

# Molecular Orbital Theory of the Electronic Structure of Molecules. 35. $\beta$ -Substituent Effects on the Stabilities of Ethyl and Vinyl Cations. Comparison with Isoelectronic Methyl Boranes. The Relative Importance of Hyperconjugative and Inductive Effects

Yitzhak Apeloig,<sup>1a</sup> Paul v. R. Schleyer,\*<sup>1b</sup> and John A. Pople<sup>1c</sup>

Contribution from the Departments of Chemistry, Princeton University, Princeton, New Jersey 08540 and Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213, and the Institut für Organische Chemie der Universität Erlangen-Nürnberg, 8520 Erlangen, West Germany. Received October 13, 1976

**Abstract:** The effect of  $\beta$ -substituents, X, on the stabilities of ethyl and vinyl cations is studied by standard ab initio procedures. The ethyl cations are examined in perpendicular (**1**) and eclipsed (**2**) conformations. X is varied systematically along the whole series of first short period substituents, Li, BeH, BH<sub>2</sub>, CH<sub>3</sub>, NH<sub>2</sub>, OH, and F. Electropositive substituents are extremely effective in stabilizing ethyl cations, e.g., 88.9 and 27.1 kcal/mol (RHF/4-31G) for  $\beta$ -Li and  $\beta$ -BeH, respectively. Hyperconjugative contributions are larger than inductive effects for most substituents. Hyperconjugation between the C-X bond and the empty 2p cationic orbital is stabilizing for electropositive (relative to hydrogen) substituents which thus prefer conformation **1**, but destabilizing for electronegative substituents which prefer conformation **2**. Very high barriers for rotation around the C-C<sup>+</sup> bond were found for  $\beta$ -lithio- and  $\beta$ -beryllioethyl cations, 49.8 and 22.8 kcal/mol (RHF/4-31G), respectively. A linear correlation exists between the rotation barriers in the ethyl cations and the isoelectronic boranes, the cations being 2.3 times more sensitive to substituent effects. The stabilization of substituted vinyl cations parallels that of the perpendicular conformation (**1**) of ethyl cations.

Carbenium ions contain a positively charged electron-deficient center which renders them particularly sensitive to electronic influences and thus ideal for the study of substituent effects. Numerous experimental<sup>2</sup> and theoretical<sup>3-9</sup> studies have been published, but most of those involved alkyl groups,<sup>2,4</sup> or highly electronegative groups such as hydroxy<sup>5</sup> and halogens.<sup>5-9</sup> Stabilization of cationic centers by  $\beta$ -carbon-metal bonds is known.<sup>10-16</sup> Thus, ferrocenyl and other metallocenyl methyl carbenium ions are very stable.<sup>10</sup> Many instances are known<sup>11</sup> in which apparent carbenium ion formation is accelerated by  $\beta$ -carbon-metal bonds. These include reactions such as the protonation of allylmetal compounds (metal = Si, Ge, Sn, Pb, Hg)<sup>12</sup> and benzylmercury halides,<sup>13</sup> the cleavage of the aryl-silicon bond of Me<sub>3</sub>SiCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SiMe<sub>3</sub><sup>11</sup> and the solvolysis rates of  $\beta$ -silylalkyl halides.<sup>14</sup> Traylor showed that  $\beta$ -Pb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>,  $\beta$ -Sn(CH<sub>3</sub>)<sub>3</sub>,  $\beta$ -HgC<sub>6</sub>H<sub>5</sub>, and similar metalloid substituents stabilize carbenium ions by as much as 6 kcal/mol.<sup>13b,15</sup> The remarkable stability of nonacarbonyltricobaltcarbon-substituted carbonium ions was recently reported by Seyferth.<sup>16</sup>

The importance of hyperconjugation in affecting the energies of  $\beta$ -substituted ethyl cations has raised considerable controversy over the past 40 years.<sup>17</sup> The importance of  $\sigma$ - $\pi$  hyperconjugation in stabilizing  $\beta$ -metal-substituted carbenium ions was pointed out by Traylor<sup>13b,15</sup> and others.<sup>12,14,16,18,19</sup> The experimental demonstration that stabilization by the metal is possible only when the carbon-metal bond is coplanar with the axis of the empty cationic p orbital is of particular importance as it appears to rule out significant contribution by the inductive effect.<sup>15a,e</sup> However, other concepts such as metal participation<sup>10a</sup> and overlap with the metal's d orbitals<sup>20</sup> have also been suggested as possible explanations. The experimental difficulties<sup>17</sup> of separating the inductive and the hyperconjugative effects and of avoiding the influence of solvation can be overcome computationally. Recent ab initio calculations<sup>3-9</sup> show that the preferred conformation of  $\beta$ -substituted cations is determined largely by the relative hyperconjugative abilities of the bonds at the  $\beta$ -carbon, and that considerable barriers for rotation around the formally single C-C<sup>+</sup> bond result.

Examples are 10 kcal/mol<sup>6</sup> for H<sub>2</sub>BCH<sub>2</sub>CH<sub>2</sub><sup>+</sup> and 8-11 kcal/mol<sup>5,6,7a</sup> for FCH<sub>2</sub>CH<sub>2</sub><sup>+</sup>. The only other  $\beta$ -metallo-substituted cation studied by ab initio methods is H<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub><sup>+</sup>, which is found to be more stable than CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub><sup>+</sup>.<sup>21</sup> A few other cations involving group 4 substituents<sup>19a,22</sup> and the  $\alpha$ -ferrocenyl cation<sup>23</sup> have been studied by semiempirical methods. Qualitative theoretical arguments show that the ability of a C-X bond to hyperconjugate depends on the electronegativity of X and predict that electropositive substituents should be especially effective.<sup>6</sup> It is therefore of interest to extend our previous ab initio study of  $\beta$ -substituted ethyl cations<sup>5</sup> to include all of the first short period groups, Li, BeH, BH<sub>2</sub>, CH<sub>3</sub>, NH<sub>2</sub>, OH, and F. We have also investigated the corresponding series of  $\beta$ -substituted vinyl cations. This allows a systematic evaluation of the electronic effects and conformational preferences produced by such  $\beta$ -substituents. Special attention is drawn to the large effects of electropositive groups, Li, BeH, and BH<sub>2</sub>. Although these particular substituted cations are not practical experimentally and may in any case rearrange to some other form (bridged or  $\alpha$ -substituted), they nevertheless provide a valuable model for  $\beta$ -substitution in carbocations where such rearrangement does not take place. We shall therefore restrict ourselves to geometries in which the  $\beta$ -carbon is constrained to have an unaltered structure (tetrahedral for ethyl and trigonal for vinyl). This paper complements our study of  $\alpha$ -substituted cations with the same series of substituents.<sup>24</sup>

## Method, Geometrical Models, and Results

Calculations were carried out at the restricted Hartree-Fock (RHF) level using the ab initio SCF-MO GAUSSIAN 70 series of programs.<sup>25</sup> The minimal STO-3G basis set<sup>26a</sup> and the split-valence 4-31G basis set<sup>26b,c</sup> were used. The 4-31G level of theory is preferable for prediction of relative energies and will be used in most of the discussion. Parallel STO-3G results will also be given as this lower level theory can be more readily extended to larger systems. The geometries of the carbenium ions and the corresponding neutral molecules are constructed from the standard models described previously.<sup>5,27</sup> For the

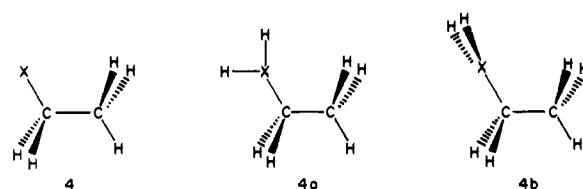
**Table I.** Total Energies (hartrees) of  $\beta$ -Substituted Ethyl Cations  $R^+$  and of Molecules  $RH^a$ 

Substituent (X)	Cation ( $R^+$ )				Neutral molecule (RH)	
	Perpendicular (1)		Eclipsed (2)		(3)	
	RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G
H	-77.405 94 <sup>e</sup>	-78.192 57 <sup>e</sup>	-77.405 94 <sup>e</sup>	-78.192 57 <sup>e</sup>	-78.305 49 <sup>e</sup>	-79.11484 <sup>e</sup>
Li	-84.239 70	-85.145 45	-84.15488	-85.066 16	-84.992 73	-85.926 01
BeH	-91.873 05	-92.822 39	-91.835 05	-92.786 07	-92.725 23	-93.701 52
BH <sub>2</sub> planar <sup>b</sup>	-102.366 16 <sup>f</sup>	-103.416 44 <sup>f</sup>	-102.348 69 <sup>g</sup>	-103.400 67 <sup>g</sup>	-103.242 17 <sup>h</sup>	
BH <sub>2</sub> perpendicular <sup>c</sup>	-102.358 39 <sup>i</sup>	-103.407 84 <sup>i</sup>	-102.342 83 <sup>j</sup>	-103.394 61 <sup>j</sup>	-103.243 02 <sup>k</sup>	-104.319 19 <sup>h</sup>
CH <sub>3</sub>	-115.992 94 <sup>e</sup>	-117.181 67 <sup>l</sup>	-115.988 93 <sup>e</sup>	-117.177 76 <sup>l</sup>	-116.885 12 <sup>e</sup>	-118.092 11 <sup>m</sup>
H <sub>2</sub> N planar <sup>b</sup>	-131.686 48 <sup>f</sup>	-133.109 92 <sup>f</sup>	-131.696 48 <sup>g</sup>	-133.122 22 <sup>g</sup>	-132.597 04 <sup>h</sup>	-134.047 95 <sup>h</sup>
NH <sub>2</sub> perpendicular <sup>c</sup>	-131.703 95 <sup>i</sup>	-133.130 64 <sup>i</sup>	-131.703 10 <sup>j</sup>	-133.131 26 <sup>j</sup>	-132.596 95 <sup>k</sup>	
OH <sup>d</sup>	-151.213 54 <sup>e</sup>	-152.904 80	-151.225 76 <sup>e</sup>	-152.923 04	-152.129 49 <sup>e</sup>	-153.854 11 <sup>m</sup>
F	-174.821 33 <sup>e</sup>	-176.869 90	-174.836 17 <sup>e</sup>	-176.892 24 <sup>f</sup>	-175.752 12 <sup>e</sup>	-177.841 54 <sup>m</sup>

<sup>a</sup> Using standard geometries. See text. <sup>b</sup> The XH<sub>2</sub> group and the CCX atoms lie in the same plane. <sup>c</sup> The XH<sub>2</sub> group and the CCX atoms define two perpendicular planes. <sup>d</sup> CCOH anti. <sup>e</sup> From ref 5 and 28. <sup>f</sup> Conformation 1a. <sup>g</sup> Conformation 2a. <sup>h</sup> Conformation 4a. <sup>i</sup> Conformation 1b. <sup>j</sup> Conformation 2b. <sup>k</sup> Conformation 4b. <sup>l</sup> Fully minimized, from ref 4a. <sup>m</sup> From ref 32.

ethyl cations, the  $\alpha$ - and  $\beta$ -carbons are constrained to be trigonal and tetrahedral, respectively, and the standard bond lengths (C-C<sup>+</sup> = 1.49, C<sup>+</sup>-H = 1.12 Å) are based on the optimized geometry of the unsubstituted ethyl cation.<sup>28</sup> In a similar manner,  $\alpha$ - and  $\beta$ -carbons of vinyl cations are taken to be linear and trigonal and standard bond lengths (C=C<sup>+</sup> = 1.28, C<sup>+</sup>-H = 1.11 Å) from the parent are used.<sup>28</sup> For hydroxyl derivatives, the conformation about the C-O bond is taken to be CCOH trans unless otherwise specified. For amino derivatives, planar arrangements around nitrogen with bond angles of 120° were used. Although these are not the preferred amino geometries, there are interpretive advantages for this choice as it allows direct comparison of NH<sub>2</sub> as a  $\pi$ -donor with BH<sub>2</sub> as a  $\pi$ -acceptor. The standard bond lengths and angles for lithium, beryllium, and boron derivatives were reported recently.<sup>29</sup>

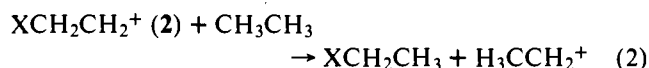
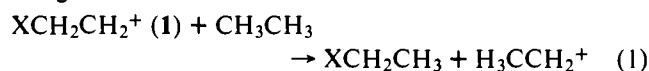
Two rotational conformations around the C-C<sup>+</sup> bond were calculated for each substituted ethyl cation, perpendicular (1) and eclipsed (2). For X = BH<sub>2</sub> and NH<sub>2</sub>, two conformations resulting from rotation around the C-X bond were calculated for both the perpendicular (1a and 1b) and the eclipsed (2a and 2b) cations. For most of the substituted vinyl cations, only the single conformation 3 has to be considered. However, for BH<sub>2</sub> and NH<sub>2</sub>, both planar (3a) and perpendicular (3b) conformations



were examined. The neutral molecules were calculated in their standard staggered conformations (4), and for X = BH<sub>2</sub> and NH<sub>2</sub>, planar (4a) and perpendicular (4b) arrangements of the XH<sub>2</sub> group relative to the C-C bond were studied. The calculated total energies for the  $\beta$ -substituted ethyl cations (1 and 2) and the corresponding neutral ethanes at both the RHF/STO-3G and the RHF/4-31G levels are given in Table I. Corresponding results for the  $\beta$ -substituted vinyl cations and corresponding ethylenes are listed in Table II.

## Discussion

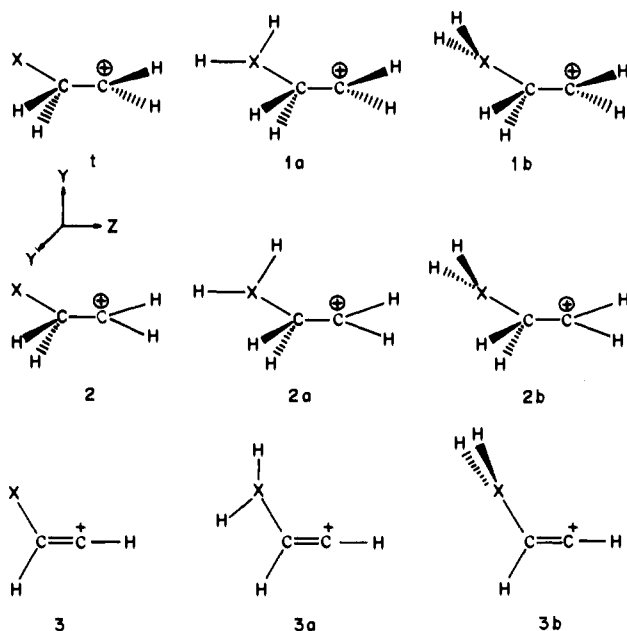
**Stabilities of  $\beta$ -Substituted Ethyl Cations.** The calculated energies for the isodesmic reactions<sup>30</sup>



(Table III) provide a comparison of the stabilities of the perpendicular (1) and eclipsed (2)  $\beta$ -substituted ethyl cations relative to the ethyl cation. A positive energy indicates a greater stabilization by X in the ethyl cation than in the corresponding substituted ethane. From previous experience, it is well known that the energies of such isodesmic reactions are generally well described even at the RHF/STO-3G<sup>30,31</sup> and the RHF/4-31G<sup>32</sup> levels. The estimated error limit for such reactions (not involving small rings) is of the order of 5 kcal/mol.<sup>4,32</sup>

The most striking result of Table III is the very large stabilization provided by electropositive  $\beta$ -substituents. BH<sub>2</sub> stabilizes the cation by 12.3 kcal/mol, BeH by 27.1 kcal/mol, and lithium by 88.9 kcal/mol (RHF/4-31G)! The calculated energies for both reactions parallel the electronegativity of the substituent. The  $\beta$ -substituted ethyl cations are more stable than the ethyl cation when the substituents are less electronegative than hydrogen, but are generally less stable than the ethyl cation when the substituents are more electronegative.

The inductive effect of a  $\beta$ -substituent should be, to a first approximation, independent of the conformation of the cation and thus is assumed to be roughly equal in 1 and in 2. C-X hyperconjugation, on the other hand, is an orientationally



**Table II.** Total Energies (hartrees) of  $\beta$ -Substituted Vinyl Cations  $R^+$  and of Molecules  $RH^a$ 

Substituent (X)	$\beta$ -Substituted vinyl cations (3)		Substituted ethylenes	
	RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G
H	-76.165 40 <sup>b</sup>	-76.977 53 <sup>b</sup>	-77.073 96 <sup>b</sup>	-77.921 88 <sup>b</sup>
Li	-83.022 47	-83.944 52	-83.784 03	-84.747 03
BeH	-90.645 55	-91.614 87	-91.508 03	-92.517 16
BH <sub>2</sub> perpendicular <sup>c</sup>	-101.133 54	-102.205 21	-102.014 19	-103.127 36
BH <sub>2</sub> planar <sup>d</sup>	-101.131 99	-102.206 36	-102.025 22	-103.140 16
CH <sub>3</sub>	-114.768 59 <sup>b</sup>	-115.975 03 <sup>b</sup>	-115.656 68 <sup>f</sup>	-116.902 03 <sup>g</sup>
NH <sub>2</sub> perpendicular <sup>c</sup>	-130.465 32	-131.917 09	-131.369 02	-132.858 90
NH <sub>2</sub> planar <sup>d</sup>	-130.493 52	-131.93439	-131.38476	-132.870 16
OH <sup>e</sup>	-149.997 07	-151.702 67	-150.908 80 <sup>f</sup>	-152.664 22 <sup>g</sup>
F	-173.592 40	-175.650 71	-174.529 41 <sup>f</sup>	-176.646 01 <sup>g</sup>

<sup>a</sup> Using standard geometries unless otherwise noted. <sup>b</sup> Fully optimized geometries from ref 5 and 28. <sup>c</sup> The XH<sub>2</sub> and the CCX atoms lie in the same plane. <sup>d</sup> The XH<sub>2</sub> group and the CCX atoms define two perpendicular planes. <sup>e</sup> CCOH anti. <sup>f</sup> From ref 31. <sup>g</sup> From ref 32 and L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 6531 (1973).

**Table III.** Ethyl Stabilization Energies (kcal/mol) for the Perpendicular (1) and Eclipsed (2)  $\beta$ -Substituted Ethyl Cations<sup>a</sup>

Substituent (X)	Electronegativity <sup>b</sup>	Reaction 1		Reaction 2	
		RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G
H	2.1	0	0	0	0
Li	1.0	91.9	88.9	38.7	39.2
BeH	1.5	29.7	27.1	5.9	4.3
BH <sub>2</sub> planar	2.0	14.2 <sup>c</sup>	12.2 <sup>c</sup>	3.3 <sup>c</sup>	2.4 <sup>c</sup>
BH <sub>2</sub> perpendicular	2.0	9.4 <sup>c</sup>	6.9 <sup>c</sup>	-0.4 <sup>c</sup>	-1.4 <sup>c</sup>
CH <sub>3</sub>	2.5	4.6	7.4	2.1	5.0
NH <sub>2</sub> planar	3.0	-6.9 <sup>c</sup>	-9.9 <sup>c</sup>	-0.6 <sup>c</sup>	-2.2 <sup>c</sup>
NH <sub>2</sub> perpendicular	3.0	4.1 <sup>c</sup>	3.1 <sup>c</sup>	3.5 <sup>c</sup>	3.5 <sup>c</sup>
OH	3.5	-10.3	-17.0	-2.6	-5.5
F	4.0	-19.6	-31.0	-10.3	-17.0

<sup>a</sup> Using energies from Table I. <sup>b</sup> After Pauling's electronegativity scale for the elements. See L. Pauling, "The Chemical Bond", Cornell University Press, Ithaca, N.Y., 1967, p 64. <sup>c</sup> Using the most stable conformation of the substituted ethanes (Table I).

**Table IV.** Orbital and Overlap Populations<sup>33</sup> for Conformations 1 and 2 of  $\beta$ -Substituted Ethyl Cations (RHF/STO-3G)

Substituent (X)	Perpendicular (1)		Eclipsed (2)	
	Mulliken population 2p(C <sup>+</sup> ) orbital <sup>a</sup>	$\pi_{C-C}$ overlap <sup>b</sup>	Mulliken population 2p(C <sup>+</sup> ) orbital <sup>a</sup>	$\pi_{C-C}$ overlap <sup>b</sup>
H	0.112	0.0748	0.112	0.0748
Li	0.484	0.1816	0.135	0.0779
BeH	0.270	0.1311	0.118	0.0743
BH <sub>2</sub> planar	0.174	0.0994	0.107	0.0712
BH <sub>2</sub> perpendicular	0.192	0.1078	0.123	0.0779
CH <sub>3</sub>	0.135	0.0836	0.113	0.0748
NH <sub>2</sub> planar	0.093	0.0637	0.146	0.0778
NH <sub>2</sub> perpendicular	0.140	0.0544	0.107	0.0728
OH	0.082	0.0614	0.121	0.0718
F	0.070	0.0512	0.116	0.0724

<sup>a</sup> Number of electrons in the formally empty 2p orbital [2p(C<sup>+</sup>)] at the carbenium center. <sup>b</sup> Overlap population of the 2p orbitals on the  $\alpha$ - and  $\beta$ -carbons.

dependent phenomenon and is at a maximum in **1**, where the empty p-orbital axis and the C-X bond are in the same plane; in **2**, these orbitals are orthogonal and C-X hyperconjugation is precluded. The much larger energy difference between lithium and fluorine in reaction 1 than in reaction 2 is consistent with the proposition that both hyperconjugative and inductive effects involving the  $\beta$ -substituent control the energy of **1**, while only the inductive effect is operating in **2**. This interpretation is supported by the Mulliken populations<sup>33</sup> of the formally vacant 2p orbitals at the carbenium center (2p(C<sup>+</sup>) orbital, Table IV). The populations of these 2p(C<sup>+</sup>) orbitals

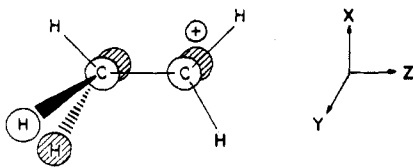
in **2** are not very dependent on the substituent as these orbitals can interact only with the  $\pi$ -type orbitals of the CH<sub>2</sub> group ( $\pi_{CH_2}$ ) and this interaction (Figure 1) is rather insensitive to the nature of X.

The small variations in the population of the 2p(C<sup>+</sup>) orbital in **2** that do occur on going from lithium to fluorine are caused by a combination of two effects: (a) The electron density of the donating  $\pi_{CH_2}$  orbital is expected to decrease slightly when the substituent X is more electronegative and thus we expect higher 2p(C<sup>+</sup>) population for lithium than for fluorine. (b) An empty 2p<sub>y</sub> orbital, if present on X, will compete for the  $\pi_{CH_2}$

**Table V.** Barriers for C–C<sup>+</sup> Bond Rotation (kcal/mol) in  $\beta$ -Substituted Ethyl Cations and C–B Bond Rotation in Substituted Methyl Boranes

Substituent (X)	Rotational barriers		
	XH <sub>2</sub> C–CH <sub>2</sub> <sup>+</sup> (2 – 1)		H <sub>2</sub> B–CH <sub>2</sub> X (6 – 5) <sup>a</sup> RHF/4-31G
	RHF/STO-3G	RHF/4-31G	
H	0	0	0
Li	53.2	49.8	20.4
BeH	23.8	22.8	9.3
BH <sub>2</sub> planar	11.0	9.9	5.5
BH <sub>2</sub> perpendicular	9.8 <sup>b</sup>	8.3	2.3
CH <sub>3</sub>	2.5	2.5	0.2
NH <sub>2</sub> perpendicular	0.5	–0.4	1.1 <sup>d</sup>
NH <sub>2</sub> planar	–6.3	–7.7	–4.9 <sup>d</sup>
HO	–7.7	–11.4	–4.9
F	–9.3	–14.0	–7.1
CCH	0.4 <sup>c</sup>		0.6 <sup>e</sup>
CN	–1.9 <sup>c</sup>		–0.6 <sup>e</sup>

<sup>a</sup> From ref 29. <sup>b</sup> A barrier of 10.4 kcal/mol (RHF/STO-3G) was reported in ref 6. The small difference in the values might be due to different geometries, which were not fully specified in ref 6. <sup>c</sup> From ref 5. <sup>d</sup> This study. The RHF/4-31G energies are –120.275 34, –120.268 92, –120.267 53, and –120.270 67 hartrees for **6a**, **6b**, **5a**, and **5b**, respectively. <sup>e</sup> At RHF/STO-3G, from ref 50.

**Figure 1.**  $2p(C^+) - \pi_{CH_2}$  interaction in **2**.

electrons and thus reduce their availability to the  $2p(C^+)$  orbital. Thus, for a BH<sub>2</sub> substituent the  $2p(C^+)$  population is higher in **2b** where the empty  $2p(B)$  and the  $\pi_{CH_2}$  orbitals are orthogonal, than in **2a** where they have a common nodal plane and can interact. A filled  $2p_y$  orbital on X, on the other hand, will somewhat enhance the  $\pi_{CH_2} \rightarrow 2p(C^+)$  donation because of the repulsive ( $4e$ )  $\pi_{CH_2} - 2p(X)$  interaction. Thus, a NH<sub>2</sub> substituent produces a higher  $2p(C^+)$  population when planar (**2a**) than when perpendicular (**2b**). A blend of these effects is responsible for the observed variations in the  $2p(C^+)$  population and for the fact that the highest population is found for a NH<sub>2</sub> substituent in planar conformation **2a**.

In the perpendicular conformation (**1**), the C–X bond is oriented properly to interact with the “empty”  $2p(C^+)$  orbital and much larger variations in its population are found. The  $2p(C^+)$  orbital is highly populated in the  $\beta$ -lithioethyl cation (0.484  $e$ ); this population decreases steadily as the electronegativity of X increases and reaches a minimum with fluorine (0.070  $e$ , Table IV). The increased population of the  $2p(C^+)$  orbital is accompanied by an enhanced  $\pi$ -type overlap between the  $2p(C^+)$  orbital and the appropriate p orbital on the  $\beta$ -carbon (the  $\pi_{C-C}$  overlap, Table IV). An increased  $\pi_{C-C}$  overlap means that the C–C<sup>+</sup> bond has a partial double bond character which should inhibit rotation around C–C<sup>+</sup> as discussed below.

The inductive effect of X influences the energies of both **1** and **2**, while hyperconjugation with the C–X bond can operate only in **1**. The C–C<sup>+</sup> rotational barrier given by the energy differences **2** – **1** provide quantitative estimates of the hyperconjugation abilities of the different C–X bonds (relative to a C–H bond). These values at both the RHF/STO-3G and the RHF/4-31G levels are given in Table V. The results are striking. Hyperconjugation stabilizes a carbenium ion by 49.8 kcal/mol (RHF/4-31G) for a C–Li bond and by 22.8 kcal/mol (RHF/4-31G) for a C–BeH bond. We find that hyperconjugation is stabilizing (positive values in Table V) for X = Li,

BeH, BH<sub>2</sub>, and CH<sub>3</sub>, the more electropositive substituents being more efficient. The perpendicular conformation **1** is then preferred. Conformation **2** (eclipsed) is more stable for the electron-withdrawing substituents NH<sub>2</sub>, OH, and F; the hyperconjugative interaction is then destabilizing (perpendicular NH<sub>2</sub> is a special case which will be discussed below).

As Traylor showed<sup>13b,15</sup>  $\beta$ -Pb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>,  $\beta$ -Sn(CH<sub>3</sub>)<sub>3</sub>,  $\beta$ -HgC<sub>6</sub>H<sub>5</sub>, and similar substituents stabilize carbenium ions by up to 6 kcal/mol. These metals have electronegativities in the range of 1.8–1.9,<sup>34</sup> intermediate between boron and beryllium. Remembering that our calculations pertain to the gas phase, and that electronic effects tend to be leveled in solution, we can say that our results showing a stabilization of around 18 kcal/mol for this electronegativity range<sup>34</sup> are consistent with Traylor's experimental data. This agreement supports the hypothesis that this stabilization arises from  $\sigma$ - $\pi$  conjugation between the empty  $2p(C^+)$  orbital and the C–metal bond,<sup>13b,15</sup> and the use of more electropositive metals should produce even larger effects. It was suggested alternatively that overlap with the metal d orbitals might be responsible for the high stabilization of carbonium ions by  $\beta$ -C metal bonds.<sup>20</sup> Our calculations do not include d orbitals and thus indicate that hyperconjugation alone may be sufficient to account for the observed effects.

For most substituents, hyperconjugation (Table V) is more important than the inductive effect (energies of reaction 2, Table III). Thus, the inductive effect contributes 39.2 and 4.3 kcal/mol (RHF/4-31G), respectively, to the additional stabilities (relative to ethyl cation) of perpendicular  $\beta$ -lithio- and beryllioethyl cations, while hyperconjugation contributes 49.8 and 22.8 kcal/mol (RHF/4-31G), respectively. Similarly, the destabilizing hyperconjugative effects for X = OH and NH<sub>2</sub> are larger than the corresponding inductive effects. The inductive effect is larger only for the highly electronegative fluorine and for a methyl where both effects are small. We conclude that, in the gas phase, hyperconjugation, rather than the substituent's inductive effect, plays the major role in determining the relative energies of  $\beta$ -substituted cations.

The change in the rotation barriers on going from lithium to hydrogen (49.8 kcal/mol at RHF/4-31G) is much larger than on going from hydrogen to fluorine (14.0 kcal/mol at RHF/4-31G) even though the electronegativity difference between H and F is larger than that between H and Li. Thus, the correlation between the additional stability provided by hyperconjugation and the electronegativity of the substituent

**Table VI.** Relative Energies (kcal/mol) for Conformations of  $\beta$ -Borano- and  $\beta$ -Aminoethyl Cations

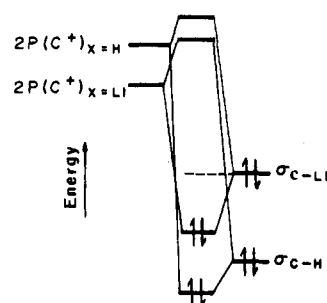
Conformation <sup>a</sup>	Relative energies, kcal/mol			
	X = BH <sub>2</sub>		X = NH <sub>2</sub>	
	RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G
<b>1a</b>	0.0	0.0	10.96	13.39
<b>1b</b>	4.88	5.40	0.0	0.39
<b>2a</b>	10.96	9.90	4.69	5.67
<b>2b</b>	14.64	13.70	0.53	0.0

<sup>a</sup> For conformation assignments, see text.

**Table VII.** Rotation Barriers (kcal/mol) around the C–X Bonds in  $\beta$ -Substituted Ethyl Cations and the Corresponding Neutral Molecules (for X = BH<sub>2</sub>, NH<sub>2</sub>)

$\beta$ -Substituent	Rotation barriers (kcal/mol)				
	<b>1a–1b<sup>a</sup></b>		<b>2a–2b<sup>a</sup></b>		<b>3a–3b<sup>a</sup></b>
	RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G	RHF/STO-3G
BH <sub>2</sub>	–4.88	–5.40	–3.68	–3.80	0.53
NH <sub>2</sub>	10.96	13.00	4.15	5.67	–0.06 <sup>b</sup>

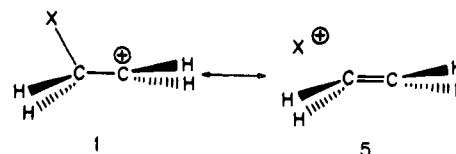
<sup>a</sup> For conformation assignments see text. <sup>b</sup> A barrier of –0.49 kcal/mol was calculated for the corresponding pyramidal conformations of ethylamine.<sup>46</sup>

**Figure 2.** Schematic interaction diagram between an empty cationic 2p orbital and a  $\beta$   $\sigma_{C-X}$  bond.

is not linear. This result can be explained by the simple perturbation theory arguments shown in Figure 2. If X is more electropositive than hydrogen, then the  $\sigma_{C-X}$  orbital (which is interacting with the empty  $2p(C^+)$  orbital) moves to higher energy,<sup>6,35</sup> and the  $2p(C^+)$  orbital to lower energy (due to stabilization by the inductive effect), thus bringing the two interacting orbitals closer together. The stabilization resulting from this interaction ( $\Delta E$ ) is inversely proportional to the energy separation of the two orbitals,<sup>36</sup> and thus should be larger for more electropositive substituents (e.g.  $\Delta E(\text{Li}) > \Delta E(\text{H})$ ). Furthermore, for electropositive substituents, the  $\sigma_{C-X}$  orbital is more localized on carbon, allowing more efficient overlap with the  $2p(C^+)$  orbital.<sup>35,36</sup> An analogous analysis accounts for the opposite effects of substituents more electronegative than hydrogen.<sup>6</sup> Other carbocations behave similarly, e.g.,  $\beta$ -substituted vinyl cations,<sup>37</sup> substituted phenyl cations,<sup>38</sup> and  $\beta$ -substituted acetyl cations.<sup>39</sup>

**Rotation Barriers around the C–C<sup>+</sup> Bond.** The sixfold rotation barrier in the ethyl cation is close to zero when regular tetrahedral and trigonal bond angles are assumed and is raised only slightly (to 0.2 kcal/mol) when distortions are allowed.<sup>40–43</sup> In  $\beta$ -substituted ethyl cations, the barrier is twofold and higher rotation barriers are expected and found (Table V). The especially large barriers for  $\beta$ -lithio- and  $\beta$ -beryllioethyl cations are due to the strong hyperconjugation with the C–Li

and C–BeH bonds. The dependence of the rotational barriers on substituent electronegativity is also consistent with the resonance representation of hyperconjugation<sup>17</sup> (**1**  $\leftrightarrow$  **5**). The



resonance contributor **5** dominates more for substituents which accommodate a positive charge better. In fact, the rotation barrier for the  $\beta$ -lithioethyl cation is only 15 kcal/mol lower than the rotational barrier in ethylene,<sup>44</sup> showing the importance of resonance structure **5**. For BeH, where the barrier is 22.8 kcal/mol (RHF/4-31G), the two resonance structures are of similar importance. Comparable rotation barriers, but with opposite signs, are predicted for the corresponding anions.<sup>6</sup> A recent analysis of experimental data emphasized the importance of lone pair–polar bond hyperconjugation.<sup>45</sup>

Many organic molecules possess partially empty 2p orbitals on carbon (such as ketones, aldehydes, esters, amides, etc.), which can hyperconjugate with  $\beta$   $\sigma$  bonds. This interaction will be smaller than that in the corresponding carbenium ion where the 2p orbital is formally empty. The strong hyperconjugation with carbon–metal bonds suggests, however, that such interactions should be of considerable importance in determining the conformation even of neutral molecules.

**Rotation around the C–XH<sub>2</sub> Bond.** A BH<sub>2</sub> or an NH<sub>2</sub> substituent can adopt two extreme conformations with respect to the plane defined by the heteroatom and the two carbons: **1a** and **1b** for the perpendicular conformation and **2a** and **2b** for the eclipsed conformation. The relative energies of the various conformers are given in Table VI and the barriers for rotation around the C–X bond for **1**, **2**, and the corresponding neutral molecules **3** are given in Table VII. As expected, the rotation barriers in the neutral molecules are much smaller than in the corresponding cations. A more accurate description of the rotational barrier for ethylamine using pyramidal nitrogen has been reported.<sup>46</sup>

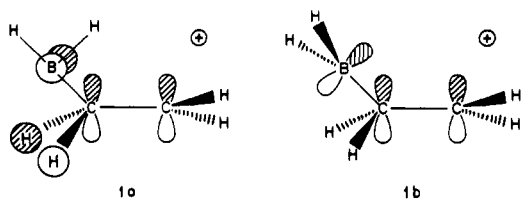


Figure 3. Orbital interactions in perpendicular  $\beta$ -boranoethyl cations **1a** and **1b**.

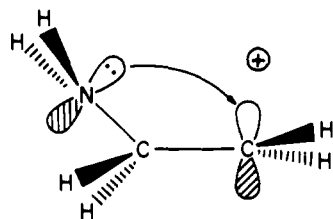


Figure 4. Overlap between an empty  $2p$  orbital and a lone pair of electrons on  $\text{NH}_2$ .

The  $\text{BH}_2$  and the  $\text{NH}_2$  groups have opposite preferences regarding the most stable arrangement around the  $\text{C-X}$  bond. Conformations **1a** and **2a** (for **1** and **2**, respectively), where the  $\text{XH}_2$  group and the  $\text{XCC}$  atoms define the same plane, are more stable for  $\text{BH}_2$ , while **1b** and **2b**, where these planes are perpendicular, are more stable for  $\text{NH}_2$ . The preference of **1a** and **2a** for  $\text{X} = \text{BH}_2$  arises from the favorable hyperconjugative interaction between the empty  $2p_y$  orbital on boron [ $2p(\text{B})$ ] and the  $\pi_y$ -type orbitals of the adjacent  $\text{CH}_2$  group (Figure 3). Rotation of the  $\text{BH}_2$  group to **1b** precludes the  $2p(\text{B})-\pi_{\text{CH}_2}$  overlap, and allows interaction only with the  $\text{C-C}^+$  bond. Hyperconjugation with a  $\text{C-C}$  bond is usually more effective than with a  $\text{C-H}$  bond (see Table V). In this case, however, one of the carbons is positively charged, and the hyperconjugative potential of the  $\text{C-C}$  bond is reduced, rendering the hyperconjugation with the  $\pi_{\text{CH}_2}$  electrons more effective. The most stable conformation for  $\text{X} = \text{BH}_2$  is **1a**, in which both the empty  $2p_x(\text{C}^+)$  and  $2p_y(\text{B})$  orbitals can hyperconjugate with the best available adjacent occupied orbitals of the proper symmetry.

For  $\text{X} = \text{NH}_2$ , the  $2p$  orbital is filled and the  $2p(\text{N})-\pi_{\text{CH}_2}$  interaction, which now involves four electrons, is destabilizing,<sup>6,35,36</sup> favoring **1b** over **1a** and **2b** over **2a**. Thus, **2b** is 5.67 kcal/mol (RHF/4-31G) more stable than **2a**, comparable to the (**2a** - **2b**) difference for  $\text{X} = \text{BH}_2$ . The "through space" interaction between the nitrogen's lone pair and the empty  $2p_x(\text{C}^+)$  orbital (Figure 4) preferentially stabilizes **1b**, causing a larger rotation barrier around the  $\text{C-N}$  bond in conformation **1** (**1a**  $\rightarrow$  **1b**) than in conformation **2** (**2a**  $\rightarrow$  **2b**) where the lone pair- $2p(\text{C}^+)$  overlap cannot take place. Conformation **1b** is affected by two opposing effects: a stabilizing interaction (lone pair- $2p(\text{C}^+)$ ) and a destabilizing hyperconjugative interaction between the  $\text{C-N}$  bond and the  $2p(\text{C}^+)$  orbital. The former is slightly larger so that a perpendicular  $\text{NH}_2$  substituent gives a positive energy for reaction **1** (Table III), although a negative value is expected since nitrogen is more electronegative than hydrogen.<sup>6</sup> The destabilizing hyperconjugative interaction is absent in **2b**, but so is the stabilizing  $\sigma_{\text{C-X}}-2p(\text{C}^+)$  interaction, and the rotation barrier **1b**  $\rightarrow$  **2b** ( $\text{X} = \text{NH}_2$ ) is very small (0.4-0.5 kcal/mol).

In the  $\beta$ -hydroxyethyl cation, the stabilizing "through space" interaction is smaller and the destabilizing hyperconjugation interaction is larger than for amino. The most stable conformation is **2**. The anti conformation ( $\angle\text{HOCC} = 180^\circ$ ) is preferred over the syn conformation ( $\angle\text{HOCC} = 0^\circ$ ) by 7.4 kcal/mol (RHF/STO-3G).

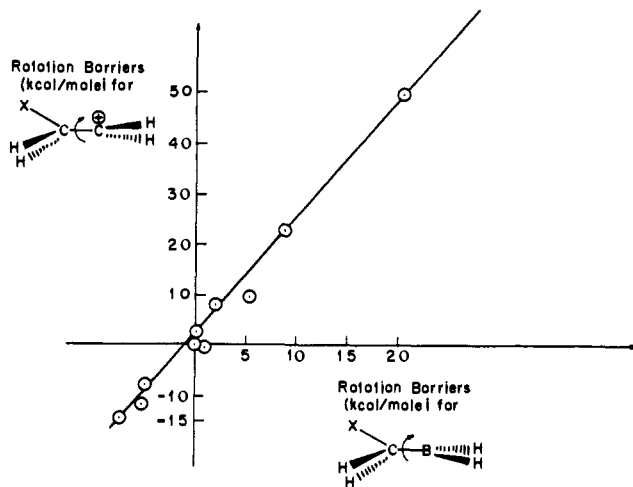
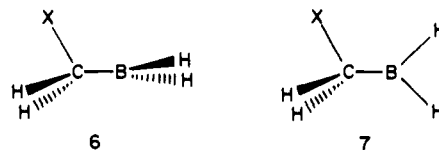


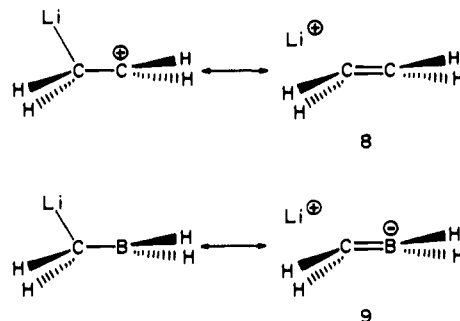
Figure 5. Correlation of the calculated (RHF/4-31G) rotation barriers around the  $\text{C-C}^+$  and  $\text{C-B}$  bond in  $\text{XH}_2\text{C}^+\text{CH}_2$  and  $\text{XH}_2\text{CBH}_2$ , respectively.

**Comparison with the Isoelectronic Boranes.** Boranes have often been suggested as models for the corresponding isoelectronic carbocations.<sup>2a,29,47-49</sup> We showed recently that  $\alpha$ -substituted boranes are reasonable analogues of the corresponding substituted methyl cations with regard to molecular geometry, but show reduced stabilization energies and  $\pi$ -bonding abilities.<sup>47</sup> A similar comparison can be made now for a  $\beta$ -substituent by comparing the  $\beta$ -substituted ethyl cations **1** and **2** with their borane analogues **6** and **7**. The barriers for



rotation around the  $\text{C-B}$  bond in substituted methyl boranes<sup>29</sup> (Table V) show a linear correlation (slope = 2.31, correlation coefficient = 0.992) with the corresponding barriers for the  $\beta$ -substituted ethyl cations (Figure 5).

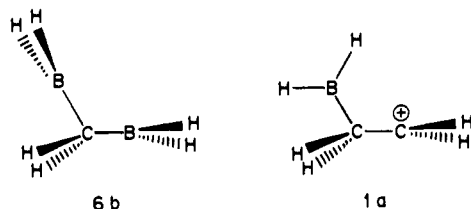
This excellent correlation shows that boranes respond in the same way as carbenium ions to changes in the electronic properties of the  $\beta$ -substituent, although to a much smaller extent. As the rotational barriers measure the energy associated with hyperconjugation, we may conclude that hyperconjugation involving a  $2p(\text{C}^+)$  orbital is 2.3 times more effective than hyperconjugation involving a  $2p(\text{B})$  orbital, a conclusion which is supported by the larger populations of the empty  $p$  orbital and larger  $\pi$  overlaps in the cations.<sup>50</sup> Qualitatively, the same conclusion can be reached by comparing the resonance structures **8** and **9**. The resonance structure **9** should



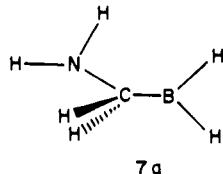
contribute less than **8** because of the charge separation involved, and because the vacant orbital energy for  $\text{C}^+$  is lower

than for boron. Both the shorter central bonds ( $C-C^+ = 1.49$ ,  $C-B = 1.57$  Å) and the presence of a positive charge will enhance hyperconjugation in the cations relative to the boranes. Shortening of the C-B bond in substituted methyl boranes to 1.49 Å does increase the rotational barriers modestly, but the barriers for the cations still remain much higher.<sup>50</sup> The positive charge is therefore the main factor responsible for the 2.3-fold difference between the two series.

For the most part, the preferred conformations are the same for both  $-BH_2$  and  $-CH_2^+$  series. The exceptions are of interest.  $H_2BCH_2BH_2$  prefers geometry **6b**, where both vacant p orbitals can hyperconjugate with BC rather than CH bonds.  $H_2BCH_2CH_2^+$ , in contrast, adopts structure **1a**, since the  $\pi_{CH_2}$

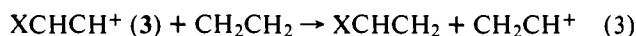


orbital hyperconjugates better than the  $C-C^+$  bond. The amino derivatives **7a** and **2b** prefer different conformations around both bonds. **7a** behaves regularly. Because of the electroneg-



ative nitrogen, the vacant B orbital of **7a** avoids hyperconjugation with the C-N bond. The lone pair N orbital conversely avoids hyperconjugation with the electron rich C-B bond. **1a** is a special case dominated by the 1,3-interaction shown in Figure 4. This interaction is expected to be greater with the carbocation center than with the  $BH_2$  group. The C- $BH_2$  and  $C^+CH_2$  rotation barriers in these exceptional cases are small, so that only small deviations (Table V) from the correlation line in Figure 5 are noted.<sup>51</sup>

**Stabilities of  $\beta$ -Substituted Vinyl Cations.** For the  $\beta$ -substituted vinyl cations (**3**), the energies of the isodesmic reactions



provide estimates of the cation stabilities relative to the parent vinyl cation. These energies are listed in Table VIII.

Changes in the substituent X are expected to have similar effects on the vinyl cations (**3**) and the perpendicular conformations of the ethyl cations (**1**). This is because the C-X bond and the axis of the  $2p(C^+)$  orbital are coplanar in both systems, so that the X inductive effect and the hyperconjugative effects between  $\sigma_{C-X}$  and  $2p(C^+)$  are both operative. It may also be pointed out that the vinyl stabilization energies do not reflect contributions from  $\pi$  conjugation between the substituent and the double bond as it is counterbalanced in reaction 3 by a similar conjugation in the substituted ethylene.

The predicted parallelism between the stabilization energies of **1** and **3** is indeed found to be close by comparison of Tables III and VIII. The range is 89 to -32 kcal/mol for vinyl cations compared with 89 to -31 for the perpendicular conformations of the ethyl cations. It is reasonable to suppose that the relative contribution of inductive and hyperconjugative effects is similar in both series, the latter being the dominant mechanism. The high predicted stabilization of vinyl cations by Li and BeH substitution (Table VIII) suggests the use of other more practical metals as a means of stabilizing the as yet unknown primary vinyl cations.

**Table VIII.** Vinyl Stabilization Energies (kcal/mol) for the  $\beta$ -Substituted Vinyl Cations (**3**)<sup>a</sup>

Substituent (X)	Reaction 3	
	RHF/STO-3G	RHF/4-31G
H	0.0	0.0
Li	92.2	89.0
BeH	28.9	26.4
$BH_2$ perpendicular	17.5	13.9
$BH_2$ planar	9.6	6.6
$CH_3$	12.8	10.9
$NH_2$ perpendicular	3.0	1.6
$NH_2$ planar	10.9	5.4
OH	-2.0	-10.8
F	-17.9	-32.0

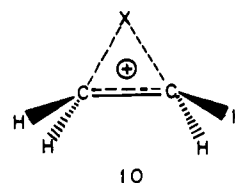
<sup>a</sup> Using total energies from Table II.

**Consequences of Geometrical Assumptions.** We have chosen to examine structures in their "standard" geometries.<sup>5,27</sup> Despite the artificiality of this approach, there are distinct advantages. We intended to investigate a graded series of  $\beta$ -substituents of greatly varying electrical character. The use of standard geometries reduces the variables which can influence the effects of these substituents, and, for example, models vertical processes.

Structural deviations from these standard models are expected, and do occur in the optimized cases already investigated.<sup>4</sup> For the perpendicular conformation (**1**), where the C-X bond hyperconjugates with the empty  $2p(C^+)$  orbital, large deviations in the C- $C^+$  and C-X bond lengths from the standard values are anticipated. If hyperconjugation is stabilizing, electrons will be transferred from the C-X  $\sigma$  bond, which will lengthen, to the C- $C^+$   $\pi$  bond, which will shorten. Indeed, the optimized C- $C^+$  bond length in **1** (X =  $CH_3$ ) is shorter (1.474 Å) than that in **2** (X =  $CH_3$ ) (1.492 Å).<sup>4</sup> Were the C- $C^+$  bond lengths in **1** to be optimized, the following trend would be expected: X = F (C- $C^+$  longest) > OH >  $NH_2$  > H >  $CH_3$  >  $BH_2$  > Li (C- $C^+$  shortest). The C-X bond lengths should show the opposite trend and should become shorter than the standard value<sup>27,29</sup> when X is a  $\sigma$  acceptor and longer when X is a  $\sigma$  donor. The latter is found when X =  $CH_3$ .<sup>4</sup> Much smaller structural changes are expected for the eclipsed conformation **2**, where the C-X bond cannot interact with the  $2p(C^+)$  orbital.<sup>52</sup>

The larger the geometrical deviation from the "standard model" the larger the resulting energy lowering should be. Optimization of the C- $C^+$  and C-X bond lengths probably will further favor conformation **1** over **2**, so that the rotation barriers around the C- $C^+$  bond reported in Table V represent minimal values for X = Li to  $CH_3$  and higher barriers should result upon geometry optimization. On the same basis, somewhat lower rotation barriers are predicted for X =  $NH_2$ , OH, and F.<sup>53</sup>

In work to be presented separately, fuller optimization of geometrical parameters of the  $C_2H_4X^+$  cations has been carried out at the RHF/STO-3G level.<sup>54</sup> Profound geometrical changes occur which emphasize the need to use standard models for our present purposes. For example, the perpendicular cations **1** (with the exception of X =  $CH_3$ )<sup>4</sup> collapse to cyclic forms **10**.<sup>54</sup> Since such rearrangement is not to be



expected in all  $\beta$ -substituted systems, e.g., those with more stable carbocation centers, the use of standard models may give a more representative picture of substituent effects.

For  $X = \text{NH}_2$ , an additional assumption, i.e., that of a planar arrangement around the nitrogen, was made in order to allow an easy separation of the  $\beta$ -amino effect into  $\sigma$  and  $\pi$  components and to allow a direct comparison with the  $\text{BH}_2$  group. Calculations using pyramidal nitrogen will not be very advantageous anyhow, since the energy difference between the pyramidal ( $C_{3v}$ ) and the planar ( $D_{3h}$ ) conformations in ammonia is underestimated by the RHF/4-31G basis set (0.4 kcal/mol<sup>55a</sup> compared to an experimental value of 5.8 kcal/mol<sup>55b</sup>). It is reasonable to assume that pyramidization at nitrogen will not change appreciably the relative energies of the different conformations investigated.

**Comparison of the RHF/STO-3G and the RHF/4-31G Results.** Our study includes a relatively large number of carbocations which were calculated using both the STO-3G and the 4-31G basis sets on the same geometries. The two basis sets show the same ordering of the calculated energies of reactions 1 and 2 (Table III) and the rotation barriers (Table V). Both basis sets predict the same conformation of a given carbocation to be the most stable; there is only one exception (**1b** and **2b**,  $X = \text{NH}_2$ ), where the energy difference between the conformations is very small ( $\sim 0.5$  kcal/mol). The STO-3G basis generally gives higher stabilization energies for reaction 1 than the 4-31G basis, especially for hydroxy and fluorine.<sup>56</sup> The STO-3G and the 4-31G results are closer for the rotation barriers, due to the cancellation of inherent basis set deficiencies. The RHF/STO-3G rotational barriers are somewhat higher than the RHF/4-31G results for  $X = \text{Li}$ ,  $\text{BeH}$ , and  $\text{BH}_2$ , and smaller for  $X = \text{NH}_2$ ,  $\text{OH}$ , and  $\text{F}$ , the largest deviations occurring for lithium, hydroxy, and fluorine.<sup>57</sup>

## Conclusions

1. Electropositive  $\beta$ -substituents, such as  $\text{Li}$ ,  $\text{BeH}$ , and  $\text{BH}_2$ , stabilize carbocations highly, lithium being the most effective. The stabilization energy in the  $\beta$ -lithioethyl and  $\beta$ -lithiovinyl cations approaches 90 kcal/mol.

2. A dissection of the total substituent effect reveals that, for most  $\beta$ -substituted ethyl cations in the perpendicular conformation, the hyperconjugative effect is larger than the inductive effect.

3. The hyperconjugative interaction between a C-X bond and the empty 2p cationic orbital in ethyl cations is stabilizing for electropositive (relative to hydrogen) substituents which thus prefer perpendicular conformations, but destabilizing for electronegative substituents which prefer eclipsed conformations. Stabilizing hyperconjugative interactions are more sensitive to changes in substituent electronegativity than are destabilizing hyperconjugative interactions.

4. Very high barriers for the rotation around the C-C<sup>+</sup> bond were found for substituted ethyl cations: 49.8 and 22.8 kcal/mol (RHF 4-31G) for  $\beta$ -lithio- and  $\beta$ -beryllioethyl cations, respectively.

5. A linear correlation is found between the rotation barriers of substituted methyl boranes and the corresponding ethyl cations. The cations are 2.3 times more sensitive to substituent effects.

6. The STO-3G and 4-31G basis sets give very similar quantitative results for  $X = \text{BeH}$ ,  $\text{BH}_2$ ,  $\text{CH}_3$ ,  $\text{NH}_2$ , while larger deviations are found for  $\text{F}$ ,  $\text{OH}$ , and  $\text{Li}$ .

7. The stabilities of  $\beta$ -substituted vinyl cations closely parallel those of  $\beta$ -substituted ethyl cations in the perpendicular conformation.

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## Organic Alloys: Synthesis and Properties of Solid Solutions of Tetraselenafulvalene-Tetracyano-*p*-quinodimethane (TSeF-TCNQ) and Tetrathiafulvalene-Tetracyano-*p*-quinodimethane (TTF-TCNQ)

E. M. Engler,\* B. A. Scott, S. Etemad, T. Penney, and V. V. Patel

Contribution from the IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598. Received December 6, 1976

**Abstract:** The selenium analogues of tetrathiafulvalene (TTF), tetraselenafulvalene (TSeF) and diselenadithiafulvalene (DSeDTF), have been synthesized by trimethyl phosphite coupling of 1,3-diselenole-2-selone and 1,3-thiaselenole-2-selone, respectively. TTF, TSeF, and DSeDTF form isostructural, metallic charge-transfer salts with tetracyano-*p*-quinodimethane (TCNQ). TSeF-TCNQ has a slightly higher conductivity and a metal-insulator transition at lower temperature compared to TTF-TCNQ. The isostructurality of TSeF-TCNQ and TTF-TCNQ permits the formation of solid solutions TSeF<sub>x</sub>TTF<sub>1-x</sub>TCNQ where  $x$  can be varied from 0 to 1. Solid solution compositions of single crystals, grown by slow cooling from saturated CH<sub>3</sub>CN solutions, were determined by elemental analysis, x-ray analysis, and electron microprobe, and found to be homogeneous. Four-probe dc conductivity measurements as a function of temperature and powder x-ray measurements of the unit cell constants were carried out over the entire solid solution range.

While organic semiconducting charge-transfer salts have been known for some time,<sup>1</sup> the metallic state in an organic solid has only recently been discovered with the preparation of tetrathiafulvalene-tetracyano-*p*-quinodimethane (TTF-TCNQ, 1-2).<sup>2,3</sup> TTF-TCNQ has been the subject of intense physical study and numerous new metal-like derivatives have been prepared.<sup>4-7</sup>

The origin of high conductivity in TTF-TCNQ derives from its segregated donor and acceptor stacked structure<sup>8</sup> (see Figure 1) and from incomplete charge-transfer which occurs between donor and acceptor stacks.<sup>4,9,10</sup> The quasi-one-dimensional structure of TTF-TCNQ makes this material prone to lattice distortions<sup>4,11</sup> (e.g., the Peierls instability) and at low

temperature TTF-TCNQ undergoes at least two phase transitions<sup>12</sup> (53 and 38 K) which convert it into an insulator.

Attempts to correlate how modifications of the molecular constituents affect the metallic state in TTF-TCNQ are complicated by unpredictable changes that can occur in the crystal structure. Not only does one have to evaluate changes due to electronic perturbations on making a molecular modification, but also changes due to solid-state structural alterations. With the synthesis of the selenium analogues of TTF (e.g., tetraselenafulvalene<sup>13</sup> (TSeF, 3) and diselenadithiafulvalene<sup>14</sup> (DSeDTF, 4)),<sup>15</sup> electronic properties were perturbed<sup>16</sup> while still maintaining essentially the same steric requirements of the original TTF-TCNQ crystal structure.