where $\bar{\mu}$ is the electric dipole operator.

The tensor components of the susceptibility, or frequency-dependent hyperpolarizability, for sum frequency generation is defined by the relation[29]

$$p_i^{(2)}\ (\omega_1 + \omega_2; -\omega_1, -\omega_2) = \chi_{ijk}^{(2)}\ (\omega_1 + \omega_2; -\omega_1, -\omega_2)\ {}^1E_{j-}{}^2E_{k-} \equiv \beta_{ijk}{}^1E_j{}^2E_k \quad \text{(A1.2)}$$

$p_i^{(2)}$ is the component of induced polarization in direction i due to the field components in directions j and k, respectively. In accordance, the tensor expressions appearing in the text are defined in such a manner that the first index always refers to the component of polarization, the second and third index to the field components one and two, respectively. We notice that the first two expressions in (A1.1), in which two-photon resonances may occur, will tend to make the predominant contribution in the wavelength range of interest.

Appendix 2

The susceptibility for the electric field-induced sum frequency generation, in particular second harmonic generation (EFISH), is a fourth rank tensor. The actual third-order electronic effect

$$\chi^{(3)}(\omega_1 + \omega_2; 0, -\omega_1, -\omega_2) \equiv \gamma_e$$

is in general very small. The temperature-dependent effect due to anisotropic averaging

$$\chi^{(3)}(\omega_1 + \omega_2; 0, -\omega_1, -\omega_2; kT) \equiv \gamma_r$$

depends on the molecular dipole moment μ_0 and the second-order hyperpolarizability $\chi^{(2)} \equiv \beta$.[30,31,61] Using the expression A2 of ref 62 allows one to easily deduce the relevant averaged quantity. If the polarization of both incident beams is parallel to the static field, one finds to first order in $(kT)^{-1}$

$$\bar{\gamma}_r = \frac{1}{5kT}[\mu_{0x}\beta_{xxx} + \mu_{0y}\beta_{yyy} + \mu_{0z}\beta_{zzz} + {}^1\!/_3\{\mu_{0x}(\beta_{xyy} + \beta_{yxy} + \beta_{yyx} + \beta_{xzz} + \beta_{zxz} + \beta_{zzx}) + \mu_{0y}(\beta_{yxx} + \beta_{xyx} + \beta_{xxy} + \beta_{yzz} + \beta_{zyz} + \beta_{zzy}) + \mu_{0z}(\beta_{zxx} + \beta_{xzx} + \beta_{xxz} + \beta_{zyy} + \beta_{yzy} + \beta_{yyz})\}] \equiv \frac{1}{5kT}\,\bar{\mu}_0\bar{\beta} = \frac{1}{5kT}\,\mu_0\bar{\beta}; \qquad \mu_0 = |\bar{\mu}_0| \quad \text{(A2.1)}$$

μ_0 is by definition always positive; μ_{0x}, μ_{0y}, and μ_{0z} are the components of the dipole moment of the molecule (unit cell) with respect to the molecule-fixed (unit cell-fixed) axes and may, according to the choice of axes, be positive or negative. If one chooses the y-axis, say, to be parallel to the dipole moment, expression A2.1 reduces to[16]

$$\bar{\gamma}_r = \frac{1}{5kT}\mu_0\{\beta_{yyy} + {}^1\!/_3(\beta_{yxx} + 2\beta_{xxy} + \beta_{yzz} + 2\beta_{zzy})\} \quad \text{(A2.2)}$$

Use has been made here of the trivial indentity for SHG, that $B_{xyx} = \beta_{xxy}$ and $\beta_{zyz} = \beta_{zzy}$. If Kleinman's symmetry rule[63] is additionally fulfilled (which in general is not, or very approximately, the case), expression A2.2 becomes

$$\bar{\gamma}_r = \frac{1}{5kT}\mu_0(\beta_{yyy} + \beta_{yxx} + \beta_{yzz}) \quad \text{(A2.3)}$$

In the absence of z-polarized transitions, such as in many of our examples, the terms β_{yzz}, β_{zzy} evidently vanish.

Registry No. 1, 57-13-6; **2**, 62-53-3; **3**, 98-95-3; **4**, 100-01-6; **5**, 99-09-2; **6**, 88-74-4; **7**, 97-02-9; **8**, 610-41-3; 9, 108-96-3; **10**, 58064-43-0; **11**, 142-08-5; **12**, 4629-58-7; **13**, 103367-99-3.

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The Stabilization of α-Substituted Methyl Cations by First- and Second-Row Substituents

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Abstract: In this paper we report the results obtained in an ab initio SCF–MO study at an extended computational level on the effects of first- and second-row substituents upon the stabilities of α-substituted carbocations. Accurate stabilization energies have been computed for the various species, and in each case we have decomposed the stabilization energy values into the following component terms: (i) the σ-effects; (ii) the nonbonded interaction effects; (iii) the d-orbital effects; and (iv) the correlation energy effects. We have found that in the comparison along a column the differences between the stabilization energies are small with the only exception of the pair NH_2, PH_2 where additional effects associated with the planarization of the XH_2 group must be considered. Futhermore, it has been found that the differences between the stabilization energies along a row are more pronounced and that the trend is determined by the π-donation effects.

(I) Introduction

The effect of first- and second-row substituents upon the stabilities of α-substituted carbocations is a chemical problem of significant interest. In fact carbocations play an important role in chemical synthesis as well as in physical organic chemistry.[1] First-row substituents (in particular OR) are known to stabilize an adjacent carbocationic center more than the second-row analogue[2] (in particular SR). For instance, chloromethyl ethyl ether hydrolyzes in aqueous dioxane about 1600 times faster than chloromethyl sulfide.[3] The reaction was assumed in both cases

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to proceed via a carbonium ion intermediate by a unimolecular mechanism.

These trends have been rationalized for many years on the basis of the assumption[4] that a first-row substituent (e.g., F or OR) is a better π-electron donor than the corresponding second-row substituent (e.g., Cl or SR), and because of this greater π-donating ability the first-row heteroatom stabilizes the adjacent cationic center more than the corresponding second-row analogue. However, in recent ab initio investigations[5] it was found that a second-row substituent is a better π-electron donor and stabilizes more an adjacent carbocationic center than the corresponding first-row substituent. Furthermore, these explanations do not rationalize the difference in the solution- and gas-phase trends.[6] It has, in fact, been observed that the trend of the effect of the substituents reverses in the gas phase. Therefore, the understanding of this problem is still limited.

In this paper we report the results obtained in an ab initio SCF–MO study at an extended level, where we have analyzed the effect of first- and second-row substituents upon the stabilities of a series of α-substituted methyl cations $H_2{}^+C–X$, with X = NH_2, OH, F, PH_2, SH, Cl. In all cases we have computed accurate stabilization energies. Then we have decomposed the stabilization energies into the component terms associated with the various types of effects that can be assumed to play a certain role in the stabilization process. These are (i) σ-effects, (ii) the nonbonded interaction effects, (iii) the d-orbital effects, and (iv) the correlation energy effects.

All the component terms associated with the various types of effects have been computed in terms of SCF–MO total energy values. The contributions associated with the σ and the nonbonded interaction effects have been computed by using total energy values obtained in the absence of the interactions under examination (total energy approach), while those associated with the d-orbital and correlation energy effects have been determined by using total energy values obtained with and without the d-orbitals in the basis set or the correlation energy corrections.

(II) Computational Methods

All the computations reported in this paper have been performed with the GAUSSIAN 80 series of programs[7] appropriately implemented for the evaluation of the total energy in the absence of nonbonded interactions.[8]

In addition to the series of α-substituted methyl cations mentioned above, the related series of $H_3C–X$ neutral molecules has also been considered.

The geometries of all the α-substituted methyl cations have been fully optimized with the gradient method at the 3-21G[9a] level, while in the case of second-row substituents, optimum geometries have been determined also with the 3-21G*[9b] basis set. For the neutral molecules we have used geometries similarly optimized.[10]

Chart I

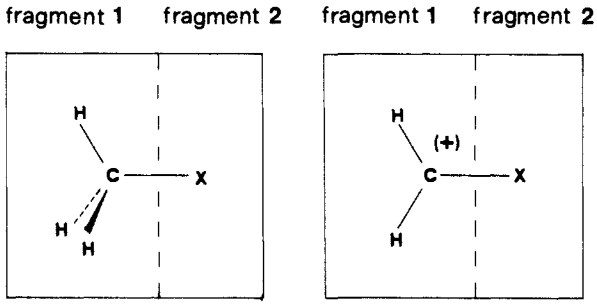
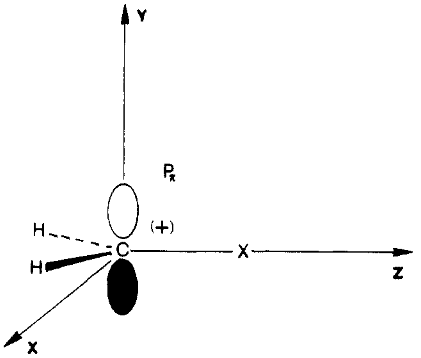


Chart II



For both $H_2{}^+C–X$ and $H_3C–X$ species single-point SCF–MO calculations have been performed at the 6-31G[11a] level with use of the 3-21G optimized geometries. Similar computations have also been carried out at the 6-31G*[11b] level without and with second-order Møller–Plesset (MP2) correlation energy corrections.[12] The geometries used in this case have been those obtained with the 3-21G basis set in the case of first-row substituents and those obtained with the 3-21G* basis set in the case of second-row substituents.

In order to compare the effect of a first-row vs. the corresponding second-row substituent upon the stability of the α-substituted carbocation $H_2{}^+C–X$, we have computed the various stabilization energies (SE) on the basis of the following equation[13]

$$SE = [E_T(H_3C–X) + E_T(H_3{}^+C)] - [E_T(H_2{}^+C–X) + E_T(CH_4)] \quad (1)$$

where E_T represents the total energy values obtained from the SCF–MO computations.

Equation 1 allows us to compare the stabilizing effect of the X substituent upon the cationic center with respect to H, more precisely a positive value of SE indicates that a given substituent is more stabilizing than H and a negative value less stabilizing than H.

In addition to the computations of the E_T values we have also carried out calculations of the total energies in the absence of the nonbonded interactions occurring between the component fragments of the molecular system under examination ($E_T{}^0$).

In the present study the two fragments are, in the case of the neutral molecules, the X substituent and the H_3C-methyl group, and in the case of the α-substituted cations, the X substitutent and the $H_2{}^+C$ group (see Chart I).

In order to perform the computations of $E_T{}^0$ we have first defined, for every molecular system, an appropriate basis representation of fragment molecular orbitals. The fragment orbitals we have chosen here are the localized fragment orbitals which have been obtained with the procedure described in ref 8b and 14. Thus for a H_3C group, within a minimal basis set scheme, we have (i) three doubly occupied orbitals σ_{CH} associated with the three C–H bonds and bonding between C and H, (ii) a singly occupied hybrid orbital σ_C pointing toward the X fragment, and (iii) three empty orbitals σ^*_{CH} associated with the three C–H bonds, but antibonding between C and H.

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Table I. Total Energies (au) of Substituted Methanes $H_3C{-}X$ and Related Methyl Cations $H_2{}^+C{-}X$ Computed at the 6-31G, 6-31G*, and MP2/6-31G* Levels

	$H_3C{-}X$			$H_2{}^+C{-}X$		
X	6-31G	6-31G*	MP2/6-31G*	6-31G	6-31G*	MP2/6-31G*
H	−40.18055	−40.19517	−40.33242	−39.21621	−39.23064	−39.32511
NH_2	−95.17024	−95.20843	−95.50459	−94.34748	−94.38307	−94.65871
PH_2	−381.42310	−381.48622	−381.73192	−380.52081	−380.58791	−380.82522
OH	−114.98760	−115.03321	−115.34542	−114.09624	−114.15437	−114.44262
SH	−437.64753	−437.70038	−437.96286	−436.73513	−436.80704	−437.05726
F	−138.99412	−139.03338	−139.33543	−138.02946	−138.09142	−138.36811
Cl	−499.05634	−499.09287	−499.36377	−498.09154	−498.14991	−498.40382

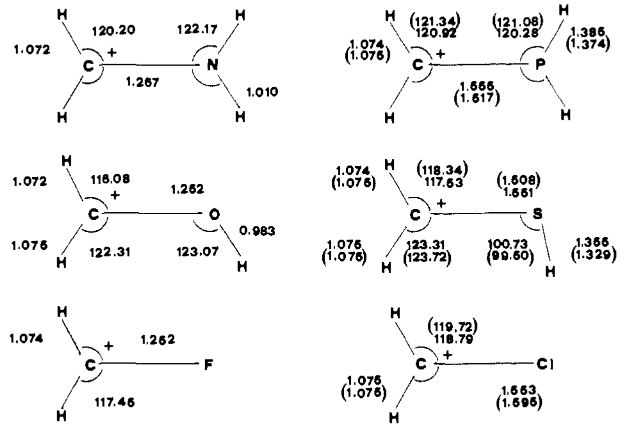

Figure 1. Geometrical parameters for the various α-substituted methyl cations computed at the 3-21G and 3-21G* (values in bracket) computational level.

In the case of a H_2C^+ group, the corresponding set of localized orbitals is formed by (i) two double occupied σ_{CH} orbitals, (ii) a singly occupied hybrid orbital σ_C analogous to that found for H_3C, (iii) an empty $2p_\pi$ orbital orthogonal to the HCH plane (see Chart II), and (iv) two empty σ^*_{CH} orbitals.

The situtation is slightly more complicated within an extended basis set scheme like that employed in this paper. At this level in fact, because of the introduction of polarization type functions in the atomic basis set, there are additional empty orbitals of higher energy with respect to those previously described.

The localized orbitals of the H_3C group are depicted in detail in ref 14b together with those of the X fragment where X = NH_2, PH_2, OH, SH. A representation of the orbitals when X = F or Cl can be found in ref 14a.

The availability of quantitative expressions for the fragment localized orbitals now makes it possible to compute the total energy of a system in the absence of the orbital interactions under examination. To this purpose we transform the Fock matrix of the composite system in the localized representation, we set to zero all the matrix elements between the orbitals of interest belonging to different fragments, and we diagonalize the resulting new matrix. In a second stage we evaluate the density matrix $\mathbf{R}^0$ from the canonical MOs obtained from the previous diagonalization, and we compute the total energy value on the basis of the following expression

$$E_T{}^0 = \mathrm{Tr}\ [(\mathbf{h}^0 + \mathbf{H}^0)\mathbf{R}^0] \qquad (2)$$

where all the matrices are defined in the localized representation. In particular $\mathbf{H}^0$ is the new Fock matrix obtained from $\mathbf{R}^0$, and $\mathbf{h}^0$ is the one-electron hamiltonian matrix.

(III) Results and Discussion

The computed geometrical parameters of the various α-substituted methyl cations are summarized in Figure 1 and those of the related substituted methanes in Figure 2, while the corresponding total energy values are given in Table I, the values of the C–X distances in Table II, and the stabilization energies in Table III.

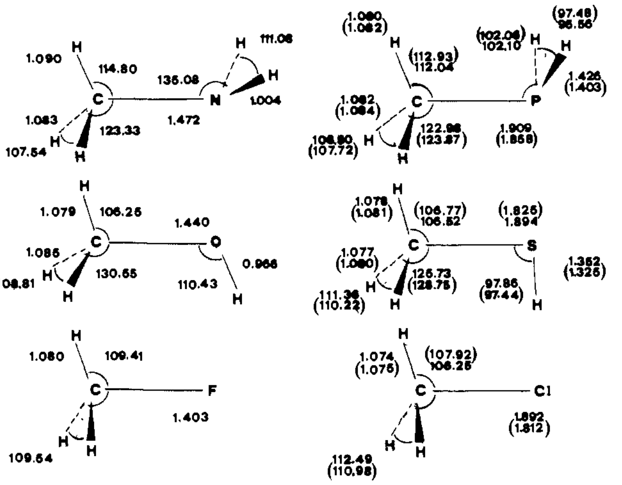

Figure 2. Geometrical parameters for the various substituted methanes computed at the 3-21G and 3-21G* (values in brackets) computational level.

Table II. Optimized C–X Bond Lengths (Å) of Substituted Methanes and Related Methyl Cations and Corresponding Bond Length Differences (ΔR)[a] Obtained at the 3-21G and 3-21G* Levels

	$CH_3{-}X$		$^+CH_2{-}X$		ΔR	
X	3-21G	3-21G*	3-21G	3-21G*	3-21G	3-21G*
NH_2	1.4716		1.2673		0.2043	
PH_2	1.9093	1.8576	1.6558	1.6166	0.2535	0.2409
OH	1.4402		1.2516		0.1886	
SH	1.8940	1.8254	1.6606	1.6078	0.2334	0.2176
F	1.4035		1.2619		0.1416	
Cl	1.8919	1.8116	1.6626	1.5946	0.2293	0.2172

[a] The term ΔR is defined, for a given computational level, as the difference between the C–X bond length value in the substituted methane and that in the corresponding α-substituted cation.

Table III. Substituent Stabilization Energies SE (kcal/mol) of α-Substituted Methyl Cations Computed at the 6-31G, 6-31G*, and MP2/6-31G* Levels

	$H_2{}^+C{-}X$			
X	6-31G	6-31G*	MP2/6-31G*	exptl[a]
H	0	0	0	0
NH_2	88.84	87.33	101.30	95
PH_2	38.94	41.55	63.13	–
OH	45.79	53.77	65.58	60
SH	32.59	44.67	63.82	64
F	−0.20	14.16	25.09	26
Cl	−0.29	13.53	29.72	32

[a] See ref 15.

The analysis of the computed geometries shows that with these substituents, i.e., substituents with π-type lone pairs, the removal of a hydride ion from the methyl group of the neutral species to form the corresponding cation is accompanied in all cases by a planarization of the molecule and by a significant shortening of

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Table IV. Contributions to the Stabilization Energies SE (kcal/mol) of Methyl Cations Associated with the σ, Nonbonded Interactions (NB), the d-Orbital (d), and the Correlation Energy (CE) Effects

X	SE(σ)	SE(NB)	SE(d)	SE(CE)	SE
NH_2	36.44	52.4	−1.51	13.97	101.30
PH_2	−56.22	95.16	2.61	21.50	63.13
OH	33.93	11.86	7.98	11.81	65.58
SH	6.97	25.62	12.14	19.09	63.82
F	−31.87	31.67	14.36	10.93	25.09
Cl	−31.12	30.83	13.83	16.19	29.72

Table V. Total Energies E_T (au) of Substituted Methanes (H_3C–X) and Related Methyl Cations ($H_2{}^+C$–X) Computed at the 6-31G Level in the Absence of the π Interactions ($E_T{}^{0'}$) and in the absence of the Nonbonded Interactions ($E_T{}^0$)

	H_3C–X	$H_2{}^+C$–X	
X	$E_T{}^0$	$E_T{}^{0'}$	$E_T{}^0$
NH_2	−95.529 17	−94.217 61	−94.622 90
PH_2	−381.696 28	−380.368 82	−380.642 35
OH	−115.260 34	−113.998 92	−114.350 07
SH	−437.828 15	−436.634 27	−436.874 92
F	−139.100 49	−137.970 35	−138.085 36
Cl	−499.102 39	−498.029 96	−498.088 46

the C–X bond length, as it is shown by the trends of the C–X values in Table II. It can be observed that the shortening is always larger for a second-row substituent than for the corresponding first-row analogue and along a row it increases with the decrease of the electronegativity.

The analysis of the stabilization energies shows that the values computed at the most accurate level, i.e., MP2/6-31G*, agree very well in all cases with the stabilization energies experimentally estimated. All these substituents have a stabilizing effect (positive SE), and in particular it is found that NH_2 has a larger stabilizing effect than PH_2, OH and SH have similar stabilizing effects, while F has a slightly smaller stabilizing effect than Cl. It is also found that the stabilization energy increases along a row with the decrease of the electronegativity.

The main purpose of this investigation is to rationalize the trends of the stabilization energies. To obtain a detailed understanding of this problem we have decomposed the SE values into the components associated with (i) σ-effects, (ii) nonbonded interaction effects, (iii) d-orbital effects, and (iv) correlation energy effects. The values of these components are listed in Table IV.

The components associated with the d-orbital and correlation energy effects have been obtained by using the SE values computed at the 6-31G, 6-31G*, and MP2/6-31G* levels (see Table III), while the components associated with the σ and the nonbonded interaction effects have been computed by using the $E_T{}^0$ and $E_T{}^{0'}$ values, which are listed in Table V; $E_T{}^{0'}$ has been computed with the same procedure used for $E_T{}^0$ and represents the total energy of a system in the absence of the π-interactions only.

We proceed now to discuss in detail the trends of the various components.

(i) σ **Effects.** The energy components of SE associated with the σ-effects have been computed by using eq 1 where the E_T values for the species H_3C–X and $H_2{}^+C$–X have been replaced by the corresponding $E_T{}^0$ values. The resulting SE(σ) values, listed in Table IV, show that this component is stabilizing when X = NH_2, OH, SH and destabilizing when X = PH_2, F, Cl.

Furthermore, it can be seen that this component favors NH_2 over PH_2 and OH over SH, while the values for F and Cl are of similar order of magnitude.

To understand these trends, it is convenient to decompose further the SE(σ) values into two energy contributions, one associated with the variation of the σ inductive effect which accompanies the transformation from H_3C–X to $H_2{}^+C$–X and the other with the variation of the C–X bond energy which accompanies the shortening of the C–X bond. Information about the inductive effect has been obtained by computing the SE(σ) values for the cations at the C–X bond distance of the corresponding monosubstituted methanes. In all cases this contribution is found to be largely destabilizing and of similar order of magnitude for each pair. Therefore, the important term in all cases is the contribution associated with the C–X bond energy variations which is always stabilizing.

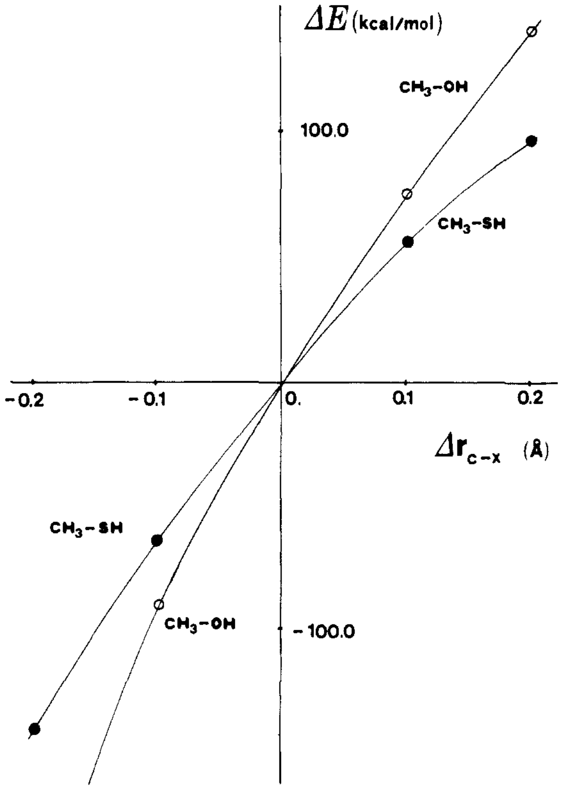

Figure 3. Trend of the variation of total energy computed in the absence of the nonbonded interactions ($E_T{}^0$) vs. the variation of the C–X bond distance for the pair H_3C–OH, H_3C–SH.

Information about the behavior of this energy contribution has been obtained by computing the $E_T{}^0$ values for the H_3C–X molecules at various values of the C–X bond length. The results for the pair OH,SH are shown in Figure 3, and similar results have been obtained for the other pairs of substituents. The abscissa of Figure 3 represents the difference $\Delta[r_{C-X} - r_{C-X}{}^0]$ where r_{C-X} denotes a given C–X bond length and $r_{C-X}{}^0$ the optimum C–X distance of the H_3C–X species, while the ordinates represent the difference $\Delta[E_T{}^0(r_{C-X}) - E_T{}^0(r_{C-X}{}^0)]$ between the $E_T{}^0$ values computed at r_{C-X} and at $r_{C-X}{}^0$. It can be seen that a decrease of the C–O and C–S bond lengths from the corresponding reference values $r_{C-X}{}^0$ is accompanied by a stabilization, while an increase is accompanied by a destabilization. Furthermore, for the same decrease the stabilizing effect is larger for the first-row substituent, while for the same increase the destabilizing effect is again larger for the first-row substituent, and the preferential stabilization or destabilization associated with first-row substituents increases with the increase of the C–X bond length variation. These trends can be explained on the basis of the fact that the orbital of the substituent X involved in the C–X bond is more contracted when X is a first-row substituent.

In the α-methyl cations under examination the shortening of the C–X bond length is always larger when X is a second-row substituent. The difference (see Table II) is small for the pairs NH_2, PH_2 and OH, SH and significantly larger for the pair F, Cl. Thus for the pairs NH_2, PH_2 and OH, SH the C–X bond energy variation remains larger for the first-row substituent and consequently the SE(σ) values favor NH_2 over PH_2 and OH over SH. On the other hand, for the pair F, Cl, the C–X bond energy variations become of similar order of magnitude and the SE(σ) values for F and Cl are almost identical.

The C–X bond energy variation determines the sign of SE(σ) for X = NH_2, OH, SH, while for F and Cl it is the inductive contribution that prevails. Also the SE(σ) value of PH_2 is negative, but in this case the sign is determined mainly by the additional

Table VI. Energy Effects $(E_T - E_T^0)^a$ Associated with the Nonbonded Interactions[b]

	H_3C–X	H_2^+C–X		
X	$E_T - E_T^0$	$E_T - E_T^0$	$E_T - E_T^{0'}$	$E_T^{0'} - E_T^0$
NH_2	225.23	172.83	−81.50	254.32
PH_2	171.42	76.26	−95.38	171.64
OH	171.14	159.28	−61.07	220.35
SH	113.34	87.72	−63.29	151.01
F	66.74	35.07	−37.09	72.17
Cl	28.90	−1.93	−38.64	36.71

[a] Values in kcal/mol.[b] [b] In the case of cations the overall effect is decomposed into a repulsive contribution $(E_T^{0'} - E_T^0)^a$ and a π-donation contribution $(E_T - E_T^{0'})$.[a]

destabilizing contribution associated with the planarization of the PH_2 fragment.

(ii) Nonbonded Interaction Effects. In each case the energy component of SE associated with the nonbonded interactions, denoted here as SE(NB), has been computed as the difference between the energy effects of the nonbonded interactions in the H_3C–X and related H_2^+C–X species. For each molecular species, the energy effect associated with the nonbonded interactions has been computed as the difference $E_T - E_T^0$, so that SE(NB) is given by the following expression

$$\mathrm{SE(NB)} = (E_T - E_T^0)_{H_3CX} - (E_T - E_T^0)_{H_2^+CX} \qquad (3)$$

The resulting SE(NB) values, which are listed in Table IV, are all positive and large. This component favors PH_2 over NH_2 and SH over OH and has similar values for F and Cl and therefore exhibits a trend opposite to that of the SE(σ) component.

To understand these trends it is convenient to analyze the trends of the $E_T - E_T^0$ values, i.e., the energy effects associated with the nonbonded interactions. In all neutral molecules this effect is always destabilizing, while in the cations it is again destabilizing in all cases except when X = Cl where this effect becomes very slightly stabilizing. Furthermore, in all cases this effect is more destabilizing in the neutral molecule than in the corresponding cation. While the $E_T - E_T^0$ values of the neutral species are almost exclusively determined by repulsive effects, those of the cations are determined by repulsive effects as well as by the π-donation effects. Thus to assess the relative importance of these terms, we have further decomposed the $E_T - E_T^0$ value of the cations into two contributions, one associated with the repulsive effects $(E_T^{0'} - E_T^0)$ and the other with the π-donation effect $(E_T - E_T^{0'})$. These values are all listed in Table VI. On the basis of this decomposition it is possible to express SE(NB) in the following way

$$\mathrm{SE(NB)} = [(E_T - E_T^0)_{H_3CX} - (E_T^{0'} - E_T^0)_{H_2^+CX}] - (E_T - E_T^{0'})_{H_2^+CX} \qquad (4)$$

where the term in the square brackets represents the contribution associated with the variation of the repulsive effects and the other that associated with the π-donation effect.

The comparative analysis of the values $(E_T - E_T^0)_{H_3CX}$ and $(E_T^{0'} - E_T^0)_{H_2^+CX}$ shows that in all cases in passing from the substituted methane to the corresponding α-methyl cation there is a significant increase of the repulsive effects, so that the related contribution to SE(NB) is large. This contribution is larger for NH_2 (29.09 kcal/mol) than for PH_2 (0.22 kcal/mol), for OH (49.21 kcal/mol) than for SH (37.67 kcal/mol), and for Cl (7.81 kcal/mol) than for F (5.43 kcal/mol).

The trends of the stabilizing contributions associated with the π-donation effect (see the $(E_T - E_T^{0'})$ values in Table VI) agree with the results of previous investigations.[5] In all cases the π-orbital interaction between the heteroatom lone pair and the LUMO of the H_2^+C fragment is controlled by the variation of the energy gap. Thus this interaction favors the second-row substituent as the heteroatom is changed along a column and the less electronegative substituent as the heteroatom is changed along a row.

From this analysis it follows that for the pairs NH_2, PH_2 and OH, SH both contributions concur to determine the trend of SE(NB), while for the pair F, Cl, where the two contributions favor one F and the other Cl, the trend of SE(NB) is determined by the variation of the repulsive effects.

(iii) d-Orbitals and Correlation Energy Effects. The energy components of SE associated with the 3d-orbital and the correlation energy effects have been computed according to the following expressions

$$\mathrm{SE(3d)} = SE(\text{6-31G*}) - \mathrm{SE(6\text{-}31G)} \qquad (5)$$

$$\mathrm{SE(CE)} = \mathrm{SE(MP2/6\text{-}31G^*)} - \mathrm{SE(6\text{-}31G^*)} \qquad (6)$$

The resulting values are listed in Table IV. Both these types of energy components can be considered as polarization effects, in one case arising specifically from the low-lying d-orbitals and in the other case from the low-lying excited states involving, in addition to the d-orbitals, also other types of low-lying empty orbitals such as σ^*_{C-X} and σ^*_{X-H}. The two types of values are of similar order of magnitude and quite large. The only exception is the d-orbital contribution in the case of the pair NH_2, PH_2, which is small.

We can see that the correlation energy component favors in all cases the second-row substituent, while the 3d-orbitals component favors the second-row substituent for the two pairs NH_2, PH_2 and OH, SH and slightly the first-row substituent for the pair F, Cl.

This behavior is roughly in agreement with the trend of polarizabilities of the atoms X and of the bonds C–X which are much larger when X is a second-row heteroatom. In the case of the d-orbital effect the preference varies from ~4 kcal/mol for the pairs NH_2, PH_2 and OH, SH to ~0.5 kcal/mol for the pair F, Cl, while in the case of the correlation energy effects the preference is almost constant (~5–7 kcal/mol).

(IV) Conclusions

In this paper we have attempted to rationalize the trends of the stabilization energies of a series of α-subtituted methyl cations with substitutents belonging either to the first or the second row. We have first computed accurate values of the stabilization energies at the MP2/6-31G* level. Then we have decomposed the stabilization energies into the component terms associated with the σ-effects, nonbonded interaction effects, and polarization effects. All these components have been computed in terms of total energy values.

The analysis of the various components has shown that all the various terms are large and have to be considered explicity. Furthermore, to obtain reliable estimates of these components, one has to compute the proper energy differences between the values of the substituted methanes and the related cations and not consider only the energy effects of the cations.

In a comparison along a column, it appears that the differences between the stabilization energies are small. In this case, in fact, the σ-effects favor NH_2 over PH_2 and OH over SH and are almost identical for F and Cl, while the nonbonded interactions and the polarization effects show the opposite trend: for each pair the preference in the two cases is of similar order of magnitude, so that the overall preference is small. The only exception is the pair NH_2, PH_2 where the stabilization energy of NH_2 is significantly larger than that of PH_2. However, in this case the preference is due to an additional effect specific of this type of substituent, i.e., the planarization of the XH_2 group, which favors largely NH_2 over PH_2, as suggested by the values of the inversion barriers of NH_3 (5.80 kcal/mol)[16a] and PH_3 (37.2 kcal/mol).[16b]

The differences between the stabilization energies along a row are more pronounced. In this case the trend is determined by the π-donation effect, which changes significantly along a row favoring the less electronegative substituent. The exception is again represented by PH_2, where we have to take into account also the additional destabilizing contribution of the planarization energy which makes the SE value of PH_2 smaller than that of SH, even if the π-donation effect has an opposite trend.

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The analysis has shown that the small differences between the stabilization energies along a column arise from large cancellations of effects of similar order of magnitude. We should also point out that the values of the various components depend critically on the geometry of the cation. Solvation will certainly change the geometry of the cation, and thus also the values of the various components, so that also the overall preference might change. Thus it can be expected that solvation might change the trend of the SE values along a column, while along a row the change is less likely.

Registry No. $H_2^+CNH_2$, 54088-53-8; H_2^+COH, 17691-31-5; H_2^+CF, 35310-31-7; $H_2^+CPH_2$, 84005-10-7; H_2^+CSH, 20879-50-9; H_2^+CCl, 59000-00-9.

Ab Initio Molecular Orbital Study of the CH_3N^{2+} Potential Energy Surface†

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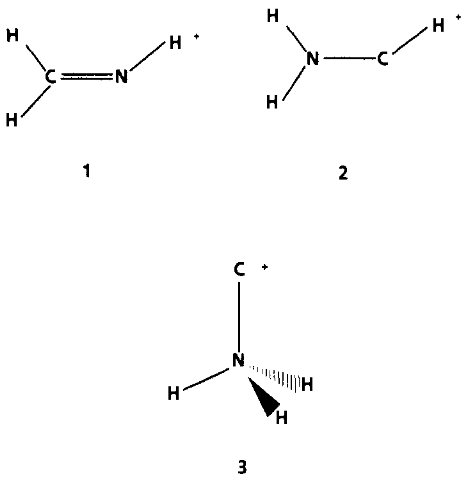
Abstract: High level MP4/6-311G(d,p)//6-31G(d)+ZPVE ab initio MO calculations predict two stable CH_3N^{2+} isomers; the global minimum corresponds to the aminomethylene dication, H_2NCH^{2+} (**5**), which at the highest level of theory is predicted to be 49 kcal/mol more stable than H_3NC^{2+} (**6**), which can be viewed as a donor/acceptor molecule. Both isomerization and dissociation pathways were studied, and the two isomers are prevented by significant barriers from isomerization as well as dissociation (charge separation). Vertical and adiabatic ionization energies for removing an electron from the corresponding, as yet unknown, monocations are estimated as are the heats of formation of the resulting dictations. For **5**, $\Delta H_f°$ is estimated to 644 kcal/mol, and for **6** a value of 700 kcal/mol has been obtained.

The remarkable chemistry and physics of multiply charged, gaseous cations is of considerable interest to both experimentalists and theoreticians.[1] Salient features of the dications which can be conveniently generated from monocations in the gas phase by charge stripping (CS) mass spectrometry[2] are the following ones: (1) reversal of stability order of dicationic isomers when compared with their mono-charged or neutral counterparts; (ii) significant structural changes which often favor anti-van't Hoff geometries for the dications;[3] and (iii) highly exothermic charge separation reactions which in the gas phase, however, are prevented by significant barriers to occur spontaneously. Thus, observation of the intrinsically thermochemically unstable dications is feasible, while in solution proton transfer to the solvent shell or transfer of negatively charged species to the dication will take place with avidity thus making it unlikely to generate under these conditions *small* organic dications as viable species. Larger organic dications or species which are stabilized intramolecularly can, of course, be generated as stable systems in solution.[4]

High-level ab initio molecular orbital (MO) calculations play a decisive role in the description and characterization of the species of interest in that they not only allow comparison of theoretically predicted and experimentally evaluated ionization energies but also provide information on the energetics of the ions, their electronic structures and their isomerization/dissociation characteristics.

While the potential energy surface of the $CH_3N^{\bullet+}$ system, which is believed to play an important role in the interstellar production of organic molecules,[5] is now quite well understood,[6] to the best of our knowledge no high-level ab initio MO calculations have been reported on the corresponding dicationic CH_3N^{2+} system, which is the subject of the present paper. For the monocations the aminomethylene cation (**2**) is predicted to be 8.8 kcal/mol (MP2/6-31G(d)//4-31G) more stable than the methyleneimine radical cation (**1**) (Chart I). A high-energy barrier (57 kcal/mol (MP2/6-31G(d)//4-31G)) for the reaction **1** → **2** largely prevents the two ions from isomerizing prior to the microsecond fragmentation. A third isomer **3**, which was not included in the earlier publications,[6] is calculated to lie 60.5 kcal/mol (MP4/6-311G-

Chart I



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† Dedicated to Professor Edgar Heilbronner, Basel, on the occasion of his 65th birthday.

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