Molecular Orbital Theory of the Electronic Structure of Organic Compounds. VI. Geometries and Energies of Small Hydrocarbons

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Abstract: An *ab initio* molecular orbital study of the geometries and energies of the neutral and positively charged C_1 and C_2 hydrocarbons is presented. Two basis sets of Gaussian-type functions are used. The first is minimal, consisting of atomic orbitals closely related to Slater-type (exponential) orbitals (STO). Each STO is fit in a least-squares sense by three Gaussians (STO-3G). The second basis (4-31G) is an extended set, containing more than the minimal number of atomic functions. These have been chosen to minimize the calculated energy of the ground-state atom. Agreement between calculated and equilibrium geometries is good. Molecular dissociation energies, proton affinities, and ionization potentials are moderately well reproduced, the extended basis being consistently superior.

There have been many *ab initio* molecular orbital studies of small hydrocarbons,[1,2] some involving limited variation of certain geometrical parameters. However, there has been no systematic study of theoretical equilibrium geometries and relative energies at a uniform level of approximation. The first aim of this paper is to present such a study of all C_1 and C_2 hydrocarbons and their positive ions, using a minimal basis of Gaussian-fitted Slater-type orbitals (STO-3G).[3] In addition, we report a partial study of the same molecules with an extended basis set of contracted Gaussian functions.

Methods

Standard quantum mechanical methods are used. The many-electron wave function is constructed using molecular orbitals which are linear combinations of basis functions ϕ_μ. The coefficients are determined from the Roothaan[4] and Pople–Nesbet[5] equations for closed- and open-shell systems, respectively. These lead to self-consistent total energies for each nuclear configuration considered.

Two basis sets ϕ_μ are used. The first (STO-3G) is closely related to a minimal basis (1s,2s,2p for C, 1s for H) of Slater-type (exponential) atomic orbitals with radial parts

$$R_n(r) = Ar^{n-1} \exp(-\zeta r) \tag{1}$$

Here A is a normalizing constant and ζ a scaling factor. The exponential functions are then replaced by linear combinations of three Gaussian functions which are fitted by least-squares methods. This permits rapid evaluation of all integrals. In this paper, we shall use the STO-3G set with standard molecular ζ values (5.67 for carbon 1s, 1.72 for carbon 2s,2p, and 1.24 for hydrogen 1s). Full details are given elsewhere.[3]

The second basis used is an extended set (4-31G).[6] The carbon 1s atomic orbital is represented by a sum of four Gaussian functions, while all valence atomic orbitals are replaced by inner (three Gaussian) and outer (one Gaussian) parts. Thus there are nine basis functions for each carbon atom and two for each hydrogen. The extra flexibility of this basis is likely to be particularly important in describing anisotropic molecular environments. However, application of the 4-31G basis is more expensive and it has not been possible to use it in a complete geometrical study.

We proceed in three steps for each molecule considered. In the first step (A), the STO-3G basis is used and *all* geometrical parameters are varied until the total energy is minimized, subject only to certain symmetry restrictions specified for each system. This is accomplished by varying each parameter in turn, each minimization being effected by a three-point fit to a parabola. The process is continued until a stationary point is achieved. The residual computational error is believed to be less than 0.003 Å for bond lengths and 0.5° for angles. Fuller details and some preliminary geometry determinations are described in an earlier publication.[7]

In the second step (B), the larger 4-31G basis set is applied, using the geometry determined with STO-3G. This has been done in all cases, leading to the lowest complete set of total energies. Finally, a third step (C) has been applied in some cases, in which the geometry is further refined to achieve the equilibrium configuration predicted by the 4-31G basis itself.

These geometries and energies are compared with experimental data where available. It should be noted that calculated bond lengths should be compared with experimental r_e values. However, these are generally unavailable for polyatomic molecules and we are forced to compare our predicted bond lengths to experimental values of r_0. However, differences between these quantities are small.

Equilibrium Geometries

The complete set of total energies found after minimization with respect to geometrical parameters is given in Tables I and II. We shall discuss the theoreti-

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Table I. Calculated Total Energies (Hartrees) for Neutral Molecules

Molecule	Point group symmetry	State	Energy[a]		
			A	B	C
H		^2S	−0.49491	−0.49928	
H_2		$^1\Sigma_g{}^+$	−1.11751	−1.12658	−1.12683
C		^3P	−37.22866	−37.63692	
CH		$^2\Pi$	−37.77026	−38.20768	−38.20801
CH_2	C_{2v}	$^3B_1$	−38.43623	−38.86881	−38.86963
	C_{2v}	$^1A_1$	−38.37230	−38.80932	−38.81035
CH_3	C_{3v}	$^2A_1$	−39.07701	−39.50392	
	D_{3h}	$^2A_2{}''$	−39.07671	−39.50484	−39.50497
CH_4	T_d	$^1A_1$	−39.72686	−40.13976	−40.13977
C_2		$^1\Sigma_g{}^+$	−74.42220	−75.26497	
		$^3\Pi_u$	−74.49845	−75.35438	
C_2H	$C_{\infty v}$	$^2\Sigma^+$	−75.19611	−76.04708	
C_2H_2	$D_{\infty h}$	$^1\Sigma_g{}^+$	−75.85625	−76.70999	−76.71141
C_2H_3	C_s	$^2A'$	−76.43572	−77.28214	
C_2H_4	D_{2h}	^1A_g	−77.07396	−77.92188	−77.92216
C_2H_5 (I)	C_s	$^2A'$	−77.66300	−78.48527	
(II)	C_s	$^2A''$	−77.66227	−78.48428	
C_2H_6	D_{3d}	$^1A_{1g}$	−78.30618	−79.11582	−79.11593
	D_{3h}	$^1A_1{}'$	−78.30160	−79.11140	

[a] A, STO-3G energy for STO-3G optimized geometry; B, 4-31G energy for STO-3G optimized geometry; C, 4-31G energy for 4-31G optimized geometry.

Table II. Calculated Total Energies (Hartrees) for Cations

Molecule	Point group symmetry	State	Energy[a]		
			A	B	C
$H_2{}^+$		$^2\Sigma_g{}^+$	−0.58270	−0.58402	−0.58408
C^+		^2P	−36.87134	−37.24348	
CH^+		$^1\Sigma^+$	−37.45638	−37.83680	−37.83988
$CH_2{}^+$	C_{2v}	$^2A_1$	−38.11894	−38.50872	−38.51257
$CH_3{}^+$	D_{3h}	$^1A_1{}'$	−38.77948	−39.17129	−39.17512
$CH_4{}^+$	C_{3v}	$^2A_1$	−39.29197	−39.68864	
	C_{2v}	^2B	−39.29262	−39.69038	
	D_{2d}	$^2B_2$	−39.29386	−39.69356	
$CH_5{}^+$	D_{3h}	$^1A_1{}'$	−39.90885	−40.31508	
	C_{4v}	$^1A_1$	−39.91589	−40.31893	
	C_s	$^1A'$	−39.91887	−40.32207	
$C_2{}^+$		$^2\Pi_u$	−74.07931	−74.85908	
		$^4\Sigma_g{}^-$	−74.19942	−74.97681	
C_2H^+	$C_{\infty v}$	$^1\Sigma^+$	−74.78462	−75.42832	
$C_2H_2{}^+$	$D_{\infty h}$	$^2\Pi_u$	−75.53549	−76.34779	
$C_2H_3{}^+$	C_{2v}	$^1A_1$	−76.16540	−76.97753	
$C_2H_4{}^+$	D_{2h}	$^2B_{3u}$	−76.79755	−77.59587	
$C_2H_5{}^+$ (I)	C_s	$^1A'$	−77.40806	−78.19496	
(II)	C_s	$^1A'$	−77.40770	−78.19449	
(III)	C_{2v}	$^1A_1$	−77.38986	−78.18418	
$C_2H_6{}^+$	D_{3d}	$^2A_{1g}$	−77.94048	−78.73354	
$C_2H_7{}^+$ (I)	C_{2v}	$^1A_1$	−78.54363	−79.33930	
(II)	C_s	$^1A'$	−78.52620	−79.32243	

[a] A, STO-3G energy for STO-3G optimized geometry; B, 4-31G energy for STO-3G optimized geometry; C, 4-31G energy for 4-31G optimized geometry.

cal equilibrium geometries for each system (and its positive ion) in turn.

H_2. The theoretical bond length is found to be 0.712 and 0.730 Å with the STO-3G and 4-31G bases, respectively. The experimental r_e value is 0.742 Å.[8]

$H_2{}^+$. The hydrogen molecule ion is calculated to have a distance of 1.061 Å with STO-3G and 1.041 Å with 4-31G. The experimental r_e value is 1.060 Å.[8]

CH. The ground state is calculated to be $^2\Pi$ with a bond length of 1.143 Å with STO-3G and 1.118 Å with 4-31G. The experimental length (r_e) is 1.120 Å.[8] An extended basis calculation by Cade and Huo[9] gives 1.104 Å.

CH^+. The ground state is found to be $^1\Sigma^+$ with a bond length of 1.185 Å with STO-3G and 1.108 Å with 4-31G. Experimentally r_e is 1.131 Å.[8] A large-scale valence-bond calculation by Moore, Browne, and Matsen[10] gives 1.17 Å.

CH_2. Methylene is well known to exist in singlet and triplet states. We have investigated both for general C_{2v} geometry. For the singlet ($^1A_1$) we obtain

$$r_{CH} = 1.123\ \text{Å} \qquad \angle HCH = 100.5° \qquad \text{(STO-3G)}$$

$$r_{CH} = 1.100\ \text{Å} \qquad \angle HCH = 105.4° \qquad \text{(4-31G)}$$

in good agreement with experimental values of 1.11 Å and 102.4° obtained by Herzberg.[11] A previous valence-bond calculation by Harrison and Allen[12] gave an angle of 108° (at a fixed CH distance of 1.058 Å).

The triplet state ($^3B_1$) is predicted to be more stable and to have

$$r_{CH} = 1.082\ \text{Å} \qquad \angle HCH = 125.5° \qquad \text{(STO-3G)}$$

$$r_{CH} = 1.069\ \text{Å} \qquad \angle HCH = 132.0° \qquad \text{(4-31G)}$$

The experimental bond length is 1.029 Å,[13] but spectroscopic evidence favors a linear structure. Most other theoretical calculations also predict a bent structure for triplet CH_2,[12,14,15] so there does appear to be some conflict with observation.[15a]

According to the STO-3G basis, the triplet is 40 kcal/mol more stable than the singlet. The fully optimized 4-31G calculation gives a separation of 37 kcal/mol. Harrison and Allen[12] obtain 32 kcal/mol by their valence-bond method. There does not appear to be any precise experimental information on this separation.

$CH_2{}^+$. The ground state is predicted to be a doublet ($^2A_1$) with

$$r_{CH} = 1.132\ \text{Å} \qquad \angle HCH = 136.0° \qquad \text{(STO-3G)}$$

$$r_{CH} = 1.079\ \text{Å} \qquad \angle HCH = 141.8° \qquad \text{(4-31G)}$$

No experimental information has been found.

CH_3. The methyl radical was considered in C_{3v} symmetry, and was found to be slightly pyramidal with

$$r_{CH} = 1.080\ \text{Å} \qquad \angle HCH = 118.3° \qquad \text{(STO-3G)}$$

for the STO basis. The angle between a CH bond and the threefold axis is 82.4°. If the system is held in the planar D_{3h} configuration, the optimized bond length is 1.078 Å and the STO-3G energy is 0.19 kcal/mol higher, giving a very low inversion barrier. The 4-31G basis gives the planar form as most stable, with

$$r_{CH} = 1.070\ \text{Å} \qquad \text{(4-31G)}$$

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(15a) NOTE ADDED IN PROOF. Recent experimental studies by electron spin resonance [E. Wasserman, V. J. Kuck, R. S. Hutton, and W. A. Yager, *ibid.*, **92**, 7491 (1970)] favor a bent structure.

The experimental study by Herzberg[13] gives $r_{CH} = 1.079$ Å and a planar (D_{3h}) structure. Other theoretical studies favor a planar or nearly planar structure.[16,17]

CH_3^+. This is predicted to be planar (D_{3h}) with

$$r_{CH} = 1.120 \text{ Å} \qquad \text{(STO-3G)}$$
$$r_{CH} = 1.076 \text{ Å} \qquad \text{(4-31G)}$$

This is the simplest carbonium ion and it is interesting to note that both methods predict a longer C–H bond in the ion than in the neutral molecule. An MO study of CH_3^+ by Kari and Csizmadia[18] gives a planar structure with $r_{CH} = 1.078$ Å. Other studies of the bond angles indicate planar structures.[19–21]

CH_4. The theoretical bond lengths using T_d symmetry are

$$r_{CH} = 1.083 \text{ Å} \qquad \text{(STO-3G)}$$
$$r_{CH} = 1.081 \text{ Å} \qquad \text{(4-31G)}$$

Both are in good agreement with the experimental r_e of 1.085 Å.[22] Other calculations have given comparable results.[23–26]

CH_4^+. This is an interesting species since the highest occupied molecular orbital bond in methane is triply degenerate. The cation is therefore expected to distort by the Jahn–Teller effect.[27,28] We have examined possible structures of C_{3v} and C_{2v} symmetry. For C_{3v}, the species is $[CH_a(H_b)_3]^+$ and we find

$$r_{CH_a} = 1.354 \text{ Å} \quad r_{CH_b} = 1.108 \text{ Å} \quad \angle H_bCH_b = 118.8°$$

For C_{2v} symmetry, the ion is $[C(H_a)_2(H_b)_2]^+$ with two independently varied CH_2 angles. Two distinct local minima were found within this symmetry. The first corresponds to closing one CH_2 angle and opening the other leading to

$$r_{CH_a} = 1.100 \text{ Å} \qquad r_{CH_b} = 1.198 \text{ Å}$$
$$\angle H_aCH_a = 118.7° \qquad \angle H_bCH_b = 72.4°$$

The ground-state wave function is ^2B, antisymmetric with respect to the H_aCH_a plane. The second structure has both HCH angles equal and larger than the tetrahedral value. This has the higher symmetry D_{2d} with parameters

$$r_{CH_a} = r_{CH_b} = 1.134 \text{ Å}$$
$$\angle H_aCH_a = \angle H_bCH_b = 137.4°$$

Both C_{2v} species are markedly distorted from the tetrahedral structure, the D_{2d} form being predicted to have a slightly lower energy. The D_{2d} puckered square-planar structure has been found in previous theoretical studies by Handler and Joy[29] and by Arents and Allen.[30] There does not appear to be any experimental information.

CH_5^+. Several possible structures can be considered for this species. For a trigonal bipyramid (D_{3h}) structure $[C(H_a)_2(H_b)_3]^+$ we find

$$r_{CH_a} = 1.136 \text{ Å} \qquad r_{CH_b} = 1.114 \text{ Å}$$

For a square-pyramid (C_{4v}) structure $[CH_a(H_b)_4]^+$

$$r_{CH_a} = 1.083 \text{ Å} \quad r_{CH_b} = 1.139 \text{ Å} \quad \angle H_aCH_b = 113.1°$$

The C_{4v} structure is predicted to be more stable than D_{3h}. However, a still lower energy is found for the C_s structure shown in Figure 1. This structure is rather like a hydrogen molecule attached to a CH_3^+ ion.[31] The geometrical parameters are

$$r_1 = 1.098 \text{ Å} \qquad r_2 = 1.106 \text{ Å}$$
$$r_3 = 1.370 \text{ Å} \qquad r_4 = 1.367 \text{ Å}$$
$$\alpha = 140.0° \qquad \beta = 83.8°$$
$$\theta = 37.2° \qquad \zeta = 117.7°$$

In order to find whether the energy relations $E(D_{3h}) > E(C_{4v}) > E(C_s)$ apply with more extensive basis sets, we note that the 4-31G energies at the same geometries are similarly ordered. In addition, we have made preliminary calculations at these same geometries using a similar basis with more Gaussian functions. This consists of a 6G 1s function and a 2s,2p shell split into 5G and 1G parts for carbon and a hydrogen 1s split into 5G and 1G (6-51G).[32] The results are

$$E(D_{3h}) = -40.3614$$
$$E(C_{4v}) = -40.3674$$
$$E(C_s) = -40.3715$$

The relative ordering is evidently the same as the other results. Van der Lugt and Ros[33] have come to similar conclusions, but with a smaller difference between the C_{4v} and C_s energies.

C_2. For the homonuclear diatomic molecule C_2, we have examined the lowest singlet ($^1\Sigma_g^+$) and triplet states ($^3\Pi_u$). For the singlet state, the theoretical distance is 1.233 Å, which may be compared with the experimental value of 1.242 Å.[34] For the triplet, the theoretical and experimental values are 1.298 and 1.312 Å, respectively.[34] It should be noted that the theory predicts the triplet to be substantially more stable (1.75 eV for STO-3G and 2.43 eV for 4-31G) than the singlet. Experimentally, Ballik and Ramsay[34] have shown $^1\Sigma_g^+$ to be 0.08 eV lower in energy. This substantial failure of the single-determinant theory has been shown to be due to configuration interaction in the $^1\Sigma_g^+$ state by Fraga and Ransil.[35] Other calculations

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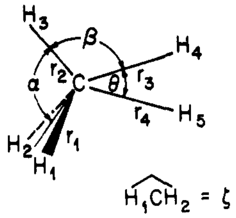

Figure 1. Protonated methane.

of C_2 bond lengths have been made by Fougere and Nesbet[36] and by Verhaegen, *et al.*[37,38]

C_2^+. For this ion, we have examined the $^4\Sigma_g^-$ and $^2\Pi_u$ states. The quartet state is predicted to be lower with a bond length of 1.456 Å. For the doublet state the length is 1.358 Å. These results are fairly close to those of Verhaegen[38] who obtained 1.412 and 1.312 Å, respectively. He also finds the ground state to be $^4\Sigma_g^-$ but, using configuration interaction, he obtains a smaller energy separation between the states. There appears to be little experimental evidence on this system.

C_2H. The geometry of this species was optimized completely and found to be linear ($^2\Sigma$) with

$$r_{CC} = 1.221 \text{ Å} \qquad r_{CH} = 1.067 \text{ Å}$$

No experimental or other theoretical information is available.

C_2H^+. This was found to be linear as a singlet state ($^1\Sigma$) with

$$r_{CC} = 1.408 \text{ Å} \qquad r_{CH} = 1.113 \text{ Å}$$

Calculations indicate that this system has low-lying triplet states rather like those of C_2. The theoretical energies lie about 0.07 hartree below the singlet energy, comparable to C_2. As the ground state of C_2 is experimentally a singlet, that of C_2H^+ is probably also a singlet, and we have not investigated the triplet states in detail.

C_2H_2. Acetylene was given C_2 symmetry for the search procedure and was found to be most stable in the linear form ($^1\Sigma_g^+$) in agreement with experimental results. The theoretical bond lengths are

$$r_{CC} = 1.168 \text{ Å} \qquad r_{CH} = 1.065 \text{ Å} \qquad \text{(STO-3G)}$$

$$r_{CC} = 1.190 \text{ Å} \qquad r_{CH} = 1.051 \text{ Å} \qquad \text{(4-31G)}$$

Corresponding experimental lengths are 1.203 and 1.061 Å.[39,40] An extended-basis Gaussian treatment by Buenker, Peyerimhoff, and Whitten[41] calculated a CC bond length of 1.205 Å keeping the CH length fixed.

$C_2H_2^+$. The acetylene cation was also given C_2 symmetry but found to be most stable in the linear form ($^2\Pi_u$). The theoretical bond lengths are

$$r_{CC} = 1.247 \text{ Å} \qquad r_{CH} = 1.102 \text{ Å}$$

Both bonds are longer than in the neutral molecule. There are no experimental data.

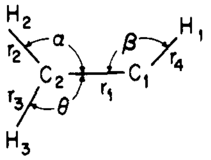

Figure 2. Vinyl radical and cation.

C_2H_3. The vinyl radical was initially assumed to be planar, as shown in Figure 2. After all lengths and angles in this structure had been optimized, rotation about the C–C bond was tested and it was found that the minimum energy occurred in the planar form. The symmetry of the ground state is $^2A'$ so that the unpaired electron is in a σ-type molecular orbital. Values for the geometrical parameters are

$$r_1 = 1.357 \text{ Å} \qquad r_2 = 1.085 \text{ Å}$$

$$r_3 = 1.083 \text{ Å} \qquad r_4 = 1.083 \text{ Å}$$

$$\alpha = 122.3° \qquad \beta = 130.8° \qquad \theta = 121.4°$$

There is no detailed experimental evidence about the structure, but electron spin resonance measurements do indicate nonequivalence of the methylene hydrogens H_2 and H_3.[42]

The only other theoretical treatment of the geometry is a calculation of the angle β by Millie and Berthier.[17] They obtain 137°.

$C_2H_3^+$. The vinyl cation is found to be planar with C_{2v} symmetry. The geometrical parameters (Figure 2) are

$$r_1 = 1.281 \text{ Å} \qquad r_2 = r_3 = 1.106 \text{ Å} \qquad r_4 = 1.106 \text{ Å}$$

$$\alpha = \theta = 120.7° \qquad \beta = 180.0°$$

Calculations by Sustmann, Williams, Dewar, Allen, and Schleyer[43] give a longer CC bond length of 1.36 Å.

C_2H_4. Ethylene was given C_2 symmetry and subjected to the additional restriction of a single CH bond length. The lowest energy was found for a planar D_{2h} structure in agreement with experiment. The theoretical geometrical parameters are

$$r_{CC} = 1.306 \text{ Å} \qquad r_{CH} = 1.082 \text{ Å} \qquad \angle HCH = 115.6° \qquad \text{(STO-3G)}$$

$$r_{CC} = 1.316 \text{ Å} \qquad r_{CH} = 1.073 \text{ Å} \qquad \angle HCH = 116.0° \qquad \text{(4-31G)}$$

The corresponding experimental results are 1.330 Å, 1.076 Å, and 116.6°.[44] The CC bond length is underestimated as it was for acetylene. The observed reduction of the HCH angle below the trigonal value of 120° is reproduced well.

$C_2H_4^+$. The ethylene cation was treated in the same manner as the neutral molecule and was also found to be planar with D_{2h} symmetry. The electron is removed from the bonding π-type molecular orbital. The theo-

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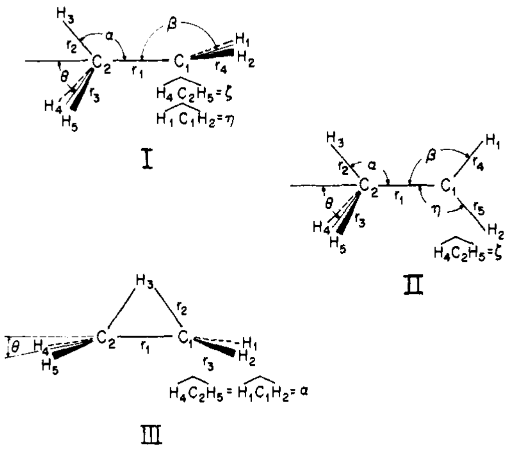

Figure 3. Ethyl radical and cation.

retical geometrical parameters are

$$r_{\rm CC} = 1.430\ \text{Å} \quad r_{\rm CH} = 1.102\ \text{Å} \quad \angle\text{HCH} = 118.4°$$

Substantial lengthening of the CC bond is found. There is no direct evidence on $C_2H_4^+$ itself; however, Merer and Schoonveld[45] have found the related first Rydberg state of ethylene to be twisted 25° from planarity with $r_{\rm CC}$ = 1.41 Å. Merer and Mulliken[46] further estimate $r_{\rm CH}$ = 1.11 Å and ∠HCH = 120° for this state. It may also be noted that Humphries, Walsh, and Warsop[47] find a planar structure for $C_2Cl_4^+$ with a CC bond length increase of 0.11 Å over the neutral molecule.

C_2H_5. The ethyl radical and cation were considered in the two C_s symmetries (I and II) and the bridged C_{2v} symmetry (III) shown in Figure 3. A very high energy was found for the bridged radical, so only I and II were examined in detail. Structure I is predicted to be most stable with parameters

$$r_1 = 1.516\ \text{Å} \quad r_2 = 1.090\ \text{Å}$$
$$r_3 = 1.087\ \text{Å} \quad r_4 = 1.083\ \text{Å}$$
$$\alpha = 111.2° \quad \beta = 157.1°$$
$$\theta = 52.6° \quad \zeta = 108.3° \quad \eta = 116.7°$$

Structure II has parameters

$$r_1 = 1.514\ \text{Å} \quad r_2 = 1.086\ \text{Å}$$
$$r_3 = 1.089\ \text{Å} \quad r_4 = 1.080 \quad r_5 = 1.081\ \text{Å}$$
$$\alpha = 111.0° \quad \beta = 121.2° \quad \theta = 52.5°$$
$$\eta = 120.3° \quad \zeta = 107.4°$$

The difference between the energies of I and II is the predicted (sixfold) rotational barrier for the C–C bond. The numerical values are 0.46 kcal/mol for STO-3G and 0.62 kcal/mol for 4-31G at the same geometry. There are no experimental values for the lengths and angles, but electron spin resonance observations imply that the radical has a classical and not a bridged structure.[42]

$C_2H_5^+$. For the ethyl cation, the classical structure I is found to give lowest energy. Geometrical parameters are

$$r_1 = 1.484\ \text{Å} \quad r_2 = 1.110\ \text{Å}$$
$$r_3 = 1.091\ \text{Å} \quad r_4 = 1.115\ \text{Å}$$
$$\alpha = 102.2° \quad \beta = 177.1°$$
$$\theta = 46.6° \quad \zeta = 113.6° \quad \eta = 116.7°$$

It should be noted that the methyl group is tilted so that the proton H_3 is moved partly toward a bridging position. The carbonium center C_1 is slightly nonplanar, the distortion being toward a "staggered" configuration about the C–C bond.

Geometrical parameters for structure II are

$$r_1 = 1.488\ \text{Å} \quad r_2 = 1.088\ \text{Å}$$
$$r_3 = 1.101\ \text{Å} \quad r_4 = 1.115\ \text{Å}$$
$$r_5 = 1.115\ \text{Å}$$
$$\alpha = 112.9° \quad \beta = 122.7°$$
$$\theta = 60.9° \quad \eta = 120.6° \quad \zeta = 105.9°$$

The energy difference between I and II is the sixfold rotational barrier. Numerical values are 0.22 kcal/mol for STO-3G and 0.29 kcal/mol for 4-31G(B).[48]

The bridged structure III has lengths and angles

$$r_1 = 1.403\ \text{Å} \quad r_2 = 1.348\ \text{Å} \quad r_3 = 1.099\ \text{Å}$$
$$\theta = 2.5° \quad \alpha = 118.8°$$

The energy difference between I and III [11.42 kcal/mol for STO-3G and 6.76 kcal/mol for 4-31G(B)] is the barrier for proton exchange between carbon centers. This agrees reasonably well with a previous calculation (9.0 kcal/mol) by Sustmann, Williams, Dewar, Allen, and Schleyer.[43]

C_2H_6. Ethane was considered in D_3 symmetry. The lowest energy was found in the staggered (D_{3d}) configuration with

$$r_{\rm CC} = 1.538\ \text{Å} \quad r_{\rm CH} = 1.086\ \text{Å} \quad \angle\text{HCH} = 108.2° \qquad \text{(STO-3G)}$$

$$r_{\rm CC} = 1.529\ \text{Å} \quad r_{\rm CH} = 1.083\ \text{Å} \quad \angle\text{HCH} = 107.7° \qquad \text{(4-31G)}$$

These parameters agree well with the experimental values of 1.531 Å, 1.096 Å, and 107.8°, respectively.[49]

In the eclipsed (D_{3h}) configuration, the optimized geometrical parameters are

$$r_{\rm CC} = 1.548\ \text{Å} \quad r_{\rm CH} = 1.086\ \text{Å} \quad \angle\text{HCH} = 107.8°$$

A predicted slight lengthening of the C–C bond with torsion should be noted. The D_{3h}–D_{3d} energy difference [2.9 kcal/mol for STO-3G and 2.8 kcal/mol for 4-31G(B)] is the threefold rotational barrier and is in good agreement with the experimental value of 2.93 kcal/mol.[50] Rather similar results were obtained by Stevens using an STO minimal basis with optimized exponents.[51]

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$C_2H_6^+$. For the ethane cation, bridged structures were considered but found to have higher energies than the D_{3d} (staggered) structure ($^2A_{1g}$).

$$r_{CC} = 1.858\ \text{Å} \qquad r_{CH} = 1.098\ \text{Å} \qquad \angle HCH = 117.1°$$

The long CC bond length arises because an electron has been removed from a molecular orbital which is primarily CC bonding.

The ethane cation is also expected to have a low-lying ^2E_g state, which will distort to some lower symmetry by the Jahn–Teller effect. For the theoretical D_{3d} geometry of the neutral molecule (0.44 eV) the STO-3G energy of the ^2E_g state is 0.0163 hartree (0.44 eV) greater than the $^2A_{1g}$ state. We have not found a geometry in which this order is reversed, but the two states of $C_2H_6^+$ are evidently close.

$C_2H_7^+$. Protonated ethane was investigated using the two structures illustrated in Figure 4. Structure I has C_{2v} symmetry and corresponds to proton attachment at the center of the C–C bond. Structure II is characteristic of an approach of a hydrogen molecule to the $C_2H_5^+$ ion in the form found to be of lowest energy. Such a structure for protonated ethane is analogous to the lowest energy structure for CH_5^+.

The bridged structure I is found to give lowest energy. The geometrical parameters are

$$r_1 = 2.362\ \text{Å} \qquad r_2 = 1.251\ \text{Å}$$

$$r_3 = 1.097\ \text{Å} \qquad r_4 = 1.094\ \text{Å}$$

$$\alpha = 52.7° \qquad \beta = 89.5° \qquad \theta = 115.6°$$

The bridging proton H_7 is found at the vertex of a very flat isosceles triangle with a long C–C distance. It was confirmed that the final structure was a potential minimum with respect to motion of H_7 parallel to the C–C line.

The optimum geometrical parameters for structure II were found to be

$$r_1 = 1.487\ \text{Å} \qquad r_2 = 1.110\ \text{Å}$$

$$r_3 = 1.091\ \text{Å} \qquad r_4 = 1.115\ \text{Å} \qquad r_5 = 2.746\ \text{Å}$$

$$\alpha = 102.3° \qquad \beta = 176.3°$$

$$\theta = 46.9° \qquad \zeta = 113.6°$$

$$\eta = 116.7° \qquad \gamma = 102.3° \qquad \delta = 15.0°$$

These correspond to a rather loose complex between a hydrogen molecule and an ethyl cation. The distance between hydrogens H_6 and H_7 is 0.716 Å, close to that for isolated H_2. It appears, therefore, that $C_2H_5^+$ has a smaller affinity for H_2 than CH_3^+, presumably because the additional methyl group donates electrons into the vacant orbital on the carbonium center, making it less available for the electrons of an approaching hydrogen molecule.

The energies quoted in Table II show that I is more stable than II with the 4-31G basis. As with CH_5^+, further calculations were carried out with the 6-51G basis and led to

$$E(\text{I}) = -79.43005$$

$$E(\text{II}) = -79.41449$$

The stabilization of I relative to II is only slightly changed.

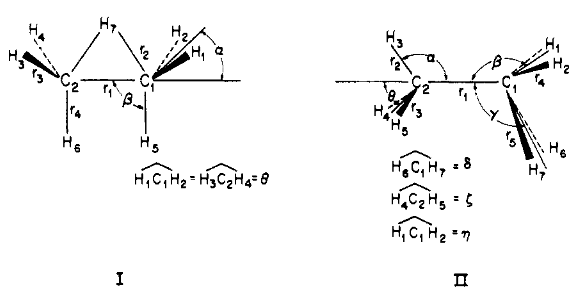

Figure 4. Protonated ethane.

A number of other structures were tested but not refined. In the trigonal-bipyramid (D_{3h}) form of CH_5^+, both equatorial and axial hydrogens were replaced by tetrahedral methyl groups and the C–C bond optimized. Other configurations of structure II with a closer approach of hydrogens H_6 and H_7 were also tested. All of these gave energies higher than those quoted in Table II. Although the complete potential surface has not been fully explored, these calculations do suggest that the bridged form I is the lowest energy configuration for $C_2H_7^+$.

Energy Comparisons

The total energies listed in Tables I and II can be used to derive theoretical dissociation energies, proton affinities, ionization potentials, and heats of a number of other reactions. In order to compare these energy differences with experimental data, we have used the heats of formation given in Table III. Some of these quantities are subject to uncertainties of several kcal/mol. It should be noted that these are all heats of formation at 298°K. The theoretical energies refer to fixed nuclei, so that comparisons should really be made with heats of formation at 0°K with corrections for zero-point vibrations. However, the vibrational frequencies are imperfectly known for many of these molecules, so it is not possible to make such comparisons systematically. We shall therefore use the 298°K heats in the tabulated comparisons.

Table III. Experimental Heats of Formation (kcal/mol) for Ground States[a]

Molecule	$\Delta H_f°$ (298°K) Neutral	Cation
H	52.095	366
H_2	0.0	356
C	171.291	431
CH	142.4	399
CH_2[b]	91.9	332
CH_3	33.2	260
CH_4	−17.88	274
C_2	199	475
C_2H	112	399
C_2H_2	54.19	317
C_2H_3	65	269
C_2H_4	12.49	253
C_2H_5	25	219
C_2H_6	−20.24	245

[a] Unless otherwise noted, J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, and K. Draxl, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS-26, National Bureau of Standards, Washington, D. C. [b] W. A. Chupka and C. Lifshitz, *J. Chem. Phys.*, **48**, 1109 (1968).

In comparing theoretical and experimental energies, we have used the triplet state for CH_2, the singlet states for C_2 and C_2H^+, and the doublet states for C_2^+ and C_2H. The theoretical energies used are those corresponding to the equilibrium configuration predicted by STO-3G (columns A and B in Tables I and II).

Table IV gives theoretical and experimental values for dissociation energies in which particular bonds are broken in neutral molecules. (A preliminary version of this table has been published previously.[52]) The theoretical dissociation energies are mostly too small, as expected, since molecular orbital theory in the form used here takes inadequate account of correlation effects. However, there are two general features in this table which are worthy of note. The first is that the deviation between theory and experiment is largest for the dissociation of the diatomic species CH and C_2. This is partly due to the importance of configuration interaction in C_2 noted in the previous section, but may also be attributed to a relatively more satisfactory description of the free carbon atom in its triplet ground state (where the single determinant wave function gives a good account of the strong correlation between electrons with parallel spins). A second significant regularity is that in the six successive C–H dissociations of ethane to C_2, the theory gives too small a value for dissociations of a singlet molecule to a radical plus hydrogen atom, whereas it gives slightly too large a value for dissociation of a radical. This is reasonable since the first process reduces the number of electron pairs and therefore decreases the correlation energy. The C–H dissociations in C_2H_5 and C_2H_3 do not alter the number of electron pairs and these energies are given well by the 4-31G basis. The excessively large value for D(C–H) in C_2H can be attributed to the poor description of C_2.

Table IV. C–H and C–C Dissociation Energies (kcal/mol) for Neutral Molecules

Reaction	D(STO-3G)	D(4-31G)	D(exptl)
$CH \rightarrow C + H$	29.3	44.9	81
$CH_2 \rightarrow CH + H$	107.3	101.6	103
$CH_3 \rightarrow CH_2 + H$	91.6	85.2	111
$CH_4 \rightarrow CH_3 + H$	97.3	85.7	103
$C_2H \rightarrow C_2 + H$	175.1	177.5	139
$C_2H_2 \rightarrow C_2H + H$	103.7	102.7	110
$C_2H_3 \rightarrow C_2H_2 + H$	53.1	45.7	41
$C_2H_4 \rightarrow C_2H_3 + H$	89.9	88.1	105
$C_2H_5 \rightarrow C_2H_4 + H$	59.1	40.5	40
$C_2H_6 \rightarrow C_2H_5 + H$	93.1	82.1	97
$C_2 \rightarrow 2C$	−22.1	−5.6	144
$C_2H_2 \rightarrow 2CH$	198.0	184.9	231
$C_2H_4 \rightarrow 2CH_2$	126.4	115.6	171
$C_2H_6 \rightarrow 2CH_3$	95.5	67.8	87

Table V compares theoretical and experimental proton affinities. Agreement is clearly better with the extended 4-31G basis set, with a mean absolute difference of about 15 kcal/mol. For the C_2 series, the theoretical values are systematically too large. This corresponds to a more accurate description of the positive ion. Since the calculation on the ion XH^+ uses a larger number of basis functions to represent the same number of electrons as in X, these differences may be reduced by further extension of the basis.

Table V. Proton Affinities[a] (kcal/mol)

X	P(STO-3G)	P(4-31G)	P(exptl)
C	142.9	125.4	138
CH	218.8	165.3	176
CH_2	215.4	188.9	198
CH_3	136.1	119.0	125
CH_4	120.5	114.4	118[b]
C_2	179.6	102.5	166
C_2H	213.0	188.7	161
C_2H_2	194.0	167.9	151
C_2H_3	227.0	196.9	178
C_2H_4	209.7	171.4	159
C_2H_5	174.1	155.5	146
C_2H_6	149.0	140.1	>118[b]

[a] Heats of reaction for $XH^+ \rightarrow X + H^+$. [b] M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **87**, 3294 (1965).

Table VI compares theoretical and experimental ionization potentials. The experimental numbers are not necessarily the best available, but are obtained from the heats of formation listed in Table III. If the theoretical energies from Tables I and II are used, these should give adiabatic ionization potentials corresponding to the energy differences between the molecule and ion, both being at their equilibrium geometry. Since many of the ions distort on ionization, we have also carried out calculations at the neutral (STO-3G) geometry leading to vertical ionization potentials. These are listed in the last two columns of the table. It is evident from the results that the theoretical ionization potentials are mostly too low. This is to be expected since the correlation energy should be smaller for the cation with its reduced number of electrons. The over-all agreement is clearly better with the 4-31G basis. However, it should be noted that for CH_2 and C_2H, the 4-31G basis gives adiabatic ionization potentials which are greater than the vertical values. This arises because the geometries are obtained with the STO-3G set and indicates that comparisons of adiabatic and vertical values cannot be properly made without geometric optimization.

Table VI. Ionization Potentials (eV)

	$IP_{adiabatic}$			$IP_{vertical}$	
Molecule	STO-3G	4-31G	Exptl[a]	STO-3G	4-31G
CH	8.54	10.09	11.13	8.57	10.03
CH_2	8.63	9.80	10.40	8.80	9.78
CH_3	8.10	9.05	9.84	8.41	9.15
CH_4	11.78	12.14	12.66	13.29	13.50
C_2	9.33	11.04	11.97	9.93	12.75
C_2H	11.20	16.84	12.45	13.38	14.72
C_2H_2	8.73	9.86	11.40	9.20	10.08
C_2H_3	7.36	8.29	8.85	8.88	9.81
C_2H_4	7.52	8.87	10.43	8.11	9.08
C_2H_5	6.94	7.91	8.41	7.29	8.18
C_2H_6	9.95	10.40	11.60	11.55	11.98

[a] Derived from values given in Table III.

Finally, the energies listed in Tables I and II may be used for the energies of several significant reactions. First consider the energy of the process

$$C_2H_6 + C_2H_2 \longrightarrow 2C_2H_4$$

Experimentally this is −9.0 kcal/mol (ΔH at 298°K), the negative sign indicating that the carbon–carbon double bond is more stable than the average of single

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[52] W. A. Lathan, W. J. Hehre, and J. A. Pople, *Chem. Phys. Lett.*, 3, 579 (1969).

and triple bonds. The corresponding theoretical numbers are +9.1 (STO-3G), −11.3 (4-31G using STO-3G geometry), and −10.7 kcal/mol (full 4-31G geometry). Thus the correct sign is not given for this comparison unless the extended basis set is used.

Next consider the reaction

$$C_2H_5 + CH_4 \longrightarrow CH_3 + C_2H_6$$

Experimentally the energy of this process is +6 kcal/mol (ΔH at 298°K from Table III). The positive sign indicates that methyl substitution of a methyl radical (to give ethyl) leads to a stabilization of 6 kcal/mol (relative to methyl substitution of methane to give ethane). This is a quantitative measure of hyperconjugation in the ethyl radical. The corresponding theoretical quantities are +4.2 (STO-3G) and +3.3 kcal/mol (4-31G using STO-3G geometry).

A similar reaction for carbonium ions is

$$C_2H_5^+ + CH_4 \longrightarrow CH_3^+ + C_2H_6$$

The experimental energy here is +39 kcal/mol (ΔH at 298°K from Table III), reflecting strong hyperconjugation in the ethyl cation. The corresponding theoretical results are +30.9 (STO-3G) and +29.9 kcal/mol (4-31G using STO-3G geometry).

Conclusions

On the basis of the studies reported in this paper, the following general conclusions may be drawn.

1. The geometries of hydrocarbons are well described by a minimal Slater-type basis set in those cases for which experimental data are available. This lends credence to predictions for other systems. Some further improvement is achieved with the extended 4-31G basis for those molecules for which a geometry search has been carried out. The most notable difference is that the extended basis leads to a planar methyl radical, whereas STO-3G gives a slightly pyramidal form.
2. Relative energies of these hydrocarbons and cations are given more satisfactorily by the extended-basis set. In particular, the correct relative energies of single, double, and triple carbon–carbon bonds are only obtained at the extended level.
3. The combination of a geometry search using the simple STO-3G basis, followed by a single calculation with the extended 4-31G set (level B), appears to be a reasonable approach when a full treatment (level C) is not practical.

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The Shapes of Simple Polyatomic Molecules and Ions. III. The Series HAB, H_2AB, and H_2ABH

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Abstract: The rough features of the shapes of molecules with the general formulas HAB, H_2AB, and H_2ABH are discussed in terms of simple molecular orbital pictures and qualitative correlation diagrams deduced from the rule of maximization of overlap and orbital symmetry considerations. Extended-Hückel correlation diagrams are presented in support of the qualitative ones. Why ions such as FHF^- have the hydrogen between the two halogens rather than at an end position as in HCN or HOCl is easily explained. This explanation is then extended to describe hydrogen-bonded dimers such as $(HF)_2$. The qualitative molecular orbital model also gives a simple picture of the difference between planar inversion processes, such as those involved in isomerizations of >C=N—R, and rotations about single bonds such as >N—O— R.

A qualitative molecular orbital (MO) model of molecular shapes was formulated by Mulliken[1] and Walsh.[2] The model has recently been modified and extended in a more practical form. The model rather easily correlates large quantities of structural information and other data of chemical interest. It has great educational potential and it can be used to suggest the direction for new experiments or detailed quantum mechanical calculations. Paper I in this series deals with the shapes of molecules with the general formulas HAAH and BAAB, where A and B are nonhydrogen atoms.[3] Paper II treats AH_2, AH_3, and AH_4 molecules.[4] A related article discusses the shapes of the H_3 and H_4 transition states in hydrogen exchange reactions.[5] The present paper (part III) surveys the shapes of HAB, H_2AB, and H_2ABH molecules. Because of the particularly high symmetry of its members, the A_2H_4 series will be the subject of another study. Walsh has already discussed the shapes of the ordinary HAB and H_2AB molecules in terms of simple MO theory.[2] Justifications for reviewing them in this paper are the somewhat different arguments and the simpler approach used here.

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