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NONPLANARITY OF π SYSTEMS. AN AB INITIO STUDY OF NORBORNENE AND NORBORNADIENE

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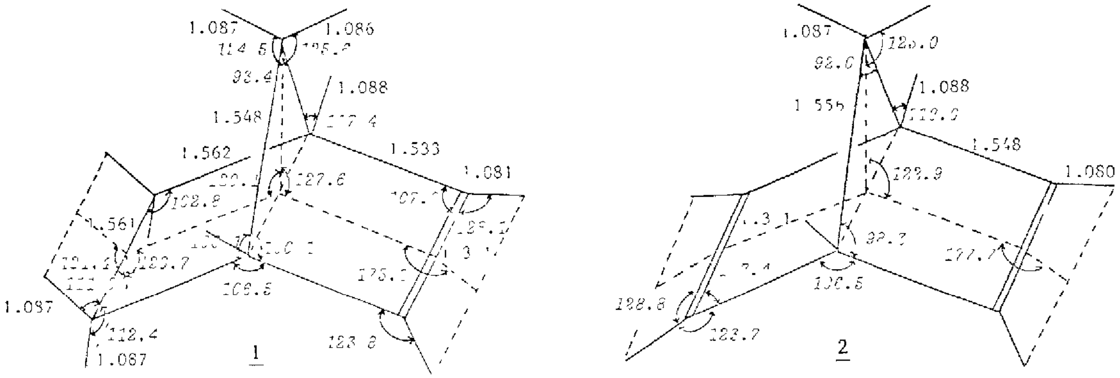
Summary. The geometry of norbornene 1 and norbornadiene 2 fully optimized by *ab initio* calculations reveals the *nonplanarity* of the π system(s). The exo addition of electrophiles on norbornene systems is analyzed in this context.

The two π faces of norbornene 1 and norbornadiene 2 are chemically non-equivalent. The most striking consequence is the exo stereoselection observed in the reaction of an electrophile with 1 and 2 [1,2]. In addition to steric effects, the following stereoelectronic effects have been advanced to rationalize this preference: (i) unsymmetrical π orbital extension [3,4] (ii) secondary interactions between the reactant and bonds neighbouring the π system [5]. Recently, the planarity of the π system in norbornadiene systems has been questioned [6], but no experimental evidence for this structural problem has been so far reported [7]. Theoretical procedures developed in the last few years permit geometry optimization, using the gradient techniques [8]. They reveal that in different conformers and epimers of 7-norbornenol 3 the π system is not strictly planar and the $C_1C_7C_4$ bridge is tilted *away* from the π bond [9]. The latter result cannot be anticipated by steric considerations and is opposite to the experimentally determined structure of 1 [7].

In this communication, we report similar features obtained from an *ab initio* study of 1 and 2. The geometry of 1 and 2 has been fully optimized, using the same technique and STO 3G basis set as was used for 3. This is followed by model calculations for electrophilic attack on 1. Our results can provide an insight into the "exceptional reactivity of the norbornene double bond" (x-factor) which has been reported recently [10].

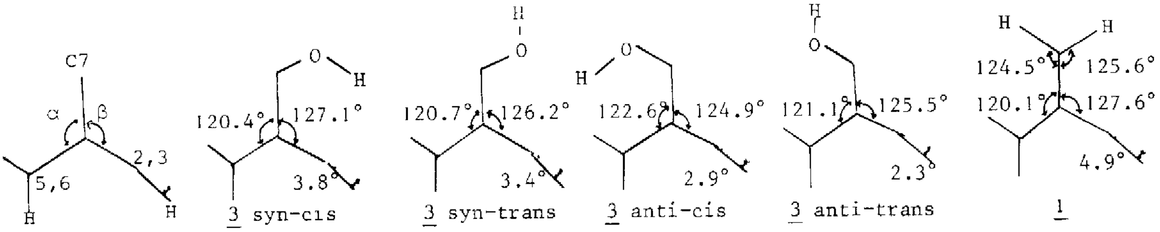
GEOMETRY DISTORTIONS. Among the geometry parameters reported in figure 1, we shall focus on those which we believe have to do with the π system asymmetry and exo/endo



1 2

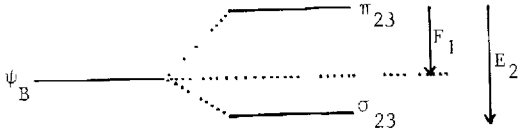
Figure 1

stereoselectivity. In 1 and 2, the C-H olefinic bonds are slightly bent endo, so that the π *system is not strictly planar*; the out-of-plane deviation is larger in 1 (4.9°) than in 2 (2.3°) and 3. Furthermore, the methylene bridge at C_7 in 1 and 3 is tilted *away* from the π_{23} bond, i.e. β is larger than α, independently of the presence and position of the 7-substituent; this difference is again larger in 1 (Δ=7.5°) than in 3 (from 2.3 to 6.7°). In 1, the C_7-H bond syn to π_{23} makes a larger angle with the central bridge (125.6°) than does the other C_7H bond (124.5°). Clearly, this cannot be due to steric effects, which are expected to give α > β in 1, and particularly in 3 anti-cis. The above structural results indicate a repulsion between the π_{23} orbital and the $C_1C_7C_4$ bridge, the geometry of the norbornene system being such as to decrease this repulsion. We shall limit the following study to the norbornene system, since it leads to larger effects than norbornadiene.

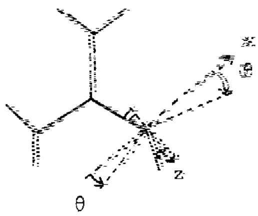


3 syn-cis 3 syn-trans 3 anti-cis 3 anti-trans 1

ORBITAL DISTORTION. As a result of the π bond nonplanarity, one might expect that the π orbital is more developed exo than endo. The same exo hybridization has been predicted by Fukui [4], using a second order perturbation theory: the π_{23} orbital mixes σ_{23} into itself, so that both π_{23} and σ_{23} are out of phase with ψ_B (ψ_B can be either the $C_1C_7C_4$ bridge or C_7-H anti, or the C_1C_6+C_4C_5 bond orbitals, at lower energy than π_{23}). Since ψ_B is more stable than π_{23}, the mixing coefficient of σ_{23} is positive, and π_{23} is more developed exo. The plot of the HOMO of 1 (figure 2b) is consistent with such interactions [11] and the coefficients at C_2 indicate a small exo rehybridization [12]; however, the electron density plot in the xy and xz planes shows almost no endo/exo difference in the HOMO (fig. 2a), probably due to the smallness of the effect. Thus, when norbornene is in its equilibrium geometry, the π orbital distortion is very weak, despite the nonplanarity of the π system. However, this is sufficient to induce a preference for exo electrophilic attack (see next).



$$\pi'_{23} = \pi_{23} + \underbrace{\frac{hh'}{E_1E_2}}_{>0}\sigma_{23} + \underbrace{\frac{h}{E_1}}_{<0}\psi_B \qquad (1)$$



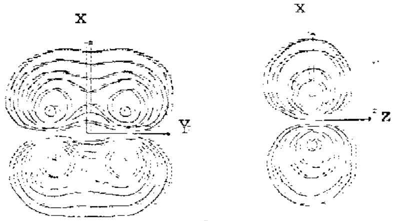


Figure 2a

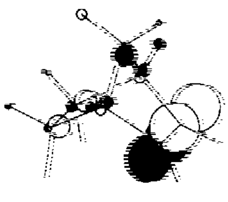


Figure 2b

The introduction of an electro-attracting substituent at the C_7 methylene bridge of 1 should decrease the repulsion between that bridge and π_{23}. As a consequence, we would expect the non planarity of the π bond and the difference between α and β to be diminished, which in fact is supported on comparing structures 1 and 3. Conversely, an electro-donating substituent at C_7 is expected to increase the π bond nonplanarity and the preference for exo electrophilic attack [13].

REACTIVITY TOWARDS ELECTROPHILES. According to the above perturbation scheme (1) a stabilization of the π_{23} orbital resulting from the field of a positive charge decreases E_1, causing an amplification of exo hybridization. As a result, the preference for electrophilic exo attack is increased, at least in the early stages of the reaction (later, more complex orbital mixing can occur). Conversely, in the case of nucleophilic attack, the exo/endo preference should be reduced, or even reversed.

Model calculations for the interaction of 1 with H^+ or H^- located at 2 Å from the midpoint of the C_2C_3 bond, at $\theta = 10°$ (C_s symmetry) support the preference for exo electrophilic attack; whereas $1H^+$ exo is more stable than $1H^+$ endo (Δ = 7.5 kcal/mole), $1H^-$ endo is more stable than $1H^-$ exo (3.4 kcal/mole)[14].

The interaction energy (INT) between 1 and H^+ calculated with the 4-31G basis set at different angles θ can be decomposed into its electrostatic (ES), polarization (PL), charge transfer (CT) and mixing (MIX) contributions [15]. The results (Table) show that

	ENDO					EXO			
θ	-10°	0°	10°	20°	30°	-10°	0°	10°	20°
INT	-109.7	-115.5 (-118.2)	-119.9	-120.8	-118.0	-123.0	-127.1 (-125.2)	-128.1	-126.1
ES	-6.9	-11.5 (-13.2)	-13.5	-13.8	-12.8	-15.3	-18.5 (-17.1)	-19.4	-18.6
PL	-42.8	-31.4 (-29.5)	-25.2	-21.8	-20.1	-31.3	-24 6 (-25.7)	-21.4	-19.9
CT	-78.0	-79.4 (-80.3)	-81.3	-81.8	-80.5	-83.4	-83.4 (-83.4)	-83.3	-82.2
MIX	+17.8	+6.9 (+4.8)	+0.1	-3.3	-4.5	+6.9	-0.6 (+1.0)	-4.1	-5.4

TABLE. Protonation of 1. Energy component analysis.

(i) the total interaction energy INT favours always exo over endo attack. (ii) The minimum corresponds to θ positive, i.e. H^+ attacking from the outside of the molecule ($\theta \sim 8°$, exo; $\theta \sim 17°$, endo; interpolated values), rather than in the π orbital plane. This releases the repulsion between H^+ and hydrogen atoms of the CH_2 groups(d $H^+_{exo}-H = 1.88$ Å, d $H^+_{endo}-H = 1.81$ Å if $\theta = 0°$) as reflected by the favourable electrostatic energy ES. (iii) CT, which is the largest contribution to INT favours exo. This is paralleled by the calculated charge on H^+ which is greater exo (0.762 e^-) than endo (0.722 e^-) at $\theta = 0°$; however, the largest endo/exo difference comes from ES. (iv) The only component in favour of endo is PL. It corresponds to the attack antiperiplanar to the more strained and hence more polarizable $C_1C_7C_4$ bridge. An electron attracting substituent at C_7 should increase PL and reduce the exo/endo preference for electrophilic attack, as expected from the above structural and perturbation results. (v) The nonplanarity of the π system is not essential for exo/endo differentiation; the above conclusions still hold when an alternative model with a planar π system is considered (values in parentheses, table). However, the nonplanarity enhances the exo/endo differences, as expected from the perturbation scheme.

In summary, three different approaches: structure optimization, perturbation theory and interaction energy analysis provide a complementary picture of the π facial non equivalence in norbornene. These results should have bearing also on other molecules in which orbital distortion is expected to perturb the planarity of the π system and thus influence the stereoselectivity of reactions [2,6], at least when an early transition state is expected. Other factors, such as interactions between non-reactive centers [16], the relaxation or deformation of geometry [17] can also play an important role

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