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The Electronic Structure of Carbonium Ions

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A large number of carbonium ions are calculated with a modified CNDO procedure. The study of the electronic structure of these electron deficient compounds using energy partitioning and localized orbital techniques leads to an understanding of the observed trends of the stabilities of carbonium ions. The stabilization of a positive charge by methyl substituents is broken down into hyperconjugative, hybridization and inductive effects. Nonclassical structures characterized by three center bonds are also investigated. The chemical reactivity of carbonium ions is explained by the ability of the empty orbital to combine steadily with bond orbitals.

Ein modifiziertes CNDO-Verfahren wurde auf eine große Zahl von Carboniumionen angewandt. Die Untersuchung der elektronischen Struktur dieser Elektronenmangel-Verbindungen mit einem Verfahren zur Energieaufteilung und mit lokalisierten Orbitalen führen zum Verständnis der beobachteten Trends in der Stabilität von Carboniumionen. Die Stabilisierung einer positiven Ladung durch Methylsubstituenten wird aufgeteilt in Beiträge der Hyperkonjugation, der Hybridisierung und des induktiven Effekts. Außerdem wurden nichtklassische Strukturen, charakterisiert durch eine Dreizentrenbindung, untersucht. Die chemische Reaktivität von Carboniumionen wird durch die Fähigkeit des leeren Orbitals erklärt, mit einem Bindungsorbital zu kombinieren.

Un procédé CNDO modifié est utilisé pour le calcul d'un grand nombre d'ions carbonium. L'étude de la structure électronique de ces composés à déficience d'électrons en utilisant des techniques de partition de l'énergie et d'orbitales localisées conduit à la compréhension des tendances observées dans la stabilité des ions carbonium. La stabilisation d'une charge positive par les substituants méthyles est décomposée en effets d'hyperconjugaison, d'hybridation et d'induction. Les structures non classiques caractérisées par des liaisons à trois centres sont aussi étudiées. La réactivité chimique des ions carbonium est expliquée par la capacité de l'orbitale vide à se lier fortement avec des orbitales de liaison.

Introduction

The question of the structure and reactivity of carbonium ions is of central interest in organic chemistry because many reactions involve such cations as key intermediates. The theoretical interest is reflected in the various *ab initio* and semiempirical MO studies which have appeared in the literature (e.g. [1–6]). *Ab initio* studies are potentially the most reliable sources of information on carbonium ions, but the complexity of such methods has restricted their use to the smallest systems, and *ab initio* calculations involving thorough minimization of the total energy with respect to the geometry have appeared only recently [1]. Semiempirical methods, on the other hand, are much less complex, and such features as charge densities and relative energies have been studied extensively for a large number of carbonium ions [2–5]. However, the prediction of structure and relative energy has often not been very satisfactory because of the lack of minimization of the energies through variation of the geometrical parameters.

The modified [7] CNDO procedure [8] used in this study has been shown to yield reasonable energies and equilibrium geometries for hydrocarbons and carbonium ions [6,7]. We have reported on several calculations of reaction paths and relative energies of various carbonium ions with this method, and have discussed the results in the light of experimental findings. In this paper we wish to emphasize the electronic structure of carbonium ions in order to gain a greater understanding of the stabilities and reactivities of such ions. For instance, the stabilization due to methyl substituents, to change in hybridization and to the presence of nonclassical bonds will be examined. In addition, the reliability and usefulness of the modified CNDO method in studies of electron deficient species will be considered.

Methods

The modified CNDO method we have used differs from the original CNDO in the evaluation of the core matrix elements $H_{\mu\nu}$[1].

$$H_{\mu\nu} = (k_A I_\mu + k_B I_\nu) S_{\mu\nu}\,; \qquad \mu \in A\,; \qquad \nu \in B\,. \tag{1}$$

The core-electron attraction V_{AB} is evaluated by:

$$V_{\mathrm{AB}} = Z_{\mathrm{B}} \left\{ (1-\alpha)\,\gamma_{\mathrm{AB}} + \frac{\alpha}{\sqrt{R_{\mathrm{AB}}^2 + 1/\mu_{\mathrm{A}}^2}} \right\}; \qquad \alpha = 0.22\,. \tag{2}$$

The interpretation of the SCF results and the investigation of the electronic structure of carbonium ions is greatly facilitated by energy partitioning analyses [9]. The total energy E of a molecule can be broken down into mono and bicentric contributions [8]

$$E = \sum_{\mathrm{A}} E_{\mathrm{A}} + \sum_{\mathrm{A<B}} E_{\mathrm{AB}} \tag{3}$$

which can be further partitioned into physical components

$$\begin{aligned} E_{\mathrm{A}} &= E_{\mathrm{A}}^U + E_{\mathrm{A}}^J + E_{\mathrm{A}}^K\,,\\ E_{\mathrm{AB}} &= E_{\mathrm{AB}}^R + E_{\mathrm{AB}}^K + E_{\mathrm{AB}}^V + E_{\mathrm{AB}}^J + E_{\mathrm{AB}}^N\,. \end{aligned} \tag{4}$$

The bond resonance energy

$$E_{\mathrm{AB}}^R = 2 \sum_{\substack{\mu \in \mathrm{A} \\ \nu \in \mathrm{B}}} P_{\mu\nu} H_{\mu\nu} \tag{5}$$

which can be interpreted as an energy weighted overlap population, is of special interest in this study. As has been demonstrated in detail [9], E_{AB} and E_{AB}^R are measures of the strength of the bond A–B.

The sum of the potential energies E_{AB}^N, E_{AB}^J and E_{AB}^V of the core-core, electron-electron and electron-core interactions, respectively, represents the electrostatic contribution to the bond A–B:

$$E_{\mathrm{AB}}^S = E_{\mathrm{AB}}^N + E_{\mathrm{AB}}^J + E_{\mathrm{AB}}^V\,. \tag{6}$$

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[1] The notation here is the same as in Ref. [7–9].

Another useful tool in the interpretation of our SCF results is the transformation of the canonical orbitals to localized bond orbitals, using the minimization of the interorbital exchange energy as the convergence criterium [10]. Some criticism has been voiced [11] at the use of this procedure within the ZDO approximation [12]. However, such localized orbitals differ essentially from those obtained without the approximation only in systems with lone pairs or multiple bonds, and localized orbitals of such systems are not studied in this article. Hence the criticism does not apply to the results reported here.

The total energies of the systems studied here have been fully minimized with respect to the molecular geometry except in a few cases where it was necessary to impose symmetry restrictions in order to maintain the conformation. For instance, a study of the features of the *n*-propyl cation was desirable despite the fact that it does not correspond to an energy minimum [6b].

Heats of Atomization and Stabilities of Carbonium Ions

The heat of atomization of a carbonium ion can be defined as the energy of the reaction

$$n\mathrm{C}_g + (m-1)\,\mathrm{H}_g + \mathrm{H}^+ \rightarrow \mathrm{C}_n\mathrm{H}_m^+ \,.$$

Table 1 lists the calculated heats of atomization of several carbonium ions for which the corresponding experimental data are available. Most of the experimental data were obtained with the use of electron impact results. The inherent uncertainty of such measurements has been discussed in the literature [13]. The experimental energies in Table 1 have been corrected for zero-point energy E° by the use of a simple empirical formula:

$$E^\circ = 3.5\, n_{\mathrm{CC}} + 6.9\, n_{\mathrm{CH}}\,(\mathrm{kcal/mol})\,.$$

Table 1. *Heats of atomization of some cations*

Carbonium ion	Formula	ΔH_f exp.[a] kcal/mol	$-\Delta H_a$ exp.[b] a.u.	$-\Delta H_a$ calc.[c] a.u.
methyl	CH_3^+	258	0.640	0.700
vinyl	$C_2H_3^+$	285	0.874	0.999
ethyl	$C_2H_5^+$	225	1.154	1.249
propargyl	$C_3H_3^+$	264	1.186	1.256
allyl	$C_3H_5^+$	229	1.428	1.501
cyclopropyl	$C_3H_5^+$	239	1.412	1.541
i-propyl	$C_3H_7^+$	190	1.674	1.761
n-propyl	$C_3H_7^+$	214	1.636	1.721
sec-butyl	$C_4H_9^+$	190	2.135	2.218
t-butyl	$C_4H_9^+$	174	2.164	2.240
i-butyl	$C_4H_9^+$	204	2.113	2.172
n-butyl	$C_4H_9^+$	211	2.105	2.180

[a] See Ref. [13].

[b] Corrected for zero-point energy: energies of sublimation and dissociation used: C 170 kcal mol, H 51,5 kcal mol. H^+ 314 kcal mol.

[c] For equilibrium geometries (for the ethyl and the *n* propyl cation within symmetry restrictions).

Table 2. *Enthalpies of some carbonium ion reactions*

No.	Reaction	Enthalpy (kcal/mol)		Ref.
		exp.	calc.	
I	$n\text{-}C_3H_7^+ \rightarrow i\text{-}C_3H_7^+$	−24	−25	[13]
II	allyl$^+ \rightarrow$ vinyl$^+ + H_2$	55	52	[22]
III	$i\text{-}C_3H_7^+ \rightarrow$ allyl$^+ + H_2$	39	48	[13]

n_{CC} is the number of C–C bonds and n_{CH} is the number of C–H bonds in the ion. The formula works well for hydrocarbons, and its accuracy for ionic species is certainly sufficient for our purpose here.

The calculated heats of atomization in Table 1 are generally around 60 kcal/mol above the experimental results. This finding indicates that the electron repulsion integrals in CNDO are somewhat too high. For the same reason, we calculate anions to be less stable than expected [14]. However, the deviation of the calculated heats of atomization from the experimental values need not be a serious defect of the theory. More decisive for the present study is the prediction of relative energies among carbonium ions. Typical examples of three key carbonium ion reactions are presented in Table 2.

a) The driving force of the rearrangement of the n-propyl cation to the isopropyl cation is the stabilization of the latter by a methyl group in the α position:

$$n - C_3H_7^+ \rightarrow i - C_3H_7^+ \,, \tag{I}$$

b) the hydrogenation energy of the vinyl cation $C_2H_3^+$ indicates the relative stability of carbonium ions with different hybridization:

$$C_2H_5^+ \rightarrow C_2H_3^+ + H_2 \,. \tag{II}$$

c) The hydrogenation energy of the allyl cation should reflect the stabilization of a carbonium ion by conjugation:

$$C_3H_7^+ \rightarrow C_3H_5^+ + H_2 \,. \tag{III}$$

The good agreement between theory and experiment for these key reactions demonstrates that the relative energies of carbonium ions are reproduced satisfactorily. Hence it can be assumed that our modified CNDO method gives a reliable picture of the electronic structure of carbonium ions.

Before comparing the stabilities of various cations, it is first necessary to decide which criteria should be used in defining the relative stability. The relative stabilities of isomeric species are reflected in their total energies, but comparisons of species of different composition must be made indirectly. There are two obvious possibilities for the definition of relative stabilities.

a) The relative enthalpies of hydride abstraction from the hydrocarbons:

$$RH_3 \rightarrow RH_2^+ + H\cdot + e \,. \tag{IV}$$

Hydride abstraction is taken as the abstraction of an H atom and an electron because the hydrogen anion is calculated by CNDO to be less stable than $H\cdot + e$.

Table 3. *Energies of protonation and hydride abstraction (values in a.u.)*

Cation RH^+	Enthalpies of the reaction	
	(IV) hydride abst.	(V) deprotonation
CH_5^+	—	0.294
CH_3^+	0.466	—
$C_2H_5^+$ classical	0.387	0.354
nonclassical	0.371	0.370
$C_2H_3^+$	0.396	0.346
C_2H^+	0.587	0.288
$C_3H_5^+$ allyl	0.364	0.366
cyclopropyl	0.367	0.371
$C_3H_7^+$ *iso*	0.327	0.396
n	0.367	0.356
prot. cyclopropane	—	0.375
$C_3H_3^+$ cyclopropenyl	0.314	—
propargyl	0.388	—

b) The relative enthalpies of proton abstraction from the carbonium ions:

$$RH_2^+ \rightarrow RH + H^+ . \tag{V}$$

The calculated values for reactions (IV) and (V) are summarized in Table 3 for a number of compounds. It would appear that both definitions lead to a reasonable order of stability. One disadvantage of such definitions of stability, though, is that the numerical value of the stabilization between species of the same composition is not that which would be expected from the total energies. On the other hand, use of these methods avoids the need to directly compare compounds with different structural features and thus gives a truer picture of the relative energies in cases such as that of the cyclopropyl and allyl cations.

The stability of a carbonium ion in the chemical sense is governed by its ability to undergo one or more of the following reactions:

a) Reaction with a nucleophile (especially the solvent).

b) Proton loss.

c) Fragmentation, rearrangement or intermolecular reactions.

Our definitions of stability plainly correspond to reactions a) and b), respectively. Cations which can be expected to react as in c) must be considered separately.

Equilibrium Geometries and Bond Strengths in Carbonium Ions

The minimization of the total energies with respect to the geometrical parameters yielded the equilibrium bond lengths[2] and valence angles listed in Tables 4 and 5. In Table 4 some general trends can be observed. Thus the C–H bonds in carbonium ions are slightly longer (by some 0.02 Å) than in hydrocarbons. C–C bonds originating from the atom carrying a formal positive charge are significantly shorter than normal C–C bonds, while neighboring bonds are much less influenced by the positive charge (e.g. *n*-propyl cation).

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[2] Calculated bond lengths for carbonium ions have also been reported in Ref. [1, 3, 5].

Table 4. *Bond properties of carbonium ions (for equilibrium geometries)*

Bond type	Carbonium ion	Bond length (Å)	Bond strengths $-E_{AB}$ (a.u.)	$-E^R_{AB}$ (a.u.)
C−H	methane[a]	1.11	0.593	0.539
	ethyl, classical, α	1.13	0.550	0.531
	ethyl, classical, β	1.12	0.57[b]	0.52[b]
	ethenyl, classical, α	1.11	0.573	0.567
	ethenyl, classical, β	1.12	0.553	0.567
	ethynyl	1.12	0.516	0.528
	i-propyl, α	1.12	0.565	0.531
C···H	ethyl, nonclassical	1.30	0.284	0.279
	ethenyl, nonclassical	1.29	0.272	0.283
	ethynyl, nonclassical	1.31	0.233	0.274
	edge prot. cyclopropane	1.29	0.296	0.291
C···C	methyl bridged ethylene	1.63	0.408	0.437
	edge prot. cyclopropane	1.67	0.321	0.363
	cyclobutyl, transannular [6c]	1.63	0.304	0.359
	cyclobutenyl, transannular [23]	1.65	0.248	0.301
C−C	ethane[a]	1.52	0.690	0.694
	ethyl, classical	1.47	0.758	0.763
	i-propyl	1.49	0.745	0.743
	n-propyl, α	1.48	0.727	0.736
	n-propyl, β	1.53	0.661	0.670
	cyclopropyl, α	1.49	0.621	0.649
	cyclopropyl, β	1.50	0.641	0.655
	edge prot. ethylene	1.52	0.624	0.636
$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$	benzene[a]	1.42	0.913	0.904
	ethyl, nonclassical	1.41	0.846	0.845
	allyl	1.41	0.921	0.909
	cyclopropenyl	1.40	0.819	0.830
	methyl bridged ethylene	1.44	0.776	0.785
	propargyl	1.36	1.007	1.016
C=C	ethylene[a]	1.34	1.128	1.067
	ethenyl, classical	1.31	1.184	1.149
$\mathrm{C}\overset{\cdots}{=}\mathrm{C}$	ethenyl, nonclassical	1.27	1.295	1.240
	propargyl	1.28	1.266	1.249
C≡C	acetylene[a]	1.21	1.576	1.465
	ethynyl, classical	1.20	1.480	1.419
	methyl ethynyl, classical	1.20	1.452	1.401
$\mathrm{C}\overset{\cdots}{\equiv}\mathrm{C}$	ethynyl, nonclassical	1.24	1.177	1.164
C≣C	C_2[a]	1.18	1.527	1.411

[a] For comparison, [7].

[b] Average value for the two types of β protons.

More interesting are bond lengths in carbonium ions with nonclassical structures. A compound is said to be nonclassical when extensive delocalization of the σ electrons is present. The nonclassical bonds can be described as multicenter bonds, three being the usual number of partners in the bond. As might be expected, distances between atoms linked only by such nonclassical bonds are considerably greater than normal single bond lengths: C···H bond lengths

Table 5. *Equilibrium angles*

Cation	A–B–C	$\measuredangle$ABC (deg.)
ethyl, classical	C_α–C_β–H[a]	109.5
	C_β–C_α–H	123
vinyl, classical	C_α–C_β–H	120
	C_β–C_α–H	180
n-propyl	C–C–C	120
isopropyl	C–C–C	130
allyl	C–C–C	123

[a] Energy minimized with the restriction of the three C_α–C_β–H angles to be equal.

are 1.26–1.30 Å and C$\cdots$C distances run from 1.63–1.67 Å. Additional bonds shorten the nonclassical bond lengths by amounts comparable to those observed in hydrocarbons. The bond length in the bridged ethyl cation is comparable to the $\mathrm{C \overset{\cdots}{-} C}$ bond length in benzene. The $\mathrm{C \overset{\cdots}{=} C}$ bond in protonated acetylene is only 1.27 Å. Surprisingly, the $\mathrm{C \equiv C}$ bond length in protonated C_2 turned out to be 1.24 Å, or somewhat longer than of the triple bond in acetylene. This anomaly will be discussed below.

The valence angles reflect the hybridization of the central atom and the steric interference of substituents. The relatively large angles in the *n*-propyl and isopropyl cations (120° and 130°, resp.) are caused by the repulsive interactions of the partially positive H atoms. These interactions are greater in the cations than in the parent hydrocarbons.

The bond strengths in Table 4 are the E_{AB} and E^R_{AB} of Eqs. (3) and (4). In general, these energy partitioning terms correlate with the bond lengths. However, some exceptions to the rule can be seen in Table 4, e.g. C$\cdots$H in protonated C_2 and protonated cyclopropane; C–C in the isopropyl and *n*-propyl cations; $\mathrm{C \overset{\cdots}{-} C}$ in the allyl cation and in protonated ethylene. However, the comparison of bond strengths in carbonium ions with those in the parent hydrocarbons leads to the same general conclusions as the consideration of bond lengths. Moreover, the energy terms reveal the changes in the electronic structures of the bonds which are responsible for the bond length changes.

The C–C bonds to positive centers have significantly higher E_{AB} and E^R_{AB} values than the corresponding C–C bonds in hydrocarbons. A detailed analysis (*vide infra*) will show that this increase in bond strength is due to the changes in hybridization ($sp^2 - sp^3$ bonding) and to hyperconjugation of the empty orbital at the positive carbon with vicinal C–H bonds. The α C–H bonds, on the other hand, are weaker than in hydrocarbons because of electrostatic repulsion, as can be seen by comparing E_{CH} and E^R_{CH} values of CH_4 and CH_3^+. The magnitude of E^R_{AB} of C$\cdots$C and C$\cdots$H bonds is about one-half of that for the corresponding single bonds. Similarly, the strength (E^R_{AB}) of $\mathrm{C \overset{\cdots}{-} C}$ bonds is about the arithmetic mean of the strengths of single and double bonds. The $\mathrm{C \equiv C}$ bond in C_2H^+ is weaker than a triple bond because the two orthogonal σ bonds are quite unfavorable energetically. Thus the Kekulé structures of organic molecules with dotted lines representing partial bonds is found to correctly represent the electronic structures.

It can also be seen in Table 4 that the trends of E_{AB} and E^{R}_{AB} are not as closely parallel as in hydrocarbons. This result is caused by the increased importance of the electrostatic terms in carbonium ions.

The Stabilization of the Positive Charge by Methyl Substituents

The stabilization of carbonium ions by methyl groups is a well established experimental fact. Calculated and experimental values of the stabilization of several carbonium ions (based on hydride abstraction) are compared in Table 6. The relative stabilities are reproduced well within isomeric series (propyl, butyl, etc.), but not quite as well between ions of different composition.

In organic chemistry, the stabilization of a positive charge by a methyl substituent is usually attributed to the electron releasing inductive effect of the methyl group. However, MO calculations predict the inductive effect of the methyl group to be just the opposite [2, 15, 16]: the central C atom in *t*-Bu$^+$ is more positive than in the methyl cation (see [16] for our values). This influence of the methyl group on charge distribution has been studied extensively (e.g. [4]). Our purpose in this section is to determine the source of the calculated stabilization.

The partitioning of the total energy difference between CH_3^+ and CH_4 is summarized in Table 7. Surprisingly, this energy difference is approximately equal to the energy of one C–H bond and one hydrogen atom in methane. The loss of an additional electron is balanced by the electronic and structural reorganization accompanying the hydride abstraction. The energy difference between $C_2H_5^+$ and ethane is smaller than that between CH_3^+ and methane by the amount of the stabilization due to a methyl group. As shown in Table 8, this energetic effect arises from the fact that the C–C bonds in cations are stronger than those in the parent hydrocarbons. Closer examination shows that the changes in the resonance energies of the C–C bonds in hydrocarbons and cations fully account for the increased stabilization.

Table 6. *The stabilization of carbonium ions*[a]

R_1^+	R_2^+	Calculated stabilization	Experimental stabilization
ethyl	methyl	0.079	0.049
n-propyl	methyl	0.098	0.063
i-propyl	*n*-propyl	0.041	0.038
n-butyl	*n*-propyl	0.014	−0.005
sec-butyl	*n*-propyl	0.052	0.025
t-butyl	*n*-propyl	0.089	0.054
i-butyl	*n*-propyl	0.021	−0.003
allyl	*n*-propyl	0.003	0.020
cyclopropyl	*n*-propyl	0.000	0.023

[a] The stabilization of the carbonium ion R_1^+ relative to the ion R_2^+ is defined as the energy of the reaction

$$R_1^+ + R_2H \rightarrow R_1H + R_2^+ .$$

Table 7. *Partitioning of the energy difference between* CH_4 *and* CH_3^+ *(values in a.u.)*

	CH_4	CH_3^+	Difference
Total energy	-8.413	-7.447	0.966
$3\,E_{CH}$	-1.776	-1.650	0.040
$3\,E_H$	-0.942	-0.810	
E_C	-4.845	-5.063	
E_{CH}	-0.592	–	0.906
E_H	-0.314	–	
E_{HH}	0.056	0.076	0.020

Table 8. *Strengths of* C–C *bonds in carbonium ions and stabilization by methyl substituents (values in a.u.)*

R =	$C_2H_5^+$	i-$C_3H_7^+$	t-$C_4H_9^+$
Calculated stabilization[a]	0.079	0.139	0.188
ΔE_{CC}[b]	0.068	0.132	0.162
ΔE_{CC}^R	0.069	0.130	0.171
$\Delta E_{p_yp_y}^R$[c]	0.045	0.066	0.081

[a] Enthalpy of the reaction $CH_3^+ + RH \rightarrow CH_4 + R^+$.

[b] $\Delta E_{CC} = (E_{CC}(RH) - E_{CC}(R^+)) \cdot n_{CC}$; n_{CC} is the number of CC bonds.

[c] All C atoms are in the xz plane.

One source of the increase in E_{CC}^R is certainly the hyperconjugation between the C–H bonds of the methyl group and the "empty" p_y orbital on the central C atom of the cation. However, the contribution of hyperconjugation ($E_{p_yp_y}^R$ in Table 8) only accounts for about 2/3 of the total increase in E_{CC}^R, the rest being caused by change of hybridization and by inductive effects.

In aliphatic hydrocarbons, the C–C bond links two sp^3 centers. In the corresponding cations, on the other hand, the C–C bond to the positive C atom links an sp^2 center with an sp^3 center. This change in hybridization strengthens the bond, as shown in Table 9 for the C–C bonds in propene and ethane. The change in hybridization increases the contribution of the s orbitals and decreases that of the p_σ orbitals (higher s character of the bond) and polarizes the σ bond in such a way that the two $2p_z - 2s$ terms of E^R are split, the higher value corresponding to the $2s$ orbital at the sp^2 center.

The comparison of ethane with propane certainly gives some idea of the importance of a change in hybridization. However, the σ-C–C bond in the ethyl cation is still stronger than in propene. A population analysis for the C atoms in $C_2H_5^+$ and propene (Table 10) indicates that the C–C σ bond in $C_2H_5^+$ (z-direction) is much more polarized than in propene. This polarization of the σ bond by the positive charge (with the methyl group at the positive end) can be ascribed to the inductive effect of the methyl group, and definitely has some effect on the contributions of the orbitals to E_{CC}^R in Table 9.

Unfortunately, it is not possible to separate the contributions of the inductive effect and the change in hybridization to the strength of C–C bonds in carbonium

Table 9. *Partitioning of the resonance energy E^R_{CC} of C–C bonds*

C_1–C_2[a]	Ethane	Propene	$C_2H_5^+$
$2s-2s$	−0.122	−0.134	−0.137
$2s-2p_z$	−0.182	−0.197	−0.225
$2p_z-2s$	−0.182	−0.177	−0.161
$2p_z-2p_z$	−0.176	−0.168	−0.162
$2p_x-2p_x$	−0.017	−0.016	−0.017
$2p_y-2p_y(\pi)$	−0.017	−0.025	−0.062
E^R_{12}	−0.694	−0.717	−0.763

[a] The C–C bonds are directed along the z axis. In the case of propene, C_2 is the methyl carbon.

Table 10. *Charge densities in hydrocarbons and carbonium ions*

		Ethane	Propene[a]	$C_2H_5^+$	CH_3^+
C_1	$2s$	1.117	1.144	1.294	1.328
	$2p_z$	0.983	0.955	1.196	1.229
	$2p_x$	0.986	0.958	1.149	1.229
	$2p_y$	0.986	0.944	0.138	0
C_2	$2s$		1.114	1.129	
	$2p_z$		0.991	0.806	
	$2p_x$		0.994	1.147	
	$2p_y$		0.992	1.101	
C_1	total	4.072	4.001	3.777	3.786
C_2	total		4.092	4.183	

[a] C_1 is the central C atom and C_2 is the methyl carbon for propene.

ions without arbitrariness. We can, however, make the reasonable assumption that the energetic contribution of the inductive effect in propene in the ground state is negligible. Thus the stabilization of the σ bond in $C_2H_5^+$ as compared with propene can be ascribed to the inductive effect of the methyl group. Finally, we are now able to partition the stabilization of the positive charge in the ethyl cation as follows:

Hyperconjugation	65%,
Change in Hybridization	20%,
Inductive effect	15%.

This estimate is, of course, arbitrary to some degree, but the difference between the influence of hyperconjugation and that of inductive effect is significant. The importance of the inductive effect of methyl groups is clearly found to be relatively small in comparison to the importance of hyperconjugation. It is interesting to note that Baird [17], using a modified INDO technique, also found a large contribution of hyperconjugation to the strength of C–C bonds in carbonium ions (13 kcal/mol in the ethyl cation).

Conjugation and Change of Hybridization

Cations are stabilized through conjugation of the positive center with a system of π bonds. The simplest example is the allylic system. Our results (Table 6) for the stabilization of the allyl cation (e.g. relative to the *n*-propyl cation) seem to be somewhat too low. However, the stabilization due to conjugation also shows up in the barrier to rotation of one of the CH_2 groups (11 kcal/mol). The maximum energy is reached after rotation through 90°, and the transition state resembles a substituted ethyl cation[3]. Recent experimental estimates of the activation barrier in substituted allyl cations run from 4 [18] to 24 kcal/mol [19]. The destabilization of the non-planar allyl cation relative to *n* alkylcations was demonstrated experimentally by Ree and Martin [20].

The cyclopropenyl cation is another system which should be stabilized by conjugation, and we find a stabilization of 0.053 a.u. relative to the cyclopropyl cation. The large stabilization is due to the aromaticity of the two electron π-system. The energetic contribution of the p_π orbitals to each C–C bond is 0.118 a.u., or about the same as in the allyl cation. The extra stability of the three membered ring comes from the third π C–C bond, which is absent in the allyl cation.

The vinyl cation in its classical form has an *sp* hybridized carbon atom with the positive charge in the *p* orbital perpendicular to the π bond. This ion is calculated to be 0.015 a.u. less stable than the open chain ethyl cation. The destabilization may be explained by the fact that the positive charge in the vinyl cation is concentrated on fewer atoms than in the ethyl cation. Thus, the C–C bond in the vinyl cation has greater electrostatic repulsive interactions (with respect to the parent hydrocarbon) than does the ethyl cation (ΔE^S_{CC} in Table 11). The hyperconjugation, on the other hand, is as effective in the vinyl cation as in the ethyl cation (ΔE^R_{pp}).

According to our calculations, C_2H^+ is of very low stability. The positive carbon atom is nearly unhybridized and has an empty orbital in the direction of the C–C bond. The C–C bond in C_2H^+ is considerably weaker than the C–C bond in acetylene. As shown in Table 11, the weakness of the C–C bond comes from the antibonding contribution of the hyperconjugation of the C–H bond with the empty *p* orbital.

Table 11. *Hybridization and stability of classical carbonium ions*[a]

	$C_2H_5^+/C_2H_6$	$C_2H_3^+/C_2H_4$	C_2H^+/C_2H_2
ΔE	0.887	0.902	1.111
ΔE_{CC}	−0.068	−0.057	0.096
ΔE^R_{CC}	−0.069	−0.082	0.046
ΔE^S_{CC}	0.019	0.041	0.053
ΔE^R_{pp} [b]	−0.045	−0.053	0.100

[a] ΔE is E in cation minus E in parent hydrocarbon (in a.u.).

[b] E^R_{pp} is E^R between the "empty" *p* orbital and the vicinal *p* orbital parallel to it, i.e. $E^R_{p_yp_y}$, $E^R_{p_zp_z}$, $E^R_{p_xp_x}$, resp.

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[3] An *ab initio* value of 45 kcal/mol for the rotational barrier was reported [24].

Non Classical Structures

The nature of the transient species in reactions involving carbonium ions is currently the theme of various investigations. Nonclassical ions have been proposed to account for various anomalies of such reactions, and their existence has been experimentally and theoretically demonstrated in some cases (e.g. [21]). MO calculations differ in their predictions of the relative stabilities of some bridged ions. *Ab initio* studies favor the classical structures for the ethyl and vinyl cations [1, 5], while semiempirical calculations tend to favor the bridged structures (e.g. [5]). Sustmann *et al.* [5] held that this discrepency was due to a basic weakness of semiempirical theories. The results in Table 12 indicate that the favoring of bridged structures can be effected by parametrization. Our modified CNDO, which is known to yield good geometries for hydrocarbons, predicts only small stabilizations of bridged structures (protonated propene is instable relative to the isopropyl cation) and the results are not unreasonable.

The partitioning of the total energies of the bridged and open forms of $C_2H_5^+$ is summarized in Table 13. Sorting the factors that tend to favor one structure or the other leads to two large energy terms, the difference of which makes up the relative energy. The bond order dependent quantities, i.e. the resonance energy E^R_{AB} and the bicentric part of the electronic exchange energy E^K_{AB}, are more favorable in the bridged structure. On the other hand, the charge distribution is energetically more favorable in the classical form, as shown by the lower

Table 12. *Relative energies of nonclassical carbonium ions*

Nonclassical ion	E_{rel}[a]
protonated ethylene	-10
protonated acetylene	$-\ 6$
protonated C_2	-15
protonated propene	$+\ 5$

[a] Energies in kcal/mol relative to the corresponding classical species.

Table 13. *Partitioning of the total energies of classical and nonclassical ethyl cations (values in a.u.)*

	Nonclassical	Classical	Difference × 10^3
E_{tot}	-14.7591	-14.7432	15.9
$\sum E_A$	-11.1950	-11.2860	$-\ 91.0$
$\sum E_{AB}$	$-\ 3.5641$	$-\ 3.4572$	106.9
$\sum E^R_{AB}$	$-\ 3.5215$	$-\ 3.3830$	138.5
$\sum E^K_{AB}$	$-\ 1.2356$	$-\ 1.1930$	42.6
$\sum E^J_{AB}$	18.0612	17.6387	$-\ 422.5$
$\sum E^V_{AB}$	-39.8348	-38.8297	1005.1
$\sum E^N_{AB}$	22.9666	22.3097	$-\ 656.9$
$\sum E^S_{AB}$	1.1930	1.1187	$-\ 74.3$
$\sum E^U_A$	-20.0018	-19.9330	68.8
$\sum E^J_A$	10.6371	10.5589	$-\ 78.2$
$\sum E^K_A$	$-\ 1.8303$	$-\ 1.9119$	$-\ 81.6$

electronic interaction terms. Thus it is clear that semiempirical theories can only be expected to give reasonable relative energies of classical and nonclassical structures if the nondiagonal one electron integrals (given by the parameter β) and the electronic interaction integrals are well balanced. Furthermore, the larger electronic repulsion energies in the nonclassical species tend to indicate that such structures will be stabilized by electron correlation. However, the correlation effects might be minimal [5].

Characteristic for nonclassical structures is the presence of three center bonds, which can be obtained from the canonical orbitals by the localization procedure described above. This bond delocalization results in an increase in the resonance energy. As shown in Table 14, the bridging H atom is bound almost exclusively by the one three center bond (the charge density at the bridge is almost entirely accounted for by the coefficient of the corresponding 1*s* orbital in the three center bond orbital). In the edge protonated cyclopropane, an additional minor contribution of the bent C–C bonds to the bonding of the bridging H atom is observed.

The protonated propene is the only case in Table 14 where the three center bond is not symmetric. The asymmetry is caused by the inductive effect of the methyl group and is responsible for the fact that the two bonds to the bridging H atom are of unequal strength (the H atom is pulled to the unsubstituted carbon atom). The correlation between the inductive effect of the methyl group and the energetic stabilization of a positive charge by methyl substituents has been discussed elsewhere [16].

The charge densities calculated by our modified CNDO method for bridged and classical ions (Table 15) yield the same qualitative picture as the results of other SCF methods. The essential feature is the transfer of negative charge in the nonclassical ions to the empty orbital of the classical ion *via* the three center bond. Thus, the carbon atoms in the bridged structures are approximately neutral, and the positive charge is shared by the hydrogens, with the bridging H atom slightly more positive than the classically bound H atoms. The charge distribution in the nonclassical ions is energetically less favorable because the charge is more concentrated on the H atoms than in the corresponding classical ions. The C_2H^+ cation is an exception to the general rule because the empty orbital of the classical form is directed along the bond axis, which causes a strong polarization of the C–H bond.

Table 14. *Localized bond orbital coefficients and total charge densities for some bridging* H *atoms*

Cation	q_H[a]	$2c_H^2$[b]
C_2H^+	0.690	0.678
$C_2H_3^+$	0.705	0.704
$C_2H_5^+$	0.768	0.767
prot. propene	0.795	0.793
edge prot. cyclopropane	0.789	0.760

[a] Charge density (electrons).

[b] c_H is the coefficient in the three center bond of the 1*s* AO centered at the bridging H atom.

Table 15. *Charge densities in bridged and classical carbonium ions*

Cation	Atom[a]	Classical	Nonclassical
$C_2H_5^+$	C_1	3.777	4.009
	$C_1\ p_y$	0.138	0.690
$C_2H_3^+$	C_1	3.781	3.924
	$C_1\ p_x$	0.150	0.714
C_2H^+	C_1	3.477	3.655
	$C_1\ p_z$	0.110	0.365
$C_2H_5^+$	H at C_1 or	0.809	0.768
$C_2H_3^+$	bridging H, resp.	0.748	0.705
C_2H^+		—	0.690
$C_2H_5^+$	C_2	3.817	
$C_2H_3^+$		3.993	
C_2H^+		3.934	
$C_2H_5^+$	H at C_2	0.807[b]	0.804
$C_2H_3^+$		0.732	0.724
C_2H^+		0.590	—

[a] The *p* orbitals listed are the "empty" *p* orbitals.
[b] Average value for the protons of the methyl group.

Chemical Reactivity

The chief characteristic of the electronic structure of carbonium ions is their electron deficiency, which leads either to an empty *p* orbital or to a three (or multiple) center bond. Carbonium ions are stabilized by such three center bonds, as well as by conjugation with vicinal π bonds or hyperconjugation with vicinal σ bonds. The reactivity of carbonium ions can be explained in terms of their electron deficiency and their stabilization by the mechanisms mentioned above.

The three center bond orbital φ_3 of a bridged carbonium ion can be formed by a steady admixture of the "empty" orbital φ_1 of the classical ion to the vicinal bond orbital φ_2 (steadily increasing λ):

$$\varphi_3 = \frac{1}{N}(\varphi_2 + \lambda\varphi_1) ; \quad N^2 = 1 + \lambda^2 . \tag{7}$$

Steadily increasing λ in (7) is roughly the orbital description of the [1, 2] migration of the substituent at C_2 of a 1-carbonium ion, and such processes should thus proceed with little or no activation energy. Computations and experimental evidence confirm this prediction (e.g. [6b]). The similar steady combination of the empty orbital with a bond orbital of another molecule should also be a thermally allowed process. Examples are the fragmentation reactions (II) and (III), which apparently proceed with at most a low additional activation energy (Table 2).

The CNDO results reported here lead in general to a satisfactory understanding of the stabilities and reactivities of carbonium ions. The data presented in this paper should also aid in finding possible deficiencies in the CNDO method by comparison with experimental and *ab initio* results.

The calculations were performed on a CDC 3300 computer using a FORTRAN program based on Pople and Segal's CNDO/2 program. Our program includes sections for minimizing the total energy with respect to the geometry, approximating reaction coordinates, transforming the canonical orbitals to localized orbitals, and calculating the "energy matrices" containing the terms of the energy partitioning.

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