The π-Type Conjugation in the Cyclopropylmethyl Cation

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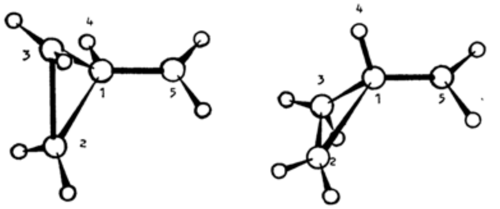
The high conjugative ability of the cyclopropyl group with an adjacent π orbital has been established experimentally1) and theoretically.2-4) For the cyclopropyl derivatives, Walsh predicted that this conjugation would be most effective when these compounds were in a "bisected" conformation (I in Fig. 1). Recently his prediction has been confirmed by Pittman and Olah through their NMR measurements.1)

In the present paper, we will treat quantitatively the electronic structures of the two conformers, "bisected" (I) and "non-bisected" (II) (see Fig. 1), of the cyclopropylmethyl cation with our newly-developed semi-empirical ASMO-SCF method.5) The geometry chosen for the cyclopropyl group is the same as that in cyclopropane, while the C_1–C_5 bond distance (in Fig. 1) is assumed to be 1.50 Å.



I II

Fig. 1. The configurations of "bisected" (I) and "non-bisected" (II) conformers. In the I form, the atoms H_4, C_1 and the terminal CH_2 group are on the same plane, and in the II form the C_1–H_4 bond is perpendicular to the plane of the terminal CH_2 group.

TABLE I. THE ATOM AND AO BOND POPULATIONS IN CYCLOPROPYL GROUP

Compound	C_1–C_2	p_1–p_2	C_1–H_4	$p_{\sigma 1}$–h
Bisected (I)	0.585	0.309	0.847	0.523
Non-bisected (II)	0.650	0.378	0.785	0.464
Cyclopropane	0.651	0.367	0.839	0.539

The calculated total energies show that the I form is more stable than the II form by 0.813 eV. The π atomic orbital (AO) population of the C_5 atom is 0.443 in I and 0.280 in II. As to the atom bond population between the C_1 and C_5 atoms, the values are 1.015 in I and 0.924 in II, while the π AO bond populations are 0.203 in I and 0.113 in II; other π AO bond values obtained by the same method include 0.425 in ethylene, 0.114 in the ethyl cation, and -0.022 in ethane. Accordingly, it may be concluded that the π-conjugation in the I form is quite strong and that it contributes greatly to the stabilization of the I form.

The atom bond populations of C_1–C_2 and C_1–H_4 are collected in Table I, together with the corresponding values in cyclopropane. The table implies that the values of C_1–C_2 in the II form and of C_1–H_4 in the I form do not suffer much change, compared with the values in the cyclopropane, while remarkable changes do occur in C_1–C_2 in I and in C_1–H_4 in II. Further, in Table I, the sum of the AO bond populations between the three p AO's belonging to the C_1 and C_2 atoms, denoted by p_1–p_2 in Table I, and the value between the pσ AO of the C_1 atom and the 1s AO of the H_4 atom ($p_{\sigma 1}$–h) are also indicated. Hence, the following conclusion may be drawn; the large changes in the atom bond population of C_1–C_2 in I and of C_1–H_4 in II are mainly caused by the changes in p_1–p_2 in I and in $p_{\sigma 1}$–h in II. As may be seen in Fig. 1, the p AO of the C_1 atom conjugating with the vacant π AO of the C_5 atom also participates in the C–C bonding in the I form and in the C–H bonding in the II form. Accordingly, the above-mentioned changes are largely due to the interactions between the p AO of the C_1 atom and the vacant π AO.

From the above discussions, it is clear that the stabilization in the I form arises mainly from π-type interaction between the vacant π AO of the sp^2 carbon and the π-like AO's in the ring carbons.

The transition energies for the first excitation may be evaluated as 6.60 eV. and 5.04 eV., and the oscillator strengths as 0.054 and 0.015, for I and II respectively. These transitions may be attributed to the intramolecular charge transfer from the cyclopropane ring to the vacant π AO of the sp^2 carbon.

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* In Ref. 1 it is stated that the energy difference between these two conformers might be larger than 8—10 kcal./mol.