Molecular Orbital Calculations on Carbonium Ions. II. The Methyl, Ethyl, and Vinyl Cations. The Series $C_3H_7^+$ [1]

R. Sustmann, J. E. Williams,[2] M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer

Contribution from the Departments of Chemistry, Princeton University,
Princeton, New Jersey 08540, and the University of Texas,
Austin, Texas 78712. *Received April 26, 1969*

Abstract: Semiempirical NDDO and *ab initio* Hartree–Fock–Roothaan SCF calculations are reported and compared for the isomeric structures of formulae $C_2H_3^+$ and $C_2H_5^+$. The NDDO (neglect of diatomic differential overlap) scheme is described. It is found that NDDO and all less complete schemes overestimate the stability of bridged ions, relative to the much more rigorous *ab initio* method. Thus NDDO favors the protonated acetylene over the vinyl cation structure by 32.0 kcal/mole, and the protonated ethylene over the ethyl cation structure by 33.2 kcal/mole. *Ab initio* calculations show the unbridged species to be more stable: the vinyl cation is favored by 25.1 kcal/mole, and the ethyl cation by 9.0 kcal/mole. NDDO calculations predict that an α-methyl substituent on a vinyl cation stabilizes the ion by 1.0–1.5 eV (*ca.* 20–35 kcal/mole) more than the methane–ethane or ethylene–propene energy differences. However, methyl substitution on protonated acetylene gives no such "extra" stabilization. NDDO calculations show the 2-propyl cation to be 18 kcal/mole more stable than the 1-propyl cation, in good agreement with experimental values. Edge-protonated cyclopropane is calculated to be 81 kcal/mole more stable than 2-propyl cation, but the validity of this result is considered dubious on theoretical grounds. Edge-protonated cyclopropane is computed to be 137 kcal/mole more stable than the face-protonated isomer by NDDO, in good agreement with the *ab initio* result of 125 kcal/mole. NDDO predicts corner-protonated cyclopropane to be some 20 kcal/mole less stable than the edge-protonated isomer.

The widespread occurrence of carbonium ions as reaction intermediates, and their more recent preparation in strong acid media, have stimulated investigations of their structure by molecular orbital methods.[3] Early extended Hückel (EHT) calculations[4] showed promise, but are not satisfactory for charged species or for calculating bond lengths. The use of more refined treatments, including electron–electron interactions and capable of predicting molecular geometries, was clearly indicated if meaningful results are to be obtained with both classical and nonclassical (bridged) structures.

While *ab initio* calculations have been performed on small cations[5,6] (and further results are reported in this paper) the need for semiempirical methods still prevails for most systems of chemical interest. Several approximate schemes have been applied to the calculation of carbonium ions.[7–10] A disadvantage of most of these procedures is that they do not account correctly for bond lengths. The most successful semiempirical treatment to date[10] uses the INDO procedure[11] for calculations on the $C_3H_7^+$ series.

In the present paper we apply a semiempirical method based on the neglect of diatomic differential overlap (NDDO), the formalism of which was proposed by Pople, Santry, and Segal.[12] This approximation of the exact Roothaan SCF scheme[13] has as yet found little application. An approximate *ab initio* method, using the NDDO scheme and orthogonalized basis set, was proposed by Cook, Hollis, and McWeeny[14] and subsequently applied in a few cases.[15] In the NDDO calculations described in this paper, only the valence electrons are included, and the inner shell is treated as part of an unpolarizable core. The integrals are evaluated in a way different from that of ref 14. The method as it is used here reproduces the carbon–carbon and carbon–hydrogen bond lengths over the range from triple to single bonds within 1–2%. We do not attempt to calculate heats of formation, which is the main objective of the MINDO procedure[16] (modified intermediate neglect of differential overlap). Our interest lies in the calculation of geometries and energy differences between geometrical isomers. Comparisons of our NDDO results with those of *ab initio* calculations in a few representative examples are highly instructive. There is much general agreement between the methods, but the great discrepancies that arise help clarify the consequences of the approximations of the NDDO method.

Method of Calculation. In the Roothaan formalism[13] the total electronic energy of a molecule is given as

$$E_{\text{electr}} = \frac{1}{2}\sum_{\mu\nu}P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) \qquad (1)$$

Starting from this scheme Pople, Santry, and Segal[12]

---

[1] Paper I [J. E. Williams, R. Sustmann, L. C. Allen, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **91**, 1037 (1969)] presented a preliminary account of part of this work.

[2] National Science Predoctoral Fellow, 1965–1969, Ph.D. Thesis, Princeton University, 1969.

[3] N. Muller and R. S. Mulliken, *J. Am. Chem. Soc.*, **80**, 3489 (1958).

[4] R. Hoffmann, *J. Chem. Phys.*, 40, 2480 (1964).

[5] R. E. Kari and I. G. Csizmadia, *ibid.*, **46**, 1817 (1967); **50**, 1443 (1969); G. von Bunau, G. Diercksen, and H. Preuss, *Intern. J. Quant. Chem.*, **1**, 645 (1967); S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, **45**, 734 (1966).

[6] J. D. Petke and J. L. Whitten, *J. Am. Chem. Soc.*, **90**, 3338 (1968).

[7] K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

[8] T. Yonezawa, H. Hakatsuji, and H. Kato, *J. Am. Chem. Soc.*, **90**, 1239 (1968).

[9] G. Klopman, *ibid.*, **91**, 89 (1969).

[10] H. Fischer, H. Kollmar, H. O. Smith, and K. Miller, *Tetrahedron Letters*, 5821 (1968).

[11] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

[12] J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, 5129 (1965).

[13] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[14] D. B. Cook, P. C. Hollis, and R. McWeeny, *Mol. Phys.*, **13**, 553 (1967).

[15] D. B. Cook and R. McWeeny, *Chem. Phys. Letters*, **1**, 588 (1968).

[16] N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); N. C. Baird, M. J. S. Dewar, and R. Sustmann, *ibid.*, **50**, 1275 (1969); N. C. Baird and M. J. S. Dewar, *J. Am. Chem. Soc.*, **91**, 352 (1969).

have derived the formulae for the F matrix elements in the NDDO approximation (eq 2 and 3). If μ and λ

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\mathrm{B}}\sum_{\lambda\sigma}{}^{\mathrm{B}} P_{\lambda\sigma}(\mu\nu/\lambda_0) - \frac{1}{2}\sum_{\lambda\sigma}{}^{\mathrm{B}} P_{\lambda\sigma}(\mu\sigma/\nu\lambda) \qquad \mu,\nu \text{ both on A} \tag{2}$$

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2}\sum_{\sigma}{}^{\mathrm{A}}\sum_{\gamma}{}^{\mathrm{B}} P_{\lambda\sigma}(\mu\sigma/\nu\lambda) \qquad \mu \text{ on A, } \nu \text{ on B} \tag{3}$$

both belong to the same atom, $H_{\mu\nu}$ has the form

$$H_{\mu\nu} = U_{\mu\nu} - \sum_{\mathrm{B}\neq\mathrm{A}} (\mu/V_{\mathrm{B}}/\nu) \tag{4}$$

$H_{\mu\nu}$ is called the resonance integral if μ and ν belong to different atoms. The total energy of the molecule is

$$E_{\text{total}} = E_{\text{electr}} + \sum_{\mathrm{A}<\mathrm{B}}\sum Z_{\mathrm{A}}Z_{\mathrm{B}}/R_{\mathrm{AB}} \tag{5}$$

Nuclear repulsions are treated as point-charge repulsions between cores.

Evaluation of Integrals. The evaluation of integrals follows closely the lines of other semiempirical valence-shell SCF procedures. The one-center repulsion integrals are the same as in the INDO procedure.[11] The repulsion of two electrons in an s orbital is calculated over Slater orbitals using Slater exponents of 1.0 for hydrogen and 1.625 for carbon, and the other integrals are derived from this with the aid of the Slater–Condon parameters.[11] The energy of an electron in a particular orbital, $U_{\mu\mu}$ in eq 4, is evaluated according to ref 11, except for hydrogen for which it is taken to be the same as in the MINDO procedure.[16]

Two-center repulsion integrals entering the NDDO approximation are computed over Slater orbitals.[17] They are first calculated in a local coordinate system and then transformed into the molecular system as it was done in the PNDO method.[18] As in other semiempirical procedures,[11,16] the two-center nuclear–electron integrals are set equal in magnitude and opposite in sign to certain electron repulsions times the charge of the core involved, thus avoiding the penetration effect.[19] If these integrals are evaluated exactly over Slater orbitals, then it is not possible to parametrize the NDDO scheme for geometries. In order to get correct bond lengths, it would be necessary to choose a very small value for each resonance integral, and this in turn does not yield meaningful covalent bonding.

There is a maximum of four different types of two-center nuclear–electron integrals involving an atom A, with four valence orbitals. These are equated to the following repulsion integrals times the effective charge of the nucleus of a second atom, B.

$$\begin{aligned}
\langle S_{\mathrm{A}}|V_{\mathrm{B}}|S_{\mathrm{A}}\rangle &= -Z_{\mathrm{B}}\langle S_{\mathrm{A}}S_{\mathrm{A}}|1/r_{12}|S_{\mathrm{B}}S_{\mathrm{B}}\rangle \\
\langle S_{\mathrm{A}}|V_{\mathrm{B}}|P\sigma_{\mathrm{A}}\rangle &= -Z_{\mathrm{B}}\langle S_{\mathrm{A}}P\sigma_{\mathrm{A}}|1/r_{12}|S_{\mathrm{B}}S_{\mathrm{B}}\rangle \\
\langle P\sigma_{\mathrm{A}}|V_{\mathrm{B}}|P\sigma_{\mathrm{A}}\rangle &= -Z_{\mathrm{B}}\langle P\sigma_{\mathrm{A}}P\sigma_{\mathrm{A}}|1/r_{12}|S_{\mathrm{B}}S_{\mathrm{B}}\rangle \\
\langle P\pi_{\mathrm{A}}|V_{\mathrm{B}}|P\pi_{\mathrm{A}}\rangle &= -Z_{\mathrm{B}}\langle P\pi_{\mathrm{A}}P\pi_{\mathrm{A}}|1/r_{12}|S_{\mathrm{B}}S_{\mathrm{B}}\rangle
\end{aligned} \tag{6}$$

The last kind of two-center integrals which needs to be specified is the resonance integral $H_{\mu\nu}$ with μ on A and ν on B. This expresses the energy of an electron occupying the overlap cloud of orbitals μ and ν. Exact evaluation of the integrals involved leads to values which are far greater than the values obtained from approximate methods. This was recognized by Cook, Hollis, and McWeeny[14] and shown to be a consequence of the nonorthogonality of the basis set. We chose the Mulliken approximation,[7] which in modified forms is used also in the MINDO[16] and PNDO[18] procedures (eq 7). The valence-state ionization potentials I_μ and

$$H_{\mu\nu} = \beta_{\mu\nu}{}^0 S_{\mu\nu}(I_\mu + I_\nu) \tag{7}$$

I_ν are readily computed from $U_{\mu\mu}$ by taking into account the one-center repulsions. The only adjustable parameter in our treatment is $\beta_{\mu\nu}{}^0$. This is taken to be a property of the type of bond under consideration. For the case of hydrocarbons, there are accordingly parameters for CC, CH, and HH bonds. The HH parameter was obtained by reproducing the correct energy for the hydrogen molecule. For $\beta_{\mathrm{CH}}{}^0$ and $\beta_{\mathrm{CC}}{}^0$ a bond-length criterion was used, as our main objective was to treat changes in geometries. They were chosen to reproduce the bond lengths in methane and ethane with an accuracy of 1–2%. Using these parameters, the same accuracy is obtained when minimizing the energy with respect to the CC bond lengths in ethylene and acetylene (Table I). Using the same parameters, a 2.2 kcal/mole rotation barrier for ethane was calculated, a value agreeing reasonably well with the experimental value of 2.88 kcal/mole.[21]

Table I. Experimental and Calculated Bond Lengths (Å)

	Calcd	Exptl[20]
Ethane (C—C)	1.515	1.534
Ethylene (C═C)	1.367	1.337
Acetylene (C≡C)	1.231	1.206
Methane (C—H)	1.095	1.093

Application to Carbonium Ions. Methyl Cation. In a preliminary communication[1] we reported *ab initio* and MINDO calculations of deformations of the methyl cation. The objective was to test the possibility that carbonium ions may be more stable in a nonplanar form when severe angle deformations are present. The results are listed in Table II along with NDDO calculations, performed for comparison.

Two sets of calculations were performed. In one, the HCH angle θ was held at 120°; in the other, θ was fixed at 90°. For each value of θ calculations were performed for geometries with the third hydrogen out of the HCH plane, this CH bond making angles φ of 0, 5, 15, and 30° with regard to the plane of the other atoms. All three types of computations show the same trend: the smaller the value of θ, the more *strongly* planarity is favored. The quantitative comparison is interesting in that while the MINDO approximation yields lower deformation energies than the more rigorous *ab initio* method, the NDDO procedure on the other hand shows the molecule to be more rigid than would be expected from the *ab initio* calculations. Taking the *ab initio* results to calibrate the semiempir-

---

(17) We thank Drs. F. A. Matsen and J. Browne for the subroutines to evaluate these integrals.

(18) M. J. S. Dewar and G. Klopman, *J. Am. Chem. Soc.*, **89**, 3089 (1967).

(19) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

(20) Tables of Interatomic Distances, Special Publication No. 11, The Chemical Society, London, 1958.

(21) J. Dale, *Tetrahedron*, 22, 3373 (1966); J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 31 (1968).

Table II. Bending Energies for Methyl Cation[a] (Kilocalories)

Deformation, degrees	NDDO[b] $\theta = 120°$	NDDO[b] $\theta = 90°$	*ab initio*[b] $\theta = 120°$	*ab initio*[b] $\theta = 90°$	MINDO[b] $\theta = 120°$	MINDO[b] $\theta = 90°$	NDDO[c] $\theta = 120°$	NDDO[c] $\theta = 90°$	MINDO[c] $\theta = 120°$	MINDO[c] $\theta = 90°$
5	0.36	0.44	0.27	0.28	0.14	0.17	0.80	0.70	0.17	0.14
15	2.80	3.57	2.13	2.47	1.15	1.35	7.47	6.36	1.60	1.19
30	12.40	14.43	8.38	9.81	4.17	5.37	29.81	25.35	6.09	4.55

[a] Relative to the planar methyl cations at $\angle$HCH = 120° and $\angle$HCH = 90°. [b] Out-of-plane movement of the third hydrogen, θ = fixed $\angle$HCH. [c] In-plane movement of the third hydrogen, θ = fixed $\angle$HCH.

ical methods, it is seen that MINDO underestimates and NDDO overestimates the energy changes. These differences obviously result from the different integral evaluation procedures in both semiempirical schemes.

The NDDO method takes the exact repulsion integrals and adjusts the nuclear–electron attractions to these, giving in general values for the integrals which are 25–30% greater than the MINDO values. In addition, many more integrals are included. The point-charge repulsion for the nuclear interaction in NDDO probably is also partly responsible for the greater rigidity.

One mode of deformation for the methyl cation was not considered in the earlier calculations: moving the third hydrogen in the plane while $\angle$HCH is kept fixed at 90 or 120°. MINDO and NDDO calculations indicate that this mode of deformation is easier at an HCH angle of 90° (columns 8–11 in Table II). In the perpendicular deformation the result was just reverse. The quantitative difference between the two calculations is remarkable. In the NDDO case E increases much more rapidly. This is again a consequence of the different approximations used in both procedures. Comparison of relative changes in total electronic and nuclear repulsion energies in the NDDO calculations shows almost exactly the same change in electronic energy for $\angle$HCH = 120 and 90°. The difference is due to the smaller increase in nuclear repulsion energies for $\angle$HCH = 90°: the separation of the hydrogen being moved is greater from the other hydrogen atoms in this geometry.

The preliminary communication[1] included also MINDO results for similar deformations on isopropyl and 7-norbornyl cations. In both molecules planarity around the carbonium-ion center was indicated to be the preferred geometry.

We conclude that classical ions prefer to be planar, even when distorted from the optimum geometry (θ = 120°). In fact, an in-plane distortion ($\theta < 120°$) increases the resistance to out-of-plane deformations. The different behavior for in-plane deformations, being easier at θ = 90°, is easily rationalized by the interplay of total electronic and nuclear repulsion energy, the latter being the more important term.

Ethyl Cation and Protonated Ethylene. The ethyl cation (I) is the simplest primary cation. Similarly, protonated ethylene (II) is one of the simplest bridged carbonium ions (Figure 1). Keeping the CH bond lengths to C_2 and to C_1 in I constant at 1.093 and 1.084 Å, respectively, the energy was minimized with respect to the CC bond length. The distance of minimum energy in the NDDO approximation is found at 1.43 Å. I has been calculated before by various authors. Wiberg[22] used a reparametrized CNDO program which reproduced CC bond lengths with accuracy comparable to that of the NDDO method. He also found the energy minimum of I at CC = 1.43 Å. Yonezawa, Nakatsuji, and Kato[8] carried out calculations with a semiempirical SCF procedure,[23] in its approximations similar to the MINDO method.[16] In this method nuclear repulsions are set equal to electron interactions. While this procedure has been shown to give good heats of formation provided standard geometries are available,[16] the results for molecules with unknown structures are only as good as the accuracy of the structures assumed.

The charge distribution given in I reflects the trends observed in other calculations.[8] The C_2 carries a negative charge whereas the positive charge is almost evenly distributed over the other atoms. The amount of positive charge distributed to C_2 hydrogens is a function of their orientation with respect to the p orbitals at C_1 and C_2. Compared to ethane the barrier to rotation in I should be reduced markedly. The calculated sixfold barrier to rotation in I is indistinguishable from zero within the error limit of the calculation. Such a low barrier is in agreement with barriers in other molecules which have sixfold rotational barriers.[21]

For II a geometry search yielded a CC length of 1.41 Å, and the distance of the bridging hydrogen from the center of the bond was found to be 1.0 Å, This geometry was obtained by varying the CC length from 1.33 to 1.44 Å and searching for the minimum position of the bridging hydrogen at each CC distance. CH bond lengths of the ethylene fragment, assumed to be planar, were kept at 1.084 Å and the HCH angle at 120°. The structure of lowest energy is 33.2 kcal/mole more stable than I. A comparison of the total electronic energy and nuclear repulsion in I and II reveals an increase of approximately 300 kcal/mole in nuclear repulsion in the bridged structure which is more than outweighed by the gain in electronic energy. The effective formation of a three-center bond in the electron-deficient bridged ethyl cation II accounts for this stabilization. The charges are more evenly distributed. Both carbon atoms in II have a very small positive charge, in contrast to the uneven distribution over the carbon atoms in I. The hydrogen atoms in II bear most of the positive charge.

Vinyl Cation and Protonated Acetylene. Recently there has been increasing interest in the chemistry of vinyl cations as intermediates in the solvolysis of vinyl compounds[24] and the electrophilic addition to triple bonds.[25]

---

(22) K. B. Wiberg, *J. Am. Chem. Soc.*, **90**, 59 (1968).

(23) T. Yonezawa, K. Yamaguchi, and H. Kato, *Bull. Chem. Soc. Jap.*, **40**, 536 (1967); H. Kato, M. Konishi, and T. Yonezawa, *ibid.*, **40**, 1017, 2761 (1967).

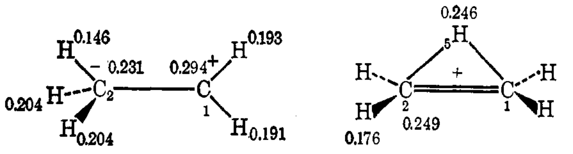
(24) L. L. Miller and D. A. Kaufman, *J. Am. Chem. Soc.*, **90**, 7282 (1968); P. E. Peterson and J. M. Indelicato, *ibid.*, **90**, 6515 (1968); P. J. Stang and R. Sommerville, *ibid.*, **90**, 4600 (1969), and references therein.

Table III. NDDO Energies of Ethyl and Vinyl Carbonium Ions

Compd	Total val. energy, eV	Electronic energy, eV	Nuclear repulsion, eV	Energy differences kcal	Energy differences eV	Energy differences eV	Recalibrated, kcal
I	−499.631	−1125.387	625.756				
II	−501.073	−1144.695	643.622	−33.24[d]			9.0[e]
III	−439.85	−875.48	435.63				
IVa	−440.809	−890.861	450.051	−22.16[a]			34.9[f]
IVb	−441.235	−890.927	449.692	−31.98[a]			25.1[e]
V	−684.967	−1661.262	976.295		−245.12[a]		
VI	−683.817	−1670.335	986.518	26.53[b]	−243.97[a]		
VII	−928.65	−2565.89	1637.24		−243.68[b]	−488.80[a]	
VIII	−927.126	−2635.685	1708.560	35.12[c]	−242.15[b]	−487.27[a]	
IX	−685.103	−1668.609	983.506	−3.78[b]	−244.29[g]		53.3[f]
X	−686.011	−1725.194	1039.183	−27.07[b]			
XI	−929.251	−2556.861	1627.610	−13.89[c]			43.2[f]

[a] Relative to III. [b] Relative to V. [c] Relative to VII. [d] Relative to I. [e] *Ab initio* result. [f] Calibrated to *ab initio* result for III — IVb difference. [g] Relative to IVa.

Molecular orbital calculations for the parent vinyl cation, $C_2H_3^+$, were first reported using the extended Hückel method[4] and more recently by a semiempirical SCF procedure.[8] Both studies treated the problem of classical *vs.* bridged structures, but the methods suffered from their inability to account satisfactorily for bond length changes.



I II

Figure 1. NDDO charge distributions for ethyl cation and protonated ethylene.

Our NDDO calculations are concerned with the structure of the vinyl cation (III) in linear and bent arrangements, where the hydrogen at the electron-deficient carbon is moved in the plane and perpendicular to the plane of the other atoms, and with the energy of isomerization to protonated acetylene (IV).

As CH bond lengths tend to be nearly invariant within classes of compounds[20] they were kept constant at 1.084 Å (the ethylene CH bond length) for III and at 1.065° for protonated acetylene (IV). The CC bond lengths obtained through minimization of the total energy are listed in Table III. The bond angles were assumed to be 120° around sp^2 centers, and 109.5° around sp^3-hybridized carbon atoms.

The effect of bending the hydrogen out of the linear arrangement is shown in Figure 2. The linear structure is the most stable, but it is easier to move the hydrogen perpendicular to, rather than in, the plane of the other atoms. This behavior reflects the fact that the out-of-plane movement produces a less unfavorable increase in nuclear repulsion and a greater increase in electronic energy. A comparison with similar deformations of the methyl cation illustrates the close similarity in results and in interpretation. Movement of a hydrogen out of the plane in the methyl cation is energetically as costly as similar out-of-plane bending of a hydrogen in III; the in-plane bending is even more difficult in both cases.

In Table III the total valence shell molecular energies of III and IV (a and b) are compared. In the geometry of minimum energy, corresponding to a bridging hydrogen distance of 1.07 Å from the center of the triple bond and 1.24 Å from the carbon atoms, IVa and IVb are more stable than III by 22.2 and 32.0 kcal/mole, respectively. The stronger binding in IVb (angle of minimum energy HCC = 165°) results from reduced nuclear repulsions. The bridged structures are favored strongly. However, it must be emphasized that these calculations apply to the isolated molecule and do not necessarily reflect the expectations in solution.

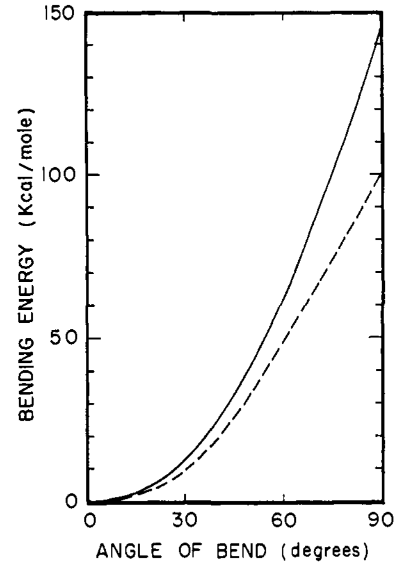


Figure 2. INDO energy for bending methine CH bond in vinyl cation III: solid line, in-plane bending; dashed line, out-of-plane bending.

Comparison of NDDO and *Ab Initio* Results. Calculations on ethyl and vinyl cations, protonated ethylene, and protonated acetylene were carried out using Roothaan's LCAO-MO-SCF procedure.[13] Basis sets employed were the same as for the methyl cation:[1] Huzinaga's atomic orbitals for carbon,[26] and Whitten's five-term hydrogen 1s.[27] During geometry searches,

---

(25) For a review, see R. C. Fahey in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience Publishers, New York, N. Y., 1968.

(26) S. Huzinaga, *J. Chem. Phys.*, 42, 1293 (1965).

(27) J. L. Whitten, *ibid.*, 39, 349 (1963); 44, 359 (1966).

Table IV. *Ab Initio* Energies and Calculated Geometries

	r(CC), Å	Distance of bridging H to center of CC bond, Å	Energy,[d] hartrees	Rel energy, kcal/mole
Ethyl cation	1.48		−78.2422	0.0[a]
Protonated ethylene	1.46[b]	1.11[b] (r(CH) = 1.33)	−78.2279	9.0[a]
Vinyl cation	1.36		−76.9847	0.0[c]
Protonated acetylene	1.34	1.18 (r(CH) = 1.36)	−76.9447	25.1[c]

[a] Relative to energy of ethyl cation. [b] Presumed value; structure of methylene groups same as for NDDO computations. [c] Relative to energy of vinyl cation. [d] A hartree ≡ 1 atomic unit = 627.502 kcal/mole.

the hydrogens had scale factors, $\eta^2 = 2.5$, found to be optimal for methyl cation. But for final energies (and while finding the best position of the bridging proton in protonated acetylene), the coefficient of the long-range term in each hydrogen orbital was allowed to be variationally evaluated. The effective "size" each hydrogen assumes is thus a result of the energy minimization for each molecule, and therefore is optimal for the molecular system as a whole. Both the four-component and one-component hydrogen orbitals were scaled, with $\eta^2 = 1.44$.

For both ethyl and vinyl cations, optimal CC distances were determined by computation. The remaining structural parameters were assumed, and were the same as those used for the NDDO calculations. Further computations, and knowledge of the NDDO results, were used to fix the CC distance and position of the bridging proton in protonated acetylene. For the latter search the two "acetylenic" hydrogens were allowed to relax so that the CCH angles were 170° instead of 180°. Using both NDDO and *ab initio* results, we found we could accurately estimate the *ab initio* minimum energy structure of protonated ethylene without recourse to a complete geometry search, and this presumed structure was used for the calculations reported in Table IV. The uncertainties in geometry thus introduced should lead to uncertainties in energy of no more than a few kilocalories per mole. *Ab initio* geometries and energies are shown in Table IV.

Our *ab initio* results indicate that the bridged ions are less stable than their nonbridged "classical" isomers, for both pairs of isomeric ions in Table IV. Semiempirical schemes used to investigate the problem, including NDDO, have generally given the contrary result. This discrepancy is not hard to account for: all semiempirical schemes neglect huge numbers of two-electron integrals which would be included in an *ab initio* Roothaan–SCF treatment. Since these integrals represent electron repulsions and exchange interactions, their neglect gives too much weight to the forces remaining, such as orbital overlap effects. Therefore, in discriminating between two isomers, semiempirical schemes in general will favor the structure displaying the greater connectivity, *i.e.*, the greater number of bonds, hence larger total bonding overlap, by an excessive amount.

This means that "bridged" or "nonclassical" structures, being more highly connected, will be favored artifically over their "unbridged" or "classical" counterparts by such semiempirical methods merely because of some of the assumptions used in the calculations.

The NDDO method, despite its being very elegant and successful in accounting for hydrocarbon bond lengths, still neglects many more of the two-electron integrals than it includes. When NDDO is used to find the energy change for a process involving a change in connectivity, *e.g.*, in going from a two-center CH bond (classical structure) to a three-center CHC bond (nonclassical structure), the electron repulsions included in the calculation are insufficient to balance the greatly increased nuclear–electron attractions, which greatly outweigh the rise in nuclear repulsion. Protonated ethylene and protonated acetylene structures are thus favored by 42.2 and 57.1 kcal/mole too much, relative to their unbridged, less highly connected ethyl cation and vinyl cation isomers. These values represent differences between the NDDO and the *ab initio* results.

Normally we would expect the conclusions from *ab initio* calculations to be correct experimentally, at least for gas-phase work. However, it is difficult in the case of the ions in Table IV to assess the effects of electron correlation (intramolecular van der Waals forces). Correlation effects generally tend to favor the more localized of two structures, presumably because the electrons in the localized case will be on the average forced to stay closer together, hence have more to gain from correlating their motions.

In going from a two-center CH to a three-center CHC bond, the CH bonding electrons expand to fill a larger volume, that is, become less localized. This expansion is indicated by the decrease in electron kinetic energies (Table V), which by analogy with the particle in a box should decrease with increasing "box" size. The loss in correlation energy expected to result from this delocalization will however be offset by the increase in electron–electron repulsions (Table V) which occurs because the CH electrons are brought into closer contact with the electrons involved in CC bonding. The "box" is larger, but there are more electrons in it. That these two effects are opposed suggests that the changes in correlation energy for the processes I → II or III → IV will be small. This suggestion is bolstered by the fact that the correlation energies of Li^+, H_2, HeH^+, and H_3^+, where two electrons are spread over one, two, and three centers, are all within 0.003 hartree (*ca.* 2 kcal/mole) of each other.[28] The *ab initio* results therefore probably correspond closely to experimental reality. However, were the predictions from NNDO to be experimentally confirmed, this agreement would have to be regarded as fortuitous, since the NDDO is formally an approximation to the *ab initio* method, and was not parametrized specifically to reproduce energies of isomerization, but to reproduce experimental geometries.

Methyl-Substituted Vinyl Cations. Methyl groups are known to stabilize carbonium-ion centers, and this experimental fact is reflected in the NDDO results for

(28) R. E. Christofferson and H. Shull, *J. Chem. Phys.*, **48**, 1790 (1968).

Table V. *Ab Initio* Energy Components^a

	Ethyl cation	Protonation ethylene	Vinyl cation	Protonation acetylene
Nuclear repulsion	37.1038	37.6850	27.7073	28.0145
Nuclear–electron attraction	−250.3146	−251.0501	−228.3802	−228.4866
Electron repulsion	57.0590	57.3439	47.5357	47.6399
Electron kinetic energy	77.9095	77.7933	76.1525	75.8875
Total energy	−78.2422	−78.2279	−76.9847	−76.9447

^{a} All energies in hartrees (1 hartree = 627.502 kcal/mole).

Table VI. NDDO Calculated CC and CH Bond Lengths for Carbonium Ions

Compound	CC bond	Length, Å	CH bond	Length, Å
I	1-2^a	1.43		
II	1-2^a	1.41	1-5^a	1.24
III	3-4^a	1.288		
IV	3-4^a	1.27	3-5^a	1.22
V	4-5^a	1.41		
VI	4-5^a	1.488		
IX	3-5^a	1.46	3-4^a	1.225
X	2-5^a	1.54		
XIIb	1-2^b	1.46		
XIIc			1-3^b	1.24
XIId	1-2^b	1.76	1-4^b	1.23
XIIe			1-4^b	1.30
XIIf	1-2^b	1.59		

^{a} Refers to Figures 1 and 3. ^{b} Refers to Figure 4.

the vinyl cation homologs and isomers listed in Table III. In the light of the *ab initio* results discussed above, some of the NDDO relative energies have been recalibrated and are presented in the last column of Table III. They were obtained from the values in column five by adding 57.1 kcal/mole to the NDDO relative energies for protonated acetylene homologs IV, IX, and XI, and 42.2 kcal/mole to the NDDO value for protonated ethylene, II. These adjustments rereference the NDDO to the *ab initio* relative energies for systems on which both types of calculations have been done, and for their homologs. The calibration for X is uncertain since a methyl is bridging instead of a proton, as in IV. Fortunately, the relative stability of X is not important for the discussion which follows, so rereferencing its energy was not attempted.

Experience has shown that the energies obtained from any semiempirical scheme are not credible unless that scheme has been carefully calibrated, either with experiment or with a rigorous and reliable theoretical method. This applies to the energies in columns six and seven of Table III for isomers differing only in position of methyl substitution, because these energies have not been so calibrated. However, these energies may be fairly accurate, because they are associated with methyl substitutions, or changes in the position of methyl groups, thus involving no changes in connectivity. Connectivity changes were the major characteristic of processes showing the large discrepancies between *ab initio* and NDDO results noted above. But for two processes not involving connectivity changes, internal rotation in ethane and the propyl cation–isopropyl cation isomerization (see below), the NDDO results agree well with experiment.

The assumptions for CH bond lengths in the vinyl cation homologs and isomers are the same as before. For each different type of CC bond length we carried out a search and subsequently used these "standard" lengths wherever they occurred. The distances determined, together with the compounds used for their determination, are listed in Table VI.

An attempt is made to predict the influence of substituents in different positions on the stability of the ions. There is a marked difference in stabilization gain depending on the position of the methyl group. The compound with the methyl group next to the carbonium-ion center (V) is more stable than the β-substituted ion VI by 26.5 kcal/mole. If one compares the unsubstituted vinyl cation III with V, the total energy difference is −245.12 eV. To evaluate the methyl group stabilization in ordinary compounds, the energy differences in methane–ethane and ethylene–propene were compared. These are −244.11 and −243.43 eV, respectively. There is an extra stabilization energy of 1.0–1.7 eV (*ca.* 23–39 kcal/mole) for V. When the methyl group is at C_2 (VI), remote from the center bearing the formal positive charge, the energy difference of −243.97 eV (relative to III) shows no extra stabilization. Only a methyl group attached to the carbonium-ion center produces significant stabilization. The additional energy gain is almost the same as the experimental difference between primary and secondary carbonium ions which is 24 kcal/mole for the pair *n*-propyl–isopropyl cation.[29] The value calculated by the NDDO method for the difference between the 1-propyl and 2-propyl cations is 18.5 kcal/mole (see Table VII).

Table VII. NDDO Energies of Carbonium Ion $C_3H_7^+$

	Total energy, Ev	Electron energy, Ev	Nuclear repulsion, Ev	Relative energy, kcal
XIIa	−743.72	−1982.07	1238.34	0.0
XIIb	−744.52	−1972.32	1227.79	−18.47
XIIc	−745.28	−1995.56	1250.28	−35.83 (6.4)^a
XIId	−748.04	−2045.20	1297.16	−99.48
XIIe	−742.12	−2085.57	1343.45	37.01
XIIf	−747.16	−2053.90	1306.74	−79.27

^{a} Recalibrated using *ab initio vs.* NDDO energy change for I → II, 42.2 kcal/mole (see Table IV).

Another interesting observation emerges from the relative stabilizations of bridged *vs.* unbridged cations by methyl groups. The energy change for methyl substitution onto protonated acetylene IVa, giving IX, is −244.29 eV, only slightly different from the methane–ethane difference. The energy change for α-methyl substitution on vinyl cation III is nearly 25 kcal/mole greater. The same conclusion applies to the dimethyl-substituted cases VII, VIII, and XI. The incremental energy addition to the total energy due to the methyl group remains constant within a small range except when the methyl is attached to the carbonium-ion center.

---

(29) J. L. Franklin in "Carbonium Ions," Vol. 1, G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, New York, N. Y., 1968.

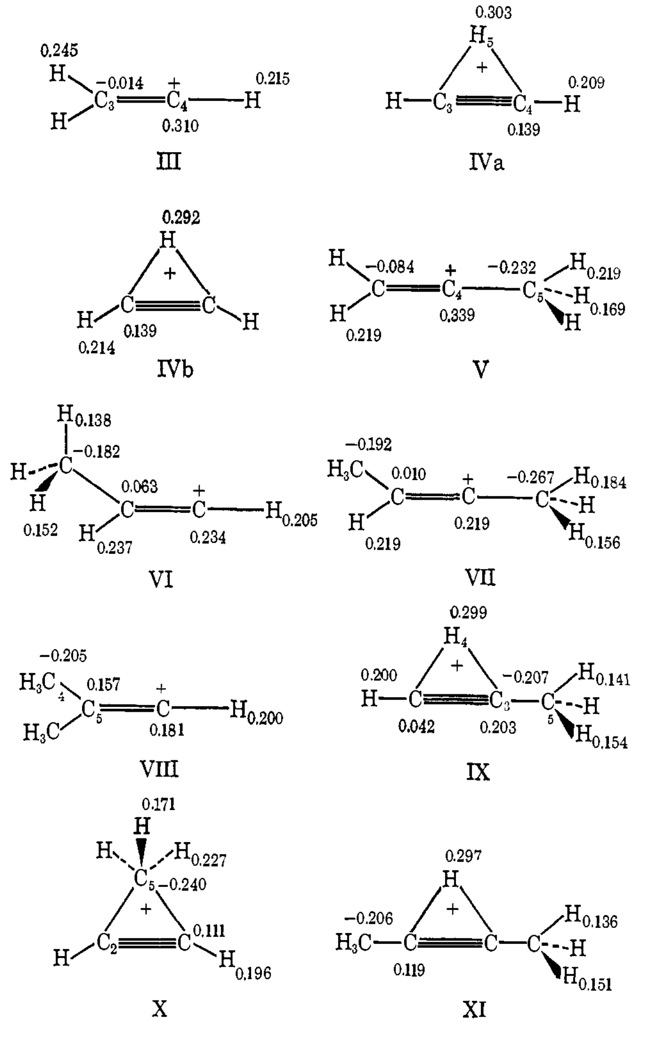


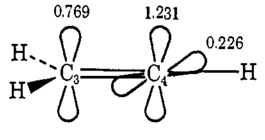
Figure 3. Structures and NDDO charge distributions in vinyl cations.

Another way to study the influence of a methyl group is to look at the energy necessary to remove a hydride ion from the parent hydrocarbon. Table VIII lists these energies. It is conceded that the total energy changes may be too high, but the relative energy differences may be more meaningful. In comparison with ethylene it becomes increasingly easier to remove a hydride ion, the effects being nearly additive as successive methyl groups are added.

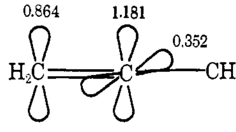
Table VIII. Energy to Remove a Hydride Ion (NDDO)

	ΔE, eV	$\Delta\Delta E$, eV
$H_2C{=}CH_2 \rightarrow H_2C{=}\overset{+}{C}H + H^-$	41.28	0.0
$CH_3CH{=}CH_2 \rightarrow CH_3CH{=}\overset{+}{C}H + H^-$	40.74	0.54
$H_2C{=}CHCH_3 \rightarrow H_2C{=}\overset{+}{C}CH_3 + H^-$	39.59	1.69
cis-$CH_3CH{=}CHCH_3 \rightarrow CH_3CH{=}\overset{+}{C}CH_3 + H^-$	38.92	2.36
trans-$CH_3CH{=}CHCH_3 \rightarrow$ $CH_3CH{=}\overset{+}{C}CH_3 + H^-$	38.70	2.58
$(CH_3)_2C{=}CHCH_3 \rightarrow (CH_3)_2C{=}\overset{+}{C}CH_3 + H^-$	39.14	2.14
$(CH_3)_2C{=}CH_2 \rightarrow (CH_3)_2C{=}\overset{+}{C}H + H^-$	40.27	1.01

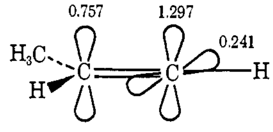
Charges are more evenly distributed in IV than in III (Figure 3). In III atom 3 (C_2) carries almost no excess charge. If one separates the charges into σ and π contributions it is seen that in III the π electrons are polarized toward atom 4 (C_1) which claims 1.231 π electrons. Additional σ electrons are also attracted by the electron-deficient center. To use the language of organic chemistry, the "empty" p orbital in III is stabilized through delocalization of 0.23 electron into this orbital out of the σ framework. In IV the similar p atomic orbital is occupied by 0.758 electron. The same analysis of the charge distribution in V and VI reveals an increased electron density in the "empty" p orbital. This is more pronounced if the methyl group is attached to the unsaturated carbon. In fact, in VI the electron density is only slightly higher than in III. Thus, the electron density in this p orbital parallels the influence of the methyl substituent on the total energy.



III



V



VI

Isomeric Ions of Composition $C_3H_7^+$. The NDDO calculations presented here for relative energy differences between the open-chain propyl cations and the protonated cyclopropanes are at a substantially lower confidence level than the calculations presented above. This is because there are no reliable data available for calibration of the NDDO energy changes on going from open to cyclic three-carbon cations. On the other hand, the 1-propyl cation protonated propene energy difference is adjusted, in the last column of Table VII, using the difference between NDDO and *ab initio* energies for protonated ethylene relative to ethyl cation, of 42.2 kcal/mole. This is the same rereferencing done for the protonated acetylene homologs in the last column of Table III.

A variety of structures can be conceived for ions of composition $C_3H_7^+$ (XIIa–f). Besides experimental studies on protonated cyclopropanes,[30] their possible structures have been investigated theoretically. *Ab initio* calculations by Petke and Whitten[6] on the energies and structures of face- and edge-protonated cyclopropane showed the latter to be more stable by 125 kcal/mole. A subsequent semiempirical study[10] using the INDO[11] and a modified CNDO procedure[12] gave the same result. In addition to the face- and edge-protonated forms, a detailed study of the possible interconversion of edge-protonated forms through corner-protonated species was considered. The availability of *ab initio* and INDO results makes the comparison with the NDDO procedure additionally interesting. Table VII contains the total energies as well as the total electronic and nuclear repulsion energies for the valence shell and various relative energies of protonated cyclo-

---

[30] C. C. Lee and L. Gruber, *J. Am. Chem. Soc.*, **90**, 3775 (1968); C. C. Lee, W. K.-Y. Chwang, and K.-M. Wan, *ibid.*, **90**, 3778 (1968), and references therein; C. J. Collins, *Chem. Rev.*, **69**, 541 (1969).

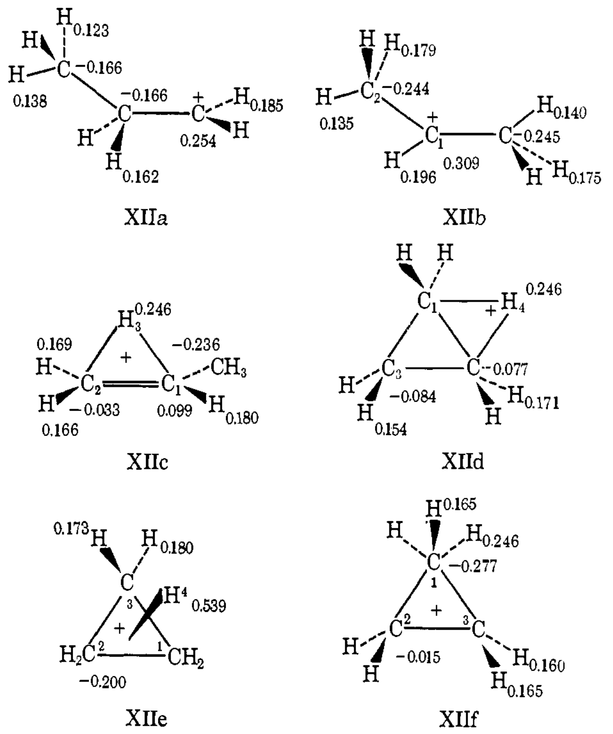
propanes and other ions of composition $C_3H_7^+$. Throughout the calculations in this series the CH bond lengths of 1.093 and 1.084 Å for sp^3 and sp^2 carbon atoms and idealized angles were used. The HCH angle in cyclopropanes was taken to be 120°; CC bond lengths were standard (1.524 Å for cyclopropanes, 1.534 Å for normal single bonds) unless they were determined and are listed in Table VI. The edge-protonated form XIId was found by NDDO to be the most stable. However, the stability of the protonated cyclopropanes XIIe and XIIf relative to the acyclic propyl ions in the NDDO approximation is probably an artifact resulting from the higher connectivities of the cyclic ions. Clearly, *ab initio* calculations aimed at this problem are desirable.

Experimentally, it has been suggested that all ions $C_3H_7^+$ collapse to protonated cyclopropane in the mass spectrometer.[31] But in SbF_5–SO_2ClF the 2-propyl cation (XIIb), and not a protonated cyclopropane, is observed by nmr.[32]

Noteworthy is the difference of 18.5 kcal/mole between the 1-propyl and 2-propyl cations, which is close to the experimental value of 24 kcal/mole.[29] Another point of interest is the close similarity in NDDO energy differences between the ethyl cation and protonated ethylene (33.3 kcal/mole) and the 1-propyl cation and protonated propene (35.8 kcal/mole). The calculations on vinyl cations showed that a methyl group does not stabilize a bridged cation appreciably. This conclusion is reinforced by the following: the replacement of a hydrogen by a methyl group in the ethyl cation to form the 1-propyl cation does not lead to an extra stabilization either. The difference in total energy between the ethyl cation and the 1-propyl cation is 244.09 eV, nearly the same as between methane and ethane.

From an overlap point of view XIIe should be more stable than XIId. The protonating hydrogen is close not only to two carbons but to all three. Partitioning of the total energy and relating it to 1-propyl cation shows that indeed the gain in valence shell molecular electronic energy is highest for XIIe but that this is outweighed by the increase in nuclear repulsions. Owing to the greater distance of the bridging proton in XIId to the third carbon, the nuclear repulsion is smaller and therefore is responsible for the greater stability. The corner-protonated form, whose geometry is, in fact, not very different from the edge-protonated species, gains more electronic energy than XIId but at the same time more nuclear repulsions. The same analysis reveals that the higher stability of the 2-propyl cation compared with the 1-propyl cation is caused by the decrease of nuclear repulsion energy and not by any gain in electronic energy.

If one arranges the ions $C_3H_7^+$ according to increasing magnitudes of electronic energy and nuclear repulsion energy, one obtains the same sequence: XIIb < XIIa < XIIc < XIId < XIIf < XIIe. The calculatated order of stability is given by the difference of both quantities. This subtle balance of effects also makes clear that there is no single physical phenomenon to explain the order of stability.



XIIa XIIb

XIIc XIId

XIIe XIIf

Figure 4. Structures and NDDO charge distributions in the $C_3H_7^+$ series.

The charge distributions given in Figure 4 do not provide a clear picture of the stability of the ions. It is true that in the least stable structure (XIIe) the bridging hydrogen carries the highest positive charge but there is no simple relationship between the amount of charge and the stability in the other compounds.

In Table IX we compare our results with those obtained by *ab initio* INDO and CNDO calculations. Except for the CNDO results the agreement seems to be excellent. Yet there is one difference which does not become apparent from these energy differences. The total binding energy for the proton given by the *ab initio* calculations is 155.0 for XIId and 30.1 kcal/mole for XIIe.[6] All the semiempirical methods yield much higher values. The NDDO method predicts differences of 442.7 for XIId and 307.2 for XIIe, while they are 235 and 76 kcal/mole in the CNDO calculations, and 321 and 120 kcal/mole for the INDO procedure.

Table IX. Comparison of Relative Energies Obtained by Different Procedures

	NDDO	*Ab initio*[a]	CNDO[b]	INDO[b]
XIId	0.0	0.0	0.0	0.0
XIIe	136.5	125.2	76	120
XIIf	20.2		10	20

[a] See ref 6. [b] See ref 10.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF 49(638)-1625, the National Science Foundation (GP 9233 and 8907), the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (AI-07766). Some of the computer time was provided by Princeton University.

---

(31) P. N. Rylander and S. Meyerson, *J. Am. Chem. Soc.*, 78, 5799 (1956); see also M. M. Bursey and F. W. McLafferty in ref 29.

(33) M. Saunders and E. L. Hagen, *J. Am. Chem. Soc.*, 90, 6881 (1968); G. A. Olah, private communication.