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ON THE MOLECULAR AND ELECTRONIC FEATURES OF *SYN*- AND *ANTI*-SESQUINORBORNENE

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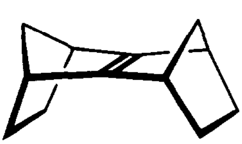
Summary: Molecular mechanics calculations of *syn*- and *anti*-sesquinorbornene indicate that the double bond is non-planar in both cases, and only by taking this non-planarity into account it is possible to rationalize the observed electronic features by molecular orbital calculations.

Since the exceptional reactivity of norbornene was discovered half a century ago,[1,2] derivatives of the norbornene system have continuously fascinated physical organic chemists, the most disputed problems probably being the classical *versus* nonclassical controversy of the norbornyl cation[3] and the high reactivity and *exo* selectivity of norbornene.[2,4]

The recently prepared *syn*- and *anti*-sesquinorbornenes, 1[5] and 2[6] respectively, which can be viewed as two fused norbornene moieties with a common double bond, have also been shown to display unusual molecular as well as electronic features: (1) X-ray crystallographic evidence for both planar[7] and bent[8] double bonds in derivatives of *anti*-sesquinorbornene 2. (2) A considerably lower π_{CC} ionization energy for the *anti* relative to the *syn* isomer.[9] In order to gain a better understanding of these and other features a joint molecular mechanics and molecular orbital study of the two sesquinorbornenes 1 and 2 are presented.



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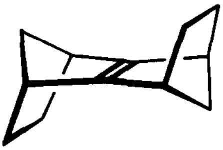

2

Several derivatives of *syn*-sesquinorbornene (1) have been studied by X-ray crystallography and in all cases the preferred conformation is characterised by having a non-planar π-system with the *endo* bending being 12-18°.[7,8,10] With Allinger's molecular mechanics method (MM2)[11] the *endo* conformation (A) is calculated to deviate from planarity by 18° in excellent agreement with experimental data and to be more stable than the *exo* conformation (B), in which the bending of the double bond is much more pronounced (35°). Accordingly the transition state for the *endo/exo* conversion is also *exo* bent (12°) and the conformation with the double bond being planar (C) is not a minimum on the conformational potential surface (cf. Figure 1 and 2).

Two apparently contradicting X-ray structures of *anti*-sesquinorbornene derivatives indicate the double bond to be practically planar[7] and puckered by 13.2°,[8] respectively, The preferred conformation of 2 is calculated by MM2 to be a puckered (26°) C_s conformation (D) only being slightly more stable than the C_{2h} conformation (E) with the planar double bond (cf. Figure 1 and 2).

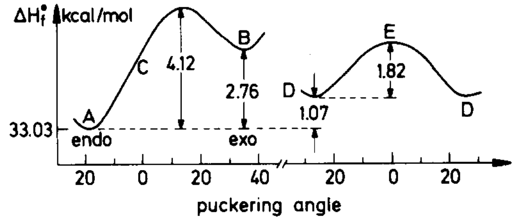

Figure 1. MM2 calculated energies for the different conformations of the sesquinorbornenes 1 and 2 as function of the puckering angle.

Ermer *et al.*[8] have already reported the corresponding values obtained with his consistent force field (CFF), but it predicts the *endo* conformation of 1 (*i.e.* the conformation preferred by the MM2 method and found experimentally by X-ray crystallography for derivatives of 1) to be less stable than the *exo* conformation and it seems to exaggerate the puckering more than the MM2 method. Furthermore, the barriers for conformational interconversion are calculated to be 2-4 times larger with the CFF than with the MM2 method. A clarification of these discrepancies between the two force field methods may necessitate further efforts and be important for achieving a better understanding of the molecular features of the sesquinorbornenes as well as for further applications of the two methods.

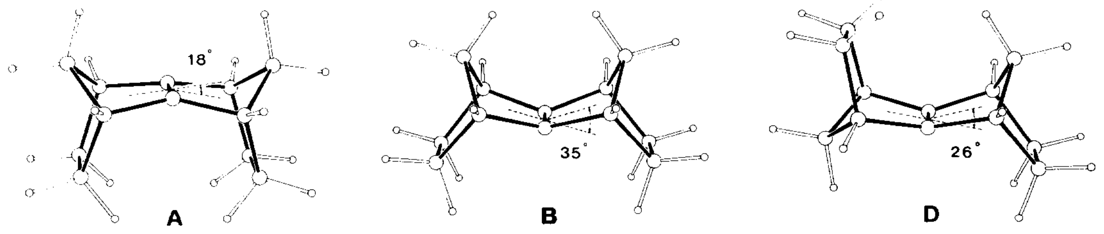

Figure 2. Computer generated three dimensional drawings of the minimum energy conformations of the sesquinorbornenes 1 (A and B) and 2 (D).

Recently, Brown *et al.*[9] determined by photoelectron spectroscopy the π ionization energies (IE_V) of *syn*- and *anti*-sesquinorbornene to be 8.12 eV and 7.90 eV, respectively, and in an attempt to mimic the large energy difference in π ionization energy the authors performed molecular orbital calculations on 1 and 2 by assuming the validity of Koopmans' theorem ($IE_V = -\varepsilon_{SCF}$) as well as by applying a direct ΔSCF principle [IE_V = E(radical cation) - E(ground state)]. Neither MINDO/3 nor *ab initio* type calculations performed on MINDO/3 fully optimized structures of 1 and 2 yielded a sizable difference in π ionization energy between the two isomers (0.06 eV with both methods), and also the MINDO/3 calculated difference between the energy of the radical cation and the ground state was negligible (ΔSCF = 0.01 eV).

Unfortunately, the geometries from the MINDO/3 geometry optimization were for both *syn*- and *anti*-sesquinorbornene characterized by having nearly planar double bonds.[9] For *syn*-sesquinorbornene the non-planarity of the double bond has been shown to be reproduced properly by the Extended Hückel method contrary to the more sophisticated NDO methods (MINDO/3 and MNDO), and the failure of the latter methods is in agreement with a hyperconjugative mechanism for the bending of the double bond.[12]

PRDDO MO calculations[13] have been performed on the previously decribed MM2 optimized structures with different degree of puckering and not surprisingly the PRDDO method also favours double bond planarity for *syn*- as well as *anti*-sesquinorbornene. The PRDDO results (cf. Table) for the planar conformations (*i.e.* conformation C and E) are as expected similar to the above molecular orbital results by not reflecting any difference between the two isomers 1 and 2. Contrary to this, the PRDDO calculations performed on the MM2 minimum energy conformations of 1 and 2 (*i.e.* conformations A and D) show the *anti*-sesquinorbornene (2) π bond to be easier to ionize than the *syn*-sesquinorbornene (1) π bond by 0.16 eV and 0.20 eV applying Koopmans' theorem and the ΔSCF principle, respectively. This is in excellent agreement with the experimental energy difference in π ionization energy of 1 and 2 on 0.22 eV,[9] and illustrates the importance of using proper optimized structures for evaluation of electronic structures by molecular orbital calculations.

For *syn*-sesquinorbornene 1 *endo* puckering leads to a poorer overlap between the π lobes and the σ orbitals of the two methylene bridges, and accordingly the π level is stabilized due to a diminished hyperconjugative effect.[12] In the case of the *anti* isomer 2 the puckering is associated with a poorer overlap with one of the methylene bridges and a better overlap with the other, which *a priori* results in a zero effect on the π level. Thus, *anti*-sesquinorbornene 2 does not relieve unfavourable ground state interactions by puckering due to a simultaneously decrease and increase in destabilizing orbital interactions, and this difference in behavior accounts for the observed difference in ionization energies between the two isomeric sesquinorbornenes 1 and 2.

Conformation	A	B	C	D	E
Koopmans' theorem	7.40	7.09	7.28	7.24	7.25
ΔSCF principle	5.91	5.54	5.73	5.71	5.71

Table. PRDDO calculated ionization energies for the different conformations of *syn*- and *anti*-sesquinorbornene (all values in eV).

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