Theoretical Study of Proton Approach towards Strained Hydrocarbon Molecules

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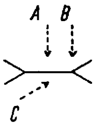
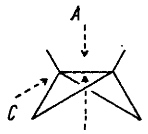
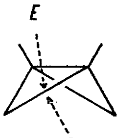
Summary *Ab initio* calculations have been performed on some paths for proton approach towards some strained hydrocarbon molecules.



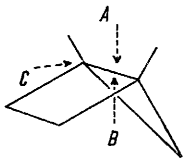
(I)



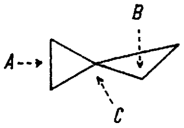
(IIa)



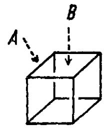
(IIb)



(III)



(IV)



(V)

Protonation paths of strained hydrocarbons represent a fascinating mechanistic problem. A theoretical study of such processes requires optimization of all geometrical parameters. Although certainly worthwhile, this becomes a major undertaking for any moderately complex molecule. In the course of a non-empirical study of molecular strain it seemed of interest to compute some paths for proton approach towards strained hydrocarbons. Using a minimal basis set of gaussian functions[1] we have optimized the total energy of the systems ethylene (I),[2] bicyclo[1,1,0]butane (II),[3] bicyclo[2,1,0]pentane (III),[4] spiropentane (IV),[5] and cubane (V)[6] while a proton approaches along the paths shown. The geometry of the hydrocarbons[2—6] has been kept unchanged throughout. Thus the resulting stabilization energies ΔE (see Table) are certainly not the protonation energies. However, if very different ΔE's are found for the various paths, the preferred path for proton approach is likely to represent correctly the preferred protonation site of a given molecule.

Table

	(I)			(IIa)			(IIb)	
Path (symmetry) ..	$A(C_{2v})$[c]	$B(C_s)$	$C(C_{2v})$	$A(C_{2v})$	$B(C_{2v})$	$C(C_s)$	$D(C_1)$	$E(C_1)$
$r_{opt.}$/Å[a]	1·24	1·22	1·22	1·06	2·17	1·12	1·06	1·16
ΔE/(kcal/mol)[b] ..	180	174	84	156	101	189	160	88

	(III)			(IV)			(V)	
Path (symmetry) ..	$A(C_s)$	$B(C_s)$	$C(C_1)$	$A(C_{2v})$	$B(C_s)$	$C(C_2)$	$A(C_{2v})$	$B(C_{4v})$
$r_{opt.}$/Å	1·04	1·89	1·78	1·12	1·24	1·26	1·15	1·32
ΔE/(kcal/mol) ..	129	98	150	159	99	141	144	79

[a] $r_{opt.}$ is the distance, corresponding to the minimum energy along the path shown, between H^+ and a carbon centre, a C–C bond, or the centre of a face. [b] ΔE is the calculated energy difference between the neutral molecule and the protonated one. [c] Values of $r_{opt.}$ = 1·15 Å and ΔE = 188 kcal/mol have been computed for an optimized bridged form.[7b]

Proton approach towards ethylene (I) has been studied in order to test whether or not meaningful results can be obtained without geometry optimization. Approach towards the π bond (paths A and B) is preferred over in-plane approach by *ca.* 100 kcal/mol. Computations with geometry optimization indicate that the ethyl cation is *ca.* 3—4 kcal/mol more stable than bridged ethylene (path A; see footnote in ref. 7b);[7] however this difference is too small to decide with certainty which form is preferred.[7b] We find path A slightly favoured over path B; one may suggest initial approach along A, as long as C_2H_4 is undeformed, followed by a bending towards path B as the ethyl cation develops.

Three different paths of proton approach, 'on the flap', A, 'under the flap', B, and 'on the corner', C, have been considered for bicyclo[1,1,0]butane (II) and bicyclo[2,1,0]pentane (III); two additional paths 'on the edge', E and D, have been computed for the bicyclobutane system. The stabilization energy is greater for the energy minimum along path A than along path B by 55 and 31 kcal/mol for (II) and (III) respectively. Indeed in the case of path A the proton approaches into a high electron density region. More striking, however, is the especially favoured 'corner' approach C on the bridgehead carbon of molecules (II) and (III). The electron density maps of (II)[8,9] and of (III)[9] display a high density region in the bridgehead corner, resulting from the back lobes of the C(2p) functions of the bridgehead carbons which make up the C–C bridging bond. Optimization of the angle between the C $\cdots$ H^+ direction and the C–C bridge in the plane containing the C–C and C–H bridge bonds yields values of 130 and 156° respectively for (II) and (III).

A population analysis of the optimized forms shows a strong polarization of the C–C bridge, with charge alternation; one finds H (+0·27) $\cdots\cdots$ C^1 (−0·26)—C^3 (+0·13) for (II) and H (+0·31) $\cdots\cdots$ C^1 (−0·18)—C (+0·05) for (III). Furthermore the overlap population between the bridge carbons decreases markedly along both paths A and C.

Approach along path D corresponds to the preferred mode according to CNDO calculations.[10] The present results, however, still favour path C by *ca.* 20 kcal/mol. It is worth noting that the two modes C and D, which are the preferred

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ones, correspond to the predominant stereochemistry of the bicyclobutane opening *via* proton addition.[10] Attack on the back lobe of the bent central C–C bond has also been proposed for the reaction of dienophiles with bicyclo[1,1,0]- and [2,1,0]-systems.[11,12]

In the case of spiropentane (IV), path *B* (approach 'on the face') leads to the least stable form, while path *A* (approach 'on the edge') is preferred over *C* by 18 kcal/mol. Along path *A* the overlap population of the attacked C–C bond decreases from 0·62 to 0·34, suggesting an easy opening to the (1-methylcyclopropyl)carbinyl cation.

Finally, proton approach towards cubane shows a strong preference for attack on the edge (path *A*) with respect to attack on the centre of a face (path *B*). In the optimum form corresponding to path *A* the overlap population of the bond under attack decreases significantly.

Many strained hydrocarbons have been shown recently to undergo complex silver-ion catalysed rearrangements.[13] A recent theoretical study of the ethylene–Ag^+ complex[14] has shown that a model in which Ag^+ is replaced by a point charge is capable of describing most of the intramolecular electron rearrangement of the ethylene unit in the complex. Thus, one may suggest (i) that the perturbation of the electronic structure of a strained system is similar for either H^+ or Ag^+ approach; (ii) that the preferred paths for proton approach are also likely to represent the preferred paths for Ag^+ approach, for instance in the Ag^+-catalysed rearrangement of cubane[13,15] and of bicyclobutane derivatives.[13,16] In the latter case, initial attack of the metal cation at the bridgehead position has been suggested.[16]

The above results may thus be of interest in the elucidation of the initial steps in mechanisms of protonation as well as of Ag^+-catalysed rearrangements.

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