Organic and Biological Chemistry

Application of the Pople–Santry–Segal Complete Neglect of Differential Overlap (CNDO) Method to Some Hydrocarbons and Their Cations[1]

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Abstract: The CNDO method has been applied to hydrocarbons, hydrocarbon cation radicals, free radicals, and carbonium ions. If the original Pople parameters are modified somewhat, it is possible to calculate structures (both bond lengths and bond angles) which are in good agreement with experimental data. In addition, if the energies calculated are considered to be in arbitrary units, a semiempirical scaling factor may be determined which permits the heats of atomization and heats of formation to be satisfactorily calculated. The CNDO method appears to have considerable promise in the investigation of organic chemical phenomena.

Much of the recent progress in the study of unsaturated organic molecules has its origin in the molecular orbital calculations based on the π-electron approximation. A similar treatment of saturated compounds would allow an examination of a wider range of phenomena. A number of approaches to such a treatment have been suggested,[2–5] and one, the extended Hückel method,[2] has been applied to a number of cases. More recently, Pople, Santry, and Segal,[4,5] have developed an approximate SCF treatment (CNDO, complete neglect of differential overlap) which has the virtue of being independent of the coordinate system used. This paper will explore the application of the method to some hydrocarbons and to the cations derived from them.

The CNDO treatment begins with extended Hückel molecular orbitals derived from the 2s and 2p atomic orbitals on carbon and the 1s atomic orbital on hydrogen. The proper linear combinations of these orbitals are obtained by constructing and diagonalizing the Hückel secular determinant in which the on-diagonal elements are the average ionization potentials and the off-diagonal elements are made proportional to the overlap integral between the atomic orbitals. The bond orders and electron densities are calculated using the occupied molecular orbitals, and from this the approximate Hartree–Fock matrix is constructed in a fashion similar to that previously used by Pople for π-electronic systems.[6] Diagonalization of the latter leads to a new set of molecular orbitals. The procedure is repeated until there is no longer a significant change in the coefficients.

The hybridization at a given carbon is not specified at the beginning of the calculation; only the coordinates of the atoms, the average ionization potential of each type of atomic orbital used, the core charge, the β-proportionality constant, and the exponent for the Slater-type atomic orbital are required. The values suggested by Pople, *et al.*, are summarized in Table I. The final hybridization is determined by the geometry initially supplied and by the difference in the above parameters between 2s and 2p orbitals.

Table I. Parameters Used in CNDO Calculations

Orbital	Av ionization potential, V	Core charge	Slater exponent	β-Proportionality constant
C, 2s	14.051	4	1.625	21
C, 2p	5.572	4	1.625	21
H, 1s	7.1761	1	1.2	9

Pople and Segal[5] have shown that the CNDO procedure, although quite good for bond angles and charge distributions, does not give the correct energy or equilibrium bond length. The parameters used are not uniquely determined from any available data, and it would appear that modification of the β-proportionality constants and the carbon average ionization potentials could be made without doing violence to the general scheme.

It seemed appropriate first to determine the sensitivity of the calculated structures to variations in the parameters used. Ethane and ethylene were chosen as test cases and the equilibrium C—C and C=C bond lengths were obtained for a number of sets of parameters. For each calculation, each of the parameters was chosen within a given range by the use of a random number generator. Thus, there was no correlation between one set of parameters and another. The results of a number

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[1] This investigation was supported by the U. S. Army Research Office, Durham.

[2] R. S. Mulliken, *J. Chim. Phys.*, **46**, 497, 675 (1949); M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, 20, 837 (1952); R. Hoffmann, *ibid.*, 39, 1397 (1963); 40, 2480 (1964); *J. Am. Chem. Soc.*, **86**, 1259 (1964); *Tetrahedron Letters*, 3819 (1965); J. A. Pople and D. P. Santry, *Mol. Phys.*, 7, 269 (1964).

[3] G. Klopman, *J. Am. Chem. Soc.*, **86**, 4450 (1964); H. A. Pohl, R. Appel, and K. Appel, *J. Chem. Phys.*, **41**, 3385 (1964); J. J. Kaufman, *ibid.*, **43**, 5152 (1965).

[4] J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129 (1965).

[5] J. A. Pople and G. A. Segal, *ibid.*, **43**, 5136 (1965); **44**, 3289 (1966).

[6] J. A. Pople, *J. Phys. Chem.*, **61**, 6 (1957).

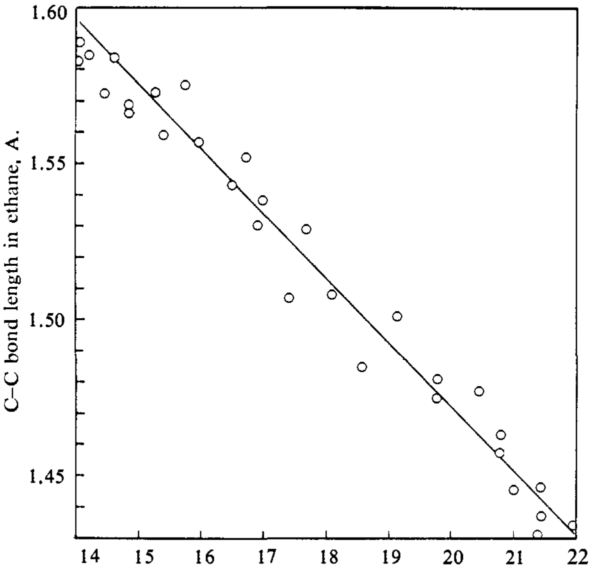

Figure 1. Effect of variation in parameters on the equilibrium C-C bond length for ethane. Although the lengths are plotted against the carbon β-proportionality constants, each of the five parameters were varied in each case. The scattering is due to the small effect of the other parameters on the bond length.

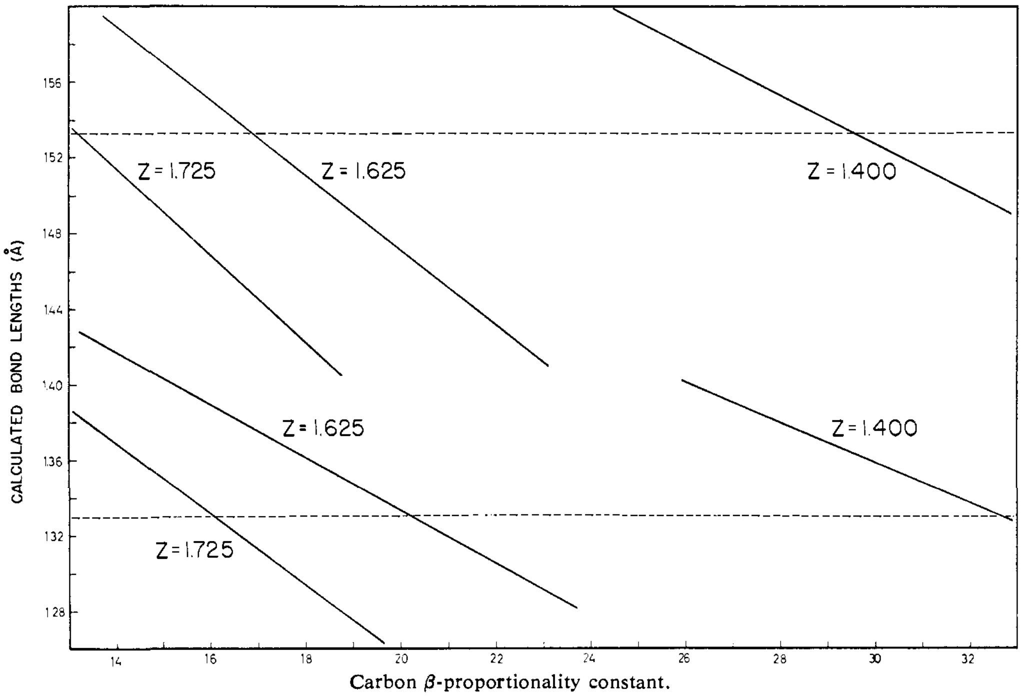

Figure 2. Effect of the carbon β-proportionality constant on the equilibrium bond lengths for ethane (upper lines) and ethylene (lower lines).

of such calculations are indicated in Figure 1. Here, the equilibrium C—C bond length in ethane is plotted as a function of the carbon β-proportionality constant. It can be seen that this constant largely determines the bond length, and that the other parameters (each of which was varied in each calculation) have relatively little effect.

The effect of the β-proportionality constant itself is shown in Figure 2. Here, the other parameters are kept constant, and the equilibrium bond lengths for ethane and ethylene are plotted against the constant. In each case, a very good linear relation is found. The effect of a variation in the Slater exponent, Z, is also indicated. The two dotted lines indicate the observed bond lengths.

It is not possible to find a value of the constant which will exactly fit both the C—C and C=C bond lengths. However, a value may be chosen (17.5) which gives 1.51 A for the C—C length and 1.36 A for the C=C length; both are close to the experimental values (1.53 and 1.33 A).[7] It was not possible to significantly improve the fit by varying Z, and thus the original values were used in all of the remaining calculations.

Having values which give reasonable bond lengths, it was now of interest to try to obtain a linear correlation between calculated and observed energies. The calculated values are the total energies for all bonding electrons. In order to convert the energies to those which may be compared with experimental data, they were converted to heats of atomization by subtracting the energies of the appropriate number of hydrogen atoms and carbon atoms. These are obtained in the same way as are the energies of the molecules being considered. Similarly, the heats of atomization may be calculated from the heats of formation knowing the heats of formation of carbon and hydrogen atoms.[8]

The calculated energies do not include zero-point energies. In order to make a valid comparison, it is necessary to use the heats of formation calculated for 0°K and to correct for zero-point energies.[9] Although the calculated energies are in atomic units, we shall for the present purpose consider them to be in arbitrary

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[7] *Cf.*, D. R. Linde, Jr., *Tetrahedron*, **17**, 125 (1962).

[8] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

[9] The vibrational frequencies were taken from R. G. Snyder and H. J. Schachtschneider, *Spectrochim. Acta*, **19**, 85 (1963).

Table II. Effect of a Variation in the MO Parameters on the Geometry and Energies of Methane, Ethane, and Ethylene

					Methane	Ethane			Ethylene			$\Delta H/\Delta E$				Ethane
β_H	β_C	I(1s)	I(2s)	I(2p)	R(CH)	R(CH)	R(CC)	HCC	R(CH)	R(CC)	HCC	Methane	Ethane	Ethylene	R	H chg
9.0	21.0	7.176	14.051	5.572	1.114	1.121	1.452	112.1	1.113	1.306	124.3	228.14	213.84	213.96	0.880	1.002
9.0	17.5	7.176	14.051	5.572	1.141	1.146	1.516	111.5	1.136	1.366	123.3	279.87	270.76	281.46	1.254	1.000
10.0	17.5	7.176	14.051	5.572	1.131	1.137	1.520	111.4	1.128	1.367	123.1	263.23	257.08	268.76	1.345	0.998
10.0	17.5	6.5	14.051	5.572	1.131	1.136	1.523	111.2	1.127	1.369	123.0	247.40	243.78	256.27	1.443	0.975
10.0	17.5	7.176	13.0	5.572	1.130	1.135	1.516	111.4	1.126	1.364	123.3	257.04	250.02	259.65	1.266	1.002
10.0	17.5	7.176	14.051	6.0	1.131	1.135	1.520	111.3	1.127	1.367	123.1	260.37	254.02	264.76	1.312	0.985
9.0	17.5	6.151	11.445	7.257	1.131	1.136	1.509	111.4	1.127	1.359	123.2	230.42	222.97	227.99	1.114	0.928
9.0	17.5	6.5	11.445	7.257	1.131	1.137	1.508	111.5	1.127	1.358	123.2	237.70	228.86	233.18	1.071	0.940
9.0	17.0	6.151	11.445	7.257	1.135	1.139	1.518	111.4	1.130	1.367	123.0	236.68	230.10	236.54	1.174	0.927
9.0	17.5	6.151	11.75	7.257	1.131	1.136	1.510	111.4	1.128	1.359	123.1	231.84	224.62	230.07	1.132	0.927
9.0	17.5	6.151	11.455	7.60	1.130	1.135	1.509	111.4	1.126	1.358	123.1	228.21	220.72	225.30	1.099	0.918
10.0	17.5	6.151	11.445	7.257	1.122	1.127	1.513	111.3	1.119	1.360	123.1	218.48	213.20	219.25	1.190	0.928
10.0	17.5	7.176	11.0	7.4	1.122	1.127	1.508	111.5	1.119	1.358	123.3	235.37	226.08	229.43	1.034	0.960
10.0	17.5	7.176	11.445	7.257	1.123	1.128	1.510	111.5	1.120	1.359	123.2	238.58	229.62	233.78	1.064	0.962
10.0	17.5	7.176	11.3	7.4	1.123	1.128	1.509	111.5	1.119	1.358	123.2	236.94	227.84	231.61	1.050	0.958
10.0	17.5	7.176	10.0	6.5	1.123	1.128	1.506	111.5	1.119	1.356	123.3	235.51	225.83	229.01	1.024	0.990
10.0	17.5	7.176	10.3	6.4	1.124	1.129	1.506	111.5	1.120	1.357	123.3	237.67	228.22	231.95	1.045	0.991
10.0	17.5	7.176	10.1	6.4	1.124	1.128	1.506	111.5	1.119	1.356	123.3	236.60	227.03	230.48	1.034	0.992

units, and we shall attempt to determine a conversion factor from these units to kilocalories/mole.

The results of a number of calculations are summarized in Table II. Here, the parameters on which the calculated energies depend are systematically varied and the equilibrium geometry is calculated for methane, ethane, and ethylene. In addition, the ratio of the experimental and calculated heats of atomization are given. The parameter R refers to the calculated heats of atomization and is given by

$$R = \frac{\Delta E(\text{ethane}) - \Delta E(\text{ethylene})}{\Delta E(\text{ethylene}) - \Delta E(\text{methane})}$$

The experimental value of this ratio is 1.034. Finally, the table also gives the calculated charge on a hydrogen in ethane.

The first set of parameters in the table are the original Pople values. A decrease of the carbon β-proportionality constant to 17.5 results in a reasonable carbon–carbon bond length. However, the value of R is not satisfactory. Small changes in the other parameters do not lead to a markedly improved value of R. All of the average ionization potentials were then considerably varied giving the second group of parameters. Here, R is considerably more satisfactory. The data suggest that there is little value in modifying the average ionization potential for hydrogen, and, since this is an experimentally determined quantity, it was returned to its original value.

The values of the β-proportionality constants were fixed by the necessity of fitting the experimental structural data. The values of the carbon ionization potentials were then set by requiring that the correct value of R be obtained, and that the charge on hydrogen be close to unity. This led to the final set of parameters in the table.

Although the correct value of R is obtained, the ratios of the observed and calculated heats of atomization are not constant, indicating that if one is plotted against the other, a small intercept would be found. It did not appear possible to eliminate the intercept.

In order to see if the new set of parameters was reasonable, the equilibrium C—C bond length and the equilibrium C—C—C and H—C—H bond angles were calculated for propane, benzene, acetylene, and allene (Table III). In each case, there is good agreement between the calculated and observed values. The bond angles agree within about 1°, and the bond lengths agree to within about 0.03 A. A further increase in the value of the hydrogen β-proportionality constant might be desirable. It should be noted that the changes in the parameters which resulted in improved agreement with the observed bond lengths also gave an improved agreement with the observed bond angles.

Table III. Observed and Calculated Geometrical Parameters

		Length, A			Value, deg		
Compd	Bond	Calcd	Obsd	Angle	Calcd	Obsd	Ref
Methane	C—H	1.124	1.106				*a*
Ethane	C—H	1.128	1.107	H-C-C	111.5	110.5	*b*
	C—C	1.506	1.536				
Propane	C—C	1.513	1.526	C-C-C	113.3	112.4	*c*
				H-C-H	105.6	106.1	
Ethylene	C—H	1.120	1.084	C-C-H	123.3	122.3	*d*
	C═C	1.356	1.332				
Benzene	C—C	1.423	1.397				*e*
Acetylene	C—H	1.103	1.059				*f*
	C≡C	1.239	1.205				
Allene	C—H	1.120	1.082	C-C-H	122.8	120.2 121.5	*g*
	C═C	1.342	1.312				

[a] L. S. Bartell, K. Kuchitsu, and R. J. de Neui, *J. Chem. Phys.*, **35**, 1211 (1961). [b] A. Almenningen and O. Bastiansen, *Acta Chem. Scand.*, **9**, 815 (1955). [c] D. R. Linde, Jr., *J. Chem. Phys.*, **33**, 1514 (1960). [d] L. S. Bartell and R. A. Bonham, *ibid.*, **31**, 400 (1959). [e] A. Almenningen, O. Bastiansen, and L. Fernholt, *Kgl. Norske Videnskab. Selskabs Skrifter*, No. 3 (1958); A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34**, 350 (1956). [f] J. H. Callomon and B. P. Stoicheff, *ibid.*, **35**, 373 (1957). [g] A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem., Scand.*, **13**, 1699 (1959).

In comparing the experimental and observed atomization energies, the bond lengths were rounded off to the nearest 0.01 A, and the parameters observed for propane were assumed also to apply to n-butane. The energies were calculated, and it was found advantageous to make an additional small correction in the carbon average ionization potentials (2s = 10.3, 2p = 6.3). The values thus obtained are summarized in Table IV. A

Table IV. Calculated and Observed Energies[a]

Compd	ΔH_f, kcal/mole	ΔH (atom.)	Zero-pt energy	Classical ΔH (atom.)	E, au	ΔE (atom.)[b]	Calcd ΔH (atom.)[c]
Methane	−15.99	392.86	27.11	419.97	−9.8155	1.7629	419.61
Ethane	−16.52	667.02	45.18	712.20	−18.1617	3.1114	713.60
Propane	−19.48	943.61	62.46	1006.07	−26.5048	4.4568	1006.91
Butane	−23.67	1221.43	79.77	1301.20	−34.8406	5.7949	1298.62
Ethylene	14.52	532.74	30.70	563.44	−16.4167	2.4213	563.14
Benzene	24.00	1308.06	62.84	1370.90	−44.9582	6.1367	1373.14
Allene	44.70	672.95	33.23	706.18	−23.0351	3.0969	710.44
Acetylene	54.33	389.69	16.18	406.50	−14.6883	1.7479	416.33

[a] $I(2s) = 10.3$ ev, $I(2p) = 6.3$ ev. [b] $E(C) = -5.9428$, $E(H) = -0.5275$. [c] $\Delta H(\text{atom.}) = 218.01 \times \Delta E(\text{atom.}) + 35.28$.

Table V. Structures and Energies of Hydrocarbon Derivatives

Species	r (CH)	r (CC)	A (CCH)	A (CCC)	E, au	ΔE (atom.)	ΔH_f (0°K), ev	ΔH (atom.), ev	Zero-pt energy, ev	Class. ΔH (atom.)	Calcd ΔH
A. Radical Cations											
CH_4^+	1.151				−9.1487	1.6236	12.29[a]	17.64	1.18	18.82	18.84
$C_2H_6^+$	1.144	1.435	114.8		−17.6101	3.0873	10.93	30.86	1.92	32.78	32.72
$C_3H_7^+$	(1.14)	1.475		121.0	−26.0242	4.5037	10.23	43.42	2.71	46.13	46.14
$\Delta H(\text{atom.}) = 9.48\Delta E + 3.45$ ev (9.48 ev = 218.7 kcal/mole)											
B. Radicals											
$CH_3\cdot$	1.127				−8.8581	1.3329	33.4[b]	291.9	20.0	311.9	311.7
$C_2H_5\cdot$	1.118	1.468	115.5		−17.2311	2.7083	27.9	571.0	38.1	609.1	609.4
2-$C_3H_7\cdot$	1.122	1.480		128.3	−25.5941	4.0736	22.9	849.6	55.4	905.0	904.8
$\Delta H(\text{atom.}) = 216.4\Delta E + 23.2$ kcal/mole											
C. Cations											
CH_3^+	1.128				−8.3849	1.3873	263[c]	376	20	396	396
$C_2H_5^+$	1.126	1.428	114.1		−16.8364	2.8411	230	682	38	720	721
2-$C_3H_7^+$	1.128	1.456		128.3	−25.2431	4.2501	205	981	55	1036	1036
$\Delta H(\text{atom.}) = 223.6\Delta E + 85.5$ kcal/mole											

[a] The values are based on the ionization potentials of the hydrocarbons (R. I. Reed, "Ion Production by Electron Impact," Academic Press Inc., London, 1962) and the heats of formation of the hydrocarbons. [b] Kcal/mole; values based on the C–H bond dissociation energies (T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press Inc., New York, N. Y., 1954) and the heats of formation of the hydrocarbons. [c] The values are based on the ionization potentials of the free radicals (F. P. Lossing, P. Kebarle, and J. B. DeSousa, *Advan. Mass Spectry.*, **1**, 431 (1959)).

least-squares fit of calculated and observed atomization energies for methane through benzene gave

$$\Delta H(\text{atom.}) = 218.01 \times \Delta E(\text{atom.}) + 35.28$$

The last column gives the heats of atomization calculated form this equation, and it can be seen that the fit is quite good. The heats of atomization of allene and acetylene were also calculated using the same equation. The result was satisfactory for allene, but was in error by 2.5% for acetylene.

The calculations summarized above suggest that it should be possible to calculate the geometries and heats of atomization of most alkanes and alkenes with only a relative small error. The fact that the energy of benzene was correctly calculated is particularly significant since this indicates the method can accommodate the energy changes due to electron delocalization.

It is quite possible that since the parameters were adjusted to fit data on hydrocarbons, they may not be appropriate for free radicals, cations, and similar species. This was tested by calculating the equilibrium geometry and energy for a group of radical cations, free radicals, and cations, giving the data shown in Table V. Both the radicals and cations were found to prefer the planer conformation. Little is known about the detailed structures of these molecules; however, the calculated bond lengths and angles appear reasonable. When the experimental energies were compared with the calculated energies, in each case the slope of the line was close to 220 kcal/mole/energy unit. Considering the errors associated with measuring the heats of formation of these species, and the fact that the ionization potential measurements lead to nonequilibrium geometries for the cations, the slopes are the same as that for the hydrocarbons within the uncertainty associated with the experimental measurements.

The intercept did vary considerably. The hydrocarbons and the free radicals gave about the same intercept, and the radical cations and cations gave about the same intercept. Thus, the magnitude of the intercept appears to be associated with the charge on the molecule. It can be seen that the CNDO method should be useful in estimating equlibrium geometry, and the difference in energy between molecules of the same charge type. It should be noted that although the Pople parameters were adjusted to give a reasonable fit to the experimental data, no attempt was made to determine the set of parameters which would give a "best fit" to a body of data. It is probable that the accuracy of the predictions could be further improved by small variations in the parameters.

Although the CNDO procedure appears very useful, one should not gain the impression that it is free from difficulties. The energies of eclipsed and staggered ethanes were calculated giving a difference of 0.0034. Using the conversion factor obtained herein, this is 0.7 kcal/mole whereas the observed value is 3 kcal/mole. Thus, for cycloalkanes and similar molecules, the energy due to the torsional barrier must be added to the calculated energy. Further, in connection with the data in Table V, the energy of the ethylene ion-radical was calculated. Unlike all the other cases, two minima were found. The first had r (CH) = 1.139, r (CC) = 1.300, A (CCH) = 138.0 and ΔE (atom.) = 2.4114. The second had r (CH) = 1.127, r (CC) = 1.450, A (CCH) = 121.7 and ΔE (atom.) = 2.4293. Using these energies, one calculates a ΔH (atom.) which is 1 ev too low. It is possible that the two conformations and the error in calculated energy are related, and that, for example, the ethylene radical cation is nonplanar. The vinyl radical and cation were not considered since the energies of these species appear not to be well established.

Experimental Section

The energies were calculated using the program written by G. A. Segal which was made available through the Quantum Chemistry Program Exchange at Indiana University. Initially, the program was modified so that the carbon and hydrogen β-proportionality constants and average ionization potentials were chosen within a predetermined range (about $\pm 20\%$ of the original value) using a random number generator. For each set of parameters, the energies of three ethane and three ethylene structures differing in C–C bond length, were calculated and the equilibrium geometry was obtained assuming a parabolic function. The data thus obtained are shown in Figure 1.

The data shown in Table II were obtained by calculating the energies of a number of structures for each molecule. For methane, three C–H bond lengths were used, and a parabolic function was assumed. For ethane and ethylene, three C–H bond lengths, three C–C bond lengths, and three C–C–H bond angles were taken. This set leads to 27 structures. Initially, the energies of each of the structures was obtained and the energies were fitted to a general quadratic function of the three geometrical parameters. A very good fit was obtained. From this, the equilibrium geometry and energy were easily obtained. The fitting procedure was repeated using only the odd-numbered structures, giving a set of 14. No significant difference in result was noted, and subsequent calculations were based on a set of 14 structures.

The data in Table III were obtained in a similar fashion, using the parameters on the last line of Table II. In the case of propane, the methyl group geometry found in ethane was assumed, and only the geometry about the central carbon was varied. The C–H bond length was taken as 1.12 A. The energies shown in Table IV were obtained using $\beta_H = 10.0$, $\beta_C = 17.5$, I (1s) = 7.176, I (2s) = 10.3, and I (2p) = 6.3. The CH bond lengths were taken as 1.12 A except for acetylene for which 1.10 A was used. The C–C lengths were rounded to the nearest 0.01 A, and the calculated bond angles were used. Butane was assumed to have the geometrical parameters calculated for propane. The heat of formation of carbon was taken as 170.39 kcal/mole and that for hydrogen was 51.62 kcal/mole.

The results summarized in Table V were obtained in the same fashion as that of Table III. The heats of atomization were calculated for the process leading to a neutral carbon atom, hydrogen atom, and, in the case of the cations, a proton. The heat of formation of the latter was taken as 365.14 kcal/mole. The zero-point energies of the radical cations were assumed to be the same as that for the hydrocarbons. The difference in zero point energy between a hydrocarbon and its radical cation might be expected to be roughly constant, leading to relatively little error in the calculated slope. The radicals were assumed to have a zero-point energy equal to that of the parent hydrocarbon less one C–H stretching vibration (3000 cm^{-1}) and two bending vibrations (1000 cm^{-1}). The cations were assumed to have the same zero-point energy as the radicals.

Solvolysis of Bicyclo[2.1.0]pentane-5-methyl and Bicyclo[3.1.0]hexane-6-methyl Tosylates[1]

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Abstract: The rates and products of the solvolysis of the *exo-* and *endo*-bicyclo[2.1.0]pentane-5-methyl and bicyclo[3.1.0]hexane-6-methyl tosylates in acetic acid and in aqueous ethanol are reported. The data suggest that ionization leads first to the cyclopropylcarbinyl cation. The nature of reactions leading from these ions to the products is discussed.

Cyclopropylcarbinyl and cyclobutyl derivatives are of considerable interest because of their high solvolytic reactivity.[3] A number of suggestions have been made concerning the structure(s) of the ions.[3,4] Recently, the tertiary cyclopropylcarbinyl cations have been shown *via* nmr spectroscopy to have an unrearranged structure.[5] We have examined the solvolysis of the bicyclo[3.1.0]hexane-6-methyl tosylates[6] and the bicylo-[2.1.0]pentane-5-methyl tosylates[7] and have concluded that the ion initially formed from these primary alcohol derivatives also must have the cyclopropylcarbinyl cation structure. The same conclusion has been reached by Schleyer and Van Dine[8] in their examination

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[2] National Science Foundation Predoctoral Fellow, 1963–1966.

[3] *Cf.*, J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509, 3542 (1951); R. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

[4] S. Winstein and E. Kosower, *ibid.*, **81**, 4399 (1959).

[5] C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998 (1965); N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *ibid.*, **87**, 3000 (1965).

[6] K. B. Wiberg and A. J. Ashe, III, *Tetrahedron Letters*, 1553 (1965).

[7] K. B. Wiberg and A. J. Ashe, III, *ibid.*, 4245 (1965).

[8] P. von R. Schleyer and G. W. Van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966).