

The 9-Barbaralyl Cation

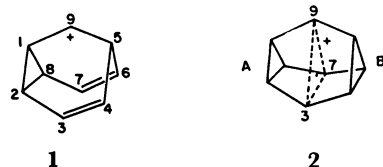
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We find that the 9-barbaralyl cation assumes a structure with 3-fold symmetry in which there is an interesting orbital pattern caused by strong conjugative interaction of the central p orbitals with the cyclopropane rings. We think this symmetrical cation is identical with the transition state for the Cope rearrangement of 9-barbaralyl cation.

At -135°C , in super acid media, the 9-barbaralyl cation **1** undergoes a sequence of rapid rearrangements which renders all protons equivalent on the NMR time scale.¹⁾ Under solvolytic conditions evidence for a somewhat faster and less degenerate rearrangement



has been obtained.²⁾ In this process positions 3,7,9 are made equivalent, as are 1,2,4,5,6, and 8.

Several mechanisms may be written for both the partially degenerate and totally degenerate rearrangements.¹⁻³⁾ For the former process an attractive transition state or intermediate which in its molecular symmetry reflects the degeneracy of the rearrangement is the D_{3h} C_9H_9^+ cation **2** suggested by Schleyer and coworkers.^{2a,b)} It also accidentally represents a confluence of four areas of our interest: the ability of a cyclopropyl group to enter into conjugation,⁴⁾ the concept of through-bond coupling,⁵⁾ the modification of the Cope rearrangement,⁶⁾ the structure and rearrangements of $(\text{XH})_n$ species.⁷⁾ We present here an analysis of its electronic structure.

Consider the interaction of the Walsh orbitals^{4,8)} of cyclopropane rings A and B of **2** with the set of three p orbitals at C_3 , C_7 and C_9 . These latter three orbitals

1) P. Ahlberg, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4454 (1970).

2) a) J. C. Barborak, J. Daub, D. M. Follweiler, and P. von R. Schleyer, *ibid.*, **91**, 7760 (1969); b) J. C. Barborak and P. von R. Schleyer, *ibid.*, **92**, 3184 (1970); c) J. B. Grutzner and S. Winstein, *ibid.*, **92**, 3186 (1970).

3) R. E. Leone and P. von R. Schleyer, *Angew. Chem.*, **82**, 889 (1970).

4) a) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); b) R. Hoffmann, *Tetrahedron Lett.*, **1965**, 3819; c) R. Hoffmann, *ibid.*, **1970**, 2907.

5) a) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968); b) R. Hoffmann, E. Heilbronner, and R. Gleiter, *ibid.*, **92**, 706 (1970); c) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

6) R. Hoffmann and W. -D. Stohrer, *J. Amer. Chem. Soc.*, **93**, 6941 (1971).

7) a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1963); b) R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963). c) W. -D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972). d) M. J. Goldstein, *ibid.*, **89**, 3657 (1967). e) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).

8) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

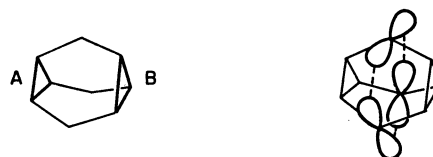
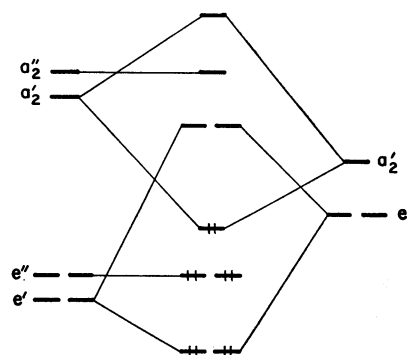


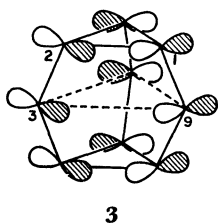
Fig. 1. Interaction of cyclopropane ring orbitals (left) with orbitals of carbons 3, 7, and 9 (right).

also generate a Walsh set, with a doubly degenerate e' orbital below a nondegenerate a_2' , but the splitting between e' and a_2' must be much smaller than in a normal cyclopropane because the C_3 - C_7 distance is long. Figure 1 shows the interaction of the orbitals of rings A and B with this inner set. The following points emerge:

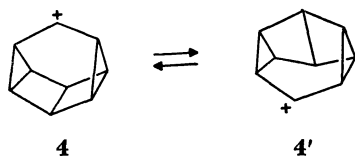
1) The highest occupied MO is a_2' . Interaction of the inner set with the Walsh orbitals of rings A and B reverses the direct overlap determined ordering e' below a_2' . This is because the overlap of a C_3 p orbital with the optimally aligned Walsh orbitals of rings A and B is greater than its overlap with C_7 or C_9 p orbitals. In an extended Hückel calculation on **2** with CCC angles of 120° at C_3 , C_7 , and C_9 the a_2' orbital emerges 2.0 eV below e' .

2) The shape of the a_2' orbital is given in **3** below. Since it is composed of the a_2' combination of inner orbitals mixed in a bonding way with the antibonding a_2' combination of outer ring orbitals it leads to stronger C_1 - C_9 , weaker C_1 - C_2 bonds (only one member of the symmetry related set is given). a_2' is 3-7, 3-9, 7-9 antibonding, and so representation **2**, if it implies any such bonding, is inappropriate.⁹⁾

9) Similar results have been obtained by S. Yoneda, S. Winstein, and Z. Yoshida, *This Bulletin*, **45**, 2510 (1972). We are grateful to Dr. Yoneda for communicating his results to us prior to publication.

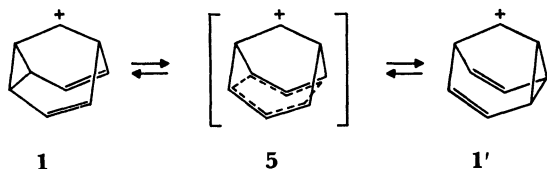


3) The collapse of **2** to **4** is a symmetry forbidden process. This is perhaps easiest seen by noting that the new 3-7 σ bond in **4** is symmetric with respect



to reflection in the symmetry plane perpendicular to that bond, but the occupied a_2' orbital of **2** is antisymmetric. Thus the hypothetical rearrangement of **4** to **4'** where the cationic center shifts from say C_7 to C_3 cannot proceed *via* the transition state or intermediate **2**. A less symmetrical circumvention, like that we have discovered in $C_5H_5^+$,^{7c)} is here made geometrically unlikely.

We now turn to the relationship of cation **2**, its electronic structure described in Fig. 1, to the transition state **5** for the degenerate Cope rearrangement of **1** \rightleftharpoons **1'**. This rearrangement was considered but dis-

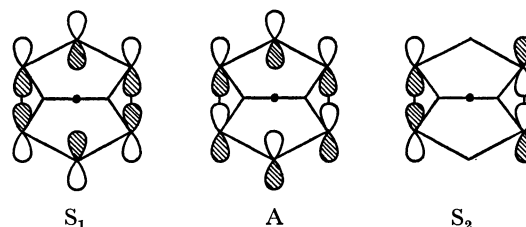


carded as a source of degeneracy in the rearrangements of the 9-barbaralyl and 9-methyl-9-barbaralyl cations by Ahlberg, Grutzner, Harris, and Winstein.^{1,10)} The basis for discounting the occurrence of a Cope

10) P. Ahlberg, J. B. Grutzner, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 3478 (1970).

rearrangement was apparently the trend in Cope rearrangement activation energies on going from barbaralone to protonated barbaralone.¹⁰⁾ However we would like to reconsider the transition state **5** in view of its geometrical similarity to cation **2**.

The interconversion of **2** and **5** is a symmetry allowed process. Let us classify levels with respect to the mirror plane containing carbons 1, 9, and 5. The occupied levels in transition state **5** (or collapsed cation **1**) are two symmetric levels and one antisymmetric, shown schematically below.⁶⁾ (The view is along the



C_2 axis, from the top toward C_9). These correlate directly to the occupied levels of **2**: S_1 and S_2 go to form the 2-8 and 4-6 σ bonds, while A by mixing with the empty p orbital at C_9 goes over into the crucial a_2' orbital of **2**.

Given the structural similarities of **2** and **5** and the fact that they have similar electronic configurations we think it is highly likely that they are not distinct molecules but one and the same species. Whether this is a transition state or intermediate can be only decided by calculations better than the ones at our command. But we propose that the rearrangement of the 9-barbaralyl cation merges with the Cope rearrangement of the same molecule—the midpoint of that reaction is of D_{3h} symmetry and simply has three possible collapse channels.

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