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ON THE EXCEPTIONAL REACTIVITY OF THE NORBORNENE DOUBLE BOND

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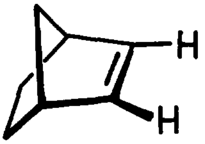
The anomalous reactivity of the bicyclo[2.2.1]*heptene double bond is interpreted in terms of hyperconjugative effects, leading to an exceptionally low endo out-of-plane deformation potential.*

The exceptional *exo* reactivity of the norbornene (1) double bond has puzzled chemists for 50 years [1,2]. Several explanations have been attempted, considering hyperconjugative, steric, torsional and ring strain effects, but none has proved unequivocally satisfactory. In a comparative study of cycloaddition rate constants for a series of cycloalkenes, Huisgen *et al.* [2] recently ascribed the "extra" reactivity of 1 to a sofar unidentified factor *x*, responsible for the greater part of the norbornene reactivity. In this communication we suggest that an important contribution to the anomalous reactivity originates in a unique coupling between hyperconjugative effects and out-of-plane deformation for the norbornene double bond, offering a straightforward interpretation of Huisgen's *x* factor.



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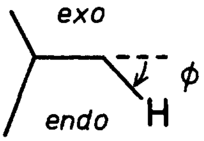

The activation energy for a chemical reaction may be expressed as the sum of an intramolecular deformation energy and an intermolecular interaction energy [3]. Here we consider the deformation energy for the norbornene substrate in the (early) transition state of a concerted *syn* addition.

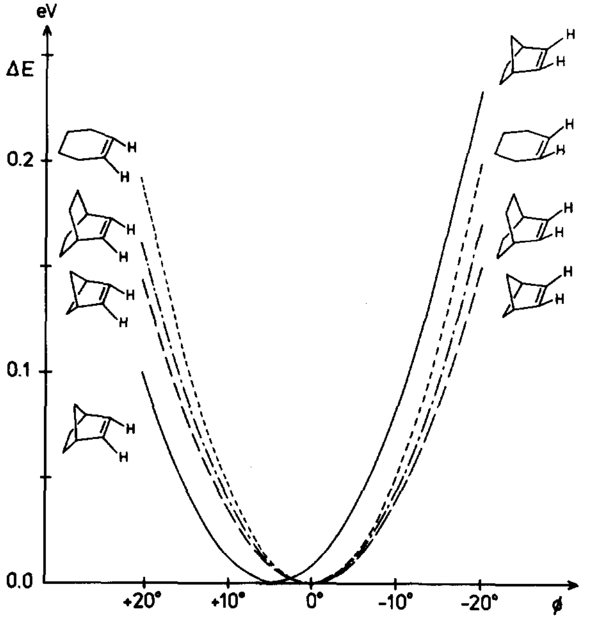

Fig. 1. Calculated out-of-plane bending potentials for the double bonds in norbornene and related cycloalkenes [5].

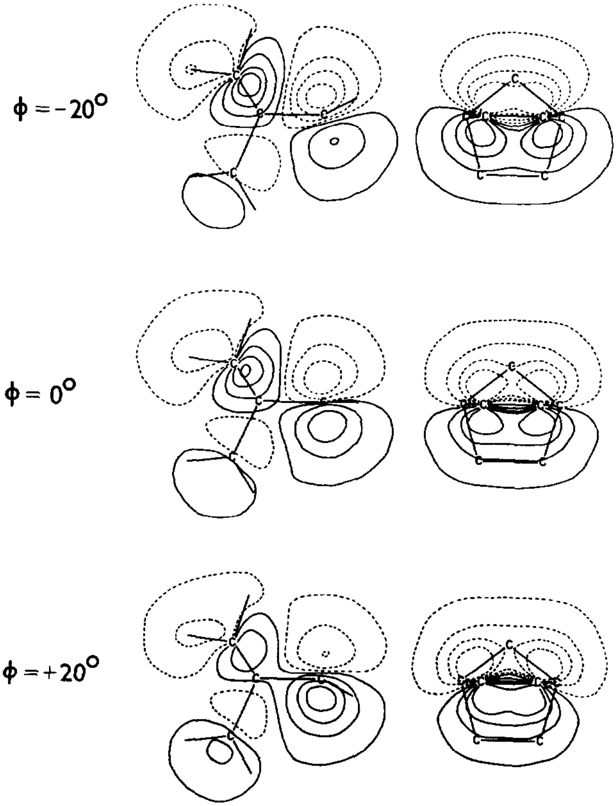

Fig. 2. Contour diagrams of the norbornene π type orbital for different out-of-plane bending angles. Amplitudes (± 0.01, ± 0.05, ± 0.10, ± 0.15) are indicated in the symmetry plane through the *exo* methylene group (*left*) and in a plane through the double bond, perpendicular to the plane containing the adjoining CC bonds (*right*).

The deformation can be approximated by a simple out-of-plane bending characterized by the dihedral angle ϕ. Fig. 1 indicates the relative bending potentials for **1** and a few related cycloalkenes calculated by the Extended Hückel (EH) method [4,5]. In the case of **1**, a marked preference for *endo* bending is predicted; the potential minimum corresponds to a significantly *endo* distorted structure ($\phi = +4.2^{\circ}$, consistent with the result of a recent *ab initio* study [8]), and an *endo* distortion characterized by a ϕ value, say, in the range 20-30° requires 10-20 kJ/mole less energy than the equivalent *exo* distortion. This result indicates a strong preference for *exo* attack (implying *endo* bending), consistent with observed *exo/endo* ratios in the order of 10^{2}-10^{3} [2]. Moreover, the *endo* bending energy for **1** is significantly smaller than the bending energies for cyclohexene, bicyclo[2.2.2]octene and bicyclo[2.1.1]hexene (Fig. 1), in accordance with the anomalous high reactivity of **1**. As a matter of fact, the predicted deformation energies parallel the observed relative cycloaddition rate constants [2], suggesting that the deformation energy is a rate determining factor.

The preference for *endo* bending of the norbornene double bond can be explained in terms of a hyperconjugative mechanism [9]. Hyperconjugative effects in **1** are characterized by a marked repulsion between the π orbital and occupied orbitals associated with the *exo* methylene bridge (Fig. 2) [8,10-12]. Bending the double bond *endo*, the π orbital is tilted away from the *exo* bridge; most significantly, however, the pπ orbital lobes are simultaneously *rotated* [13] such that overlap with σ orbitals of the bridge is efficiently reduced (bending *exo*, the trends are reversed) [7]. As a result, repulsive interactions are reduced during *endo* bending (but increased during *exo* bending). In the case of *syn*-sesquinorbornene, the effects are magnified, with correspondingly drastic consequences [7]. Similar effects operate in envelope cyclopentene, although to a smaller degree.

A full understanding of the norbornene reactivity requires investigation also of those contributions to the activation energy which depend on the reaction partner [3,8]. However, our tentative interpretation of Huisgen's

x factor is appealing in that it provides a common reason for all exceptional features of norbornene reactivity: *exo* selectivity and increased rate constants in all addition reactions, remarkably *independent* of reagent, mechanism and orbital control [2].

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