

# Pseudo-aromaticity and -anti-aromaticity in Cyclopropyl Cation and Anion

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**Summary** Non-empirical LCAO-MO-SCF calculations with GTF have been performed on cyclopropyl cation and anion respectively, to give numerical values for the pseudo-aromaticity of the former and pseudo-anti-aromaticity and barrier to inversion of the latter.

In a recent communication<sup>1</sup> the results of non-empirical calculations have been presented on the aromaticity and anti-aromaticity of cyclopropenyl cation and anion, respectively. It has previously been pointed out<sup>2</sup> that the planar cyclopropyl system, Figure 1 (hydrogen attached to C-1 in the plane of the ring) possesses a pseudo- $\pi$ -system constructed from  $2p_z$ -orbitals on each carbon and the appropriate anti-symmetric combination of hydrogen  $1s$ -orbitals. It is therefore of interest to investigate the possibility of an analogous stabilizing and destabilizing delocalization for the cation and anion as in the cyclopropenyl case. Further points of interest are the acidity of hydrogens in cyclopropane with respect to those in cyclopropene, and barrier to inversion in cyclopropyl anion.

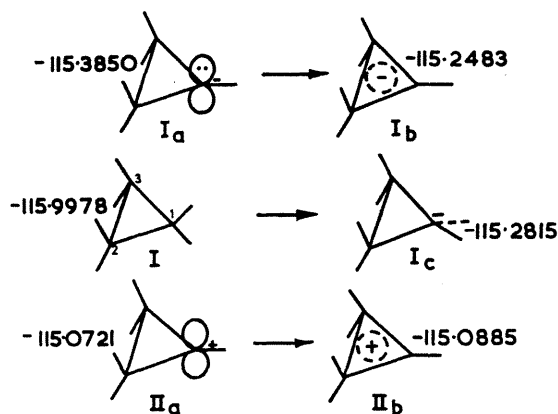


FIGURE 1. (Total energies in a.u.)

We define pseudo-anti-aromaticity in the case of cyclopropyl anion as being the increase in energy on allowing the delocalization of the electrons in the doubly occupied orbital of  $\pi$ -symmetry at C-1 into the pseudo- $\pi$ -system associated with  $2p_z$ -orbitals at C-2 and C-3, and the corresponding anti-symmetric combinations of hydrogen  $1s$ -orbitals, Figure 1 ( $I_a \rightarrow I_b$ ). This may readily be computed as has been outlined for the cyclopropenyl system. Similarly the pseudo-aromaticity of the cation may be defined as the decrease in energy on allowing the delocalization of the pseudo- $\pi$ -system into the vacant  $2p_z$ -orbital of  $\pi$ -symmetry at C-1 ( $II_a \rightarrow II_b$ ).

The calculations described in this work have been carried out as previously described,<sup>1</sup> using a medium size basis set of  $5s$  and  $6p$  Gaussian type functions for each carbon and  $2s$  for each hydrogen, (a total of 43 GTF for the cyclopropyl systems and 45 GTF for cyclopropane). The geometry of

the cyclopropyl ring system was taken to be that of cyclopropane.<sup>3</sup>

The energy increase involved in the process ( $I_a \rightarrow I_b$ ) *i.e.* the pseudo-anti-aromaticity of planar cyclopropyl anion, is calculated to be 85.77 kcal./mole. This is considerably lower than the value of 143.16 kcal./mole obtained for the anti-aromaticity of cyclopropenyl anion.<sup>1</sup> The pseudo-anti-aromaticity can be relieved to a considerable extent by the out-of-plane bending of the C-1-H bond. Figure 2

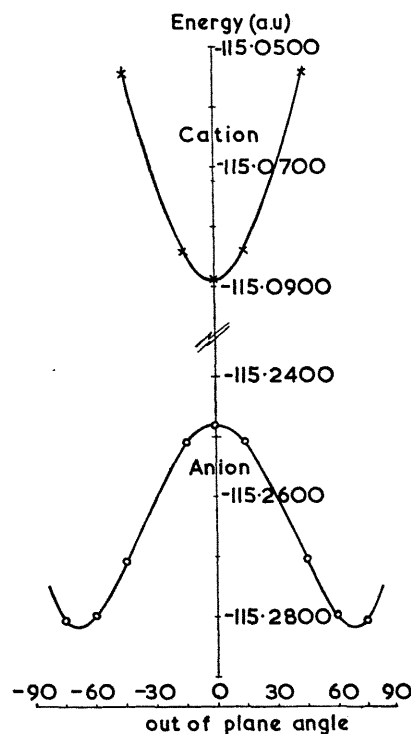


FIGURE 2

shows the potential energy curve for this out of plane bending. Cyclopropyl anion is predicted to be *nonplanar* with the C-1-H bond at 68° to the plane of the ring, with a barrier to inversion of 20.85 kcal./mole. This is substantially lower than for cyclopropenyl anion which reflects the larger anti-aromatic character for the planar configuration of the latter. However as for the cyclopropenyl anion, the barrier to inversion for cyclopropyl anion is higher than for the isoelectronic nitrogen heterocycle aziridine<sup>4</sup> (20.85 and 15.50 kcal./mole, respectively), although the difference is not as large as for the unsaturated systems.<sup>1,4</sup>

It is of interest to compare the energy involved in removing a methylene proton from cyclopropane and cyclopropene, respectively since there are experimental data available for substituted derivatives of the two ring

systems.<sup>5</sup> The calculated energy change for cyclopropane (Figure 1, I  $\rightarrow$  I<sub>c</sub>), 449.46 kcal./mole, may be compared with that previously reported for the methylene group in cyclopropene, 459.63 kcal./mole.<sup>1</sup> If the reasonable assumption is made that the differences in enthalpies of solvation and entropies for these two processes will be similar then the saturated hydrocarbon is substantially more acidic, the enthalpy difference with respect to cyclopropene amounting to some -10.17 kcal./mole. This would appear to be an entirely reasonable estimate. For example in the case of *cis*-2,3-diphenyl-*trans*-1-benzoylcyclopropane and the corresponding cyclopropene, the activation energy difference for deuterium exchange amounts to 5.7 kcal./mole,<sup>5</sup> the entropy terms being almost identical. However it should be noted that the calculations show that the vinylic hydrogens in cyclopropene<sup>1</sup> should still be considerably more acidic than the methylene protons in cyclopropane.

For the process (II<sub>a</sub>  $\rightarrow$  II<sub>b</sub>), Figure 1, the calculated energy lowering, the pseudo-aromaticity of the cyclopropyl cation amounts to 10.28 kcal./mole. This is considerably lower than the corresponding aromaticity of the cyclopropenyl system,<sup>1</sup> 49.57 kcal./mole, but is by no means insignificant. As expected the most stable conformation

has the hydrogen atom at C-1 in the plane of the ring, and it is of interest to investigate the energy required to bend the C-1-H bond out of the plane of the ring to reduce the pseudo-aromaticity of the system. The potential energy curve for this process is shown in Figure 2. For a 45° out-of-plane angle the energy required amounts to 21.30 kcal./mole, which is somewhat smaller than for the cyclopropenyl cation,<sup>1</sup> 24.54 kcal./mole. For the saturated species, it should be remembered that any out-of-plane bending is more expensive in terms of increased nuclear repulsion energy than for the unsaturated species, so that the energies required for out-of-plane bending are quite similar despite the fact that the pseudo-aromaticity of the former is considerably smaller than for the latter. Nevertheless, the interesting feature common to both is the relatively small amount of energy required to displace the hydrogen at C-1 out of the plane of the ring. As we have previously pointed out,<sup>2</sup> however, if the methylene groups are rotated in the correct disrotatory fashion and the C-2-C-3 bond lengthened, the resulting distorted cyclopropyl cation is actually lowered in energy by a small out-of-plane bending of hydrogen at C-1.

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<sup>1</sup> D. T. Clark, *Chem. Comm.*, 1969, 637.

<sup>2</sup> D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, 1969, **13**, 365.

<sup>3</sup> *Chem. Soc. Special Publ. No. 11*, 1958.

<sup>4</sup> D. T. Clark, International Symposium, Quantum Aspects of Heterocyclic Compounds in Chemistry and Biochemistry, Jerusalem 1969. (To be published by the Israel Academy of Sciences and Humanities).

<sup>5</sup> R. Breslow, J. Brown, and J. Gazewski, *J. Amer. Chem. Soc.*, 1967, **89**, 4383.