STRUCTURE AND REACTIVITY OF NORBORNENE AND SYN-SESQUINORBORNENE

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Abstract—The origin of the observed non-planarity of the syn-sesquinorbornene (syn-tetracyclo-[6.2.1.1^{3,6}.0^{2,7}]dodec-2(7)-ene) π system is discussed in terms of simple molecular orbital theory. Calculated out-of-plane bending energies for the double bonds in cyclohexene, bicyclo[2.2.2]oct-2-ene, bicyclo[2.1.1]hex-2-ene, bicyclo[3.2.1]oct-6-ene, and bicyclo[2.2.1]hept-2-ene closely parallel the published cycloaddition rate constants for these compounds, indicating that ease of deformation may be a rate determining factor. The "staggering effect" considered by Houk et al. is discussed and it is demonstrated that this effect is not equivalent with the norbornene "x" factor introduced by Huisgen et al.

Evidence has long been accumulating that the electronic structure of the norbornene ring system (1) predisposes it towards rapid reaction on the exo face of the double bond. Several theoretical explanations have been attempted,[1–10] but the origin of the exceptional reactivity has eluded unequivocal physical detection. The recent synthesis[3] of the syn-sesquinorbornene ring system (2) opens the interesting possibility of investigating the effect of two co-operating norbornene systems. X-ray analyses of crystalline derivatives reveal that the π system of 2 deviates from planarity, exhibiting a highly significant hinge-like endo bending ($\phi = 16$–$18°$).[11,12] This result is consistent with the observation that thermal additions to the double bond of 2 occur exclusively on the exo face. On the other hand, light induced hydrogen addition was found to take place mainly from the endo side, implying a reversal of the ground state bend in the excited state.[13]

1   2
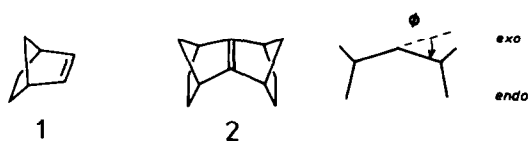
In this paper, we first investigate the electronic origin of the ground and excited state distortions of 2, then discuss electronic effects associated with cycloaddition reactions of 1 and related compounds, with particular emphasis on calculated out-of-plane deformation energies and a discussion of the "staggering effects" considered recently by Houk et al.[7]

Interrelation of hinge-like bending and hyperconjugative effects for the syn-sesquinorbornene π system

Non-planarity has been previously observed or predicted for several classes of substituted ethylenes.[4–19] However, the case of 2 is unique. The observed bending is surprisingly large for a flexible olefin and it cannot easily be explained by steric, torsional or ring strain effects. It is well known that "zero-bridge olefins" with small C=C—C bond angles exhibit small out-of-plane bending force constants.[14,19] However, in view of the larger steric interference of the two endo bridges in 2 one

would expect preference of exo bending; this expectation is supported by the results of sophisticated force-field calculations[19] but is in disagreement with the experimental evidence.[11,12] Some additional effect, overcompensating the mutual repulsion of the endo bridges, must be responsible for the observed endo bending in the ground state. Bartlett et al.[11,13] offered a simple explanation, based on the steric demand of the π orbital of the double-bond. They suppose that in the ground state of 2 the double bond exerts a steric force on the endo hydrogens of the monatomic bridges, 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 monatomic bridges; the balance of forces may thus be reversed, causing presumably a reversal of the ground state bend.

The hypothesis of Bartlett et al. is intuitively appealing. However, all-valence-electrons MO methods like MINDO/3[20] and MNDO[21] fail to reproduce these effects.[10,12] They hardly predict any ground state distortion at all: ϕ values equal to $+0.7°$ and $-1.0°$ are predicted by MINDO/3 and MNDO, respectively. The failure is disappointing since these sophisticated procedures were optimized explicitly to reproduce molecular geometries and they are generally considered to be the best methods of their kind. Vogel et al.[12] felt that electronic correlation effects must be considered in order to approach an explanation.

Fortunately, it turns out that ordinary Extended Hückel[22] (EH) calculations offer a rationalization of the observed phenomena.[23] In Fig. 1(a) are indicated the calculated total energies for ground and excited states of 2 as a function of the bending 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 $+13°$ and $-30°$, respectively, in excellent consistency with the experimental evidence. It is obviously of interest to analyse these results and to investigate why the EH method succeeds where MINDO/3 and MNDO fail.

Hinge-like bending of an ethylenic π system induces π–σ mixing.[14] The admixture of σ and σ^* contributions would be expected to destabilize the π and stabilize the
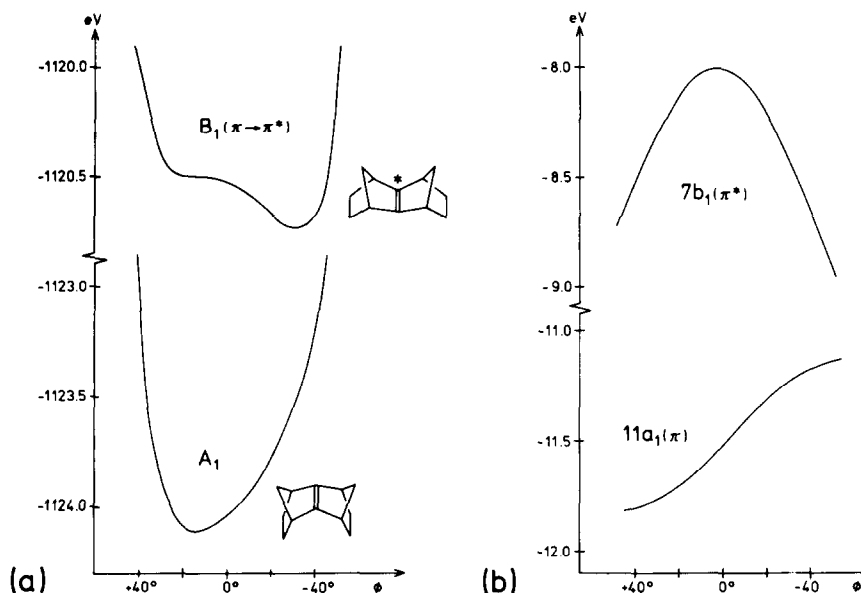
Fig. 1(a). Calculated total energies for ground and excited state of **2** as a function of the bending angle ϕ. (b) HOMO and LUMO energies of **2** as a function of the bending angle ϕ.

π^* orbital. However, in the case of **2**, only the π^* level is found to behave as expected; as indicated in Fig. 1(b), the π orbital is monotonously stabilized with increasing ϕ value in the region $-40° < \phi < +40°$.

In order to understand this result it is necessary to consider in more detail what happens to the π orbital during bending. The admixture of a σ contribution corresponding to the double bond can be described as causing a disrotatory motion of the p lobes composing the π orbital.[14] Bending endo, thereby increasing ϕ, leads to a rotation of the p lobes in the sense indicated in the Newman projection in Fig. 2. EH predicts rotation angles ρ equal to $-17°$, $-4°$, and $+13°$ for bending angles ϕ equal to $-20°$, $0°$, and $+20°$, respectively; rehybridization, involving admixture of s orbital character into the π orbital is found to be negligible for the structures studied, in contrast to the results of Fukui *et al.*[24]

As indicated by Fig. 2, the rotation leads to less effective overlap with the σ orbitals associated with the monatomic bridges. This effect is of particular significance since hyperconjugation in the norbornene ring system is characterized by a marked repulsion between the π orbital and occupied σ orbitals of the exo methylene bridge[8,10,24] (see Fig. 4). In **2** the repulsive interactions on the exo face are doubled; however, relief is obtained by bending endo, essentially as a result of the
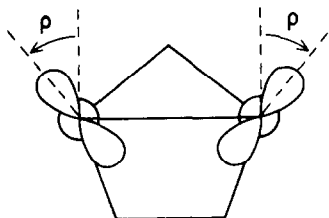

Fig. 2. Newman projection of **2**, indicating the disrotatory distortion of the π orbital during endo bending.
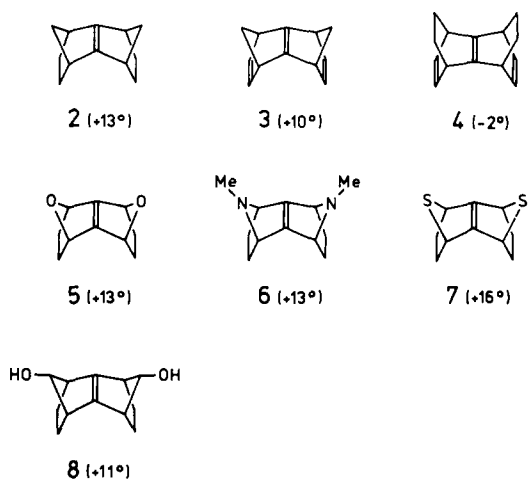
rotation of the p lobes in the distorted π orbital. Simultaneously, overlap with the two endo hydrogens of the monatomic bridges is reduced, as pointed out by Bartlett *et al.*[11,13] but this contribution is less significant to the result of the EH calculation.

The results in Fig. 1 can thus be explained by a decrease of repulsive hyperconjugative effects during endo bending, leading to stabilization of the π orbital and a net stabilization of the ground state when ϕ is increased above zero. When one electron is removed from the π orbital, thereby creating a radial cation, the contribution due to hyperconjugative effects is halved and a ϕ value close to $-5°$ is predicted, corresponding to a slightly exo-bent structure. This demonstrates that in **2**, hyperconjugative interactions are responsible for the predicted endo bending. Returning the electron into the π^* orbital, thereby generating the lowest excited state, leads to further exo bending, a result which can be understood in view of the nodal properties of the π^* orbital.[13]

A possible explanation for the failure of MINDO/3 and MNDO also becomes apparent. 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. In an average sense, neglect of these contributions is compensated for in MINDO/3 and MNDO by introduction of empirical parameters, e.g. by adjustment of the core-core repulsion terms;[20,21] but specific effects, such as the face asymmetric repulsion operating in the norbornene system, are evidently not reproduced. A number of problems with NDO methods in the description of non-bonded interactions are now well known and most of these have been ascribed to an insufficient treatment of overlap effects.[25-29] 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.

In Scheme 1 we summarize the ϕ values predicted for **2** and a few related species by the EH method (using
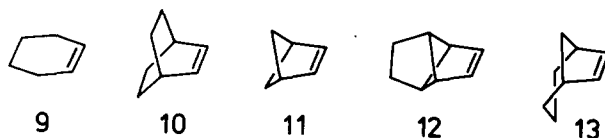
MINDO/3 skeleton geometries). A relatively small bending angle is predicted for syn-sesquinorbornadiene **3**. This can be explained as a result of repulsive interactions on the endo side, involving the three ethylenic π orbitals; in case of **4**, similar interactions lead to prediction of a small exo bending. Introduction of a hetero-atom as in the case of **5–7** has no drastic influence on the calculated bending angle. The predicted distortion is comparatively large in the case of **7** which contains two sulfide bridges. This can be explained by the relatively low binding energy of the C—S bond orbitals, favouring hyperconjugation, and by repulsive through-space interaction between the π orbital and the diffuse sulfide lone-pair orbitals. Similar through-space interaction has been discussed previously in the case of thiapropellenes.[30,31] Substitution at the exo methylene groups as in **8** leads to the prediction of slightly smaller bending angles, consistent with the results of sophisticated calculations on the corresponding norbornene derivatives.[5,8]

Encouraged by the excellent performance of simple EH theory in the rationalization of the observed non-planarity and stereochemistry of the syn-sesquinorbornene double bond, we have calculated the relative EH out-of-plane bending potentials for the double bonds in **1**, **9**, **10**, **11** and **13**. The potential energy curves shown in Fig. 3 indicate total EH energies as a function of the bending angle ϕ. All other structural parameters were kept constant and were taken as those predicted by MINDO/3. Calculated bending energies for $|\phi|$ equal to $10°$ and $20°$ are given in Table 1.
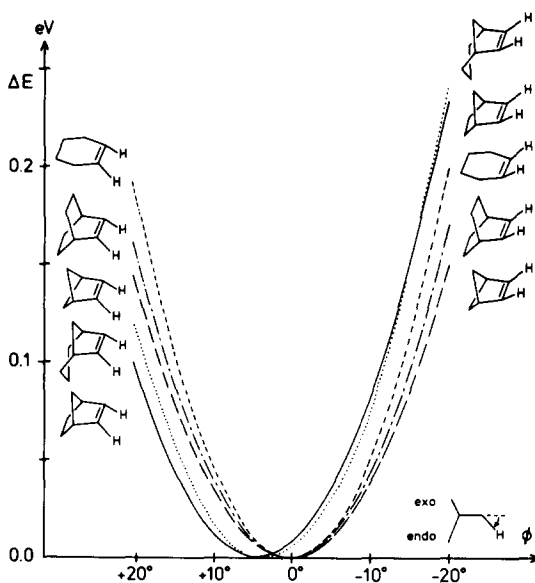
Scheme 1.

Fig. 3. Calculated out-of-plane bending potentials for the double bonds in cyclohexene (**9**), bicyclo[2.2.2]oct-2-ene (**10**), bicyclo[2.1.2.1]hex-2-ene (**11**), bicyclo[3.2.1]oct-6-ene (**13**) and bicyclo[2.2.1]hept-2-ene (norbornene) (**1**).

Correlation of deformation energies and reactivities for norbornene and related cycloalkenes

Huisgen et al.[1] have recently investigated the relative cyclo-addition rate constants for a series of cycloalkenes, including norbornene (**1**), cyclohexene (**9**), bicyclo[2.2.2]oct-2-ene (**10**), bicyclo[2.1.1]hex-2-ene (**11**), and tricyclo[3.3.0.0²,⁶]oct-3-ene (**12**). In order to account for the surprising observation that exo addition to norbornene occurs even faster than addition to the more strained species **11** and **12**, Huisgen et al. introduced an unidentified factor "x", responsible for the extra norbornene reactivity. Under the assumption that the rate increase of **11** and **12** over **10** can be ascribed exclusively to increased strain release in the transition state, and that, percentage-wise, the strain release is the same for norbornene, factor "x" was estimated to lower the activation energy for cyclo-additions to norbornene by 1–3 kcal mol.$^{-1}$

As expected, a significant preference for endo bending is predicted for norbornene (**1**) and bicyclo[3.2.1]oct-6-ene (**13**), as indicated by the calculated ground state ϕ values $+4.2°$ and $+3.5°$, respectively. The preference for endo bending can be explained in terms of a hyperconjugative mechanism, as discussed in the case of **2**, although other factors such as torsional strain between the olefinic CH bonds and the bridgehead hydrogens contribute to the trend.[5,8,9,19,32] As illustrated by the contour diagrams in Fig. 4, during endo bending the π orbital is tilted away from the exo bridge; most significantly, however, the p lobes of the π orbital simultaneously undergo a disrotatory motion such that repulsive interactions with the σ orbitals of the exo bridge are efficiently reduced. Bending exo, the trends are reversed.

However, the most interesting result is the close correlation between calculated bending energies and observed relative cycloaddition rate constants for the five
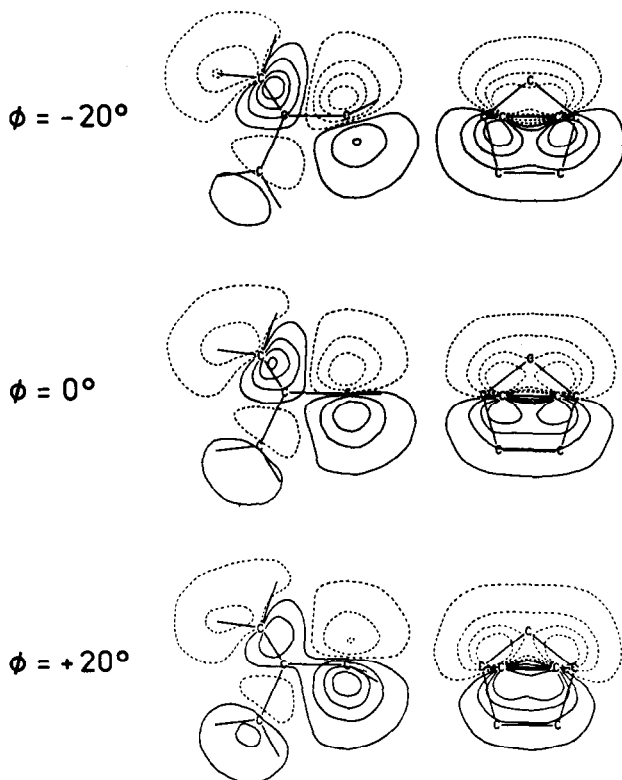
Fig. 4. Contour diagrams of the norbornene (1) π type orbital for different out-of-plane bending angles ϕ. Amplitudes (± 0.01, ± 0.05, ± 0.10, ± 0.15) are indicated in the symmetry plane through the exo methylene group (left) and in a plane containing the double bond, perpendicular to the plane of the adjoining CC bonds (right). The orbitals were calculated by the EWMO method.[33,34]

Table 1. Calculated bending energies for norbornene (1) and related cycloalkenes for bending angles $|\phi|$ equal to $10°$ and $20°$. Experimental relative rate constants k_{rel} for addition of 2,4,6-trimethylbenzonitrile oxide at 25°C in CCl$_4$ are indicated for comparison[1,7]

Cycloalkene		Bending energy (kcal/mole)		k_{rel}
		$10°$	$20°$	
cyclohexene (9)		1.1	4.5	1
bicyclo[2.2.2]oct-2-ene (10)		0.9	3.7	5
bicyclo[2.1.1]hex-2-ene (11)		0.8	3.3	1900
bicyclo[3.2.1]oct-6-ene (13)	$\phi > 0$	0.4	2.7	$\sim$ 2000
	$\phi < 0$	1.8	5.3	
bicyclo[2.2.1]hept-2-ene (1)	$\phi > 0$	0.3	2.3	2600
	$\phi < 0$	1.8	5.2	

compounds considered (Table 1). Taken at its face value, this result suggests that the ease of deformation may be a rate determining factor.[10]

Following Nagase and Morokuma,[35] the activation energy for a chemical reaction can be expressed as the sum of an intramolecular deformation energy and an intermolecular interaction energy. According to the results of *ab initio* calculations,[35] the deformation energy for ethylene in the syn cycloaddition of HCl accounts for 40% of the total activation energy, indicating the significance of olefin deformation in the (late) transition state. Unfortunately, the corresponding investigation of the norbornene reactivity by Wipff and Morokuma[8] did not consider the deformation energy. Our simple EH results suggest that different "deformabilities" could easily explain the relative cycloaddition rates for norbornene and related alkenes, at least in those cases where other contributions, such as staggering effects,[7] are estimated to be of similar magnitude (e.g. 1 (exo), 11, 13 (exo)).

In the case of exo addition to norbornene, the required pyramidalization of the olefinic carbon atoms in the transition state is exceptionally cheap, so to speak; this also means that more pyramidalization may be invested in order to increase the bonding frontier orbital overlap contributions to the interaction energy, thereby further lowering the total activation energy. Huisgen *et al.*[1] introduced factor "x" to account for the puzzling observation that 1 is more reactive than 11 and 12; in this sense, we consider the exceptional endo deformability of the norbornene double bond a promising candidate for factor "x".

The "staggering effect"

In a recent publication,[7] Houk *et al.* have investigated the origin of the exceptional norbornene reactivity. In this work, Huisgen's factor "x" is assigned specifically to an ideal staggering of allylic and partially formed bonds in the transition states of exo addition to norbornene. It was previously pointed out by Houk *et al.*[4,5] that endo out-of-plane bending of the norbornene double bond is easier than exo bending, leading to the prediction of an endo distorted ground state structure and increased reactivity on the exo face. However, in the interpretation of factor "x", this effect is considered to be insignificant; it is merely observed that "alkene pyramidalization contributes slightly to the staggered arrangement in norbornene reactions".[7]

The staggering model is down-to-earth and appealing in its simplicity: any organic chemist is familiar with the preference of staggered over eclipsed conformations. A straightforward consideration of staggering effects in the transition state allows a beautiful rationalization of the exo selectivity of cycloadditions to 1 and 13 and the increase by orders of magnitude of the reactivity of 1, 11, 12 and 13 relative to that of 10; the favourable staggered arrangement is almost perfectly realized for attack on those faces with monatomic allylic bridges, but much less so for attack on those with two- or three-membered bridges. Inspection of estimated torsional angles[7] for (exo) attack on 1, 11 and 13 indicates that staggering effects should be rather similar in these cases. This is nicely consistent with the observed reactivities which differ by less than an order of magnitude (Table 1).[1,7]

The staggering effect is thus a useful concept. Nevertheless, there is a difficulty with Houk's interpretation of factor "x". Huisgen's original analysis is based on the explicit assumption that the total rate difference between 10 and 11 is accounted for by strain release in the transition state.[1] In contrast, Houk *et al.* assign the increased reactivity of 11 over 10 to the staggering effect. Moreover, Huisgen's factor "x" refers specifically to the norbornene ring system and accounts for the additional rate increase for 1 relative to 11, after tentative correction for strain release effects. The staggering effect discussed by Houk *et al.* operates in 11 as well as in 1 and does not obviously account for the rate difference between these compounds (*vide infra*). Huisgen's and Houk's analyses are based on different premises and it is evidently unjustified to identify Huisgen's factor "x" with the staggering effect.

As shown by Houk *et al.*[7] exo attack on 1 can occur with nearly ideal staggering of the partially formed bonds with respect to the CC and CH bonds to the bridgehead carbons. Attack on 11 involves 9° greater eclipsing with the allylic CC bond but 22° less eclipsing with the allylic CH bond. It is not immediately obvious to us that these shifts in torsional angles should indicate reduced reactivity for 11, as claimed by Houk *et al.*[7] Comparison of estimated torsional angles for 1 and 13 yields a similar result; exo attack on 13 should be as rapid as that on 1, but 1 is observed to react faster.[7] Houk *et al.* explain this result by considering a release of around one third of the added strain relief in 1 in the transition state, thereby referring to Huisgen's numerical estimate.[1] Now, in the first place, it is obviously inconsistent to consider explicitly strain release effects in the comparison of 1 and 13 and not in the comparison of 1 and 11. Secondly, Huisgen's numerical estimate is based on assumptions inconsistent with Houk's approach, as pointed out above. Actually, as emphasized in the concluding remarks of Huisgen's review,[1] the presumption that a large part of the total strain release becomes effective in the transition state is rather unlikely; Huisgen would prefer a zero value for strain release in the very early transition state.

Interpretation of the relative reactivities of 1, 11 and 13 in terms of the staggering principle is problematic. This, of course, is not a serious limitation of the usefulness of this principle, since the rate constants for these compounds are quite similar[1,7] (as they should indeed be, according to the staggering principle). We believe that the relative reactivities of 1, 11 and 13 may depend on other factors, such as the different deformabilities discussed in the preceding section, providing also an alternative interpretation of Huisgen's "x" factor.[10]

CONCLUDING REMARKS

In the course of time, numerous effects have been made responsible for the anomalous exo reactivity of norbornene: steric, torsional, strain, rehybridization, hyperconjugation, pyramidalization, ease of deformation, staggering, etc. All kinds of contributions seem of importance to the phenomenon, but the organic chemist tends to prefer a simple picture; he would like a nice and tidy solution, preferably in terms of a single "effect". This is probably to ask for too much, although some of the contributions listed above seem less significant than others, e.g. the hybridization of the olefinic carbons in norbornene is predicted to be normal by most calculational procedures, and strain energy release in the transition state is not the general solution.[1] Also, at least with increasing theoretical sophistication, several or most of the contributions are interrelated and may be difficult to separate unambiguously. Nevertheless, as

emphasized by Huisgen in his recent review,[1] a consistent picture seems to emerge. Among the bridged cycloalkenes considered, those with allylic monoatomic bridges exhibit similar increased reactivity. As we have seen, this structural element is associated with favourable staggering effects, and, in the case of exo–endo asymmetry, with a preferred distortion mode for the double bond. The two effects in combination could easily explain the observed trends; the relative importance of the individual contributions can only be settled on the basis of accurate calculational and experimental data.

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