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THE ENERGY SURFACE OF $[(CH)_3(CH_2)]^+$ CATIONS

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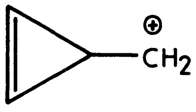
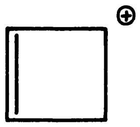
Potential curves calculated for the $[(CH)_3(CH_2)]^+$ system show that the cyclopropenylcarbinyl, planar cyclobutenyl, and bicyclobutyl cations, are all surrounded with relatively low energy barriers, if at all, and that they would readily collapse to the most stable conformer, puckered homocyclopropenyl cation 2b.

Our interest in the $[(CH)_n(CH_2)_m]^+$ species[1] has been extended to $[(CH)_3(CH_2)]^+$ cations. Included in this group are cyclopropenylcarbinyl (1), cyclobutenyl (2), and bicyclobutyl (3), and the entire system has now been theoretically examined.[2] While we were being involved in sophisticated and extremely difficult experiments to seek for evidence, there appeared recently a note, analyzing the conversion of 3 to its degenerate isomer.[3] This has prompted us to summarize our extensive study on this system and to comment on the experimental feasibility of testing the theoretical prediction.



1



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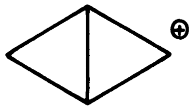
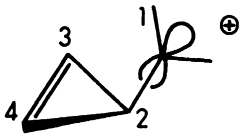


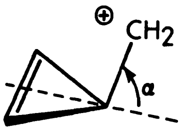
3

Adopting MINDO/2,[4] we have first examined potential surfaces in the neighborhood of cations 1, 2, 3, vertically generated from the corresponding precursors. Application of the OPTMO program[5] has automatically created the geometry corresponding to an energy minimum. For those conformers which are not minima, the most likely arrangement of nuclei has been assumed in order to remove undue strain.[6]

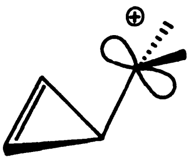
Cyclopropenylcarbinyl (1). There are two conformers (bisected) **1a** and (eclipsed) **1b** conceivable for this species. The former is a local minimum, surrounded with energy walls, as is shown by changing dihedral angle α defined in A. The interaction of the empty *p*-orbital of C(1) with an asymmetrical (σ plane) orbital of the cyclopropenyl moiety is significant, resulting in shortening of both the C(3)-C(4) double bond (1.25 Å) and C(1)-C(2) single bond (1.35 Å), and elongation of the C(2)-C(3) single bond (1.57 Å) as well as in the development of the positive charge at C(3) and C(4). In contrast, **1b** represents an energy maximum and leads to **1c** and **1d** with an increase and decrease of angle α, respectively. Apparently the interaction of the *p*-orbital [C(1)] with the cyclopropene is insignificant in **1b**, compared with that observed in **1a** (*vide supra*).



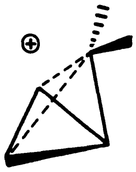
1a



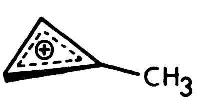
A



1b

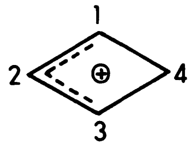


1c

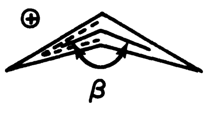


1d

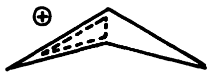
Cyclobutenyl (2). This cation is formally the homocyclopropenyl cation discussed by Winstein.[7] In its planar form (C_{2v})(**2a**), the energy of the system is not minimal and the type of electron delocalization is allylic rather than homoaromatic. Thus, carbons 1 and 3 are 1.89 Å apart and the charge densities at carbons 1 and 2 are +0.29 and -0.03, respectively. As one bends this system as shown below, it reaches an energy minimum with angle β = 142° (conformer **2b**). The bond length between carbons 1 and 3 is now shortened to 1.65 Å and the system is assumed to be homoaromatic in nature. The C(1)-C(3) bicentric energies[8] of **2a** and **2b** are -0.5 and -4.94 eV, respectively. The energy difference (16 kcal/mole) between the two conformers can be taken as an inversion barrier for this bent cyclobutenyl cation.



2a

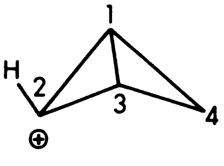


B

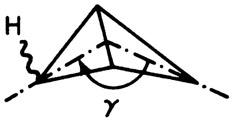


2b

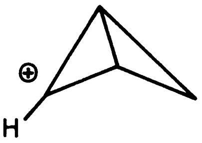
Bicyclobutyl (3). A potential minimum corresponding to this system has not been found. Therefore, a most likely geometry[9] is assumed to have an angle, γ = 120°. The energy of this system is very sensitive to the geometry of the hydrogen indicated in **3a**, **3b**, and **3c**. Thus conformer **3b** with the hydrogen atom in the plane of carbons 1, 2, 3 is stable with respect to **3a** and **3c**. As one expands angle γ from 120°, all three conformers lead to cyclobutenyl cation **2b**, while the decrease converts **3c** to **1c**.



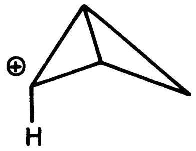
3a



C



3b



3c

As described above, **1**, **2**, and **3** are interrelated as a function of angle α or γ, and the entire energy diagram with the relative energy of each representative conformer is shown in Figure 1. Curves to connect two conformers are somewhat arbitrarily chosen and pathways that are not shown here are of course conceivable. For example, if degenerate isomerization of **3** proceeds through **1**,[3,10] ([1,2]sigmatropic isomerization), then the preferred reaction would involve **1a** rather than **1b**, the former being some 20 kcal/mol more stable than the latter (*vide supra*). Stereochemically, this would bring about a rearrangement *with inversion* at the migrating center, a process that violates *formally* the orbital symmetry selection rule.[11] Experiments to test this prediction are difficult to devise, due to the anticipated collapse of **3a-c** into **2b**. Thus we feel that any $[(CH)_3(CH_2)]^+$ cations once generated, would undergo facile rearrangement to provide **2b**, which would be the only carbocation observable under currently feasible experimental conditions. The inversion barrier for **2b** appears to be within a range measurable by n.m.r. spectroscopy. Diphenylcyclo*propenyl*carbinyl tosylate solvolyzes only three times faster than diphenylcyclo*propyl*carbinyl tosylate and eleven times faster than anisylphenylcyclo*propenyl*carbinyl tosylate.[13] Thus the effect of the cyclopropenyl double bond and methoxy group on the rate is negligible. This fact is consistent with the above result that a cation similar to **1a** rather than **1b** is involved in the reaction and the stability of **1a** arises from a type of interaction analogous to that now well-accepted for the cyclo*propyl*carbinyl cation.

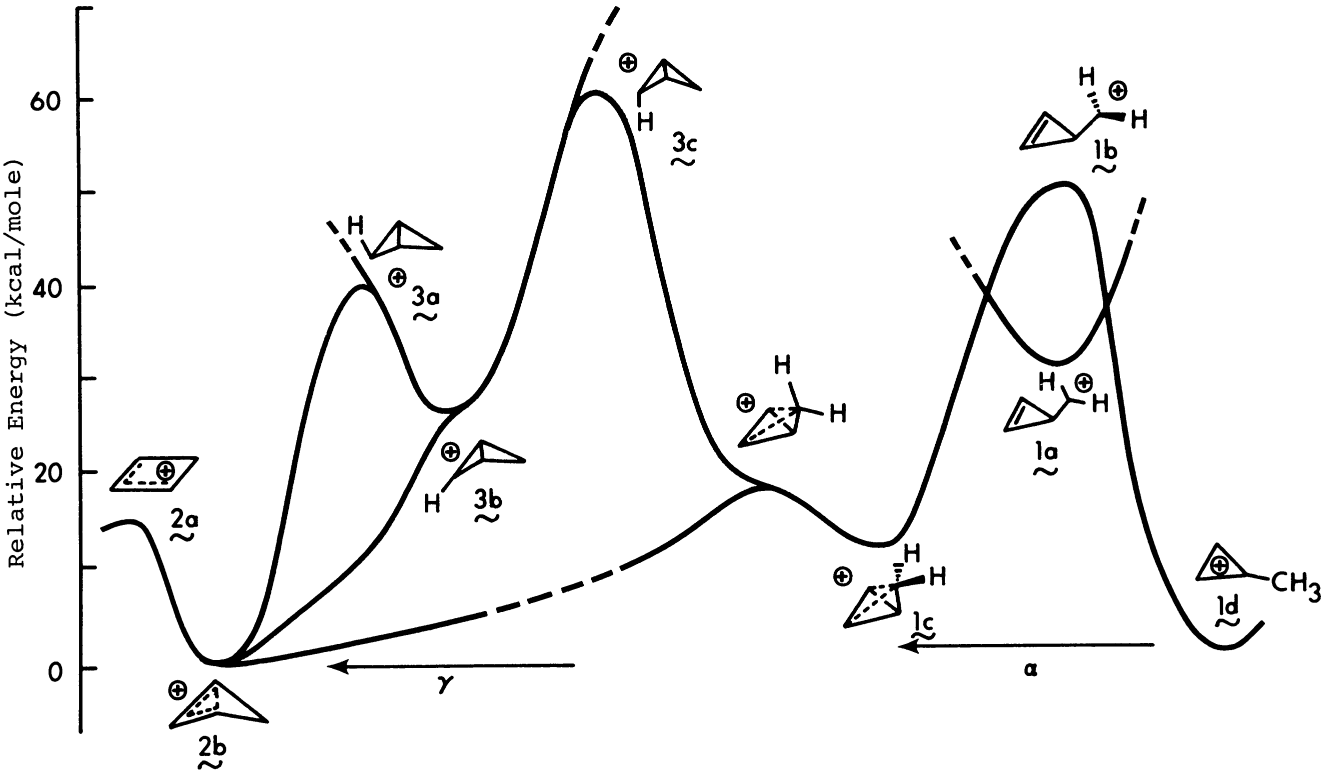
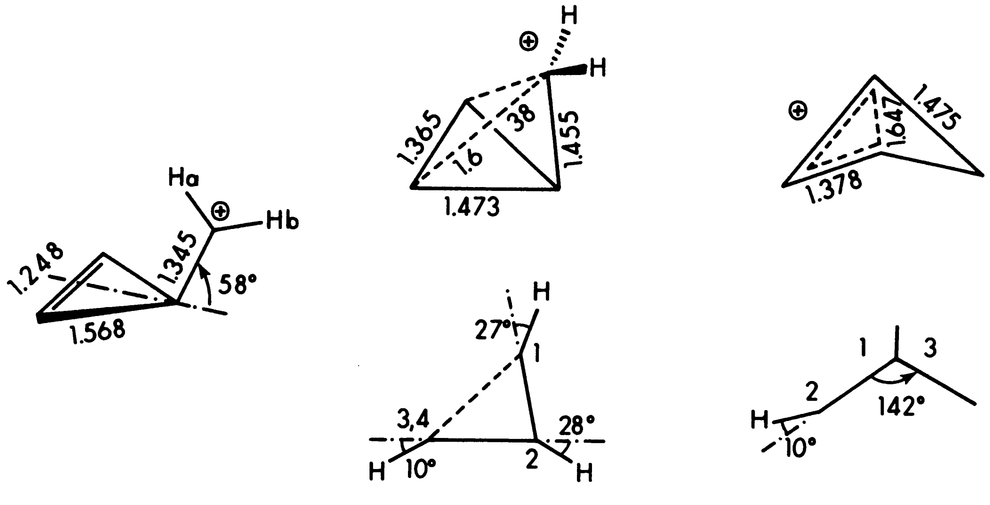


FIGURE 1. $\left[(CH)_3(CH_2)\right]^+$



1a 1c 2b

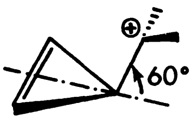
FIGURE 2. OPTIMIZED STRUCTURES OF 1a, 1c, AND 2b.

Table 1. Charge Distributions of 1a, 1c, and 2b.

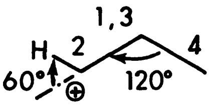
Compounds	Carbon Atoms	Charge	Hydrogen Atoms	Charge
1a	C(1)	+0.202	$H_a(1)$	+0.086
			$H_b(1)$	+0.054
	C(2)	+0.038	H(2)	+0.054
	C(3)	+0.141	H(3)	+0.141
1c	C(1)	+0.067	H(1)	+0.097
	C(2)	+0.077	H(2)	+0.121
	C(3)	+0.150	H(3)	+0.121
2b	C(1)	+0.168	H(1)	+0.094
	C(2)	+0.116	H(2)	+0.125
	C(4)	+0.079	$H(4)_{equat.}$	+0.070
			$H(4)_{axial}$	+0.087

REFERENCES AND NOTES

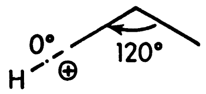
1. For a short summary of $[(CH)_n(CH_2)_m]^+$ chemistry, see N. Nakamura and S. Masamune, Yûki Gôsei Kagaku Kyôkai-shi (Japan), in press.
2. Presented before the Annual Congress of the Chemical Society (London), April 3, 1974.
3. A.J.P. Devaquet and W. J. Hehre, J. Amer. Chem. Soc., 96, 3644 (1974).
4. M.J.S. Dewar and E. Haselback, ibid, 92, 590 (1970); N. Bodor, M.J.S. Dewar, and E. Haselbach, ibid, 92, 3854 (1970).
5. No. 217 Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.
6. For the conformers that fall in this category are 1b, 3a-c, and the geometries are assumed to be as shown below.



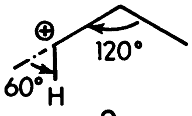
1b



3a



3b



3c

7. S. Winstein, Quarterly Reviews, *23*, 141 (1969).

8. *E.g.* J.A. Pople and D.L. Beveridge, "Approximate Molecular Orbital Theory," McGraw Hill Inc., New York, N.Y., 1970, Chap. 3.

9. K.W. Cox, M.D. Haronony, G. Nelson, and K.B. Wiberg, J. Chem. Phys., *50*, 1976 (1969).

10. The MINDO/2 treatment is known to underestimate strain energy. Thus the result that **1c** is stable with respect to **1a** is not reliable.

11. R.B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie Gmbh., Weinheim 1970, Chap. 7. The selection rule, as it is formulated, automatically neglects the unique orbital interaction, present in the system involving cyclopropane (Walsh type)[12] and cyclopropene but normally absent in those containing ordinary, larger ring systems. This case manifests this special property of the small ring systems, thus representing a rare exception to the rule.

12. R. Hoffmann and R. Davidson, J. Amer. Chem. Soc., *93*, 5699 (1971).

13. R. Breslow, J. Lockhart, and A. Small, ibid, *84*, 2793 (1962).

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