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Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XVI. Conformations and Stabilities of Substituted Ethyl, Propyl, and Butyl Cations[1]

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Abstract: *Ab initio* molecular orbital theory is used to study the effects of substitution on the conformations and stabilities of ethyl, propyl, and butyl cations. A separation of the substituent effect into hyperconjugative and inductive contributions is achieved by assuming that the former is conformationally dependent and the latter conformationally independent. The preferred *conformation* of the cations is determined largely by the *relative* hyperconjugative abilities of the bonds at the β carbon. The *stabilities* of the substituted cations depend, in addition, on the inductive effect of the substituent. The theoretical predictions of the relative stabilities of alkyl cations are in reasonable agreement with available gas-phase experimental data.

Because simple alkyl cations contain an electron-deficient (positively charged) carbon atom, they are likely to be more sensitive to the electronic effects of substituents than corresponding neutral molecules and may therefore provide a useful basis for studying substituent effects. However, only a limited amount of experimental data on these systems is currently available. On the other hand, these cations are quite amenable to theoretical investigation and we have undertaken such an approach in this study. We report here results of *ab initio* molecular orbital calculations on a number of substituted ethyl, propyl, and butyl cations and related neutral molecules. In order that our calculations serve as models for larger experimentally accessible systems, we have employed a set of fixed standard geometries. On the basis of this study, we attempt to make some predictions and generalizations concerning the influence of substituents on the conformations and stabilities of carbonium ions.

Method

Standard LCAO–SCF molecular orbital theory has been used. The molecular orbitals (ψ_i) are written as linear combinations of atomic orbitals (ϕ_μ)

$$\psi_i = \sum_\mu c_{\mu i}\phi_\mu$$

Solution of the Roothaan equations[3] leads to the coefficients $c_{\mu i}$ and energy for each nuclear configuration considered. For the functions ϕ_μ we take a least-squares fit of three Gaussian functions to each exponential function in a minimal basis set of Slater type orbitals. This STO-3G basis set[4] has previously been applied successfully to studies of rotational barriers[5,6] and the energies of isodesmic reactions.[7,8]

The geometries of the carbonium ions and neutral molecules are constructed from a standard model described previously.[9] In addition, the carbonium center is taken to be trigonal with standard bond lengths $C^+–C = 1.49$, $C^+–H = 1.12$, these values being taken from the optimized geometry of the ethyl cation.[6] The geometries for the cyclopropyl and cyclobutyl skeletons are taken from experimental geometries for chlorocy-

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[1] Parts of this work have been reported in preliminary communications: (a) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 6380 (1970); (b) *ibid.*, **92**, 6987 (1970).

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[9] J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

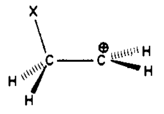
Table I. Total Energies (hartrees) of Molecules RH and Total Energies (hartrees) and Rotational Barriers (kcal mol^{-1}) for Primary Carbonium Ions R$^+$

	X	Y	Cation (R$^+$) conformations A (perpendicular)	Cation (R$^+$) conformations B (cis)	Neutral molecule (RH) C	Barrier (B–A)
I.	CH_3		−115.99294	−115.98893	−116.88512	2.52
	CCH		−152.11870	−152.11799	−153.02467	0.45
	H		−77.40594	−77.40594	−78.30549	0
	CN		−167.91735	−167.92046	−168.85032	−1.95
	OH		−151.21354	−151.22576	−152.12949	−7.67
	F		−174.82133	−174.83617	−175.75212	−9.31
II.	H	CH_3	−154.57320	−154.57747	−155.46511	−2.68
	CH_3	CH_3	−193.15890	−193.15889	−194.04502	0.01
	H	F	−272.27260	−272.26522	−273.21460	4.63
	F	F	−369.72487	−369.72489	−370.68983	−0.01
	CH_3	F	−310.87168	−310.85921	−311.80148	7.82
	F	CH_3	−252.00071	−252.01840	−252.91913	−11.10
III.	H	$n = 0$	−153.34926	−153.37722	−154.24765	−17.54
	H	$n = 1$	−191.96003	−191.96654	−192.84664	−4.09
	CH_3	$n = 0$	−191.93640	−191.96189	−192.83028	−16.00
	CH_3	$n = 1$	−230.54646	−230.55015	−231.42854	−2.32
VI.			−193.15059	−193.15578	−194.03972	−3.26
VII.	CH_3		−154.57682	−154.57088	−155.46457	3.73
	H		−115.99294	−115.98893	−116.88512	2.52
	CCH		−190.70776	−190.70390	−191.60448	2.42
	F		−213.42878	−213.42542	−214.33172	2.11
	OH		−189.81070	−189.80925	−190.70902	0.91
	CN		−206.51636	−206.51498	−207.43037	0.87
VIII.	CH_3		−193.15832	−193.15146	−194.04400	4.30
	CCH		−229.29316	−229.28684	−230.18402	3.97
	H		−154.57682	−154.57088	−155.46457	3.73
	F		−252.01654	−252.01078	−252.91123	3.61
	OH		−228.39771	−228.39233	−229.28865	3.38
	CN		−245.10777	−245.10312	−246.01003	2.92

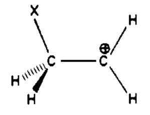
clopropane[10] and cyclobutane,[11] respectively. Conformations are chosen to be staggered unless otherwise specified. For hydroxyl derivatives, the conformation about the C–O bond is taken to be CCOH trans. Orbital, atomic, and overlap electron populations have been calculated using Mulliken's method.[12]

Results and Discussion

Conformations of Mono-β-substituted Ethyl Cations. It has generally been found that sixfold rotational barriers are very small.[13] In particular, recent *ab initio* molecular orbital calculations[6,14–17] have shown that the barrier in the ethyl cation [E(IB) − E(IA), X = H] is close to zero when regular tetrahedral and trigonal bond angles are assumed and is raised only slightly (to 0.2 kcal mol^{-1}) when distortions are allowed. However, substitution in the β position of the ethyl cation makes the barrier twofold and would be expected to increase the energy difference between IA and IB. Calculated total energies and rotational barriers for mono-β-substituted ethyl cations (IA, IB) are included in Table I. It may be seen that the magnitudes of the twofold barriers are indeed different from the zero value in the ethyl cation itself. A previous *ab initio* calculation[18] on the 2-fluoroethyl cation gave a large rotational barrier (10.53 kcal mol^{-1}) which is moderately close to the present value (9.31 kcal mol^{-1}).



IA



IB

There is a strong correlation between the conformational preferences (*i.e.*, IA or IB) and the populations of the formally vacant 2p orbital at the carbonium center (which we shall call the 2p(C$^+$) orbital) listed in Table II. Thus, IA is favored when X is CH_3 and the population of the 2p(C$^+$) orbital in IA is high (0.135) while IA is a highly unfavorable conformation when X is F and the 2p(C$^+$) population is low (0.070). The 2p(C$^+$) populations in IA, in turn, measure the relative *hyperconjugative* abilities of the C–X bonds, *i.e.*, the ability of the C–X bonds to release electrons into the 2p(C$^+$) orbital.

In general, the more strongly electron-withdrawing substituents (CN, OH, F) lead to a decrease in the 2p(C$^+$) populations in the perpendicular conformation IA and a reduced π-type overlap population between the 2p(C$^+$) orbital and the appropriate p orbital on the β carbon (which we shall call the π_{C-C} overlap). This may be caused by withdrawal of electrons in the

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Table II. Orbital and Overlap Populations for Conformations A and B of Primary Carbonium Ions

	X	Y	A (perpendicular)			B (cis)	
			2p(C$^+$) orbital[a]	π_{C-C} overlap[b]	σ_{C-X} overlap[c]	2p(C$^+$) orbital[a]	π_{C-C} overlap[b]
I.	CH_3		0.135	0.0836	0.0122	0.113	0.0748
	CCH		0.115	0.0604	0.0224	0.115	0.0742
	H		0.112	0.0748		0.112	0.0748
	CN		0.092	0.0562	0.0154	0.107	0.0728
	OH		0.082	0.0614	0.0026	0.121	0.0718
	F		0.070	0.0512	0.0090	0.116	0.0724
II.	H	CH_3	0.124	0.0788		0.144	0.0872
	CH_3	CH_3	0.144	0.0868		0.144	0.0868
	H	F	0.083	0.0568		0.063	0.0420
	F	F	0.058	0.0384		0.058	0.0384
	CH_3	F	0.109	0.0670		0.064	0.0408
	F	CH_3	0.079	0.0534		0.153	0.0864
III.	H	$n = 0$	0.124	0.0714		0.250	0.1360
	H	$n = 1$	0.165	0.0896		0.186	0.1058
	CH_3	$n = 0$	0.138	0.0782		0.261	0.1376
	CH_3	$n = 1$	0.182	0.0978		0.189	0.1058
VI.			0.128	0.0794		0.154	0.0908
VII.	CH_3		0.148	0.0874	0.0142	0.113	0.0746
	H		0.135	0.0836	0.0122	0.113	0.0748
	CCH		0.144	0.0860	0.0104	0.114	0.0752
	F		0.143	0.0880	0.0092	0.113	0.0752
	OH		0.132	0.0840	0.0090	0.116	0.0766
	CN		0.125	0.0794	0.0094	0.110	0.0742
VIII.	CH_3		0.155	0.0892	0.0154	0.114	0.0748
	CCH		0.153	0.0876	0.0152	0.112	0.0744
	H		0.148	0.0874	0.0142	0.113	0.0746
	F		0.146	0.0854	0.0154	0.111	0.0740
	OH		0.143	0.0858	0.0140	0.112	0.0742
	CN		0.139	0.0840	0.0134	0.110	0.0736

[a] Population of formally vacant 2p orbital [2p(C$^+$)] at the carbonium center. [b] Overlap population of 2p orbitals on α and β carbons as shown in Figure 1a. [c] Overlap population of 2p orbitals on α carbon atom and X as shown in Figure 1b.

C–X bond leading to a decreased population of the p orbital on the β carbon and hence withdrawal of electrons from the 2p(C$^+$) orbital as shown in Figure 1a. A partially compensating factor (which is largest for X = CN) is a σ-type overlap population between a p orbital on X and the 2p(C$^+$) orbital (which we shall call the σ_{C-X} overlap). This is shown in Figure 1b and the σ_{C-X} values are included in Table II.

On the other hand, the 2p(C$^+$) populations in the cis conformation IB all fall in a narrow range as do the π_{C-C} overlap populations. It seems that in this conformation in which the C–X bond is orthogonal to the 2p(C$^+$) orbital there is only a slight interaction of the 2p(C$^+$) orbital with the substituent X. The small variation in the 2p(C$^+$) population that does occur (*i.e.*, an increase when X = OH and decrease when X = CN) cannot be attributed to a *direct* 1,3-type π overlap since the corresponding populations are slightly negative.

When X is CH_3 (*i.e.*, the 1-propyl cation), the 2p(C$^+$) population and the π_{C-C} overlap population in IA both increase significantly rendering this perpendicular conformation more stable. However, the mechanism of the electron donation into the 2p(C$^+$) orbital is not clear since the Mulliken populations indicate the methyl group to be slightly electron withdrawing (relative to hydrogen). The relative orientation of the β C–H and C–CH_3 bonds and the 2p(C$^+$) orbital in the 1-propyl and related cations has important consequences regarding the rates of 1,2-hydride and 1,2-alkyl shifts and of β-cleavage reactions; these have been discussed recently.[19a]

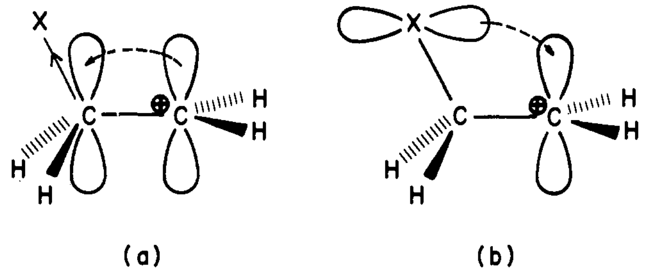


Figure 1. Electronic interactions in substituted ethyl cations.

We are led to suggest that the major effect causing the barriers in substituted ethyl cations is a relative destabilization of the perpendicular form IA due to withdrawal of electrons from the 2p(C$^+$) orbital when X is CN, OH, or F and a relative stabilization of IA due to donation of electrons into the 2p(C$^+$) orbital when X is CH_3 or C≡CH. The relative stabilities of conformations IA and IB reflect the relative hyperconjugative abilities of the C–X bonds. If we take the hyperconjugative effect of the C–X bond in conformation IB to be zero, then the hyperconjugative stabilizations are given simply by the differences in energy between IA and IB, *i.e.*, the rotational barriers, in Table I. These range from a slightly stabilizing hyperconjugative effect for the C–CH_3 bond (2.5 kcal mol^{-1}) to a strongly destabilizing effect for C–F (−9.3 kcal mol^{-1}).

(19) (a) D. M. Brouwer and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **89**, 211 (1970). (b) The solvolysis of 2,2,2-trifluoroethyl trifluoromethanesulfonate (triflate) has been studied, but the mechanism undoubtedly is SN2: R. L. Hansen, *J. Org. Chem.*, 30, 4322 (1965).

Thus we find in particular that C–C hyperconjugation is more effective than C–H hyperconjugation. This will be discussed in more detail below.

Stabilities of Mono-β-substituted Ethyl Cations. Having examined the relative stabilities of IA and IB, we now compare the stabilities of substituted ethyl cations with that of the ethyl cation itself. This can be done *via* reaction 1 and supplements information

$$XYZCCH_2^+ + CH_3CH_3 \longrightarrow XYZCCH_3 + CH_3CH_2^+ \quad (1)$$

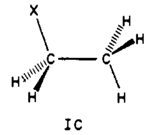
provided by the rotational barriers. The energy change in this reaction represents the effect of the substituents X, Y, and Z on the ethyl cation compared with their effect on ethane. For the sake of brevity, we shall refer to the energy change in (1) as the *ethyl cation stabilization energy*. A *positive* ethyl cation stabilization energy indicates a *greater* substituent stabilization in the ethyl cation than in ethane.

The ethyl cation stabilization reaction 1 is *isodesmic*, *i.e.*, the number of bonds of each type is conserved. We should point out that energy changes in isodesmic reactions involving neutral molecules have been found to be given moderately well by STO-3G calculations.[7,8] Ethyl cation stabilization energies for IA and IB are listed in Table III. In order to derive these values, total energies for the neutral molecules RH (IC) related to each cation R^+ are required. These are included in Table I.

Table III. Ethyl Stabilization Energies[a] (kcal mol^{-1}) for Conformations A and B of Primary Carbonium Ions

	X	Y	A (perpendicular)	B (cis)
I.	CH_3		+4.6	+2.1
	H		0	0
	OH		−10.3	−2.6
	CCH		−4.0	−4.4
	F		−19.6	−10.3
	CN		−20.9	−19.0
II.	H	CH_3	+4.8 (+5.5)	+7.5 (+8.1)
	CH_3	CH_3	+8.5 (+10.2)	+8.5 (+10.2)
	H	F	−26.6 (−25.3)	−31.2 (−34.6)
	F	F	−41.0 (−44.9)	−41.0 (−44.9)
	CH_3	F	−18.9 (−20.6)	−26.8 (−32.5)
	F	CH_3	−11.8 (−14.1)	−0.7 (−2.2)
III.	H	$n = 0$	+0.8	+18.3
	H	$n = 1$	+8.2	+12.2
	CH_3	$n = 0$	+3.6	+19.6
	CH_3	$n = 1$	+11.0	+13.3
VI.			+6.6	+9.8
VII.	CH_3		+7.4	+3.7
	H		+4.7	+2.1
	OH		+0.8	−0.1
	CCH		+1.8	−0.6
	F		−2.1	−4.2
	CN		−9.0	−9.9
VIII.	CH_3		+8.7	+4.4
	H		+7.4	+3.7
	OH		+5.4	+2.1
	CCH		+5.5	+1.5
	F		+3.1	−0.5
	CN		−1.7	−4.6

[a] Values in parentheses calculated from additivity rules (see text).

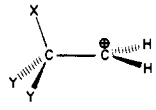


IC

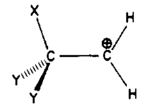
Ethyl cation stabilization energies vary widely. This is true even in the cis conformation IB for which we found little interaction of the 2p(C^+) orbital with the substituent X. This result suggests that in addition to the hyperconjugative effect which stabilizes or destabilizes conformation IA relative to IB, there is an *inductive* type of effect which stabilizes or destabilizes IB relative to the unsubstituted ethyl cation. We assume this effect is not dependent on conformation and therefore is also present in conformation IA.

The stabilization energies for conformation IB listed in Table III provide quantitative estimates of the inductive effects of the substituents. These range from a slightly stabilizing methyl substituent (+2.1 kcal mol^{-1}) to a strongly destabilizing cyano substituent (−19.0 kcal mol^{-1}).

Poly-β-substituted Ethyl Cations. In order to test the additivity of the hyperconjugative and inductive effects, we have performed calculations on a number of poly-β-substituted ethyl cations (IIA, IIB) and related neutral molecules (IIC). Total energies for these species are listed in Table I, relevant electron populations in Table II, and ethyl cation stabilization energies in Table III. The stabilization energies may alternatively be predicted from the inductive and hyperconjugative parameters derived from the monosubstituted cations and assuming (a) that the inductive effects are simply additive and (b) the hyperconjugative stabilization $V(\theta)$ for each C–X or C–Y bond follows a simple cosine potential function, $V(\theta) = (V_2/2)(1 + \cos 2\theta)$ where V_2 is the hyperconjugative stabilization parameter for X or Y and θ the dihedral angle between the C–X or C–Y bond and the 2p(C^+) orbital.



IIA



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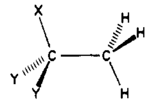
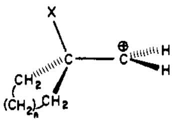


IIC

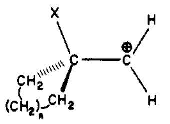
These predicted values are included in parentheses in Table III. The agreement between the calculated stabilization energies and those predicted from the additivity relationships above is reasonably good although absolute magnitudes are somewhat overestimated. This scheme may be useful in predicting stabilization energies for other polysubstituted cations. The results in Table III support our subdivision of stabilization energies into angular dependent hyperconjugative and angular independent inductive terms; predictions of the stabilization energies of polysubstituted ethyl cations assuming simple additivity give much poorer results. For example, the isobutyl cation (II, X = H, Y = CH_3) has less than twice the stabilization energy of the 1-propyl cation, and the neopentyl cation (II, X = CH_3, Y = CH_3) considerably less than three times the stabilization energy of the 1-propyl cation.

The actual values of orbital populations and stabilization energies for the polysubstituted ethyl cations are also of some interest. The 2p(C^+) population, which is increased from its value (0.112) in the ethyl cation to 0.135 by a single β-methyl substituent in conformation A of the 1-propyl cation, increases further to 0.144 with a second β-methyl substituent (conformation B of the isobutyl cation). However, a third β-methyl substituent (conformation B of the neopentyl cation) does not add to the $2p(C^+)$ population since the additional $C-CH_3$ bond is orthogonal to the $2p(C^+)$ orbital. Similar considerations apply to the effect of poly-β-fluoro substitution. The decrease in $2p(C^+)$ population caused by the first fluorine is much greater than the further decrease with the second and third β-fluoro substituents. The π_{C-C} overlap populations follow the same trend. Finally, the ethyl cation stabilization energies range from +8.5 kcal mol^{-1} for the neopentyl cation to −41.0 kcal mol^{-1} for the 2,2,2-trifluoroethyl cation.[19b]

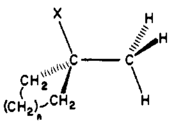
Cyclopropylcarbinyl and Cyclobutylcarbinyl Cations. The ability of adjacent cyclopropane rings to stabilize carbonium ions is now very well established.[20,21] This ability is illustrated in the present and prior calculations[22] on the cyclopropylcarbinyl cation. The stabilization in both the cyclopropylcarbinyl and the 1-methylcyclopropylcarbinyl cations is shown in Table II, by the very large $2p(C^+)$ orbital populations and π_{C-C} overlap populations in conformation IIIB (cis or bisected), and in Table III by the unusually large ethyl cation stabilization energies in the same (IIIB) conformation. Similar data for the perpendicular conformation IIIA of the cyclopropylcarbinyl systems (Tables II and III) show that there is only a small ethyl cation stabilization energy; the value obtained (0.8 kcal mol^{-1}) is considerably smaller than that produced by two methyl groups in the perpendicular conformation of the isobutyl cation (+4.8 kcal mol^{-1}). The 1-methyl group in the perpendicular (A) conformation of the 1-methylcyclopropylcarbinyl cation produces an additional stabilization of 2.8 kcal mol^{-1}, relative to the parent cyclopropylcarbinyl system. While this stabilization is to be expected because of the favorable hyperconjugative arrangement of the $C-CH_3$ bond, the magnitude is smaller than that found (+4.6 kcal mol^{-1}) in going from the ethyl cation to the perpendicular conformation of the *n*-propyl cation, or the 3.7 kcal mol^{-1} change calculated in going from the perpendicular conformation of the isobutyl cation to the neopentyl cation.



III A

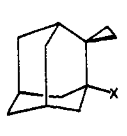


III B

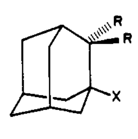


III C

Recently, experimental studies of cyclopropylcarbinyl systems have been reported in which the cyclopropylcarbinyl moiety is locked into the unfavorable perpendicular conformation.[20b,21] The solvolytic rate constants observed in IV are approximately 10^3 smaller than those found for model compounds, V. Thus, instead of the normal strong rate enhancing effect by adjacent cyclopropane rings, a marked decrease in reactivity was observed for IV. While some of this decrease may be due to less favorable hyperconjugative interaction in IV, relative to V (as indicated by the theoretical results above), steric strain effects inhibiting planarity in the cation derived from IV are probably also responsible.[21a] The magnitude of the difference between the solvolytic rate depression found in IV and the rate enhancement found ordinarily in unconstrained cyclopropylcarbinyl systems[21] is in general agreement with both the rotational barrier we have calculated (Table I) and an experimental determination of the rotational barrier in the dimethylcyclopropylcarbinyl cation.[23]



IV

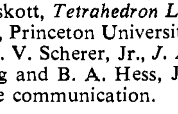


V (R = H or CH_3)

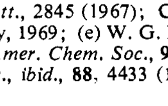
The indicated behavior of the cyclobutylcarbinyl and 1-methylcyclobutylcarbinyl cations is of considerable interest since such systems have received much less experimental attention.[24] Although the rates of solvolysis of cyclobutylcarbinyl systems are typically appreciably accelerated, this acceleration has generally been attributed to the relief of steric strain *via* σ participation leading to cyclopentyl products.[24] Thus, it is difficult to differentiate experimentally between the rate enhancement in cyclobutylcarbinyl systems due to (1) ring enlargement and (2) enhanced hyperconjugation.

While Table I indicates barriers to rotation in the cyclobutylcarbinyl and 1-methylcyclobutylcarbinyl cations which are only slightly larger than those in the propyl or isobutyl cations, the ethyl cation stabilization energies of Table III reveal that these barriers themselves are misleading. Rather surprisingly, *both* the perpendicular (IIIA) and bisected (IIIB) conformations of the cyclobutylcarbinyl cations are *strongly stabilized.* Thus, the small barrier to rotation is a result of a small difference in the stabilization in the two different conformations. This stabilization is also reflected in the $2p(C^+)$ orbital and π_{C-C} overlap populations (Table II).

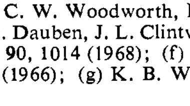
Examination of Table III reveals that the perpendicular conformations of the cyclobutylcarbinyl cations are behaving somewhat anomalously. Unlike the perpendicular conformations of the corresponding cyclopropylcarbinyl cations, a strong *stabilization* is indicated, a stabilization even larger than that found in the isobutyl cation and the model acyclic cation, VI. Thus, the cyclobutane ring has an unusually large car-



VI A



VI B



VI C

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(20) For extensive bibliographies, see (a) P. v. R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966); (b) P. v. R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969); (c) Reviews: H. G. Richey in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1972; K. B. Wiberg, B. A. Andes, Jr., and A. J. Asche, Jr., ref 20c; also see ref 21 and 23.

(21) (a) J. C. Martin and B. Ree, *J. Amer. Chem. Soc.*, **91**, 5882 (1969); B. Ree and J. C. Martin, *ibid.*, **92**, 1660 (1970); (b) V. Buss, R. Gleiter, and P. v. R. Schleyer, *ibid.*, **93**, 3927 (1971).

(22) Summarized in ref 20b and 21b.

(23) D. S. Kabakoff and E. Namanworth, *J. Amer. Chem. Soc.*, **92**, 3234 (1970).

(24) (a) C. E. Wilcox and M. E. Mesirov, *ibid.*, **84**, 2757 (1962); (b) A. P. Krapcho and M. Benson, *ibid.*, **84**, 1036 (1962); (c) S. Winstein and N. J. Holness, *ibid.*, **77**, 3054 (1955); (d) P. v. R. Schleyer and E. Wiskott, *Tetrahedron Lett.*, 2845 (1967); C. W. Woodworth, Ph.D. Thesis, Princeton University, 1969; (e) W. G. Dauben, J. L. Clintwood, and K. V. Scherer, Jr., *J. Amer. Chem. Soc.*, **90**, 1014 (1968); (f) K. B. Wiberg and B. A. Hess, Jr., *ibid.*, **88**, 4433 (1966); (g) K. B. Wiberg, private communication.

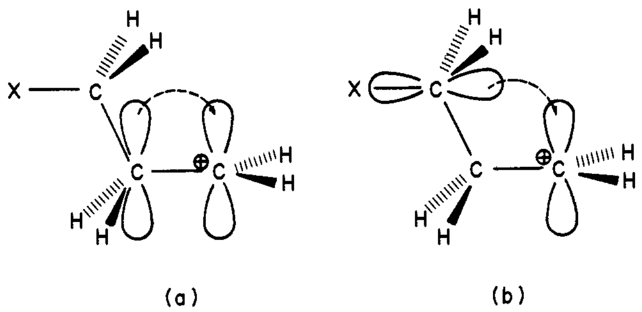


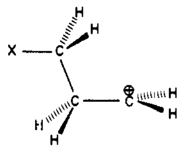
Figure 2. Electronic interactions in substituted 1-propyl cations.

bonium ion stabilizing ability in the perpendicular conformation.

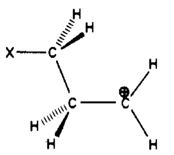
The behavior in the bisected (cis) conformation is regular. There is a progression in the ethyl stabilization energies in going from the isobutyl (+7.5 kcal mol^{-1}) to the cyclobutylcarbonyl (+12.2 kcal mol^{-1}) to the cyclopropylcarbinyl (+18.3 kcal mol^{-1}) cations, as would be expected because of enhanced C–C hyperconjugation in the strained ring compounds.

A qualitative analysis of the behavior of the cyclobutylcarbinyl system has been provided recently by Hoffmann and Davidson[25] in terms of the Walsh orbitals of cyclobutane. The highest occupied molecular orbitals of cyclobutane are a degenerate pair with symmetries which permit stabilization of adjacent cationic centers in both perpendicular and bisected conformations; the stabilizing interaction is indicated to be greater in the latter instance. From an analysis of the photoionization spectrum of cyclobutyl bromide, Heilbronner[26] has recently reached similar conclusions regarding the ability of the cyclobutane ring to interact with adjacent π-deficient centers.

Substituted 1-Propyl Cations. In the 1-propyl cation (VIIA, VIIB, X = H), conformation A is 2.52



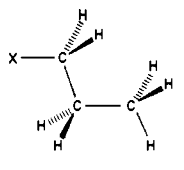
VII A



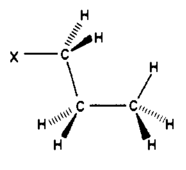
VII B

kcal mol^{-1} more stable than B. Substituted 1-propyl cations (VIIA, VIIB, X = CH_3, C≡CH, F, OH, CN) were examined to determine (i) whether the γ substituent X influences the relative stabilities of VIIA and VIIB (*i.e.*, the rotational barriers) and (ii) whether it stabilizes or destabilizes VIIA and VIIB relative to the unsubstituted 1-propyl cation. The barrier to rotation (*E*(VIIB) − *E*(VIIA), Table I) is found to be strongly dependent on X. This behavior is in marked contrast to the barrier to rotation of the terminal methyl groups in the similarly substituted propanes (VIIC, VIID, Table IV) where the barrier is nearly independent of X.

In the 1-propyl cations, conformation VIIA is favored in each case. The relative stabilization of VIIA can be rationalized in terms of the interactions in Figure 2 leading to increased population of the 2p(C$^+$) orbital (Table II). These interactions are favored when the CH_2X group is electron releasing (X = CH_3) and disfavored when it is electron attracting (X = CCH, F, OH, CN). The magnitude of the barrier and the 2p(C$^+$) populations show a reasonable correlation with the charge donated by the CH_2X group (Table V).



VII C



VII D

Table IV. Total Energies (hartrees) and Rotational Barriers [*E*(VIID) − *E*(VIIC), kcal mol^{-1}] for Substituted Propanes

X	VIIC (staggered)	VIID (eclipsed)	Rotational barrier
CH_3	−155.46457	−155.45878	3.63
H	−116.88512	−116.87924	3.69
CCH	−153.02467	−153.01868	3.76
F	−214.33172	−214.32621	3.46
OH	−190.70912	−190.70356	3.49
CN	−207.43037	−207.42457	3.64

Table V. Charge on CH_2X Group in Conformations of Substituted 1-Propyl Cations (VII)

X	A (perpendicular)	B (cis)
CH_3	+0.201	+0.132
H	+0.178	+0.117
F	+0.178	+0.110
CCH	+0.174	+0.104
OH	+0.163	+0.105
CN	+0.139	+0.079

Ethyl cation stabilization energies for the 1-propyl cations are listed in Table III. The γ substituent X influences the stability of both VIIA and VIIB. The inductive stabilizing effect of a γ substituent may be compared with that of a β substituent by calculating ethyl cation stabilization energies for conformation B of substituted ethyl cations and *1-propyl cation stabilization energies* for conformation B of substituted 1-propyl cations (Table VI). The latter quantity is simply the energy change in reaction 2 with the energies of con-

Table VI. Ethyl, 1-Propyl, and 1-Butyl Stabilization Energies (kcal mol^{-1}) for Conformation B of Substituted Ethyl (I), 1-Propyl (VII), and 1-Butyl (VIII) Cations, Respectively

X	Ethyl	1-Propyl	1-Butyl
CH_3	2.1	1.6	0.7
H	0	0	0
OH	−2.6	−2.2	−1.6
CCH	−4.4	−2.7	−2.2
F	−10.3	−6.3	−4.2
CN	−19.0	−12.0	−8.3

$$XCH_2CH_2CH_2^+ + CH_3CH_2CH_3 \longrightarrow XCH_2CH_2CH_3 + CH_3CH_2CH_2^+ \quad (2)$$

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(25) R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, **93**, 5699 (1971). We are indebted to Professor Hoffmann for sending us a preprint of this paper.

(26) F. Brogli and E. Heilbronner, *Helv. Chim. Acta*, **54**, 1423 (1971); F. Brogli, J. A. Hashmall, and E. Heilbronner, *ibid.*, in press; and E. Heilbronner, private communication.

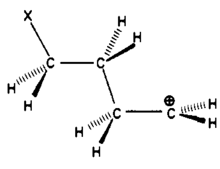
Table VII. Total Energies (hartrees) and Energy Differences (kcal mol^{-1}) for Secondary (IX) and Tertiary (X) Carbonium Ions R$^+$ and Neutral Molecules RH

	X	Cation (R$^+$) conformations A	B	C	Neutral molecule (RH)[a] D	E(B) − E(A)
IX.	CH_3	−154.60944	−154.60600	−154.59633		2.16
	H	−116.02406	−116.02397	−116.02410		0.05
	CN	−206.53838	−206.54077	−206.53791		−1.50
	OH	−189.83351	−189.84380	−189.84586		−6.46
	F	−213.44289	−213.45535	−213.45720		−7.82
X.	CH_3	−193.21925	−193.21221	−193.20590	−194.03972	4.42
	H	−154.63521	−154.63591	−154.63445	−155.46511	−0.44
	F	−252.05692	−252.06937	−252.06827	−252.91180	−7.81

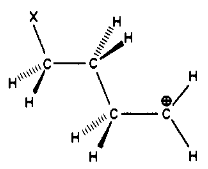
[a] The neutral molecules RH related to the substituted 2-propyl cations (IX) are listed in Table I as VIIC.

formation B being used for the 1-propyl cations. The inductive effect of the substituents in 1-propyl cations parallels that in the ethyl cations but is reduced in magnitude[27] by approximately one-third. An important point is that the inductive effect of a γ substituent may be of considerable magnitude. For example, when X = CN there is a destabilization of 12.0 kcal mol^{-1}.

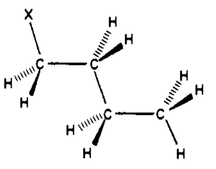
Substituted 1-Butyl Cations. In view of the results for 1-propyl cations, it was of interest to carry out calculations on the substituted 1-butyl cations (VIIIA, VIIIB) in which the substituent is at the δ position. The results are included in Tables I–III. We find that the rotational barriers in substituted 1-butyl cations (Table I) are still dependent on the substituent X although the variation with X is somewhat smaller than for the substituted 1-propyl cations. Again, the conformational preference is reflected in the 2p(C$^+$) populations (Table II).



VIIIA



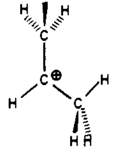
VIIIB



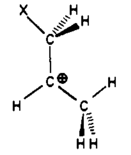
VIIIC

Inductive stabilization energies at the δ position (Table VI) are surprisingly large. The values are about $^2/_3$ those calculated for the correspondingly substituted 1-propyl cations[27] and range from +0.7 (X = CH_3) to −8.3 (X = CN) kcal mol^{-1}.

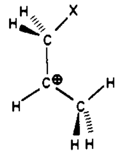
Secondary and Tertiary Cations. Since most experimental data on reactions involving carbonium ions are for cases where the ions are secondary or tertiary, it is of particular importance to see whether the general trends with regard to the effect of substituents on conformations and stabilities, discussed above for primary ions, also hold true for secondary and tertiary ions. For this reason, we have performed calculations on conformations of the 2-propyl cation (IXA, IXB, IXC, X = H) and substituted 2-propyl cations (X = CH_3, CN, OH, F). Conformation IXC is complicated by steric and other possible interactions between X and H, so we shall primarily be concerned with conformations IXA and IXB and the energy differences between them. These are analogous to the conformations IA and IB of substituted ethyl cations.



IXA



IXB



IXC

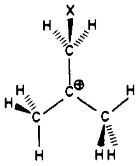
The energy differences between IXA and IXB (Table VII) range from a small relative stabilization (2.16 kcal mol^{-1}) for A when X = CH_3 to a strong destabilization (7.82 kcal mol^{-1}) when X = F. These are very similar to the values for the ethyl cations (Table I) only slightly reduced in magnitude. In addition, the *2-propyl cation stabilization energies* (Table VIII) for A and B, *i.e.*, the energy changes in reaction 3, are almost as large as the ethyl cation stabilization energies for the corresponding primary cations (Table VIII).

$$\mathrm{XCH_2\overset{+}{C}HCH_3 + CH_3CH_2CH_3 \longrightarrow CH_3\overset{+}{C}HCH_3 + XCH_2CH_2CH_3} \qquad (3)$$

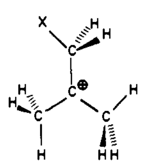
Table VIII. Ethyl, 2-Propyl, and *tert*-Butyl Stabilization Energies (kcal mol^{-1}) for Primary (I), Secondary (IX), and Tertiary (X) Carbonium Ions, Respectively

X	Conformation A (perpendicular) I	IX	X	Conformation B (cis) I	IX	X
CH_3	+4.6	+3.7	+6.0	+2.1	+1.5	+1.5
H	0	−0.1	−0.4	0	0	0
OH	−10.3	−9.1		−2.6	−2.6	
F	−19.6	−17.4	−15.6	−10.3	−9.6	−7.8
CN	−20.9	−19.4		−19.0	−17.9	

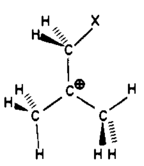
We have considered three tertiary cations, the *tert*-butyl cation and two substituted *tert*-butyl cations (XA, XB, XC, X = H, CH_3, and F) and their neutral analogs (XD). The most stable conformation of the *tert*-butyl cation is of some interest since it is one of the few aliphatic carbonium ions upon which some de-



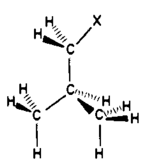
XA



XB



XC



XD

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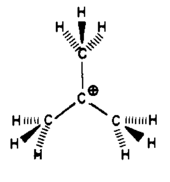
[27] The "falloff factor" of $^2/_3$ is essentially identical with that found experimentally for the addition of trifluoroacetic acid to substituted olefins as well as for the trifluoroacetolysis of ω-halo-substituted tosylates: P. E. Peterson, C. Casey, E. U. P. Tao, A. Agtorop, and G. Thompson, *J. Amer. Chem. Soc.*, **87**, 5163 (1965); P. E. Peterson, R. J. Bopp, D. M. Chevli, E. C. Curran, D. E. Dillard, and R. J. Kamal, *ibid.*, **89**, 5902 (1967).

Table IX. Orbital and Overlap Populations for Conformations A and B of Secondary (IX) and Tertiary (X) Carbonium Ions

		A (perpendicular)				B (cis)			
		Orbital	Overlap			Orbital	Overlap		
	X	2p(C+)	π_{C1-C2}	π_{C1-C3}	π_{C1-C4}	2p(C+)	π_{C1-C2}	π_{C1-C3}	π_{C1-C4}
IX.	CH_3	0.198	0.0720	0.0626		0.182	0.0636	0.0640	
	H	0.185	0.0644	0.0648		0.183	0.0638	0.0646	
	CN	0.174	0.0578	0.0684		0.182	0.0612	0.0672	
	OH	0.163	0.0516	0.0676		0.186	0.0608	0.0642	
	F	0.160	0.0434	0.0696		0.187	0.0610	0.0656	
X.	CH_3	0.242	0.0632	0.0556	0.0546	0.237	0.0580	0.0560	0.0574
	H	0.233	0.0564	0.0570	0.0560	0.234	0.0566	0.0566	0.0566
	F	0.218	0.0378	0.0606	0.0600	0.242	0.0542	0.0572	0.0594

tailed structural work has been carried out using vibrational spectroscopy. Olah and his associates[28] concluded that the carbon skeleton was planar and that the structure in solution probably had C_{3v} symmetry (XE), possibly because of the easier access of the counterion in that conformation. While we have not carried out a complete geometry optimization, our calculations indicate a preference for a C_{3h} structure (XB, X = H). This is found to be about 1.4 kcal mol^{-1} more stable than the C_{3v} form.



XE

Calculated results for all the tertiary cations examined are included in Tables VII–IX. The *tert-butyl cation stabilization energies* refer to the energy change in reaction 4. Again, the energy differences between

$$XCH_2C^+(CH_3)_2 + CH_3CH(CH_3)_2 \longrightarrow XCH_2CH(CH_3)_2 + CH_3C^+(CH_3)_2 \quad (4)$$

A and B and their stabilization energies are quite close to the corresponding values for the similarly substituted primary and secondary cations. The results in some cases are affected by steric interactions. For example, when X = CH_3, the standard values of bond lengths and angles that we use lead to destabilizing steric interactions in XB, XC, and XD which affect the calculated stabilization energies. Nevertheless, the results we have obtained for secondary and tertiary cations suggest quite strongly that the same β-substituent effects as in the primary cations are operative and are only slightly diminished in magnitude.

Table X. Calculated and Experimental Heats of Formation (kcal mol^{-1}) for Alkyl Carbonium Ions

Cation	Calcd[a]	Exptl[b]
1-Propyl	+209	+208
2-Propyl	+190	+192
1-Butyl	+202	+201
Isobutyl	+199	+199
2-Butyl	+181	+183
tert-Butyl	+163	+167
1-Pentyl	+195	+171[c]
2-Methyl-1-butyl	+192	
Neopentyl	+190	+196[c]
tert-Amyl	+152	+164[c]

[a] Calculated using $\Delta H°_f$ for the ethyl cation (+219 kcal mol^{-1}) from ref 29 and $\Delta H°_f$'s for neutral hydrocarbons from F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953. [b] From ref 29 unless otherwise noted. [c] "Best values" from ref 37.

Table XI. Relative Energies (kcal mol^{-1}) for Isomeric Alkyl Carbonium Ions

	Calcd		
Cation	(i)[a]	(ii)[b]	Exptl[c]
1-Propyl	0	0	0
2-Propyl	−20	−19	−16
1-Butyl	0	0	0
Isobutyl	0	−3	−2
2-Butyl	−20	−21	−18
tert-Butyl	−37	−39	−34
1-Pentyl	0	0	0
2-Methyl-1-butyl	+2	−3	
Neopentyl	0	−5	+25
tert-Amyl	−38	−43	−7

[a] Calculated as straight energy difference. [b] From calculated heats of formation in Table X. [c] From experimental heats of formation in Table X.

Experimental information concerning the effect of substituents on the stabilities of secondary and tertiary cations seems compatible with our predictions. The available gas-phase data[29] for the various propyl and butyl cations (see Tables X, XI and discussion below) are in close agreement with our calculations. On the other hand, a study[30] of the solvolysis rates of uncrowded tertiary species has shown only a small variation with β-alkyl substitution. It is possible that solvent stabilization in these cases attenuates the differences between the various substituted cations. Indeed, the solvolysis of simple secondary alkyl tosylates in trifluoroacetic acid, a solvent of low nucleophilicity, shows a marked rate enhancement by β-alkyl substituents.[30,31] A large rate depression is found for substituents like cyano in solvolysis studies on tertiary systems.[32] Finally, the observation[33] that the three isomeric *tert*-hexyl cations (XI, XII, XIII) exist in approximately equal concentrations in superacid is

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(28) G. A. Olah, J. R. DeMember, A. Kommeryas, and J. L. Brides, *ibid.*, **93**, 459 (1971).

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

(30) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971).

(31) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *ibid.*, **87**, 5169 (1965).

(32) P. v. R. Schleyer and C. W. Woodworth, *ibid.*, **90**, 6528 (1968).

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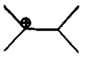
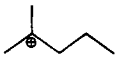


XI



XII

XIII

consistent with the similar values of calculated stabilization energies for cations like isobutyl and *n*-butyl (Table III).

Effect of α-Methyl Substitution on the Methyl Cation. Successive α-methyl substitution in the methyl cation has several interesting effects which are summarized in Table XII. It leads to (a) a large increasing stabilization energy, (b) increasing 2p(C+) population, (c) increasing *total* π_{C-C} overlap population, but (d) decreasing π_{C-C} overlap population per C–C bond, and (e) increasing positive charge on the central carbon.

Table XII. Effect of Methyl Substitution on the Methyl Cation

Cation	MCSE,[a] kcal mol^{-1}	2p(C+)	π_{C-C}[b]	q_{C^+}[c]
CH_3^+	0	0		+0.225
$CH_3CH_2^+$	30.0	0.112	0.0748	+0.249
$(CH_3)_2CH^+$	54.2	0.186	0.0646	+0.283
$(CH_3)_3C^+$	74.2	0.234	0.0565	+0.328

[a] Methyl cation stabilization energy, *i e.*, the energy of $XYZC^+ + CH_4 \rightarrow XYZCH + {}^+CH_3$. [b] Average π_{C-C} overlap population for *each* C–C bond. [c] Total charge on central carbon atom.

Results (b) and (c) simply reflect the expected increase in hyperconjugative interaction of the larger number of β C–H bonds. The increasing stabilization energies (a) include contributions from both the hyperconjugative and inductive stabilizing effects of the methyl substituents. In this regard, we should note that an α-methyl substituent has a much larger effect than a β-methyl group. A less obvious result is (d) which indicates that there is decreasing double bond character in the C–C bonds in the sequence ethyl, 2-propyl, and *tert*-butyl cations. We have recently found[34] that the C–C bond length in the 2-propyl cation is larger than in the ethyl cation which is consistent with this result. The fact that methyl substitution leads to an increase in the positive charge at the central carbon (e) and also an increase in the 2p(C+) population (b) suggests that the methyl group is a σ acceptor and a π donor in this situation (Figure 3). These conclusions are, of course, subject to the inherent limitation of the Mulliken method[12] of defining atomic charges. Olah and White[35] have recently observed that the ^{13}C chemical shift of the carbonium ion carbon (C_2) in the *tert*-butyl cation is shifted upfield by 10.4 ppm from the value obtained for the similar carbon in the 2-propyl cation. Because of a postulated relationship between ^{13}C chemical shifts and electron density, they conclude that the central carbon atom in the *tert*-butyl cation is slightly more positive than that in the 2-propyl cation. This result is thus in accord with our calculations and with previous theoretical conclusions.[36]

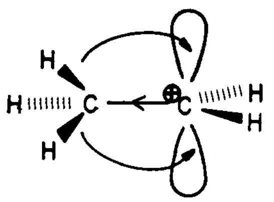


Figure 3. π-Electron donation and σ-electron withdrawal by methyl in the ethyl cation.

Ab initio molecular orbital theory has been used to study hyperconjugation in the ethyl cation in other recent publications.[16,36d] The results of a population analysis[16b] confirm that hyperconjugation is important. Williams, Buss, and Allen[36d] have estimated the hyperconjugative effect in the ethyl cation by carrying out calculations with and without the 2p(C+) orbital. When the 2p(C+) orbital is included, they obtain a methyl cation stabilization energy (defined in Table XII) of 18 kcal mol^{-1} which can be compared with our value of 30 kcal mol^{-1} (Table XII), an extended basis set, optimized geometry value[6] of 30 kcal mol^{-1}, and an experimental value of 40 kcal mol^{-1}. When the 2p(C+) orbital is excluded and hyperconjugation is therefore suppressed, the corresponding stabilization energy is only 6 kcal mol^{-1} indicating that a major part of the calculated stabilization energy is in fact due to hyperconjugation.

General Comparisons of Calculated and Experimental Energy Data. Calculated ethyl cation stabilization energies for the $C_3H_7^+$ and $C_4H_9^+$ cations are compared with experimental values derived from a recent electron impact study by Lossing and Semeluk[29] in Table XIII. There is good agreement between the two sets of values. The success of the theory in predicting ethyl cation stabilization energies has important consequences. It means that heats of formation for substituted ethyl cations may be predicted from the more readily available heats of formation of the appropriately substituted ethane, ethane itself, and the ethyl cation together with the calculated ethyl cation stabilization energy.

Table XIII. Ethyl Cation Stabilization Energies (kcal mol^{-1}) for Alkyl Carbonium Ions

Cation	Calcd	Exptl[a]
1-Propyl	5	6
2-Propyl	24	22
1-Butyl	7	8
Isobutyl	8	8
2-Butyl	28	26
tert-Butyl	44	40

[a] Calculated from data in ref 29.

Heats of formation for the $C_3H_7^+$, $C_4H_9^+$, and $C_5H_{11}^+$ cations computed in this way are listed in Table X. There is a wide divergence between calculated heats of formation for the $C_5H_{11}^+$ cations and the experimental "best values" from ref 37. Because of the close agreement between the calculated heats for $C_3H_7^+$

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and $C_4H_9^+$ and the experimental data of Lossing and Semeluk,[29] we have some confidence in our calculated values for the $C_5H_{11}^+$ cations which we therefore feel warrant experimental reexamination.

The relative energies for the isomeric alkyl carbonium ions are listed in Table XI. The calculated relative energies have been obtained both from (a) direct total energy differences and (b) differences in calculated heats of formation. The calculated and experimental values for the $C_3H_7^+$ and $C_4H_9^+$ (but not $C_5H_{11}^+$) cations are in reasonable agreement.

The gas-phase experimental and calculated relative energies (Table XI) are also in remarkably good agreement with values obtained indirectly from solution kinetics involving isomerization processes in superacid media.[38-41] For example, the process leading to mixing of all of the hydrogens in the 2-propyl cation has[38] $E_a = 16.4 \pm 0.4$ kcal mol^{-1}. Since this mixing process is believed to proceed through the 1-propyl cation, this value (less an undetermined but small energy representing the activation needed for transforming the 1-propyl to the 2-propyl cation) should thus represent roughly the energy difference between the 1-propyl and 2-propyl cations; comparable values are 16 kcal mol^{-1} (experimental, gas phase) and 19–20 kcal mol^{-1} (present calculations, Table XI).

Similarly the isomerization of the 2-butyl cation to the *tert*-butyl cation, believed to proceed through the isobutyl cation in the rate-limiting step,[39] has $E_a \sim 18$ kcal mol^{-1}, as compared with the experimental difference of 16 kcal mol^{-1} and our calculated values of 18–20 kcal mol^{-1}. Similar processes thought to involve the conversion of tertiary cations to secondary cations in their rate-limiting steps are found[40] to have E_a's consistently around 15 kcal mol^{-1}. These processes include methyl mixing in the *tert*-amyl cation, isomerization of the diethylmethylcarbonium ion to the dimethylpropylcarbonium ion, and methylene hydrogen exchanges in the methylcyclopentyl cation.[40] Although we have not specifically calculated these systems nor are experimental heats of formation data available, energy differences between tertiary and secondary cations are typically on the order of 14–20 kcal mol^{-1} (Table X). Only one interconversion of tertiary and primary cations seems to have been studied (most isomerizations involve protonated cyclopropane intermediates instead of classical species). Saunders and Rosenfeld[40] have estimated the barrier to hydrogen mixing in the *tert*-butyl cation (*via* the isobutyl cation) to be at least 28 kcal mol^{-1}, a value to be compared with experimental estimates of 34 kcal mol^{-1} (Table XI)[41] and 32.5 ± 9 kcal mol^{-1},[42] and the calculated values of 36–37 kcal mol^{-1} (Table XI).

C–C *vs.* C–H Hyperconjugation. It is commonly assumed by chemists that C–H hyperconjugation is more important than that involving C–C bonds.[43] This assumption rests primarily on the observation of a "Baker–Nathan order"

$$CH_3 > C_2H_5 > i\text{-}C_3H_7 > t\text{-}C_4H_9 \qquad (5)$$

of reactivities in systems such as para-substituted benzyl derivatives. However, explanations other than hyperconjugation have also been advanced to account for this ordering, notably, that it is due to a solvent effect, and the subject has stimulated a great deal of controversy.[43]

A direct indication that C–C hyperconjugation is more effective than C–H hyperconjugation comes from the observation (Table I) that the favored conformation of the propyl cation is IA ($X = CH_3$) and that the 2p(C^+) population in this conformation of the propyl cation (Table II) is greater than in the corresponding ethyl cation (IA, X = H). Further substitution of the β hydrogens by methyl groups leads to additional increases in the 2p(C^+) population.

We find also that the calculated stabilization energies (Table III, Table XIII) of the cations RCH_2^+ follow the "normal inductive order"

$$R = t\text{-}C_4H_9 > i\text{-}C_3H_7 > C_2H_5 > CH_3 \qquad (6)$$

which is the reverse of the Baker–Nathan order (5). This conclusion is confirmed by gas-phase experimental results (Table XIII). As we have discussed above, the β-methyl stabilizing effect includes contributions from both inductive and hyperconjugative effects. By assuming that hyperconjugation but not induction is conformationally dependent, we have been able to separate out the two effects (Tables I and III). The C–C hyperconjugation and the inductive effects make approximately equal contributions to the stabilization of primary cations. The important point to note is that *both* inductive and hyperconjugative stabilization energies are in the normal inductive order (6) and *not* the Baker–Nathan order (5).

Summary and Conclusions

The following important conclusions may be drawn from this work.

(1) Whereas conformations IA and IB of the ethyl cation have approximately the same energy, β substituents X change the energies of IA and IB by different amounts so that one or other conformation is preferred. This conformational preference is associated with the number of electrons in the formally vacant 2p orbital at the positive carbon in IA and is largely a measure of the relative *hyperconjugative* abilities of C–H and other C–X bonds. In particular, C–C hyperconjugation is found to be more effective than C–H hyperconjugation.

(2) Both conformations IA and IB are stabilized or destabilized relative to the unsubstituted ethyl cation by an *inductive* type of effect.

(3) Substituents in γ and δ positions (in substituted 1-propyl and 1-butyl cations, respectively) both modify the hyperconjugative interaction with the positive car-

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bon (and hence affect the relative energies of conformations A and B) and also have an inductive stabilizing or destabilizing effect of considerable magnitude. The falloff factor in the inductive effect is found to be approximately $^2/_3$ for each interposed CH_2 group.

(4) Substituent effects observed in primary cations are also operative in secondary and tertiary cations and only slightly diminished in magnitude.

(5) Calculated heats of formation, relative energies, and stabilization energies are in reasonable agreement with available gas-phase experimental data.

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A Semiempirical Molecular Orbital Study of ^{199}Hg–^{1}H Coupling Constants. I. The Method and Aliphatic Systems

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Abstract: An extended Hückel procedure for calculating ^{199}Hg–^{1}H coupling constants is outlined and results for a variety of methylmercury (CH_3HgX) systems are given. These results suggest that orbital contraction for the 6s orbital of mercury with increasing electronegativity of the substituent X is an important contributing factor to the large range spanned by these coupling constants. The calculated vicinal and geminal coupling constants in the ethylmercury moiety agree well with experimental values. It is suggested that this agreement might be useful in some conformational studies of organomercurials. No support for significant employment of mercury 5d orbitals in bonding is found in these systems.

In recent years a great deal of information on heavy atom proton spin–spin couplings has been accumulated,[1,2] particularly for mercury systems.[3,4] Perhaps the most outstanding general features of these couplings are their large absolute magnitudes and the degree to which they are influenced by substitution at the heavy atom.[4,5]

Hatton, Schneider, and Siebrand[4] have shown that the relative magnitudes of the geminal coupling constants in methane (^{1}H–C–^{1}H) and dimethylmercury (^{199}Hg–C–^{1}H) are approximately accounted for by assuming that both are due solely to the Fermi contact mechanism and including the relative optical hyperfine structure constants for hydrogen and mercury.

Evans, *et al.*,[5,6] have shown that the pattern of ^{1}H–^{1}H coupling constants in benzene is largely reproduced by ^{205}Tl–^{1}H couplings and ^{199}Hg–^{1}H couplings in the appropriate metal-substituted benzene.

These and other studies strongly suggest that the magnitudes of heavy metal proton spin–spin coupling constants are largely determined by the Fermi contact mechanism although several authors have questioned this.[6,7]

Orgel[8] has argued that one of the principal causes of the different stereochemical preferences of Hg (linear) and Zn (tetrahedral) is the involvement of the d_{z^2} orbital of mercury in forming digonal hybrids with a significant amount of d orbital character. Baldeschwieler[9] has interpreted the relative magnitudes of $J(M–H_\alpha)$ and $J(M–H_\beta)$ in ethyl compounds of Sn, Pb, Tl, and Hg as evidence for involvement of the metal d orbitals in bonding. However, a recent esr study[10] of radical anions of several arylmercury systems gave little evidence that the d orbitals of mercury play a significant role in bonding.

Because of these divergent views we have undertaken to calculate the Fermi contact contribution to $J(^{199}Hg–^{1}H)$ for a variety of systems. Mercury was chosen for this investigation because of the accuracy and variety of both structural and nuclear magnetic resonance data available. The low coordination number of mercury also makes the MO calculations easier and less expensive. Extended Hückel semiempirical MO methods have been shown to provide reasonable results for many proton proton couplings.[11,12]

Method

In the one-electron MO approximation the Fermi contact contribution, $J^{(3)}_{AB}$, to the coupling of nuclei

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