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Molecular Orbital Calculations for Norbornene and Some Related Nonclassical Intermediates

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Abstract: The geometrical and electronic structures of norbornene and its 7 ions and 7 radical have been investigated using approximate SCF–MO theory. The results from these investigations were used to discuss whether the structures of the ions and radical are classical or nonclassical. It was found that under electron delocalization criterion the structure of the 7 anion is classical whereas the structures of the 7 radical and 7 cation are equally nonclassical. However, using the nonclassical stabilization energy as a criterion, the 7 radical was found to be intermediate between the 7 anion and the 7 cation. This suggests that nonclassical stabilization energy is the better criterion for nonclassical structures.

The molecular orbital calculations of Winstein,[1] Roberts,[2] and their coworkers have been of fundamental importance to the development of current theories of the bonding in nonclassical ions. These calculations, for example, demonstrated the importance of the 1–4 interaction to the stabilization of nonclassical ions which contain the homoallyl group. Important results have also been obtained by Hoffmann[3] and Klopman[4] which have contributed significantly to this field.

Although the above studies have yielded valuable qualitative descriptions of the bonding in these systems, they are severely limited at the semiquantitative level by the fact that the geometries of nearly all nonclassical intermediates are completely unknown. In view of the sensitivity of molecular orbital calculations to changes in molecular geometry, this lack of experimental data tends to detract from the credibility of even the qualitative results from these calculations. Klopman[4] has attempted to remedy this situation by repeating his calculations for two or three intuitively chosen structures. Although this represents an improvement over calculations based on a single structure, the only satisfactory solution to this problem is to use molecular orbital theory to calculate the necessary structural data for the molecule under investigation. Once the geometry has been established, the results from the molecular orbital calculation can be used to discuss the bonding in the ion. Experiences with semiempirical molecular orbital methods suggest that they are capable of yielding very satisfactory geometrical data, but unfortunately the large number of internal degrees of freedom ($3N - 6$), for molecules of chemical interest, renders this approach too time consuming. Clearly, some approximation must be devised which will limit the number of geometrical parameters which need to be calculated. In this paper we report such a scheme for molecules of the norbornene series.

A second, but probably less serious, problem is the neglect of electron repulsion in all of the calculations discussed above. Although this type of approximation has been shown to be satisfactory for neutral nonpolar molecules, it tends to lead to unsatisfactory charge distributions for ions, and is completely unsatisfactory for radicals. As ions and a radical are included in the list of molecules under discussion, all of the calculations were based on an approximate self-consistent field (SCF) method.

Systematic Treatment of Molecular Geometry

Although the structure of the norbornene molecule could in principle be calculated by minimizing the molecular energy with respect to ($3N - 6$) internal coordinates, the computation time required would be prohibitively long. Fortunately, a reasonable guess can be made for many of the bond lengths and bond angles of the C_1–C_2–C_3–C_4–C_6 skeleton, so that the calculation can be drastically curtailed. However, some care must be exercised in the choice of the structure for this fragment, otherwise a spurious energy minimum could be calculated which would lead to the prediction of a structure for the molecule which is only metastable with respect to the equilibrium structure. In view of this possibility the structure chosen for the C_1–C_6 skeleton will be specified in some detail.

The method proposed for calculating the geometry of the norbornene series of molecules is based on the calculation of the four bond angles θ_1, θ_2, θ_3, and θ_4 shown in Figure 1. Essentially, the molecular energy is calculated for a systematically chosen set of values for these variables and then minimized graphically. It is clear from Figure 1 that the positions of the atoms in the C_1–C_6 skeleton depend on both θ_1 and θ_4, and that some means must be devised of calculating their coordinates in terms of these angles. The method used in the present calculation is as follows.

A value is assigned to θ_1 and the coordinates of atoms C_7, C_1, and C_4 are calculated using a carbon–carbon bond length of 1.54 Å. The coordinates of C_7 can then be adjusted for changes in θ_2. Using the coordinates of C_1 and C_4 the coordinates of carbon atoms 2, 3, 5, and 6 are calculated by applying the conditions that

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(1) R. J. Piccolini and S. Winstein, *Tetrahedron Suppl.*, 2, 423 (1963).

(2) M. E. H. Howden and J. D. Roberts, *ibid.*, 2, 403 (1963).

(3) R. Hoffmann, *J. Am. Chem. Soc.*, 86, 1259 (1964).

(4) G. Klopman, *ibid.*, 91, 89 (1969).

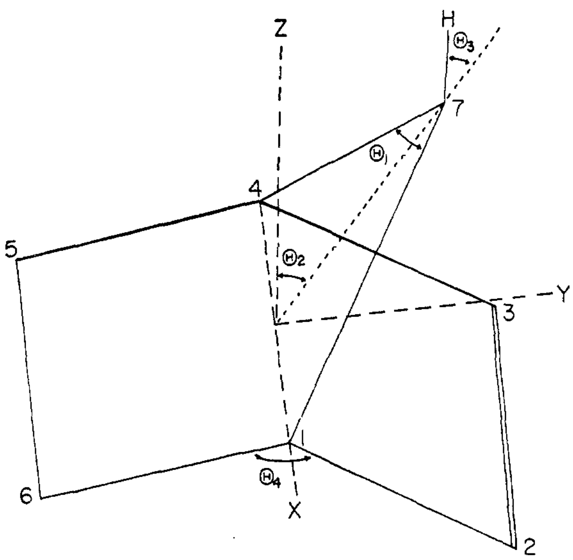

Figure 1. Molecular axes for the norbornene series of molecules.

the angle between the bonds 1–6 and 1–2 is bisected by the *xz* plane and has the value assigned to θ_4, and that the C_2–C_3 and C_5–C_6 bond lengths are 1.33 and 1.54 Å, respectively. The coordinates of atoms 3 and 5 are calculated using the *yz* reflection plane. The coordinates of H_1, the proton attached to C_1, are calculated by assuming that the angles between the H_1–C_1 bond and the C_1–C_4 and C_1–C_6 bonds are tetrahedral. The coordinates for the proton H_2 are calculated on the assumption that it lies in the $C_1C_2C_3$ plane and the C_2–H_2 bond bisects the $C_1C_2C_3$ bond angle. A bond length of 1.09 Å is assumed for all C–H bonds. The coordinates of H_3 are obtained by reflection. The coordinates of the *exo* and *endo* C_6 protons are calculated on the assumption that the angle between the C_6–H_6^{endo} and the C_6–H_6^{exo} bonds is tetrahedral, that the $H_6^{exo}C_6H_6^{endo}$ plane bisects the angle $C_5C_6C_1$, and that the protons are symmetrically situated above and below the $C_5C_6C_1$ plane. The coordinates for the corresponding C_5 protons are obtained by reflection.

Molecular Orbital Calculation

All of the calculations reported here are based on the CNDO (complete neglect of differential overlap) approximation[5,6] to the full SCF (self-consistent field) equations of Roothaan.[7] Calculations for the radical were based on the Pople–Nesbet approximate open-shell method.[8] A complete specification of this method together with a discussion of the approximations are given in references.[5,6,8] These calculations were carried through to a level of self-consistency where the energies were accurate to the sixth decimal place.

The calculation of the geometry was organized as follows. The angle θ_1 was first calculated, by minimizing the molecular energy, assuming $\theta_2 = \theta_3 = 0$, and $\theta_4 = 109°$. (In the case of the norbornene molecule the initial value of $2\theta_3 = 109° 27'$.) Using the computed value for θ_1, θ_2 was calculated, then θ_4, and finally θ_3. With the new values for θ_2, θ_3, and θ_4, θ_1 was recalculated. This process was repeated until an absolute minimum in energy with respect to all four angles was obtained. In the present calculations the angles were calculated to within 2 or 3°.

Results for Norbornene, 7-Norbornene Cation, Anion, and Radical

a. Geometrical Structures. As the above method is intended for the calculation of the geometry of molecules which are not amenable to experimental investigation, it is desirable to test it against molecules of known structure. Two molecules which are suitable for this purpose are norbornene and norbornane. Although the structures of these two molecules are unknown, the structures of substituted norbornenes and norbornanes have recently been determined by X-ray analysis.[9,10] The substituents are generally a *p*-bromosulfonate group attached to C_7 and a ring system fused to C_2–C_3 or C_5–C_6. Unfortunately, our calculations suggest that these types of substituents could lead to a significant change in the molecular geometry. Nevertheless these data do provide a good semiquantitative check on our method.

A value of 94° was calculated for the bridge angle (θ_1) in norbornane, which agrees quite well with the experimental value of 97° for *anti*-8-tricyclo[3.2.1.0^{2,4}]octyl *p*-bromobenzenesulfonate.[10] A value of 89° was calculated for the bridge angle (θ_1) for norbornene which agrees fairly well with the experimental value of 96° for norboramide.[9]

The energy surfaces for the ions and radical were found to be complicated functions of all four angles, such that the independent calculation of any one angle could lead to a significant error. For example, the independent calculation of θ_1 and θ_2 yielded values of 108 and 46°, respectively, whereas the final values are 101 and 51°.

The theoretical structures for norbornene, the 7 ions, and the 7 radical are given in Table I. The significant differences found in the structures for this series of closely related molecules can be understood in terms of a modified three-center bond between C_7, C_2, and C_3. The molecular orbitals associated with this bond are modified by relatively small yet significant contributions from 2p atomic orbitals centered on atoms C_1 and C_4. These contributions are such as to give the C_1C_2 and C_3C_4 bonds considerable bonding π character in the bonding three-center molecular orbital, and consider-

Table I. Theoretical Bond Angles for Norbornene and Its 7 Ions and 7 Radical

	Molecule			
	Norbornene	7 anion	7 radical[b]	7 cation
	Angle, deg			
θ_1	89	88	95	101
θ_2	−2	5	55	51
θ_3	53	58	26	12
θ_4	(109° 27′)[a]	105	113	112

[a] Assumed. [b] The asymmetric structure in which C_7 was bent toward C_2 was also investigated, but it was found to be of higher energy than the above structure.

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(6) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

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(9) T. Sato, M. Shiro, and H. Koyama, *J. Chem. Soc., B*, 935 (1968).

(10) A. C. Macdonald and J. Trotter, *Acta Cryst.*, **18**, 243 (1965).

Table II. Net Atomic Charges Computed for Norbornene and Its 7 Ions and 7 Radical

	Molecule			
Atom	Norbornene	7-Norbornene Anion	7-Norbornene Radical	7-Norbornene Cation
H_1	−0.026	−0.109	−0.001	0.083
H_2	0.005	−0.064	0.006	0.090
H_3 *exo*	−0.009	−0.051	−0.021	0.041
H_3 *endo*	−0.008	−0.072	−0.012	0.035
H_7 *anti*	−0.016	−0.120	0.021	0.083
H_7 *syn*	−0.009			
C_1	0.046	0.083	−0.045	0.009
C_2	−0.023	−0.037	−0.078	0.095
C_3	0.012	0.014	0.020	0.010
C_7	0.029	−0.407	0.242	0.191

able antibonding π character in the lowest antibonding three-center molecular orbital.

The highest occupied level in the 7 cation is found to be the bonding orbital associated with the three-center bond. The corresponding antibonding orbitals are vacant. As a result of the occupation of this orbital the C_7 carbon bends toward the double bond to a point where the energy gained by strengthening the three-center bond is offset by the increase in strain energy for the remainder of the molecule. This change in θ_2 is of course accompanied by significant changes in the other bond angles θ_1, θ_2, and θ_4. According to the present calculations the final value for θ_2 is 51° and corresponds to a high degree of bonding between C_7, C_2, and C_3. An interesting feature of this ion is the existence, according to the present calculations, of two equilibrium positions for the C_1–C_6–C_5–C_4 bridge. These two bridge positions are of almost equal energy and are separated by a small barrier. The bond angles θ_1, θ_2, θ_3, and θ_4 for this second structure are 94, 37, 15, and 135°, respectively.

According to the present calculations, the unpaired electron in the 7 radical occupies the lowest antibonding orbital of the three-center bond. The highest doubly occupied level is found to be the corresponding bonding molecular orbital. The geometrical effects of adding a single electron to the antibonding three-center orbital do not appear to be very great. Although the nonclassical stabilization energy (next section) is decreased in magnitude, suggesting a significant weakening of the three-center bond, θ_2 actually increases slightly rather than decreasing as expected. One of the reasons for this is probably related to the changes in the other bond angles, θ_1, θ_3, and θ_4, between the radical and cation. Our calculations show, for example, that the equilibrium value of θ_2 is very sensitive to θ_1 and θ_3.

The addition of another electron to the antibonding orbital, to form the 7 anion, gives an over-all antibonding character to this bond. As a result, the equilibrium geometry of the anion is very close to the parent molecule, norbornene. The highest occupied orbital is strongly localized on C_7 and is very close to sp^3 in character. This is reflected by the large value of 58°, approximately half the tetrahedral angle, calculated for θ_3.

b. Charge Densities and Stabilization Energies. The charge densities for all of the molecules under discussion are given in Table II. The spin density distribution for the 7 radical is given in Table III.

Table III. Spin Densities for the 7 Radical

Atom	C_1	C_2	C_3	C_7
Density	0.09	0.44	0.02	−0.09

A particularly interesting question, which the present calculations should help to answer, is whether the 7 ions and 7 radical have classical or nonclassical structures. According to Bartlett's definition,[11] a nonclassical ion (or radical) has delocalized bonding σ electrons in its ground state. An almost perfect example of a classical ion under this definition is provided by the 7 anion. The lone-pair electrons in this ion occupy an orbital which is almost completely localized on C_7 and which is almost sp^3 in character. Thus the electron distribution in this ion bears a close resemblance to that of norbornene. On the other hand, the 7 anion and 7 radical are almost ideal nonclassical systems under Bartlett's definition. There are σ electrons in both of these molecules strongly delocalized over atoms C_7, C_1, C_2, C_3, and C_4. The delocalization over atoms C_1 and C_4 is strongest in the 7 cation, and is the result of the bonding π character which the bonding three-center molecular orbital gives to the C_1–C_2 and C_4–C_3 bonds. In the case of the radical this is diminished by the antibonding π character of the antibonding three-center orbital. The high degree of σ-electron delocalization in the radical is reflected by the high spin densities calculated for atoms C_2 and C_3, and the small spin density for atom C_7.

Another property of considerable interpretive interest is the nonclassical stabilization energy. It is difficult to define this quantity theoretically, but we may approximate it by the quantity W, where W = energy of ion or radical calculated at its equilibrium geometry minus the energy of ion or radical calculated at the equilibrium geometry of the parent molecule.

$$W = E_{\text{equilibrium}} - E_{\text{parent}} \text{ (always negative or zero)}$$

This definition is appropriate since the σ electrons are usually localized for the parent geometry, and it is the delocalization of the σ electrons which is generally responsible for any significant change in geometry between parent molecule and the ion or radical. Clearly, a large negative stabilization energy will facilitate the formation of the intermediate and hence result in a strongly accelerated reaction.

The nonclassical stabilization energies for the 7 cation, 7 radical, and 7 anion are respectively −8, −3, and −1 V. Thus although the 7 cation and 7 radical are equally nonclassical under Bartlett's definition, the 7 radical in fact appears to fall midway between the strongly nonclassical ion, the 7 cation, and the almost ideal classical ion, the 7 anion, in stabilization energy. These results are in keeping with the chemistry of these intermediates.

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[11] P. D. Bartlett, "Non-Classical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965, p V.