and the diene **3** to predict the difference, ΔEA, between the E_A's of ethylene and the monoene **2**. This procedure yields $x = 0.27$ eV and $y = 0.14$ eV, or $x - y = +0.13$ eV, in agreement with experiment. The σ'^*,π^* and σ',π^* interactions are significantly smaller than the σ,π interactions in the same systems on account of the large energy gap between the $\pi^* - \pi^*$ MO and the σ' MO and the relatively poor overlap between the $\pi^* + \pi^*$ MO and the σ'^* MO.

The present study indicates two salient features of π^*-OITB: (1) these interactions result from the mixing of the $\pi^* \pm \pi^*$ symmetry-adapted orbitals with both σ and σ^* frontier MO's, with the latter predominating (i.e., $x > y$); (2) the net splitting in the π^* manifolds is nearly the same as in the π manifolds. This follows because the $\pi^* \pm \pi^*$ combinations are shifted in *opposite* directions through mixing with the σ and σ^* MO's, while the $\pi \pm \pi$ combinations are shifted in the *same* direction through mixing with the occupied σ orbitals.

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Registry No. 2, 1076-12-6; **3**, 83602-18-0; **4**, 36012-52-9; **5**, 15914-93-9; **6**, 15914-94-0; **7**, 1076-12-6; **8**, 1076-13-7; norbornene, 498-66-8.

Diprotonated Methane, CH_6^{2+}, and Diprotonated Ethane, $C_2H_8^{2+}$

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The stabilization of the *pentacoordinate* CH_5^+ ion[1] finds its origin in the interaction of the electron-deficient carbon with two ligands (three center, two electron (3c-2e)). The size of this effect is reflected in the heat of hydrogenation of CH_3^+, experimentally deduced as 40 kcal/mol[2a] and calculated as 34.5 kcal/mol by ab initio molecular orbital theory (MP3/6-31G** + ZPE).[2b] The 3c-2e stabilization is a common phenomenon in larger systems, like the norbornyl cation,[3] although its magnitude reduces as illustrated by the heats of hydrogenation of $C_2H_5^+$ (11.8 kcal/mol) and $C_3H_7^+$ (2.3 kcal/mol).[2a]

The concept of hypercoordination of electron-deficient species can also be applied to dications. From our ab initio theoretical[4] studies on small carbocations, the prototypes of new unprecedented types of hypercoordinate ions emerged, i.e., diprotonated methane, CH_6^{2+}, and diprotonated ethane, $C_2H_8^{2+}$. In the context of pentacoordinate carbon stabilization we also restudied the ethane dication, $C_2H_6^{2+}$.

Table I. Total (hartrees) and Relative Energies (kcal/mol) Using the 6-31G** Basis and HF/6-31G* Geometries and Zero-Point Energies (kcal/mol)

geometry	HF	MP3	zero point
1, C_{2v}	−40.30397 (0)	−40.49674 (0)	37.9
2, C_{2v}	−40.29730 (4.2)	−40.49264 (2.6)	35.8
3, C_2	−79.45620 (0)	−79.80097 (0)	58.1[a]
4, D_{4d}	−79.44122 (9.4)	−79.79618 (3.0)	55.8[a]
7, C_{2v}	−78.27287 (5.9)	−78.56410 (3.5)	43.2[a]
8, C_s	−78.28234 (0)	−78.56969 (0)	44.4[a]
5, D_{2d}	−77.09538	−77.32626	30.1[a]

[a] Zero-point vibrational energy obtained with the 3-21G basis.

Scheme I

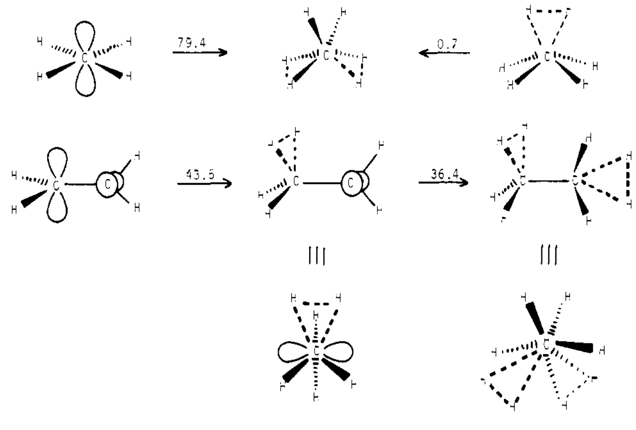
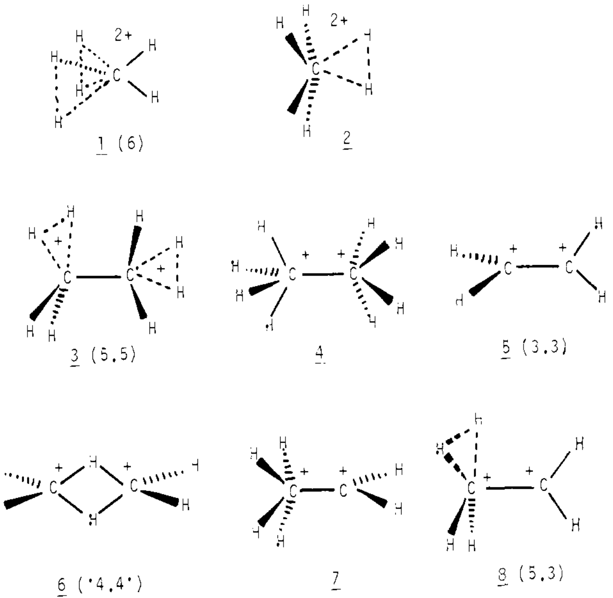


Chart I



In order to describe these hypercoordinate species, we have used single-point calculations with the flexible 6-31G** basis set, which has polarization functions on both hydrogen and carbon, for geometries optimized within the Hartree–Fock limit at the 6-31G* (d functions) level.[5] Furthermore, at this level we have included electron correlation corrections with the Møller–Plesset perturbation theory[6,7] to the third order with frozen core (MP3/6-

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31G**) for all data and used these throughout the text (see Table I). All species reported are considered to be equilibrium structures, since the force-constant matrix obtained from the 6-31G* (CH_6^{2+}) and 3-21G[5] ($C_2H_4^{2+}$, $C_2H_6^{2+}$, and $C_2H_8^{2+}$) optimized geometries have no negative eigenvalues, except **2**, which has one. The zero-point vibrational energies deduced from these force constants (see Table I) are after scaling[8] included as our final adjustment in all subsequent reaction energies given at the MP3/6-31G** level (Scheme I).

The methane dication, CH_4^{2+}, is trivalent and tetracoordinate with a planar (D_{4h} symmetry) geometry.[9] Interaction of molecular hydrogen with the empty p_z orbital of CH_4^{2+} results in CH_6^{2+}. Diprotonated methane is *hexacoordinate*. The minimum-energy equilibrium structure **1** (Chart I) calculated for CH_6^{2+} (see Table I) has two orthogonal 3c-2e interactions (C_{2v} symmetry), emphasizing the importance of this effect. The structure **2** with only one such interaction may be regarded as the transition for transfer of one 3c-2e interaction in **1** and is 2.6 kcal/mol higher in energy. The stabilization of **1** gained with respect to CH_4^{2+} amounts to 79.4 kcal/mol. Intuitively one expects carbodications to be highly unstable because of electrostatic repulsion. Indeed CH_6^{2+} has a high exothermicity of 63.1 kcal/mol for proton loss and of 126.8 kcal/mol toward dissociation to CH_3^+ and H_3^+. However, our studies indicate a barrier of 40 kcal/mol (MP3/6-31G**) for the deprotonation and suggest even more for loss of H_3^+. Since CH^{2+}, CH_2^{2+}, CH_3^{2+}, and CH_4^{2+} have already been reported in a gas-phase study,[10] CH_6^{2+} may be also a viable species. The calculated heat of formation of 651 ± 3 kcal/mol is actually the lowest of the C_1 dications.

In diprotonated ethane, $C_2H_8^{2+}$, *each carbon is pentacoordinate.* We may regard $C_2H_8^{2+}$ as hydrogenated ethane dication, $C_2H_6^{2+}$ (see later). Even better, $C_2H_8^{2+}$ can be considered as doubly hydrogenated ethylene dication, $C_2H_4^{2+}$, with each of the orthogonal vacant p_z orbitals in strong interaction with a hydrogen molecule. This view is confirmed through the calculations. For the equilibrium structure with minimum energy we find C_2 symmetry (**3**) with the two 3c-2e interactions at about a 90° dihedral angle. The Newman projection (Scheme I) shows that complexation of the two hydrogen molecules only slightly distorts the perpendicular ethylene dication skeleton **5** (D_{2d} symmetry). At the 6-31G** level **3** is 9.4 (HF) and 3.0 (MP3) kcal/mol more stable than the second equilibrium structure **4** (D_{4d} symmetry) and therefore underlines the importance of 3c-2e interactions. The heat of hydrogenation of $C_2H_4^{2+}$ to give diprotonated ethane is 79.8 kcal/mol. The most likely dissociation of $C_2H_8^{2+}$ is toward CH_5^+ and CH_3^+ and is exothermic by 100.1 kcal/mol. A significant barrier for dissociation is expected, however, because of the distinct reorganization of atoms needed in the transition state.

We reported recently[11] the structure of the ethane dication as the doubly bridged, diborane-like dication **6** (D_{2d} symmetry). Schleyer et al.[12] subsequently found the carbenium–carbonium structure **7** (C_{2v} symmetry) to be 9.0 kcal/mol more stable (MP4SDQ/6-31G**//6-31G*). The preference of **7** was explained by the reduced electrostatic repulsion for the hydrogens lying farther apart and the stronger C–C bonding through hyperconjugation.[12] Structure **7** has a *tri- and a tetravalent* carbon with *tri- and pentacoordination*, respectively. In the context of the present concept one might formulate $C_2H_6^{2+}$ as hydrogenated $C_2H_4^{2+}$. Complexation of molecular hydrogen with a vacant orbital on one of the carbons of the ethylene dication **5** is then expected to result in the carbenium–carbonium dication $C_2H_6^{2+}$, with the carbonium center involved in a 3c-2e interaction as in **8** (C_s symmetry). This is indeed confirmed by our calculations on a reinvestigation of $C_2H_6^{2+}$. The equilibrium structure **8** is 3.5 kcal/mol (MP3/6-31G**) more stable than **7**, reported by Schleyer et al.[12] (see Table I). The Newman projection of **8** shows the orthogonality of the 3c-2e interaction and the vacant p orbital and also suggests a somewhat larger hyperconjugation as in **7**. The hydrogenation of the ethylene dication **5** is exothermic by 43.5 kcal/mol. The kinetic stability of $C_2H_4^{2+}$ combined with the reported barrier for dissociation of $C_2H_6^{2+}$,[12] now adjusted for **8**, of 30 kcal/mol may render the ethane dication feasible for experimental observation.

The calculations further suggest that all three hypercoordinate dications, CH_6^{2+}, $C_2H_8^{2+}$, and $C_2H_6^{2+}$, with coordination numbers 6, 5-5, and 5-3, respectively, may be viable species. A possible route to experimental observation could be via hydrogenation of the appropriate carbodication precursors, obtained by the mass spectroscopic charge-stripping technique in the presence of hydrogen in the neutral gas.

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Registry No. CH_6^{2+}, 83561-00-6; $C_2H_8^{2+}$, 83561-01-7; CH_4^{2+}, 34557-54-5; $C_2H_4^{2+}$, 54509-73-8.

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Bimolecular Substitution at Carbon in Neopentyl-Like Silylcarbinyl Sulfonates

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There is considerable current synthetic and mechanistic interest in silicon chemistry. It has been reasonably well established that carbocations are stabilized by β-silicon substitution and largely by implication that they are destabilized by α-silicon substitution.[1,2] For example, no detectable reaction of $(CH_3)_3SiCH_2X$ (X = Br, Cl) was observed in aqueous solvents at 70 °C.[3] Furthermore, $PhCMe(SiMe_3)Br$ reacts slower than $PhC(CH_3)_2Br$, as does $(CH_3)_3SiC(CH_3)_2Br$ compared to $(CH_3)_3CC(CH_3)_2Br$.[4]

The effect of silicon substitution at the reaction center on a bimolecular displacement at carbon is even less well understood. Thus, while $(CH_3)_3SiCH_2Br$ reacts 2600 times more rapidly with ethoxide in ethanol than does $(CH_3)_3CCH_2Br$,[5] $(CH_3)_3SiCH_2Cl$ reacts slower than CH_3CH_2Cl with I^- in aqueous ethanol and faster than CH_3CH_2Cl with I^- in acetone.[3]

The solvolysis reaction of neopentyl-X compounds proceeds with considerable k_Δ character in many solvents, resulting in

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