Tetrahedron. Vol. 27, pp. 4401 to 4406. Pergamon Press 1971. Printed in Great Britain

GROUND STATES OF σ-BONDED MOLECULES—XIII*

7-NORBORNYL, 7-NORBORNENYL, AND 7-NORBORNADIENYL IONS AND RADICALS

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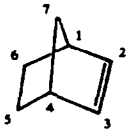
(*Received in the USA* 16 *March* 1971; *Received in the UK for publication* 17 *May* 1971)

Abstract—MINDO/2 calculations are reported for 7-norbornyl, 7-norbornenyl and 7-norbornadienyl ions and radicals, for the parent hydrocarbons, and for the degenerate rearrangement by "flipping" of 7-norbornadienyl cation.

INTRODUCTION

THE STRUCTURES of the 7-norbornyl (**1a**) and 7-norbornadienyl (**2a**) cations have been the subject of much speculation and controversy.[1] While it now seems to be generally agreed that they are last represented by "nonclassical" π complex structures,[1–4] stabilized by dative bonding from a double bond to the cationic center, no reliable theoretical studies have as yet appeared concerning these ions or the possible intervention of analogous interactions in the corresponding anions or radicals.[‡]



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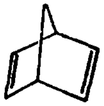

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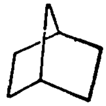

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a, 7-cation
b, 7-anion
c, 7-radical
d, parent hydrocarbon

Here we report calculations for **1a**, **2a**, the 7-norbornyl cation **3a**, the corresponding anions (**1b–3b**), and radicals (**1c–3c**), and the parent hydrocarbons (**1a–3d**), using the MINDO/2 method.[8] While this has given good results for heats of atomization and geometries in a wide variety of molecules, it has not yet been tested for nonclassical structures such as those believed to occur in the cations **1a** and **2a**; however it has proved successful[8,9] in treating the analogous delocalized structures

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[*] Part XII: Michael J. S. Dewar and Muthanna Shanshal, *J. Chem. Soc.*, in press

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[‡] Calculations for **1a** and **2a** by the extended Hückel method have been reported by Hoffmann,[5] and for norbornene by the CNDO/2 method by H. O. Ohorodnyk and D. P. Santry, *J. Amer. Chem. Soc.* **91**, 4711 (1969). As Hoffmann himself has pointed out,[5] the use of the extended Hückel method for ions is incorrect in principle, while the CNDO/2 method is also open to objection on the grounds that it gives estimates of heats of atomization that are in error by chemically huge amounts.[7]

that occur as transition states in various reactions, and it also gives good estimates[9, 10] of the energies of the ion-radicals formed by ionization of normal molecules. There is therefore reason to believe that its extension to the systems considered here should give meaningful results.

PROCEDURE AND RESULTS

The calculations were carried out with the CDC 6600 computer at the University of Texas Computation Center, using the parameters of ref 7b. The energies of radicals were calculated by the "half-electron" method.[11] Geometries were found by minimizing the energy with respect to variation of all bond lengths and bond angles, assuming only that each structure has a plane of symmetry passing through atom 7 and the midpoints of the 2,3 and 5,6 bonds. The minimization was carried out by an iterative procedure based on the simplex method;[12] the program (SIMPLEX) for the minimization was written by Dr. A. Brown. The results are shown in Table 1, using the notation of Fig 1.

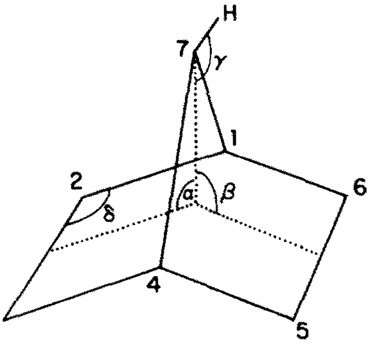

FIG 1. Key to angles (α,β,γ,δ) and numbering of atoms and bonds in Table 1

DISCUSSION

In the cations **1a** and **2a**, the bridgehead methine group is predicted to be tilted towards the 2,3 double bond and the 7-hydrogen away from it (*cf.* [5]), as one would expect[2] if the ion is indeed a π complex; for the tilting will increase the overlap between the π MO of the 2,3 bond and the vacant AO in the 7 position while pyramidal distortion of the 7 carbon atom will both further increase this overlap and reduce I-strain. In the case of **2a**, this geometry is consistent with the NMR spectrum.[5]

It is surprising to find the same kind of distortions in the saturated cation **3a**; presumably relief of I-strain at the 7-position and the favourable geometry conspire to favour a σ-complex* structure **6** in which the 2,3 σ bond acts as donor to the 7 position.

The radicals **1c** and **2c** show similar but smaller distortions, implying that the

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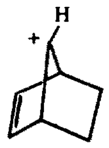
* Since the term π complex was introduced[13] to describe structures in which the π electrons of a double or triple bond are used to form dative bonds to acceptors, it seems logical to use the term "σ complex" to describe similar structures in which a σ bond acts as donor. Edge protonated cyclopropane and the non-classical ion postulated as an intermediate in the solvolysis of 2-bicyclo[3,1,0]hexyl esters would be possible examples.[2]

Table 1. Calculated geometries and heats of formation of **1**, **2** and **3**

Compound	Bond lengths (Å)					Angles (degrees)				Heat of formation at 25° (kcal/mole)
	1,7	1,2	2,3	4,5	5,6	α	β	γ	δ	
1a	1·532	1·495	1·392	1·528	1·566	77·4	153·6	164·5	104·8	173·2
1b	1·479	1·508	1·353	1·544	1·546	123·6	127·2	202·0	102·0	22·1
1c	1·504	1·492	1·344	1·528	1·559	115·8	126·8	176·9	102·3	25·8
1d	1·543	1·482	1·362	1·540	1·541	125·0	122·1	—	102·7	1·9
2a	1·540	1·501	1·381	1·465	1·339	77·2	154·8	172·3	109·3	201·7
2b	1·499	1·493	1·353	1·513	1·329	118·4	133·0	227·5	104·8	48·7
2c	1·509	1·466	1·341	1·528	1·346	117·3	124·3	176·1	108·8	53·6
2d	1·528	1·516	1·346	b	c	124·2	124·7	—	106·3	29·4
3a	1·478	1·545	1·579	b	c	98·9	142·0	176·9	105·1	179·0
3b	1·461	1·565	1·523	b	c	122·7	126·4	183·2	101·5	−5·2
3c	1·496	1·538	1·554	b	c	121·3	122·2	176·7	104·1	−0·2
3d	1·538	1·527	1·564	b	c	121·6	126·3	—	102·2	−23·6



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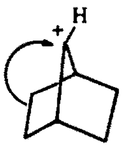

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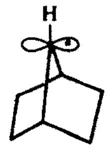

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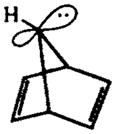
interaction between the double bond and the radical center, while less than in the cation, still has a stabilizing effect. As might have been expected on this basis, the saturated radical **1c** is predicted to have a symmetrical structure **7**, the 7-CH group lying almost on a plane of symmetry passing through C_1 and C_4. As one might also have expected, the parent hydrocarbons **1d**–**3d** are predicted to have similar symmetrical structures.

The anion **2b** on the other hand shows an unexpected distortion in which both the bridge atom, C_7, and the hydrogen atom attached to it are tilted towards the same double bond. This can be understood if the interaction between the double bond and the anionic center is repulsive, as of course one would expect it to be; tilting the hydrogen atom at the 7-position towards the 2,3 bond replaces the 2*p* lone pair AO at C_7 by a hybrid AO which overlaps less with the π electrons of the 2,3 bond, while tilting the bridge reduces overlap between the major lobe of this hybrid AO and the π electrons of the 4,5 bond. This situation is indicated in **8**.



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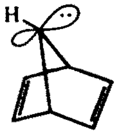

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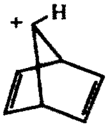
The anion **1b** is predicted to show comparable though smaller distortions (**9**); presumably the repulsive interactions between the lone pair electrons and σ bonds are less than the lone pair-interaction in **8**; in agreement with this, the saturated anion **10** shows even smaller distortions, although again in the same direction.

There are of course two equivalent isomeric structures **10** and **11** for the unsymmetrical cation **2b**; the interconversion of these should represent a typical narcissistic rearrangement.[14] The transition state for this process could be the symmetrical structure **12**; alternatively there could be two mirror image transition states **13** and **14**, the 7-H failing to "flip" until C_7 has crossed the midpoint between bonds 2,3 and 5,6. A third possibility would be that **12** might be a stable intermediate, the two transition states being intermediate between **10** and **12** and **11** and **12**.



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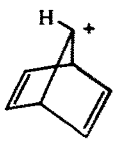

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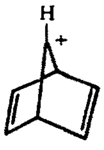

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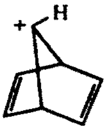

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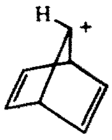

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Calculations for a structure in which the carbon skeleton has a plane of symmetry passing through atoms 1, 4, and 7 showed that the most stable state is the symmetrical one **12**; according to these calculations, the reaction does not therefore exemplify the interesting possibility envisaged by Salem *et al.*,[14] *i.e.* that the forward and backward reactions in a case such as this might take place by different mirror image paths. Further calculations in which the position of C_7 was varied showed that **12** is predicted to be the transition state rather than a stable intermediate; the calculated reaction path is indicated in Fig 2, the reaction coordinate being the angular deviation of the bridge from the central position (*i.e.* $\frac{1}{2}(\alpha-\beta)$ in the notation of Fig 1).

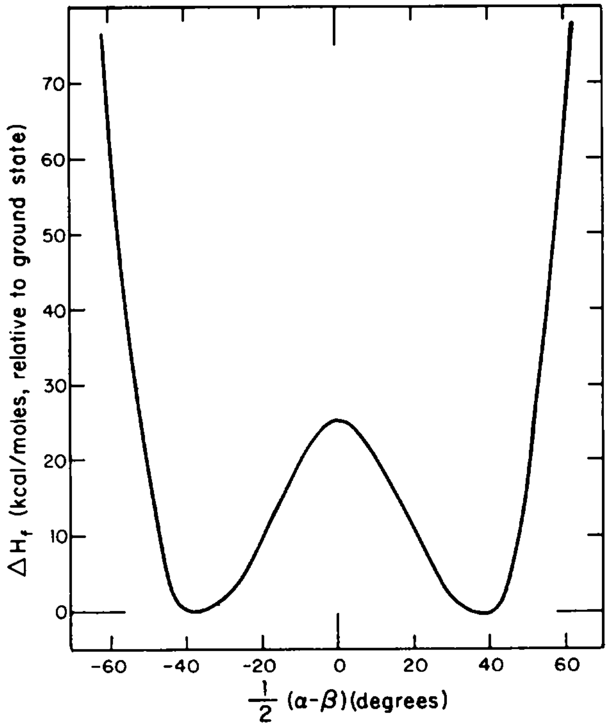

FIG 2. Plot of calculated heat of formation vs $\frac{1}{2}(\alpha-\beta)$ for the interconversion of **10** and **11**

Winstein *et al.*[3] have studied the barrier to "flipping" of **10** to **11**; unfortunately they could only fix a lower limit (19·55 kcal/mole) to it since the ion underwent side reactions on heating before flipping became fast on the NMR time scale. Our calculations (see Fig 1) lead to an estimated barrier height of 26 kcal/mole, consistent with the experimental evidence.

Two previous estimates of the barrier have been reported, both apparently too low. Hoffmann,[5] using the extended Hückel method, arrived at a value of 8 kcal/mole. Konishi *et al.*,[6] using a method somewhat similar to MINDO, but in which the parameters were fixed by reference to spectroscopic data rather than ground state properties, estimated the barrier to be 17·25 kcal/mole.

Acknowledgement—This work was supported by the Air Force Office of Scientific Research through Contract No. F44620-70-C-0121.

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