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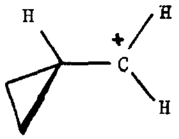
THE 1-BICYCLOBUTYLCARBINYL CATION AND RELATED MOLECULES: THEORETICAL CALCULATIONS

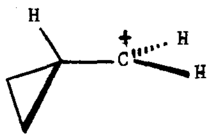
Arthur Greenberg
Department of Chemical Engineering and Chemistry
New Jersey Institute of Technology
Newark, New Jersey 07102

Interactions between substituents such as Li, F, CN, CF_3, CH_2^+, CH_2^-, and O^- and the strained carbocyclic networks to which they are attached form an active area of current interest.[1] Effects at the bridgehead position of bicyclobutane should be particularly significant because of the high p character (ca. 96%[2]) attributed to the central bond between C1 and C3. This bond is envisioned as a pi orbital formed by overlap of two canted p orbitals. Unlike the pi orbital of ethylene, the electronic distribution of the C1-C3 pi orbital is highly unsymmetrical with the electron density on the molecule's exo surface differing greatly from that on the endo surface. Such unsymmetric electronic distribution should itself present some interesting conjugative aspects. Presently, there is little structural or thermochemical data on substituted bicyclobutanes. A published thermochemical study[3] on 1-cyanobicyclobutane appears to indicate an apparent stabilization (relative to the parent hydrocarbon and pivalonitrile) of about 10 kcal/mole, although the investigators find no apparent thermochemical stabilization in cyanocyclopropane.

The 1-bicyclobutylcarbinyl cation is a specie having an extremely strong pi electron withdrawing substituent at the bridgehead position (assuming that the CH_2^+ group adopts a suitable conformation). We have applied ab initio molecular orbital calculations, using the STO-3G basis set in the Gaussian 70 series of programs,[4] to a study of idealized structures of this cation and related molecules. Similar calculations have been performed on conformers of the idealized cyclopropylcarbinyl cation constructed by substitution of an idealized trigonal CH_2^+ group for the chlorine atom in chlorocyclopropane.[5] These calculations led to the conclusion that the bisected conformation, **1**, is more stable by some 17.5 kcal/mole than the eclipsed conformation **2**, and this is consistent with a wealth of experimental data.[6] A later STO-3G study, in which optimal geometries were calculated, found the bisected conformer, which exhibits marked departures from the idealized geometry, to be 27.9 kcal/mole more stable than the eclipsed conformer which has essentially idealized geometry.[7] (The corresponding energy difference found with the 4-31G basis set is 30.3 kcal/mole[7]). While the interaction in **1** is strongly stabilizing, that in **2** is actually mildly



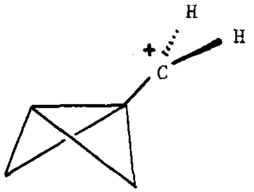
1



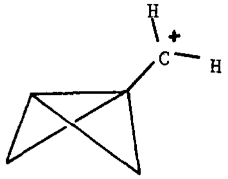
2

destabilizing.[5] This is readily understood by considering the substituent in 2 to act as a sigma electron withdrawer offering no significant pi conjugation. Dill has discussed the stabilization offered by sigma-releasing, pi-withdrawing substituents.[8] In 1,obviously pi withdrawal overwhelms sigma withdrawal to provide net stabilization.

The total energies (T.E.); in hartrees, obtained from STO-3G calculations of the two extreme conformers of 1-bicyclobutylcarbinyl cation are listed in parenthesis under their structures (3 and 4). The bicyclobutane ring was assigned the geometry of the parent hydrocarbon,[9] a $C\text{-}CH_2^+$ bond length of 1.47 Å and ideal trigonal geometry about the substituent were assumed. The calculated energy difference favoring (idealized) eclipsed conformation 3 over bisected conformation 4 is 31.8 kcal/mole - almost twice the energy difference calculated for idealized structures 1 and 2.[5] It is clear that optimization of



3
(-190.73700)



4
(-190.68621)

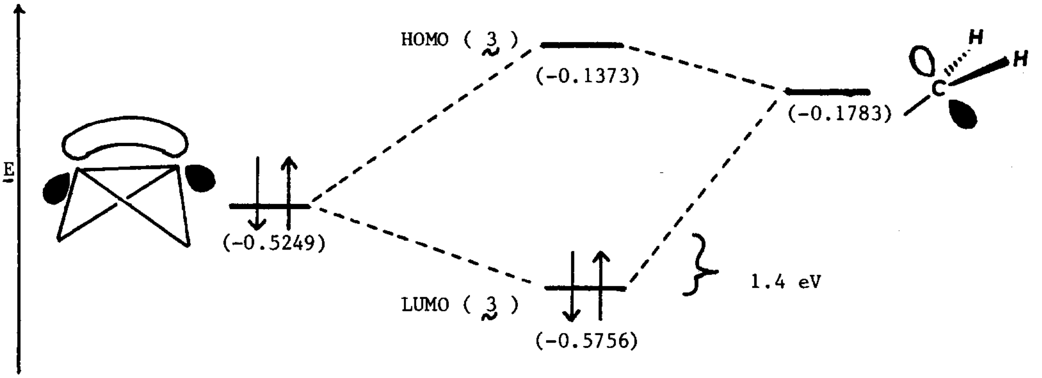
the geometries of 3 and 4 will accentuate this energy difference by enhancing the stabilization in 3 relative to that in 4. Furthermore, comparison with STO-3G results for neopentyl cation,[5] in the manner of the isodesmic reactions 1 and 2, in a manner very similar to the approach taken in reference 5, indicates that 3 is stabilized by 28.2 kcal/mole while 4 is destabilized by 3.6 kcal/mole (1 hartree = 627 kcal/mole). The origin of the effect is a

1) T.E.(3) = T.E.(neopentyl cation) + T.E.(bicyclobutane) - T.E.(isobutane)
model (-190.69193) = (-193.15890) + (-152.99802) - (-155.46499)
STO-3G Result: T.E.(3) = -190.73700; Stabilization = 28.2 kcal/mole

2) T.E. (4) = T.E.(neopentyl cation) + T.E.(bicyclobutane) - T.E.(isobutane)
STO-3G Result: T.E.(4) = -190.68621; Destabilization = 3.6 kcal/mole

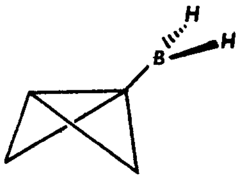
highly stabilizing interaction between the substituent's vacant p orbital and the highest occupied molecular orbital (HOMO) of bicyclobutane which is the pi orbital connecting C1 and C3 discussed earlier. Figure 1 depicts this interaction where the eigenvalues of the substituent's "unperturbed" vacant p orbital and bicyclobutane's "unperturbed" HOMO are actually the LUMO and HOMO , respectively, in 4 which is employed as a standard.

Figure 1. Interaction of "bicyclobutane HOMO" and "vacant ρ orbital" in 3. The numbers in parenthesis are orbital energies in hartrees.

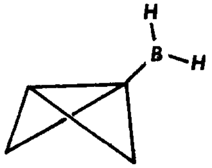


The large stabilization calculated for 3 is consistent with the observed solvolytic reactivity of 1-bicyclobutylcarbinyl p-nitrobenzoate, which is at least 1000 times more reactive than cyclopropylcarbinyl p-nitrobenzoate.[10] (2-Bicyclobutylcarbinyl tosylates solvolyze at rates comparable to those of cyclopropylcarbinyl tosylates[11]). Although this does not establish that the 1-bicyclobutylcarbinyl cation has actually been generated experimentally, the solvolytic data is not inconsistent with the intermediacy of this highly stabilized cation. It is also tempting to attribute the anomalously rapid solvolyses of bridgehead bicyclo(1.1.1)pentyl derivatives[12] to rate-determining formation of 3.However, Chandrasekhar and Schleyer have obtained an extremely interesting calculational result in which the 1-bicyclo(1.1.1)pentyl cation (best understood as a stable complex of CH^+ and trimethylenemethane) rearranges extremely rapidly to the 3-methylenecyclobutyl cation (STO-3G T.E. -190.76776 hartree) without the intervention of 3.[13]

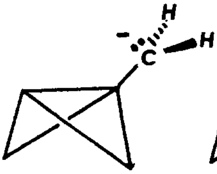
The total energies have also been calculated for eclipsed(5) and bisected (6) conformations of 1-bicyclobutylborane (trigonal geometry at boron, C-B = 1.57 Å, B-H = 1.16 Å) as well as eclipsed (7) and bisected (8) conformations of 1-bicyclobutylcarbinyl anion. The latter were assigned the same geometries as 3 and 4. The validity of calculated results on anions has been discussed.[14] The calculated rotational barrier in



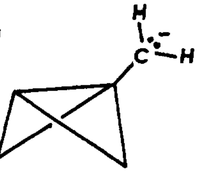
5
(-177.95811)



6
(-177.94363)



7
(-190.71258)



8
(-190.70685)

1-bicyclobutylborane is only 9.1 kcal/mole consistent with the relatively small pi electron demand of neutral BH_2 compared with CH_2^+. Furthermore, even the less stable conformer **6** is stabilized by 9.4 kcal/mole (in the manner of equations 1 and 2) because the substituent is an appreciable sigma donor. The rotational barrier in 1-bicyclobutylcarbinyl anion is only about one ninth that calculated for the cation. This is in marked contrast with the rotational barriers calculated for "3-propenyl cation" and "3-propenyl anion" (C1-C2 = 1.35 Å, C2-C3 = 1.47 Å) which are 32.2 and 40.7 kcal/mole respectively. (Obviously allyl cation[5,7] and allyl anion[15] are more stable than these ions; it is our purpose here to examine the interactions between idealized CH_2^+ and vinyl substituents.) If rotational barriers are employed as measures of the pi conjugation of unsaturated systems with the substituents investigated, then it appears that the central bond in bicyclobutane is comparable to the vinyl group in its ability to stabilize a carbocationic center but quite inferior in its ability to stabilize a carbanionic center.

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