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AB INITIO CALCULATIONS ON THE STRUCTURE OF THE CYCLOPROPENYL ANION

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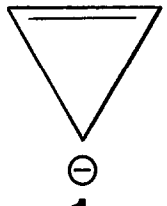
Abstract: Calculations at the SCF level and with inclusion of correlation were carried out on a portion of the potential $^1A'$ state of the cyclopropenyl anion which was found to be nonplanar in its most stable geometry.

The question of cyclic destabilization in Hückel 4n monocyclic systems has been of great interest to both synthetic and theoretical chemists for many years with particular focus on the simplest 4n molecular system, cyclobutadiene (n=1). It now appears that experiment[1,2] and theory[3-8] agree that cyclobutadiene has a rectangular structure. Calculations predict that this molecule has unusually long single bonds which perhaps indicates that the two double bonds repel one another. One might therefore conclude that systems with four π electrons in a ring do indeed possess cyclic destablization.

A related system which also potentially contains four π electrons is cyclopropenyl anion (1). Experimental evidence on the high instability of 1 and its derivatives has been obtained



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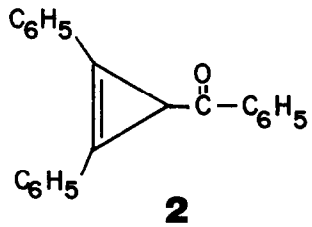
by Breslow. He has observed that the substituted cyclopropene 2 undergoes base-catalyzed exchage 6000 times more slowly than the saturated system 3[9], and that the pK_a of triphenyl cy-



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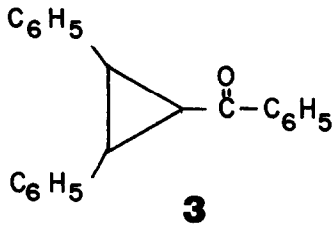

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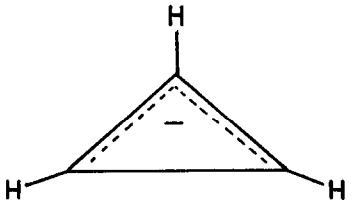
clopropene is greater than 51.[10] More recently Breslow has also been able to obtain an estimate of the pK_a of the parent anion. This pK_a of 61 is extremely high, and the lifetime of the anion is very short[11]. He attributes all these observations to the high instability (antiaromaticity) of the cyclopropene anion. It therefore seems that the parent anion 1 will be difficult to isolate, and theoretical studies of this relatively small system might aid in the prediction of its properties.

Previous calculations have been done by both semi-empirical[12-17] and ab initio[18-20] methods. The only complete geometry optimization was by Pancíř and Zahradník with the CNDO/2 approximation.[17] They found two minima, one of D_{3h} symmetry (presumably a triplet) and a second with C_s symmetry (presumably a singlet). The D_{3h} ground state was 8 kcal lower in energy than the minimum of C_s symmetry. Pancíř and Zahradník also examined the planar cyclopropene anions of C_{2v} symmetry, and with this symmetry constraint found two "minima" 4 and 5 very similar in energy. Structure 4 was about one kcal/mole higher than 5. 5 was 17 kcal higher in energy than the minimum with C_s symmetry.



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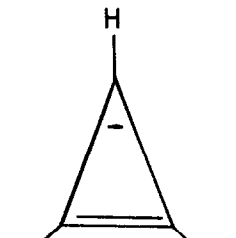

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Davidson and Borden have also examined several of these forms with ab initio calculations which included CI. Of the structures they studied they found the lowest in energy to be a $^3A_2'$ state of D_{3h} symmetry in agreement with Pancíř's and Zahradník's results. They also found two "minima" of C_{2v} symmetry corresponding to 4 and 5 ($^1A'$), although their stabilities were reversed, and a much larger energy difference (22 kcal/mole) was computed. Unfortunately, they did not relax the symmetry of 4 or 5 and therefore did not treat the $^1A'$ state with potentially lower symmetry such as that found by Pancíř and Zahradník (C_s). In this work we have undertaken the geometry optimization of the $^1A'$ state with constraints of both C_s and C_{2v} symmetry.

At the SCF level, calculations were performed with the modest basis set, 3-21G,[21] and the larger basis set, 6-31G*.[22] In both cases a diffuse p function (α = 0.034) was also included[23] for each carbon since it has been found that these are necessary to obtain reasonable results for carbanions.[24-28] Correlation energy was computed using second order perturbation theory with Møller-Plesset partitioning of the Hamiltonian[29] (MP2) and the 6-31G* + diffuse p wave function. The optimized geometries of 6 (with C_s symmetry constraint) obtained at each of the three levels are given in Table I along with total energies. We note that the highest occupied MO is bound whereas a previous ab initio calculation of double zeta quality (without a diffuse p) gave a positive orbital energy.[18] This provides further evidence for the necessity of including a diffuse p on carbons when treating carbanions.

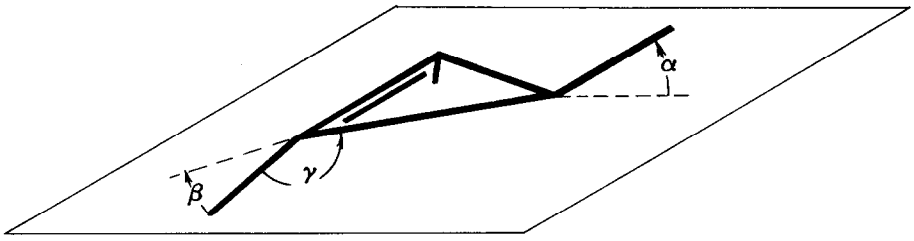

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Table I. Geometry and Energy of Cyclopropenyl Anion (6)[a]

parameter	3-21G + p	6-31G* + p	6-31G* + p/MP2	CNDO/2[b]
R_{C-C}	1.630	1.559	1.559	1.51
$R_{C=C}$	1.293	1.285	1.312	1.36
R_{-C-H}	1.117	1.119	1.125	1.14
$R_{=C-H}$	1.068	1.076	1.091	1.11
α	71.93	69.15	66.14	55.4
β	-4.16	-5.28	-9.34	0.
γ	149.22	148.55	147.61	149.5
energy	-114.4689	-115.1210	-115.5132	

[a]Bond distance are Å, angles in degrees and energies in Hartrees.
[b]Reference 17.

With one exception the geometries obtained are in reasonable agreement with those found previously using the CNDO/2 method. We find that not only is the unique hydrogen out of the plane of the cyclopropene ring but so too are the hydrogens attached to the double bond. They are found to be trans to the unique hydrogen. One can conclude that the cyclopropene anion like cyclobutadiene, is apparently doing all that is possible to avoid cyclic conjugation of the four π electrons. Not only is the charge apparently localized on a single carbon; but unlike other conjugated anions this carbon possesses sp^3 hybridization rather than sp^2. The lack of conjugation in 1 is also born out by the unusually long C-C bonds. This is reminiscent of the predicted behavior of cyclobutadiene.

As observed previously, two "minima" corresponding to 4 and 5 were found with a C_{2v} symmetry constraint. We find structure 4 to be more stable than 5 at the 6-31G*/MP2 level by 5 kcal/mole. This ordering is the same as that found by Davidson and Borden, however our energy difference of 5 kcal/mole is significantly smaller than their 22 kcal/mole value.

All the above results are for the $^1A'$ state of the cyclopropenyl anion. There is still the question whether this or the triplet ($^3A_2'$) is the actual ground state of the ion. We have carried out a single point calculation (6-31G*/UMP2) on the triplet state with D_{3h} symmetry (C-C = 1.40Å and C-H = 1.08Å), and find it to be 19 kcal/mole higher in energy than the nonplanar singlet which suggests that the $^1A'$ might be the ground state. However for this to be established more certainly will require extensive CI or MCSCF calculations.

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