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ORIGIN AND DIRECTION OF NONEQUIVALENT ORBITAL EXTENSION AND STEREOCHEMICAL BEHAVIORS OF PLANE-ASYMMETRIC OLEFINS. EXO-ELECTROPHILIC ADDITION TO NORBORNENE

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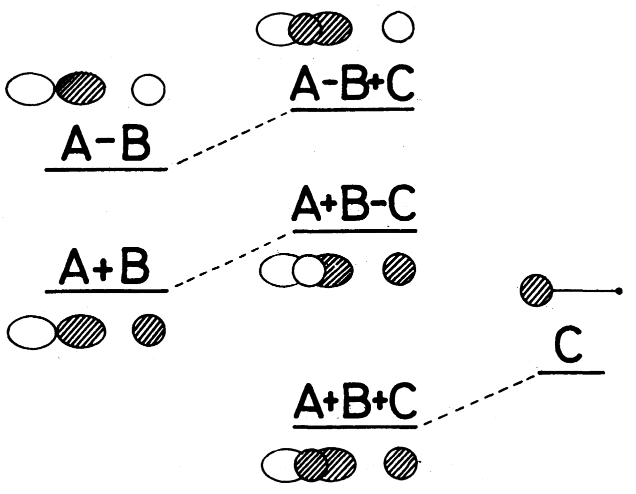
Origin and direction of nonequivalent extending of orbitals with symmetric density distribution under influence of weakly conjugative entity was considered in a general manner. An application of the obtained results was found to shed new light on exo-stereoselectivity in electrophilic addition to norbornene.

Exo-stereoselection has been observed in the reactions of norbornene with a variety of electrophiles.[1-8] Brown[3] and Schleyer[4] attributed this selectivity to stereochemical features of norbornene, i.e., steric interference by endo-hydrogens at C_5 and C_6, and a torsional effect exerted between bridgehead hydrogens and the neighboring olefinic hydrogens, respectively. The steric hindrance explanation is questionable on the basis of the similar selectivity observed in the oxymercuration[5,6] and in the hydrochlorination[7] of 7,7-dimethylnorbornene. On the other hand, the uniform distribution between the possible isomeric exo-products from the reactions of 1-methylnorbornene with unsymmetrical electrophilic reagents, mercuric salts[5] and formic acid[8], and the inverted ratios of one to the other on slightly different conditions of hydrochlorination reaction[8] may also throw a doubt on the predominant role of the torsional effect in determining the stereochemical path. In this study we attempt to seek a reason for these matters in the electronic structure of norbornene. During the work a remarkable electronic difference between the exo- and the endo-directions has been predicted and confirmed, which can provide a good ground for understanding the preference of exo- over endo-attack of electrophiles.

According to the concept of orbital interaction[9], the charge-transfer interaction involving the highest occupied (HO) molecular orbital (MO) is the most important in characterizing behavior toward an electrophile. A precise description of the HOMO is indispensable to scrutinizing electrophilic reaction mechanisms. Briefly speaking for our present purpose, an electrophile approaches norbornene in the direction of higher HOMO electron density.

We will consider origin and direction of nonequivalent orbital extension in general. Suppose that the orbital system with originally plane-symmetrical distribution of electron density and one which weakly interacts with it to introduce the asymmetrical environments are represented by p-type orbital (A) with energy E_A and by s-type orbital (B) with E_B, respectively. we can assume $E_A>E_B$ without altering our final conclusions. The interaction between the orbitals A and B gives rise to a new set of orbitals; one by in-phase combination A+B, the other by out-of-phase one A-B in which $E_{A+B}<E_B<E_A<E_{A-B}$. Although, needless to say, the orbital A in bonding A+B orbital appears to extend in the direction of B and vice versa on account of orbital overlap effect, our concerns are not associated with such an effect on orbital extension but with the effect of mixing of the third orbital C newly induced into the same system as A by the perturbation with conjugative entity. As a p-type orbital is employed as A, s-type orbital is now appropriate to the C orbital. The orbitals A and C have opposite symmetry property with respect to reflection in the nodal plane of A so that net interaction is negligible. Accordingly the sign relation between B and C determines the height of C-containing orbital energy.

We will first discuss the case of $E_C<E_{A+B}(<E_{A-B})$. New orbitals through mutual mixing by the interaction of nondegenerate orbitals — one (in-phase) with lower and the other (out-of-phase) with higher orbital energy — are composed mainly of the original lower and the higher orbitals, respectively. The A+B and the A-B lie high above C so that they are modified by mixing C into themselves with the signs opposite to B. This is summarized in the schematic representation of orbital interaction shown below. The same signs between A and C show that the A orbital is endowed with the trend to extend in the direction of B and vice versa. It follows that the A orbital with originally plane-symmetrical electron density has more extension in the direction for and against the conjugative part B in the out-of-phase and in-phase combinations of A and B, respectively. If $E_A>>E_B$, the A orbital is mainly characterized by the former statement.



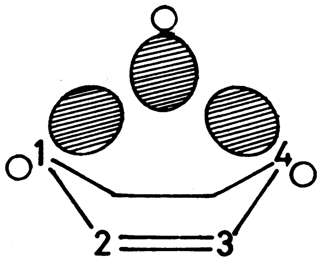
TABLE

case \ orbital	A+B	A-B
$E_{A-B}>E_{A+B}>E_C$	-C	+C
$E_{A-B}>E_C>E_{A+B}$	+C	+C
$E_C>E_{A-B}>E_{A+B}$	+C	-C

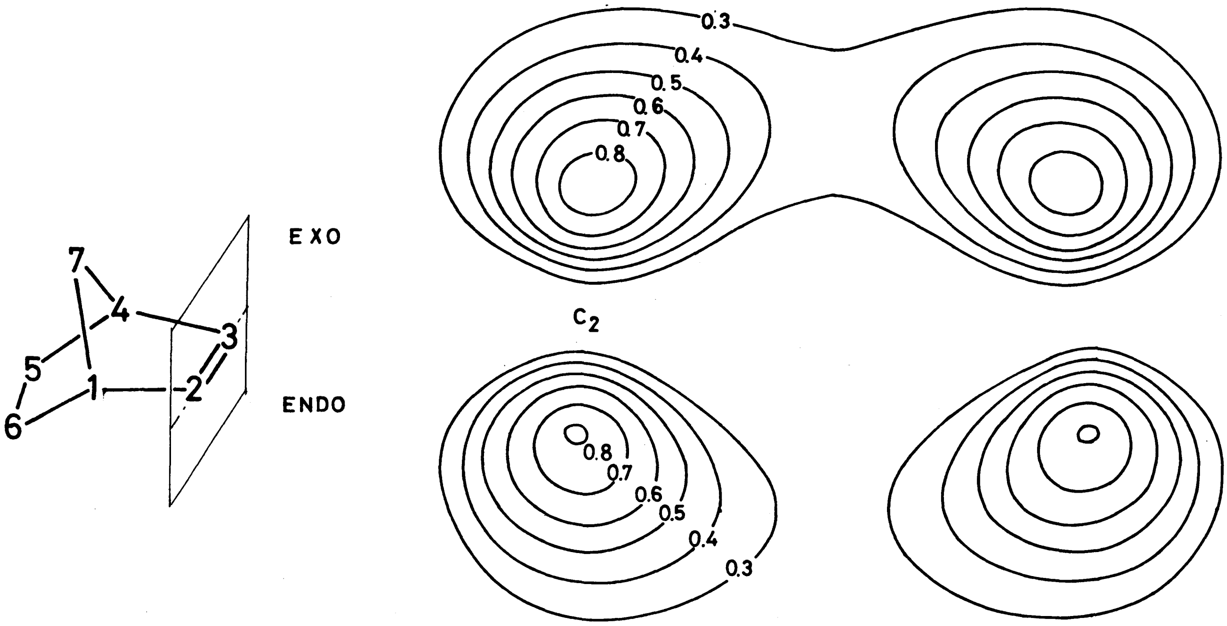
Figure. Schematic representation of origin and direction of nonequivalent orbitals extending in case of $E_C<E_{A+B}<E_{A-B}$.

The similar arguments hold for the cases of $E_{A+B}<E_C<E_{A-B}$ and $E_{A+B}<E_{A-B}<E_C$. The results are listed together with the case of $E_C<E_{A+B}<E_{A-B}$.

Direction of nonequivalent extension of norbornene HOMO is the case of $E_A>E_B$ and $E_{A-B}>E_C$, in which unperturbed π orbital and σ orbital located in $C_1C_2C_3C_4$ bond region can be unquestionably assigned for A and C orbitals, respectively. The alternative assignment of carbon-chain σ bond orbitals involving methano- or ethano-bridge for B orbital holds the keys since the preceding conclusion for $E_A>E_B$ shows that the A orbital tends to extend in the direction of more conjugative entity. Simple semi-empirical extended Hückel$^{10)}$ and CNDO$^{11)}$ calculations on the assumed structure constructed by hybridizing norbornane$^{12)}$ for the saturated moiety and norbornadiene$^{13)}$ for the unsaturated moiety suggest stronger hyperconjugation of the methano-bridging bonds than that of the ethano-bridging one with the π orbital. The orbital amplitude at C_7 is larger than that at C_5 in the HOMO. The methano-bridge orbital conjugating with A can be represented as shown. We can now predict that the HOMO extends in the direction of the methano-bridge or in the exo-direction. The sign relation between the

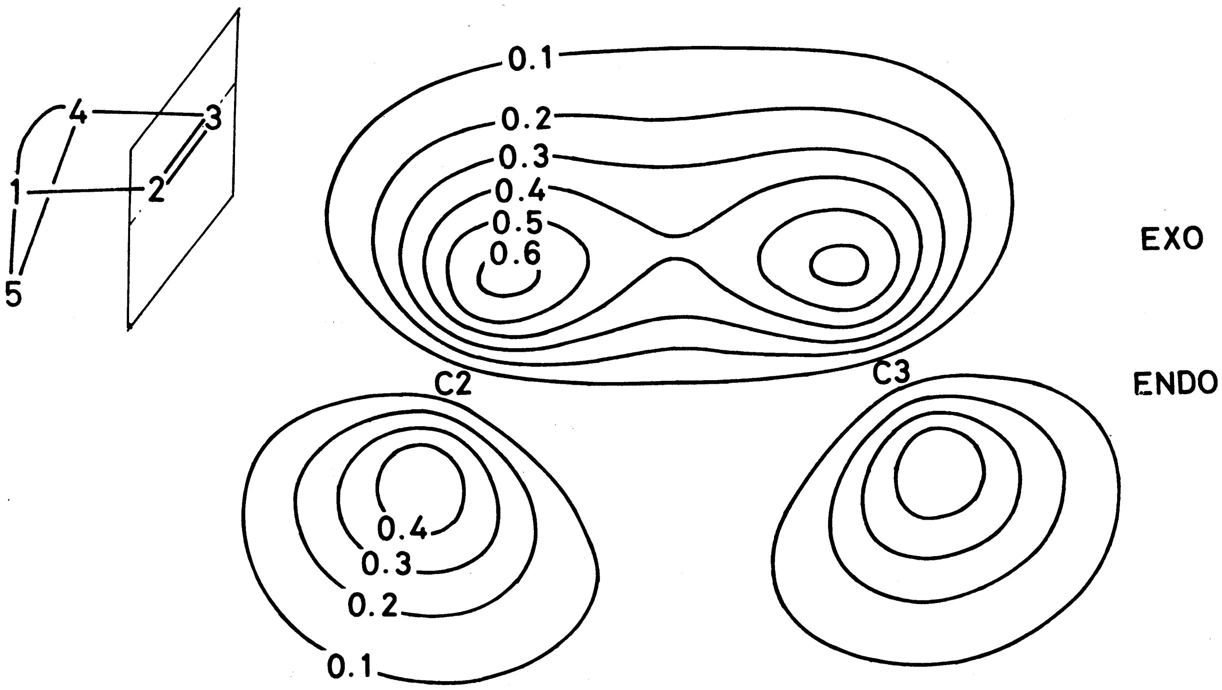


mixing π and σ orbitals is in fact confirmed with the prediction; the coefficient of s-atomic orbitals on C_2 and C_3 has the same sign as that of exo-lobes of pπ-orbitals. In addition to the s-character the effect of pσ component at the C_2-C_3 bond should be noted which causes the unperturbed parallel p-atomic orbitals to tilt in such a way that the π orbital may become more conjugative with C_1-C_7-C_4 as can be easily predicted by the analogous arguments. The inclination of pπ atomic orbitals gives rise to more orbital overlapping or to more electron crowding in the exo-region to assist exo-electrophilic attack. With a view to visualizing the spatial extension of the HOMO, a contour map of the HOMO electron density is depicted on the plane perpendicular to the $C_1C_2C_3C_4$ coplane. A nonequivalent extension along the exo-endo direction is discernible obviously.



Additional supports for direction of nonequivalent orbital extension and for its relation to exo-endo-stereoselectivity are available, although steric factor is also possible to contribute to some degree. The π-HOMO of bicyclo[2.1.0]-pentene is predicted to extend in the exo-direction. That can be readily understood when the unperturbed π-orbital at C_2-C_3, the σ-bond at C_1-C_4 bent in the exo-direction and the σ-bonds localized at $C_1C_2C_3C_4$ are assigned for A, B and C defined above. The prediction is confirmed by the contour map perpendicular to

$C_1C_2C_3C_4$ coplane on the basis of the extended Hückel MO. The calculation was performed on the molecular structure determined by microwave spectrum.14) The electronic feature of the π-orbital is consistent with the direction of attack of diimide15), which is an electrophilic reagent.16) The similar role of the bent bond is observed in electrophilic additions to bicyclo[3.1.0]hexene of DCl, and of $DOCH_3$ in the presence of TsOD.17)



This way of explanation is similarly applicable to the problem of exo-selectivity in free radical reactions of norbornyl18,19) and 7-oxabicyclo[2.2.1]-hept-2-yl.19)

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