potential whereas further fluorination progressively reduces it.

It should be noted that calculations of ionization potentials, using a SCF MO π approximation, failed completely to reproduce these trends.[21]

D. Dipole Moments. Table XI compares calculated[22,23] and observed dipole moments of some fluorinated hydrocarbons. The agreement is obviously satisfactory. Note in particular the correct prediction of the rather strange changes in dipole moment along the series CHF_3, CH_2F_2, CHF_3 and the correct prediction of the moments of CH_2F_2 and $CH_2{=}CF_2$. While the absolute values for the moments are somewhat too large, so too are those given by recent *ab initio* SCF calculations.[24] The CNDO/2 method fails to reproduce the observed trends.[25]

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[21] M. J. S. Dewar, A. J. Harget, and N. Trinajstić, unpublished results.

[22] N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, 50, 1262 (1969).

[23] R. N. Dixon, *Mol. Phys.*, **12**, 83 (1967).

[24] M. E. Schwartz, C. A. Coulson, and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 447 (1970).

[25] J. A. Pople and M. S. Gordon, *ibid.*, **89**, 4253 (1967).

Ground States of σ-Bonded Molecules. XVIII.[1]
An Improved Version of MINDO/2 and Its Application to Carbonium Ions and Protonated Cyclopropanes[2]

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Abstract: (a) Modifications of MINDO/2 lead to correct CH bond lengths; (b) calculations are reported for several classical carbonium ions, the estimated heats of formation agreeing with experiment; (c) calculations for the various species derived by protonation of cyclopropane are in marked disagreement with *ab initio* calculations but in better accord with experiment; (d) calculations for protonated methylcyclopropanes support the π-complex theory of electrophilic addition to cyclopropane.

While the MINDO/2 method[5,6] has proved remarkably successful in a number of connections,[5-7] the original version[6] suffered from several serious defects. (1) Dipole moments were overestimated by 50%. (2) Bond lengths involving hydrogen were overestimated by 0.1 or 0.15 Å. (3) Strain energies of small rings were underestimated, the errors for cyclopropane and cyclobutene being 10 and 25 kcal/mol, respectively. (4) The treatment of heteroatoms was not satisfactory, the bond angles being much too large and large errors appearing in the lengths and bond energies of bonds involving pairs of adjacent heteroatoms.

One problem of much topical interest where reliable calculations would be of value is that concerning the existence and nature of "nonclassical carbonium ions." However, it seemed unlikely that calculations by MINDO/2 could prove useful in this connection until steps had been taken to remedy the first two objections above. Errors in calculated dipole moments imply errors in the calculations of charge distributions which could have serious consequences in the case of ions while errors in bond lengths would clearly be inconvenient in the comparison of related classical and nonclassical ions.

The first of these difficulties was overcome[1] by a change in the method used to determine the values of one-center integrals for spectroscopic data. Here we describe a further small modification which leads to correct CH bond lengths. The new parameters have been used in several calculations carried out recently in these laboratories.[7g] Here we have applied them to various carbonium ions and to the various species that can be formed by protonation of cyclopropane and its methyl and dimethyl derivatives.

Theoretical Procedure

The original version[6] of MINDO/2 led to dipole moments that were too large by *ca.* 50% and to CH bond lengths that were systematically too long by 0.1 Å. As noted above, the first of these defects has already been corrected[1] by a change in the estimation of one-center integrals.

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[1] Part XVII: M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.*, **94**, 5296 (1972).

[2] This work was supported by the Air Force Office of Scientific Research through Contract F44620-70-C-0121 and by the Robert A. Welch Foundation through Grant F-126. A preliminary account of some of it has appeared: N. Bodor and M. J. S. Dewar, *ibid.*, **93**, 6685 (1971).

[3] Robert A. Welch Postdoctoral Fellow.

[4] On leave of absence from the Chemical-Pharmaceutical Research Institute, Cluj, Romania.

[5] M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

[6] N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

[7] (a) M. J. S. Dewar, E. Haselbach, and M. Shansal, *ibid.*, **92**, 3505 (1970); (b) N. Bodor and M. J. S. Dewar, *ibid.*, **92**, 4270 (1970); (c) A. Brown, M. J. S. Dewar, and W. W. Schoeller, *ibid.*, **92**, 5516 (1970); (d) M. J. S. Dewar and W. W. Schoeller, *ibid.*, **93**, 1481 (1971); (e) M. J. S. Dewar and J. S. Wasson, *ibid.*, **93**, 3081 (1971); (f) M. J. S. Dewar, M. Kohn, and N. Trinajstic, *ibid.*, **93**, 3437 (1971); (g) M. J. S. Dewar and S. Kirschner, *ibid.*, **93**, 4290, 4291, 4292 (1971); (h) M. J. S. Dewar, Z. Náhlovská, and B. D. Náhlovský, *Chem. Commun.*, 1377 (1971).

For reasons indicated in part X,[6] the one-electron core resonance integrals (β_{ij}^c) and the core–core repulsion function ($(CR)_{mn}$) are represented in MINDO/2 by the following parametric functions:

$$\beta_{ij}^c = S_{ij}(I_i + I_j)f_1(R_{mn}, S_{ij}) \qquad (1)$$

$$(CR)_{mn} = Z_m Z_n\,[\gamma_{mn} + (e^2/R_{mn} - \gamma_{mn})f_2(R_{mn})] \qquad (2)$$

Here R_{mn} is the internuclear separation between atoms m and n of which i and j are AO's, Z_m and Z_n on the corresponding core charges in units of the electronic charge e, and the remaining symbols have their usual significance. The functions f_1 and f_2 were chosen after extensive trials, the original[5,6] version being

$$f_1 = B_{mn};\; f_2 = e^{-\alpha_{mn}R_{mn}} \qquad (3)$$

where B_{mn} and α_{mn} are parameter characteristics of the atom pair mn and chosen to fit (least squares) the heats of atomization and geometries of a set of standard molecules.

Table I. Functions and Parameters in the Modified Version of MINDO/2

Bond	f_1	B_{mn}	f_2	α_{mn}
CC	B_{CC}	0.3512	$e^{-\alpha_{CC}R_{mn}}$	1.6737
CH	B_{CH}	0.2823	$\alpha_{CH}e^{-R_{mn}}$	0.4929
HH	$B_{HH(1+\|S_{ij}\|)^{-1}}$	0.3313	$\alpha_{HH}\gamma_{mn}$	1.0005

Initial attempts to correct the CH bond lengths by varying the functions f_1 and f_2 in eq 1 and 2 failed. We therefore tried using different core repulsion functions for CH and CC bonds. This procedure can be justified on physical grounds since the carbon core, unlike that of hydrogen, includes inner shell electrons. One might on this basis expect the appropriate form of f_{mn} to depend on the rows in the periodic table in which the elements m and n occur. In the case of HH, we had also to modify the function f_1 in the expression for the resonance integral. The final expressions for f_1 and f_2, and the values for the parameters B_{mn} and α_{mn} found by a least-squares fit[5,6] to the heats of formation and geometries of a set of standard hydrocarbons, are shown in Table I.

As indicated above, the one-center parameters were those of part XVII. The calculations otherwise followed the same pattern as before,[5,6] molecular geometries being calculated by the Simplex method.[7c,8] For convenience, the calculated heats of atomization were converted to heats of formation at 25°, using the following values for the heats of formation of gaseous atoms

$$\text{C, 170.89 kcal/mol; H, 52.102 kcal/mol} \qquad (4)$$

For convenience we shall refer to this version of MINDO/2 as MINDO/2′.

Results and Discussion

A. Hydrocarbons. Calculations for a number of hydrocarbons are compared with experiment in Table II. It will be seen that the calculated CH bond lengths

Table II. Comparison of Calculated and Observed Heats of Formation (ΔH_f) and Geometries of Hydrocarbons

	ΔH_f (kcal/mol at 25°)				
		Method			Geometry,[k]
Molecule	Obsd[a]	A[l]	B[m]	C[k]	calcd (obsd)
HC≡CH	54.3	57.7	60.3	62.0	R(C≡C) = 1.214 (1.205)[b] R(C—H) = 1.047 (1.059)
$CH_2{=}CH_2$	12.50	13.5	17.6	12.4	R(C═C) = 1.343 (1.338)[c] R(C—H) = 1.072 (1.08$_6$))
CH_3CH_3	−20.2	−22.8	−24.6	−27.8	R(C—C) = 1.497 (1.532$_7$)[d] R(C—H) = 1.083 (1.10)[e]
CH_4	−17.9	−16.2	−19.9	−19.3	R(C—H) = 1.060 (1.093)[f]
$CH_3CH{=}CH_2$	4.9	0.7	4.9	4.5	R(C═C) = 1.333 (1.336)[f] R(C—CH_2) = 1.496 (1.501) R(═C—H) = 1.092 (1.090)
Benzene	19.3	19.8	21.5	18.8	R(C—C) = 1.411 (1.397)[g] R(C—H) = 1.097 (1.087)
Cyclopropane	12.7	−7.1	−2.6	−2.3	R(C—C) = 1.505 (1.510)[h] R(C—H) = 1.085 (1.089)
Cyclopropene	66.6	40.9	45.5	48.1	R(C═C) = 1.327 (1.300)[i] R(C—H) = 1.486 (1.515) R(C—H vinyl) = 1.059 (1.070), methylene = 1.083 (1.087)
Cyclobutene	37.5	9.4	19.2	14.9	R(C═C) = 1.340 (1.342)[j] R(C—C) = 1.508 (1.517) R(C—C) = 1.528 (1.566) R(C—H vinyl) = 1.075 (1.083), methylene = 1.095 (1.094)

[a] "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953. [b] J. H. Callomon and B. P. Stoicheff, *Can. J. Chem.*, **35**, 373 (1957). [c] H. C. Allen and E. K. Plyer, *J. Amer. Chem. Soc.*, **80**, 2673 (1958). [d] L. S. Bartell and H. K. Higginbotham, *J. Chem. Phys.*, **42**, 851 (1965). [e] L. S. Bartell, K. Kuchitsu, and R. J. de Neui, *ibid.*, **35**, 1211 (1967). [f] D. R. Lide, Jr., and D. Christensen, *ibid.*, **35**, 1374 (1961). [g] A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34**, 350 (1956). [h] O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964). [i] P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and W. G. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959). [j] B. Bak, J. J. Led, L. Nygaard, J. Rastrop-Anderson, and S. Sorenson, *J. Mol. Struct.*, **3**, 364 (1969). [k] Calculated from the present method. [l] Calculated by the MINDO/2 method. [m] Calculated by the method in part XVII.

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(8) See J. A. Nelder and R. Mead, *Comput. J.*, 7, 308 (1964).

are now in good agreement with experiment while the errors in CC bond lengths and in the calculated heats of formation are still about the same as before.[1,6] The modifications described here have not improved the results for compounds containing small rings. The calculated heats of formation are still too negative, implying that the strain energies in such systems are underestimated. Ionization potentials, calculated using Koopmans' theorem, agree closely with those given by the original version of MINDO/2 and so with experiment.[5,6,9]

B. Carbonium Ions. All the methods currently available for the study of organic molecules are essentially empirical and can be trusted only insofar as they have been checked against experiment. This is just as true for *ab initio* SCF methods as for semiempirical ones since the errors in the SCF energies are enormous in a chemical sense. If the results of *ab initio* calculations are useful, this can be so only through a cancellation of errors which cannot be justified on theoretical grounds and can only be established empirically.

In the case of nonclassical carbonium ions, there are unfortunately no experimental data that can be used to check our procedures. However, we should at least show that they are valid for as many related systems as possible. We therefore carried out calculations for several classical carbonium ions in the usual way, the geometries being optimized by the Simplex method.[7c,8]

No problems arose in the case of the methyl, ethyl, isopropyl, 2-butyl, 2-amyl, or *tert*-butyl cations. The *n*-Pr$^+$ and *n*-Bu$^+$ ions, however, proved unstable with respect to rearrangement to edge-protonated cyclopropanes (see below). The energy of the classical carbonium was therefore estimated by assuming the terminal CCC bond angle to have the same value (110.5°) as in the corresponding alkane. The various calculated heats of formation are shown in Table III.

Table III. Calculated and Observed Heats of Formation of Gaseous Cations

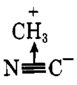
Ion	Heat of formation (kcal/mol at 25°) Calcd	 Obsd[a]
CH_3^+	276	260[b]
$CH_3CH_2^+$	225	219[b]
$CH_3CH_2CH_2^+$	216,[c] 188[d]	209,[b] 222[e]
$CH_3CH_2CH_2CH_2^+$	209,[c] 173[d]	218[e]
$CH_3CH^+CH_3$	191	190[b]
$CH_3CH_2CH^+CH_3$	183	183,[f] 192[e]
$(CH_3)_3C^+$	171	170,[g] 176[e]

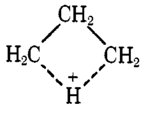
[a] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," National Bureau of Standards, Washington, D. C., 1969. [b] From photoionization, ionization potential of radical. [c] Value calculated for classical ion (see text). [d] Value for equilibrium species (edge-protonated cyclopropane). [e] From electron-impact ionization potential of radical (semilog plot). [f] From photoionization appearance potential of ion from 2-methylbutane and 2-ethylbutane. [g] From photoionization appearance potential of ion from neopentane.

Table III also shows experimental values estimated from the best available photoionization and electron-impact data. Except for methyl, the agreement is satisfactory, considering the uncertainties in the experimental values. Thus the differences between the photoionization (8.1 eV) and electron-impact (8.69 ± 0.05 eV) ionization potentials (ref *a* of Table III) of propyl radical are far greater than the claimed experimental errors and the heat of formation of *n*-Bu$^+$ (218 kcal/mol) is clearly out of step with those for Et$^+$ (219 kcal/mol) and *n*-Pr$^+$ (209 kcal/mol).

The calculated geometries and distributions of formal charge are shown in Table IV. The predicted conformation of *n*-Pr$^+$, *i.e.*, with methyl hyperconjugation, agrees with that predicted by Pople, *et al.*[10] The more interesting features of these results are (1) the marked increase in $^+$C–H bond length with alkyl groups at the cationic center; (2) the surprisingly small difference in charge at the cationic center between 1-Pr$^+$ and 2-Pr$^+$ and between 1-Bu$^+$ and 2-Bu$^+$; (3) the very short C–C$^+$ bond lengths; and (4) the striking difference in formal charge between configurationally different hydrogen atoms in methyl or methylene groups.

C. Protonated Cyclopropanes. The present version of MINDO/2 thus seems to deal adequately with classical carbonium ions. It has also been used successfully in the study of several reactions involving ions,[7g,11] implying that it gives a reasonable account of the nonclassical intermediate phases of reactions involving such ions. Further confirmation of its ability to deal with nonclassical systems was provided by a study[12] of the rearrangement of methyl isocyanide to acetonitrile which involves a π-complex intermediate **1**. We therefore felt that MINDO/2 calculations for "nonclassical" carbonium ions should lead to reasonably meaningful conclusions and so might be assistance in this rather turbid area.


1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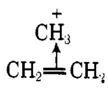
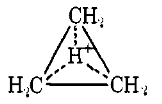

3


4

One such problem which has aroused much attention recently is the nature of the species formed by protonation of cyclopropane and the fate of *n*-propyl cation in solution.[10,13,14] Four such species have been considered, *i.e.*, *n*-Pr$^+$, the edge-protonated cyclopropane **2**, the π complex **3** ("corner-protonated cyclopropane"), and center-protonated cyclopropane **4**.

When we applied our Simplex procedure starting with geometries corresponding to *n*-Pr$^+$ or **3**, the structures changed continuously at each iteration until they both converged on the edge-protonated isomer **2**. According to our calculations, **2** is therefore the *only* stable species formed by protonation of cyclopropane.

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(9) N. Bodor, M. J. S. Dewar, and S. D. Worley, *J. Amer. Chem. Soc.*, **92**, 19 (1970); N. Bodor, M. J. S. Dewar, W. B. Jennings, and S. D. Worley, *Tetrahedron*, **26**, 4109 (1970).

(10) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 1813 (1971).

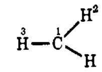
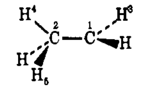
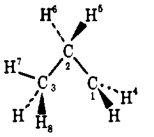
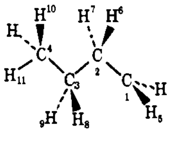
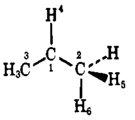
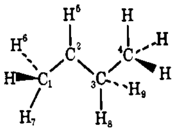
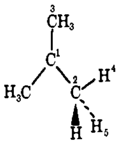
(11) M. J. S. Dewar and W. W. Schoeller, *Tetrahedron*, **27**, 4401 (1972).

(12) M. J. S. Dewar and M. C. Kohn, *J. Amer. Chem. Soc.*, **94**, 2704 (1972).

(13) (a) R. Hoffman, *J. Chem. Phys.*, 40, 2480 (1964); (b) C. C. Lee and J. E. Kruger, *Tetrahedron*, **23**, 2539 (1967); J. D. Petke and J. L. Whitten, *J. Amer. Chem. Soc.*, **90**, 3338 (1968); H. Fischer, H. Kollmar, and H. O. Smith, *Tetrahedron Lett.*, 5821 (1968).

(14) C. J. Collins, *Chem. Rev.*, **69**, 543 (1969); G. J. Karabatsos, C. Zioudrou, and S. Meyerson, *J. Amer. Chem. Soc.*, **92**, 5996 (1970), and papers cited therein.

Table IV. Calculated Geometries and Distributions of Formal Charge for Carbonium Ions

Ion	Bond lengths,[a] A	Bond angles,[a] deg	Formal charge[b]
	$\overline{12}$, 1.062	$\overline{213}$, 120	1, 0.5764
	$\overline{12}$, 1.421 $\overline{13}$, 1.082 $\overline{24}$, 1.093 $\overline{25}$, 1.081	$\overline{213}$, 126 $\overline{124}$, 112 $\overline{125}$, 113	1, 0.4514 2, −0.1170 3, 0.0901 4, 0.2108 5, 0.1373
	$\overline{12}$, 1.435 $\overline{23}$, 1.534 $\overline{14}$, 1.085 $\overline{25}$, 1.082 $\overline{36}$, 1.081 $\overline{37}$, 1.090	($\overline{123}$, 110.5)[c] $\overline{214}$, 127 $\overline{526}$, 106 $\overline{237}$, 111 $\overline{238}$, 113	1, 0.4267 2, −0.0225 3, 0.0142 4, 0.0800 5, 0.0987 7, 0.1083 8, 0.0580
	$\overline{12}$, 1.429 $\overline{23}$, 1.575 $\overline{34}$, 1.519 $\overline{15}$, 1.089 $\overline{26}$, 1.082 $\overline{38}$, 1.080 $\overline{4}$, $\overline{10}$, 1.081 $\overline{4}$, $\overline{11}$, 1.090	($\overline{123}$, 110.5)[c] $\overline{234}$, 111.5 (ass) $\overline{215}$, 126 $\overline{627}$, 104 $\overline{839}$, 105 $\overline{34}$, $\overline{10}$, 111 (ass) $\overline{34}$, $\overline{11}$, 113 (ass)	1, 0.4068 2, −0.0520 3, 0.0949 4, −0.0607 5, 0.0776 6, 0.0990 8, 0.0600
	$\overline{12}$, 1.452 $\overline{14}$, 1.098 $\overline{25}$, 1.093 $\overline{26}$, 1.082	$\overline{213}$, 130 $\overline{125}$, 113 $\overline{126}$, 111	1, 0.4281 2, −0.1236 4, 0.0429 5, 0.1508 6, 0.0865
	$\overline{12}$, 1.455 $\overline{23}$, 1.466 $\overline{34}$, 1.539 $\overline{25}$, 1.094 $\overline{38}$, 1.089 $\overline{39}$, 1.093	$\overline{521}$, 114.1 $\overline{523}$, 116.7 $\overline{234}$, 112 $\overline{238}$, 110.6 $\overline{239}$, 109.5 $\overline{218}$, 113 (ass) $\overline{217}$, 111 (ass)	1, −0.1202 2, 0.426 3, −0.0424 4, −0.0119 5, 0.0409 6, 0.1491 7, 0.0840 8, 0.0587 9, 0.1191
	$\overline{12}$, 1.483 $\overline{24}$, 1.093 $\overline{25}$, 1.082	$\overline{124}$, 110.5 $\overline{125}$, 112	1, 0.3907 2, −0.1200 4, 0.0784 5, 0.1222

[a] All angles and bond lengths were optimized by the Simplex procedure, except the angles in the methyl groups of 1-Bu$^+$ and 2-Bu$^+$. These were assumed to be the same as in *n*-Pr$^+$ since the values in *n*-Pr$^+$ were also the same as those for the lower paraffins. [b] In units of the electron charge. [c] See text.

It, and the isopropyl cation, represent the only minima on the $C_3H_3^+$ potential surface.

Estimates of the energy of *n*-Pr$^+$, **3**, and **4** were obtained by applying geometrical restraints. In *n*-Pr$^+$ the CCC bond angle was fixed (see above), in **3** the CH bond lengths in the apical group were assumed equal, and in **4** the central hydrogen was assumed to be equidistant from all three carbons. The geometries were otherwise optimized (except as indicated below in Table VI). The calculated heats of formation are shown in Table V together with that of the isomer isopropyl cation. Their values relative to *n*-Pr$^+$ are also listed together with those calculated by Pople, *et al.*,[10] by two *ab initio* SCF procedures.

It will be seen that our results agree with those of Pople, *et al.*,[10] in predicting **4** to be very unstable and in the relative energies of *n*-Pr$^+$ and *i*-Pr$^+$. Our conclusions differ seriously from theirs, however, in the case of the "nonclassical" ions **2** and **3**. We predict both these to be much more stable than *n*-Pr$^+$, the edge-protonated isomer being the more stable of the two, whereas Pople, *et al.*,[10] predict **3** to be much less stable than *n*-Pr$^+$ or **2**, the latter being comparable with *n*-Pr$^+$.

Table V. Calculated Heats of Formation at 25° (ΔH_f) of $C_2H_3^+$ Isomers

Ion	ΔH_f, kcal/mol	ΔH_f relative to *n*-Pr$^+$, kcal/mol		
		This paper	STO-3G[a]	4-31G[a]
n-Pr$^+$	216.0	0	0 (+0.8)[b]	0 (−0.5[b])
i-Pr$^+$	191.5	−24.5	−19.7	−17.4
2	187.6	−28.4	+3.1	−0.1
3	195.0[c]	−21	+7.4	+9.7
4	247.5	+31.5	+141.3	+122.3

[a] Reference 10; the values are relative to the methyl-staggered conformer of *n*-Pr$^+$. [b] Value for methyl-eclipsed conformer. [c] Value almost independent of orientation of methyl (*i.e.*, the methyl is predicted to rotate freely).

The experimental evidence[14] shows very clearly that n-Pr$^+$ can rearrange in aqueous solution to protonated cyclopropane. The evidence also suggests,[14] though with less certainty, that **2** is the most stable form. Now the solvation energy in water of the classical ion n-Pr$^+$ must be much greater than those of the nonclassical isomers **2** or **3** because not only is the charge in n-Pr$^+$ more localized but there is an empty 2p AO not used directly for bonding. In **2** and **3** all the carbon AO's participate in two- or three-center covalent bonds. It seems fairly certain that the lifetime of n-Pr$^+$ in aqueous solution must be very short so rearrangement could hardly occur if it involved any appreciable endothermicity. If these arguments are accepted, it follows that either **2** or **3** must be much more stable than n-Pr$^+$ and that this is probably true in particular of **2**.

Our calculations predict **2** to be more stable than i-Pr$^+$. The difference is, however, probably within the limits of accuracy of the MINDO/2 method. It is known that i-Pr$^+$ is more stable than **2** in solution but, of course, this could be due to the greater solvation energy of the classical isopropyl cation.

The difference in energy between n-Pr$^+$ and i-Pr$^+$ calculated by Pople, *et al.*, is in better agreement than ours with a recent experimental estimate (16 kcal/mol[15]). This is not surprising because detailed studies by Pople and his collaborators[16] have shown that their procedures, particularly 4-13G, give very good estimates indeed of the relative energies of isomers containing similar numbers of similar bonds. This demonstration does not, however, extend to situations where very different types of bonds are present and, of course, it is well recognized that SCF procedures lead to very poor estimates of dissociation energies and force constants. It would not therefore be surprising if they failed likewise in a comparison of isomeric classical and nonclassical structures.

We have also carried out calculations for protonated methylcyclopropanes and protonated *cis*-1,2-dimethylcyclopropanes. The calculated heats of formation are shown in Chart I.

These results are in good agreement with the predictions of simple MO theory. Thus the bond between the basal atoms and apical atoms in a π complex is a dative bond.[17] It should be strengthened by −I substituents (*e.g.*, alkyl) in the donor component and weakened by such substituents in the acceptor component. One would therefore expect protonation of an alkylated cyclopropane to occur preferentially at the least alkylated carbon. Our calculations confirm this both for methylcyclopropane and for *cis*-1,2-dimethylcyclopropane. On the other hand, the three-center bond in an edge-protonated cyclopropane is a covalent bond. The carbon atoms are now all effectively quadricovalent. The effect of methyl substituents should be small and less dependent on their position (since they are roughly equidistant for the center of charge). The calculated heats of formation of the isomeric edge-protonated isomers are indeed very similar and the balance between π complex and edge-protonated isomers swings over to the former with introduction of methyl groups.

Chart I. Calculated Heats of Formation (kcal/mol at 25°) for Protonated Methylcyclopropane and Protonated *cis*-1,2-Dimethylcyclopropane

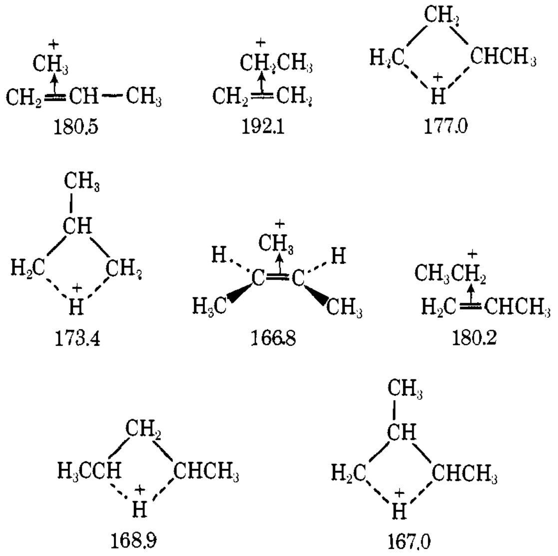
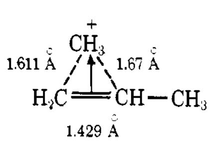
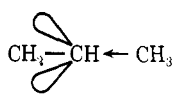


Table VI shows calculated geometries and distributions of formal charge in **2**, **3**, and their monomethyl and dimethyl derivatives. The bond lengths calculated for **3** by Pople, *et al.*,[10] are included for comparison.

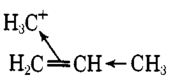
It will be seen that our calculations are in complete accord with the predictions of simple π-complex theory[17] according to which the apical group in a π complex such as **3** should be attached to the ethylene moiety by a strong dative bond. Thus the distance of the apical methyl carbon in **3** from a line joining the basal carbons is 1.46 Å and while the basal carbons carry large positive charges, the apical one is slightly negative. The CC bond lengths found by Pople, *et al.*,[10] are much longer than ours, corresponding to their prediction that **3** should be no more stable than the isomeric primary carbonium ion. Moreover the bond lengths in the propene–methyl π complex **5** correspond to earlier intuition.[17] It was there supposed that the inductive effect of the methyl would polarize the adjacent double bond in the manner indicated in **6** so that the methyl in the π complex would be attached off-center (**7**). A similar polarization was noted earlier in the calculated[12] structure of the π complex **1**.



5

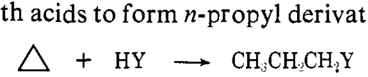


6

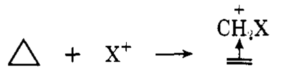


7

D. Electrophilic Addition to Cyclopropane. These results also support the π-complex theory[17a] of electrophilic addition to cyclopropanes, for example, their reactions with acids to form n-propyl derivatives.



It was supposed[17a] that the first step is addition of an electrophile X$^+$ to form a π complex


(5)

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(15) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

(16) W. J. Mehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970).

(17) (a) M. J. S. Dewar, "The Electron Theory of Organic Chemistry, Clarendon Press, Oxford, 1949; (b) *Bull. Soc. Chim. Fr.*, **18**, C71 (1951); (c) "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

Table VI. Calculated Geometries and Charge Distributions in Protonated Cyclopropanes

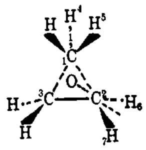
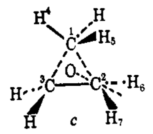
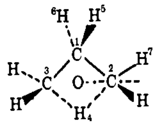
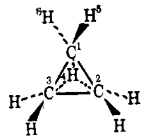
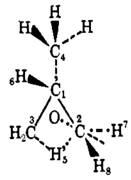
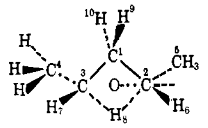
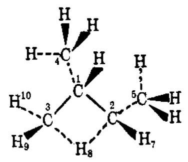
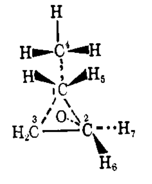
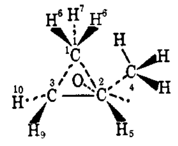
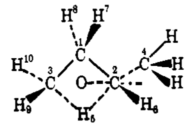
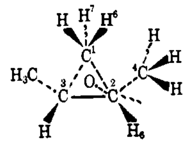
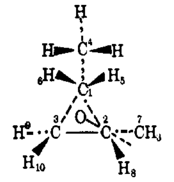
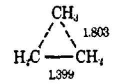
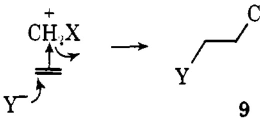
Structure	Bond lengths, Å	Bond angles,[a] deg	Atom no.	Formal charge[b]
	$\overline{12}$, 1.628	$\overline{023}$, 17.2	1	−0.0708
	$\overline{23}$, 1.419	$\overline{014}$, 118.8	2	0.1386
	$\overline{14}$, 1.087		4	0.0861
	$\overline{26}$, 1.081		5	0.1542
			6	0.1054
			7	0.0941
	$\overline{12}$, 1.627	$\overline{023}$, 16.8	1	−0.0662
	$\overline{23}$, 1.419	$\overline{014}$, 17.6	2	0.1392
	$\overline{14}$, 1.082		3	0.1360
	$\overline{26}$, 1.089		4	0.1755
			5	0.1083
			6	0.1002
			7	0.0993
	$\overline{12}$, 1.500	$\overline{023}$, 29.8	1	0.0176
	$\overline{23}$, 1.673	$\overline{516}$, 108.7	2	0.0907
	$\overline{24}$, 1.272		4	0.1746
	$\overline{15}$, 1.081		5	0.1091
			7	0.1022
	$\overline{12}$, 1.531	$\overline{123}$, 60	1	−0.0907
	$\overline{14}$, 1.377	$\overline{231}$, 60	4	0.5484
	$\overline{15}$, 1.080		5	0.0802
			6	0.1612
	$\overline{12}$, 1.521	$\overline{023}$, 35	1	0.1026
	$\overline{23}$, 1.675	$\overline{016}$, 119.2	2	0.0583
	$\overline{14}$, 1.508	$\overline{014}$, 129	4	−0.0474
	$\overline{25}$, 1.255		5	0.1756
	$\overline{16}$, 1.081		6	0.0741
	$\overline{27}$, 1.079		7	0.0927
			8	0.0965
	$\overline{12}$, 1.508	$\overline{023}$, 27.8	1	−0.0310
	$\overline{23}$, 1.767	$\overline{9110}$, 108.8	2	0.1564
	$\overline{24}$, 1.524		4	−0.0694
	$\overline{28}$, 1.278		6	0.0707
	$\overline{26}$, 1.079		8	0.1070
	$\overline{19}$, 1.081		9	0.0938
			10	0.0964
	$\overline{12}$, 1.526		1	0.0628
	$\overline{13}$, 1.515		2	0.1328
	$\overline{23}$, 1.699		3	0.0508
	$\overline{28}$, 1.335		4	−0.0481
	$\overline{38}$, 1.218		5	−0.0710
	$\overline{14}$, 1.519		6	0.0801
	$\overline{25}$, 1.527		7	0.0684
			8	0.1510
			9	0.0920
			10	0.0889
	$\overline{12}$, 1.645	$\overline{023}$, 15	1	−0.0125
	$\overline{23}$, 1.415	$\overline{014}$, 115.9	2	0.1284
	$\overline{14}$, 1.549	$\overline{015}$, 118.8	4	−0.0626
	$\overline{15}$, 1.087		5	0.1325
	$\overline{16}$, 1.081		6	0.0906
			7	0.1003
	$\overline{12}$, 1.677	$\overline{023}$, 16.8	1	−0.0769
	$\overline{23}$, 1.429	$\overline{032}$, 17.8	2	0.2013
	$\overline{13}$, 1.611	$\overline{017}$, 118.8	3	0.1016
	$\overline{24}$, 1.519	$\overline{024}$, 127.2	4	−0.0772
	$\overline{16}$, 1.087		5	0.0800
	$\overline{25}$, 1.081		6	0.0878
			7	0.0924
			8	0.1357
			9	0.1399
			10	0.0804

Table VI (*Continued*)

Structure	Bond lengths, Å	Bond angles,[a] deg	Atom no.	Formal charge[b]
	$\overline{12}$, 1.508 $\overline{13}$, 1.500 $\overline{23}$, 1.719 $\overline{24}$, 1.521 $\overline{25}$, 1.329 $\overline{35}$, 1.210 $\overline{26}$, 1.079	$\overline{026}$, 126.1 $\overline{024}$, 127.8	1 2 3 4 5 6 7 8 9 10	−0.0062 0.1637 0.0776 −0.0738 0.1419 0.0755 0.1019 0.1003 0.0973 0.0953
	$\overline{12}$, 1.643 $\overline{23}$, 1.438 $\overline{24}$, 1.509 $\overline{16}$, 1.087	$\overline{023}$, 23.4 $\overline{024}$, 127	1 2 4 5 6 7	−0.0793 0.1659 −0.657 0.0615 0.1298 0.0686
	$\overline{12}$, 1.709 $\overline{13}$, 1.627 $\overline{23}$, 1.427 $\overline{14}$, 1.549 $\overline{27}$, 1.519 $\overline{16}$, 1.087 $\overline{28}$, 1.081		1 2 3 4 5 7 8 9	0.0886 0.1931 0.0788 −0.0563 0.1175 −0.0732 0.0476 0.0875
	*d*			

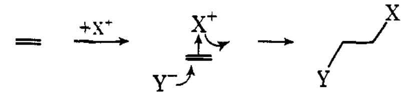
[a] The point 0 lies in the plane of the ring on a line bisecting the external HCH angle, as indicated. [b] In units of the electron charge. [c] Differs from above only in the conformation of methyl, the barrier to rotation of which is negligible (<0.1 kcal/mol). [d] π complex calculated by Pople, *et al.*[10]

This then reacts with the nucleophile Y^- in the same way as the corresponding π-complex intermediates in electrophilic addition to olefins



8 **9** (6)

CF.

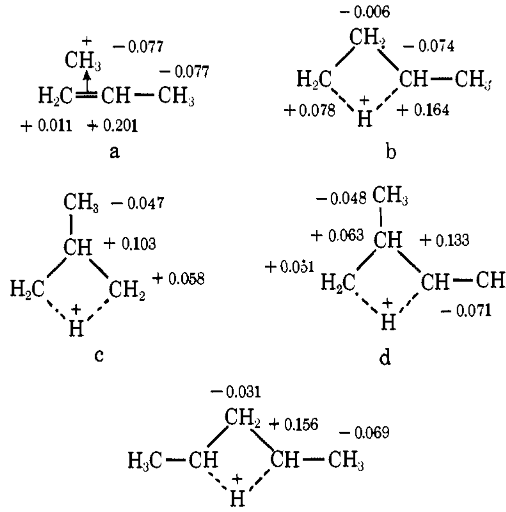


10 **11** (7)

The arguments given above, which are supported by the calculations reported here, imply that in alkylcyclopropanes the initial attack should take place at the least alkylated carbon atom. Likewise, analogy between the secondary attack on the π complex **8** to form **9**, and on the π complex **10** to form **11**, implies that the secondary reaction should occur at the most alkylated carbon. This argument accounts for the fact that such addition reactions obey Markovnikov's rule, the bond broken being that between the least alkylated and most alkylated carbon atoms in the cyclopropane ring.

The orientation of attack by the nucleophile on **8** or **10** was attributed[17a,b] to two contributing factors. In the first place, the asymmetry of the π complex (see **5**, **7**), due to polarization of the basal π electrons by the inductive effect of alkyl (see **6**), should favor a reaction in which the apical methyl migrates to the nearer basal atom. Secondly, the π polarization (**6**) should lead to a lower electron density at the more alkylated basal carbon, thus facilitating approach of the nucleophile. It has already been pointed out that our calculations support the predicted distortion of the π complex (see **5**). The calculated formal charges of the basal atoms are also in accord with the second prediction (Chart II).

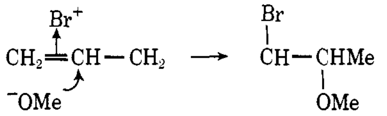
Chart II. Distributions of Formal Charges in Protonated Cyclopropanes



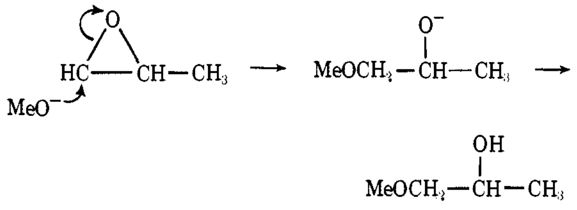
This discussion is based on the assumption that the intermediate is a π complex rather than a protonated cyclopropane. Our calculations and experiment[12] indicate that the isomeric edge-protonated cyclopropanes are comparable in stability with the most stable π complex and with each other and all these species probably undergo rapid interconversion. Since the edge-protonated isomers differ little in energy, unlike the π complexes (Chart I), the fact that addition follows Markovnikov's rule must imply either that the π complex reacts more readily with nucleophiles or that one of the edge-protonated forms reacts more readily than the others.

While we have not yet calculated reaction paths for attack by nucleophiles on these ions, the calculated charge distributions in the edge-protonated dimethylcyclopropanes (Chart II, d and e) would certainly lead one to expect d to react more easily, the positive charges on the carbon atoms in the C–H–C unit being smaller in d than in e. One must therefore find some reason why the π complex should react more readily with nucleophiles than does an edge-protonated isomer.

One of the curious aspects of electrophilic addition to olefins is the orientation of the secondary attack by nucleophiles (**10** → **11**). This is directly opposite to the orientation observed in the ring opening of epoxides or azirines by nucleophiles. Thus, nucleophiles attack the propene–Br$^+$ π complex at the substituted carbon while they attack propene oxide at the unsubstituted carbon; *e.g.*



$$\overset{Br^+}{CH_2{=}CH}{-}CH_2 \;\; {}^-OMe \longrightarrow \overset{Br}{CH}{-}\underset{OMe}{CHMe} \qquad (8)$$



(9)

This was attributed[17] to the relative planarity of the basal ethylene unit in the π complex, the approach of the reagent being normal to this plane and so relatively unhindered by methyl, whereas the opening of the ring in eq 9 is a typical S$_N$2 process and so subject to steric hindrance ("F strain") by α-methyl groups.

Our calculations (Table VI) support this intuition, the terminal groups in the ethylene units being bent out of the plane by only 17°. Now the three-center C–H–C bond in the edge-protonated cyclopropanes should behave as normal covalent bonds so far as the terminal carbon atoms are concerned; the attack by a nucleophile on such a system should therefore be analogous to a normal S$_N$2 reaction and subject to hindrance by α-methyl groups. While such hindrance should be less at the unsubstituted carbon atoms in the ions of Chart II (b–d), these atoms are predicted to carry only small positive charges. It is therefore not unreasonable to expect nucleophiles to react preferentially with the intermediate protonated cyclopropanes in their π-complex tautomeric forms.

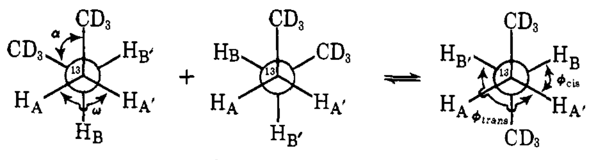
The Conformational Analysis of *n*-Butane[1]

Paul B. Woller and Edgar W. Garbisch, Jr.*[2]

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received September 7, 1971*

Abstract: The conformational analysis of 1,1,1,4,4,4-butane-d_6 (**1**) has been accomplished utilizing the temperature dependences of three nuclear magnetic resonance spectral parameters. The observed temperature dependences of the sum and the difference of the two vicinal spin–spin coupling constants and the chemical shift of the four equivalent methylene protons were correlated with the gauche ⇌ anti conformational equilibrium of **1**. The enthalpy difference for this equilibrium was found to be -681 ± 35 cal/mol at $\Delta S = -1.376$ eu. The CD_3CCCD_3 dihedral angle in the gauche conformer was calculated to be $66 \pm 1°$.

The simplest hydrocarbon capable of exhibiting gauche ⇌ anti conformational isomerism (eq 1)



(1)

1a gauche **1b** anti

is *n*-butane and as such it reflects the importance of nonbonded repulsive interactions that contribute to the relative stability of molecular conformers. This system has been the subject of a rather large number of theoretical calculations directed at accurately determining the correct form of the potential function for internal rotation about the central C–C bond and semiempirically estimating the conformational geometry and energy of the molecule.[3] In contrast, reports of direct experimental measurements regarding conformation and the barrier to internal rotation are somewhat meager.[4] The energy difference between the gauche

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(1) Presented in part by E. W. G. at the 159th National Meeting of the American Chemical Society, Feb 1969, Houston, Tex.

(2) Correspondence may be directed to E. W. G., The Nature Conservancy, P.O. Box P, St. Michaels, Md. 21663.

(3) (a) J. R. Hoyland, *J. Chem. Phys.*, **49**, 2563 (1968); (b) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7036 (1967); (c) P. Geneste and G. Lamaty, *Bull. Soc. Chim. Fr.*, 4456 (1967); (d) R. A. Scott and H. Scheraga, *J. Chem. Phys.*, **44**, 3054 (1966); (e) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 631 (1966); (f) A. Opschor, *Makromol. Chem.*, **85**, 249 (1965); (g) N. P. Borisova and M. V. Volkenstein, *Zh. Strukt. Khim.*, **2**, 469 (1961).

(4) (a) G. J. Szasz, N. Sheppard, and D. H. Rank, *J. Chem. Phys.*, **16**, 1704 (1948); (b) N. Sheppard and G. J. Szasz, *ibid.*, **17**, 86 (1949); (c)