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ON THE GROUND STATE AND FIRST EXCITED STATE GEOMETRIES OF SYN-SESQUINORBORNENE

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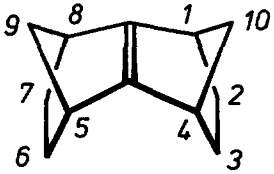
Extended Huckel calculations on the title compound (1) predict hinge-like bending of the double bond corresponding to interplanar angles of 167° for the ground state and 210° for the first excited state. The predictions are discussed in terms of hyper-conjugative interactions.

Recent X-ray analyses reveal that the π-system of *syn*-sesquinorbornene (1) derivatives deviates considerably from planarity, exhibiting a dihedral angle in the range 162-164° [1,2]. This result is consistent with the observation that thermal additions to the double bond of 1 occurs exclusively on the *exo* face. On the other hand, light induced hydrogen addition was found to take place mainly from the *endo* side, implying that the dihedral angle ϕ is drastically increased in the excited state of 1 [3].



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Bartlett *et al.* [1,3] offered a simple explanation of these findings, based upon a consideration of the steric demand of π and π* orbitals of the double bond. They suppose that in the ground state of 1 the double bond exerts a steric force on the *endo* hydrogens of the methylene bridges, H(9en) and H(10en), leading to the observed distortion. In the excited state, a π electron is promoted to the π* orbital which has a nodal plane through the methylene bridges; the balance forces may thus be reversed, causing presumably a reversal of the ground state bend. Vogel *et al.* [2], however, found that the observed geometries did not agree well with those predicted by NDO type MO calculations and felt that electronic correlation effects must be considered in order to approach an explanation.

To contribute to this discussion, which is also important towards an understanding of the exceptional *exo* reactivity of norbornene [4], we present here the results of Extended Huckel (EH) [5] calculations on 1. In Fig. 1a are indicated the calculated total energies for ground and excited states as a function of the dihedral angle ϕ; the remaining geometrical parameters were kept constant and were taken as those predicted by MINDO/3. The EH calculation predicts minimum ground and excited state energies for ϕ values close to 167° and 210°, respectively, in consistency with the experimental evidence.

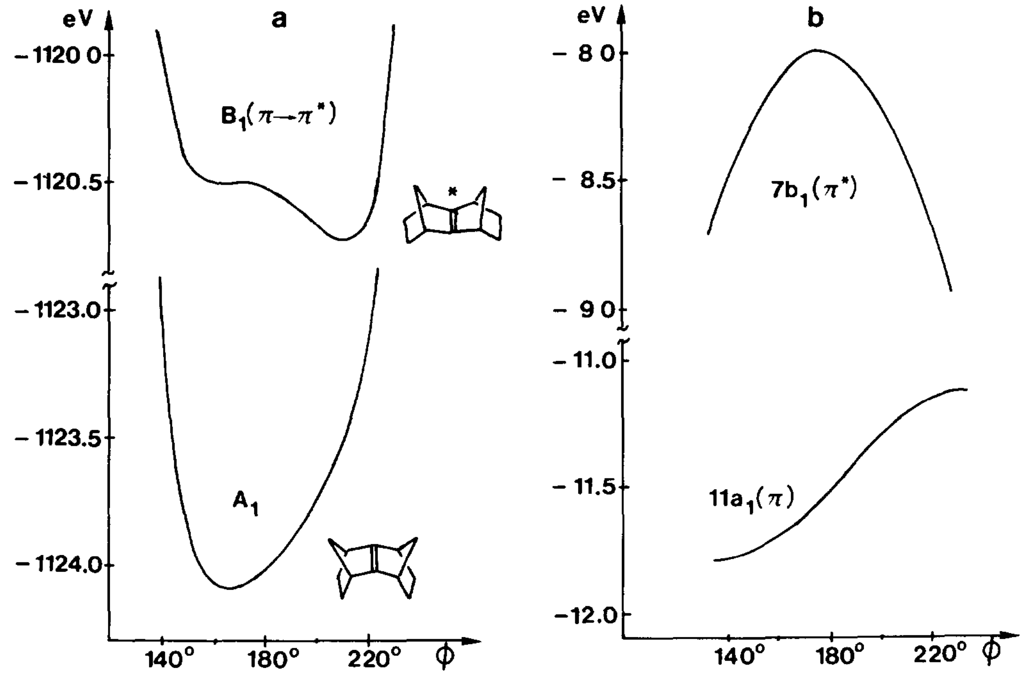

Fig. 1a) Calculated total energies for ground and excited state of 1 as a function of the dihedral angle ϕ.

b) 11a$_1$(π) and 7b$_1$(π^*) orbital energies as a function of the dihedral angle ϕ.

Hinge-like bending of an ethylenic π-system induces σ-π mixing, leading to rotation of the π lobes [6]. The admixture of σ and σ^* contributions tend to destabilize the π and stabilize the π^* orbital. However, in the case of 1, only the π^*level is found to behave as expected for a normal π system. The π level shows a monotonic decrease in energy with decreasing ϕ angle in the region 140 - 220° (Fig. 1b). Reducing ϕ causes a rotation of π lobes in the direction of more *negative* ρ values (Fig. 2), resulting in less overlap with the cyclopentane ribbon orbitals, in particular the part associated with the monatomic bridges. At the same time, overlap with H(9en) and H(10en) is reduced, but this seems less important to the result of the EH calculation. The combined effects lead to a remarkable reduction of hyperconjugative interactions, resulting in a *stabilization* of the π level and a net stabilization of the ground state when ϕ is decreased below 180°. When one electron is removed from the π orbital, thereby creating a radical cation, the contribution due to hyperconjugative effects is halved and a ϕ value close to 185° is predicted. Returning the electron into the π^* orbital, thereby generating the lowest excited state of 1, leads to further increase of ϕ, a result which can be understood in view of the nodal properties of the π^* orbital [3].

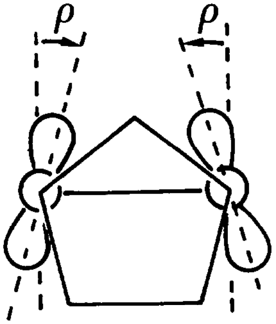

Fig. 2 Newman projection of 1 to indicate rotation of the π lobes by an angle ρ [6].

Given that a reduction of hyperconjugative interactions is the driving force behind the observed ground state bend for *syn*-sesquinorbornenes, it is understandable why NDO methods fail to predict this phenomenon [2,7]. Hyperconjugation involving interaction between filled π and σ orbitals is a net destabilizing contribution. However, the repulsion between closed shells is a second order overlap effect and is not reproduced by NDO methods. It seems significant that in the present case the simple EH model, which is based on an explicit treatment of orbital overlap, is superior to the sophisticated NDO procedures.

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References

[1] W. H. Watson, J. Galloy, P. D. Bartlett, A. A. M. Roof, J. Chem. Soc. 103, 2022 (1981).

[2] J.-P. Hagenbuch, P. Vogel, A. A. Pinkerton, D. Schwarzenbach, Helv. Chim. Acta 64, 1818 (1981).

[3] P. D. Bartlett, A. A. M. Roof, W. J. Winther, J. Am. Chem. Soc. 103, 6520 (1981).

[4] R. Huisgen, P. H. J. Ooms, M. Mingin, N. L. Allinger, J. Am. Chem. Soc. 102, 3951 (1980); R. Huisgen, Pure & Appl. Chem. 53, 171 (1981); G. Wipff, K. Morokuma, Tet. Lett. 21, 4445 (1980); U. Burkert, Angew. Chem. 93, 602 (1981); Angew. Chem. Int. Ed. Engl. 20, 572 (1981).

[5] R. Hoffmann, J. Chem. Phys. 39, 1397 (1963); P. K. Mehrotra, R. Hoffmann, Theoret. Chim. Acta 48, 301 (1978) and lit. cited.

[6] H.-U. Wagner, G. Szeimies, J. Chandrasekhar, P. v. R. Schleyer, J. A. Pople, J. S. Binkley, J. Am. Chem. Soc. 100, 1210 (1978). In the case of 1, EH predicts rotation angles ρ equal to -13°, $+4^{\circ}$, and $+17^{\circ}$, for dihedral angles ϕ equal to 160°, 180°, and 200°, respectively. For a definition of ρ, see Fig. 2.

[7] In the case of 1, MINDO/3 [8] and MNDO [9] predicts ϕ values close to 179° and 181°, respectively.

[8] R. C. Bingham, M. J. S. Dewar, D. H. Lo, J. Am. Chem. Soc. 97, 1285 (1975); P. Bischof, QCPE 12, 383 (1979).

[9] M. J. S. Dewar, W. Thiel, J. Am. Chem. Soc. 99, 4899 (1977).

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