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Structure of the Cyclopropane Cation Radical and Its Energy Barrier to Pseudorotation

Charles E. Hudson,[*,†] C. S. Giam,[†] and David J. McAdoo[‡]

Department of Marine Sciences, Texas A&M University at Galveston, Galveston, Texas 77551, and
Marine Biomedical Institute, The University of Texas Medical Branch, Galveston, Texas 77555

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Ionized cyclopropane is predicted theoretically to have one long C–C bond and two others of nearly normal length. A recently published structure for this ion is actually the transition state for migration of the long bond from one site to another (pseudorotation). No evidence was found for a previously proposed stable scalene triangle structure.

It is well established that the HOMO of cyclopropane is doubly degenerate,[1] another success of the Walsh model.[2] The a_1 component of the Walsh pair is bonding between two of the atoms (C1 and C3) and nonbonding between C2 and the others. Removal of an electron from this orbital would be expected to result, via Jahn–Teller distortions, in a structure with a long C1–C3 bond and nearly normal C1–C2 and C2–C3 bond lengths, a 2N1L (2 normal, 1 long) structure. The b_2 component is bonding from C2 to both C1 and C3, while the C1–C3 interaction is antibonding. Removal of an electron from this orbital should result in a structure with long bonds between C1 and C2 and between C2 and C3 and a short bond between C1 and C3 (2L1S).

Radom et al.[3] found both structures showed that the 2N1L form was lower in energy when the structures were optimized at the UHF/6-31G* level and that the 2L1S structure had one imaginary vibrational frequency at the UHF/3-21G level. The 2N1L structure was predicted[3] to have only positive vibrational frequencies. Borden[4] extended the finding of positive vibrational frequencies to the 6-31G* level. We became interested in this ion when it was shown to result from the elimination of water from ionized 1-propanol.[5] After establishing that the 2N1L structure was of lower energy at the UHF/3-21G level, our subsequent calculations focused on this structure exclusively. Others also treated this geometry as the important one.[6,7] It was therefore surprising to see a recent calculation of the ionization potential of cyclopropane which gave the 2L1S structure for this ion[8] optimized at the MP2/6-31G* level.

Inclusion of electron correlation can invert the order of electronic states of hydrocarbon cation radicals. For example, optimization of ionized ethane by UHF theory fails to converge to the diborane-like component of the ^2E_g state at all,[9,10] even though it is the most stable one for C–C bond lengths near that of the neutral[9] and may be the global minimum.[11-13] We assessed the relative energies and vibrational stabilities of the two forms of ionized cyclopropane, treating correlation with second-order Moller–Plesset (MP2) theory, since the previous calculations[3,4] used only UHF methods in the optimizations and more recent calculations[5-7] did not consider the 2L1S form.

We find that the 2N1L structure is the more stable at all levels of theory that we used (Table I). In addition a numerical frequency calculation of the tightly optimized 2L1S structure at the MP2/6-31G* level (which reproduces the published parameters of ref 8) shows that it has one imaginary frequency with $\nu = 172.7i$ cm^{-1} and $\mu = 7.924$ amu. The 2N1L structure has the expected 21 positive frequencies.

The reduced mass and displacements of the imaginary vibration suggested that 2L1S is the TS for interconversion of the possible long bond isomers of the 2N1L structure. Addition of 0.1 of the displacements calculated in the imaginary vibration to the coordinates of the optimized 2L1S form followed by reoptimization resulted in a 2N1L structure with the long bond between C1 and C2.

The ESR spectrum of the cyclopropane cation radical has been recorded in frozen media of low reactivity[14,15] and is in better accord with the predictions of our calculations (6-311+G** basis set) for the 2N1L structure

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[†] Texas A&M University.

[‡] The University of Texas.

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(13) The two most serious attempts to determine the ground state of ionized ethane are refs. 9 and 11b which come to different conclusions. The former has a more extensive treatment of correlation while the latter uses the larger basis set. However the lack of analytical gradients in the former treatment means that the geometry optimizations are only approximate. We have found in several calculations, the best of which is QCISD(T)6-311+G(2df,2p)//MP2/6-311+G(2df,2p)+ZPVE, that the diborane-like structure is marginally more stable than the long bond isomer (submitted for publication). The diborane-like isomer is also more consistent with the fact that in the gas phase $C_2H_6^{+\bullet}$ loses $H^\bullet$ rather than $CH_3^\bullet$ and with the ESR spectrum.[14]

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Table I. Energies of Ionized Cyclopropane Species (Hartrees)

species	2N1L	2L1S	ΔE (kJ/mol)[a]
MP2/6-31G*//MP2/6-31G*	−117.111354	−117.109313	4.5
MP2/6-311+G**//MP2/6-311+G**	−117.232898	−117.230835	4.5
MP4(SDTQ)/6-311+G**//MP2/6-311+G**	−117.232644	−117.229663	6.9
ZPVE (kJ/mol)	210.7	209.8	

[a] Includes ZPVE.

Table II. ESR Parameters of the Cyclopropane Cation Radical

	2N1L	2L1S	experimental[a]
ratio of proton splittings[c]	−1.11	−5.97	−1.68 to −2.18[b]

[a] Reference 14a. [b] Depends on the medium. [c] From the Fermi contact analysis, triplet splitting/quintet splitting.

Table III. Energies of Cyclopropane Cation Radical Species

species	2N1L	2L1S	ΔE (kJ/mol)
ROHF/6-31G*	−116.742327	−116.734337	7.8
MP4(SDTQ)/6-31G**//ROHF/6-31G*	−117.146699	−117.143541	8.3
NRE[a]	+73.660052	+74.008003	913.5
ERE[b]	+105.104027	+105.382054	730.0
ENAE[c]	−412.216855	−412.838615	−1632.4
KE[d]	+116.710448	+116.709221	−3.2

[a] Nuclear repulsion energy. [b] Electron repulsion energy. [c] Electron-nuclear attraction energy. [d] Kinetic energy.

than with the 2L1S structure. Table II compares our estimates with experiment. It has been shown that anihilation of contaminating states of higher multiplicity (a capability we do not have) is important in predicting the ESR splittings[15] of this cation radical. In addition the observation of pseudorotation at 77 K[14,15] is fully consistent with the low barrier we calculate for this process, and our highest level calculations predict the same barrier as does ref 3 at the MP3/6-31G*//UHF/3-21G level.

Having successfully used the Walsh model to understand the degeneracy of the HOMO in cyclopropane and the types of Jahn–Teller distortions that the cyclopropane ion may undergo, we next used that model to attempt to identify the reason for the lower energy of the 2N1L form as compared to the 2L1S form. This attempt failed because of inconsistencies of the Walsh model with modern MO theory. The Walsh model posits that the three C–C bonds in cyclopropane are composed of an MO of a′ symmetry formed by overlap of sp^2 orbitals in the center of the ring and an e′ pair of MOs formed by overlap of p orbitals around the periphery. This implies that there should be an MO of a′ symmetry with the largest contributions coming from carbon 2p and 2s orbitals in the ratio of ±1.414. Of the three a′ orbitals that are occupied in neutral cyclopropane, the lowest is formed primarily from 1s orbitals. A calculation using Slater orbitals shows that the remaining two combine 2p and 2s in the ratio of 0.33 and 12.0,[1d] contrasting to the predictions of the Walsh model.

More seriously in our problem, the Walsh formulation predicts that the a_1 component of the degenerate HOMOs should have a node at C2. If this were correct, than it should be preferable to place the odd electron in this orbital because C2 would then provide a haven for the β electrons, as Borden has argued.[16] This leads to the correct prediction that the 2N1L structure should be the more stable and attributes the difference to correlation effects. We performed some calculations to test this hypothesis that correlation is responsible for the lower energy of the 2N1L form.

First we optimized the two structures using restricted open-shell Hartree–Fock (ROHF) theory, which takes no account of correlation. Then from this geometry we assessed the correlation energy using MP4 theory. Table III gives the results. The 2N1L structure is the more stable whether correlation is included or not, and the additional stabilization accounted for by correlation effects is less than one-tenth of the difference. The most likely reason for the minimal effect of correlation is that there is no node at C2 in either component of the degenerate pair in any modern treatment of cyclopropane. The a_1 component has fairly substantial contribution from C2 in an orbital directed into the center of the ring. In the 2N1L form of the ion at the ROHF/6-31G* level the 3s, 2p, and 3p basis functions on C2 have coefficients about half as large as the largest ones in the MO. These are the $2p_x$ and $2p_y$ on C1 (which are about the same) and the identical coefficients on C3. Table III also shows that the 2L1S form has both a more negative potential energy from electron nuclear attractions and a more positive potential energy from e–e and n–n repulsions. The electron kinetic energies are similar in the two forms. It is concluded that the relative energies of the 2N1L and 2L1S structures result from the complex interplay of several different factors. We were unable to formulate a rule to make an easy prediction concerning the relative stabilities of the two forms.

Finally, we were unable to find any evidence for the scalene triangle structure at the MP2/6-31G* level of theory which has been proposed[17] for this ion. To explore the possibility of this structure, we fixed the ring in the geometry of ref 17. The positions of the hydrogens (which were not specified) were then optimized subject only to the same C_s (plane of the ring) symmetry that Collins and Gallup[17] used. The constraints on the ring (but not the C_s) were then removed and the structure reoptimized. The result was the 2N1L structure. Another study reached the same conclusions using very similar but not quite identical methods.[7] While the previous work[7] established that the scalene triangle was not the global energy minimum as had been claimed,[17] we have shown that it is very unlikely that a scalene structure forms even a local minimum.

In summary, we have shown that the structure of the cyclopropane cation radical is little changed whether electron correlation is employed in optimizing the structure or not, that the barrier to pseudorotation is low (in accord with a previous prediction and experiment), and that two structures that have been proposed for this ion in the literature are without theoretical justification. We have also discussed some successes and failures of the Walsh model.

Facilities and Methods. Calculations were performed using the Gaussian 90 Revision H suite of programs[18] as

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implemented on the Cray YMP at the University of Texas Center for High Performance Computing in Austin. Optimization were run using the Berny algorithm with standard cutoffs except where the results were to be used to calculate vibrational frequencies, in which case opt = tight was used. The position of the hydrogen atoms in assessing the Collins–Gallup structure[17] was also tightly optimized.

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