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Dihedral Angle-Dependent Orbital Distortions Arising from Vicinal Bonds in Norbornene and 2-Norbornanone

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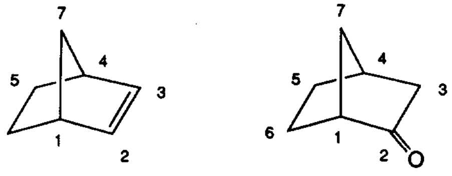
Abstract

Exo reactivities of norbornene with respect to electrophilic addition and of 2-norbornanone with respect to nucleophilic addition are classical examples of the influence of distorted π faces of sp^2- trigonal centers of olefin and carbonyl groups. Intuitively, it seems likely that the asymmetry of π orbitals is an intrinsic feature of the nonequivalent environment around the trigonal centers arising from the unsymmetrical substituents, *methano* and *ethano* bridges in these cases. In this paper we will propose an orbital interaction motif (orbital diffusion effect) to describe a dihedral angle-dependent magnitude of interaction in the methano and ethano bridges. This divergent interaction provides an explanation for the origin of the unsymmetrical π face of norbornene and norbornanone. These two systems involve the mixing of C-C σ (σ^*) orbitals of the methano and ethano bridges into π or π^* orbitals of the trigonal carbon centers. These interactions are *primary* interactions, although these mixing will not create by themselves a secondary hybridization or tilting of the π or π^* orbitals to one face of the π bond. However these primary interactions involve intrinsically divergent orbital diffusion of the π (π^*) orbitals which unsymmetrize the p face toward the attack of the reagents. In norbornene, out-of-phase interaction of the π orbital (π_{CC}) of the olefin group with the less acute allylic $\sigma_{C\text{-}C}$ orbital of the ethano bridge leads to greater depletion of the electron density of the π_{CC} orbital on the endo face, favoring exo addition of electrophiles. In 2-norbornanone, the π^* orbital (π^*_{CO}) of the carbonyl group is perturbed by the in-phase combination of the vacant $\sigma^*_{C\text{-}C}$ orbital of the less acute ethano bridge at the back-side lobe. This mixing builds up a larger virtual bonding region on the exo face which is to be attacked by a nucleophile. Ab initio calculations of 1-butene and 2-fluoroacetaldehyde as models for norbornene and 2-norbornanone supported the involvement of interactions with dihedral angle-dependent magnitude.

Exo reactivities of norbornene **1** (with respect to electrophilic addition such as oxymercuration and hydroboration) [1] and of 2-norbornanone **2** (with respect to nucleophilic addition such as reduction with hydride) [2] are classical examples of the effects of distorted π faces of sp^2- trigonal centers of olefin and carbonyl groups (Chart 1). Various theoretical interpretations of the bias have been proposed. [3] Two basic explanations have been previously given, that is, the torsional based arguments [3d] and the stereoelectronic arguments. [3c, e, f] Fukui and collaborators proposed unsymmetrical π orbital extension of the olefin in **1** due



1 **2**

Chart 1

to the orbital mixing with the σ_{CC} bond of the olefin skeleton through the intervention of the σ orbital of the methano bridge.[3e] This mixing leads to hybridization of the π orbital of the olefin (Chart 2 (a)). Another orbital distortion was also previously proposed, namely π-orbital tilting (Chart 2 (b)) due to the combination of $2p\pi$-$2p\sigma$ orbitals on the same rigonal carbon atom through the intervention of the π-type group orbital of the methylene group (π_{CH2}) of the methano and ethano bridges in **1**.[3f] A similar π orbital tilting of norbornadiene was also proposed which involves the mixing of the π orbitals with the σ_{CC} orbitals of the bridges. Although these orbital interactions successfully interpreted the norbornene problem, these distortions stem from secondary orbital interactions, and are arbitrary in some cases.[3h] Intuitively, it seems likely that the asymmetry of π orbitals is an intrinsic feature of the nonequivalent environment around the trigonal centers arising from the unsymmetrical substituents, *methano* and *ethano* bridges in these cases. It is still worthwhile to consider what is the difference between the orbital interaction of π (π^*) orbitals with the methano bridge and that with the ethano bridge in **1** and **2**. In this paper we will propose a dihedral angle-dependent orbital interaction motif to account for the origin of unsymmetrical π face of norbornene and norbornanone. The mixing of C-C σ (σ^*) orbitals of the methano and ethano bridges into π or π^* orbitals of the trigonal carbon centers are *primary* interactions, although these mixing will not create by themselves a hybridization nor tilting of the π or π^* orbitals to one face of the π bond. However these primary interactions involve intrinsically divergent orbital diffusion of the π (π^*) orbitals (Chart 2 (c), *vide infra*) which unsymmetrizes the π face toward the attack of the reagents.

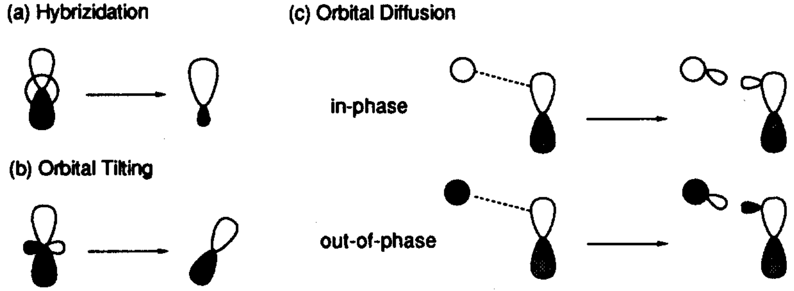
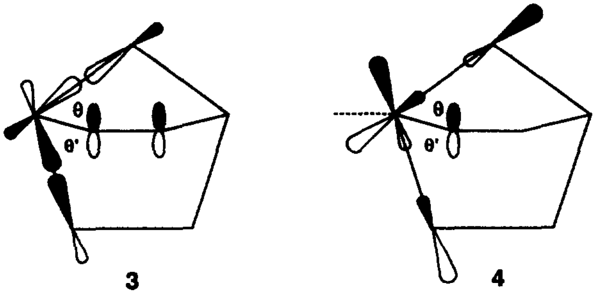


Chart 2

Orbital Interaction Principles

Our postulate is based on simple, well-defined principles of orbital interactions, as follows. Principle 1: in-phase mixing of orbitals (A and B) leads to buildup of bonding electrons along the internuclear region (A-B); out-of-phase mixing of orbitals (A and B) depletes the bonding electrons from the internuclear region (A-B).[4] In order to emphasize electron density distribution of the internuclear region in addition to the phase relation of the interacting orbitals, we adopted the diagram depicted in Chart 2(c): the buildup of bonding electron is equivalent to diffusion of the electron into each bonding region along the bond axis; the removal of bonding electron from the internuclear region can be regarded as diffusion of the electron of each fragment into each antibonding region along the internuclear axis. In the case of orbital interactions of two vacant orbitals, the depletion and buildup of the orbital electron density (or the diffusion of orbital into the



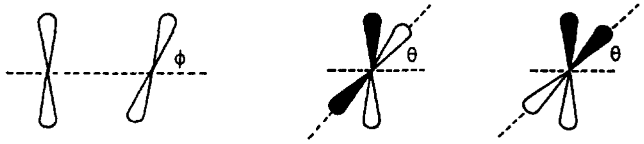
3 4

Chart 3

internuclear region) are notional because there is no electron present. However, we are interested in the interpretation of the reaction in terms of frontier orbital theory. We thus consider the virtual electron density (and virtual orbital diffusion region) which is to be attacked by electrons of an occupied orbital (e.g., the HOMO) of a reagent. The bonding or antibonding diffusion depends on energy difference and on overlap: interactions of orbitals with a smaller energy gap or with a larger set of overlap intergrals perturbed more significantly the electron density distribution in the interacting region. Principle 2: out-of-phase combination of HOMO (A) and HOMO (B), if symmetry permits, results in a hybridized HOMO, activated energetically; while in-phase combination of LUMO (A) and LUMO (B), if symmetry permits, results in a hybridized LUMO, activated energetically.[5,6] These principles can also describe orbital distortions in π-π interactions in spiro[cyclopentane-1,9'-fluorene] systems[7] and dibenzo[2.2.2]-bicyclooctene.[8]

Orbital Interactions in Norbornene

An electrophilic reaction of an olefin involves interaction of the occupied π orbital of the olefin group (π_{CC}) with an unoccupied orbital (LUMO) of the reagent.[10] In norbornene **1** the π_{CC} of the olefin moiety can interact with CC framework orbitals of the methano and ethano bridges, i.e., σ_{CC} orbitals (rather than σ_{CC}^* orbitals) of the vicinal CC bonds judging from the small energy difference.[9] Owing to the higher energy level, the π_{CC} orbital mixes out-of-phase with the occupied σ_{CC} orbitals (precisely, σ_{CC} bond orbitals)[10] of the vicinal C-C bonds (C_1-C_6 and C_4-C_5 in the ethano bridge ; C_1-C_7 and C_4-C_7 in the methano bridge) to give an energetically potent HOMO (principle 2) (3, Chart 3).[11] The bonding nature of the σ_{CC} orbitals allows mixing with the π_{CC} orbitals. This mixing involves a π type overlap of these orbitals whose magnitude exhibits dihedral angle-dependence. In the Wolfsberg-Helmholz formula,[12] the orbital interaction energy between two orbitals is approximated to be negatively proportional to the overlap integral. In a simple arrangement of two parallel 2p atomic orbitals (AO's) (Chart 4, ϕ=90 °) the angular variation of π-type overlap of these 2p AO's is a sine function ($\sin\theta$) of the angle θ.[13, 14] Here θ is defined as the



Two angle parameters in overlap of 2p-2p atomic orbitals. Dashed lines indicated molecular planes. One of the planes is a π plane. (a) Out-of-phase combination. (b) In-phase combination.

Chart 4

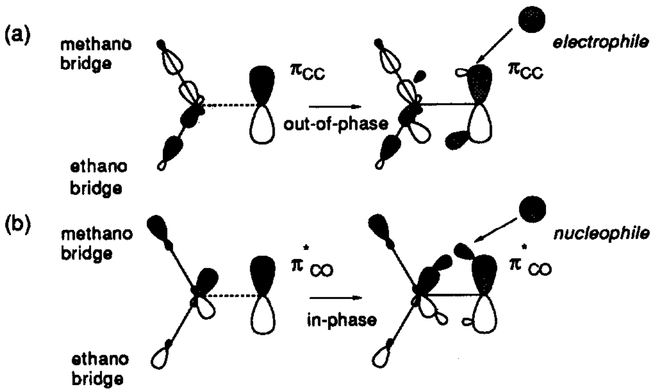
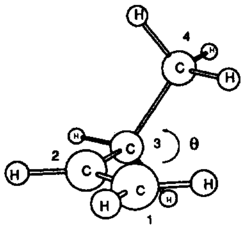


Chart 5

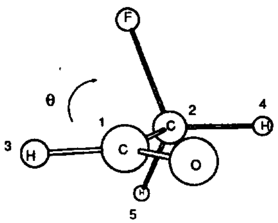
dihedral angle of the molecular planes (one of the planes is a π plane in these cases) rather than that of the orbitals as in Chart 4, (a) and (b); overlap greatly increases as the angle (θ) increases ($0° \leq \theta \leq 90°$). In out-of-phase mixing, the greater the angle, the stronger the interaction (Chart 4(a)), and thus, the larger the depletion of the bonding electrons (principle 1). Owing to symmetry agreement, the C-C bond orbitals take part in this π-type overlap with p orbitals of the olefin moiety (3). Because of the less acute angle of the σ bonds of the ethano bridge (θ (dihedral angle, $\angle C_7C_1C_2C_3$ or $\angle C_7C_4C_3C_2$) > θ' (dihedral angle $\angle C_6C_1C_2C_3$ or $\angle C_5C_4C_3C_2$) in **3**, out-of-phase mixing of the σ_{CC} orbital of *the ethano bridge* more markedly depletes the electron density of the π_{CC} orbital of the olefin on the endo face, favoring exo addition of electrophiles (Chart 5a).[7, 8] This unsymmetrical π face character will be conserved during the attack of a reagent.[15]

Orbital Interactions in 2-Norbornanone

In the related ketone, 2-norbornanone **2**, the vacant π orbital of the carbonyl group (π^*_{CO}) plays a predominant role in nucleophilic reactions.[5] Because of the small difference in energy, the π^* orbital can interact with the vacant C-C σ^* orbitals (i.e., $\sigma^*_{C\text{-}C}$ bond orbitals) of the methano and ethano bridges.[9] Thus the lower-lying π^*_{CO} is perturbed by in-phase mixing of the σ^* orbitals of the vicinal C_1-C_7 and C_1-C_6 bonds to give an energetically activated LUMO (principle 2) (4, Chart 3). In this case, however, owing to the antibonding nature of the $\sigma^*_{C\text{-}C}$ orbitals, the overlap effect of the π^* orbital of the carbonyl group is cancelled. Instead, the π^*_{CO} orbital can interact with the back-side lobes of the $\sigma^*_{C\text{-}C}$ orbitals centered on the



5



6

Chart 6

bridgehead carbon atom (C_1) in an in-phase manner. This interaction motif bears a close resemblance to orbital interactions in the transition state associated with a back-side nucleophilic attack (S_N2) on a tetrahedral carbon center.[16] Owing to symmetry agreement , these interactions can be approximated to the π-type overlap of the π^*_{CO} orbital with 2p AO components of these $\sigma^*_{C\text{-}C}$ orbitals. The magnitude of the interaction is also dihedral angle-dependent: the greater the angle (θ), the greater the overlap of the orbitals (Chart 4(b)). Thus, the in-phase mixing with less acute orbitals (θ') of *the ethano bridge* involves larger build-up of the virtual internuclear bonding region on the exo face which is to be attacked by electrons of an occupied orbital of a nucleophilic reagent (principle 1) (Chart 5b).[7,8] This orbital distortion is consistent with the experimental exo reactivity of **2**.

Model Calculation of Dihedral-Dependent Orbital Distortion

In order to shed light on the dihedral angle dependence of the magnitude of orbital interactions in 1-norbornene **1** and 2-norborenone **2**, we carried out ab initio molecular orbital calculations of 1-butene (**5**) and 2-fluoroacetaldehyde (**6**) as models of **1** and **2**, respectively (Chart 6).[17] Because complete optimization of all geometrical parameters in all possible conformations is very difficult and time-consuming, we used the partial flexible rotor approximation [18, 19] of the anti conformation of **5** with respect to the C_3-C_4 bond, and of the *s*-trans conformation of **6** with respect to the C-C bond with minimal STO-3G basis sets.[20] The carbon-carbon single bond in 1-butene (**5**) required optimization of the bond angles $C_1C_2C_3$ (α) and $C_2C_3C_4$ (β) for each choice of dihedral angles ($\angle C_1C_2C_3C_4$) (Chart 6 and Table 1). The energy level of the π orbital (HOMO) decreases monotonously (i.e., destabilizing) as the dihedral angle (θ) increases in the range of 0 ° to 60 °. Total energy showed broad maxima, not simply related to the energy level of the HOMO. Contour plots of the HOMO (the 16 th) of **5**, e.g. in the case of the dihedral angle of 60 °, illustrated out-of-phase mixing of the p orbital of the olefin with canonical bonding σ orbitals derived from both vicinal CC and CH bonds (Figure 1a). This variation of the energy level of the π orbital (the HOMO) indicated dihedral angle-dependent magnitude of the mixing of the π orbital with the σ_{CC} orbital in an out-of-phase manner.[17] In 2-fluoroacetaldehyde **6**, the angles $\angle OC_1C_2$ (α) and $\angle C_1C_2F$ (β) were subjected to optimization with a specified dihedral angle ($\angle H_3\check{C}_1C_2F$) (Chart 6 and Table 2). In this case the energy of the vacant π orbital

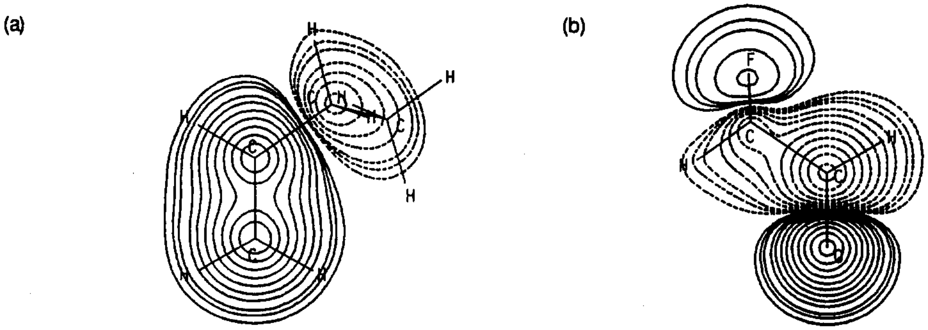


Figure 1 Contour Plots for Frontier Orbitals of **5** and **6**. (a)The HOMO (the 16 th) of **5**, (b) the LUMO (the 17 th) of **6** at the dihedral angle of 60 °. Contours are geometric, differing by a factor of 1.5, with the lowest contour of 0.005 (e.Å^{-3}). The slices through the molecular orbitals were at 0.20 Å above the molecular planes of the olefin and the carbonyl groups.

Table 1 Angular Dependence in 1-Butene 5

dihedral angle (θ)	angle (α) [a]	angle (β) [b]	E_{Total} [c]	E_{CC} [d]
0.0	126.56	114.20	-154.23548	-0.30472
15.0	126.55	114.18	-154.23502	-0.30444
30.0	126.17	113.99	-154.23406	-0.30370
60.0	124.47	112.67	-154.23451	-0.30202
75.0	124.12	112.12	-154.23538	-0.30188
90.0	124.23	111.80	-154.23646	-0.30229

a) $\alpha = \angle C_1C_2C_3$ b) $\beta = \angle C_2C_3C_4$ c) Total energies in a. u. d) The HOMO (the 17th orbital) energy in a.u.

($\pi_{CO}{}^*$) of the carbonyl group (LUMO) decreases monotonously (stabilizing) as the dihedral angle increases in the range from 0 ° to 90 °. Here, lowering of the LUMO involves stabilization of the total energy. Contour plots of the LUMO (the 17 th) of **6** in the case of the dihedral angel 60 ° indicated in-phase mixing of the π^*_{CO} orbital with canonical σ^* MO orbitals of the vicinal CH and CF bonds (Figure 1b). The stabilization of the $\pi_{CO}{}^*$ orbital on increase of the dihedral angle can also be interpreted in terms of dihedral angle-dependent magnitude of the in-phase mixing of the $\pi_{CO}{}^*$ orbital with the lower-lying vacant $\sigma_{CF}{}^*$ bond orbital, representing the $\sigma_{CC}{}^*$ orbital in norbornanone.[17] Similar dihedral angle-dependent orbital distortions can interpret the biased reactions of bicyclo[3.2.2.]nona-6-one, bicyclo[3.2.2]nona-6-ene [21], and bicyclo[3.2.1]-octane-6-one.[22]

Table 2 Angular Dependence in 2-Fluoroacetoaldehyde 6

dihedral angle (θ)	angle (α) [a]	angle (β) [b]	E_{Total} [c]	$E_{CO}{}^*$ [d]
0.0	125.05	109.92	-248.38629	0.27414
15.0	125.01	109.94	-248.38636	0.27357
30.0	124.86	110.00	-248.38647	0.27200
45.0	124.63	110.08	-248.38645	0.26976
60.0	124.34	110.17	-248.38609	0.26733
75.0	124.03	110.26	-248.38537	0.26529
90.0	123.74	110.34	-248.38451	0.26426

a) $\alpha = \angle OC_1C_2$ b) $\beta = \angle C_1C_2F$ c) Total energy in a.u. d) The LUMO (the 17th orbital) energy in a.u.

Calculational Methods

The calculations have been performed at the Computer Center of the University of Tokyo. The ab initio calculations were carried out by using a modified version of the Gaussian 80 computer programs (Gaussian 80H).[23] Contour plots of the orbitals were obtained by using the basis sets and orbital coefficients based on the geometries partially optimized with the STO-3G basis sets.[18, 19]

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9) The σ_{CH} or σ^*_{CH} orbitals centered on the bridgehead carbon atoms do not contribute to the perturbation of the π (π^*) orbitals of **1** and **2** because of symmetry disagreement.

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14) As shown in ref 13, the overlap integral is dependent on two angular parameters, $\sin\theta\sin\phi$ (Chart 3). The angle ϕ is the dihedral angle of the molecular planes, rather than that of the orbitals. In the calculated geometry of norbornene with STO-3G basis sets, a pair of dihedral angles ϕ, between the methano bridge ($C_1C_7C_4$ plane) and the olefin plane ($C_{11}C_2C_3C_4$ plane), and between the ethano bridge ($C_{11}C_6C_5C_4$ plane) and the olefin plane ($C_{11}C_2C_3C_4$ plane) are optimized to be 127.6 and 112.3 °, respectively (Wipff, G.; Morokuma, K., *Tetrahedron Lett.*, **1980**, *21*, 4445). Judging from the small discrepancy in sin (ϕ), we can assume that difference in $\sin(\theta)$ is overwhelmingly effective in the overlap integral.

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