# A High-Level ab Initio and Density Functional Investigation of Cyclopropenyl Anion and Its Mono-, Di-, and Trisubstituted Derivatives

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**Abstract:** High-level *ab initio* and density functional theory calculations were carried out on cyclopropenyl anion (**1**) and related species. The parent c-$C_3H_3^-$ ion is predicted to be unstable with respect to electron loss whereas its cyano-substituted derivatives are attractive synthetic targets. MCSCF structures for singlet and triplet cyclopropenyl anion are reported and contrasted to the results obtained from more modest computations. Energetic quantities for **1** were computed including its proton affinity, destabilization energy, singlet−triplet gap, electron binding energy, and ring-opening isomerization energy. The allylic C−H bond strength for cyclopropene also is given. Mono-, di-, and tricyanocyclopropenyl anions were investigated too, and their conjugate acids have lower p$K_a$'s than cyclopropene by up to 70.4 kcal/mol or 52 p$K_a$ units.

## Introduction

Aromaticity is a topic that has intrigued experimental and theoretical chemists ever since Faraday's discovery of benzene in 1825 and Kekule's (or Loschmidt's) subsequent deduction of its structure.[1,2] Numerous working definitions of aromaticity have been offered which address the reactivity, thermodynamic stability, and magnetic properties of aromatic compounds, but no single definition has met with universal acceptance. Perhaps the most common and generally useful definition is given by Hückel's rule, which states that aromatic compounds are fully conjugated, monocyclic, planar species with $4n + 2$ ($n = 0, 1, ...$) $\pi$-electrons. Analogous compounds with $4n$ ($n = 1, 2, ...$) $\pi$-electrons are termed nonaromatic or antiaromatic depending upon their stability.

Antiaromatic compounds are destabilized by cyclic conjugation. Like their aromatic counterparts, they have captured the imagination of chemists and have been the subject of numerous studies.[3−5] The simplest examples of these species are cyclopropenyl anion (**1**), cyclobutadiene (**2**), and cyclopentadienyl cation (**3**) of which **1** is the archetype. Consequently, it is not surprising that cyclopropenyl anion and its derivatives have been long sought after and extensively investigated. Breslow has shown in a series of seminal studies that cyclopropenyl anions

are among the most basic compounds known in solution.[3b−g] Their conjugate acids have p$K_a$'s in excess of 50 p$K_a$ units and are less acidic than many simple alkanes. A stable derivative, which can be spectroscopically interrogated, has yet to be prepared in the liquid phase, and many questions thus remain unanswered.
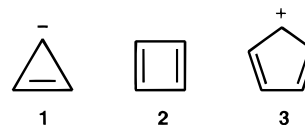


We have recently synthesized a stable cyclopropenyl anion derivative in the gas phase via the DePuy reaction (i.e., the formation of a carbanion via the fluoride-induced desilylation of an appropriately substituted trialkylsilyl derivative, eq 1).[6,7]
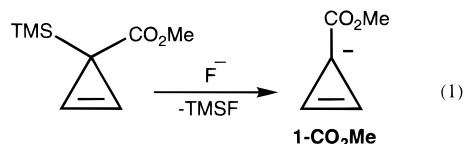


After establishing the ion's structure, the proton affinity of **1-CO$_2$Me** was measured and compared to its saturated analog (eq 2). These experimental results show that the double bond

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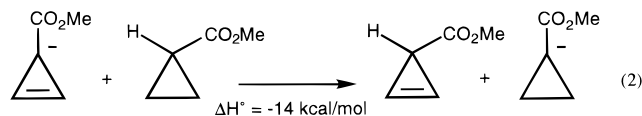
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in the cyclopropenyl anion is destabilizing as would be expected for an antiaromatic species.

$$\text{(structure)} + \text{(structure)} \xrightarrow{\Delta H° = -14 \text{ kcal/mol}} \text{(structure)} + \text{(structure)} \quad (2)$$

Computational studies on cyclopropenyl anion abound in the literature and are of particular value given the lack of experimental data.[8] This literature, beginning in the early 1960s, offers an historical perspective on the evolution of modern theoretical methods. Many of the conclusions were based on low-level, incomplete, or unsophisticated (by current standards) methodologies. In fact, the current picture of the structure of cyclopropenyl anion is based upon single-determinant computations even though multiconfigurational calculations may be more appropriate.[8g-k] At present, the "best" structural data in the literature for singlet cyclopropenyl anion comes from full optimizations with the 6-31+G(d) basis set,[8c] which includes a set of diffuse sp functions and six d-orbitals on each carbon atom; it is well-known that diffuse functions are needed to describe adequately anionic structures and that polarization functions are essential for small-ring compounds.[8h,9] Characterization of the corresponding potential energy surface, however, has only been carried out at the HF/3-21+G level of theory.

The lowest energy singlet has $C_s$ symmetry in which one hydrogen lies above and the other two hydrogens are somewhat below the plane of the three-membered ring (Figure 1). A $C_2$ transition structure, corresponding to the interconversion of $C_s$ species by pseudorotation, was found at the HF/3-21+G level. The MP3/6-31++G(d,p)//HF/6-31+G(d) energy difference is 4.3 kcal/mol ($\Delta E = E(C_2) - E(C_s)$), but $\Delta E$ varies with the computational method and has been reported by Winkelhofer et al. to be as low as $-0.5$ kcal/mol (estimated MP2/6-31+G-(d)//HF/4-31+G) and as high as 13.4 kcal/mol (LSD/3−21+G//HF/3−21+G).[8e] Additional point groups also have been examined, including the fully delocalized $D_{3h}$ structure, but all were found to be considerably higher in energy.

Triplet cyclopropenyl anion has been explored too, but with the smaller 4-31+G basis set. The nature of the stationary



**Figure 1.** Different symmetry types for singlet cyclopropenyl anion.

points (i.e., minima, transition structures, etc.) was not reported, but the classical $D_{3h}$ structure is higher in energy than those with $C_s$ and $C_{3v}$ symmetry.[8e,i] Cyclopropenyl anion is, therefore, predicted to be a ground state singlet, and it appears, at least in the gas phase, to be less stable than its corresponding radical; this makes **1** an unbound ion. From a practical standpoint, this means that it will be more difficult to probe the cyclopropenyl anion experimentally. In principle, techniques such as electron transmission spectroscopy[10] and the DePuy kinetic acidity method[11] are still applicable and could potentially provide useful information. In the absence of such data, computations take on added importance.

Quite recently, a G2 study was reported on cyclopropenyl anion and some related compounds.[8a] This approach typically provides energies within 2 or 3 kcal/mol of experiment for small (≲6 heavy atoms) main group compounds and has been successfully applied to a wide range of species.[12] The original G2 procedure is not an especially reliable method, however, for obtaining anion geometries or characterizing the nature of their potential energy surfaces. Geometry optimizations and vibrational frequency analyses are carried out with the 6-31G-(d) basis set, which does not include diffuse functions. This can lead to serious differences with results obtained with the 6-31+G(d) basis set[9] and has led to the development of the G2+ procedure by Gronert.[13,14] The original G2 protocol also calls for Hartree−Fock (HF) frequencies, but MP2(full) structures. This is undesirable, particularly for anions, because the nature of a stationary point can change with the computational method. In some cases, a structure will not even exist on the potential energy surface at both the HF and MP2 levels of theory. The method also is applicable only to those systems which are adequately described by a single determinant wave function.

In carrying out MP2 and density functional theory (DFT) calculations on cyclopropenyl anion, we were somewhat surprised to find that the $C_2$ singlet is no longer a transition structure but a minimum on the potential energy surface. We therefore undertook the current high-level *ab initio* (CCSD(T)//MCSCF) study to establish reliably the structure and energetics

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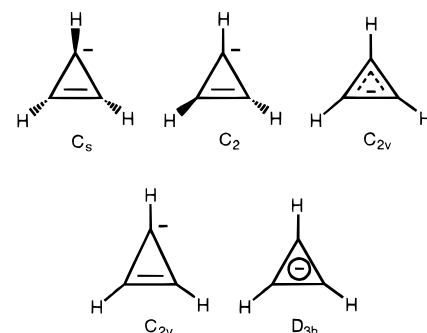
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(14) The C1−C3 bond length in the $C_2$ (¹A) cyclopropenyl anion contracts 0.035 (or 0.034) Å upon adding diffuse functions to the basis set (i.e., HF/6-31G(d) vs HF/6-31+G(d) or MP2/6-31G(d) vs MP2/6-31+G-(d)) and elongates by 0.080 (or 0.083) Å upon going from the HF to the MP2 level. The average unsigned difference in the vibrational frequencies with and without diffuse functions is 58 (HF) and 53 cm⁻¹ (MP2).

of cyclopropenyl anion and its conformers. These results have been used to benchmark less computationally demanding methodologies (DFT) which could then be applied to larger (substituted) cyclopropenyl anions. Mono-, di-, and tricyano-cyclopropenyl anions were also investigated in order to assess the impact of electron-withdrawing substituents and provide information which might facilitate the preparation of a stable cyclopropenyl anion derivative in solution.

## Computational Methods

All structures were fully optimized with the 6-31+G(d,p) basis set. The *ab initio* optimizations were performed within the Hartree−Fock (HF), Møller−Plesset second-order perturbative (MP2), and multiconfigurational self-consistent field (MCSCF) formalisms.[15] Three density functionals (B-VWN5, B-LYP, and Becke3-LYP (B3-LYP))[16−20] were also used for obtaining geometries as density functional theory is computationally less demanding and has shown great promise. The curvatures associated with the potential energy surfaces in the vicinity of each stationary point were determined via full vibrational analyses at the same theoretical level at which the optimization were conducted. Zero-point energy, but not thermal, corrections were applied, using the following scaling factors: 0.9135 (HF), 0.9646 (MP2), and 1.00 (all others).[21] Single-point calculations were subsequently performed on the lowest energy minima and transition structures. With the exception of the HF geometries, which employed the 6-31+G(d,p) basis, all single-point calculations were carried out with the larger 6-311+G-(2df,2pd) set of functions. MP2 and coupled-cluster (CCSD(T):[22] full single, double, and quadruple excitations; triple excitations via the noniterative approximation of Pople et al.)[22d] single-point energies were calculated for the HF and MCSCF structures, respectively. All other single-point calculations were undertaken at the same level as that used in the optimization (e.g., MP2/6-311+G(2df,2pd)//MP2/6-31+G (d,p), etc.).

A few comments are in order with respect to the various levels of theory. (1) Closed-shell systems were treated with spin-restricted wave functions. Hartree−Fock optimizations and their subsequent MP2 single-point energy calculations on open-shell species were performed similarly (i.e., ROHF and ROMP2, respectively). In all other open-shell cases, spin-unrestricted wave functions were employed. (2) MP2 structures and energies were obtained by using the frozen-core (fc) approximation. (3) Density functional calculations were performed with a numerical quadrature that made use of a "fine" integration grid. This grid was formed from 75 radial shells per atom and 302 angular points per shell. The grid was subsequently "pruned" to yield approximately 7000 integration points per atom. (4) The MCSCF calculations employed the following active spaces: **cyclopropenyl systems**—three C−C σ bonds, one C=C π bond, the lone pair of electrons (or an unpaired electron in the case of the radical), three C−C σ* bonds, and one C=C π* bond (i.e., MCSCF-[10(9),9]); **acetonitrile systems**. The C−C and C−N σ bonds, both C=N π bonds, the lone pair of electrons on nitrogen, the lone pair of electrons (or an unpaired electron in the radical) on carbon, the C−C and C−N σ* bonds, and both C=N π* bonds (i.e., MCSCF[12(11), 10]); **cyclopropyl systems**—three C−C σ bonds, the lone pair of electrons (or an unpaired electron in the radical), and all three C−C σ* bonds (i.e., MCSCF[8(7),6]); **allyl systems**—both C−C σ bonds, one C=C π bond, the lone pair of electrons (or unpaired electron in the radical), two C−C σ* bonds, and the C=C π* bond (i.e., MCSCF-[8(7),6]). These active spaces represent the full valence except for the C−H bonds. All MCSCF calculations made use of the full optimized reaction space (FORS) model; this method is equivalently known as complete active space, self-consistent field (CASSCF) MCSCF.

The RHF, ROHF, ROMP2, and MCSCF calculations were performed with the GAMESS program.[23] All of the other computations were carried out using Gaussian 94.[24]

## Results and Discussion

**Cyclopropenyl System.** The potential energy surfaces for cyclopropene, cyclopropenyl radical, and cyclopropenyl anion (singlets and triplets) were extensively examined at the HF/6-31+G(d,p) and MP2/6-31+G(d,p) levels of theory. Within any given point group at the Hartree−Fock level, the full range of electronic states were investigated. The resulting lowest energy minima and transition structures served as the basis for further study at other theoretical levels.

As no detailed structural or energetic data are available experimentally for either the cyclopropenyl radical or anion,[25] direct comparisons between computational and experimental results are obviously not possible. Therefore, the geometries and energies obtained at the highest level of *ab initio* theory, CCSD(T)/6-311+G(2df,2pd)//MCSCF[10(9),9]/6-31+G(d,p) (referred to below as CCSD(T)//MCSCF), will be used as the benchmark for the results obtained at the other levels of theory. This provides a consistent means of evaluation. It also is reasonable given that some of the $C_3H_3$ species are not well described by a single configuration, and CCSD(T)//MCSCF thermochemical data have been shown to be quite reliable (*vide infra*).

**Structures.** Figure 2 depicts structures calculated at the MCSCF[10(9),9]/6-31+G(d,p) level. Upon deprotonation at the C3 position of the $C_{2v}$ ($^1A_1$) neutral (**4**), the $C_s$ ($^1A'$) anion (**5**)

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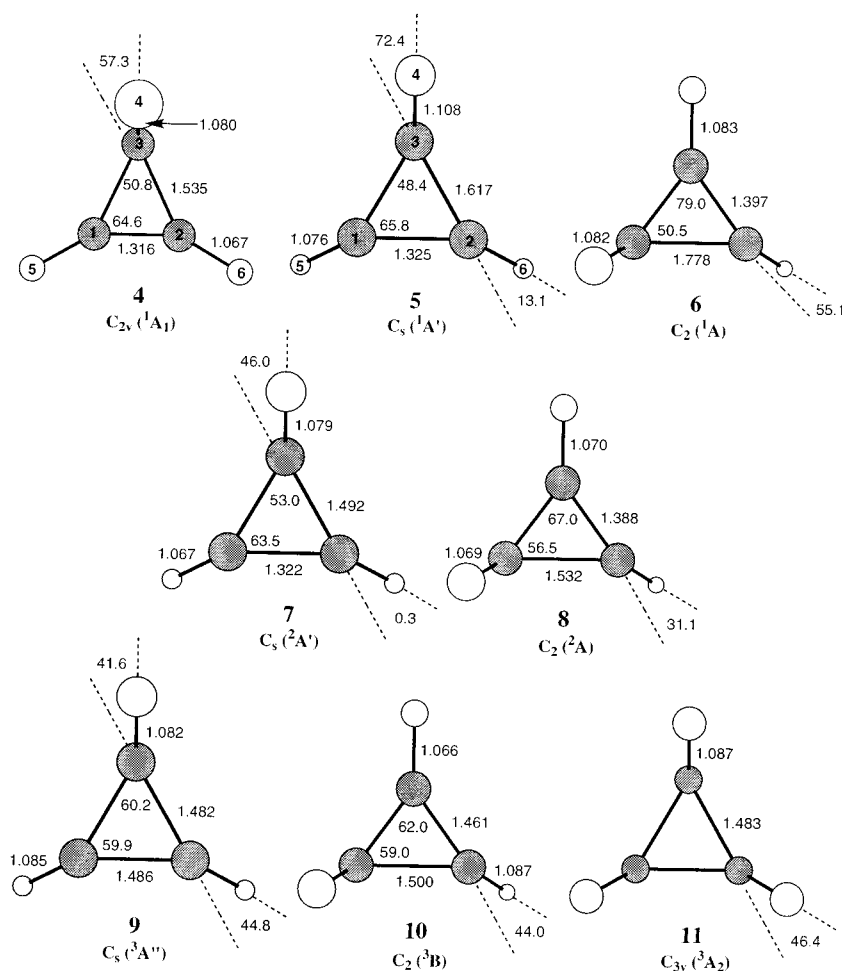
**Figure 2.** Cyclopropene and cyclopropenyl MCSCF[10(9),9]/6-31+G(d,p) optimized structures. All bond distances and angles are given in angstroms and degrees, respectively.

results.[26] Examination of the anion's structure (Table 1) reveals that the paraffinic bonds (C1—C3 and C2—C3) have increased by 0.082 Å and the C3—H4 distance has stretched by 0.028 Å. The olefinic hydrogens are now bent 13.1° out of the plane of the ring and have assumed a trans orientation to that of the unique hydrogen atom (H4). This hydrogen (H4), instead of bending toward the ring plane and thus increasing the overlap between the lone pair of electrons and the $\pi$-bond, moves 15.1° in the opposite direction and is 72.4° out of the plane. Mulliken population analysis (Supporting Information) of the change in the charge density upon deprotonation at the CCSD(T)/6-311+G(2df,2pd) level reveals that more than a third (0.42 e⁻) of the negative charge has been distributed to the two olefinic carbons and well over half (0.58 e⁻) still remains at the C3 position.[27]

Taken together the above changes in structure and charge density reflect an attempt by the ¹A′ anion to reduce the highly unfavorable interaction between the $\pi$-bond and the lone pair of electrons that results upon deprotonation of cyclopropene. A Jahn—Teller distortion away from the completely delocalized ion, which results from occupied degenerate (or near degenerate) orbitals, is accomplished primarily by stretching of the paraffinic bonds and partitioning the negative charge on opposite sides of

the cyclopropenyl ring. The charge localized ¹A′ anion stands in sharp contrast to that of the completely charge delocalized $D_{3h}$ cation (in this case the degenerate orbitals are unoccupied) and serves to accentuate the former's antiaromatic character.

Examination of the individual configurations that make up the ¹A′ MCSCF wave function reveals it to be fairly well-described by the closed-shell, ground-state determinant (~91%).[28] The remainder of the wave function is formed mainly from eight additional open-shell configurations (i.e., excited singlets). Alternatively, the natural orbital occupation numbers (NOONs)[29] are all within 0.1 electron (e⁻) of the doubly occupied or unoccupied values although two {1.9228 ($\pi$ (a′)) and 0.0793 ($\pi$* (a″))} are greater than 0.07 e⁻.[30] This also indicates that the structure is fairly well reproduced at the HF level.

Interconversion between identical $C_s$ (¹A′) cyclopropenyl anions (**5**) is achieved via a $C_2$ (¹A) transition structure (**6**) possessing an imaginary frequency along the reaction coordinate of 537i cm⁻¹. This structure for pseudorotation assumes an allylic quality by a 30.6° widening of the C1—C3—C2 angle. This results in a stretching of the (formerly) olefinic bond by 0.453 Å and a 0.220 Å shortening of the two paraffinic bonds.

(26) Cyclopropene is well-described by a single configuration and thus the MCSCF geometry would not be expected to reproduce the experimental structure any better than the HF data. For experimental data, see: (a) Benson, R. C.; Flygare, W. H. *J. Chem. Phys.* **1969**, *51*, 3087. (b) Stigliani, W. M.; Laurie, V. W.; Li, J. C. *J. Chem. Phys.* **1975**, *63*, 1890.

(27) In this work all of the reported atomic charges have the hydrogen contributions summed into the carbon atoms.

(28) The cyclopropenyl anion wave functions contain anywhere from 2676 (**5**) to 7560 (**11**) configurations. The CSF coefficient is 0.956 and thus 9% of the MCSCF wave function is made up of open-shell configurations.

(29) Löwdin, P. O. *Phys. Rev.* **1955**, *97*, 1474.

(30) When NOONs deviate by more than 0.07—0.1 from the closed-shell configuration, a multiconfiguration wave function is generally warranted. (a) Bone, R. G. A.; Pulay, P. *Int. J. Quantum Chem.* **1993**, *45*, 133. (b) Bofill, J. M.; Pulay, P. *J. Chem. Phys.* **1989**, *90*, 3637. (c) Pulay, P.; Hamilton, T. P. *J. Chem. Phys.* **1988**, *88*, 4926.

**Table 1.**   Geometric Parameters for Cyclopropene, Cyclopropenyl Anion, and Cyclopropenyl Radical[a]

| | curvature[b] | C2−C3 | C1−C2 | C3−H4 | C2−H6 | C1−C3−C2 | C1−C2−C3 | α | β |
|---|---|---|---|---|---|---|---|---|---|
| **4** ($C_{2v}$, $^1A_1$) | | | | | | | | | |
| MCSCF | min. | 1.535 | 1.316 | 1.080 | 1.067 | 50.8 | 64.6 | 57.3 | |
| B-VWN5 | min. | 1.526 | 1.306 | 1.096 | 1.082 | 50.7 | 64.7 | 56.8 | |
| B3-LYP | min. | 1.512 | 1.297 | 1.093 | 1.079 | 50.8 | 64.6 | 56.7 | |
| expt[c] | | 1.509 | 1.296 | 1.088 | 1.072 | 50.8 | 64.6 | 57.3 | |
| **5** ($C_s$, $^1A'$) | | | | | | | | | |
| MCSCF | min. | 1.617 | 1.325 | 1.108 | 1.076 | 48.4 | 65.8 | 72.4 | 13.1 |
| B-VWN5 | 244i cm$^{-1}$ | 1.598 | 1.314 | 1.127 | 1.092 | 48.5 | 65.7 | 71.0 | 13.8 |
| B3-LYP | min. | 1.573 | 1.305 | 1.119 | 1.087 | 49.0 | 65.5 | 70.2 | 13.8 |
| **6** ($C_2$, $^1A$) | | | | | | | | | |
| MCSCF | 537i cm$^{-1}$ | 1.397 | 1.778 | 1.083 | 1.082 | 79.0 | 50.5 | | 55.1 |
| B-VWN5 | min. | 1.385 | 1.748 | 1.106 | 1.100 | 78.2 | 50.9 | | 54.4 |
| B3-LYP | 238i cm$^{-1}$ | 1.375 | 1.682 | 1.098 | 1.096 | 75.4 | 52.3 | | 53.2 |
| **7** ($C_s$, $^2A'$) | | | | | | | | | |
| MCSCF | min. | 1.492 | 1.332 | 1.079 | 1.067 | 53.0 | 63.5 | 46.0 | 0.3 |
| B-VWN5 | min. | 1.476 | 1.327 | 1.097 | 1.083 | 53.4 | 63.3 | 45.1 | 0.5 |
| B3-LYP | min. | 1.463 | 1.317 | 1.093 | 1.080 | 53.5 | 63.2 | 44.6 | 0.6 |
| **8** ($C_2$, $^2A$) | | | | | | | | | |
| MCSCF | 824i cm$^{-1}$ | 1.388 | 1.532 | 1.070 | 1.069 | 67.0 | 56.5 | | 31.1 |
| B-VWN5 | 682i cm$^{-1}$ | 1.375 | 1.518 | 1.087 | 1.086 | 67.0 | 56.5 | | 29.1 |
| B3-LYP | 785i cm$^{-1}$ | 1.366 | 1.500 | 1.083 | 1.082 | 66.7 | 56.7 | | 28.4 |
| **9** ($C_s$, $^3A''$) | | | | | | | | | |
| MCSCF | min. | 1.482 | 1.486 | 1.082 | 1.085 | 60.2 | 59.9 | 41.6 | 44.8 |
| B-VWN5 | min. | 1.467 | 1.471 | 1.100 | 1.104 | 60.0 | 59.9 | 39.5 | 42.7 |
| B3-LYP | min. | 1.455 | 1.458 | 1.095 | 1.100 | 60.0 | 60.0 | 39.0 | 42.2 |
| **10** ($C_2$, $^3B$) | | | | | | | | | |
| MCSCF | 847i cm$^{-1}$ | 1.461 | 1.500 | 1.066 | 1.087 | 62.0 | 59.0 | | 44.0 |
| B-VWN5 | 719i cm$^{-1}$ | 1.448 | 1.485 | 1.082 | 1.106 | 61.7 | 59.0 | | 42.3 |
| B3-LYP | 723i cm$^{-1}$ | 1.436 | 1.472 | 1.078 | 1.100 | 61.6 | 59.2 | | 42.0 |
| **11** ($C_{3v}$, $^3A_2$) | | | | | | | | | |
| MCSCF | min. | 1.483 | | 1.087 | | | | 46.4 | |
| B-VWN5 | min. | 1.471 | | 1.106 | | | | 44.4 | |
| B3-LYP | min. | 1.458 | | 1.100 | | | | 44.0 | |

[a] All bond distances, angles, and vibrational frequencies are in angstroms, degrees, and cm$^{-1}$, respectively. Atomic labels are as shown in Figure 2 for **4** and **5**. α and β correspond to the H4 and H5(H6) out-of-plane angles, respectively. [b] Curvature associated with the potential energy surface in the vicinity of the stationary point:  min. ≡ minimum energy structure; $x$i cm$^{-1}$ ≡ transition structure. [c] Reference 26.

The negative charge is now almost completely localized on the terminal carbons (C1 and C2). These electronic changes are also somewhat reflected in the configurations that make up the $^1A$ MCSCF wave function. The relative weight of the closed-shell, lowest energy determinant has decreased (88.5%).[31] In terms of the NOONs, the highest energy σ (a) and lone-pair (a) orbitals and the lowest energy π* (b) and σ* (b) orbitals are occupied by 1.9338, 1.9322, 0.0708, and 0.0996 electrons, respectively, so **6** is in general less well described than **5** by a single configuration.

Excitation from the singlet to triplet potential energy surface leads to two minimum energy structures (**9** and **11**). The lower energy triplet is the $C_{3v}$ ($^3A_2$) anion (**11**). As this structure possesses 3-fold symmetry, the C−C and C−H bonds have equalized at 1.483 and 1.087 Å, respectively. The hydrogen atoms are bent 46.4° out of the plane of the ring, and the charge density is equally distributed among the three carbon atoms. The slightly higher energy $C_s$ ($^3A''$) anion (**9**) is structurally very similar to **11** except that one of the hydrogen atoms is now trans to the other two. Also, unlike its $C_s$ singlet counterpart (**5**), the negative charge has been shifted much more to the olefinic (C1 and C2) moiety.

Hückel theory predicts that cyclopropenyl anion should be a $D_{3h}$ ground state triplet. While this is clearly not the case (*vide infra*), it is interesting to evaluate the above triplet structures in light of this approximate theory. The equalization of the C−C bonds in the two anions, coupled with the more even charge distribution (especially for the $C_{3v}$ anion), is reminiscent of the

predictions made by Hückel theory. The unpairing of electrons in the singlet results in an appreciable reduction in the repulsive orbital overlap experienced by the triplets. From a structural standpoint, the triplet species have not undergone the same distortion experienced by the singlets. The two triplets can be viewed as cis and trans isomers of one another given that their MCSCF wave functions are nearly identical (e.g., the ground state determinant makes up 95% of both wave functions).[32] This also indicates that both species appear to be well-described by single configuration wave functions and is in accord with all of the NOONs being within 0.042 e$^-$ of their expected values.

As was the case for the $C_2$ ($^1A$) singlet anion (**6**), the $C_2$ ($^3B$) triplet (**10**) is a transition structure corresponding to pseudorotation between identical $^3A''$ anions. This structure differs markedly from that of the $^1A$ anion in that the C1−C3−C2 angle is 17.0° more acute, the olefinic (C1−C2) bond is 0.278 Å shorter, the paraffinic bonds (C1−C3 and C2−C3) are 0.064 Å longer, and the vinyl hydrogens are bent 11.1° less severely out of the plane of the ring. The charge distributions for the two $C_2$ anions also differ from each other. Whereas the negative charge has been largely shifted to the terminal carbons (C1 and C2) in **6**, it is essentially unchanged in the $^3B$ anion. Again, the lowest energy configuration makes up the preponderance of the wave function (95%),[33] and all of the NOONs are within 0.04 e$^-$ of their unoccupied, singly occupied, or doubly occupied values (0, 1, or 2).

(31) The CSF coefficient is 0.941, and thus 11.5% of the wave function is made up of open-shell determinants.

(32) The CSF coefficients for the lowest energy open-shell configuration are both 0.973.

(33) In this case the CSF coefficient is 0.974.

Electron loss from either the ${}^1$A′ singlet or ${}^3$A″ triplet leads to a ${}^2$A′ doublet with $C_s$ symmetry (**7**).[8e,34] Like the triplets, a substantial reduction (0.125 Å) in the paraffinic (C1−C3 and C2−C3) bonds is evident for **7** relative to **5**. The olefin distance (C1−C2) is essentially the same as in cyclopropene and the ${}^1$A′ anion, while the H4 and H5(H6) out-of-plane angles (α and β, respectively) are now only 46.0° and 0.3°, respectively. This corresponds to a 26.4° and 12.8° reduction in α and β relative to **5**. These structural changes are analogous to those seen for the triplets and is not surprising given that there is one less electron.

A comparison of the charge density differences between the singlet and triplet anions and the radical is uninformative given that the total number of electrons has been reduced by one in the later species. The spin distribution in **7**, based upon the Mulliken population analysis (0.94 e⁻ (C3) and 0.03 e⁻ (C1 and C2)) provides little indication of delocalization of the unpaired electron. The wave function for the ${}^2$A′ radical is reasonably described by the lowest energy doublet configuration (92.5% of the wave function) and an excited configuration (1.6% of the wave function).[35] All of the natural orbital occupation numbers are within 0.04 e⁻ of the predicted values except for the π (a′) and π* (a″) orbitals which have values of 1.9378 and 0.0646 electrons, respectively.

As can be readily guessed from the above discussion of the $C_2$ anions, the analogous $C_2$ radical (${}^2$A, **8**) is also a transition structure connecting identical ${}^2$A′ radicals via a pseudorotation process. While **8** is substantially allylic in nature, the C1−C2 bond is 0.246 Å shorter than in the ${}^1$A anion. The hydrogen atoms attached to C1 and C2 also are not bent as sharply out of the plane of the ring (31.1° vs 55.1°), and the spin density (C1-(C2) = 0.82 and C3 = −0.64) is spread more evenly around the ring than in the $C_s$ radical. Analysis of the wave function reveals there are appreciable contributions from excited configurations. In particular, quadruple and double excitations play an important role; the lowest energy doublet configuration makes up 89% of the MCSCF wave function, while configurations corresponding to quadruple and double excitations contribute 3.8% and 6.4%, respectively.[36] This is also reflected in the π (b) and π* (b) orbitals which have NOONs of 1.9134 and 0.0907 e⁻, respectively.

To summarize briefly these MCSCF results, it is clear that, while all of the wave functions are primarily composed of a single (lowest energy) configuration, each multiplicity shows a definite pattern with regard to contributions from excited configurations. It is thus possible to rank the wave functions with respect to the increasing importance of these additional configurations: triplets < doublets < singlets; in other words, a Hartree−Fock calculation on the triplets is apt to provide a better description of the wave function than similar computations on the doublets, etc.[37]

Structures for **4**−**11** were also optimized with more modest levels of *ab initio* theory (i.e., HF and MP2). While these results will not be discussed in detail, the geometric parameters and

Mulliken charges are provided in the Supporting Information. As for the nature of the stationary points, these levels reproduce the MCSCF results except for the $C_2$ (${}^2$A) radical and the $C_2$ (${}^1$A) anion. Hartree−Fock theory (ROHF) predicts the former species to be a stable energy minimum, while the latter ion is a minimum at the MP2 level. This last result represents a sporadic problem that we have encountered with MP2 optimizations.[38]

Three levels of density functional theory were also employed in this work (B-VWN5, B-LYP, and B3-LYP), and they yield structures which are for the most part consistent with one another and the MCSCF results. B-VWN5 most closely reproduces the MCSCF geometries, and in the worst case, the ${}^1$A anion, the C1−C2 bond distance differs by only 0.030 Å. The B-VWN5 and B-LYP functionals, like MP2 theory, do not reproduce the nature of the MCSCF stationary points on the singlet potential energy surface. In particular, B-VWN5 and B-LYP predict the $C_2$ (${}^1$A) anion to be a minimum energy structure and the $C_s$ (${}^1$A′) anion to be a transition structure. As has been previously noted in the literature, density functional theory tends to yield loose TS's.[39] This propensity is also found for the cyclopropenyl systems (e.g., the vibrational frequency along the reaction coordinate for the ${}^2$A radical is calculated by the B-VWN5 functional to be 142 cm⁻¹ less than that of the corresponding MCSCF frequency). Population analyses based upon B-VWN5 wave functions also reproduce results found for MP2 wave functions.

The poorest agreement between the density functional and MCSCF results occurs for the B3-LYP functional. Carbon−carbon single and double bond distances are always underestimated, usually by more than 0.020 Å. Conversely, C−H bonds are always overestimated, occasionally by greater than 0.020 Å. Given the rather poor structural agreement, it is interesting that, unlike the other two functionals, B3-LYP reproduces the curvatures of the MCSCF potential energy surfaces. The vibrational frequencies along the TS reaction coordinate are always predicted to be lower, but this difference is far less dramatic than that found for the other two functionals. One is led immediately to speculate on the importance of the inclusion of "exact" exchange in reproducing the essential features of the potential energy surfaces.[19]

The above structural and charge density comparisons enable us to rank the abilities of the different methodologies to reproduce the CCSD(T)//MCSCF results: B-VWN5 ≥ B-LYP > MP2 ≥ B3-LYP > MP2//HF, i.e., the B-VWN5 functional most closely duplicates the high-level *ab initio* results, followed by B-LYP, etc. This ordering, while clearly promising given the potential computational savings associated with density functional methods, must be tempered by the confusion surrounding the true nature (i.e., curvature) of the singlet potential energy surface.

**Energetics**. A number of thermochemical quantities can be calculated for the cyclopropenyl system. Unfortunately, very few experimental data are available with which to compare. The

(34) For recent calculations on the cyclopropenyl radical, see: (a) Byun, Y.-G.; Saebo, S.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 3689. (b) Jensen, F. *Chem. Phys. Lett.* **1989**, *161*, 368. (c) Usha, G.; Rao, B. N.; Chandrasekhar, J.; Ramamurthy, V. *J. Org. Chem.* **1986**, *51*, 3630. (d) Hoffmann, M. R.; Laidig, W. D.; Kim, K. S.; Fox, D. J.; Schaefer, H. F. *J. Chem. Phys.* **1984**, *80*, 338.

(35) The CSF coefficients are 0.962 and 0.127, respectively.

(36) Coefficients associated with the lowest energy doublet and the sums of the quadruple and doubly excited CSFs are 0.945, 0.195, and 0.253, respectively.

(37) The total deviations from the expected NOON values are 0.204 (**9**), 0.205 (**11**), and 0.199 (**10**) e⁻ for the triplets, 0.289 (**7**) and 0.339 (**8**) e⁻ for the doublets, and 0.350 (**5**) and 0.423 (**6**) e⁻ for the singlets.

(38) If a larger basis set than 6-31+G(d) or 6-31+G(d,p) is used (i.e., 6-311+G(2df,2pd)) or an MP3 optimization is carried out, the structure changes relatively little (especially in the former case), but the anion does become a TS.

(39) (a) Merrill, G. N.; Gronert, S.; Kass, S. R. *J. Phys. Chem. A* **1997**, *101*, 208. (b) Baker, J.; Andzelm, J.; Muir, M.; Taylor, P. R. *Chem. Phys. Lett.* **1995**, *237*, 53. (c) Latajka, Z.; Bouteiller, Y.; Scheiner, S. *Chem. Phys. Lett.* **1995**, *234*, 159. (d) Pederson, M. R. *Chem. Phys. Lett.* **1994**, *230*, 54. (e) Johnson, B. G.; Gonzales, C. A.; Gill, P. M. W.; Pople, J. A. *Chem. Phys. Lett.* **1994**, *221*, 100. (f) Stanton, R. V.; Merz, K. M., Jr. *J. Chem. Phys.* **1994**, *100*, 434. (g) Fan, L.; Ziegler, T. *J. Am. Chem. Soc.* **1992**, *114*, 10890.

**Table 2.** Calculated Proton Affinities (in kcal/mol) at 0 K for Cyclopropenyl and Mono-, Di-, and Tricyanocyclopropenyl Anions[a]

| substituent | MP2//HF | MP2 | CCSD(T)//MCSCF | B-VWN5 | B-LYP | B3-LYP |
|---|---|---|---|---|---|---|
| −H | 422.3 | 418.5 (420.9) | 418.9 [417.8][b] | (419.3) | (412.7) | 418.4 |
| −CN | 388.1 | 384.7 (404.2) | | 385.6 | 379.2 | 383.7 |
| −(CN)$_2$ | 379.1 366.2[b] | 375.6 363.4[c] | | (360.6) | (354.3) | 359.7[b] |
| −(CN)$_3$ | 350.7 | 348.1 (351.1) | | 346.3[b] | 340.3[b] | 345.0[b] |

[a] Parenthetical values are for the $C_2$ ($^1A$) anion. [b] G2 value from ref 8a. [c] Value for $C_1$ ($^1A$) anion.

results obtained at the CCSD(T)//MCSCF level of theory given their high degree of reliability will, therefore, once again serve as benchmarks for the values obtained with the other computational methods.

The proton affinity (PA) of cyclopropenyl anion is defined as the enthalpic change for eq 3 and is calculated to be 418.9 kcal/mol at the CCSD(T)//MCSCF level. This anion is thus
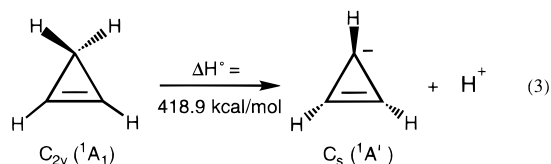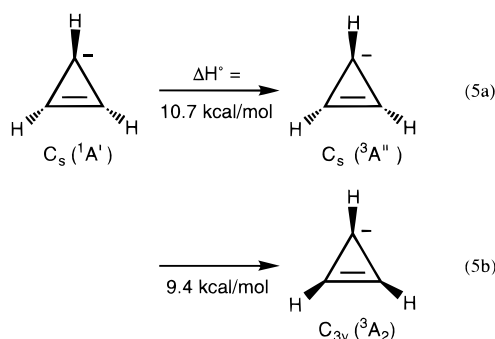


predicted to be more basic than methyl anion (PA(CH$_3^-$)$_{expt}$ $_{(0K)}$ = 415.2 ± 0.8 kcal/mol),[40] the strongest base that has been prepared in the gas phase. It also is less stable than cyclopropyl anion, and the difference, 5.8 kcal/mol (eq 4),[41] can be taken as a measure of the destabilization associated with cyclopropenyl anion (i.e., its antiaromaticity).
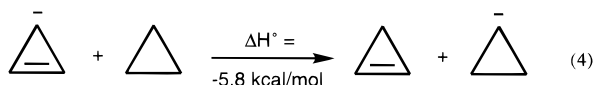


Calculated proton affinities of cyclopropenyl anion at other levels of theory are presented in Table 2. With the exception of the MP2//HF and B-LYP results, all of the other methods reproduce the CCSD(T)//MCSCF proton affinity to within 0.5 kcal/mol and are in good accord with species with known experimental values (Table 5). The MP2//HF proton affinity is too high by 3.4 kcal/mol, while that for B-LYP is too low by 6.2 kcal/mol. As we have noted in another study, the B-LYP functional consistently yields PA's that are too low.[42] It is also important to remember that the B-VWN5 and B-LYP PA's correspond to the $^1A$, and not the $^1A'$, anion; the PA's for the $^1A'$ transition structures are 420.1 and 413.5 kcal/mol, respectively, for the B-VWN5 and B-LYP functionals.

The CCSD(T)//MCSCF level of theory predicts that two low-lying electronic transitions between the singlet and triplet potential energy surfaces are possible: $^1A' \leftarrow {}^3A''$ and $^1A' \leftarrow {}^3A_2$ (eq 5). The calculated changes in enthalpy for eqs 5a and

(40) The experimental proton affinity was corrected to 0 K by using MP2/6-31+G(d,p) vibrational frequencies. For a critical review of measured thermodynamic data, see: Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

(41) The proton affinity of the cyclopropyl anion is calculated to be 411.3 and 413.2 kcal/mol at the CCSD(T)//MP2/6-31+G(d,p) and CCSD(T)// MCSCF[6,6]/6-31+G(d,p) levels, respectively. These results are in good agreement with an experimental determination of 411.5 (see ref 11). For the purposes of comparison (and consistency), we have employed the calculated value using the MCSCF geometry.

(42) Merrill, G. N.; Kass, S. R. *J. Phys. Chem.* **1996**, *100*, 17465.

5b are 10.7 and 9.4 kcal/mol, respectively. Values at other





theoretical levels are listed in Table 3, and they reproduce the relative ordering (i.e., $\Delta H°(5a) > \Delta H°(5b)$). However, the magnitude of the singlet−triplet splittings, except for the MP2 result, is underestimated. The largest discrepancies on average are 5.5 and 4.6 kcal/mol at the MP2//HF and B3-LYP levels, respectively. The other two density functionals do a good job at reproducing the CCSD(T)//MCSCF values; the B-VWN5 and B-LYP splittings are smaller on average by 1.2 and 1.9 kcal/mol, respectively (these mean values increase to 1.9 and 2.7 kcal/mol, respectively, when the $^1A'$ anion is used to calculate these splittings).

Any time an unrestricted calculation is performed, it is possible to infer something with regard to the quality of the wave function via the expectation value for the total spin, $\langle S^2 \rangle$. If the calculated value is within ±10% of that expected for a given multiplicity (e.g., 0.0 for singlets, 0.75 for doublets, 2.0 for triplets, etc.), the wave function is usually considered to be relatively free from contamination by higher multiplicities.[9] The current calculations reveal that none of the triplet wave functions are particularly suspect. On average, the calculated $\langle S^2 \rangle$ values are within 2.0, 0.3, 0.3, and 0.5% of the expected values for the MP2, B-VWN5, B-LYP, and B3-LYP levels of theory, respectively.[43]

The electron affinity (EA) of radicals has proved notoriously difficult to calculate directly. This is due primarily to the fact that the radical and its corresponding anion possess different numbers of electrons, and thus rather sophisticated treatments of electron correlation are generally required. Direct calculation of the EA, the change in enthalpy for eq 6, for the $^2A'$ radical
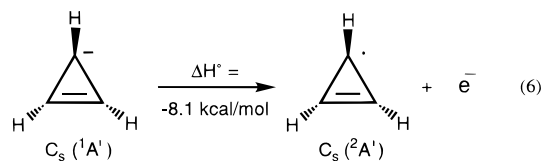


yields a value of −8.1 kcal/mol at the CCSD(T)//MCSCF level of theory. This result, as previously reported,[8e] indicates that the $^1A'$ anion is unbound with respect to spontaneous electron loss and should not, therefore, exist as a stable species in the gas phase. This does not mean (of course) that this species is "fictitious" in that it can be probed via techniques such as electron transmission spectroscopy and possibly the DePuy kinetic method.[10,11] Table 4 provides a complete listing of the directly calculated EA's. With one exception (B-VWN5), all of the methods predict the $^2A'$ ($^2A$) radical to be more stable than the corresponding $^1A'$ ($^1A$) anion.[44]

(43) The MP2//HF calculations were carried out within the restricted open-shell formalism and thus $\langle S^2 \rangle = 0.750$. The CCSD(T) wave function yields a $\langle S^2 \rangle$ value of 0.763.

(44) The $\langle S^2 \rangle$ values for the radical wave functions are 0.753, 0.752, 0.753, and 0.762 for B-VWN5, B-LYP, B3-LYP, and MP2, respectively.

**Table 3.** Singlet−Triplet Splittings (in kcal/mol) at 0 K for Cyclopropenyl and Cyanocyclopropenyl Anions[a]

| compound | transition | MP2//HF | MP2 | CCSD(T)//MCSCF | B-VWN5 | B-LYP | B3-LYP |
|---|---|---|---|---|---|---|---|
| cyclopropenyl anion | $^1A'(C_s) \leftarrow \,^3A_2(C_{3v})$ | 4.3 | 10.6 | 9.4 [13.0][b] | (7.6) | (6.7) | 4.8 |
| | $^1A'(C_s) \leftarrow \,^3A''(C_s)$ | 4.8 | 11.5 | 10.7 [14.2][b] | (8.7) | (8.0) | 6.1 |
| | $^1A(C_2) \leftarrow \,^3A_2(C_{3v})$ | (3.2) | 8.2 | (6.5) | 8.3 | 7.5 | (3.8) |
| | $^1A(C_2) \leftarrow \,^3A''(C_s)$ | (3.7) | 9.1 | (7.8) | 9.5 | 8.8 | (5.0) |
| cyanocyclopropenyl anion | $^1A'(C_s) \leftarrow \,^3A''(C_s)$ | 9.8 | 19.5[c] | (14.7)[d] | 7.7 | 7.3 | 6.1 |
| | $^1A'(C_s) \leftarrow \,^3B(C_2)$ | (9.3) | (20.1) | | 8.5 | 8.2 | 6.8 |

[a] Parenthetical values represent transitions from singlets that are *not* minima. [b] G2 values from ref 8a are given in brackets. [c] The $^1A(C_2) \leftarrow \,^3A''$ ($C_s$) transition is thermoneutral (0.6 kcal/mol). [d] In this case MP2/6-31+G(d,p) geometries were used (i.e., CCSD(T)/6-311+G (2df,2pd)//MP2/6-31+G(d,p) energies were employed).

**Table 4.** Electron Affinities at 0 K for Cyclopropenyl and Cyanocyclopropenyl Radicals (in kcal/mol) Calculated Directly and via the Isogyric Reaction c-$C_3H_2Y$ + $X^-$ → X + c-$C_3H_2Y^-$ (Y = H or CN; X = $CH_3$, c-$C_3H_5$, $CH_2CHCH_2$, and $CH_2CN$)[a]

| substituent | method | MP2//HF | MP2 | CCSD(T)//MCSCF | B-VWN5 | B-LYP | B3-LYP |
|---|---|---|---|---|---|---|---|
| −H | direct | −15.0 | −1.0 | −8.1[−4.2][c] | 2.5 | (−6.0) | −7.4 |
| | | −6.9[b] | (−3.3) | | (3.3) | | |
| | X = $CH_3$ | −4.2 | 2.1 | −3.4[−3.3][c,d] | (−4.8) | (−6.1) | −7.3 |
| | | 3.9[b] | (−0.2) | | | | |
| | X = c-$C_3H_5$ | −7.8 | −1.5 | −6.8[−4.7][c] | (−4.4) | (−4.7) | −6.6 |
| | | 0.3[b] | (−3.8) | | | | |
| | X = $CH_2CHCH_2$ | −14.1 | −8.0 | −5.6 | (−5.5) | (−6.4) | −8.4 |
| | | −6.0[b] | (−10.3) | | | | |
| | X = $CH_2CN$ | −8.5 | −9.9 | −5.9 | (−4.0) | (−4.6) | −8.2 |
| | | −0.4[b] | (−12.2) | | | | |
| | mean[e] | −8.6 | −4.3 | −5.4 | (−4.7) | (−5.4) | −7.6 |
| | | −0.6[b] | (−6.6) | | | | |
| −CN | direct | 16.9 | 34.5 | | 29.2 | 19.7 | 20.8 |
| | | 29.6[b] | (15.0) | | | | |
| | X = $CH_3$ | 27.7 | 37.6 | | 21.1 | 19.6 | 20.9 |
| | | 40.4[b] | (18.1) | | | | |
| | X = c-$C_3H_5$ | 24.1 | 34.0 | | 21.5 | 21.0 | 21.6 |
| | | 36.8[b] | (14.5) | | | | |
| | X = $CH_2CHCH_2$ | 17.8 | 27.5 | | 20.4 | 19.3 | 19.8 |
| | | 30.5[b] | (8.0) | | | | |
| | X = $CH_2CN$ | 23.4 | 25.6 | | 21.9 | 21.1 | 20.0 |
| | | 36.1[b] | (6.1) | | | | |
| | mean[e] | 23.2 | 31.2 | | 21.2 | 20.2 | 20.6 |
| | | 36.0[b] | (11.7) | | | | |

[a] Parenthetical values correspond to the $C_2(^1A)$ anion being converted to the $C_s(^2A')$ radical. [b] Value for the $C_s(^1A')$ anion going to the $C_2(^2A)$ radical. [c] G2 values from ref 8a are given in brackets. [d] RHF and ROHF structures were used for $CH_3^-$ and $CH_3$. [e] Only the results from the isogyric reactions were averaged.

Given the intrinsic difficulties associated with the direct calculation of EA's, computations were also carried out on four radicals with known experimental EA's so as to assess the reliability of the various theoretical levels. These results can be found in Table 5. Three of the methods perform in a superior fashion: B3-LYP, B-LYP, and CCSD(T)//MCSCF with absolute mean errors of 0.7, 0.8, and 2.7 kcal/mol, respectively. With the exception of B3-LYP and B-LYP, all of the methods had trouble reproducing the experimental EA for the methyl radical (1.8 ± 0.7 kcal/mol).[40] If methyl radical is excluded, the absolute mean error associated with the CCSD(T)//MCSCF calculation drops to 2.0 kcal/mol. It is also interesting to note that, while the MP2//HF and CCSD(T)//MCSCF levels consistently yield EA's that are too low, those obtained with the B-VWN5 functional are always too high. The wide range of errors for the MP2//HF and MP2 levels shows that these methods are unreliable for use in the direct calculation of electron affinities.

Isogyric reactions, in which the number of paired and unpaired electrons is conserved, have been employed in an attempt to avoid the shortcomings associated with the above direct calculations. This approach often leads to EA's that are in good agreement with those determined experimentally.[45] An added benefit to this approach is that low levels of theory, which

(45) Pople, J. A.; Schleyer, P. v. R.; Kaneti, J.; Spitznagel, G. W. *Chem. Phys. Lett.* **1988**, *145*, 359.

take little or no account of electron correlation, can often be used. The following isogyric reaction (eq 7) was employed in
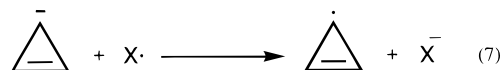


the current study where X is $CH_3$, c-$C_3H_5$, $CH_2CHCH_2$, or $CH_2$-CN. The EA for the species of interest, the cyclopropenyl radical, is then computed via eq 8 and the results are given in

$$EA(\text{c-}C_3H_3) = \Delta H°(7)_{calc} + EA(X)_{expt} \qquad (8)$$

Table 4. The average value derived for the CCSD(T)//MCSCF level is −5.4 kcal/mol, 2.7 kcal/mol greater than that calculated directly. This value is exactly reproduced by the B-LYP functional. The largest improvements are seen for the B-VWN5 and MP2 methods. The B-VWN5 functional had previously predicted the $^1A$ anion to be more stable than the $^2A'$ radical. Now, via the isogyric reactions, cyclopropenyl radical is found to be more stable and its EA differs from that calculated at the CCSD(T)//MCSCF level by only 0.7 kcal/mol! This represents an improvement of 10.7 kcal/mol. The average MP2 EA, depending upon which anion is used in the calculation, is either too high by 1.1 kcal/mol ($^1A'$) or too small by 1.2 kcal/mol ($^1A$). In contrast, at the MP2//HF level, the agreement between the average EA values obtained via the isogyric scheme depends upon which radical is used (mean difference = 4.8 ($^2A$) and

**Table 5.** Comparison of Experimental and Directly Calculated Proton Affinities (PA's), Electron Affinities (EA's), and Bond Dissociation Energies (BDE's) in kcal/mol[a]

|  | expt[b] | MP2//HF | MP2 | CCSD(T)//MCSCF[c] | B-VWN5 | B-LYP | B3-LYP |
|---|---|---|---|---|---|---|---|
| **PA (X⁻)** |  |  |  |  |  |  |  |
| $CH_3^-$ | 415.2 ± 0.8 | 419.7 | 416.0 | 418.8 [416.9] | 418.4 | 411.2 | 415.2 |
| $c\text{-}C_3H_5^-$ | 410.1 ± 2.0 | 416.1 | 411.3 | 413.1 [413.7] | 414.0 | 407.5 | 411.8 |
| $CH_2CHCH_2^-$ | 389.6 ± 2.1 | 391.9 | 386.3 | 390.4 | 389.3 | 382.2 | 386.0 |
| $^-CH_2CN$ | 371.3 ± 2.1 | 375.6 | 372.6 | 374.0 | 373.9 | 367.1 | 369.8 |
| $\alpha\text{-}c\text{-}C_3H_4CN^-$ | 374.0 ± 2.2[d] | 378.7 | 374.8 |  | 376.2 | 369.9 | 373.7 |
| mean error[e] |  | 4.4 | 0.2 | 2.5 | 2.3 | −4.5 | −0.7 |
| mean absolute error |  | 4.4 | 1.5 | 2.5 | 2.4 | 4.5 | 1.4 |
| **EA (X)** |  |  |  |  |  |  |  |
| $CH_3$ | 1.8 ± 0.7 | −9.0 | −1.3 | −2.9 [0.9] | 9.9 | 1.9 | 1.7 |
| $c\text{-}C_3H_5$ | 8.4 ± 2.0 | 1.2 | 8.9 | 7.1 [8.9] | 16.1 | 7.1 | 7.6 |
| $CH_2CHCH_2$ | 10.9 ± 0.2 | 10.0 | 17.9 | 8.4 | 19.7 | 11.3 | 11.9 |
| $CH_2CN$ | 35.6 ± 0.3 | 29.1 | 44.5 | 33.4 | 42.9 | 34.2 | 36.4 |
| mean error[e] |  | −6.4 | 3.3 | −2.7 | 8.0 | −0.6 | 0.2 |
| mean absolute error |  | 6.4 | 4.9 | 2.7 | 8.0 | 0.8 | 0.7 |
| **BDE (HX)** |  |  |  |  |  |  |  |
| $CH_3-H$ | 103.3 ± 0.1 | 98.1 | 101.0 | 102.3 [104.0] | 102.3 | 100.9 | 101.7 |
| $c\text{-}C_3H_5-H$ | 104.8 ± 0.3[f] | 104.6 | 106.6 | 106.6 [108.8] | 104.0 | 102.4 | 104.2 |
| $CH_2CHCH_2-H$ | 86.7 ± 2.1 | 89.2 | 90.6 | 85.1 | 82.9 | 81.2 | 82.8 |
| $H-CH_2CN$ | 93.3 ± 2.1 | 92.1 | 103.5 | 93.7 | 90.7 | 89.0 | 91.1 |
| mean error[e] |  | −1.0 | 3.4 | −0.1 | −2.0 | −3.7 | −2.1 |
| mean absolute error |  | 2.3 | 4.6 | 1.2 | 2.0 | 3.7 | 2.1 |

[a] All values at 0 K. [b] The experimental proton affinities and the c-C₃H₅−H BDE were temperature corrected to 0 K using MCSCF vibrational frequencies. See ref 40 for the 298 K data. [c] G2 values come from ref 8a and are in brackets. RHF and ROHF structures were used for CH₄, CH₃⁻, and CH₃. [d] Corrected to 0 K using MP2 vibrational frequencies. [e] Mean error: $E_{error} = \sum_n (E_{calc} - E_{expt})/n$. Mean absolute error: $E_{error} = \sum_n |E_{calc} - E_{expt}|/n$. [f] The 298 K value comes from: McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

3.2 (²A′) kcal/mol; direct = 1.2 (²A) and 6.9 (²A′) kcal/mol. Finally, the B3-LYP mean value decreased only slightly from −7.4 kcal/mol to −7.6 kcal/mol, while the discrepancy with the benchmark increased from 0.7 kcal/mol to 2.2 kcal/mol.

Anions that are energetically less stable than their corresponding radicals are often referred to as metastable or temporary species. The cyclopropenyl anion by virtue of its negative EA is just such one example. These anions present unique computational challenges. As has been observed by Jordan and co-workers, solutions to the eigenvalue problem for metastable anions fall within the continuum for electron−molecule scattering.[46] As the basis set used to describe these wave functions increases in flexibility, solutions risk convergence to the neutral plus free-electron limit. Closed-shell systems (i.e., those represented within the restricted formalism) are not expected to suffer from this potential problem as the energetic costs associated with removing two electrons to infinite separation are prohibitive. This is not the case for open-shell species with their half-filled orbitals.

Within the present context, the calculations performed upon the cyclopropenyl triplets are thus suspect. To investigate the possibility that our triplet solutions correspond to the cyclopropenyl radical plus a free electron, stabilization calculations along the lines proposed by Jordan et al.[46b] were carried out, and their effect upon the singlet−triplet splittings was examined. Briefly, the singlet and triplet cyclopropenyl anions were surrounded by a "sphere" of positive charge (*Q*) and radius (*R*), the sphere being simulated by a series of partial charges (*q*). It has been shown previously that such an approach is capable of converting unbound systems into bound ones. The radius of and the charge on the sphere were varied, and their impact upon the singlet−triplet gap explored. It was found that, over a wide range of values for *R* and *Q*, the calculated gap did not change

significantly (<2 kcal/mol) from the directly determined value (i.e., without the positively charged sphere). The conclusion to be drawn is that the 6-31+G(d,p) and 6-311+G(2df,2pd) bases do not lead to radical plus free electron solutions for the cyclopropenyl triplets.[47]

The C−H bond dissociation energies (BDE's) are presented in Table 6 and correspond to the enthalpy change for eq 9. The



$$C_{2v}\ (^1A_1) \xrightarrow[\text{97.2 kcal/mol}]{\Delta H^\circ =} C_s\ (^2A') + H^\bullet \qquad (9)$$
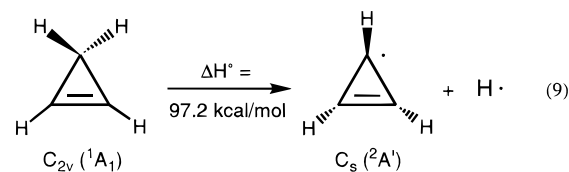
CCSD(T)//MCSCF level of theory predicts a C−H bond dissociation energy of 97.2 kcal/mol. With the exception of the MP2 calculation, which is overbound by 6.7 kcal/mol, all of the other levels yield a narrow range of values: 94.5 to 96.5 kcal/mol. The performance of the B-VWN5 functional is especially noteworthy given its rather poor ability to duplicate experimental EA's. Both thermodynamic quantities (BDE's and EA's) require the determination of enthalpies for processes in which a closed-shell system is converted to an open-shell one. The additional energy contribution for the hydrogen atom in the above BDE calculation may serve to diminish errors associated with open-shell species.[48]

As the allylic C−H BDE for cyclopropene is of some interest and the experimental value of 90.6 ± 4.0 kcal/mol has been called into question,[25] isogyric reactions similar to those used for calculating the electron affinity of cyclopropenyl radical (eq 7) were employed (eq 10, X = CH₃, c-C₃H₅, CH₂CHCH₂, or

(46) (a) Falcetta, M. F.; Jordan, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 2903. (b) Chao, J. S.-Y.; Falcetta, M. F.; Jordan, K. D. *J. Chem. Phys.* **1990**, *93*, 1125.

(47) It is also worth noting that if one carries out a "free" electron calculation (see ref 46) to obtain the one-electron continuum, the singly occupied MO energy level lies above that of the anion. This also suggests that our calculations do not correspond to radical + free electron solutions.
(48) The B-VWN5/6-311+G(2df,2pd) energy for H• is −0.51969 hartree, which is in error by 12.3 kcal/mol from the exact value of −0.5 hartree.

**Table 6.** C−H Bond Dissociation Energies (in kcal/mol) at 0 K for Cyclopropene and Cyanocyclopropene via Direct Calculation and the Isogyric Reaction c-C₃H₃Y + X → c-C₃H₂Y + HX (Y = H or CN; X = CH₃, c-C₃H₅, CH₂CHCH₂, and CH₂CN)[a]

| substituent (Y) | method | MP2//HF | MP2 | CCSD(T)// MCSCF[b] | B-VWN5 | B-LYP | B3-LYP |
|---|---|---|---|---|---|---|---|
| −H | direct | 94.6 (102.7) | 103.9 | 97.2 [99.9] | 96.5 | 94.5 | 95.9 |
| | X = CH₃ | 99.8 (107.9) | 106.2 | 98.2 [98.3] | 97.5 | 96.9 | 97.5 |
| | X = c-C₃H₅ | 94.8 (102.9) | 102.1 | 95.4 [95.0] | 97.3 | 96.9 | 96.5 |
| | X = CH₂CHCH₂ | 92.1 (100.2) | 100.0 | 98.8 | 100.3 | 100.0 | 99.8 |
| | X = CH₂CN | 95.8 (103.9) | 93.7 | 96.8 | 99.1 | 98.8 | 98.1 |
| mean[c] | | 95.6 (103.7) | 100.5 | 97.3 | 98.6 | 98.2 | 98.0 |
| mean absolute error[d] | | 2.9 (6.5) | 5.0 | 1.2 | 1.4 | 1.2 | 1.1 |
| −CN | direct | 92.4 (105.0) | 105.6 | | 88.7 | 86.7 | 89.4 |
| | X = CH₃ | 97.6 (110.2) | 107.9 | | 89.7 | 89.1 | 91.0 |
| | X = c-C₃H₅ | 92.6 (105.2) | 103.8 | | 89.5 | 89.1 | 90.0 |
| | X = CH₂CHCH₂ | 89.9 (102.5) | 101.7 | | 92.5 | 92.2 | 93.3 |
| | X = CH₂CN | 93.6 (106.2) | 95.4 | | 91.3 | 91.0 | 91.6 |
| mean[c] | | 93.4 (106.0) | 102.2 | | 90.8 | 90.4 | 91.5 |
| mean absolute error[d] | | 4.0 (16.6) | 12.8 | | 1.4 | 1.2 | 2.1 |

[a] Parenthetical values are for the C₂ (²A) radical. [b] G2 values are in brackets and come from ref 8a. RHF and ROHF structures were used for CH₄ and CH₃. [c] Mean of four isogyric reactions. [d] Relative to the CCSD(T)//MCSCF direct value. [e] Relative to the B3-LYP direct value.



$$\text{(10)}$$
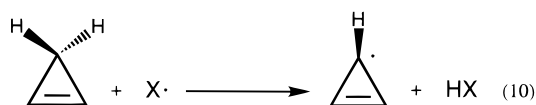
CH₂CN). The desired bond dissociation energy is obtained via eq 11, and the results are summarized in Table 6. All of the

$$\text{BDE(c-C}_3\text{H}_3\text{−H)} = \Delta H°(10)_{\text{calc}} + \text{BDE(HX)}_{\text{expt}} \quad (11)$$

theoretical methods, except MP2, show good agreement between the various isogyric values and the directly calculated C−H BDE. The mean values span a narrow range from 95.6 to 98.6 kcal/mol except for the MP2 result (100.5 kcal/mol). From these data it appears that the bond strength is around 98 kcal/mol at 0 K, which is in excellent accord with the values of Petersson (99.0 kcal/mol, CBS-QCI/APNO)[49] and Glukhovtsev et al. (99.9, G2).[8a] All are slightly smaller than Chen's estimate at 298 K of ~104 kcal/mol.[25,50] In any case, an experimental reinvestigation of this quantity is warranted.

The final thermodynamic value of relevance to the current work concerns the enthalpic change associated with the symmetry-forbidden ring-opening process (eq 12).[8e] ROHF and



$$\text{(12)}$$
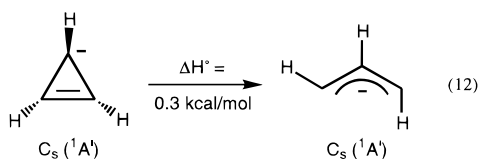
UMP2 calculations predict that the C_s (¹A′) isomer is the most

(49) Montgomery, J. A., Jr.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900.

(50) At 0 K this value will drop to ~102 kcal/mol.

stable open C₃H₃ anion, and so it was optimized at the MCSCF level. It too is an energy minimum on the potential energy surface. A similar structure was obtained with B3-LYP, whereas B-VWN5 and B-LYP give C₁ (¹A) minima. Structural comparisons between the various theoretical levels lead to conclusions that closely parallel those for the cyclic isomers (for more information on this species see the Supporting Information). Energetically, the ring-opening is found to be essentially thermoneutral (ΔH° = +0.3 kcal/mol) at the CCSD-(T)//MCSCF level. More endothermic enthalpies are obtained at the MP2//HF (3.3 kcal/mol) and MP2 (4.4 and 6.8 kcal/mol) levels of theory, while exothermic processes are found for the DFT methods (B-VWN5 = −4.0 kcal/mol; B-LYP and B3-LYP = −2.5 kcal/mol). The C₃H₃⁻ acyclic anion, unlike its cyclic counterpart, was found to be stable with respect to electron loss, but it will not be discussed further within the context of this work other than to note that experimental investigations into this unusual anion are presently being carried out in our laboratory. A computational study at the same levels of theory as performed in this paper has been completed and will be reported in due course.

**Cyanocyclopropenyl System.** Introduction of an electron-withdrawing group on to a cyclopropenyl anion (e.g., c-C₃H₂Z⁻, where Z = CF₃, CO₂Me, CN, etc.) will stabilize the ion with respect to its conjugate acid and corresponding radical. The substituted species will thus be less basic and more tightly bound than the parent. These changes should facilitate the preparation of a stable cyclopropenyl anion and, consequently, the cyano-cyclopropenyl anion was examined. MCSCF structures would be desirable, but the comparable active space to that used for the parent system (20 electrons in 18 orbitals, i.e., an MCSCF-[20,18] calculation) is prohibitively large. Optimizations were, therefore, carried out at the other theoretical levels used for the
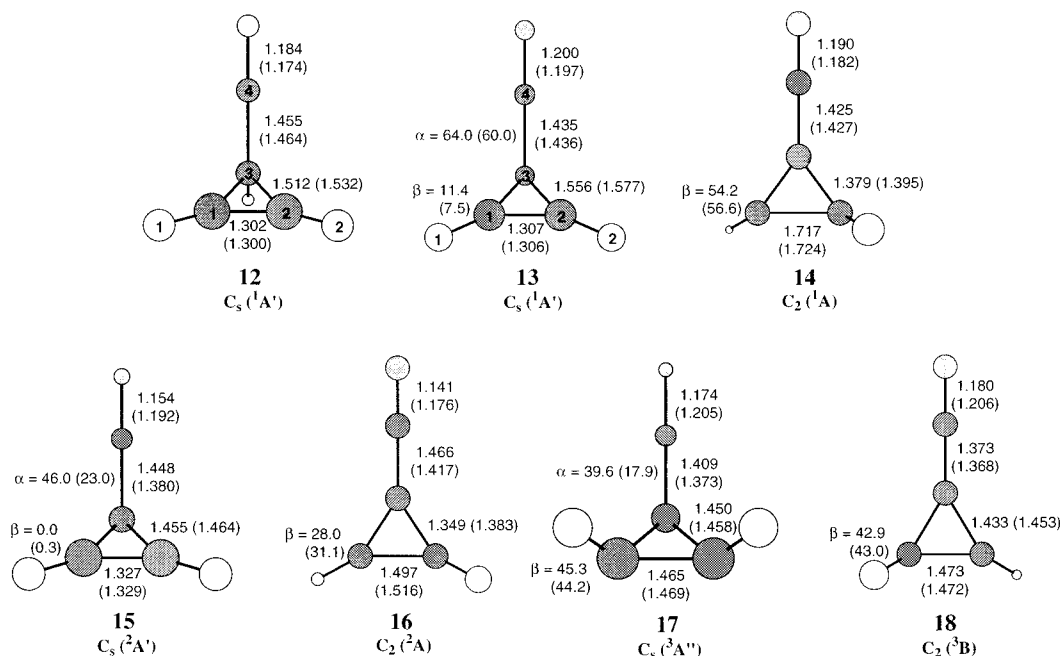
[MP2/6-31+G(d,p) structural parameters are given. Parenthetical values are for the B-VWN5/6-31+G(d,p) geometries.]

**Figure 3.** Cyanocyclopropene and cyanocyclopropenyl B-VWN5/6-31+G(d,p) optimized structures. All bond distances and angles are given in angstroms and degrees, respectively.

**Table 7.** Geometric Parameters for Cyanocyclopropene, Cyanocyclopropenyl Anion, and Cyanocyclopropenyl Radical[a]

| | curvature[b] | C2–C3 | C1–C2 | C3–C4 | C4–N | H3–C3 | H1–C1 | C1–C3–C2 | C2–C1–C3 | N–C4–C3 | α | β |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **12** ($C_s$, $^1$A′) | | | | | | | | | | | | |
| MP2 | min. | 1.512 | 1.302 | 1.455 | 1.184 | 1.086 | 1.074 | 51.0 | 64.5 | 178.9 | 56.5 | 0.3 |
| B-VWN5 | min. | 1.532 | 1.300 | 1.464 | 1.174 | 1.094 | 1.081 | 50.2 | 64.9 | 179.3 | 55.7 | 0.6 |
| expt[c] | | 1.511 | 1.292 | 1.453 | 1.162 | 1.092 | 1.071 | 50.6 | 64.7 | | 57.1 | |
| **13** ($C_s$, $^1$A′) | | | | | | | | | | | | |
| MP2 | min. | 1.556 | 1.307 | 1.435 | 1.200 | | 1.079 | 49.6 | 65.2 | 171.2 | 64.0 | 11.4 |
| B-VWN5 | min. | 1.577 | 1.306 | 1.436 | 1.197 | | 1.087 | 49.0 | 65.5 | 168.6 | 60.0 | 7.5 |
| **14** ($C_2$, $^1$A) | | | | | | | | | | | | |
| MP2 | min. | 1.379 | 1.717 | 1.425 | 1.190 | | 1.089 | 77.0 | 51.5 | | | 54.2 |
| B-VWN5 | 195i cm$^{-1}$ | 1.395 | 1.724 | 1.427 | 1.182 | | 1.100 | 76.4 | 51.8 | | | 56.6 |
| **15** ($C_s$, $^2$A′) | | | | | | | | | | | | |
| MP2 | min. | 1.455 | 1.327 | 1.448 | 1.154 | | 1.075 | 54.2 | 62.9 | 180.0 | 46.0 | 0.0 |
| B-VWN5 | min. | 1.464 | 1.329 | 1.380 | 1.192 | | 1.082 | 54.0 | 63.0 | 173.5 | 23.0 | 0.3 |
| **16** ($C_2$, $^2$A) | | | | | | | | | | | | |
| MP2 | 1236i cm$^{-1}$ | 1.349 | 1.497 | 1.466 | 1.141 | | 1.076 | 67.4 | 56.3 | | | 28.0 |
| B-VWN5 | 1091i cm$^{-1}$ | 1.383 | 1.516 | 1.417 | 1.176 | | 1.086 | 66.4 | 56.8 | | | 31.1 |
| **17** ($C_s$, $^3$A″) | | | | | | | | | | | | |
| MP2 | min. | 1.450 | 1.465 | 1.409 | 1.174 | | 1.090 | 60.6 | 59.7 | 177.6 | 39.6 | 45.3 |
| B-VWN5 | min. | 1.458 | 1.469 | 1.373 | 1.205 | | 1.103 | 60.4 | 59.8 | 175.8 | 17.9 | 44.2 |
| **18** ($C_2$, $^3$B) | | | | | | | | | | | | |
| MP2 | 130i cm$^{-1}$ | 1.433 | 1.473 | 1.373 | 1.180 | | 1.089 | 62.0 | 59.0 | | | 42.9 |
| B-VWN5 | min. | 1.453 | 1.472 | 1.368 | 1.206 | | 1.100 | 60.8 | 59.6 | | | 43.0 |

[a] All bond distances, angles, and vibrational frequencies are in angstroms, degrees, and cm$^{-1}$, respectively. Atomic labels are as shown in Figure 3 for **12** and **13**. α and β correspond to the C4 and hydrogen out-of-plane angles, respectively. [b] Curvature of the potential surface in the vicinity of the stationary point. [c] See: Staley, S. W.; Norden, T. D.; Su, C.-F.; Rall, M.; Harmony, M. D. *J. Am. Chem. Soc.* **1987**, *109*, 2880.

cyclopropenyl system (HF, MP2, B-VWN5, B-LYP, and B3-LYP). The resulting structures are discussed below in terms of those obtained with the B-VWN5 functional as this method reproduced the MCSCF [10(9),9]/6-31+G(d,p) geometries for the parent ion most closely.

**Structures.** Substitution of a cyano group on to the cyclopropenyl ring eliminates any potential for 3-fold symmetry and reduces the number of permissible point groups. All of the possible symmetries ($C_1$, $C_s$, $C_2$, or $C_{2v}$) were examined; the important species (minima and transition structures) are illustrated in Figure 3 and summarized in Table 7.

Upon deprotonation of the $C_s$ ($^1$A′) neutral (**12**),[51] a $C_s$ ($^1$A′) anion (**13**), similar to **4**, results. The two paraffinic bonds (C1–C3 and C2–C3) in **13** are 0.045 Å longer than those in **12**, the

cyano group is bent farther from the ring plane (α = 60.0° vs 55.7°), and the olefinic hydrogens are bent 7.2° farther from the ring in the direction opposite to the nitrile. The C3–C4–N angle (168.6°) has also decreased significantly from near linearity (179.3°). Smaller structural changes, such as a reduction of the C3–C4 (C–CN) and a lengthening of the C4–N (C≡N) bonds, are evident too. This substituted ion is flatter than its parent (α = 60.0° vs 71.0° and β = 7.5° vs 13.8°)

(51) The isomeric 1-cyanocyclopropene is 1.4 kcal/mol higher in energy than **12** at the MP2/6-31+G(d)//HF/6-31+G(d) level. The corresponding cyclopropenyl anion also was found to be an energy minimum at the HF level. It is 9.5 kcal/mol higher in energy than **13** (MP2/6-31+G(d)//HF/6-31+G(d)) and disappears from the potential surface at the MP2 level. For further details, see: Sachs, R. K. Ph.D. Thesis, University of Minnesota, 1993.

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as would be expected given that the cyano group is a resonance-stabilizing substituent. The $\alpha$ out-of-plane angle is comparable to that found for cyanocyclopropyl anion ($\alpha = 53.7°$), the saturated analog of **13**. This is presumably because of inductive stabilization of the charge. As in the case of cyclopropenyl anion, these structural changes represent an attempt to reduce the repulsive interaction between the olefinic moiety and the negative charge. The Mulliken population analysis supports this conclusion in that only a little of the negative charge has been shifted to the C1 and C2 positions and most of it remains concentrated at C3. Some of the charge, of course, has also shifted to the more electronegative nitrogen atom.

Four of the five calculations that were carried out (HF, B-VWN5, B-LYP, and B3-LYP) indicate that the $C_2$ ($^1A$) cyanocyclopropenyl anion is a transition structure. The sole exception is at the MP2 level where the $^1A$ anion is found to be a minimum energy structure as was the case with the $C_2$ ($^1A$) cyclopropenyl anion. There also are large differences with regard to the vibrational frequency along the TS reaction coordinate. All three density functionals underestimate the HF frequency by anywhere from 591 (B3-LYP) to 849 (B-LYP) cm$^{-1}$. As for the structures, the HF geometry shows the greatest variation from the others. The paraffinic, C≡N triple, and (especially) the C1−C2 bonds are all much shorter. This last bond distance is also much shorter (0.052 Å vis-à-vis the B-VWN5 calculation) in the B3-LYP structure. Otherwise, there is good agreement between the different methods.

All five of the computational approaches predict that the $C_s$ ($^3A''$) triplet (**17**) is a minimum energy structure, and the resulting geometries are for the most part in good agreement with one another. The HF and MP2 structures have longer C1−C4 (C−CN) and shorter C4−N (C≡N) bond lengths than those calculated with density functional theory; the cyano group is also bent more steeply out of the ring plane for the *ab initio* methods. In addition, the paraffinic bonds are somewhat shorter at the HF level than for the other methods. The charge density distributions for the $^3A''$ triplet (**17**) differ significantly from those of the $^1A'$ singlet (**13**). All of the negative charge has been transferred from the C3 carbon atom to the cyano group (specifically the C4 position) and the olefinic C1 and C2 carbons. This shifting of the charge out of the cyclopropenyl ring results in the near equalization of the C−C bonds, a fact that corresponds to a significant reduction in the repulsive forces within the cyclopropenyl ring.

Somewhat surprisingly, all three density functionals predict the $C_2$ ($^3B$) triplet to be a minimum energy structure. This stands in sharp contrast to the results from the two *ab initio* methods and the previously discussed data for the $C_2$ cyclopropenyl species. Regardless of this discrepancy, the geometries are extremely similar at all levels with the notable exception of that obtained with the Hartree−Fock method. Again, the carbon−nitrogen triple bond distances are most at variance. The charge densities mirror those found for the $^3A''$ triplet although there are some differences which depend upon the computational method. In addition, both of the triplet wave functions ($^3A''$ and $^3B$) determined at all five levels of theory are relatively free of contamination from higher multiplicities.

The minimum energy structure on the doublet potential energy surface has $C_s$ ($^2A'$) symmetry. Relative to the $^1A'$ neutral, reductions in the paraffinic and an increase in the olefinic bonds are predicted. The *ab initio* geometries display their characteristically short carbon−nitrogen triple bonds, the C3−C4 (C−CN) distances are too long, and the cyano group is bent much farther out of the plane of the ring. As for the $C_2$ ($^2A$) cyclopropyl radical, the corresponding cyano radical is found

to be a transition structure except at the HF level. The imaginary frequencies along the TS reaction coordinate are all in good agreement with one another, but the DFT geometries are more "allylic-like" than their *ab initio* counterparts. Like their $C_s$ ($^2A'$) counterparts, the HF and MP2 structures have longer C3−C4 (C−CN) and shorter C1−C2 (olefinic) bonds. There is considerable spin contamination of the $^2A$ UMP2 wave function, $\langle S^2 \rangle = 1.065$, and thus the overall reliability of this calculation is called into question. The expectation value for the $^2A'$ MP2 radical, $\langle S^2 \rangle = 0.817$, is also somewhat high. Once again, there is little spin contamination in the density functional wave functions.

**Energetics.** The proton affinity of the $^1A'$ ($C_s$) cyanocyclopropenyl anion was calculated, and the MP2, B-VWN5, and B3-LYP values (384.7, 385.6, and 383.7 kcal/mol), as was found for the parent ion (**1**), are in good accord with one another (eq 13, Table 2). Similarly, the relative ordering of the proton



$$\text{C}_s\ (^1A') \xrightarrow[\Delta H° = 385.6\text{ kcal/mol}]{} \text{C}_s\ (^1A') + \text{H}^+ \qquad (13)$$
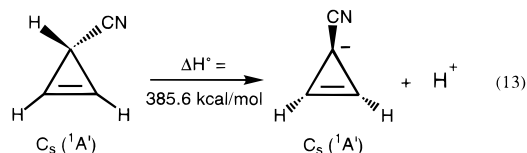
affinities is the same as for **1** (i.e., MP2/HF > B-VWN5 > MP2 > B3-LYP > B-LYP), and the MP2/HF and B-LYP energies are once again approximately 3 and 6 kcal/mol too high and low, respectively. The calculated proton affinity of cyanocyclopropyl anion (Table 5) is 9.6 kcal/mol smaller than that of cyanocyclopropenyl anion,[52] indicating that the latter is less stable than its saturated counterpart (eq 14). This desta-



$$\xrightarrow[\Delta H° = -9.6\text{ kcal/mol}]{} \qquad (14)$$
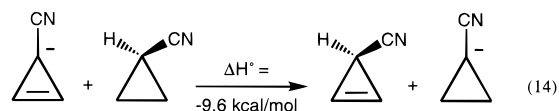
bilization energy is larger than for the unsubstituted case (5.8 kcal/mol, eq 4), because the cyano group stabilizes cyclopropyl anion 3.7 kcal/mol *more* than cyclopropenyl anion. One might have expected exactly the opposite: the cyano substituent removes electron density from the unsaturated three-membered ring and should diminish the unfavorable $4\pi$ electron interaction. Substitution of a hydrogen atom by a cyano group in cyclopropyl or cyclopropenyl anion, however, results in a flattening of the ion (e.g., the out-of-plane angle ($\alpha$) diminishes by 7.0° and 5.6°, respectively, at the MP2 level) in order to delocalize some of the charge at the C3 position on to the nitrogen. This also leads to an increase in the unfavorable overlap between the lone pair orbital on C3 and the $\pi$-bond. These conflicting effects are absent in the saturated system, and it is stabilized to a greater extent by the cyano group. In accord with this explanation, the cyanocyclopropenyl anion inversion barrier is 12.1 kcal/mol larger than that for cyanocyclopropyl anion at the MP2/6-31+G(d)//HF/6-31+G(d) level.[51] It is also worth adding that if one forces the out-of-plane nitrile in cyanocyclopropenyl anion (or the corresponding hydrogen in **1**) into the plane of the ring, the carbon−carbon olefinic distance dramatically increases and the two (formerly) vinyl hydrogens bend significantly to minimize the unfavorable $4\pi$ electron interaction (Tables 1 and 7). If these distortions are prevented, as in the $C_{2v}$ ($^1A_1$, c-C₃H₂-CN⁻) or $D_{3h}$ ($^1A_1'$, C₃H₃⁻) ions, the resulting structures are

(52) For comparison purposes, the average of the MP2/HF, MP2, B-VWN5, B-LYP, and B3-LYP differences (i.e., 9.4, 9.9, 9.4, 9.3, and 10.0 kcal/mol, respectively) was used. In addition, PA(cyclopropyl anion−cyanocyclopropyl anion) − PA(cyclopropenyl anion−cyanocyclopropenyl anion) = 37.7 − 34.0 or 3.7 kcal/mol.

higher-order saddle points and energetically unfavorable (e.g., $\Delta E(C_{2v} - \mathbf{13}(C_s)) = 20.4$ kcal/mol at the MP2/6-31+G(d,p) level).[53]

Adiabatic electronic transitions between the singlet and triplet cyanocyclopropenyl potential energy surfaces (eqs 15a and 15b) have been calculated, and the values are tabulated in Table 3.
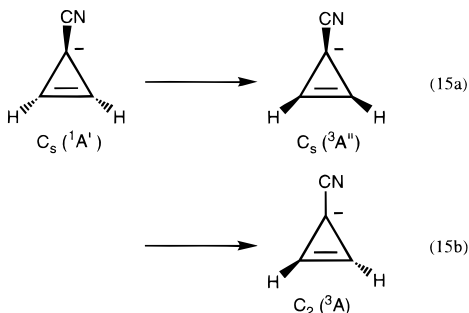


The density functional and MP2//HF singlet−triplet gaps are in reasonable agreement with each other whereas the MP2 energy difference is considerably larger. In contrast, the cyclopropenyl anion singlet−triplet gaps are in good agreement at the MP2, B-VWN5, and B-LYP levels as well as with the CCSD(T)//MCSCF value; here, the MP2//HF and B3-LYP splittings appear to be ∼5 kcal/mol too small. CCSD(T)/6-311+G(2df,2pd)//MP2-6-31+G(d,p) single point calculations were, therefore, carried out and the singlet−triplet gap was found to decrease only slightly (4.8 kcal/mol) from the MP2 result. Consequently, even though DFT has shown promise for accurately reproducing singlet−triplet splittings,[54] it is difficult to assess in this instance whether the cyano group increases the energy gap (as indicated by the changes in the *ab initio* calculations) or has little bearing on it. Further discussion of this quantity, therefore, is not warranted at this time.

Direct calculation of the electron affinity of cyanocyclopropenyl radical (eq 16) yields a wide range of values; these are
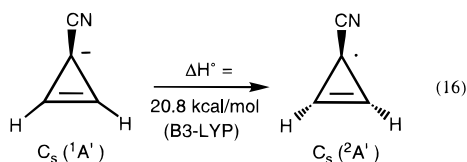


compiled in Table 4 along with those for the cyclopropenyl radical. Given the difficulties associated with this type of calculation (*vide supra*), the present discussion will not dwell on EA's derived in this manner other than to note that, unlike the parent, all of the methods predict cyanocyclopropenyl anion (**13**) to be bound (i.e., stable with respect to electron loss). This is expected given the electron-withdrawing nature of the CN group and is in accord with recent experimental studies in our laboratory.

Table 4 also lists the individual and average electron affinities calculated via the isogyric scheme used for the parent system. While the B-LYP and B3-LYP mean EA's vary only slightly from those calculated directly, the MP2//HF and B-VWN5 mean values change significantly. With the exception of the MP2 result, the other levels of theory all yield average EA's from the isogyric procedure within a narrow range of energies (i.e., 20.2 to 23.2 kcal/mol). These data, and the fact that the

B-VWN5 electron affinity of hydroxyl radical is 9.2 kcal/mol too large, appear to indicate that this functional destabilizes radicals compared to their corresponding anions by ∼8 kcal/mol.

The allylic carbon−hydrogen bond dissociation energy for cyanocyclopropene was calculated directly and via isogyric reactions (Table 6). All of the computational methods (except MP2) indicate that there is a modest decrease in the BDE relative to cyclopropene, the mean values spanning a fairly narrow range from 90.4 to 93.4 kcal/mol. The approximately 6 kcal/mol reduction seems reasonable, in contrast to an increase at the MP2 level of 1.9 kcal/mol, given that the same substitution on methane (i.e., $D_0(CH_3-H) - D_0(NCCH_2-H)$) leads to an experimentally determined reduction of 10.0 kcal/mol.[40]

α-Elimination of cyanide from cyanocyclopropenyl anion (**13**) is a potential pathway that could interfere with the preparation of this ion (eq 17), so the thermochemistry of this process was
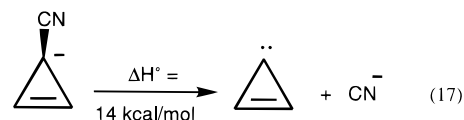


examined. The heat of formation of **13** (obtained from its calculated proton affinity and a G2 determination of the heat of formation of **12**)[55] combined with the experimental values for cyclopropylidene and cyanide leads to a reaction enthalpy of +14 kcal/mol.[57] This quantity is in good agreement with a calculated MP2/6-31+G(d) reaction energy of 12.8 kcal/mol[51,58] and indicates that α-elimination should not pose a problem in the gas phase. This conclusion is further reinforced by the fact that *ab initio* calculations indicate that a significant activation barrier for α-elimination exists.[51]

**Di- and Tricyanocyclopropenyl Systems.** Since one cyano substituent stabilizes cyclopropenyl anion by 34 kcal/mol relative to its conjugate acid and converts the substituted species into a bound ion, di- and tricyano derivatives also were examined.

**Structures.** 1,2-Dicyanocyclopropene (**19**), 1,3-dicyanocyclopropene (**20**), and 1,2,3-tricyanocyclopropene (**24**) were fully optimized along with their corresponding conjugate bases, and the results are summarized in Figures 4 and 5 and Table 8.[59] The structures are discussed in terms of the B-VWN5 functional as was done for the monocyanocyclopropenyl system, and geometries at the other computational levels are given in the Supporting Information.

Deprotonation of the di- and trisubstituted cyanocyclopropenes affords similar $C_s$ ($^1A'$), $C_2$ ($^1A$), and $C_1$ ($^1A$) structures

(53) The $C_{2v}$ cyanocyclopropenyl anion has one imaginary frequency at the HF/6-31+G(d,p) level (411i), but this increases to three at the MP2/6-31+G(d,p) level (167i, 195i, 635i).

(54) Cramer, C. J.; Dulles, F. J.; Storer, J. W.; Worthington, S. E. *Chem. Phys. Lett.* **1994**, *218*, 387.

(55) The G2 and G2₂₉₈ values for **12** are −208.50187 and −208.49610 hartrees, respectively; the temperature correction was carried out by using scaled (0.8929) 6-31G(d) vibrational frequencies. Calculating the atomization energy by using the latter quantity, and combining it with the experimental (298 K) heats of formation for C (171.3 kcal/mol), H (52.1 kcal/mol), and N (113.0 kcal/mol) [see ref 12] leads to $\Delta H°_{f\ 298}(\mathbf{12}) = 101.2$ kcal/mol. This result is in reasonable accord with an estimate of 97 kcal/mol from Benson's additivity approach (ref 56), and can be combined with the proton affinity of **13** at the MP2/6-31+G(d,p) level, 386.2 kcal/mol at 298 K, to afford $\Delta H°_{f\ 298}(\mathbf{13}) = 122$ kcal/mol.

(56) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley and Sons: New York, 1976.

(57) $\Delta H°_{f\ 298}(CN^-) = 17.7$ kcal/mol (ref 40), and $\Delta H°_{f\ 298}(c\text{-}C_3H_2) = 118$ kcal/mol (ref 25).

(58) This quantity was corrected to 298 K by using MP2/6-31+G(d) vibrational frequencies and a scaling factor of 0.9427.

(59) 1,2-Dicyanocyclopropene (**19**) is slightly more stable than **20** at most levels of theory that were explored (i.e., $\Delta E(\mathbf{20} - \mathbf{19}) = -2.64$ (HF), −0.11 (MP2//HF), 0.41 (MP2), 2.95 (B-VWN5), 2.74 (B-LYP), and 1.34 (B3-LYP) kcal/mol.
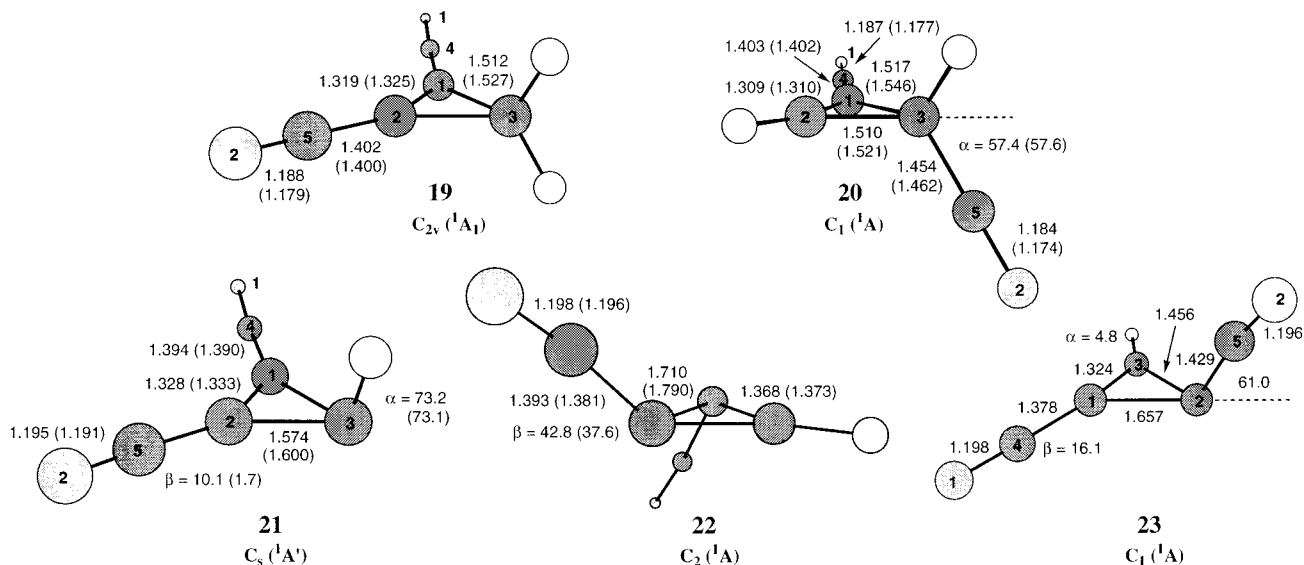
¹MP2/6-31+G(d,p) structural parameters are given. Parenthetical values are for the B-VWN5/6-31+G(d,p) geometries.

**Figure 4.** Dicyanocyclopropene and dicyanocyclopropenyl B-VWN5/6-31+G(d,p) optimized structures. All bond distances and angles are given in angstroms and degrees, respectively.
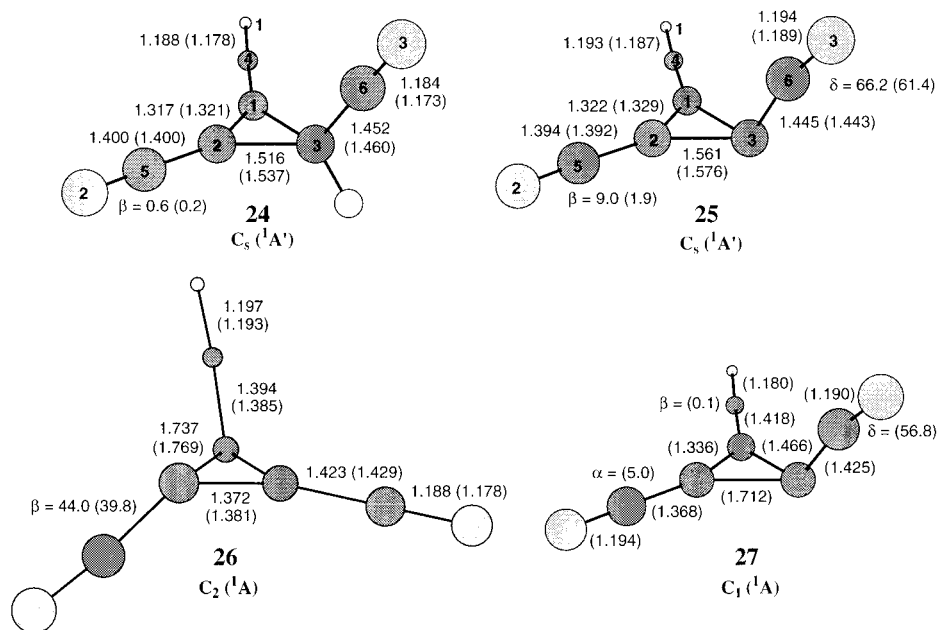


¹MP2/6-31+G(d,p) structural parameters are given. Parenthetical values are for the B-VWN5/6-31+G(d,p) geometries.

**Figure 5.** Tricyanocyclopropene and tricyanocyclopropenyl B-VWN5/6-31+G(d,p) optimized structures. All bond distances and angles are given in angstroms and degrees, respectively.

which are analogous to their cyanocyclopropenyl analogues.[60] For example, the paraffinic bonds (C1−C3 and C2−C3) in **21** and **25** elongate 0.073 and 0.039 Å, respectively, the hydrogen and unique cyano group bend 15.4° (H) and 5.6° (CN) farther out of the ring plane, and in both cases the olefinic nitriles move 1.7° in the opposite direction. These ions are a little more pyramidal than their less substituted counterparts ($\alpha = 73.1°$ vs 71.0° for **21** and **5**, respectively; $\alpha = 61.4°$ vs 60.0° for **25** and **13**, respectively), which contrasts with what would be expected if increased resonance stabilization by the remote cyano groups was the dominant interaction. Instead, it appears that field and inductive effects are responsible for stabilizing

these species. The Mulliken population analyses indicate that in **21** a significant fraction of the charge has shifted from C3 to C1/C2 and is more equally distributed than in **5** or **13**. This is not the case for **25** where the negative charge is concentrated at C3.

The geometries for the di- and trisubstituted $C_s$ ions are similar at the other levels of theory, except for the Hartree−Fock structures, but the nature of the stationary points varies with the computational method. All three density functional procedures indicate that both ions are transition states whereas they are energy minima at the HF and MP2 levels. These differences are a little less surprising for the tricyano derivative because the relative energies for the $C_s$, $C_2$, and $C_1$ conformers span a narrow range of less than 3.2 kcal/mol (Table 9). The

(60) Other symmetries were explored but were found to be second-order or higher saddle points.

**Table 8.** Geometric Parameters for Di- and Tricyanocyclopropene and Their Conjugate Bases[a]

| | curvature[b] | C1−C2 | C1−C3[c] | C1−C4[d] | C3−C6 | C4−N1[e] | C6−N3 | C3−H[f] | C2−C1−C3[g] | C1−C3−C2 | C1−C4−N1[h] | C3−C6−N3 | $\alpha$[i] | $\beta$[j] | $\delta$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **19** ($C_{2v}$, $^1A_1$) | | | | | | | | | | | | | | | |
| MP2 | min. | 1.319 | 1.512 | 1.402 | | 1.188 | | 1.085 | 64.0 | 51.7 | 178.5 | | 58.0 | | |
| B-VWN5 | min. | 1.325 | 1.527 | 1.400 | | 1.179 | | 1.093 | 64.3 | 51.4 | 178.2 | | 57.7 | | |
| **20** ($C_1$, $^1A$) | | | | | | | | | | | | | | | |
| MP2 | min. | 1.309 | 1.517 | 1.403 | | 1.187 | | 1.086 | 64.0 | 51.2 | 178.4 | | 57.4 | 0.6 | |
| | | | (1.510) | (1.454) | | (1.184) | | (1.076) | (64.7) | | (179.7) | | (57.0) | (0.4) | |
| B-VWN5[k] | min. | 1.310 | 1.547 | 1.402 | | 1.177 | | 1.094 | 63.7 | 50.6 | 177.9 | | 57.6 | 0.7 | |
| | | | (1.521) | (1.462) | | (1.174) | | (1.082) | (65.7) | | (179.2) | | (55.7) | (0.2) | |
| **21** ($C_s$, $^1A'$) | | | | | | | | | | | | | | | |
| MP2 | min. | 1.328 | 1.574 | 1.394 | | 1.195 | | 1.110 | 65.0 | 49.9 | 176.8 | | 73.2 | 10.1 | |
| B-VWN5 | 412i cm$^{-1}$ | 1.333 | 1.600 | 1.390 | | 1.191 | | 1.125 | 65.4 | 49.2 | 176.3 | | 73.1 | 1.7 | |
| **22** ($C_2$, $^1A$) | | | | | | | | | | | | | | | |
| MP2 | 60i cm$^{-1}$ | 1.710 | 1.368 | 1.393 | | 1.198 | | 1.085 | 51.3 | 77.3 | 174.4 | | | 42.8 | |
| B-VWN5 | min. | 1.790 | 1.373 | 1.381 | | 1.196 | | 1.096 | 49.3 | 81.4 | 173.7 | | | 37.6 | |
| **23** ($C_1$, $^1A$)[k] | | | | | | | | | | | | | | | |
| MP2 | min. | 1.657 | 1.324 | 1.378 | | 1.198 | | 1.083 | 57.2 | 73.0 | 177.3 | | 4.8 | 16.1 | |
| | | | (1.456) | (1.429) | | (1.196) | | | (49.8) | | (171.7) | | | (61.0) | |
| B3-LYP | min. | 1.666 | 1.327 | 1.370 | | 1.182 | | 1.089 | 55.2 | 74.6 | 177.4 | | 1.6 | 17.1 | |
| | | | (1.419) | (1.407) | | (1.180) | | | (50.2) | | (172.3) | | | (52.2) | |
| **24** ($C_s$, $^1A'$) | | | | | | | | | | | | | | | |
| MP2 | min. | 1.317 | 1.516 | 1.400 | 1.452 | 1.188 | 1.184 | 1.086 | 64.3 | 51.5 | 178.3 | 180.0 | 58.0 | 0.6 | 57.1 |
| B-VWN5 | min. | 1.321 | 1.537 | 1.400 | 1.460 | 1.178 | 1.173 | 1.093 | 64.5 | 50.9 | 178.2 | 179.3 | 58.3 | 0.2 | 55.8 |
| **25** ($C_s$, $^1A'$) | | | | | | | | | | | | | | | |
| MP2 | min. | 1.322 | 1.561 | 1.394 | 1.445 | 1.193 | 1.194 | | 64.9 | 50.0 | 177.8 | 170.7 | | 9.0 | 66.2 |
| B-VWN5 | 296i cm$^{-1}$ | 1.329 | 1.576 | 1.392 | 1.443 | 1.187 | 1.189 | | 65.0 | 49.9 | 177.2 | 168.1 | | 1.9 | 61.4 |
| **26** ($C_2$, $^1A$) | | | | | | | | | | | | | | | |
| MP2 | min. | 1.737 | 1.372 | 1.394 | 1.423 | 1.197 | 1.188 | | 50.7 | 78.6 | 174.0 | | | 44.0 | |
| B-VWN5 | 51i cm$^{-1}$ | 1.769 | 1.381 | 1.385 | 1.429 | 1.193 | 1.178 | | 50.2 | 79.6 | 173.2 | | | 39.8 | |
| **27** ($C_1$, $^1A$)[l] | | | | | | | | | | | | | | | |
| B-VWN5 | min. | 1.336 | 1.466 | 1.418 | 1.425 | 1.180 | 1.190 | | 75.2 | 49.0 | 178.2 | 169.6 | 5.0 | 0.1 | 56.8 |
| | | | (1.712) | (1.368) | | (1.194) | | | (55.9) | | (177.4) | | | | |

[a] All bond distances, angles, and vibrational frequencies are in angstroms, degrees, and cm$^{-1}$, respectively. Atomic labels are as shown in Figures 4 and 5 for **19** and **24**. $\alpha$, $\beta$, and $\delta$ correspond to the hydrogen (or C5 in **27**), C4, and C6 out-of-plane angles, respectively; see Figure 5. [b] Curvature associated with the potential energy surface in the vicinity of the stationary point: min. ≡ minimum energy structure; $xi$ cm$^{-1}$ ≡ transition structure. [c] Parenthetical values correspond to C2−C3 bond distances. [d] Parenthetical values correspond to C2−C5 or C3−C5 bond lengths. [e] Parenthetical values correspond to the C5−N2 bond distance. [f] Parenthetical values correspond to the C2−H bond lengths. [g] Parenthetical values correspond to the C1−C2−C3 bond angle. [h] Parenthetical values correspond to the C2−C5−N2 or C3−C5−N2 bond angles. [i] Parenthetical values correspond to the H−C3 out-of-plane angles. [j] Parenthetical values correspond to the C5 out-of-plane angle. [k] Attempts to locate $C_1$ structures with B-VWN5 and B-LYP led to $C_2$ structures. [l] Attempts to locate HF and MP2 $C_1$ structures led back to the $C_2$ species.

**Table 9.** Relative Energies (in kcal/mol) for the Different Dicyano- and Tricyanocyclopropenyl Anions (**21**−**23** and **25**−**27**, Respectively)[a]

| | | rel energy | | | | |
|---|---|---|---|---|---|---|
| compd no. | pt grp | HF | MP2 | B-VWN5 | B-LYP | B3-LYP |
| **21** | $C_s$ | 12.9 | 12.2 | 13.3 | 13.5 | 13.2 |
| **22** | $C_2$ | −0.04 | 1.1 | 0.0 | 0.0 | 0.3 |
| **23** | $C_1$ | 0.0 | 0.0 | | | 0.0 |
| **25** | $C_s$ | 0.0 | 0.0 | 1.4 | 0.2 | -0.4 |
| **26** | $C_2$ | 1.8 | 3.1 | 0.7 | 0.7 | 2.4 |
| **27** | $C_1$ | | | 0.0 | 0.0 | 0.0 |

[a] Single-point energy calculations, as described in the computational section (e.g., CCSD(T)/6-311+G(2df,2pd)//MP2/6-31+G(d,p)). All energies include a zero-point energy correction.

dicyanocyclopropenyl anion, **21** ($C_s$), is 12.2−13.5 kcal/mol less stable than **22** ($C_2$) and **23** ($C_1$), but the variation in the nature of the potential energy surface is in keeping with results for the parent and monocyanocyclopropenyl ions.[51]

Most of the calculations that were carried out indicate that the $C_2$ ($^1A$) ions are transition structures—the exceptions being B-VWN5 and B-LYP for **22** and MP2 (as was the case for **6** and **14**) for **26**. All of the computations indicate that these species (**22** and **26**) are energetically low lying and structurally similar to their less substituted analogs. In particular, **22** and **26** have characteristically long C1−C2 bonds (1.790 and 1.769 Å, respectively), short C1−C3 (C2−C3) bonds (1.373 and 1.381 Å, respectively), and significant CN out-of-plane angles ($\beta$ = 37.6° and 39.8°, respectively). These changes lead to an

essentially complete shift in the charge density from the C3 to C1 and C2 sites.

An additional $C_1$ species was located on the potential energy surface in those cases where the $C_2$ ($^1A$) ions were found to be transition structures.[61] This was expected for the dicyano compound because substitution of a cyano group for a hydrogen atom in the $C_s$ cyanocyclopropenyl anion (**13**) breaks the symmetry. In the tricyano derivative this need not be the case, and the existence of a $C_1$ structure is startling; this may represent a failing of DFT as analogous structures were not located at the HF or MP2 levels. Regardless, in both cases (**23** and **27**) the geometries are similar. Their most striking features are the presence of long paraffinic bonds (**23**, 1.657 Å (MP2); **27**, 1.712 Å (B-VWN5)), much shorter paraffinic bonds (**23**, 1.456 Å (MP2); **27**, 1.466 Å (B-VWN5)), and normal olefinic distances (1.324 and 1.336 Å, respectively). *These structures suggest that heavily substituted cyclopropenyl anions may be susceptible to ring-opening processes.*

**Energetics.** Since substitution of a single electron-withdrawing group converts cyclopropenyl anion into a bound (with respect to spontaneous electron loss) species, additional substituents will only increase the stability of the anion with respect to the radical and lead to larger electron affinities. These values, along with the related bond dissociation energies, are of interest but were not calculated. The singlet−triplet gaps for the di- and trisubstituted species also were not computed given that the compounds are far too large to treat at the appropriate level

(61) The only exception to this is at the HF level where **26** is a TS but no corresponding $C_1$ structure could be located.

**Table 10.** Substituent Effects on the Acidity and p$K_a$ of Cyclopropene

| compd | $\Delta H^{\circ}_{\text{acid}}$ | $\Delta E$ | $\Delta$p$K_a$ | p$K_a$ |
|---|---|---|---|---|
| cyclopropene (**4**) | 418.5 | 0.0 | 0.0 | 61[a] |
| cyanocyclopropene (**12**) | 384.7 | 33.8 | 24.8 | 36 (41−44)[b] |
| dicyanocyclopropene (**19**) | 363.4 | 55.1 | 40.4 | 21 (25−28) |
| tricyanocyclopropene (**24**) | 348.1 | 70.4 | 51.6 | 9 (14−17) |

[a] Reference 3c. [b] Parenthetical values are based on a previous estimate of the acidity of 3-carbomethoxycyclopropene. See ref 6.

(CCSD(T)//MCSCF) of theory (*vide supra* the inconclusive results of the cyanocyclopropenyl anion).

The proton affinities of di- and trisubstituted cyclopropenyl anions are critically important in planning their syntheses and ultimately probing these ions' reactivity, spectral properties, stability, and structures. Therefore, we calculated this quantity via the same methods that were used for cyanocyclopropenyl anion, and the results are given in Table 2. It can be seen immediately that the second and third cyano groups have a profound effect on the basicity. At the MP2 level, one CN group reduces the proton affinity of cyclopropenyl anion by 33.8 kcal/mol (25 p$K_a$ units), the second nitrile lowers the proton affinity by an additional 21.3 kcal/mol (16 p$K_a$ units), and the third substituent drops the PA another 15.3 kcal/mol (11 p$K_a$ units, Table 10); similar results are obtained with all three density functionals. While the stabilizing effect clearly diminishes with increasing substitution, *three CN substituents lower the proton affinity relative to the parent ion by 70.4 kcal/mol or 52 p$K_a$ units!*

If one assumes that the computed differences are mirrored in solution and that the ΔPA's reflect the Δp$K_a$'s, then by using Breslow's p$K_a$ of 61 for cyclopropene,[3c] a p$K_a$ of 9 would be predicted for 1,2,3-tricyanocyclopropene. If instead our estimate of 41−44 for the p$K_a$ of a monosubstituted cyclopropene is employed,[62] then a value of 14−17 is obtained. These results are in reasonable accord with a previous estimate of near 20 p$K_a$ units for this quantity based upon the measured difference between triphenylmethane (Ph₃CH) and 1,2,3-triphenylcyclopropene and an estimated acidity for tricyanomethane (CH-(CN)₃).[63] It thus appears that di- and, particularly, trisubstituted cyclopropenes with electron-withdrawing groups are remarkably acidic. Consequently, the difficulty in generating substituted cyclopropenyl anions appears to be a kinetic problem (deprotonation vs nucleophilic attack at the activated double bond) and not a thermodynamic one.[64]

## Conclusions

Singlet and triplet cyclopropenyl anion and cyclopropenyl radical were explored via high-level *ab initio* (CCSD(T)//MCSCF) calculations. The wave functions for these species are largely composed of a single determinant (ground state), but the contribution from additional configurations increases in the following order: triplet < doublets < singlets. The anion is predicted to be a ground state singlet with $C_s$ symmetry, and in accord with the notion of antiaromaticity, it is destabilized relative to its saturated counterpart (cyclopropyl anion). Several thermodynamic quantities were calculated ($\Delta H_{\text{acid}}$(c-C₃H₄), $\Delta S - T$(C₃H₃⁻), EA(c-C₃H₃), and BDE(c-C₃H₃−H)) at the CCSD-(T)/6-311+G(2df,2pd)//MCSCF[10(9),9]/6-31+G(d,p) level, and the results were compared to more modest HF, MP2, and DFT computations.

Electron-withdrawing substituents stabilize cyclopropenyl anion with respect to its conjugate acid and corresponding radical. One cyano group is sufficient to convert the anion to a bound species, and additional nitriles have a dramatic effect on the ion's proton affinity. In particular, three cyano groups are found to lower the proton affinity of cyclopropenyl anion by 70.4 kcal/mol or 52 p$K_a$ units; this is probably due to field and inductive effects. This leads to a predicted p$K_a$ of roughly 10−15 for 1,2,3-tricyanocyclopropene and suggests that this compound may be more acidic than water in a polar aprotic solvent such as dimethyl sulfoxide (DMSO). The preparation of a stable di- or trisubstituted cyclopropenyl anion thus is a very inviting target.

(62) This value was derived for 3-carbomethoxycyclopropene (see ref 6), but the stabilizing difference between CO₂Me and CN should be small and can be ignored for these purposes.

(63) Breslow, R.; Cortes, D. A.; Jaun, B.; Mitchell, R. D. *Tetrahedron Lett.* **1982**, *23*, 795.

(64) Ring-opening processes and radical chemistry via the triplet also must be circumvented if a stable cyclopropenyl anion is to be prepared.