

A High Level *Ab Initio* Study of Corner-protonated Cyclopropane

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Calculations have been carried out at the MP4SDQ//6-31G* level for corner-protonated cyclopropane that show it to have an unsymmetrical π complex structure, the formal charges on the basal atoms being in the ratio 3 : 2; implications concerning the norbornyl cation are discussed.

The role of 'nonclassical' carbocations has been of major interest to organic chemists for many years. The properties and structures of such ions remain uncertain because of an unfortunate but inevitable lack of experimental data. Very high level *ab initio* procedures have to be used in theoretical studies of such species if the results are to be meaningful and calculations using such procedures are currently restricted to relatively small molecules. The $C_3H_7^+$ potential surface is therefore of especial importance because this is the simplest system where the existence of a nonclassical species ('protonated cyclopropane') has been established by experiment.¹

Two reasonably high level *ab initio* calculations^{2,3} have been reported for this system. Both predicted the existence of two

nonclassical species, one the ethylene-carbenium ion π complex, (1) ('corner-protonated cyclopropane'), the other a species (2) with a three-centre two-electron bond ('edge-protonated cyclopropane'). Both procedures predicted (1) to have C_s symmetry, and (2) to have C_{2v} symmetry, as indicated in the formulae, and both (1) and (2) were predicted to be intermediate in energy between the n-propyl (3) and isopropyl (4) cations. However, while one calculation² predicted (1) to be lower in energy than (2), the other³ led to the opposite conclusion.

Both these calculations were carried out some years ago and were consequently restricted by the performance of available computers. As a result, the methods used to calculate

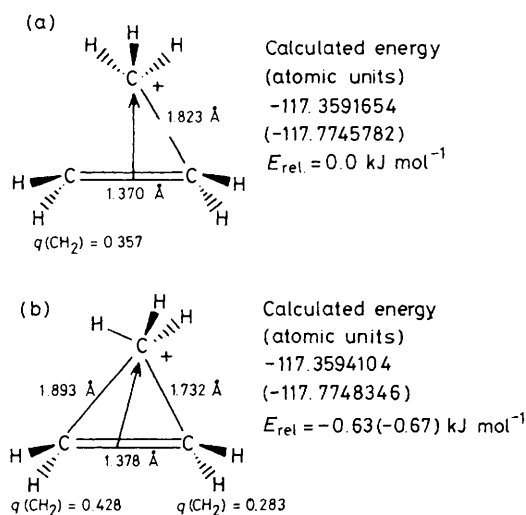
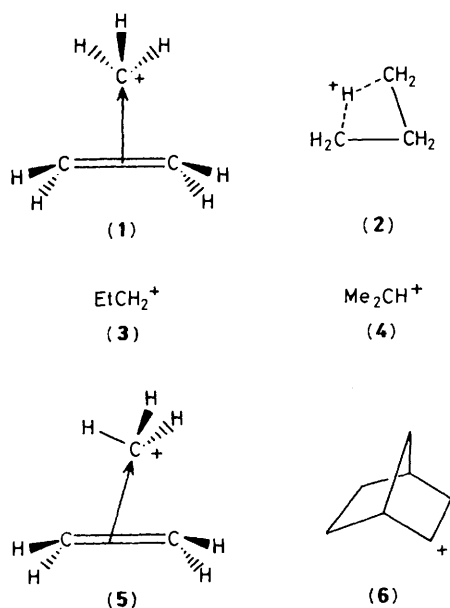


Figure 1. Charges, CC bond lengths, and SCF (MP4SDQ/6-31G*) energies of (a) the symmetrical π complex (1) and (b) the unsymmetrical π complex (5).

geometries were not acceptable by present standards. In one case³ a minimum basis was used for optimization while in the other,² where symmetry was assumed, no adequate steps were taken to check that the corresponding point on the potential energy (p.e.) surface corresponded to a minimum and not to a stationary point of some other kind. We therefore decided to repeat the calculations for the C_3H_7^+ system, using the improved procedures and computers now available. Our results for (1) proved to be unexpected and interesting and we report these herein.

A 6-31G* calculation for (1), using the GAUSSIAN 82 program⁴ and assuming C_s symmetry, led to a geometry and energy almost identical with those reported previously;² see Figure 1(a). While Pople *et al.*² implied this to be a minimum on the p.e. surface, they did not characterize it by calculating force constants, a surprising omission given that force constants were calculated for (2). When we calculated force constants for (1), using the same (6-31G*) basis set, one was found to be negative. Thus (1) is *not* a minimum on the p.e. surface. It is a saddle point, *i.e.* a transition state. The transition co-ordinate (imaginary frequency, $93i \text{ cm}^{-1}$) corresponded to rotation of the methyl group. When we rotated it through 30° and reoptimized the geometry, we found a genuine minimum (5) on the p.e. surface, lower in energy by 0.63 kJ mol^{-1} and with a distinctly unsymmetrical structure; see Figure 1(b). The symmetrical species is thus the transition state for interconversion of (5) with its mirror image.

Since the energies of such π complexes, relative to those of isomeric classical carbenium ions, are known^{2,3} to be underestimated by RHF procedures, we recalculated the energies of (1) and (5), using fourth order Møller-Plesset perturbation theory⁴ with single, double, and quadruple excitations (MP4SDQ). The corresponding energies, and relative energies, are shown in parentheses in Figure 1. Note that inclusion of electron correlation has led to essentially no change in the relative energies of (1) and (5). Therefore although the difference in energy between them is very small, the conclusion that (1) is not a minimum on the p.e. surface seems strong.

The difference in geometry between (1) and (5) is surprisingly large. The orientation of the methyl group in (5) is also surprising, corresponding to eclipsing with the adjacent

methylene. Conversion of (5) into (3) thus involves another rotation of methyl, through 60° . The fact that (5) is lower in energy than (1) presumably reflects back-co-ordination,⁵ involving a hyperconjugative interaction between the CH bonds of the apical methyl group and the empty antibonding π M.O. of the basal ethylene moiety in the π complex.⁵ Hyperconjugative interactions are strongest when one of the bonds involved eclipses the A.O., or in this case the M.O., interacting with it.

Even more surprising is the large difference between the Mulliken formal charges on the basal atoms in (5); see Figure 1(b). These are in the ratio 2 : 3. Their sum, however, is almost the same as that of the corresponding charges in (1), Figure 1(a). Making the π complex unsymmetrical leads to a major charge displacement. Several significant conclusions follow.

(a) Our results illustrate once again the need for proper characterization of stationary points, particularly when the latter have been located assuming symmetry. In such cases it is *essential* that force constants be calculated properly. No reliance can be placed on the 'Hessian' generated during the geometry optimization by typical gradient procedures, particularly if the optimization has been carried out with assumed symmetry. Indeed, the 'Hessian' generated in this way for (1) had no negative eigenvalue.

(b) Our results throw new light on the controversy concerning the structure of the norborn-2-yl cation (6). It has been claimed^{6,7} that high level *ab initio* calculations show (6) to be symmetrical. However, no attempt was made in either of these studies to calculate force constants with the basis set used in optimizing their geometries. There is therefore no reason to believe that the symmetrical structure was not in fact the transition state for interconversion of two unsymmetrical π complexes, as the ESCA spectrum suggests.⁸ If the difference in energy between the symmetrical and unsymmetrical forms of (6) are as small as that between (1) and (5), interconversion could well be fast on the n.m.r. time scale, even at 0 K, since such a barrier could be eliminated by zero point energy. Indeed, the zero point energy estimated for (5) from our calculated vibration frequencies is greater than that for (1) by 0.50 kJ mol^{-1} , virtually eliminating the differences in energy between them. As long as the potential surface has a double minimum, the ESCA spectrum will correspond to the un-

symmetrical structure, the ESCA measurement being effectively instantaneous on the time scale of molecular vibrations.

The fact that the charges at the basal atoms in (5) are so different strongly supports this suggestion. The 1s ionization energies estimated for the basal atoms in (5), using our 6-31G* orbital energies and Koopmans' theorem, differ by 1.22 eV. Such a difference would be sufficient to account for the observed⁸ ESCA spectrum. The fact that so large a change in charge involves so small a change in energy implies moreover that the ions must be extremely polarizable. The difference between the two 1s ionizations in the case of (6) could thus well have been accentuated by ion pairing or solvent interactions under the conditions used in the ESCA measurements.

(c) Our results imply that π complexes with apical alkyl groups are *not* symmetrical, as has always been supposed. The work reported here thus supports recent calculations⁹ for biomimetic cyclizations which predicted that they take place *via* unsymmetrical π complexes as intermediates.

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