mation, B(S···O), computed by the definition of Mayer.

As far as the structural changes in the X—S—A=B—Y(Z)=O system were concerned we have established the following pattern: (i) Substitution in X enhances the "strength of the S···O interaction in the following order: F > OH > $NH_2 \simeq$ SH > CH_3. (ii) Changes at position **B** influence the "strength of interaction" in the order HC(sp^2) < N(sp^2). It is quite likely that changes at position A will respond analogously. (iii) Changes at the O=Y—Z moiety influence the "strength of interaction" in the order OCH > ONO. The position of the nitroso group ($O\ddot{N}/$) in that order is hard to establish since rotation about the B–Y bond changes a 1,5 S···O interaction to a 1,4 S···N interaction or visa versa.

We have shown that, in addition to electrostatic forces, changes in the Mayer bond index (covalent interactions) are associated with formation of short S···O close contacts. The proper description of these covalent interactions, as measured by the Mayer bond order index, cannot be achieved without the inclusion of sulfur d orbitals.

Finally, the strongest S···O interactions may be regarded as "premature" hypervalent bonds similar to those found in certain nonsymmetric dioxysulfurane derivatives.

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Supplementary Material Available: Tables including the optimized geometries at STO-3G, 3-21G, and 3-21G+ levels and total energies and structures **2–5** (15 pages). Ordering information is given on any current masthead page.

The Ethyl Dication ($CH_3CH_2^{\cdot 2+}$): Classical (Open) or Nonclassical (Bridged)?

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Abstract: Ab initio molecular orbital theory using basis sets up to 6-311G** and with electron correlation incorporated at the fourth-order Møller–Plesset level has been used to examine the ethyl radical (**1**), cation (**2**), and dication (**3**). Previously demonstrated preferences for an open (or classical) structure (**1a**) for the ethyl radical and for a bridged (or nonclassical) structure (**2c**) for the ethyl cation have been confirmed. This trend is reversed, however, in the ethyl dication, which returns to a preference for an open structure (**3a**). The ethyl dication is characterized by a short C–C bond (1.433 Å), quite long β C–H bonds (1.121, 1.202 Å), and facile interconversion between staggered (**3a**) and eclipsed (**3b**) conformations. It lies in a moderately deep potential well, being separated from highly exothermic fragmentation to $CH_2^{\cdot +}$ + CH_3^+ and to $C_2H_4^{\cdot +}$ + H^+ by barriers of more than 100 kJ mol^{-1}. The calculated difference (0.5 eV) between vertical and adiabatic ionization energies of the ethyl radical agrees well with a value (0.41 eV) derived from recent experimental data. Our calculated ionization energy for the process $C_2H_5^+ \rightarrow C_2H_5^{\cdot 2+}$ (19.7 eV) is reasonably close to a recent experimental value (19.1 eV).

The ethyl cation has been the subject of considerable recent attention as a prototype for the comparison of classical (open) and nonclassical (bridged) species.[1] There is now substantial theoretical[2] and experimental[3] evidence that the preferred structure of the ethyl cation is bridged rather than open. This contrasts with the situation for the ethyl radical, which has a preferred open structure.[4] Indeed, the experimental observation of a significant difference between vertical and adiabatic ionization energies for the ethyl radical has been taken as evidence for the qualitative difference in structure between the radical (open) and cation (bridged).[3] We present here theoretical evidence that removal of an additional electron, leading to the ethyl dication, reverses the change produced by the initial ionization, returning to a preference for an open isomer. The implications regarding vertical and adiabatic ionization processes that yield the ethyl dication are discussed.

Method and Results

Standard ab initio molecular orbital calculations were carried out with modified versions[5,6] of the Gaussian 80[7] and Gaussian 82[8] series of programs. Optimized geometries were obtained with the 6-31G* basis set[9] at both Hartree–Fock (HF) and second-order Møller–Plesset (MP2)[10] levels of theory using gradient techniques.[11] Unless otherwise noted, it is the latter values which are quoted in the text. Improved relative energies were obtained through calculations with the 6-311G** basis set[12] and with

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Table I. Calculated Total Energies (hartrees) and Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1}) for Open (**a**, **b**) and Bridged (**c**) Structures of the Ethyl Radical (**1**), Cation (**2**), and Dication (**3**) and Related Species[a]

structure	state	Ni^b	HF/6-31G*[c]	$\langle S^2\rangle^d$	MP2/6-31G*	MP4/6-31G*	HF/6-311G**	MP2/6-311G**	ZPVE[e]
1a	$^2A'$	0	−78.597 15	0.76	−78.835 60	−78.872 41	−78.619 54	−78.902 95	166.3
1b	$^2A''$	1	−78.596 87	0.76	−78.835 35	−78.872 19	−78.619 29	−78.902 70	164.7
1c	$^2B_2$	1	−78.505 31	0.79	−78.757 87	−78.794 58	−78.532 56	−78.831 36	155.1
2a	$^1A'$	0	−78.311 23	0	*f*	*f*	*f*	*f*	169.2
2b	$^1A'$	1	−78.310 21	0	−78.542 19	−78.579 61	−78.331 42	−78.600 67	168.5
2c	$^1A_1$	0	−78.309 94	0	−78.552 31	−78.588 40	−78.334 43	−78.613 36	170.8
1a^{+g}	$^1A'$			0	−78.533 93	−78.571 83	−78.326 51	−78.592 18	
3a	$^2A''$	1	−77.620 30	0.76	−77.824 06	−77.861 36	−77.647 08	−77.878 33	142.3
3b	$^2A'$	0^h	−77.621 05	0.76	−77.825 28	−77.862 53	−77.645 92	−77.878 31	141.8
3c	^2A	1^h	−77.589 98	0.77	−77.811 17	−77.848 74	−77.613 68	−77.867 44	141.7
3c′	$^2A_1$	1	−77.585 85	0.76	−77.793 37	−77.832 04	−77.615 89	−77.851 82	148.8
3c″	$^2A_2$	2	−77.562 97	0.77	−77.810 80	−77.845 23	−77.592 20	−77.865 89	145.3[i]
1a^{2+j}	$^2A''$			0.76	−77.780 81	−77.819 09	−77.600 24	−77.831 94	
2c^{+k}	$^2A_2$			0.77	−77.782 77	−77.817 27	−77.560 77	−77.838 14	
3d	$^2A'$	1	−77.580 20	0.77	−77.769 05	−77.809 62	−77.611 77	−77.825 50	143.6
$CH_2^{\bullet +}$	$^2A_1$	0	−38.566 19	0.75	−38.635 37	−38.653 50	−38.566 04	−38.635 37	46.8
CH_3^+	$^1A_1'$	0	−39.230 64	0	−39.325 38	−39.346 18	−39.243 56	−39.356 18	88.5
$C_2H_4^{\bullet +}$	$^2B_{3u}$	0	−77.712 33	0.75	−77.917 70	−77.952 47	−77.731 59	−77.966 00	139.5
$C_2H_4^{2+}$	$^1A_1$	0	−77.086 70	0	−77.273 17	−77.309 69	−77.106 53	−77.315 55	128.4
$H^\bullet$	^2S		−0.498 23	0.75	−0.498 23	−0.498 23	−0.499 81	−0.499 81	0

[a] Based on MP2/6-31G* geometries, unless otherwise noted. [b] Number of imaginary frequencies (6-31G*//6-31G* unless otherwise noted). [c] Based on HF/6-31G* geometries. [d] Expectation value of S^2 from 6-31G* wave function. [e] 6-31G*//6-31G* values. [f] Collapses to **2c** upon optimization at the MP2/6-31G* level. [g] Structure arising from vertical ionization of **1a**. [h] Confirmed at the MP2/6-31G*//MP2/6-31G* level. [i] Taken as the mean of the ZPVEs for **3c** and **3c′** due to difficulties encountered in the calculation of the vibrational frequencies for **3c″** itself. [j] Structure arising from vertical double ionization of **1a**. [k] Structure arising from vertical ionization of **2c**.

Table II. Calculated Relative Energies (kJ mol^{-1}) for Open (**a**, **b**) and Bridged (**c**) Structures of the Ethyl Radical (**1**), Cation (**2**), and Dication (**3**) and of the Transition Structure (**3d**) and Products for Fragmentation of the Dication[a]

structure	HF/6-31G*	MP2/6-31G*	MP4/6-31G*	HF/6-311G**	MP2/6-311G**	MP4/ 6-311G**[b]	MP4/ 6-311G**[c]
1a	0	0	0	0	0	0	0
1b	0.7	0.7	0.6	0.7	0.7	0.6	−0.9
1c	241	204	204	228	188	188	178
2c	0	0	0	0	0	0	0
2b	−0.7	27	23	8	33	30	32
1a$^+$		48	44	21	56	51	51[d]
3a	0	0	0	0	0	0	0
3b	−2.0	−3.2	−3.1	3.1	0.1	0.2	−0.3
3c	80	34	33	88	29	28	27
3c′	91	81	77	82	70	66	72
3c″	151	35	42	144	33	40	43
1a^{2+}		114	111	123	122	119	119[e]
2c$^+$		108	116	227	106	113	113[e]
3d	105	144	136	93	139	130	131
$CH_2^{\bullet +} + CH_3^+$	−464	−359	−351	−427	−297	−290	−283
$C_2H_4^{\bullet +} + H^+$	−242	−246	−239	−222	−230	−224	−221
$C_2H_4^{2+} + H^\bullet$	93	138	140	107	165	167	154

[a] Calculated with total energies from Table I. [b] MP4/6-311G** value calculated with eq 1. [c] MP4/6-311G** value together with zero-point vibrational contribution. [d] Zero-point energy assumed to be the same as in **2c**. [e] Zero-point energy assumed to be the same as in **3a**.

electron correlation incorporated at the full fourth-order Møller–Plesset level.[13] Spin-unrestricted calculations were used throughout for open-shell systems. Harmonic vibrational frequencies were calculated at the 6-31G*//6-31G* level in order to characterize stationary points as minima (representing equilibrium structures) or saddle points (representing transition structures) and to provide zero-point vibrational corrections to relative energies. The directly calculated frequencies were scaled by 0.9 for the latter purpose.[14] Our best relative energies correspond to MP4/6-311G**//MP2/6-31G* values, evaluated with use of the additivity approximation[15]

$$\Delta E(\text{MP4/6-311G**}) \approx \Delta E(\text{MP4/6-31G*}) + \Delta E(\text{MP2/6-311G**}) - \Delta E(\text{MP2/6-31G*}) \quad (1)$$

together with zero-point vibrational contributions. Structures **a**, **b**, and **c** of the ethyl radical (**1**), cation (**2**), and dication (**3**) were examined in this manner and the results are shown in Figure 1 (optimized structures) and Tables I (total energies) and II (relative energies). Some of the information for the radical and cation has been reported previously[2,16] but is included here for ease of comparison.

Additional calculations were carried out to investigate specific points. Thus, the three bridged structures (**1c**, **2c**, **3c′**) were optimized with the 6-31G** basis set[9] to see whether *p* polarization functions on hydrogen have a significant effect on the calculated geometries. The results (Figure 2) show that the effect is small and provide some justification for our use of MP2/6-31G* geometries as the basis for energy comparisons.

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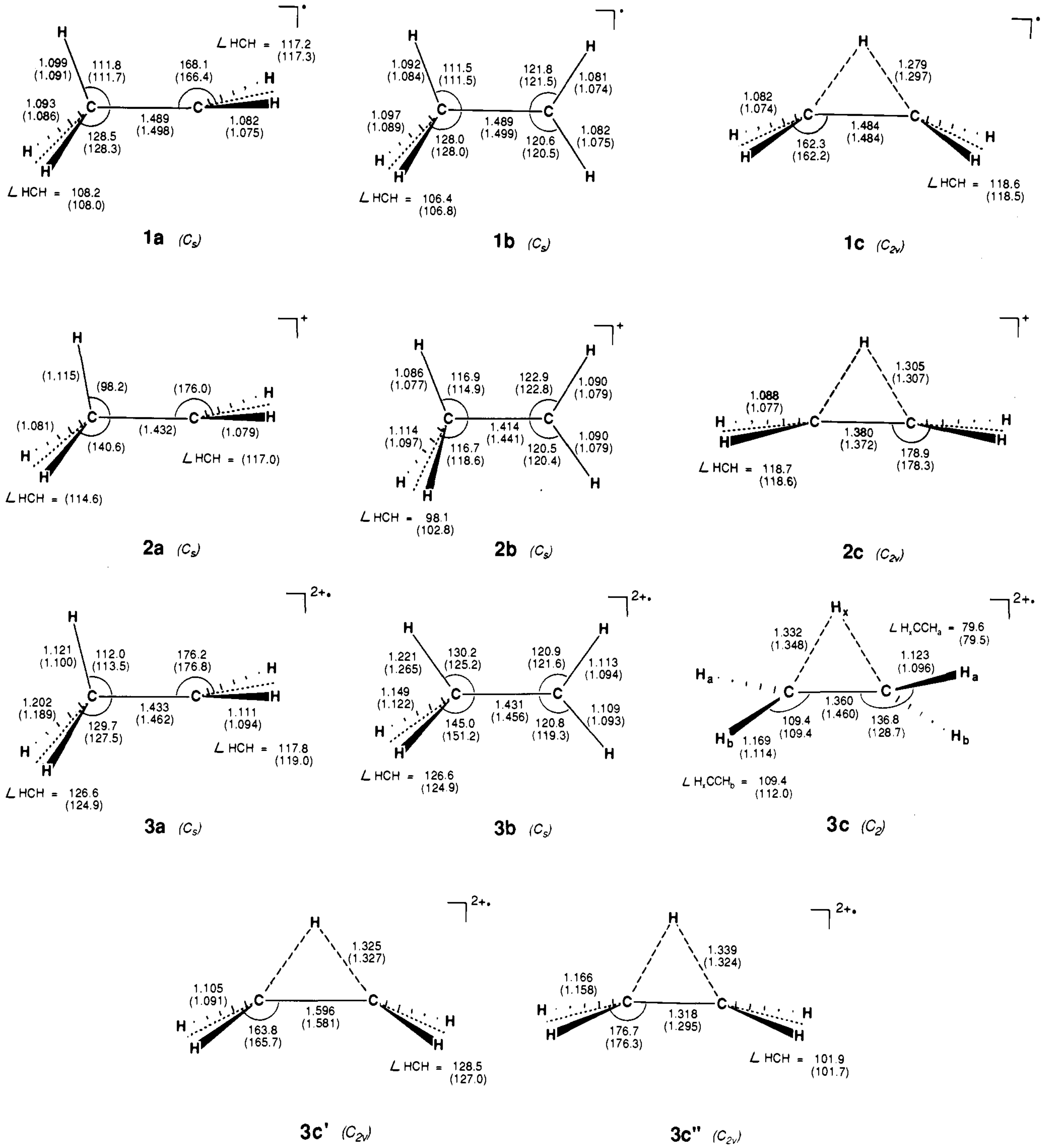


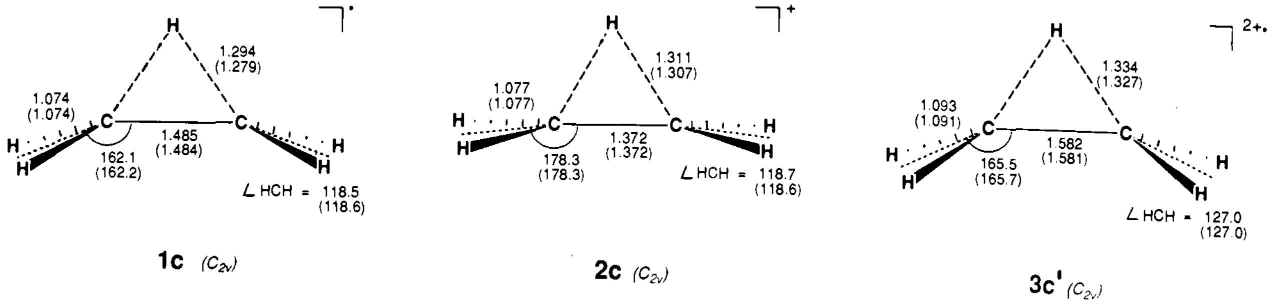
1a (C_s) 1b (C_s) 1c (C_{2v})

2a (C_s) 2b (C_s) 2c (C_{2v})

3a (C_s) 3b (C_s) 3c (C_2)

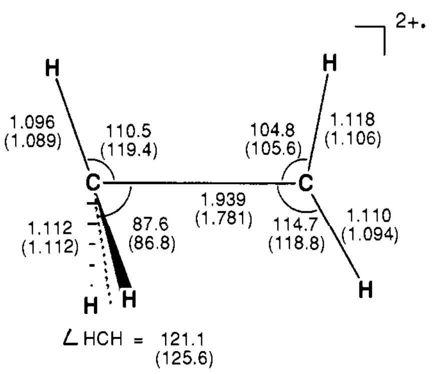
3c' (C_{2v}) 3c" (C_{2v})

Figure 1. Optimized geometries (MP2/6-31G* with HF/6-31G* values in parentheses) for open (**a**, **b**) and bridged (**c**) structures of the ethyl radical (**1**), cation (**2**), and dication (**3**).



1c (C_{2v}) 2c (C_{2v}) 3c' (C_{2v})

Figure 2. Optimized geometries (HF/6-31G** with HF/6-31G* values in parentheses) for bridged structures (**c**) of the ethyl radical (**1**), cation (**2**), and dication (**3**).



3d (C_s)

Figure 3. Optimized geometry (MP2/6-31G* with HF/6-31G* values in parentheses) for the transition structure (**3d**) for fragmentation of the ethyl dication (**3a**) to $CH_3^+ + CH_2^{\bullet+}$.

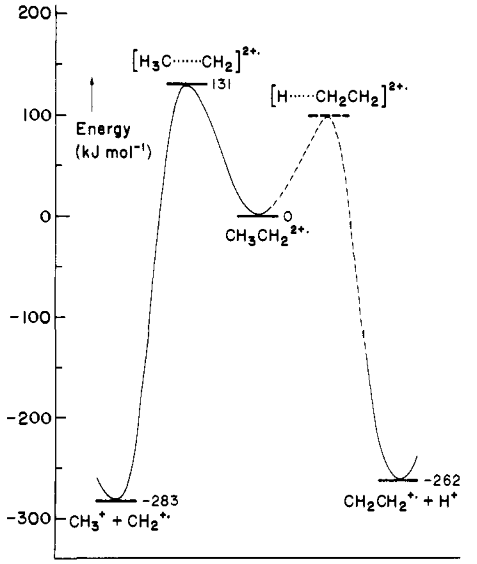


Figure 4. Schematic potential energy profile for fragmentation of the ethyl dication (**3a**).

Calculations were also carried out for possible fragmentation products of the ethyl dication ($CH_3^+ + CH_2^{\bullet+}$, $C_2H_4^{\bullet+} + H^+$) and for the transition structures (**3d**, **3e**) for such fragmentation. Optimized geometries are displayed in Figure 3 while calculated energies are included in Tables I and II. Figure 4 shows a schematic potential energy profile for the fragmentation pathways of the ethyl dication.

Finally, vertical (IE_v) and adiabatic (IE_a) ionization energies were calculated for the various ionization processes connecting $C_2H_5^\bullet$, $C_2H_5^+$, and $C_2H_5^{\bullet 2+}$. These were obtained as differences in calculated total energies. In addition, IE_v values were determined for the ionization process $C_2H_5^+ \rightarrow C_2H_5^{\bullet 2+}$ by using the equations-of-motion (EOM) procedure[17] and the MOLECULE,[18] EPSCF,[19] and EOM[20] program packages. A partial third-order approach[21] was employed, and all noncore occupied orbitals and the lowest 30 virtual orbitals were included in the EOM calculations. Such an approach has been previously found to be successful in the calculation of ionization energies.[22] Relevant results are shown in Table III and Figure 5.

Table III. Calculated Ionization Energies (eV) for Processes Involving the Ethyl Radical, Cation, and Dication

process	IE_a	IE_v	EOM[a]	exptl[b]
$C_2H_5^\bullet \rightarrow C_2H_5^+$	7.9	8.4[c]		8.1[d]
$C_2H_5^+ \rightarrow C_2H_5^{\bullet 2+}$	19.7	20.8[e]	21.5	19.1
$C_2H_5^\bullet \rightarrow C_2H_5^{\bullet 2+}$	27.6	28.9[e]		

[a] Vertical ionization energy calculated with the EOM procedure. [b] See text. [c] ZPVE for **1a**$^+$ assumed to be the same as for **2c**. [d] IE_a. [e] ZPVE for **2c**$^+$ and **1a**$^{2+}$ assumed to be the same as for **3a**.

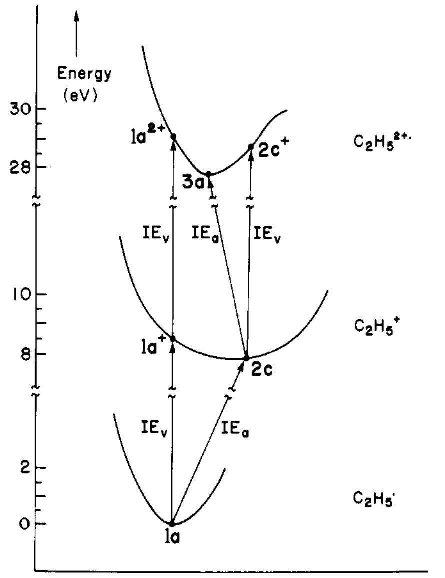


Figure 5. Schematic potential energy diagram showing ionization processes involving the ethyl radical (**1a**), cation (**2c**), and dication (**3a**).

Discussion

Ethyl Radical (1). Consistent with previous calculations,[4,23] the equilibrium structure of the ethyl radical is found to be the open, staggered form (**1a**, Figure 1). After inclusion of zero-point vibrational effects, the open eclipsed structure (**1b**) drops slightly below **1a** in energy (Tables I and II), suggesting that internal rotation about the C–C bond should occur relatively freely. The bridged structure (**1c**), while having very reasonable C–C and bridging C- - -H bond lengths (1.484 and 1.279 Å, respectively, with MP2/6-31G*), has a very high energy, 178 kJ mol⁻¹ above **1a**. An energy difference of 194 kJ mol⁻¹ was found[4] in a previous study based on a generalized-valence-bond approach with partial geometry optimization. Clearly, the ethyl radical has a strong preference for an open (or classical) structure over a bridged structure.

Ethyl Cation (2). The ethyl cation has been the subject of extensive previous theoretical studies,[2,24] and it is sufficient here to summarize the main findings. The open staggered structure (**2a**), although a local minimum at the HF/6-31G* level, collapses at MP2/6-31G* to the bridged structure **2c**. The open eclipsed structure (**2b**) remains a minimum, provided C_s symmetry is maintained, but when this constraint is relaxed it too collapses to **2c**. The bridged (or nonclassical) structure (**2c**) is, in fact, the only minimum found on the $C_2H_5^+$ potential surface. Thus, in this case, there is a preference for a bridged over an open structure.

Our calculated energies for **1a** and **2c** allow the adiabatic ionization energy of the ethyl radical to be evaluated. The calculated IE_a of 7.9 eV (Table III) is somewhat lower than ex-

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perimental values of 8.39 and 8.25 eV reported in photoelectron studies,[3a,c] a point which will be addressed further below. The vertical ionization energy can also be obtained from our calculations, as the difference in energy of **1a** and the ion resulting from vertical ionization (represented as **1a**$^+$ in Tables I and II). In this case, the calculated value (8.4 eV) is reasonably close to the experimental IE_v[3a,c] of 8.51 eV.

The difference between IE_a and IE_v, as determined by photoelectron spectroscopy (0.12 eV,[3a] 0.26 eV[3c]), is somewhat less than our present best estimate (0.5 eV). Other experimental work[3b,c] also suggests that the photoelectron values[3a,c] may be too small. It is possible that the Franck–Condon factors for transitions from the open form of the ethyl radical (**1a**) to the bridged form of the ethyl cation (**2c**) are sufficiently small that the adiabatic ionization was not observed in the photoelectron experiments.[3a,c] An alternative estimate of the experimental adiabatic ionization energy may be obtained from a photoion-photoelectron coincidence (PIPECO) determination[3b] of $\Delta H_f{}^\circ{}_{298}$ for the ethyl cation (901 ± 4 kJ mol^{-1}) and a very recent and precise determination[25] of $\Delta H_f{}^\circ{}_{298}$ for the ethyl radical (119 ± 2 kJ mol^{-1}). This leads to an IE_a value of 8.10 eV and a difference in IE_v and IE_a of 0.41 eV which is now in satisfactory agreement with our theoretical value of 0.5 eV.

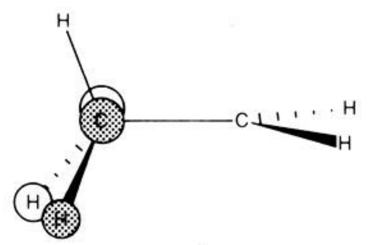
Ethyl Dication (3). Having confirmed the preferred open structure for the ethyl radical (**1a**) and the preferred bridged structure for the ethyl cation (**2c**), we now come to the ethyl dication. Is its preferred structure open or bridged?

We note first that the energies of the two open structures (**3a** and **3b**) lie close together and the preference for one or the other changes with different levels of theory and with incorporation of zero-point vibrational energy (Table II). At our highest level, the equilibrium structure is **3a** but the difference in energy between **3a** and **3b** is not significant. Internal rotation about the C–C bond is clearly a facile process.

We have considered a number of possibilities (**3c**, **3c′**, and **3c″**) for the bridged structure of the ethyl dication. All of these lie significantly higher in energy than the open structures **3a** and **3b**. Thus, the preference for a bridged (or nonclassical) structure in the ethyl monocation is reversed in the dication which prefers an open structure.[26] Observation of a preferred open structure for the ethyl dication is consistent with the preference for an open structure for the ethane dication, a result attributed to minimizing electrostatic repulsion between the positive charges which lie mainly on the hydrogen atoms.[27]

Under C_{2v} symmetry, $^2A_1$ and $^2A_2$ states are possible for the bridged dication and the optimized structures (**3c′** and **3c″**) have one and two imaginary frequencies, respectively. Examination of the imaginary frequencies indicates that, in both cases, a distortion to C_2 symmetry should lead to a lowering in energy. This is indeed found to be the case: optimization from either **3c′** or **3c″** under C_2 symmetry leads to **3c** which is the preferred bridged structure and represents the true transition structure for 1,2-hydrogen migration in **3a** or **3b**. Our best estimate of the barrier for this process is 27 kJ mol^{-1}.

There are interesting structural features for the ethyl dication (Figure 1) that warrant discussion. These may be readily understood by considering the effect of ionization on the structure of the appropriate monocation. For example, the open staggered dication (**3a**) can be considered formally to arise through ionization from the 2a″ orbital (**4**) of the monocation. This orbital, which is concentrated in the out-of-plane β C–H bonds, is C–H bonding but H- - -H antibonding. Ionization from it leads to a lengthening of the out-of-plane β C–H bonds (to 1.202 Å) but a shortening of the H- - -H distance (to 1.453 Å). For **3b**, on the other hand, ionization occurs from the 7a′ orbital (**5**) which is concentrated in the in-plane β C–H bond. As a result, this bond lengthens to 1.221 Å. Because of the bonding relationship between the out-of-plane hydrogens in **5**, the HCH angle widens (to 126.6°) on ionization to give **3b**. For the $^2A_1$ bridged structure (**3c′**), ionization occurs from the $4a_1$ orbital (**6**) which is concentrated in the three-center bridging CCH region. The main consequence of ionization in this case is the lengthening of the C–C bond which, at 1.596 Å, is even longer than a normal single bond. For the $^2A_2$ bridged structure (**3c″**), ionization occurs from the $1a_2$ orbital (**7**) which is antibonding with respect to C–C and bonding with respect to the C–H bonds. The results are quite striking: a short C–C bond of 1.318 Å, long C–H bonds of 1.166 Å, and a narrow HCH angle of 101.9°.



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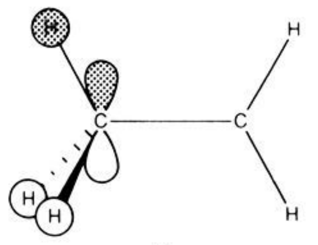

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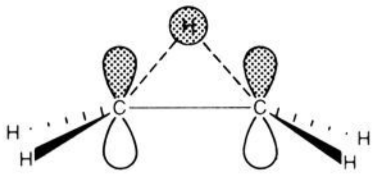

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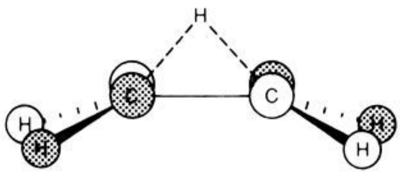

7

The stability of the ethyl dication with respect to unimolecular decomposition depends on the magnitude of the barriers separating this species from fragmentation products. Two of these fragmentation processes are highly exothermic: by 283 kJ mol^{-1} for the production of $CH_2{}^{\bullet +} + CH_3{}^+$ and by 221 kJ mol^{-1} for the production of $C_2H_4{}^{\bullet +} + H^+$. However, the barriers to such fragmentation are sufficient to ensure that the ethyl dication is observable (cf. Figure 4). Thus, decomposition to $CH_2{}^{\bullet +} + CH_3{}^+$ via the transition structure **3d** requires 131 kJ mol^{-1}. Determination of the transition structure for decomposition to $C_2H_4{}^{\bullet +} + H^+$ through single-configuration calculations presented difficulties, and we are planning to carry out multi-configuration calculations to examine this process. However, the results which we have obtained to date suggest a barrier comparable to that for the decomposition to $CH_2{}^{\bullet +} + CH_3{}^+$ and certainly greater than 100 kJ mol^{-1}.

The only experimental information available for the ethyl dication comes from charge-stripping mass spectrometry experiments.[28] These yield Q_{min} values, corresponding to the ionization process $C_2H_5{}^+ \rightarrow C_2H_5{}^{\bullet 2+}$, of 19.1 ± 0.5 eV. This is slightly lower than our best estimated IE_a (19.7 eV) and somewhat further below our calculated IE_v values (20.8 and 21.5 eV, Table III). A low experimental Q_{min} value could arise, in principle, if the monocations were not in their vibrational ground state. There appear to be increasing indications[29] that the charge-stripping process may be accompanied by structural changes and that the Q_{min} values may therefore not represent vertical ionization energies as originally believed. Our results are consistent with this point of view in that the experimental Q_{min} is closer to the calculated IE_a than to the IE_v.

Examination of Figure 5 shows that vertical ionization of the ethyl cation (**2c**) produces the ethyl dication (**2c**$^+$) with consid-

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(26) An interesting alternative structure, $CH_4CH^{\bullet 2+}$, of $C_2H_5{}^{\bullet 2+}$ is found (Schleyer, P. v. R., unpublished data) to lie considerably higher in energy than the structures examined here. We thank Professor Schleyer for bringing this result to our attention.

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erable excess energy. However, it lies below the lowest fragmentation barrier, consistent with its experimental observation via charge stripping. A striking additional result is that double ionization of the ethyl radical also produces an ethyl dication (**1a**$^{2+}$) which lies below the lowest fragmentation barrier. It should therefore be possible to produce the ethyl dication from the ethyl radical in the source of a mass spectrometer. This contrasts with the situation for molecules such as methane for which double ionization in the source does not lead to a stable dication but for which production of the dication can be achieved through charge stripping of the methane monocation.[29a-c,30]

Concluding Remarks

Several important points emerge from this study.

(i) In contrast to the ethyl cation, which has a bridged (or nonclassical) structure, the ethyl dication has an open (or classical) structure, returning in a qualitative sense to the preference found in the ethyl radical.

(ii) The ethyl dication lies in a moderately deep potential well, being prevented by barriers of more than 100 kJ mol^{-1} from undergoing highly exothermic fragmentation reactions to $CH_2^{\bullet+}$ + CH_3^+ and $C_2H_4^{\bullet+}$ + H^+.

(iii) The various forms of the ethyl dication display unusual structural features (e.g., long β C–H bonds in the open forms) which may be readily rationalized with use of qualitative orbital arguments.

(iv) The calculated difference between vertical and adiabatic ionization energies for the ethyl radical, reflecting the difference in structures for these two species, is somewhat larger than the value originally reported from photoelectron spectroscopy but is in good agreement with more recent experimental thermochemical data.

Acknowledgment. We thank Dr. Eric Kingston for some stimulating discussions regarding the charge-stripping process.

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Ylides and Ylidions: A Comparative Study of Unusual Gas-Phase Structures

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Abstract: Ab initio molecular orbital calculations with split-valence plus polarization basis sets and incorporating electron correlation and zero-point energy corrections have been used to study the structures and stabilities of prototype ylides CH_2XH and ylidions $\dot{C}H_2X^+H$ (X = NH_2, OH, F, PH_2, SH, Cl). Detailed potential energy surfaces are presented for the 12 systems studied, and comparisons are made across the periodic table, between first- and second-row compounds and between the ylides and ylidions. The ylidions are confirmed to be much more stable with respect to unimolecular rearrangement or decomposition than their neutral counterparts. For both ylides and ylidions, this stability decreases across a row of the periodic table. For the ylides, the first-row species tend to be less stable energetically than the second-row species, while the reverse is true for the ylidions. The effects of higher level calculations have been examined for ylides, ylidions, and their conventional isomers, and the results are compared with recent experimental data.

Experimental and theoretical studies have firmly established the existence in the gas phase of simple organic ions with unusual structures whose neutral counterparts are unknown or extremely reactive. One of the earliest examples to receive high-level treatment both theoretically[2] (by using ab initio calculations) and experimentally[3] (by using collisionally activated dissociation (CAD) mass spectrometry) was the methyleneoxonium radical cation, $CH_2OH_2^{\bullet+}$. This species has quite a short C–O bond and, perhaps surprisingly, lies lower in energy than the methanol radical cation, $CH_3OH^{\bullet+}$. In contrast, the neutral ylide (CH_2OH_2) resembles a weak complex of methylene with water.[4]

We have introduced[5] the term *ylidion* to describe the class of radical cations corresponding to such ionized ylides.[6] The ylidions may be written with the charge and radical sites on adjacent centers (e.g., $\dot{C}H_2O^+H_2$) and are members of the more general class of *distonic*[7] radical cations in which the charge and radical sites are formally separated.

In this paper, we present a comprehensive survey of the first- and second-row ylidions $\dot{C}H_2X^+H$ (X = NH_2, OH, F, PH_2, SH, Cl) and their corresponding ylides CH_2XH.[8] The main emphasis is on the ylidions, with the ylides being briefly included largely for comparison purposes. Our general aim is to compare structural features and relative stabilities of the various species at uniform and moderately high levels of ab initio theory. In particular, we wish to elucidate trends in these properties in three specific areas: (i) across a row of the periodic table, (ii) between first- and second-row compounds, and (iii) between neutral and charged species.

Method

Standard ab initio molecular orbital calculations were carried out with modified versions[9,10] of the Gaussian 80[11] and Gaussian 82[12] programs.

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