The Structure of the Norborn-2-en-7-yl Radical

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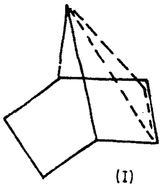
THE first experimental evidence supporting the assignment[1] of a non-classical structure to the norborn-2-en-7-yl radical was recently reported:[2] tri-n-butyltin deuteride reacts with the norborn-2-en-7-yl radical almost exclusively at the *anti*-C-7 position. Since a classical norborn-2-en-7-yl radical would be expected to react almost equally at both the *syn* and *anti* positions, this result strongly supports a non-classical structure (I).


(I)

Calculations are reported here for the norborn-2-en-7-yl radical. These calculations are all based on the CNDO (complete neglect of differential overlap) approximate self-consistent field molecular orbital theory[3,4] used in conjunction with the Pople–Nesbet[4,5] open shell theory.

As the geometry of the radical is unknown, it was necessary to calculate certain key bond-angles before calculating the spin and charge densities. The theoretical angles for the norborn-2-en-7-yl radical are listed in Table 1. We calculate the C-1–C-7–C-4 bridge angle (θ_1) as 94°, and the H-7 out-of-plane angle ϵ as 26°. Unlike that in the norbornene molecule,[6] the C-7 bridge is bent away from the perpendicular position by an angle of 56° towards the double bond. The stereospecificity of the reactions which involve this intermediate are easily understood in terms of this result. Clearly, attack at the *syn* position will be sterically hindered by C-2 and C-3, whereas attack at the *anti* position will be relatively unhindered. The structure in which C-7 was bent towards C-2 or C-3 was also

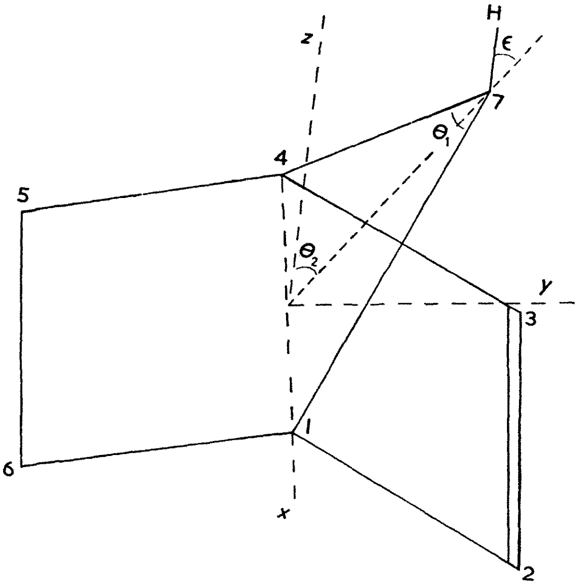


FIGURE. *Angles for the norborn-2-en-7-yl radical:* θ_1 *is the* C-1–C-7–C-4 *bridge angle,* θ_2 *the displacement of* C-7 *from the vertical towards the* C-3–C-2 *double bond and* ϵ *the displacement of* 7-H *from the* C-4–C-7–C-1 *plane.*

investigated, but was found to be higher in energy than the structure in Table 1.

TABLE 1

Bond angles for the norborn-2-en-7-yl radical

Angle	Theoretical Value
θ_1	94°
θ_2	56°
ϵ	26°
C-1–C-2–C-3	107°
C-4–C-5–C-6	103°

The distribution of charge within the radical, as represented by the atomic charge and spin densities, is shown in Table 2. A striking feature of this distribution is the large positive charge centered on C-7, and the large negative charges which reside on atoms C-2 and C-3. The non-classical nature of the radical is clearly illustrated by the spin densities. The classical structure for this radical has the unpaired electron completely localized on C-7, and negligible bonding between C-2 and C-7. However, according to the present calculations, almost all of the radical character has been transferred from C-7 to atoms C-2 and C-3 as the result of the formation of bonds between C-7 and both C-2 and C-3. This description is supported by the relatively short C-2–C-7 and C-3–C-7 bond lengths of 1·58 Å calculated for the radical, and the very high spin densities predicted for C-2 and C-3. This delocalization leads to a significant decrease in the C-2–C-3 π-bond-order for the norborn-2-en-7-yl radical as compared with the norborn-2-ene molecule.[6]

TABLE 2

Charge and spin densities for the norborn-2-en-7-yl radical

Atom Density	C-1	C-2	C-5	C-7
Charge[a]	−0·045	−0·078	+0·020	+0·242
Spin	0·09	0·44	0·02	−0·09

[a] Charge density = 4 minus electron density.

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