Orbital Unsymmetrization of Olefins Arising from Non-equivalent Orbital Interactions. σ–π Coupling in Bicyclo[2.2.2]octenes

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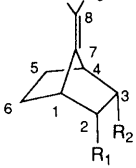
We characterized experimentally the substituent effect of a 5-*exo* substituent on the π facial selectivities of bicyclo[2.2.2]octenes toward electrophilic oxidative reactions such as epoxidation and dihydroxylation, and we discuss the underlying orbital interactions of vicinal σ orbitals and the olefinic π orbital involved in bicyclo[2.2.2]octenes, and commonly in methylenenorbornanes. Of significance is the out-of-phase motif of these σ–π couplings. Electron-withdrawing substituents such as cyano and carboxylic acid groups unequalize the relevant σ–π coupling, leading to the observed *syn*-facial preference. Alkyl substituents exhibit an electron-donative perturbing effect, depending on the bicyclic ring system.

Key words bicyclo[2.2.2]octene; olefin; orbital unsymmetrization; σ–π coupling; methylenenorbornane

The π orbitals of trigonal carbon atoms of an olefin have a symmetric property, *i.e.*, they are symmetric in magnitude and antisymmetric in sign. This nodal property constitutes the symmetric π face (π plane) of olefin groups. However, some olefinic compounds afford a biased pair of reaction products even when the stereogenic center is free from steric bias.$^{1)}$ Remote substituents asymmetric with respect to the π plane can provide an asymmetric π face. le Noble *et al.* showed such effects of remote substituents in the case of 2-methyleneadamantane derivatives,$^{2)}$ while Mehta *et al.* studied 7-methylenenorbornane **1a**$^{3a)}$ and 7-isopropylidenenorbornane **1b**$^{3b)}$ bearing an *exo* substituent, and Jones and Vogel recently investigated the substituent effect of a 5,6-bis(methoxycarbonyl) group in bicyclo[2.2.2]octene (**2i**).$^{4)}$ The π facial selectivities of carbonyl groups arising from unsymmetrical σ-frameworks have been extensively studied in the cases of 2-adamantanones,$^{5)}$ 7-norbornanones,$^{6)}$ 7-norbornenones,$^{7)}$ and 7-benzonorbornanone,$^{8)}$ bicyclo[2.2.2]octanones,$^{9)}$ and related benzobicyclo[2.2.2]octanones,$^{10)}$ and theoretical rationalizations based on electrostatic$^{11)}$ or hyperconjugative stabilization$^{12)}$ or steric and torsional destabilization,$^{11)}$ and orbital mixing perturbation$^{13,14)}$ have been proposed and examined with the help of *ab initio* calculations on the ground and transition structures involved in the additions.$^{15)}$ On the other hand, few experimental studies have been reported on detection of the facial selectivities of olefinic groups, in particular of rigid bicyclic compounds,$^{16)}$ and the theoretical background for the biases has also received little attention. It is not necessarily the case that factors similar to those for the carbonyl group are also operative in the case of the olefin. Theoretical evaluation of the reaction mechanisms of olefins is also not well advanced, though transition structures of prototype reactions of an olefin, epoxidation of ethylene with a peracid,$^{17)}$ and dihydroxylation with osmium tetroxide$^{18)}$ were recently elucidated. The aims of this paper are to characterize the substituent effect of a single 5-*exo* substituent on the facial selectivities of bicyclo[2.2.2]octenes **2b**—**h**, and to discuss the underlying orbital interactions of vicinal σ orbitals and the olefinic π orbital involved in bicyclo[2.2.2]octenes **2** and commonly in methylenenorbornanes **1**.

The HOMOs of unsubstituted methylenenorbornane **1a** and bicyclo[2.2.2]octene **2a**, which are most significant in the reaction with electrophiles, are intrinsically comprised of the π orbital of the ethylene and the σ orbitals of the ethano bridges, the coupling being in an out-of-phase fashion (Fig. 1). The π orbitals of the olefins of **1a** and **2a** are symmetric because of equivalent σ–π coupling with respect to the π plane. We will postulate here that asymmetric σ–π coupling is a cause of unsymmetrization of the π face, although such mixings will not by themselves



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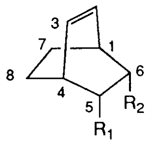

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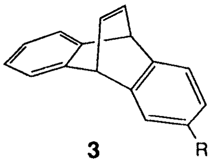

3

	R_1	R_2	R_3
1a:	H	H	H
1b:	H	H	CH_3
1c:	CN	CN	H
1d:	CH_3	CH_3	H

	R_1	R_2
2a:	H	H
2b:	CN	H
2c:	CO_2CH_3	H
2d:	CONHPh	H
2e:	CO_2H	H
2f:	CH_2OCH_3	H

	R_1	R_2
2g:	CH_2OTs	H
2h:	CH_3	H
2i:	CO_2CH_3	CO_2CH_3
2j:	CN	CN
2k:	CH_3	CH_3

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create a hybridization of the π orbitals to one face of the π bond.[19] It is known that the olefin group in 2-substituted dibenzobicyclo[2.2.2]octatrienes (2-substituted-9,10-dihydro-9,10-ethenoanthracenes) **3** is facially biased through σ-type overlaps of the π orbitals of aromatic and olefinic groups,[20] in a similar manner to longicyclic conjugation.[21] Because bicyclo[2.2.2]octenes **2** and dibenzobicyclo[2.2.2]octatrienes **3** have a similar bicyclic σ skeleton, we can compare the tendency and the origin of the substituent effects in aromatic **3** with those in the case of aliphatic **2**.

Results and Discussion

Biases in Electrophilic Oxidative Reactions of the Olefins 2 Epoxidation and dihydroxylation of the olefin moiety of 5-*exo*-substituted bicyclo[2.2.2]octenes (**2b**—**h**) were investigated. The results are summarized in Table 1. 5-*exo*-Cyanobicyclo[2.2.2]octene (**2b**) underwent preferential *syn*-addition (with respect to the face of the cyano group) of peroxidic reagents, *i.e.*, *m*-chloroperbenzoic acid (*m*CPBA) and osmium tetroxide. In the epoxidation of **2b** with *m*CPBA, the *syn*-epoxide is favored over the *anti*-epoxide. In the dihydroxylation with osmium tetroxide, the *syn*-diol is also favored over the *anti*-diol. Values of diastereomeric excess observed in these reactions ranged from 70% to 72%. Direct intervention of the *exo*-substituent at the reaction center, such as a coordinative interaction, can be ruled out, because of the rigid structure of the bicyclo[2.2.2]octene system, and of the dangling position of the *exo*-substituent. 5-*exo*-Methoxycarbonylbicyclo[2.2.2]octene (**2c**) also preferentially gave the *syn*-epoxide (de 36%) and the *syn*-diol (de 68%). Electron-withdrawing nature of the substituent is important for *syn*-preference, as judged from the findings that phenylcarbamoyl **2d** and carboxylic acid **2e** substituents distorted the olefinic π face similarly to the methoxycarbonyl group, whereas the methoxymethyl group **2f** imparted reduced (in the case of dihydroxylation, de 20%) or absent (in the case of epoxidation) selectivity. Tosylation of the methyl alcohol functionality (**2g**) restored the *syn*-selectivity to some extent in hydroxylation and particularly in the epoxidation. On the other hand, the 5-methyl derivative **2h** showed a negligible preference in both reactions.

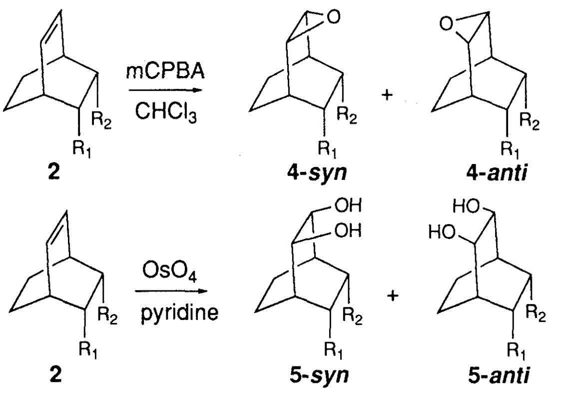


Table 1. Electrophilic Oxidations of 5-*exo*-Substituted Bicyclo[2.2.2]-oct-2-enes[a,b]

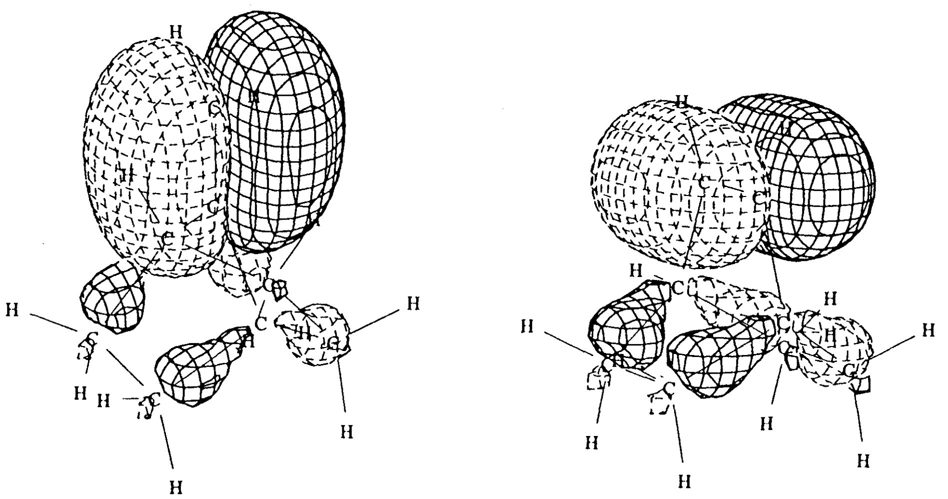
	R_1	R_2	Reagent	Time (h)	Yield (%)	*syn* : *anti*
2b	CN	H	*m*CPBA	2	98	85 : 15
2c	CO_2CH_3	H	*m*CPBA	6	88	68 : 32
2d	CONHPh	H	*m*CPBA	2.5	95	81 : 19
2e	CO_2H	H	*m*CPBA	2.5	90	74 : 26
2f	CH_2OCH_3	H	*m*CPBA	2	91	50 : 50
2g	CH_2OTs	H	*m*CPBA	3	92	63 : 37
2h	CH_3	H	*m*CPBA	3	72	52 : 48
2i	CO_2CH_3	CO_2CH_3	*m*CPBA	10		73 : 27[c]
2b	CN	H	OsO_4	3	83	86 : 14
2c	CO_2CH_3	H	OsO_4	2.5	93	84 : 16
2d	CONHPh	H	OsO_4	2.5	85	62 : 38
2e	CO_2H	H	OsO_4	2.5	62	76 : 24
2f	CH_2OCH_3	H	OsO_4	3	89	60 : 40
2g	CH_2OTs	H	OsO_4	3	86	63 : 37
2h	CH_3	H	OsO_4	3	70	54 : 46
2i	CO_2CH_3	CO_2CH_3	OsO_4	3		83 : 17[d]

a) $CHCl_3$, 0 °C. *b*) Pyridine, −23 °C. *c*) CH_2Cl_2, room temperature. Taken from ref 4. *d*) Et_3NO, acetone : water (6 : 1), 0 °C. Taken from ref. 4.

The *syn*-preference arising from the electron-withdrawing groups is consistent with the preference observed in the case of the bis(methoxycarbonyl) group **2i** (de 46% in the epoxidation; de 66% in the dihydroxylation).[4] A single substituent is sufficient to perturb the π face in the bicyclo[2.2.2]octene system. This observation coincides with the case of methylenenorbornanes **1**.[3] Furthermore, this bicyclo[2.2.2]octane system exhibited the same preference as those found in 7-methylene- (**1a**) and 7-isopropylidenenorbornanes (**1b**), except for the electron-donating alkyl groups: in 7-methylidenenorborane the ethyl substituent favored *anti*-addition in the epoxidation with *m*CPBA.

Finally, the bicyclo[2.2.2]octenes **2** and the dibenzobicyclo[2.2.2]octatrienes **3** exhibited similar substituent effects: an electron-withdrawing substituent such as a cyano or methoxycarbonyl group (in the case of **2**) and a "frontier-electron withdrawing" nitro or fluoro group (in the case of **3**) gave a large to moderate bias (preferred *syn* attack with respect to the substituents) whereas an "electron-donating" methyl (in the case of **2**) or methoxy (in the case of **3**) substituent exhibited a small or negligible bias.

σ–π Coupling in Bicyclo[2.2.2]octenes Interacting σ Components Even though π and σ orbitals are separated by a significant energy gap, symmetry allows a high-lying σ orbital to interact with a low-lying π orbital. The HOMO of the bicyclo[2.2.2]octene is approximated as a combination of the π orbital of the olefin and σ fragments of a cyclohexane (CHA) (in a boat conformation). Because the π orbital is higher in energy, the combination which perturbs the π orbital is an out-of-phase motif.[22] Substitution can perturb four possible types of σ fragment orbitals of CHA, *i.e.*, parallel C–C bonds (a), vicinal C–C bonds (b), *exo*-C–H bonds (c), and *endo*-C–H bonds (d) (Fig. 2). The nodal property of the σ bonds can exclude the contribution of parallel C–C bonds (Fig. 2 (a)), and inefficient overlap (owing to unfavorable directions and small amplitudes of orbitals) disfavors *endo*-C–H bonds (c) and *exo*-C–H bonds (d). Therefore the π orbital of the olefin should interact exclusively with the vicinal C–C σ orbitals in the bicyclo[2.2.2]octene system **2** (see Fig. 1). This is because the vicinal σ_{C-C} orbitals are aligned to



1a **2a**

Fig. 1. Orbital Pictures of the HOMOs of the Two Bicyclic Systems **1a** and **2a**

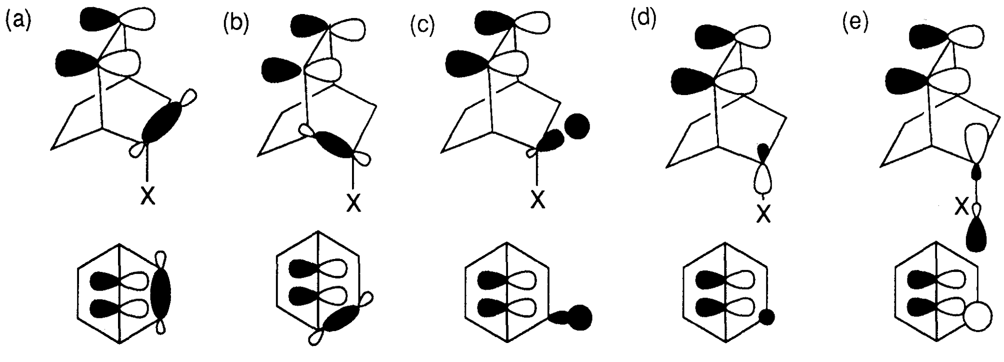


Fig. 2. σ-Components of Bicyclo[2.2.2.]octenes

(a) Parallel σ_{C-C}, (b) vicinal σ_{C-C}, (c) *exo* σ_{C-H} (σ_{C-X}), (d) *endo* σ_{C-H} (σ_{C-X}), (e) *exo* σ^*_{C-X}.

overlap distinctly with the π orbital of the olefin in a π-type fashion. The orbital pictures of CHA were obtained on the basis of HF/6-31G* optimized geometry (C_s).[23] Owing to the maximum degree of the out-of-phase motif in higher-lying σ orbitals of CHA (Fig. 3), the π orbital of the ethylene bridge cannot interact with the HOMO (the 24th orbital, an out-of-phase combination of vicinal σ orbitals) of the CHA because of the orbital symmetry disagreement, as pointed out by Hoffmann *et al.*[24]: the π orbital is intrinsically antisymmetric in phase with respect to the π plane and symmetric on either side of the π plane. The orbitals from the 23rd to the 19th of CHA are non-interacting: the 23rd and 19th occupied orbitals of CHA correspond to the parallel C–C bonds, and the 22nd to the 20th orbitals involve *exo*-C–H σ orbitals. Instead, a set of four vicinal σ_{C-C} orbitals, the next highest vicinal σ orbitals (the 18th occupied orbital of CHA), can interact with the π orbital of the olefin in an antibonding manner to constitute the perturbed HOMO of the bicyclo[2.2.2]-octenes (Figs. 2 (a) and 4(a)). Thus the orbital is selected by symmetry, not by the order of the energy level.[12,13] There is no indication of significant orbital rehybridization of the olefinic carbon atoms, *i.e.* 2p(C)–2p(C) or 2s(C)–2p(C) mixing, which seems to be operative in some cases.[25]

In 7-methylidenenorborane (**1a**) the HOMO is also assumed to be built from the same components, CHA and the ethylene, but in a different arrangement (Fig. 1). Symmetry allows a similar σ–π coupling (Figs. 1 and 4 (e) for **1a**).

π Orbital Unsymmetrization Arising from σ–π Coupling A substituent modifies the orbital energy level of the vicinal bonds. An electron-withdrawing group lowers the energy of the vicinal σ orbital significantly. In order to evaluate energetic changes on substitution, we calculated molecular orbitals of substituted ethanes (C_2H_5X) using HF/3-21G[23] and HF/6-31G* basis sets.[26] In ethane (C_2H_6) itself the gauche (D_{3d}) and eclipsed (C_{2v}) forms both involve a σ_{C-C} orbital of a similar energy.[27] Changing the substituent from a cyano to a methoxy-carbonyl, carboxylic acid, hydroxymethyl or methyl group causes the energy of the σ_{C-C} orbital of the substituted ethane to rise, in the case of the hydroxymethyl group to an energy level comparable to that of the σ_{C-C} orbital of the parent ethane (Fig. 5). A higher-lying occupied orbital can be a better electron-donor in the framework of the frontier orbital theory.[28] Thus, substitution of an electron-withdrawing group at the C_5 position of **2** decreases the contribution of the vicinal σ_{C-C} orbital (C_4–C_5 bond) to the HOMO of the whole

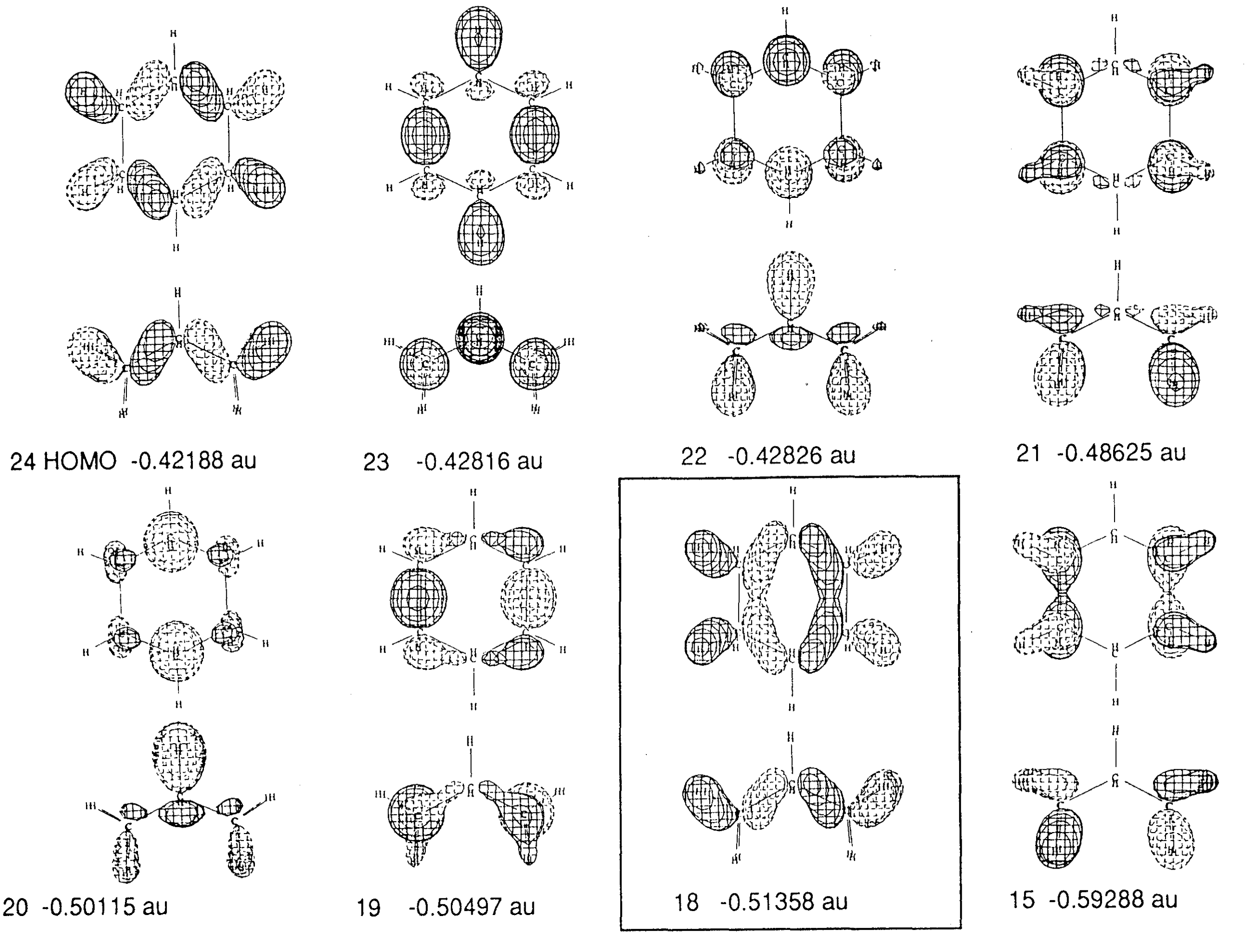


Fig. 3. Orbital Pictures of Occupied σ Orbitals of CHX Based on the HF/6-31G* Optimized Geometries

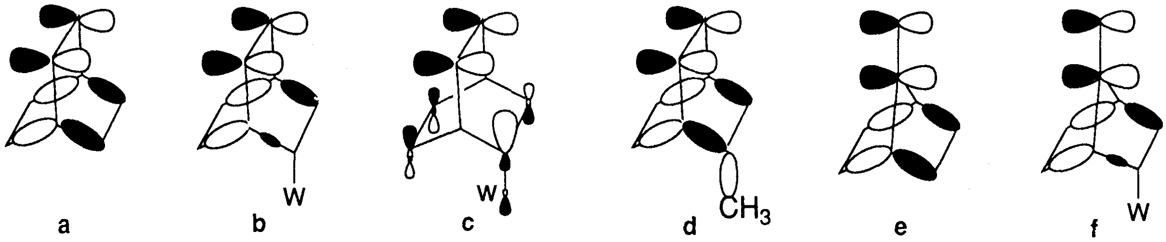


Fig. 4. Principle Orbital Interactions (W = an Electron-Withdrawing Group)

bicyclo[2.2.2]octene molecule (Fig. 4 (b)). Therefore, antibonding nature is weakened on the side of the substituent: the antibonding orbital on the side of the substituent is less diffused.[29] σ-Type reagents having an early transition state[30] (such as *m*CPBA (the σ^*_{O-O} orbital)[17] and OsO_4 (the vacant diffused $3d_z$ orbital)[18] favor attack on the side of the less diffused antibonding region.[13,19,20] Therefore the *syn* addition is favored. A similar orbital interaction diagram is also valid in the case of 5-substituted 7-methylidenenorbornane **1** (Fig. 4 (f)). The outcome of orbital unsymmetrization by the unsymmetrical σ–π coupling coincides with the result anticipated by using Cieplak's transition-state stability postulation (attack opposite a better vicinal σ-donor) (Fig. 6 (a)).[12]

We could also confirm different amplitudes of σ–π coupling in model compound **2j** ($R_1 = R_2 = CN$) in the HF/6-31G* optimized geometry. The responsible orbital, as is suggested by the above discussion, consists of the bridged olefin and the 18th orbital of CHA. The HOMO orbital is composed by mixing of C_2 and C_6 and C_7 (and C_3 and C_5 and C_8) *p*-orbitals. The HOMO (Φ_{HOMO}) of **2j** is expressed as

$$\begin{aligned}\Phi_{HOMO} = {} & [0.3564\phi_{2p}(C_2) + 0.3008\phi_{3p}(C_2)] + [0.0965\phi_{2p'}(C_6) \\ & + 0.0399\phi_{3p'}(C_6)] + [0.0987\phi_{2p''}(C_7) + 0.0484\rho_{3p''}(C_7)] \\ & + (C_3 \text{ component}) + (C_5 \text{ component}) + (C_8 \text{ component}) \quad (1)\end{aligned}$$

wherein $\phi_{2p}(C_2)$ is the π orbital of the olefinic carbon atom (C_2) and ϕ_{3p} (C_2) is the corresponding diffusion function component, $\phi_{2p'}$ (C6) and $\phi_{3p'}$ (C6) represent σ components of the C6 carbon atom comprising the C_6C_1 bond orbital, and $\phi_{2p''}$ (C7) and $\phi_{3p''}$ (C7) are σ components of the C7 carbon atom comprising the C_7C_1 bond orbital. Equation 1 indicates that the cyano substituent decreases the amplitude of the σ component of the C_6 atom carrying the substituent. The conclusion from the analysis of the wavefunction was the same as

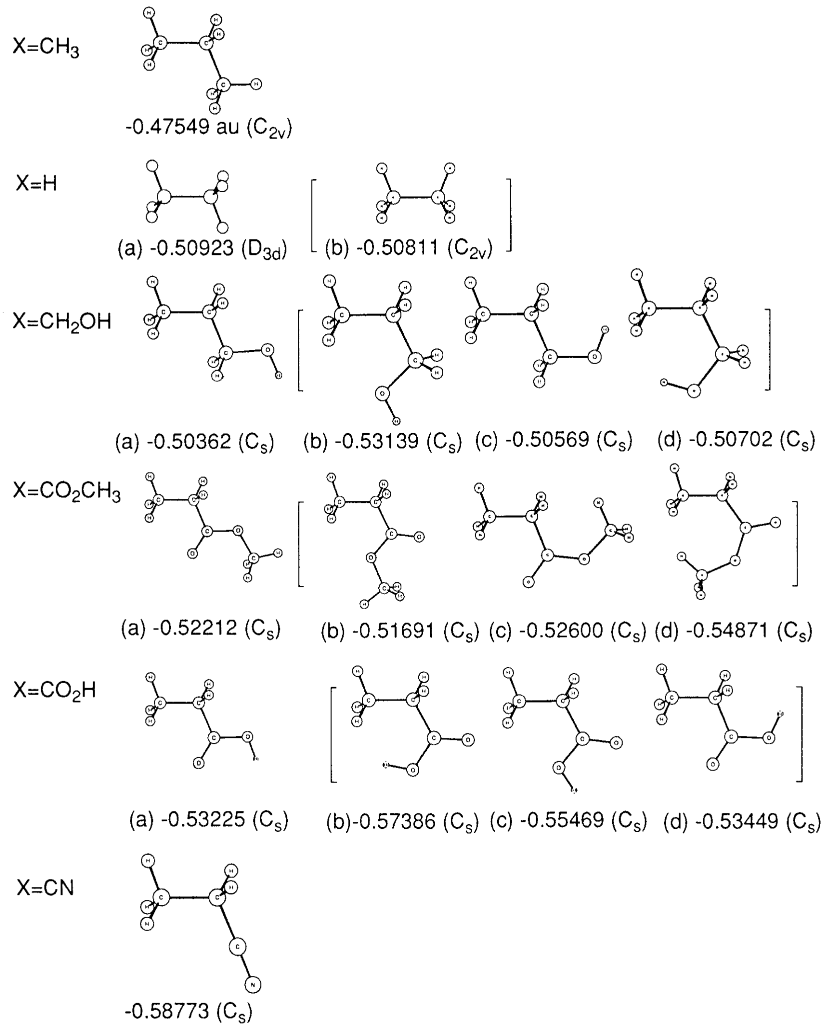


Fig. 5. Occupied σ_{C-C} Orbitals of Substituted Ethanes (C_2H_5X) at HF/6-31G* Basis Sets (Minimum Structures and Other Possible Conformations in Brackets)

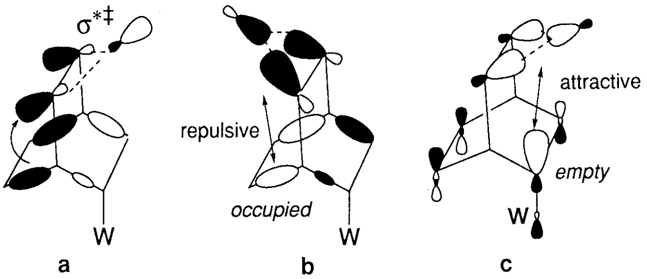


Fig. 6. Principle Interactions in Alternative Rationalization

that derived from the simple (and rather intuitive) perturbation model of the fragment orbitals described. A quantitative estimation of the orbital unsymmetrization along this line is in progress.

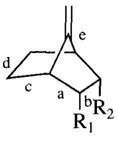
The energy level of σ_{C-C} orbitals of substituted ethanes (C_2H_5X) are apparently dependent on the conformation (Fig. 5).[27] This may be reflected in fluctuation in the magnitude of the observed bias of **2c**—**g**, depending on the reaction, reagent, solvent and temperature. This idea was based on the constant biases observed in the cases of the cyano and methyl groups, which are rigid rotors. Of course, a different reaction has a different transition state, so there exists a divergent substituent effect. However, the above possibility is worthy of consideration because the influence of conformational variations on the energy of the transition structures has already been computed in the cases of cyclohexanone[11a] and norbornane derivatives.[11b]

Additional σ^*–π Coupling Substitution of an electron-withdrawing group (W) makes the relevant carbon atom (C–W) more electronegative which leads to a situation where the σ bonding orbitals are weighted more heavily on the atom W and the σ antibonding orbitals are weighted more heavily on the relevant carbon atoms.[31] The π orbital of the olefin in **2b**—**e** can interact efficiently with the *exo*-σ^*C–W orbital in an in-phase manner (Fig. 2 (e)), which provides a more extended bonding region on the side of the substituent in the cases of electron-withdrawing substituents (Fig. 4 (c)). This reinforces the *syn*-preference.[32]

Comparison of Norbornane Systems Owing to the energetic perturbation arising from the methyl substituent on the substituted ethane (Fig. 5), the contribution of the vicinal orbital bearing the methyl group will be increased in the σ–π coupling, and therefore *anti*-preference should exist. This is indeed observed in 7-methylidenenorbornane (2-ethyl-7-methylidenenorbornane), but no definite bias was detected in the case of bicyclo[2.2.2]octene **2h**. In spite of the energetically perturbing effect of the methyl group, evaluation of the orbital interaction may be exaggerated due to the neglect of the effect of overlap: because of the equal contribution of the two σ_{C-C} orbitals in the model propane (Figs. 4(d) and 5), the coefficient of each σ_{C-C} orbital in the real bicyclic systems is decreased to compensate for the energetic effect.[33)]

In order to shed light on the different behavior of the two bicycles (bicyclo[2.2.2]octenes and 7-methylidenenorbornanes), Bader topological one-electron density analysis[34)] was performed on the HF/6-31G* optimized geometries (Table 2) (see Computational Methods). Due to symmetrical benefit and the anticipated similar substituent effects, we calculated the molecules bearing two substituents (**1a**, **c**, **1** and **2a**, **j**, **k**), imposing C_s symmetry. The parent bicyclo[2.2.2]octene (**2a**) is a cage structure, characterized by the presence of three ring critical points on each convex 6-membered ring and also containing a cage critical point. Methylenenorbornane (**1a**) is an open structure with two curved five-membered ring surfaces with one common carbon (C_7). Therefore the two bicyclic systems have different electron networks as pointed by Wiberg *et al.*[35)] One-electron densities (ρ) at the bond critical points indicated that the methyl substituent did not increase the electron density of the vicinal bond (bond a, C_1–C_2 and C_1–C_6, Table 2), but rather decreased it as compared with the vicinal bond (bond c, C_4–C_8 and C_4–C_5) opposite to the methyl group. Unexpectedly, this was the case for both 5,6-*exo*,*exo*-dimethylbicyclo[2.2.2]octene **2k** and 2,3-*exo*,*exo*-dimethyl-7-methylidenenorbornane **1d** in the present calculations. On the other hand an electron-withdrawing group such as a cyano group decreases the electron-density of the adjacent vicinal bond. Wiberg *et al.* also defined the strain energy of the bicyclic molecules in terms of the Bader charge[34)] of the bridgehead carbon atoms[35)]: as strain (or strain energy) is increased on going from the bicyclo[2.2.2]octene system to the norbornane system, the bridgehead carbon atoms increase in both electronegativity and stability.[36)] Therefore, a charge flow from the peripheral methylene groups to the bridgehead carbons in the norbornanes **1** is encouraged. Thus, the electron-donation of the methyl group is enhanced to refill the electron-deficiency of the peripheral methylene group in the norbornanes (**1**). This electron shift is supported by slightly smaller values of ρ and $\nabla^2\rho$ and ellipticity (ε) of the C_2–CH_3 (C_3–CH_3) bonds in the dimethylnorbornane (**1d**) as compared with those of dimethylbicy-

Table 2. HF/6-31G* Critical Point Data of Methylidenenorbornanes and Bicyclo[2.2.2]octenes[a)]



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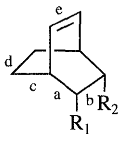

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Substrate	Bond	ε	ρ	$\nabla^2\rho$
1a	a	0.010	0.250	−0.641
	b	0.011	0.241	−0.603
	c	0.010	0.250	−0.641
	d	0.011	0.241	−0.603
	e	0.480	0.361	−1.173
1c	a	0.009	0.245	−0.619
	b	0.049	0.233	−0.563
	c	0.009	0.251	−0.643
	d	0.011	0.242	−0.607
	e	0.479	0.362	−1.180
	C–CN	0.020	0.270	−0.836
1d	a	0.007	0.246	−0.617
	b	0.024	0.233	−0.564
	c	0.012	0.247	−0.622
	d	0.010	0.236	−0.578
	e	0.481	0.364	−1.194
	C–CH_3	0.005	0.251	−0.653
2a	a	0.007	0.249	−0.635
	b	0.004	0.246	−0.626
	c	0.007	0.249	−0.635
	d	0.004	0.246	−0.626
	e	0.455	0.364	−1.179
2j	a	0.019	0.243	−0.612
	b	0.044	0.237	−0.584
	c	0.005	0.249	−0.638
	d	0.007	0.246	−0.630
	e	0.457	0.365	−1.186
	C–CN	0.024	0.268	−0.824
2k	a	0.014	0.247	−0.625
	b	0.018	0.239	−0.593
	c	0.008	0.248	−0.633
	d	0.004	0.246	−0.629
	e	0.458	0.364	−1.182
	C–CH_3	0.007	0.252	−0.657

a) ρ values are in $e/\text{Å}^3$. $\nabla^2\rho$ values are in $e/\text{Å}^5$.

Table 3. HF/6-31G* Mulliken Charges of Methylenenorbornanes and Bicyclo[2.2.2]octenes

Structure	Atom	Charge
1a	1	−0.033
	2	0.020
	5	0.020
	7	0.131
	8	−0.143
1c	1	0.012
	2	0.041
	5	0.062
	7	0.103
	8	−0.088
	C	0.325
	N	−0.448
1d	1	−0.027
	2	0.019
	5	0.018
	7	0.126
	8	−0.147
	CH_3	0.001
2a	1	−0.049
	2	0.009
	5	0.020
	7	0.020
2j	1	−0.015
	2	0.036
	5	0.047
	7	0.063
	C	0.318
	N	−0.449
2k	1	−0.046
	2	0.009
	5	0.022
	7	0.019
	CH_3	0.020

Table 4. ^{13}C-NMR Chemical Shifts of Monosubstituted Bicyclo[2.2.2]octenes

Structure	Atom	ppm
2b	1	27.1
	2	32.3
	3	135.3
	4	28.60
	5	31.9
	6	30.5
	7	20.8
	8	24.8
	CN	123.2
2c	1	29.2
	2	133.7
	3	135.1
	4	32.4
	5	42.5
	6	28.2
	7	21.1
	8	25.0
	CO	175.8
	CH_3	51.6
2d	1	29.4
	2	133.7
	3	135.5
	4	33.8
	5	45.2
	6	28.0
	7	20.7
	8	25.2
	CO	173.0
	C_o	119.6
	C_m	129.0
	C_p	124.0
	C_{ipso}	138.2
2e	1	29.2
	2	133.7
	3	135.2
	4	32.3
	5	42.6
	6	28.0
	7	21.0
	8	25.0
	CO	182.0
2f	1	29.6
	2	135.8
	3	134.0
	4	30.5
	5	36.1
	6	30.3
	7	19.4
	8	25.9
	CH_2	58.7
	CH_3	19.4
2g	1	29.2
	2	134.3
	3	135.0
	4	29.8
	5	35.4
	6	29.3
	7	18.8
	8	25.5
	C_{ipso}	144.7
	C_{ipso}	133.1
	C_o	129.8
	C_m	127.9
	CH_2	72.9
	CH_3	21.6
2h	1	30.3
	2	133.1
	3	136.6
	4	30.6
	5	35.6
	6	34.8
	7	18.8
	8	26.3
	CH_3	20.5

clo[2.2.2]octene (**2k**). Even in terms of Mulliken charges[37] (based on the HF/6-31G* optimized geometries) (see Table 3), while in the bicyclo[2.2.2]octene system, the carbon atoms (C_5 and C_6) bearing the methyl groups (**2k**) tend to obtain a slightly more positive charge as compared with the parent bicyclo[2.2.2]octene (**2a**) (*vide ante*), the C_2 (C_3) carbon atom shows lower positive charge on substitution of the methyl groups in the methylenenorbornane system (**1d**), indicating electron-donation of the methyl groups of **1d**.

Alternative Hypothesis As reasonably suggested by the computed Mulliken charges (Table 3), an electron-withdrawing group such as a cyano group (**2j**) creates positive charge at the C_5 (C_6) position and also on the olefinic C_2 (C_3) position of the bicyclo[2.2.2]octene systems. We also used ^{13}C-NMR chemical shifts of the olefinic and the bridge carbons (C_5) as a probe to examine the charge distribution in the real monosubstituted bicyclo[2.2.2]octenes **2c**—**h** (Table 4).[38] As jugded from the ^{13}C-NMR chemical shifts, the C_5 (the substituted carbon) of the carboxylic acid derivatives, the ester (**2c**), amide (**2d**) and acid (**2e**), are apparently deshielded compared to those of the methoxymethyl (**2f**), tosylate (**2g**) and methyl (**2h**) derivatives. The shielding effect of the cyano group (though it is a strong electron-withdrawer) might suggest π-donating nature of the cyano group.[39] Thus, there is no obvious relation between the ^{13}C-deshielding of the attached carbon (C_5) and the magnitude of facial bias; rather the bias is apparently correlated with the Hammet σ (σ^*) values (the larger the positive value of σ, the larger the bias).[40] Although we could not reach a conclusion as to the role of electrostatic interactions between the positively charged C_5 and the reagents, the lack of a perturbing effect of the methyl group in the bicyclo[2.2.2]octene system (**2h**) superficially seems to be related (at least partially) to inefficient charge accumulation at the C_5 position.

Conclusion

We highlighted the common σ–π orbital interactions involved in two bicyclic systems, 7-methylidenenorbornanes **1** and bicyclo[2.2.2]octenes **2**. Of significance is the out-of-phase motif of these σ–π couplings. Generally, electrophilic reactions of an olefin involve in-phase interaction of the HOMO of the olefin and the LUMO of the electrophile. Therefore, reactions of the two bicyclic systems **1** and **2** intrinsically involve orbital-phase-disfavored HOMO–LUMO interactions which are relieved by the trajectory and larger amplitude of the π component in the HOMOs of **1** and **2**. Electron-withdrawing groups such as cyano or carboxylic acid shrink the unfavorable antibonding σ component, resulting in the observed *syn*-preference. This scheme can be also applied to the *syn* preference of 5-fluoro-2-methylideneandmantane.[2] From the viewpoint of electron-density, the weak σ–π coupling implies the relief of electron repulsions through attack of the reagent, which agrees with the interpretation in terms of the Felkin model (Fig. 6 (b)).[41,42] The σ–π coupling is strengthened by bonding σ^*–π coupling in the case of an electron-withdrawing substituent. This interaction may coincide with the electron flow of the attacking reagent to the peripheral acceptor, proposed by Ahn (Fig. 6 (c)).[41,43]

Experimental

General Methods All the melting points were measured with a Yanagimoto hot-stage melting point apparatus (MP-500) and are uncorrected. Proton (400 MHz) and carbon (100 MHz) NMR spectra were measured on a JEOL GX-400 NMR spectrometer with tetramethylsilane (^{1}H) and the middle peak of $CDCl_3$ (77.0 ppm, ^{13}C) as an internal references in $CDCl_3$ as the solvent unless otherwise specified. High-performance liquid chromatography (HPLC) was run on a Shimadzu LC-6AD system on silica gel SIL S-5 (G-040-5 and S-5, YMC, Japan) packing (50 mm × 20 cm) with ethyl acetate and *n*-hexane as the eluents. Column chromatography was performed on silica gel (Kieselgel 60, 70—230 mesh, Merck) with the specified solvent. The combustion analyses were carried out in the microanalytical laboratory of this Faculty. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-SX102 spectrometer.

Preparation of 5-Substituted Bicyclo[2.2.2]octenes. 5-*exo*-Cyanobicyclo[2.2.2]oct-2-ene (2b) Cycloaddition of 1,3-cyclohexadiene (5.1 g) with acrylonitrile (5.0 g, 1.5 eq) was performed in a sealed tube at 150 °C for 18 h. The residue after the removal of unchanged starting materials by distillation, was chromatographed with methylene chloride to give a mixture of cycloadducts (4.8 g, 58%) (*exo* : *endo* = 55 : 45). The cycloadducts were separated by column chromatography (ethyl acetate: *n*-hexane = 1 : 20) to give the *endo*-isomer (534 mg) and *exo*-isomer **2b** (184 mg).

2b: Colorless plates, mp 51.5—52.0 °C (molecular distillation: 31 °C/3.0 mmHg). ^{1}H-NMR: 6.31 (1H, t, J = 7.1 Hz), 6.24 (1H, t, J = 7.0 Hz), 2.78 (1H, br q), 2.62 (1H, br t), 2.44—2.42 (1H, m), 2.07—2.02 (1H, m), 1.75—1.73 (2H, m), 1.69—1.64 (1H, m), 1.32—1.30 (2H, m). ^{13}C-NMR: 135.3, 132.3, 123.1, 34.0, 31.9, 30.5, 28.6, 27.1, 24.8, 20.8. HRMS: Calcd for $C_9H_{11}N$: 133.0891. Found: 133.0875. *endo*-Isomer of **2b**: ^{1}H-NMR: 6.46 (1H, t, J = 7.3 Hz), 6.31 (1H, t, J = 7.0 Hz), 2.88 (1H, br q), 2.72 (1H, dq, J = 10.1, 2.2 Hz), 2.65 (1H, br t), 1.96 (1H, ddd, J = 21.0, 10.3, 2.5 Hz), 1.55—1.44 (3H, m), 1.37—1.26 (2H, m).

Bicyclo[2.2.2]oct-2-ene-5-*exo*-carboxylic Acid (2e) Bicyclo[2.2.2]-oct-5-ene-2-*exo*-carboxylic acid **2e** was prepared by the cycloaddition reaction of 1,3-cyclohexadiene and methyl acrylate (sealed tube, 180 °C, 14 h), followed by hydrolysis, and *exo*-**2e** was separated through iodolactonization of the undesired major *endo* isomer (Chart 1).[44] A mixture of *endo*- and *exo*- (**2c**) cycloadducts of 1,3-cyclohexadiene and methyl acrylate (6.1 g, *endo* : *exo* = 88 : 12) was hydrolyzed with aqueous NaOH in methanol at 60 °C for 2 h to afford the corresponding acids (5.5 g, 98% yield). The acids were subjected to iodolactonization: a solution of the acids (5.1 g) in methylene chloride (35 ml) was treated with aqueous 2 N NaOH, followed by aqueous KI (0.35 g in 10 ml of water). To this mixture, iodine (7.4 g) was added in portions. The whole was treated with aqueous $Na_2S_2O_3$. Extraction with methylene chloride and evaporation of the solvent gave the halo-lactone, 5-*exo*-iodobicyclo[2.2.2]octane-2,6-carbolactone (8.2 g, 94% conversion based on the *endo*-acid adduct). Acidification of the aqueous phase, followed by extraction with methylene chloride gave *exo*-**2e** (564 mg, 87% conversion based on the *exo*-acid adduct) as a white powder.

2e: mp 47.5—48.5 °C (colorless plates, recrystallized from *n*-hexane). ^{1}H-NMR: 12.0—10.2 (1H, br m), 6.32 (2H, dq, J = 5.6, 2.2 Hz), 2.90 (1H, br q), 2.58 (1H, br q), 2.47 (1H, dq, J = 11.5, 2.8 Hz), 1.95 (1H, ddd, J = 7.7, 5.0, 2.2 Hz), 1.73—1.66 (1H, m), 1.63—1.55 (1H, m), 1.53—1.46 (1H, m), 1.30—1.12 (2H, m). ^{13}C-NMR: 182.0, 135.2, 133.7, 42.6, 32.3, 29.2, 28.0, 25.0, 21.0. HRMS: Calcd for $C_9H_{12}O_2$: 152.0837. Found: 152.0808.

5-*exo*-Methoxycarbonylbicyclo[2.2.2]oct-2-ene (2c) Methylation of the corresponding acid **2e** with ethereal diazomethane gave the methyl ester **2c** quantitatively.

2c: Colorless oil, bp 75 °C/2 mmHg. ^{1}H-NMR: 6.35—6.25 (2H, m), 3.70 (3H, s), 2.85—2.80 (1H, m), 2.60—2.55 (1H, m), 2.45—2.35 (1H, m), 2.00—1.90 (1H, m), 1.65—1.55 (2H, m), 1.50—1.45 (1H, m), 1.30—1.11 (2H, m). ^{13}C-NMR: 175.8, 135.1, 133.7, 51.6, 42.5, 32.4, 29.2, 28.2, 25.0, 21.1. HRMS: Calcd for $C_{10}H_{14}O_2$: 166.0994. Found: 166.0979.

Bicyclo[2.2.2]oct-2-en-5-*exo*-carboxanilide (2d) The corresponding acid **2e** was treated with thionyl chloride at 65 °C for 2 h to prepare the acid chloride, which was coupled with aniline in pyridine to give the anilide **2d** in 82 % overall yield.

2d: Colorless plates, mp 132.5—133.5 °C (recrystallized from *n*-hexane–ethyl acetate). ^{1}H-NMR: 7.53 (2H, d, J = 7.7 Hz), 7.31 (2H, t, J = 7.7 Hz), 7.27 (1H, br s), 7.08 (1H, t, J = 7.3 Hz), 6.35—6.33 (2H, m), 2.78—2.75 (1H, m), 2.64—2.58 (1H, m), 2.42—2.36 (1H, m), 2.09—2.03 (1H, m), 1.89—1.80 (1H, m), 1.72—1.65 (1H, m), 1.51—1.42 (1H, m), 1.30—1.21 (1H, m), 1.17—1.08 (1H, m). ^{13}C-NMR: 173.0, 138.2, 135.5, 133.7, 129.0, 124.0, 120.0, 45.2, 33.8, 29.4, 28.0, 25.2, 20.7. *Anal.* Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 78.98; H, 7.52; N, 6.15.

5-*exo*-Hydroxymethylbicyclo[2.2.2]oct-2-ene Reduction of the acid **2e** to the corresponding hydroxymethyl compound was carried out in ether with lithium aluminum hydride (LAH) (reflux, 24 h).

Colorless oil, bp 80 °C/1.5 mmHg. ^{1}H-NMR: 6.38 (1H, t, J = 7.3 Hz), 6.35 (1H, t, J = 7.3 Hz), 3.69 (1H, dd, J = 10.6, 6.6 Hz), 3.54 (1H, dd, J = 10.1, 9.2 Hz), 2.53 (1H, br q), 2.47 (1H, br q), 1.72—1.63 (2H, m), 1.54—1.46 (1H, m), 1.44—1.37 (2H, m), 1.29—1.20 (1H, m), 1.15—1.06 (1H, m), 0.87 (ddd, 1H, J = 12.5, 5.5, 2.2 Hz). ^{13}C-NMR: 135.6,134.2, 66.1, 38.9, 30.0, 29.5, 25.8, 19.2. HRMS: Calcd for C9H14O: 138.1045. Found: 138.1061.

5-*exo*-*p*-Toluenesulfonylbicyclo[2.2.2]oct-2-ene (2g) The tosylate (**2g**) of the above hydroxymethyl derivative was prepared as usual with TsCl in pyridine at 0 °C to the ambient temperature.

2g: Colorless cubes, mp 38.5—39.0 °C (recrystallized from *n*-hexane–ethyl acetate). ^{1}H-NMR ($CDCl_3$): 7.80 (1H, d, J = 8.4 Hz), 7.35 (1H, t, J = 7.6 Hz), 6.30 (1H, t, J = 7.4 Hz), 6.24 (1H, t, J = 6.7 Hz), 4.04 (1H, dd, J = 9.5, 6.6 Hz), 3.91 (dd, 1H, J = 10.1, 8.5 Hz), 2.46 (5H, br s), 1.86—1.77 (1H, m), 1.51—1.41 (2H, m), 1.36—1.28 (1H, m), 1.24—1.16 (1H, m), 1.09—1.00 (1H, m), 0.79 (1H, ddd, J = 12.8, 5.5, 2.2 Hz). ^{13}C-NMR ($CDCl_3$): 144.7, 135.0, 134.3, 133.1, 129.8, 127.9, 72.9, 35.4, 29.8, 29.3, 29.2, 25.5, 21.6, 18.8. HRMS: Calcd for $C_{16}H_{20}O_3S$: 292.1133. Found: 292.1134.

5-*exo*-Methoxymethylbicyclo[2.2.2]oct-2-ene (2f) Methylation of the precursor alcohol was performed with an excess amount of methyl iodide in the presence of NaH in *N*,*N*-dimethylformamide (DMF) at ambient temperature. The residue after removal of the solvent by distillation was flash-chromatographed (ethyl acetate : *n*-hexane = 1 : 40).

2f: Colorless oil. ^{1}H-NMR ($CDCl_3$): 6.38 (1H, t, J = 7.4 Hz), 6.23 (1H, t, J = 7.4 Hz), 3.37 (1H, m) 3.35 (3H, s, CH_3), 3.33 (1H, m), 2.51—2.42 (2H, m), 1.80—1.63 (2H, m), 1.51—1.36 (2H, m), 1.27—1.19 (1H, m),

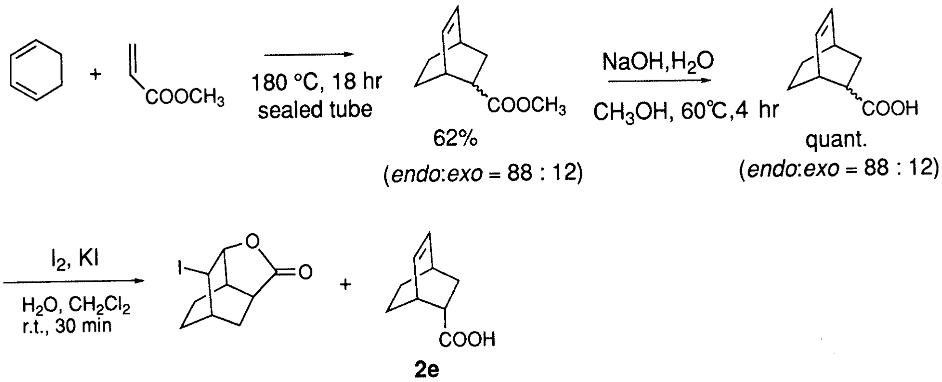

Chart 1

1.14—1.06 (1H, m), 0.91—0.84 (1H, m). HRMS: Calcd for $C_{16}H_{20}O_3S$: 292.1133. Found: 292.1134.

5-*exo*-Methylbicyclo[2.2.2]oct-2-ene (2h) The tosylate **2g** was treated with LAH (2.2 eq) in ether at 0 °C and then the mixture was heated at reflux for 24 h. The crude product was purified by bulb-to-bulb distillation at atmospheric pressure.

2h: Colorless oil, bp 105 °C/760 mmHg. ^{1}H-NMR ($CDCl_3$): 6.38 (1H, t, J=7.0 Hz), 6.18 (1H, t, J=7.0 Hz), 2.41 (1H, br q), 2.14 (1H, br q), 1.82—1.73 (1H, m), 1.60—1.50 (2H, m), 1.48—1.40 (1H, m), 1.26—1.16 (1H, m), 1.10—1.00 (1H, m), 1.01 (3H, d, J=6.6 Hz), 0.90—0.81 (1H, m). ^{13}C-NMR ($CDCl_3$): 136.6, 133.1, 35.6, 34.8, 30.6, 30.3, 26.3, 20.5, 18.8. HRMS: Calcd for C_9H_{14}: 122.1095. Found: 122.1090.

General Procedure of Epoxidation of the 5-Substituted Bicyclo[2.2.2]-octenes A solution of the olefin **2** (0.4 mmol) in 2 ml of chloroform was treated with *m*CPBA (200 mg, 2 eq) at 0 °C. Stirring was continued for specified time, then an aqueous solution of Na_2HSO_3 (300 mg in 5 ml of water) was added. The whole was stirred for one night, then extracted with methylene chloride, and the organic phase was washed with saturated aqueous sodium bicarbonate and water, and dried over $MgSO_4$, followed by evaporation of the solvent. The residue was chromatographed to obtain a mixture of stereoisomers of the epoxide. The ratios of the diasteromeric epoxides were determined by integration of the proton signals in the ^{1}H-NMR spectra. Separation of the diasteromers was achieved by repeated flash-column chromatography or by HPLC with a specified eluent. Configurations of the epoxide moieties were elucidated on the basis of the characteristic deshielding of the *endo*-H5 and *endo*-H6 protons (in the case of the *syn*-epoxides) or *endo*-H7 and *endo*-H8 protons (in the case of the *anti*-epoxides) and shielding of *exo*-H6 proton (in the case of the *syn*-epoxides) or *exo*-H7 and *exo*-H8 protons (in the case of the *anti*-epoxides) owing to the anisotropic effect of the epoxide ring.[20,45] The assignments of the ^{1}H-NMR signals of the starting materials **2b**—**h** were based on INDOR (internuclear double resonance) measurements.

Epoxidation of 5-*exo*-Cyanobicyclo[2.2.2]oct-2-ene (2b) A crude mixture of the epoxides was obtained by column chromatography (ethyl acetate : *n*-hexane = 1 : 2). Diastereomers were isolated by column chromatography (ethyl acetate : *n*-hexane = 1 : 3).

4b-*syn*: Colorless oil. ^{1}H-NMR ($CDCl_3$): 3.30 (1H, t, J=4.8 Hz), 3.24 (1H, t, J=4.8 Hz), 2.98—2.93 (1H, m), 2.42—2.39 (1H, m), 2.24—2.20 (1H, m), 2.14—2.03 (2H,m), 1.73—1.58 (3H, m), 1.47 (1H, dq, J=3.0, 15.8 Hz). HRMS: Calcd for $C_9H_{11}NO$: 149.0841. Found: 149.0833.

4b-*anti*: Colorless oil. ^{1}H-NMR ($CDCl_3$): 3.26—3.21 (2H, m), 2.78—2.75 (1H, m), 2.48—2.43 (1H, m), 2.25—2.21 (1H, m), 2.10—2.02 (1H, m), 1.87 (1H, dq, J=4.8, 15.6 Hz), 1.81—1.65 (3H, m), 1.40—1.28 (1H, m). HRMS: Calcd for $C_9H_{11}NO$: 149.0841. Found: 149.0812.

Epoxidation of 5-*exo*-Methoxycarbonylbicyclo[2.2.2]oct-2-ene (2c) A crude mixture of the epoxides was obtained by column chromatography (ethyl acetate : *n*-hexane = 1 : 8). Diastereomers were isolated by column chromatography (ethyl acetate : *n*-hexane = 1 : 4).

4c-*syn*: Colorless oil. ^{1}H-NMR ($CDCl_3$): 3.67 (3H, s), 3.29 (1H, t, J=4.8 Hz), 3.21 (1H, t, J=4.8 Hz), 2.84—2.78 (1H, m), 2.52—2.48 (1H, m), 2.21—2.17 (1H, m), 1.79—1.74 (2H, m), 1.62—1.39 (4H, m). HRMS: Calcd for $C_9H_{11}NO$: 182.0943. Found: 182.0962.

4c-*anti*: Colorless oil. ^{1}H-NMR ($CDCl_3$): 3.82 (3H, s), 3.32 (1H, t, J=4.8 Hz), 3.24 (1H, t, J=4.8 Hz), 2.70—2.64 (1H, m), 2.51—2.47 (1H, m), 2.19—2.10 (2H, m), 1.89—1.51 (3H, m), 1.29—1.19 (1H, m). HRMS: Calcd for $C_9H_{11}NO$: 182.0943. Found: 182.0937.

Epoxidation of Bicyclo[2.2.2]oct-5-en-2-*exo*-carboxanilide (2d) A crude mixture of the epoxides was obtained by column chromatography (ethyl acetate : *n*-hexane = 1 : 2). Diastereomers were isolated by column chromatography (ethyl acetate : *n*-hexane = 1 : 4).

4d-*syn*: Colorless needles, mp 191—192 °C (recrystallized from diethyl ether). ^{1}H-NMR ($CDCl_3$): 7.50 (2H, d, J=7.7 Hz), 7.30 (3H, t, J=8.5 Hz), 7.08 (1H, t, J=7.3 Hz), 3.35 (1H, t, J=4.8 Hz), 3.29 (1H, t, J=4.8 Hz), 2.82—2.77 (1H, m), 2.44—2.42 (1H, m), 2.29—2.25 (1H, m), 1.90—1.83 (2H, m), 1.79—1.67 (2H, m), 1.59—1.51 (1H, m), 1.46—1.39 (1H, m). *Anal.* Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.83; H, 6.98; N, 5.61.

4d-*anti*: White powder, mp 137.0—137.5 °C (recrystallized from *n*-hexane–ethyl acetate). ^{1}H-NMR ($CDCl_3$): 7.50 (2H, d, J=7.7 Hz), 7.30 (3H, t, J=8.5 Hz), 7.08 (1H, t, J=7.3 Hz), 3.35 (1H, t, J=4.8 Hz), 3.29 (1H, t, J=4.8 Hz), 2.82—2.77 (1H, m), 2.44—2.42 (1H, m), 2.29—2.25 (1H, m), 1.90—1.83 (2H, m), 1.79—1.67 (2H, m), 1.59—1.51 (1H, m), 1.46—1.39 (1H, m). *Anal.* Calcd for $C_{15}H_{17}NO_2 \cdot 1/5H_2O$: C, 72.97; H, 7.10; N, 5.67. Found: C, 73.05; H, 7.08; N, 5.65.

Epoxidation of Bicyclo[2.2.2]oct-2-ene-5-*exo*-carboxylic Acid (2e) A crude mixture of the solid epoxides (**4e**-*syn* and **4e**-*anti*) was methylated with ethereal diazomethane, and the diastereomers were isolated by column chromatography as described above to give esters identical to authentic **4c**-*syn* and **4c**-*anti*.

Epoxidation of 5-*exo*-Methoxymethylbicyclo[2.2.2]oct-2-ene (2f) A crude mixture of the epoxides was obtained by column chromatography (ethyl acetate : *n*-hexane = 1 : 4). No adequate solvent for separating the mixture of diasteromers could be found. The mixture of the epoxides (**4f**-*syn and* **4f**-*anti*) gave satisfactory spectra and HRMS value: HRMS: Calcd for $C_{10}H_{16}O_2$: 168.1151. Found: 168.1137. **4f**-*syn*: ^{1}H-NMR: 3.31 (s 3H, OCH_3), 3.30—3.14 (4H, m), 2.19 (1H, m), 2.10 (1H, m), 2.02 (1H, m), 1.79 (1H, m), 1.70 (1H, m), 1.56 (1H, m), 1.47—1.37 (1H, m), 1.35 (1H, m), 1.07—1.01 (1H, m). **4f**-*anti*: ^{1}H-NMR: 3.38 (2H, m), 3.31 (3H, s, OCH3), 3.30—3.20 (2H, m), 2.19 (1H, m), 2.10 (1H, m), 1.79 (1H, m), 1.70 (1H, m), 1.56 (1H, m), 1.55—1.50 (1H, m), 1.47—1.37 (1H, m), 1.16—1.07 (1H, m), 0.67—0.63 (1H, m).

Epoxidation of 5-*exo*-*p*-Toluenesulfonylbicyclo[2.2.2]oct-2-ene (2g) A crude mixture of the epoxides was obtained by column chromatography (ethyl acetate : *n*-hexane = 1 : 4). Diastereomers were isolated by HPLC (ethyl acetate : *n*-hexane = 1 : 4).

4g-*syn*: Colorless oil. ^{1}H-NMR: 7.78 (2H, d, J=8.0 Hz), 7.34 (2H, t, J=8.0 Hz), 3.87—3.78 (2H, m), 3.25 (1H, t, J=5.1 Hz), 3.19 (1H, t, J=4.0 Hz), 2.46 (3H, s), 2.28—2.17 (2H, m), 2.11—2.07 (1H, m), 1.81—1.70 (1H, m), 1.60—1.48 (2H, m), 1.40—1.30 (2H, m), 0.62—0.57 (1H, m). HRMS: Calcd for $C_9H_{11}NO$: 308.1082. Found: 308.1069.

4g-*anti*: Colorless oil. ^{1}H-NMR: 7.79 (2H, d, J=8.4 Hz), 7.35 (2H, t, J=8.0 Hz), 4.07 (1H, dd, J=10.5, 7.5 Hz), 3.94 (1H, t, J=9.5 Hz), 3.22—3.18 (2H, m), 2.46 (3H, s), 2.16—2.07 (3H, m), 1.82—1.74 (1H, m), 1.69—1.59 (1H, m), 1.54—1.45 (1H, m), 1.17—1.08 (1H, m), 1.06—0.95 (2H, m). HRMS: Calcd for $C_9H_{11}NO$: 308.1082. Found: 308.1083.

Epoxidation of 5-*exo*-Methylbicyclo[2.2.2]oct-2-ene (2h) No adequate solvent for separating the mixture of diastereomeric epoxides could be found. The mixture of the epoxides (**4h**-*syn* and **4h**-*anti*) gave satisfactory spectra and HRMS value. HRMS: Calcd for $C_9H_{14}O$: 138.1045. Found: 138.1035. **4h**-*syn*: ^{1}H-NMR: 3.261 (2H, dd, J=4.76, 4.76 Hz), 2.050—1.150 (8H, m), 0.887 (3H, d, J=6.96 Hz), 0.6781 (1H, ddd, J=2.93, 3.29, 12.45 Hz). **4h**-*anti*: ^{1}H-NMR: 3.201 (2H, dd, J=4.76, 4.76 Hz), 2.050—1.150 (8H, m), 1.049 (3H, d, J=6.6 Hz), 1.017 (1H, dd, J=8.06, 2.20 Hz).

General Procedure of Dihydroxylation of 5-Substituted Bicyclo[2.2.2]-octenes A solution of the olefin **2** (0.4 mmol) in 1 ml of pyridine was added in portions to a solution of osmium tetroxide (123 mg, 1.2 eq) in 1.5 ml of pyridine, at −23 °C (dry ice-acetonitrile). The mixture was stirred for a specified time, then an aqueous solution of $NaHSO_3$ (300 mg in 5 ml of water) was added. The whole was stirred for one night, then extracted with methylene chloride, and the organic layer was washed with diluted hydrochloric acid and water, and dried over $MgSO_4$. The residue after evaporation of the solvent was chromatographed to obtain a mixture of stereoisomers of the epoxide. Separation of the diastereomers were performed by repeated column chromatography or by HPLC with a specified eluent. Configurations of the diols were elucidated on the basis of the characteristic deshielding of the *endo*-H5 and *endo*-H6 protons (in the case of the *syn*-diols) or *endo*-H7 and *endo*-H8 protons (in the case of the *anti*-diols) and shielding of *exo*-H6 proton (in the case of the *syn*-diols) or *exo*-H7 and *exo*-H8 protons (in the case of the *anti*-diols) owing to the anisotropic effect of the hydroxy groups.[20,45] The assignments of the ^{1}H-NMR signals of the starting materials **2b**—**h** were based on INDOR (internuclear double resonance) measurements.

Dihydroxylation of 5-*exo*-Cyanobicyclo[2.2.2]oct-2-ene (2b) A crude mixture of the diols were obtained by column chromatography (ethyl acetate only). Diastereomers were isolated by column chromatography (ethyl acetate : *n*-hexane = 1 : 4).

5b-*syn*: White powder, mp 156—157 °C (recrystallized from *n*-hexane–ethyl acetate). ^{1}H-NMR ($CDCl_3$): 3.96—3.88 (2H, m), 3.24 (1H, br m), 3.19—3.14 (1H, m), 2.95 (1H, br m), 2.34—2.28 (1H, m), 2.03—1.92 (2H, m), 1.85—1.68 (2H, m), 1.59—1.46 (3H, m). *Anal.* Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.37. Found: C, 64.60; H, 8.14; N, 8.44.

5b-*anti*: White powder, mp 127—128 °C (recrystallized from *n*-hexane–ethyl acetate). ^{1}H-NMR ($CDCl_3$): 3.84 (2H, br m), 2.82 (1H, br m), 2.70—2.65 (1H, m), 2.58 (1H, br m), 2.04 (1H, br m), 1.95—1.82

(5H, m), 1.81—1.73 (1H, m). HRMS: Calcd for $C_9H_{13}NO_2$: 167.0946. Found: 167.0937.

Dihydroxylation of 5-*exo*-Methoxycarbonylbicyclo-[2.2.2]-oct-2-ene (2c) A crude mixture of the diols were obtained by column chromatography (ethyl acetate : *n*-hexane = 1 : 4). Diastereomers were isolated by HPLC (tetrahydrofuran : *n*-hexane = 1 : 3).

5c-*syn*: Colorless oil. ^{1}H-NMR ($CDCl_3$): 3.91 (2H, br m), 3.69 (3H, s), 3.01—2.96 (1H, m), 2.86 (1H, br m), 2.55 (1H, br m), 2.09—1.97 (2H, m), 1.84—1.79 (2H, m), 1.64—1.60 (2H, m), 1.41—1.32 (2H, m). HRMS: Calcd for $C_{10}H_{16}O_4$: 200.1049. Found: 200.1058.

5c-*anti*: Colorless oil. ^{1}H-NMR (CD_3OD): 4.10 (1H, dd, $J=8.0$, 2.6 Hz), 4.03 (1H, dd, $J=8.4$, 2.2 Hz), 3.92 (3H, s), 2.85—2.79 (1H, m), 2.32—2.21 (2H, m), 2.12—1.98 (2H, m), 1.93—1.83 (2H, m), 1.56—1.46 (2H, m). HRMS: Calcd for $C_{10}H_{16}O_4$: 200.1049. Found: 200.1077.

Dihydroxylation of Bicyclo[2.2.2]oct-2-en-5-*exo*-carboxanilide (2d) A crude mixture of the diols were obtained by column chromatography (ethyl acetate only). Diastereomers were isolated by column chromatography (ethyl acetate only).

5d-*syn*: Colorless oil. ^{1}H-NMR ($CDCl_3$): 7.72 (1H, br s), 7.51 (2H, d, $J=7.7$ Hz), 7.30 (2H, t, $J=7.7$ Hz), 7.08 (1H, t, $J=7.3$ Hz), 3.95—3.91 (2H, m), 3.81 (1H, br m), 2.94 (2H, br t), 2.03—1.94 (3H, m), 1.89—1.83 (2H, m), 1.76—1.70 (1H, m), 1.40—1.31 (2H, m). HRMS: Calcd for $C_{15}H_{19}NO_3$: 261.1365. Found: 261.1399.

5d-*anti*: White powder, mp 164—165 °C (recrystallized from diethyl ether). ^{1}H-NMR ($CDCl_3$): 7.50 (2H, d, $J=7.7$ Hz), 7.32 (2H, t, $J=7.3$ Hz), 7.10 (1H, br t, $J=7.7$ Hz), 3.95—3.92 (2H, m), 2.98 (1H, br m), 2.47 (2H, br q), 2.31—2.25 (1H, m), 2.00 (1H, br m), 1.84—1.78 (3H, m), 1.66—1.48 (2H, m). HRMS: Calcd for $C_{15}H_{19}NO_3$: 261.1365. Found: 261.1369.

Acetonide of the *syn*-Diol (5d-*syn*) The *syn*-diol obtained from **2d** (**5d**-*syn*) was treated with acetone in the presence of *p*-toluenesulfonic acid and benzene at reflux. The reaction mixture was column-chromatographed (ethyl acetate : *n*-hexane = 1 : 5) to give the acetonide of **5d**-*syn*. White powder, mp 139.5—140.5 °C (recrystallized from diethyl ether). ^{1}H-NMR ($CDCl_3$): 7.52 (2H, d, $J=7.7$ Hz), 7.31 (2H, t, $J=8.5$ Hz), 7.24 (1H, br m), 7.08 (1H, t, $J=7.7$ Hz), 4.16—4.14 (2H, m), 2.92—2.86 (1H, m), 2.14—2.00 (1H, m), 2.02—1.92 (2H, m), 1.90—1.83 (2H, m), 1.81—1.74 (1H, m), 1.56 (3H, s), 1.40 (3H, s), 1.31—1.25 (2H, m). *Anal.* Calcd for $C_{18}H_{23}NO_3 \cdot 4/5H_2O$: C, 68.46; H, 7.85; N, 4.44. Found: C, 68.26; H, 7.64; N, 4.60.

Dihydroxylation of Bicyclo[2.2.2]oct-2-ene-5-*exo*-carboxylic Acid (2e) A crude mixture of the diols (**5e**-*syn* and **5e**-*anti*) was methylated with ethereal diazomethane to give esters identical to authentic **5c**-*syn* and **5c**-*anti*.

Dihydroxylation of 5-*exo*-Methoxymethylbicyclo[2.2.2]oct-2-ene (2f) No adequate solvent for separating the mixture of diastereomers could be found. A mixture of the diols (**5f**-*syn* and **5f**-*anti*) gave satisfactory spectra and HRMS value. HRMS: Calcd for $C_{10}H_{19}O_3$ (M+H): 187.1334. Found: 187.1330. **5f**-*syn*: ^{1}H-NMR: 3.894 (2H, br s), 3.336 (3H, s), 3.294 (2H, s), 2.332 (1H, m), 1.987 (1H, m), 1.850—1.229 (6H, m), 0.816 (1H, m). **5f**-*anti*: ^{1}H-NMR: 3.868 (2H, br s), 3.343 (3H, s), 3.312 (2H, s), 1.850—1.229 (8H, m), 1.089 (1H, m).

Dihydroxylation of 5-*exo*-*p*-Toluenesulfonylbicyclo[2.2.2]oct-2-ene (2g) A crude mixture of the diols was obtained by column chromatography (methylene chloride). Diastereomers were isolated by HPLC (ethyl acetate : *n*-hexane = 1 : 5).

5g-*syn*: Colorless oil. ^{1}H-NMR: 7.79 (2H, d, $J=8.0$ Hz), 7.34 (2H, t, $J=8.0$ Hz), 4.10—4.05 (2H, m), 3.96—3.89 (2H, m), 2.80 (2H, s), 2.45 (3H, s), 2.39—2.29 (1H, m), 1.95—1.80 (3H, m), 1.62—1.53 (1H, m), 1.50—1.41 (1H, m), 1.36—1.25 (1H, m), 1.21—1.12 (1H, m), 0.73—0.63 (1H, m). HRMS: Calcd for $C_{16}H_{22}O_5S$: 326.1188. Found: 326.1196.

5g-*anti*: Colorless oil. ^{1}H-NMR: 7.79 (2H, d, $J=8.1$ Hz), 7.35 (2H, t, $J=8.0$ Hz), 4.10—3.91 (4H, m), 2.70 (2H, br s), 2.45 (3H, s), 2.00—1.85 (1H, m), 1.85—1.50 (6H, m), 1.40—1.10 (4H, m), 1.05—1.00 (1H, m). HRMS: Calcd for $C_{16}H_{22}O_5S$: 326.1188. Found: 326.1162.

Dihydroxylation of 5-*exo*-Methylbicyclo[2.2.2]oct-2-ene (2h) No adequate solvent for separating the mixture of diastereomers could be found. The mixture of the diols (**5h**-*syn* and **5h**-*anti*) gave satisfactory spectra and HRMS value. HRMS: Calcd for $C_{10}H_{19}O_3$ (M+H): 187.1334. Found: 187.1330. HRMS: Calcd for $C_9H_{16}O_2$: 156.1151. Found: 156.1168. **5h**-*syn*: ^{1}H-NMR: 3.853 (2H, br s), 2.148—1.255 (8H, m), 0.957 (3H, d, $J=6.59$ Hz), 0.792 (1H, m). **5h**-*anti*: ^{1}H-NMR: 3.853 (2H, br s), 2.148—1.255 (8H, m), 1.051 (1H, m), 1.027 (3H, d, $J=6.59$ Hz).

Computational Methods *Ab initio* calculations were performed with GAUSSIAN 92 package programs.[46] Geometries were optimized with specified symmetry constraint on the split-valence HF/3-21G basis sets (data not shown),[23a] followed by full optimization with HF/6-31G* basis sets.[23b] Orbital pictures were drawn with PSI88[47] on the HF/6-31G* optimized geometries with a contour level of 0.048 (Fig. 1) and 0.084 (Fig. 3), respectively.[48]

The bonding properties of the HF/6-31G* optimized bicyclic species **1** and **2** were investigated by means of Bader's topological electron density analysis.[34] The program SADDLE was used to characterize the one-electron density properties.[49] The one-electron density distribution $\rho(\mathbf{r})$ was analyzed with the aid of its gradient vector field $\nabla\rho(\mathbf{r})$. The zero-flux lines $[\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})=0]$ define the boundaries of the atomic basins in the molecular space. Extreme or critical points in ρ [where $\nabla\rho(\mathbf{r})=0$] are classified according to rank and signature or curvature. In a basin the electron density is maximum at the nuclear position and is characterized as a (3,-3) critical point. Of particular importance in this study are the (3,-1) or bond critical points. Their value of ρ is a minimum along the line linking nuclei (bond path, positive curvature) and it is a maximum along the interatomic surface (negative curvature) as defined by the trajectories which terminate at the critical point. Generally the σ and π character of a bond can be estimated from its ellipticity ε, which is defined as $\varepsilon=\lambda_1/\lambda_2-1$ (λ_1 and λ_2 are the two negative curvatures of the bond critical point). The sign of the Laplacian $\nabla^2\rho(\mathbf{r})$ provides information about where the electronic charge is locally concentrated (negative) or depleted (positive).

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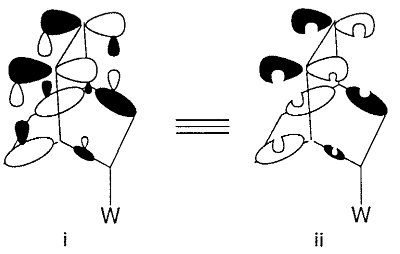
29) In order to emphasize electron density distribution of the internuclear region of the less-diffused orbital state in addition to the phase relation of the interacting orbitals, we adopted the diagrams depicted in (i) and (ii). See references 19 and 20.



Unsymmetrization of π Orbital of the Olefin Arising from Antibonding Interaction

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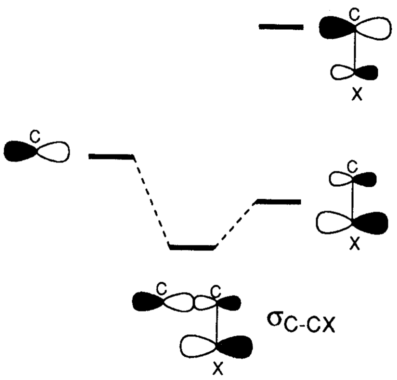
31) In a substituted ethane ($H_3C\text{-}CH_2\text{-}X$) the σ_{C-C} orbital is assumed to be constructed by orbital interactions between the two relevant carbon atoms wherein one carbon atom (C–X) has electronegativity perturbation (X represents a cyano or carbonyl group) (Scheme i). The $2p$ orbital of the carbon atom of the C–X fragment, comprising the C–C bond, is perturbed by π-type overlapping of the π orbital of X. In π-type interaction of the CX bond, the π bonding orbitals are weighted more heavily on the atom X and the π antibonding orbitals are weighted more heavily on the relevant carbon atoms. Thus, the in-phase interaction of C_{2p} orbitals of the two carbon atoms provides a higher amplitude on the $C(H_3)$ fragment than on the $C(XH_2)$ fragment, although the group electronegativity is higher in the CX portion. This can be seen in the drawing.



Scheme i. Schematic Representation of σ_{C-CX} Orbital of Ethane Substituted with an Electron-withdrawing Group

32) An analogous π–π^* interaction can be present in dibenzobicyclo[2.2.2]octatrienes **3** (ref. 20) and other conjugated systems (ref. 19). Due to the symmetry agreement, the π orbital of the olefins can interact with the vacant aromatic π^* orbitals (NXLUMO or LUMO) of the aromatic moiety, *e.g.*, dihydroanthracene in the case of **3**, which creates a bonding region. When the substituent is electron-withdrawing, the aromatic π^* orbitals of the substituted benzene have lowered energy, and thus the π–π^* interaction is activated on the side of the substituent. This can at least partially explain the observed *syn*-preference inherent to electron-withdrawing substituents in **3** and other systems.

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