= 348.5 kcal/mol[35]), while the gas-phase acidities of formic acid and methanol are 345.2 kcal/mol[35] and 379.2 kcal/mol,[35] respectively. The order of basicity of the anions is $CH_3O^- > O_2^-\cdot > HCOO^-$. We considered it possible that the reaction would proceed via the S_N2 pathway because $HCOO^-$ might be a better leaving group than $O_2^-\cdot$. This was not observed. Apparently, $HCOO^-$, is not a good enough leaving group or the required reaction intermediate is unstable and the reaction does not proceed fast enough to be observed.

Conclusion

For reaction of NH_2^- with methyl formate, under the low-pressure conditions reported here, it has been established that two primary competitive pathways, the $B_{AC}2$ and proton abstraction reactions, exist. In contrast with previous ICR results, our FTMS study clearly contradicts the conclusion that methoxide results exclusively from a proton abstraction process. Direct observation of the NH_2^- solvated methoxide anion establishes that it has far greater stability than assumed by Isolani and Riveros. The present results with hydroxide generally confirm those of previous flowing afterglow and ICR studies. O^- reacts in a manner similar to that described earlier. However, this study establishes that product earlier attributed solely to the secondary reaction of OH^- are, in fact, derived from O^- reaction, as well. When OH^- is continually ejected, proton abstraction by O^- is dominant.

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Nonplanar Structures of the Singlet and Triplet Cyclopropenyl Anions. An ab Initio Study

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Abstract: Both the singlet and the triplet cyclopropenyl anions are found by ab initio MO theory to be strongly distorted from planarity. Discussions of these "antiaromatic" species which have assumed planarity are not realistic. Furthermore, the ground state is a $^1A'$ singlet (C_s) (not a triplet) with one hydrogen strongly out of plane and the other two hydrogens bent out of plane in opposite direction; a C_2 form is also lower in energy than either of the planar Jahn–Teller distorted (C_{2v}) forms. The triplet cyclopropenyl anion, about 15 kcal/mol less stable than the lowest singlet, also prefers nonplanar geometries in order to reduce electron repulsion. Triplets with C_{3v}, C_s, and C_2 symmetries are all over 10 kcal/mol more stable than the D_{3h} form. Open-chain (CH)$_3^-$ species also are low in energy, but ring opening is symmetry forbidden. The cyclopropenyl anion is indicated not to be stable toward spontaneous ejection of an electron in the gas phase.

The cyclopropenyl anion, (CH)$_3^-$, the smallest possible Hückel 4π electron system, is often regarded as the "antiaromatic" prototype.[1-3] Breslow's experimental pK_a estimate in solution emphasizes the thermodynamic instability of this species;[3a] no gas-phase studies have been reported and the "disquieting" question has been raised whether (CH)$_3^-$ can exist at all as an isolated entity.[4] Many prior theoretical investigations of the cyclopropenyl anions have assumed planarity of both singlet and triplet states, which we will show in the present paper to be incorrect. Simple Hückel theory assumes the trigonal (D_{3h}) planar form to be a ground-state triplet. Davidson and Borden[4] have discussed the Jahn–Teller distortions of the planar (C_{2v}) singlets which lead to quite unequal C–C bond lengths, but did not compute forms involving out-of-plane movements of the hydrogen atoms. A model study of the same group on the isoelectronic (NH)$_3^{2+}$ dications indicated that nonplanar forms might be important.[5]

Clark first pointed out that the "antiaromaticity" of the planar singlet cyclopropenyl anion could be relieved most effectively by the out-of-plane bending of one of the hydrogens,[6] but only limited geometry optimization was carried out at the ab initio level.

Similar results were obtained by Ha, Graf, and Günthard.[7] The fully optimized diffuse function-augmented study of Chandrasekhar et al.[8] indicated an inversion barrier ($C_s \rightarrow C_{2v}$) of 28.9 kcal/mol for the singlet cyclopropenyl anion at a correlated level (MP2/4-31+G//4-31+G), but triplet forms were not considered. All hydrogens were found to lie out of the carbon plane in the C_s singlet. Hess, Schaad, and Čársky found similar results at the MP2/6-31G* + diffuse p function level, but also did not compute the triplet.[9] In the most extensive prior computational study of (CH)$_3^-$ species (but with CNDO/2 semiempirical theory), Pancir and Zahradnik found a planar D_{3h} triplet ground state to lie

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[‡] Bulgarian Academy of Sciences. We are saddened by the death of our colleague, Filip Fratev, on March 31, 1984.
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Table I. Absolute Energies (au) of Cyclopropenyl Anion Forms, Related $C_3H_3^-$ Isomers, and Cyclopropenyl Radical

state	symmetry	3-21+G//3-21+G	4-31+G//4-31+G	6-31+G*//4-31+G	LSD/3-21+G//3-21+G	MP2/4-31+G//4-31+G
$^1A'$	1 C_s	-114.477 61	-114.948 39	-115.126 56[b]	-115.193 17	-115.236 10[c]
^1A	2 C_2	-114.457 51	-114.931 30	-115.112 38	-115.171 81	-115.234 03
^3B	6 C_2	-114.445 98[a]	-114.952 32	-115.130 11		-115.213 00
$^3A''$	7 C_s	-114.445 33[a]	-114.960 90	-115.141 24		-115.221 38
$^3A_2$	8 C_{3v}	-114.443 29[a]	-114.961 79	-115.143 35		-115.221 01
$^3A_2'$	9 D_{3h}	-114.431 32[a]	-114.931 04	-115.103 03		-115.190 98
$^1A_1$	3 C_{2v}	-114.421 73	-114.896 49	-115.068 08	-115.132 93	-115.190 08
$^1A_1$	4 C_{2v}	-114.415 74	-114.891 63	-115.064 14	-115.127 55	-115.179 82
$^1E'$	5 D_{3h}	-114.388 96[a]				
$^1A_1$	10 C_{2v} EE	-114.516 32	-114.987 35	-115.155 84	-115.229 26	-115.244 24
$^1A'$	11 C_s ZE	-114.517 02	-114.987 99	-115.156 22	-115.230 78	-115.244 10
$^1A_1$	12 C_{2v} ZZ	-114.508 42	-114.979 56	-115.149 28	-115.225 10	-115.234 84
$^2A'$	13 C_s	-114.537 28	-115.009 16	-115.196 54[b]	-115.231 43	-115.256 05[c]

[a] Calculated with IVO. [b] The 6-31+G*//6-31+G* energy for 1 is -115.127 57 au and for 13 -115.197 12 au. [c] The MP2/6-31+G*//6-31+G* energy for 1 is -115.527 74 au and for 13 -115.556 29 au.

Table II. Relative Energies (kcal/mol) of Cyclopropenyl Anion Forms, Related $C_3H_3^-$ Isomers, and Cyclopropenyl Radical

state	symmetry	3-21+G//3-21+G	4-31+G//4-31+G	6-31+G*//4-31+G	LSD/3-21+G//3-21+G	MP2/4-31+G//4-31+G	MP2/6-31+G*//4-31+G est[b]
$^1A'$	1 C_s	0.0	0.0	0.0	0.0	0.0	0.0
^1A	2 C_2	12.6	10.7	8.9	13.4	1.3	-0.5
^3B	6 C_2	19.8[c]	-2.5	-2.2		14.5	14.2
$^3A''$	7 C_s	20.3[c]	-7.9	-9.2		9.2	7.9
$^3A_2$	8 C_{3v}	21.5[c]	-8.4	-10.5		9.5	7.4
$^3A_2'$	9 D_{3h}	29.0[c]	10.9	14.8		28.3	32.2
$^1A_1$	3 C_{2v}	35.0	32.6	36.7	37.8	28.9	33.0
$^1A_1$	4 C_{2v}	38.8	35.6	39.2	41.2	35.3	38.9
$^1E'$	5 D_{3h}	55.6[c]					
$^1A_1$	10 C_{2v} EE	-24.3	-24.4	-18.4	-22.6	-5.1	0.9
$^1A'$	11 C_s ZE	-24.7	-24.9	-18.6	-24.9	-5.0	1.3
$^1A_1$	12 C_{2v} ZZ	-19.3	-19.6	-14.3	-20.0	0.8	6.1
$^2A'$	13 C_s	-37.4	-38.1	-43.9[a]	-24.0	-12.5	-18.4[a]

[a] At 6-31+G*//6-31+G* the radical 13 is 43.6 kcal/mol more stable than 1; at MP2/6-31+G*//6-31+G* the difference is 17.9 kcal/mol. [b] Values are estimates; see text. [c] Calculated with IVO.

somewhat below the best (nonplanar, C_s) singlet.[10] Azirene, an isoelectronic model for $C_3H_3^-$ with lower inherent symmetry, has been calculated to have a nonplanar C_s structure where the hydrogens attached to the carbons are bent trans to that on the nitrogen.[11] The present paper reports the first comprehensive examination of $(CH)_3^-$ species at adequately high ab initio levels with more extensive searches of the singlet and triplet potential energy surfaces. We also examine the relative and thermochemical stability of these species.

Computational Procedures and Results

All calculations employed the GAUSSIAN 76[12] and the GAUSSIAN 82[13] series of programs with suitable modifications. Geometry optimizations used analytically calculated atomic forces[14] in a Davidon–Fletcher–Powell multiparameter search routine.[15] The diffuse function augmented basis sets 3-21+G,[16,17] 4-31+G,[8,17] and 6-31+G*[18,19] were used in order to achieve a proper wave

function for the anion. The influence of polarization functions (3d) at the carbon atoms was studied. Electron correlation corrections were taken into account by the MP2[20] (second-order Møller–Plesset theory) procedure as well as by the LSD formalism (local spin density).[21] The MP2 calculations did not involve the nonvalence orbital (frozen core approximation).[20] Singlet states were calculated by the RHF method.[22]

Triplet states were calculated by the unrestricted Hartree–Fock (UHF) method[23] and, for comparison, by the use of improved virtual orbitals (IVO).[24] The latter method has been successfully applied not only for singly excited states but also in the case of degenerate or nearly degenerate doubly excited electronic configurations as they occur with cyclobutadiene[25] and is now applied to $C_3H_3^-$. The improved triplet orbital energy shows immediately, in the sense of Koopmans' theorem, the position of the triplet state relative to the ionization limit.

The well-known relation between the relative energies of the singlet and triplet states for an excited configuration . . .(a)^1(b)^1 is

$$\text{singlet:} \quad \epsilon_b - \epsilon_a - J_{ab} + 2K_{ab}$$

$$\text{triplet:} \quad \epsilon_b - \epsilon_a - J_{ab}$$

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Table III. Valence Orbital Energies (au) for the Lowest Singlet and Triplet States of the Cyclopropenyl Anion[a]

1	$C_s(^1A')$	−0.196 (a′)	−0.135 (a″)	−0.029 (a′)	
4	$C_{2v}(^1A_1)$	−0.248 (b₁)	−0.210 (b₂)	0.061 (b₁)	
5	$D_{3h}(^1E')$	−0.298 (a₂′)	−0.291 (a₂″)	0.069 (eₓ″)	0.075 (e_y″)
3	$C_{2v}(^1A_1)$	−0.247 (b₁)	−0.142 (a₁)	0.042 (a₂)	
2	$C_2(^1A)$	−0.189 (b)	−0.147 (a)	−0.027 (a)	
6	$C_2(^3B)$	−0.216 (a)	−0.212 (b)	0.024 (a)	0.021 (b)
7	$C_s(^3A'')$	−0.236 (a″)	−0.198 (a′)	0.022 (a′)	−0.014 (a″)
8	$C_{3v}(^3A_2)$	−0.236(a₂)	−0.222(a₂)	0.032(eₓ)	−0.019 (e_y)
9	$D_{3h}(^3A_2')$	−0.288 (a₂′)	−0.277 (a₂″)	0.066 (eₓ″)	0.030 (e_y″)

[a] The last two orbitals of the open-shell states are singly occupied; improved virtual orbitals are utilized for the last orbital. (Three Rydberg states are slightly below $^1E'$.)
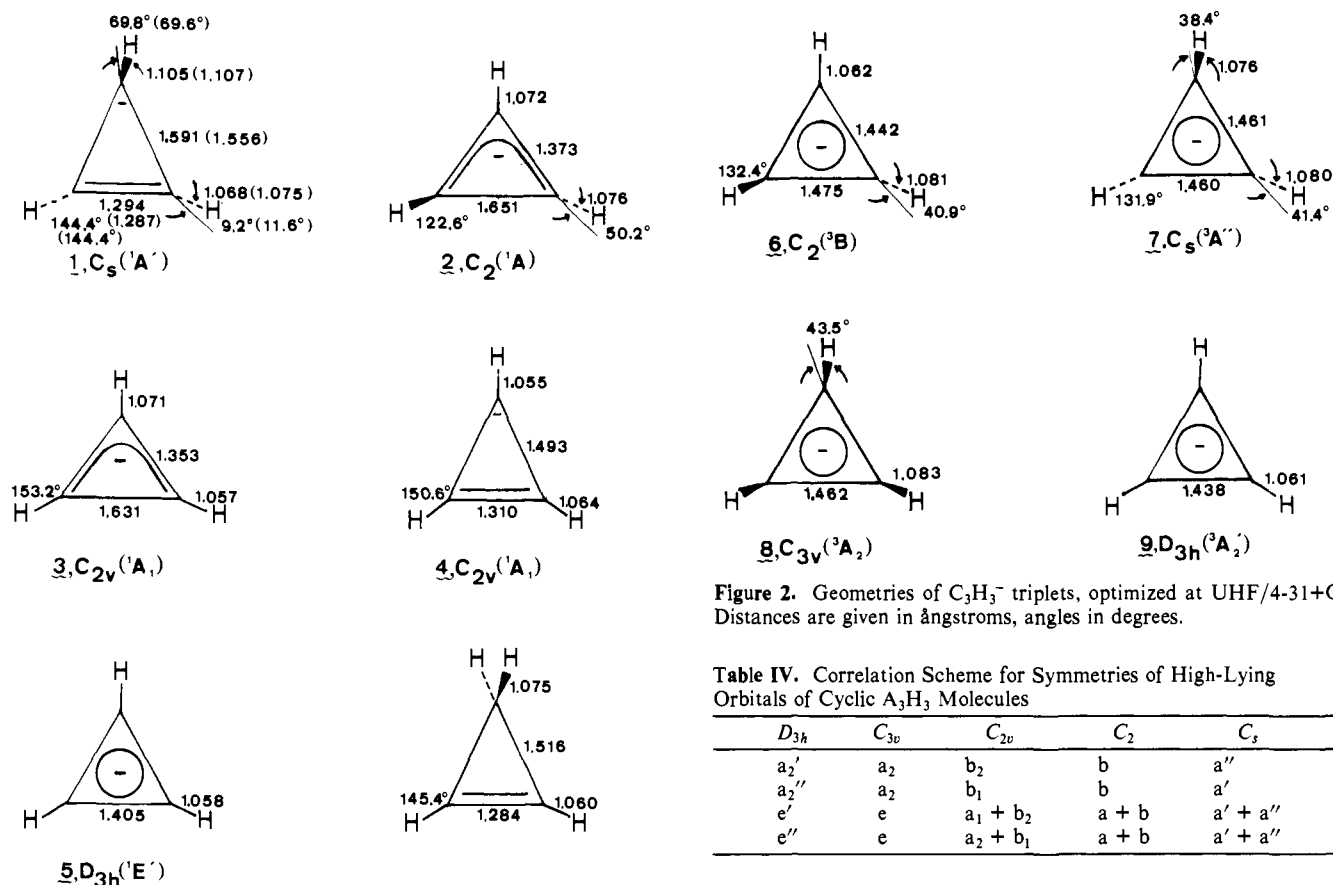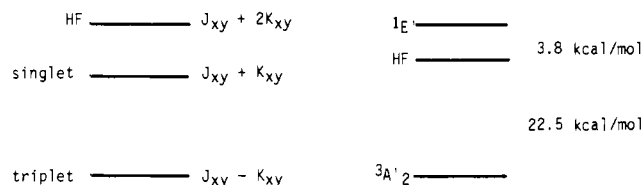

Figure 1. Geometries of $C_3H_3^-$ singlets, optimized at 4-31+G. Similar results were obtained at 3-21+G. Distances are given in ångstroms, angles in degrees. The 6-31+G* data for **1** are given in parentheses.

where ϵ_a and ϵ_b are the energies of the SCF orbitals a and b, respectively; J_{ab} and K_{ab} are the usual two-electron Coulomb and exchange integrals, respectively. In the case of degenerate orbitals x and y the Hartree–Fock energy of the configuration . . .(x)²(y)⁰ divides the singlet–triplet interval externally with the ratio 1:3. However, the use of a common excited orbital y for singlet *and* triplet may be a rather crude approximation. Within the IVO formalism the excited orbital y is variationally optimized for each state and results to have a much more diffuse character in the singlet than in the triplet state, so that the calculated energies of the states differ from the usual diagram.

The lack of diffuse functions in the basis set employed in Davidson and Borden[4] and their use of the more contracted triplet orbitals for the description of the much more diffuse singlet wave

Figure 2. Geometries of $C_3H_3^-$ triplets, optimized at UHF/4-31+G. Distances are given in ångstroms, angles in degrees.

Table IV. Correlation Scheme for Symmetries of High-Lying Orbitals of Cyclic A_3H_3 Molecules

D_{3h}	C_{3v}	C_{2v}	C_2	C_s
a₂′	a₂	b₂	b	a″
a₂″	a₂	b₁	b	a′
e′	e	a₁ + b₂	a + b	a′ + a″
e″	e	a₂ + b₁	a + b	a′ + a″

functions probably is responsible for their longer CC distances of 1.443 Å for the $^1E'$ state with respect to 1.405 Å of the present work.

The absolute energies of all species considered are listed in Table I at the various theoretical levels. Relative energies are given in Table II. The ordering of the lower states of the anion is visualized, with respect to the radical, in Figure 4. It is noteworthy that several Rydberg states are found between the valence states $^1E'$ and $^3A'_2$ in D_{3h} symmetry. The lowest of them, $^1E''$ and $^3E''$, happen to be almost identical in their energies. The MP2/6-31+G* estimates were obtained by assuming additivity.[26] That is, the MP2 correction at the 4-31+G level was added to the 6-31+G* results. Since the number of electron pairs in the singlets and triplets differ, only relative energies of these species at correlated levels provide meaningful comparisons (the last three columns in Table II; triplets at the SCF-IVO level are automatically correlation-corrected with respect to the corresponding singlets).

To facilitate comparison, the 4-31+G optimized geometries are presented in Figure 1 for the $C_3H_3^-$ singlets (**1–5**), in Figure 2 for the corresponding triplets (**6–9**), and in Figure 3 for the open-chain $(CH)_3^-$ singlets (**10–12**).

The energies of a few of the higher lying orbitals along with their symmetry specifications are given in Table III. In order

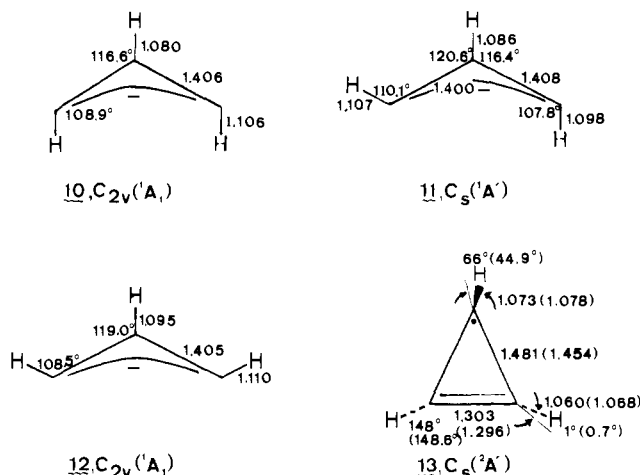(26) McKee, M. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 4673.

Figure 3. Geometries of open-chain $C_3H_3^-$ singlets optimized at 4-31+G and of the C_3H_3 radical optimized at UHF/3-21+G (6-31+G* data for the radical given in parentheses). Distances are given in ångstroms, angles in degrees.
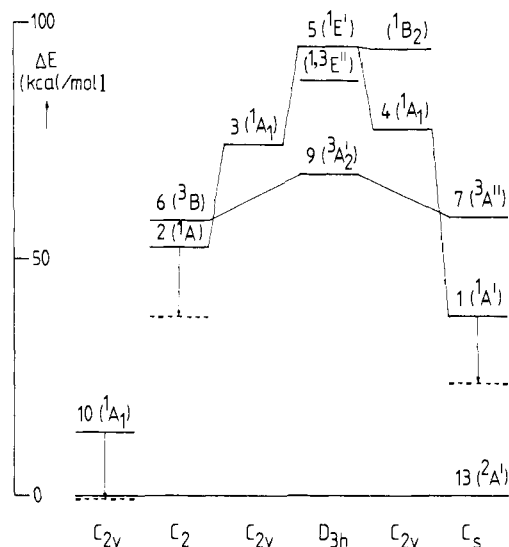

Figure 4. Energy levels of the lowest singlet and triplet states of the cyclopropenyl anion for different symmetries; **10** is the open-chain structure. The levels are drawn with respect to the energy of the cyclopropenyl radical. The methods employed are SCF for closed-shell states, SCF IVO for open-shell states, and UHF for the radical; the basis set is 3-21+G. Electron correlation corrections (LSD) are indicated by broken lines and are referred to the correlation corrected energy of the radical ($\Delta E = 0$).

to facilitate a comparison of orbital energy changes of related MO's in the various species, the correlation scheme for the irreducible representations spanned by the orbitals of cyclic A_3H_3 molecules with various symmetries is shown in Table IV.

Jahn–Teller Effect for Planar Cyclopropenyl Anion

The theory of the Jahn–Teller effect for D_{3h} species is extensively described by Davidson and Borden.[4] At first, we repeated the calculations of these authors with our methods for comparison and then, in addition, we performed a pointwise construction of the energy surfaces of those states which contribute to a Jahn–Teller analysis. In agreement with Davidson and Borden, we found that the first-order Jahn–Teller effect is small, so that strong in-plane distortions are caused by the second-order effect which occurs with degenerate configurations.

Although the SCF states suffer from the lack of the proper symmetry of D_{3h}, the single determinant approach can be used to construct symmetry-adapted wave functions very quickly. We started with one of the degenerate SCF wave functions

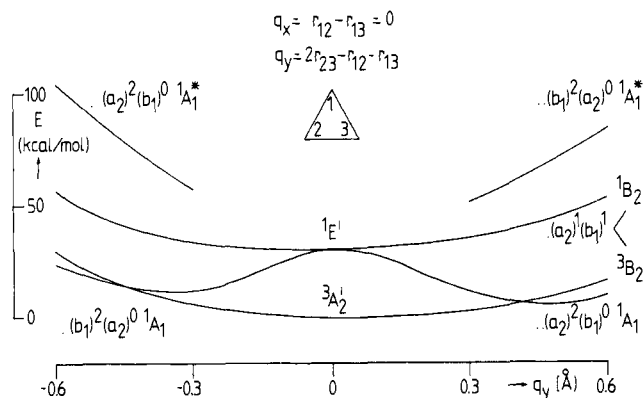$$e_x''\bar{e}_x'' \quad (\text{or } e_y''\bar{e}_y'')$$

Figure 5. First- and second-order Jahn–Teller effect on planar cyclopropenyl anion. The geometries of the ... $(b_1)^2(a_2)^0\,^1A_1$ saddlepoint and of the ... $(a_2)^2(b_1)^0\,^1A_1$ minimum on the (q_x,q_y) surface are listed in Figure 1 (structures **4** and **3**, respectively); the geometry of ... $(b_1)^1(a_2)^1$ $^1B_2$ is $r_{23} = 1.389$ Å, $r_{12} = r_{13} = 1.419$ Å.

and then transformed the virtual orbitals into improved virtual orbitals (IVO)[24] which immediately yield the wave functions

$$1/\sqrt{2}(e_x''\bar{e}_y''(S) + \bar{e}_x''e_y''(S)) \qquad ^1E' \qquad (I)$$

and

$$1/\sqrt{2}(e_x''\bar{e}_y''(T) - \bar{e}_x''e_y''(T)) \qquad ^3A'_2$$

as well as their corresponding energies. The second degenerate component of $^1E'$ is

$$1/\sqrt{2}(e_x''\bar{e}_x'' - e_y''(S)\bar{e}_y''(S)) \qquad ^1E' \qquad (II)$$

Upon the reduction of symmetry ($D_{3h} \rightarrow C_{2v}$) by the variation of the coordinate $q_y = 2r_{23} - r_{12} - r_{13}$ ($q_x = r_{12} - r_{13} = 0$) the configurations $e_x''\bar{e}_x''$ and $e_y''\bar{e}_y''$ become decoupled, so that the SCF wave functions are proper approximations for the $^1A_1$ states as is shown in Figure 5. The steep descent of the energy of the $^1A_1$ state is caused by the decrease of electron repulsion.

The first-order effect of $^1E'$ ($\rightarrow^1B_2$) is so small as to be almost invisible in Figure 5, and it predicts an ethylenic structure ($q_y < 0$) for $^1B_2$. The other component of $^1E'$ ($\rightarrow^1A_1$), for which the allylic structure ($q_y > 0$) is slightly favored, is strongly distorted from D_{3h} symmetry owing to the predominating second-order effect. Consequently, the energy of the lowest singlet surface becomes competitive with the triplet energy.

Discussion

Singlet Cyclopropenyl Anions. As has been found in previous studies, the C_s deformed $C_3H_3^-$ anion (**1**) was the lowest energy singlet. This species can also be regarded as a complex between a perpendicularly oriented singlet CH⁻ anion and acetylene. While decomposition of **1** into CH⁻ triplet (the ground state) and C_2H_2 is indicated by our highest level calculations to be slightly endothermic (2 kcal/mol), this process is symmetry forbidden.

In **1**, the interaction between the localized anion and the double bond is clearly antibonding. The single C–C bonds are lengthened (1.591 vs. 1.516 Å in cyclopropene, Figure 1), and the unique CH bond is bent out of the ring plane by 70°. As a consequence of this distortion of the π system, which thus strives to relieve repulsive interactions, the other two hydrogens bend out of plane in the other direction by 9.2°. The small bond angles associated with three-membered rings also lead to an increase in s character of the anion lone-pair orbital, and an increase in the inversion barrier. However, the 35.4-kcal/mol (MP2/4-31+G//4-31+G) energy difference between **1** and the corresponding planar form, **4** (C_{2v}), is considerably larger than the 15.1-kcal/mol inversion barrier calculated for the cyclopropyl anion.[8] This also demonstrates the "antiaromatic" character of the cyclopropenyl anion, that is, the repulsive 4π electron interaction between the localized lone pair electrons in the p orbital in **4** and the double bond.

Distortion of only two hydrogens from the ring plane (2, C_2 symmetry) also gives a substantial lowering in energy relative to all planar alternatives (3–5). However, 2 is about 10 kcal/mol less stable than 1. The electronic structure of 2 can be described as being highly "twisted". The antibonding interaction between the termini of the allyl anion-like system is relieved, as much as possible, by a lengthening of the unique C–C bond (to 1.694 Å), and the bending of the two hydrogens to 56.7° in opposite directions out of the ring plane.

The planar singlets, 3–5, are much less stable than 1 and 2 and are not minima on the potential energy surface. Besides out-of-plane bending, 3 → 2 and 4 → 1, there is a smooth descent from 4 to 3 by pseudorotation. As expected from qualitative MO considerations, the D_{3h} singlet (5) is 20 kcal/mol higher in energy than the Jahn–Teller deformed C_{2v} structure 3. In qualitative agreement with the calculations of Borden and Davidson,[4] we in addition find 3 (the allyl anion-like form) to be more stable than 4 by 6 kcal/mol (at the estimated MP2/6-31+G* level). Note that the stability ordering 3 < 4 is reversed when full geometry optimization is allowed (1 < 2).

Triplet Cyclopropenyl Anions. As in calculations on the isoelectronic $(NH)_3^{2+}$,[5] we find that the triplet cyclopropenyl anion also prefers nonplanar structures. Three deformations, to C_2 (6), C_s (7), and C_{3v} (8) symmetries, are possible. While our quantitative ordering of 6–8 varies with the theoretical level (Table II), the planar D_{3h} form 9 is always higher in energy (at least by 10 kcal/mol). In all four structures (Figure 2) the C–C bond lengths are nearly equal and range only from 1.438 Å in 9 to 1.475 Å in 6. This reflects the more even electron distribution in the triplets, relative to the singlets. However, the out-of-plane deformations of the hydrogen atoms in the triplets are not always smaller than in the singlets. This is especially notable in 7 where the large bending of the two identical hydrogens is noteworthy (compare 1).

The C–C bond length in the D_{3h} triplet (9), 1.438 Å, is substantially longer than that in the cyclopropenyl cation, $C_3H_3^+$ (1.361 Å at 4-31G; 1.349 Å at 6-31G*). This shows in yet another way that the 4π electron anion is less favorable than its 2π cation counterpart. The two extra electrons in 9 must occupy antibonding π orbitals.

Singlet vs. Triplet Stabilities. If a planar trigonal (D_{3h}) geometry is assumed, the triplet 9 is, in accord with Hückel theory, lower in energy than the singlet state (5). If the restriction of planarity is maintained but Jahn–Teller deformation allowed, the more favorable C_{2v} singlet (3) becomes competitive with the D_{3h} triplet (9) in energy (Table II; the results at different correlated levels vary somewhat). If, however, full geometry relaxation is allowed, the nonplanar singlet 1 becomes the ground state; the best triplets (6–8, depending on the method) are 14 kcal/mol or more higher in energy at correlated levels.

Open-Chain (CH)$_3^-$ Species. The small angles in three-membered rings result in energy raising. Nevertheless, cyclopropene, for example, is considerably more stable (by 36.6 kcal/mol, GVB(4)CI)[27] than its ring-opened vinylcarbene counterpart.

In contrast, the (CH)$_3^-$ open-chain singlet anion isomers, 10–12, are found, surprisingly, at many levels of theory (Table II) to be much lower in energy than the cyclopropenyl anion (1). While the stability order reverses at our highest estimated level (MP2/6-31+G*), the competitive nature of the open-chain (CH)$_3^-$ species is still remarkable.

These isomers (10–12) have the electronic structure indicated in Figure 3 with only 2π electrons and two lone pairs on the terminal carbenes. The lone pairs are best oriented away from one another; hence, the trans–trans (10) and cis–trans (11) geometries are energetically more favorable than the cis–cis form (12).

Even if 10–12 were to be more stable than the cyclopropenyl anion (1), ring opening should not be facile, since the reaction is symmetry forbidden. Nevertheless, it might be possible to

observe such species when an appropriate metal counterion is present. We will consider organometallic models in a subsequent publication.

While triplet states of 10–12 were not found to be competitive with the singlets, these open-chain triplets were more stable than some of the triplet cyclopropenyl anion forms.

Thermochemical Considerations. Can the Cyclopropenyl Anion Exist?

The central question, already raised by Borden and Davidson,[4] is whether the cyclopropenyl anion can exist at all as an isolated species. Their CI calculations indicated the planar cyclopropenyl anion not to be bound in the gas phase. While we find the nonplanar singlet (1) to be much lower in energy, it still might be unstable toward spontaneous loss of an electron.

As shown in Table III, the singlet cyclopropenyl anion HOMO energies of only 1 and 2 are negative. All but the C_{3v} triplet also are unfavorable in this regard. However, a negative HOMO energy does not ensure that an anionic species will be stable toward electron loss. The comparison between the lowest state of the anion with that of the radical, both in their optimized structures, indicates an unstable anion (cf. Figure 4). Since the electron affinities are difficult to evaluate accurately by direct calculations, we employ indirect procedures using isodesmic reactions.

$$CH_3^{\cdot} + \triangle^{(-)} \longrightarrow \triangle + CH_3^- \quad (1)$$
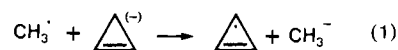
Thus, the energy of eq 1, which compares the electron affinities of CH$_3$, and C$_3$H$_3$, can be evaluated using MP2/6-31+G* data and the known heats of formation of the methyl radical,[28] methyl anion,[29] and the cyclopropenyl radical.[30] This gives an estimated $\Delta H_f°(C_3H_3^-) = 110 \pm 5$ kcal/mol. Alternatively, eq 2 can be

$$CH_3^- + \triangle \longrightarrow \triangle^{(-)} + CH_4 \quad (2)$$

employed to obtain $\Delta H_f°(C_3H_3^-) = 122.3$ kcal/mol. This utilizes the difference in proton affinities of the methyl and cyclopropenyl anions calculated at the MP2/6-31+G* level (1.9 kcal/mol; CH$_3^-$ is more stable), and experimental heats of formation of cyclopropene,[30] CH$_3^-$,[29] and methane.[31]

Both methods agree. The electron affinity of CH$_3^-$ is about 18 kcal/mol more favorable than C$_3$H$_3^-$. Since the electron affinity of CH$_3^-$ is known experimentally to be only +1.8 kcal/mol, the cyclopropenyl anion is thus indicated *not to be bound*. This means that all theoretical investigations are dealing with a fictitious species. Quantum mechanical calculations, such as those we report in this paper on C$_3$H$_3^-$, are only possible because of deficiencies in the theory of the levels we have employed. If the basis sets were sufficiently large, an electron would fly off to infinity. Only the use of more restricted descriptions prevents this from happening.

Do such inadequate calculations have any meaning? Real cyclopropenyl anion systems undoubtedly do exist in condensed phases, since they can be stabilized by solvation or especially by the presence of a gegenion. We will consider model C$_3$H$_3$Li systems in a separate publication and will show close parallels with our results on the C$_3$H$_3^-$ anions. In particular, the geometries of the carbanionic moieties are quite similar. Experimental structures of a number of anions are known to be reproduced well at modest theoretical levels. It is also possible that the energies we have calculated reflect the relative stabilities of the various geometries, even though no absolute significance can be attached to the values.

The "stabilization energy" of C$_3$H$_3^-$ depends on the definition one prefers. A simple evaluation employs eq 3 which corrects to

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(30) DeFrees, D. J.; McIver, R. T.; Hehre, W. J. *J. Am. Chem. Soc.* 1980, 102, 3334.
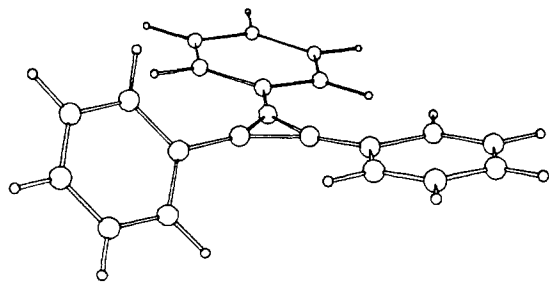(31) Rossini, F. D. *J. Res. Natl. Bur. Stand.* 1931, 6, 37.

Figure 6. The MNDO optimized structure of the triphenylcyclopropenyl Anion.

a large extent the "angle strain" present in the three-membered rings.

The calculated data indicate the cyclopropenyl anion to be *destabilized* relative to the cyclopropyl anion, but only by 3.5 kcal/mol. This is a measure of the "antiaromaticity" associated with **1** and, in comparison with values deduced similarly for cyclobutadiene (eq 4), is surprisingly small. Of course, much of
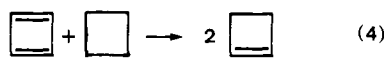
$$-38.2 \text{ kcal/mol } (6\text{-}31G^*//6\text{-}31G^*)^{35}$$

the unfavorable electronic character of $C_3H_3^-$ is relieved by the strong geometrical distortion exhibited by **1**. In addition, it can be argued that the olefinic carbons in **1** are electron withdrawing inductively and help to stabilize the negative charge.

By contrast, the stabilization energies of the cyclopropenyl radical and cation, evaluated by equations similar to eq 3, are 15 and 70 kcal/mol, respectively. Both the 3π and 2π electron species thus are stabilized relative to their cyclopropyl counterparts.

Triphenylcyclopropenyl Anion. The full MNDO[32] geometry optimization of the experimentally known triphenylcyclopropenyl anion,[3a] starting from a skeleton structure similar to **1**, led to a nearly perfect C_{2v} structure of the allyl-type for the cyclopropenyl part of the molecule (Figure 6). The two short C–C bonds had an average length of 1.392 Å; the C^1–C^2 distance was 1.517 Å. All three phenyl rings are only slightly twisted (average: 12°) relative to the plane of the cyclopropenyl ring. Good conjugative stabilization of the negative charge should occur. The total negative charge on all three cyclopropenyl carbon atoms is –0.45. Thus, 55% of the negative charge is delocalized to the phenyl rings. The stabilizing effect of the phenyl groups is so high that the cyclopropenyl part of the molecule favors a **3**-like structure rather than a geometry corresponding to **1**. The 33-kcal/mol preference of **1** over **3** in $C_3H_3^-$ thus is overcome in the triphenylcyclopropenyl anion. This agrees with the experimental conclusion. In addition, our calculations indicate the potential energy surface to be quite flat.

The Cyclopropenyl Radical. The structure of the cyclopropenyl radical[33] poses similar problems to its cyclopropenyl anion counterpart. The ground-state doublet has 3π electrons, and Jahn–Teller distortion from D_{3h} symmetry is expected. The theoretical studies which allowed full geometry optimizations found out-of-plane distortions to be most effective in reducing the energy.[10,34,35] All agree that a C_s form ($^2A'$) with a double bond and a highly bent radical center to be the most stable. Pople's data[35] at UHF/6-31G*//6-31G* give the following relative energies, in kcal/mol: C_s ($^2A'$) 0.0; C_2 (^2A) 2.6; C_s ($^2A''$) 3.0; C_{2v} ($^2A_2$) 8.6; C_{2v} ($^2B_2$) 12.0; and D_{3h} (^2E) 15.0. This ordering is similar to that found for the singlet cyclopropenyl anion in the present study.

We examined only the most stable ($^2A'$) C_s form of the cyclopropenyl radical (**13**), but this was optimized at several levels including 6-31+G*. Geometrical details (given in **13**) show that the distortions are similar to those formed in the corresponding anion (**2**).

Conclusions

We conclude that the most stable cyclopropenyl anion is the nonplanar (C_s) singlet (**1**). Nonplanar triplets also are more stable than the planar D_{3h} form (**9**), but are not competitive in energy with **1**. Movement of the hydrogens out of the ring plane is much more effective in relieving the unfavorable electronic interactions than second-order Jahn–Teller distortion of the C–C bond lengths in planar arrangements. Open-chain $(CH)_3^-$ isomers with 2π electrons and two nonbonding lone pairs are competitive in energy with **1**. The latter is destabilized relative to the cyclopropyl anion and, most important, is indicated not to be bound toward loss of an electron. Since the loss of an electron is assumed to have no barrier, the lower energy cyclopropenyl radical should be formed spontaneously. No cyclopropenyl anion should thus be experimentally observable in the gas phase.[36]

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