bond angle.