CHEMISTRY LETTERS, pp. 1107-1111, 1974. Published by the Chemical Society of Japan

THEORETICAL EVALUATION OF TRISHOMOCYCLOPROPENYL AND BISHOMOSQUARE PYRAMIDAL CATIONS

Kazuhiko MORIO and Satoru MASAMUNE

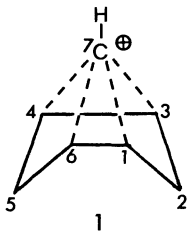
Department of Chemistry, University of Alberta,

Edmonton, Alberta, Canada

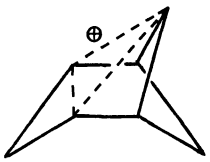
The lowest energy minimum is calculated for two systems, bicyclo[3.1.0]hex-3-yl and tricyclo[3.1.1.$0^{2,4}$]hept-6-yl, and corresponds to the C_{3v} and C_{2v} structures, respectively.

Since the symmetry of a species exhibited by n.m.r. spectroscopy of necessity is subject to the limitation of the n.m.r. time scale, the molecular geometry that satisfies the required symmetry does not always represent the lowest energy minimum of the system, but an intermediate or a transition state intervening between a degenerate pair of less symmetrical structures. To evaluate this often encountered, subtle problem, one normally utilizes arguments based on the chemical shift and coupling constant and further applies other spectroscopic methods.[1,2] Two bishomosquare pyramidal cations (1 and 2) recently generated[3,4] in our laboratories are not exceptional in this sense, and our tentative conclusion that (1) appears to be more stable than (1a) (trishomocyclopropenyl derivative) and (1b) rests on indirect evidence. Now that the parent trishomocyclopropenyl cation (3)[5] and its derivative (4)[6] have been successfully generated, it is most appropriate to record calculations for these systems to lend further support to the conclusions derived earlier.

Using MINDO/2,[7] the potential energy surfaces of the bicyclo[3.1.0]hex-3-yl(trishomocyclopropenyl) and tricyclo[3.1.1.$0^{2,4}$]hept-6-yl(bishomopyramidal) system were calculated as a function of dihedral angle α as shown in Diagram 1. Since no structural data are available for the systems, we optimized geometries that correspond to energy minima, utilizing the OPTMO procedure available from Q.C.P.E. For each value of α the energy was minimized with respect to other variables, in particular the orientation and length of the C-H bond to eliminate undue strain energy.

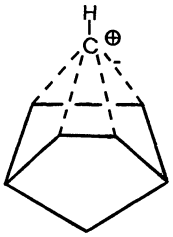


1

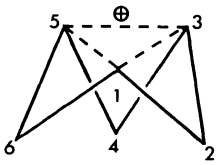


1a

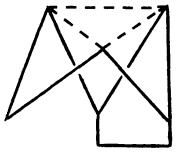
1b



2



3



4

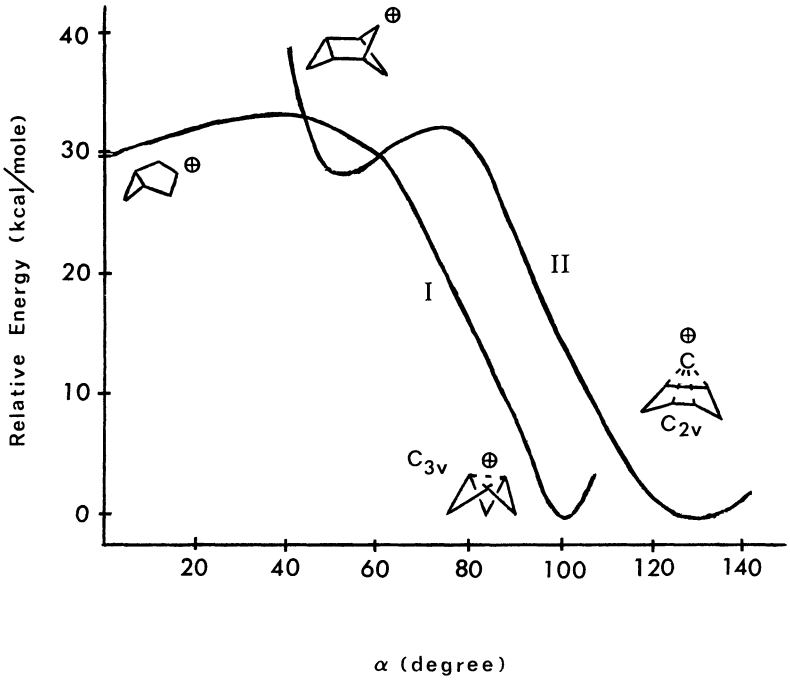


DIAGRAM 1

Trishomocyclopropenyl Series. Two energy minima on the potential curve I correspond to planar cyclopentyl(α=0°) and the structure of C_{3v}(α=101°), the former being ca. 30 kcal./mole less stable than the latter. The geometry of C_{3v} is shown in Figure 1 and the charge distribution and bond index[9] are summarized in Table I. The C(1)-C(3)[10] bond distance is 1.68 Å, thus allowing effective overlap of three p-rich-orbitals (a_1 level). The positive charge is, as expected, evenly distributed over C(1), C(3), and C(5) and the fact that 51.3% of the total charge now resides on the hydrogen atoms of the cation, attracts interest (vide infra). The calculated $J_{13_{C-H}}$ values agree well with those found experimentally.[11]

Table I. Bond Index and Atomic Charge of 3

	E_{A-B} (eV)	Bond Index
C(1)-C(2)	-13.81	0.95
C(1)-C(3)	- 6.30	0.46

	Atomic Charge	Total
C(1)	0.129	0.486
C(2)	0.033	
H(1)	0.053	
$H(2)_{axial}$	0.045	0.513
$H(2)_{equat.}$	0.073	

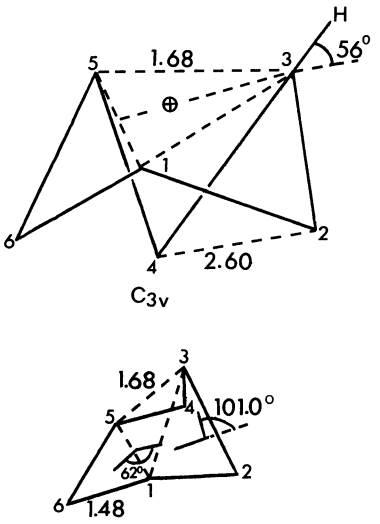


Figure 1

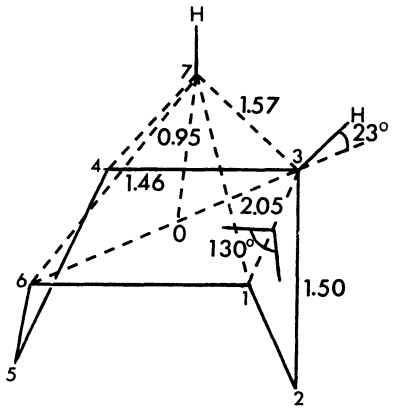
Bishomosquare Pyramidal Series. Of two minima on the potential curve II calculated for this system, the one of higher energy corresponds to the structure with α = 50°, stabilized in a manner similar to the cyclobutonium cation.[9] The other, representing the lowest energy minimum, appears at α = 127° and the corresponding geometry possesses C_{2v} symmetry, but not C_s(trishomocyclopropenyl derivative). Interesting features of the structure shown in Figure 2 are: i) The C(1)-C(7) bond distance is 1.57 Å, being nearly a C-C single bond, and ii) while the C(1)-C(6) bond length,1.46 Å, is shorter than the normal single bond, C(1) and C(3) are stretched out 2.05 Å apart. Thus, the C_{2v} species resembles bent cyclohexa-1,4-diene complexed to $(CH)^+$ and in order to achieve effective overlap of the orbitals of the two segments, the hydrogen atoms attached to the basal carbons are directed

upwards (23°). As shown in Table II, most of the charge is located at the basal carbons and the hydrogens attached to them, and to our surprise, the apical carbon is the least positively charged atom.

Table II. Bond Index and Atomic Charge of 2

	Bicentric Energy	Bond Index
C(1)-C(6)	-14.86	1.06
C(1)-C(7)	- 9.82	0.72
C(1)-C(3)	- 0.50	0.04
C(1)-C(2)	-14.26	0.97

	Atomic Charge	Total
C(7)	0.018	
C(1)	0.104	0.510
C(2)	0.038	
H(7)	0.062	
H(1)	0.063	0.492
$H(2)_{equat.}$	0.057	
$H(2)_{axial}$	0.032	



C_{2v}

Figure 2

This result is in accord with at least two experimental observations i) the ^{13}C.m.r. signal assigned to C(1) of (2) appears at extraordinarily high field (δ_{TMS} -17.15) and ii) quenching of (2) induces nucleophilic attack of solvent (methanol) at a basal carbon, although the mechanism involved in this reaction is complicated and the present interpretation is obviously oversimplified. When C(3) and C(4) of (1) are compressed inward, the calculation shows that the charge density at C(7) increases. Cation 2 may presumably respond to this effect, thus the chemical shift of the apical carbon shifts downfield by ca. 20 p.p.m. and the quenched products now consist of two compounds, showing that both the apical and basal positions are attacked.

The above theoretical results are, at least qualitatively consistent with the earlier observations and conclusions regarding the structures. Even with full awareness of the limitation[12] imposed on the semi-empirical treatment, the outcome

is extremely gratifying.

References and Notes

1. E.g., G. A. Olah, G. D. Mateescu, L. A. Wilson, and M. H. Gross, J. Amer. Chem. Soc., 92, 7231 (1970).
2. E.g., G. A. Olah, A. M. White, J. R. DeMember, A. Commeyas, and C. Y. Lui, ibid., 92, 4627 (1970).
3. S. Masamune, M. Sakai, A. V. Kemp-Jones, H. Ona, A. Venot, and T. Nakashima, Angew. Chem. Int. Ed. Eng., 12, 769 (1973); also see H. Hart and M. Kuzuya, J. Amer. Chem. Soc., 94, 8958 (1972).
4. S. Masamune, A. V. Kemp-Jones, and N. Nakamura, J. Chem. Soc., Chem. Comm., 109 (1974).
5. S. Masamune, M. Sakai, and A. V. Kemp-Jones, and T. Nakashima, Can. J. Chem., 52, 855 (1974).
6. S. Masamune, M. Sakai, and A. V. Kemp-Jones, ibid., 52, 858 (1974).
7. M. J. S. Dewar and E. Haselbach, J. Amer. Chem. Soc., 92, 590 (1970); N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, ibid., 92, 3854 (1970).
8. R. Hoffmann, Tetrahedron Lett., 3819 (1965).
9. K. B. Wiberg, Tetrahedron 24, 1083 (1968); K. B. Wiberg, and G. Szeimies, J. Amer. Chem. Soc., 92, 571 (1970).
10. The numbering system of the cations is arbitrary.
11. The EH treatment of the same system reported earlier[8] showed a minimum at $\alpha = 76°$ (C_s), presumably due to neglect of variables other than the dihedral angle.
12. Semi-empirical treatments such as MINDO/2 utilized in the present work tend to lower unduely the energy of a structure of higher symmetry as opposed to a less symmetrical one. Thus, the results shown above should be taken as qualitative rather than quantitative.

(Received May 15, 1974)