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DOES DOUBLE HYPERCONJUGATION PLAY A ROLE IN 1-BICYCLO[2.2.2]OCTYL CATION ?
THE THROUGH-SPACE EFFECT OF POLAR SUBSTITUENTS

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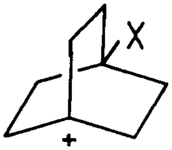
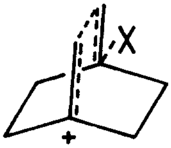
Summary. The calculated structure (ab initio,STO-3G) of 1-bicyclo[2.2.2]octyl cation does not reveal stabilization by double hyperconjugation,postulated recently. The calculated energetic effect of 5 polar groups at C4 show the dominance of the through-space effect.

Hyperconjugation[1] has now become a well defined concept; the stabilizing effect of a ß-substituent in ethyl cations can be estimated by calculating the energy difference of the perpendicular vs. the bisected conformations of such cations[2].

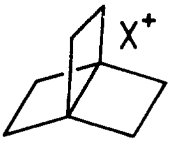
Recently Grob and Rich[3], on the basis of solvolysis experiments on 18 4-substituted bicyclo[2.2.2]octyl nisylates, postulated the existence of a previously unobserved hyperconjugative effect in 1-bicyclo[2.2.2]octyl cations I,termed twofold CC- or HC-CC- hyperconjugation, to explain the enhanced solvolysis rate for some substituted as well as for the parent compound (X=H).



I



II



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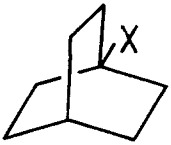


IV

The authors suggest a hyperconjugatively stabilized transition state,leading to a cation as illustrated in II. If II does imply participation of the C4-H or C4-X σ-bond in stabilizing the cationic center at C1 and does not merely depict one out of the three equivalent resonance hybrids representing normal and expected ß-CC-hyperconjugation in I, it is basically difficult to interpret Grob's concept in a physical sense.

It is the purpose of this communication to show that theory provides no support for a twofold CC- or HC-CC- hyperconjugative mechanism nor any significant homohyperconjugative stabilization as indicated in III - an alternative structure which could account for a stabilization of the bridgehead cation.

Therefore we have studied cation I and hydrocarbon IV theoretically using MINDO/3[4] and ab initio methods at the RHF/STO-3G level[5]. In the calculations of the structures I and IV the geometry of the carbon framework, as well as the bridgehead hydrogen, was optimized assuming C_{3v}-symmetry for either species[6]. In Table 1 all relevant parameters are summarized.

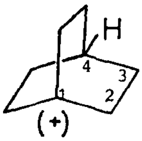
Table 1. Geometry of cation I and hydrocarbon IV; bond lengths in [Å], angles in deg.

species	parameter	MINDO/3[a]	MINDO/3[b]	STO-3G	exp.[c]
cation I (X=H)	C1-C2	1.497	1.498	1.500	
	C2-C3	1.554	1.544	1.587	
	C3-C4	1.554		1.552	
	C4-H	1.116		1.088	
	C1-C4	2.345	2.348	2.364	
	∢C4C1C2	80.2		80.2	
	∢C1C4C3	69.8		70.3	
hydrocarbon IV (X=H)	C1-C2	1.549	1.549	1.545	1.538
	C2-C3	1.531	1.531	1.552	1.552
	C4-H	1.120		1.089	
	C1-C4	2.591	2.593	2.596	
	∢C4C1C2	70.0		70.3	

[a] this work [b] from ref.7 [c] from ref.8

It is apparent that the C2-C3 bond in the cation is elongated substantially (STO-3G), showing efficient hyperconjugation of the ß σ-bonds. The value is comparable to that of 1.59 Å calculated for the ß bond in the perpendicular form of 1-propyl cation[2]. For the bridgehead hydrogen on C4 a C-H bond lenght of 1.088 Å is calculated - almost the same as in the uncharged species IV (1.089 Å). Charge distribution and overlap populations of parent cation I compared to hydrocarbon IV gives further information about the character of the species (see Table 2). By none of the three tests can a contribution of structure II or III be substantiated.

Table 2. Charge distribution and overlap population of I and IV



charge distribution

atom	species I	species IV
C1	+0.280	-0.028
C2	-0.132	-0.104
H on C2	+0.122	+0.048
C3	-0.100	-0.104
H on C3	+0.104	+0.048
C4	-0.046	-0.028
H on C4	+0.107	+0.050

overlap population

bond	species I	species IV
C1-C2	0.750	0.724
C2-C3	0.641	0.716
C3-C4	0.721	0.724
C4-H	0.770	0.716
C1-C4	-0.035	-0.032

Effect of polar substituents

In order to evaluate the influence of polar substituents at the bridgehead position on the stability of cation I, we calculated the energetic effect of five groups; X= CH_3, CCH, OH, F, and CN on the isodesmic reaction (1) and compared this result with the effect of substituents for isodesmic reactions (2) and (3)[9].

(1)[a] $RX^+ + HR'H \rightleftharpoons RH^+ + HR'X$

(2)[b] $X(CH_2)_4^+ + CH_3(CH_2)_2CH_3 \rightleftharpoons CH_3(CH_2)_3^+ + X(CH_2)_3CH_3$

(3)[c] $XCH_3...CH_3^+ + CH_4...CH_4 \rightleftharpoons CH_4...CH_3^+ + XCH_3...CH_4$

[a] R = cation I,without bridgehead substituent;optimized as described
R'= hydrocarbon IV,without bridgehead substituents;optimized as described
for all bridgehead substituents standard geometry was used

[b] standard geometry used;see ref.2

[c] see text below for explanation

Recent calculations,on an ab initio basis,of remote substituent effects in cationic species such as protonated benzenes have been shown to be consistent with experimentally determined gas-phase values[10].In Table 3 the energy change of isodesmic reaction (1) is compared with the published values of δ-substituent effects of the bisected form of the 1-butyl cation[2](isodesmic reaction(2)). To get further information about the nature of the substituent effects we simulated the system by a model described as follows : The three ethano groups connecting the bridgehead carbons in I and IV respectively are replaced by hydrogens.Bridgehead carbons are fixed in the same positions as in I and IV,respectively.Where in I or IV a C(bridgehead)-C(bridging) bond was present,we now introduced a C(bridgehead)-H bond with standard bond lengths (C-H 1.09 Å; C^+-H 1.12 Å; angles XCH are the same as XCC in I or IV;bond lengths C-X are standard values).In this model no interaction between the center of positive charge and the substituents through bonds is possible.Transmission of polar effects is expected to reflect the electrostatic interaction between the center of the positive charge of the cation and the field of an electric dipole created by the polar C-X bond.This approach is to some extent similar to the electrostatic field model developed by Kirkwood and Westheimer[11].The isodesmic reaction (3) for our model is compared with reactions (1) and (2) (see Table 3).

Table 3.Calculated ΔE-values of isodesmic reactions (1),(2),and (3) for various substituents X in kcal mole^{-1}

substituent X	ΔE of (1)	ΔE of (2)	ΔE of (3)
CH_3	1.1	0.7	2.6
H	0.0	0.0	0.0
CCH	-2.6	-2.2	-5.1
OH	-4.4	-1.6	-6.8
F	-6.8	-4.2	-11.4
CN	-11.6	-8.3	-14.9

We draw the following conclusions from these results :

(1) Effects of substituents on the relative stability of the cations are larger in bicyclic systems than the normal δ-effect in alicyclic compounds.

(2) Substituent effects on the relative stability of bicyclic compounds and their cations parallel those found in the model,indicating the dominance of the through-space effect .Not surprisingly,substituent effects on the stability of cations are even larger in the model than in bicyclic cations

themselves; in the latter case the positive charge can be delocalized on a larger number of atoms.

(3) According to our analysis a methyl substituent on the bridgehead leads to a stabilization of the cation relative to a hydrogen substituent. The decreased rate observed for the methyl substituent in solvolysis of bicyclo [2.2.2]octyl sulfonate and adamantyl bromide[12] has to be attributed to alternative factors such as solvent effects[13]. Steric hindrance to solvation in transition states leading to cationic intermediates is generally accepted as important for cases in which a Baker-Nathan order is observed[14].

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