Non-empirical LCAO–MO–SCF Calculations with Gaussian Type Functions on the Aromaticity and Anti-aromaticity of Cyclopropenyl Cation and Anion

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Summary Non-empirical LCAO–MO–SCF calculations with G.T.F. have been performed on cyclopropenyl cation and anion, respectively, to give numerical values for the aromaticity of the former and anti-aromaticity and barrier to inversion of the latter.

THE 2π- and 4π-electron systems of *planar* cyclopropenyl cation and anion, respectively, are the simplest aromatic and anti-aromatic systems. Breslow and co-workers[1] have defined anti-aromaticity as the decreased π electron stability of cyclic compounds compared to open chain compounds, and by carrying out PPP–SCF–MO calculations on planar cyclopropenyl anion and allyl anion suggested that for the singlet states the anti-aromaticity amounted to 46 kcal./mole. However leaving aside the fundamental objections to PPP–SCF treatments of these systems,[2] the quantity defined is somewhat artificial in that the geometries of the two systems are radically different. An *ab initio* treatment allows a more satisfactory definition of anti-aromaticity as being; the increase in energy on allowing the delocalization of the electrons in the doubly-occupied orbital of π symmetry at C-1 into the C-2–C-3 double bond system [Figure 1 (Ia) → (Ib)]. This is readily computed by carrying out calculations on cyclopropenyl anion, and cyclopropenyl anion in which the $2p_z$ orbital at C-1 is a doubly occupied symmetry orbital restrained from interacting with the C-2–C-3 π system. Similarly the aromaticity of the cation may be defined as; the decrease in energy on allowing the delocalization of the C-2–C-3 double bond system into the vacant $2p_z$ orbital of π-symmetry at C-1[(IIa) → (IIb)].

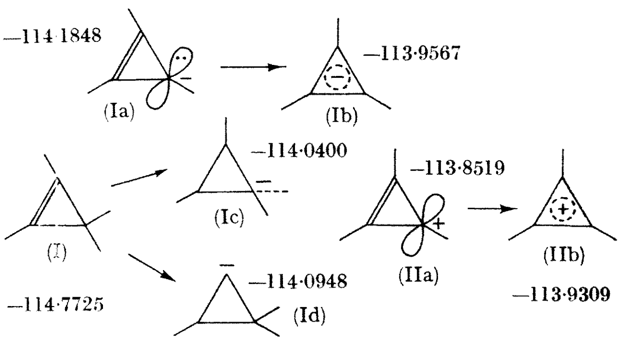

FIGURE 1

The calculations described in this work have been carried out using the POLYATOM system,[3] implemented on the Northumbrian Universities IBM 360/67 Multiple Access Computer (NUMAC), using a medium size basis set of 5 *s* and 6 *p* Gaussian type functions (G.T.F.) for each carbon and 2 *s* for each hydrogen (a total of 39 G.T.F. for the cyclopropenyl systems and 41 G.T.F. for cyclopropene). The geometry of the cyclopropenyl ring system was taken to be that of cyclopropene[4] rather than an equilateral triangle (whose bond lengths are unknown), the reason for this being twofold. Firstly in cyclopropenyl anion, distortion along one of the twofold axis splits the degeneracy of the highest occupied orbitals to give a closed-shell singlet state. This does not apply to the cation, however it is an efficient use of computer time to employ the integrals generated for a given internuclear configuration in as many calculations as possible. Hence for the cyclopropene ring geometry it is possible to use the same set of integrals in four different SCF procedures for (Ia), (Ib), (IIa), and (IIb). Secondly we were interested in comparing the energetics of the processes for removing a methylene and vinylic proton from cyclopropene, since there is experimental evidence,[5] concerning the rates of exchange at the two sites.

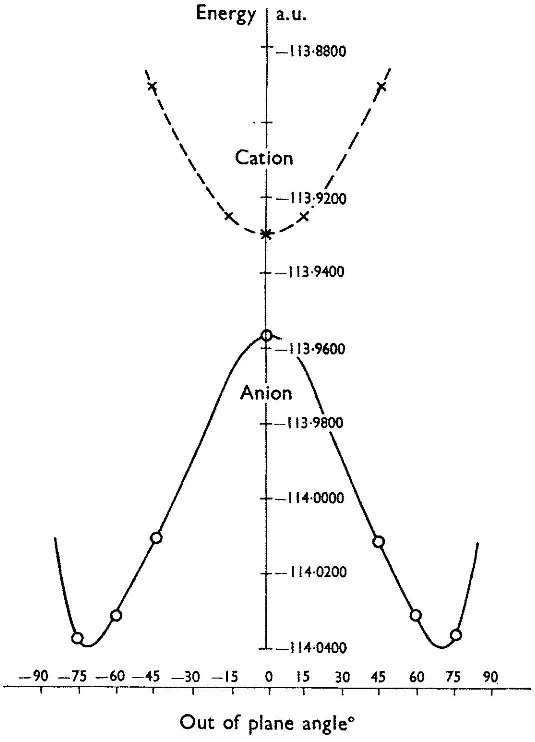

FIGURE 2

The energy increase involved in the process (Ia) → (Ib) *i.e.* the anti-aromaticity of *planar* cyclopropenyl anion, is calculated to be 143·16 kcal./mole. Although previous workers[1] have discussed in detail the anti-aromatic character of cyclopropenyl anion, the point seems to have been missed that the anti-aromaticity can be relieved to a considerable extent by the out of plane bending of the C-1–H bond. Figure 2 shows the potential energy curve for this out of plane bending. Cyclopropenyl anion is predicted to be *non planar* with the C-1–H bond at 68° to the plane of the ring, with a barrier to inversion of 52·3 kcal./mole. This is considerably higher than the value of 35·14 kcal./mole calculated for the isoelectronic 2-azirene ring systems.[6]

This interesting result has important ramifications in the interpretation of experimental data, however little is known of cyclopropenyl anion itself, most of the data pertaining to 1-substituted derivatives. For example derivatives of the 1-cyano-substituted species have been investigated,[1] and we are currently undertaking calculations on the parent species.

The calculations show that in cyclopropene the vinylic hydrogens (I) → (Id) are more acidic than the methylene protons (I) → (Ic) and this is in accord with the experimental data.[5] The enthalpy of isomerization of the non-planar cyclopropenyl anion to the vinylic anion amounts to −34·4 kcal./mole.

For the process (IIa) → (IIb) the calculated energy lowering (the aromaticity of the cyclopropenyl cation) amounts to 49·57 kcal./mole. It is also of interest to investigate the energy required to bend the C-1–H bond out of the plane of the ring to reduce the aromaticity of the system. The potential energy curve for this process is shown in Figure 2. The interesting feature here is the comparatively small amount of energy required to push the hydrogen at C-1 out of the plane of the ring; for a 45° out-of-plane angle this only amounts to 24·54 kcal./mole.

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