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SECONDARY ORBITAL INTERACTION VS. ORBITAL DISTORTION IN STEREOSELECTIVITY

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Abstract: Stereoselectivities in reactions such as electrophilic additions to norbornene and 1-methoxycyclohexene-2, and reductions of cyclohexanone derivatives and a benzocycloheptenone one have been interpreted using frontier orbital theory. We concluded that the secondary orbital interaction is more important for the selectivities than the orbital distortion at the reaction center. This conclusion may be a motive for reexaminations of factors in stereoselectivities which could not be interpreted by the orbital distortion at the reaction center.

One of the theoretical ways to predict stereoselectivity is Inagaki *et al.*[1] and Liotta's[2] attribution of it in some reactions to the distortion of the frontier orbital at the reaction center, although this was criticized by Houk[3] and Kahn *et al.*[4] They pointed out that the distortion of the frontier orbital was too small to cause the stereoselectivities in the reactions. Houk noted that the most important factor in stereoselectivity was steric hindrance in the transition state of the reaction. Kahn *et al.* proposed the importance of electrostatic interaction.

Another way to interpret the stereoselectivity by frontier orbital theory is to include the secondary orbital interaction. Houk noted that the secondary orbital interaction between the LUMO of the reagent and the HOMO distribution of norbornene at the ethano bridge might have some effects on the *exo/endo* stereoselectivity in electrophilic additions to norbornene.[3] However, he did not believe that the interaction was the main origin of the stereoselectivity.

One of the purposes of this article is to compare the effects of the secondary orbital interaction on stereoselectivities with those of the orbital distortion at the reaction center. Electrophilic additions to norbornene and 1-methoxycyclohexene-2, and reductions of cyclohexanone derivatives and a benzocycloheptenone one are discussed. Houk *et al.* took up stereoselectivity in the reduction of a benzocycloheptenone derivative as an example which could not be interpreted by frontier orbital theory.[5] They underestimated the power of frontier orbital theory, since they

gave their attention only to the orbital distortion at the reaction center. Interpreting this stereoselectivity by frontier orbital theory is another purpose.

Method

Molecular structures and molecular orbitals were obtained by the AM1 method[6] integrated into MOPAC.[7] Geometries were fully optimized by the Broyden-Fletcher-Goldfarb-Shanno algorithm.[8] Molecular orbitals were also obtained at the restricted Hartree-Fock level using the STO-3G basis set (HF/STO-3G) and the geometries optimized by the AM1 method. The GAUSSIAN 82[9] was used for the HF/STO-3G calculations. Molecular orbital coefficients obtained by the HF/STO-3G calculation were renormalized within the valence orbital part by neglecting overlap integrals to compare them with those obtained by the AM1 method. These coefficients were used to calculate the integrals described below.

To compare the effects of the secondary orbital interaction on stereoselectivity with those of the orbital distortion at the reaction center, $h_{H,i}$ defined by equation 1 was calculated.

$$h_{H,i} = \langle \chi_H | h | \phi_i \rangle \approx \sum_r 0.5 \, (\beta_H + \beta_r) \langle \chi_H | \chi_r \rangle \, C_{ri} \qquad (1)$$

In this equation, h is the one-electron Hamiltonian. χ_H is the 1s atomic orbital of hydrogen, which is used as a probe orbital. ϕ_i is the frontier orbital of the reactant and is approximated by $\sum_r \chi_r C_{ri}$, where χ_r is the atomic orbital of the reactant. β_H and β_r are the resonance integrals for χ_H and χ_r, respectively. The AM1 parameters were used for them. The square of $h_{H,i}$ is approximately the numerator of the perturbation equation on which frontier orbital theory has its base. Therefore, the effects of the orbital interaction on stereoselectivity can be estimated by putting a probe orbital (1s atomic orbital of hydrogen) on each side of the enantiomeric face and calculating $h_{H,i}$. The probe orbital was put at the point defined by the direction of the p-component of the frontier orbital at the reaction center (p-axis, Figure 1-(a) and (b)). The distance between the centroid of the probe orbital and the reaction center was set at 2.0 Å referring to the transition state geometry of LiH-acetone reaction.[10] For electrophilic additions to norbornene, the 2p-orbital of carbon was also used as a probe orbital in order to examine the dependence of results on the nature of the probe orbital. The points where the p-type probe orbital was put were defined by the direction of the p-axis. Direction of the p-type probe orbital was the same as that of the p-axis (Figure 1-(c) and (d)). Dependence of results on the distance between the centroid of the probe orbital and the reaction center was also examined for the reaction.

Electrostatic potential was calculated at the same point as that at which the s-type probe orbital was put (Figure 1-(a) and (b)) using the HF/STO-3G wave function. The PROP option of GAUSSIAN 82[9] was used for the calculation.

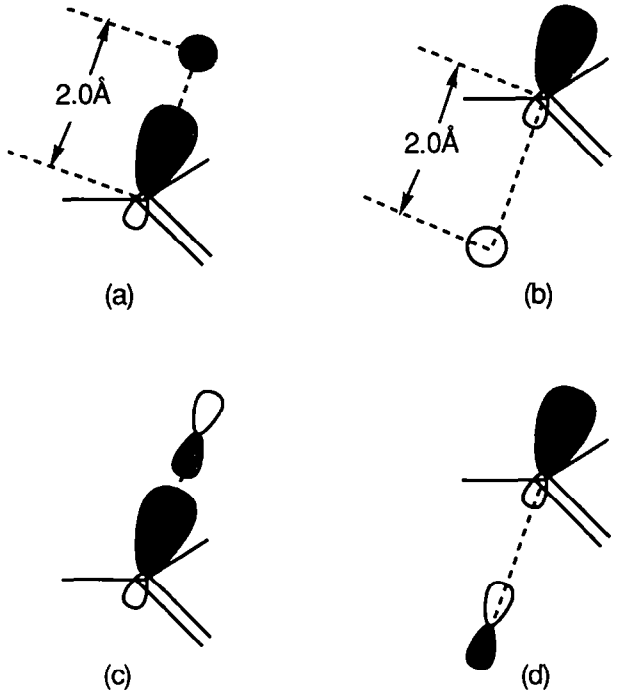


Figure 1. Definition of the point at which a probe orbital is put.
(a), (b) : The 1s atomic orbital of hydrogen is the probe orbital.
(c), (d) : The 2p atomic orbital of carbon is the probe orbital.

Electrophilic additions to norbornene

Exo stereoselection has been observed in the reactions of norbornene with a variety of electrophiles.[11] According to the AM1 and HF/STO-3G calculations, the 2s coefficients of HOMO at C_2 (Figure 2), which is considered to be the reaction center, are 0.009 and 0.017, respectively, while the $2p_z$ coefficients are 0.638 and 0.633, respectively. Therefore, it is concluded that HOMO distorts in the *exo* direction at C_2. This has already been pointed out by Inagaki *et al.*[1] and is consistent with the selectivity. However, the effects of the orbital distortion at the reaction center are smaller than those of the secondary orbital interaction. In Table I, contributions to $h_{H,HOMO}$ from the atom X ($h^X_{H,HOMO}$) are listed. The effects of the orbital distortion at

C_2 are estimated to be -0.027 (-0.768+0.741) and -0.050 (-0.773+0.723) ev at the AM1 and HF/STO-3G levels, respectively. On the other hand, for *endo* attack, the effects of the secondary orbital interaction with the HOMO distribution at the ethano bridge (C_1, C_4, C_5, C_6, H_1, H_4, H_5, H_5', H_6, and H_6' ; Figure 2) are estimated to be 0.201 (0.054+0.018+0.033+0.111-0.008-0.002-0.003+0.001-0.006+0.003) and 0.245 (0.049+ 0.014+0.052+0.153-0.008-0.002-0.004-0.000-0.008-0.001) ev at the AM1 and HF/STO-3G levels, respectively. For *exo* attack, they are estimated to be 0.097 and 0.090 ev at the AM1 and HF/STO-3G levels, respectively. Therefore, the differences in the secondary orbital interaction with the HOMO distribution at the ethano bridge between *exo* and *endo* attacks are -0.104 and -0.155 ev at the AM1 and HF/STO-3G levels, respectively. Main term is the difference in $h^{C6}{}_{H,HOMO}$ between *exo* and *endo* attacks. As a whole, differences in $h_{H,HOMO}$ between *exo* and *endo* attacks are estimated to be -0.045 (-0.949+0.904) and -0.109 (-0.939+0.830) ev at the AM1 and HF/STO-3G levels, respectively. This is consistent with the selectivity. It became quantitatively clear that the secondary orbital interaction with the HOMO distribution at the ethano bridge, which has been pointed out qualitatively by Houk,[3] is more important for the *exo*/*endo* stereoselectivity in the electrophilic additions to norbornene than the orbital distortion at the reaction center caused by the mixing of the C_2C_3 σ orbital with the π orbital, which has been pointed out by Inagaki *et al.*[1]

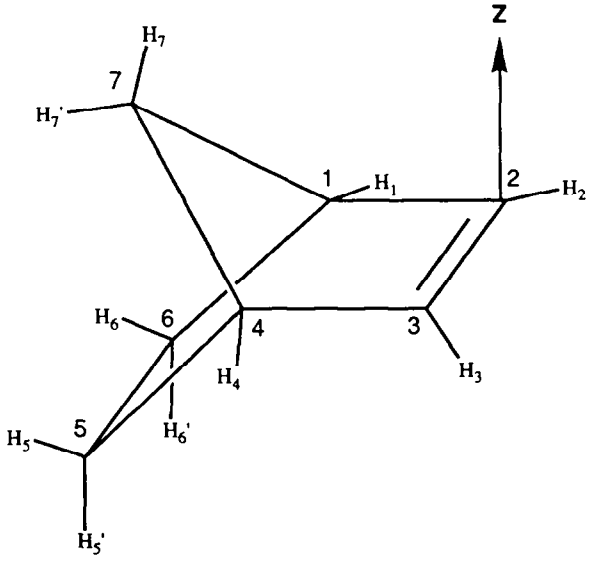


Figure 2. Numbering of atoms in norbornene and definition of z axis.

Table I. $h^{X}_{H,HOMO}$ (ev) for norbornene.

/ X	C_1	C_2	C_3	C_4	C_5	C_6
exo (AM1)	0.067	-0.768	-0.312	0.020	-0.004	-0.009
exo (HF/STO-3G)	0.062	-0.773	-0.325	0.020	-0.005	-0.010
endo (AM1)	0.054	-0.741	-0.346	0.018	0.033	0.111
endo (HF/STO-3G)	0.049	-0.723	-0.327	0.014	0.052	0.153

C_7	H_1	H_2	H_3	H_4	H_5	H_5'	H_6
0.080	0.019	0.003	0.001	0.004	0.000	0.000	0.000
0.113	0.018	0.006	0.002	0.004	0.000	0.000	0.001
-0.017	-0.008	-0.003	-0.001	-0.002	-0.003	0.001	-0.006
-0.020	-0.008	-0.006	-0.002	-0.002	-0.004	-0.000	-0.008

H_6'	H_7	H_7'	$h_{H,HOMO}$
0.000	-0.042	-0.007	-0.949
0.000	-0.043	-0.008	-0.939
0.003	0.001	0.002	-0.904
-0.001	0.001	0.002	-0.830

Numbering is shown in Figure 2.

Next, we examined the dependence of results on the nature of the probe orbital. Dependence of results on the distance between the centroid of the probe orbital and the reaction center was also examined. Results are shown in Figure 3 and 4. Effects of the secondary orbital interaction are always more important than those of the orbital distortion estimated with the s-type probe orbital. This is also the case for the effects estimated with the p-type probe orbital at the points around the transition state (R ≈ 2.0 Å). Hence, only the s-type probe orbital was used and the distance between the centroid of the probe orbital and the reaction center was set at 2.0 Å in the following section.

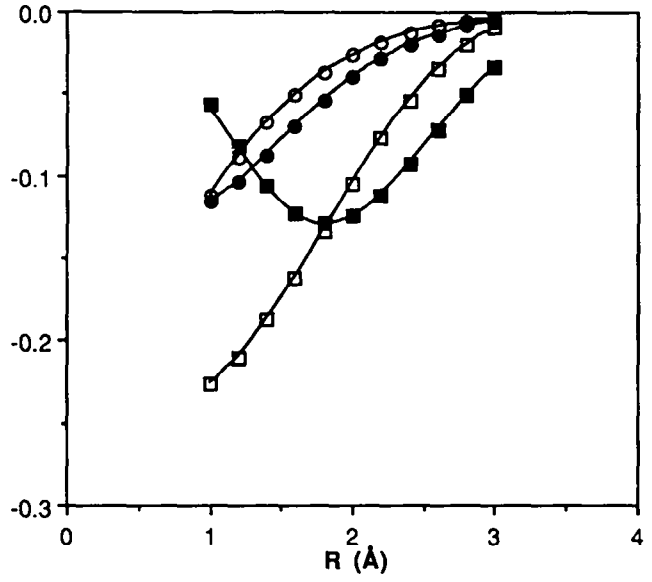


Figure 3. Effects of the secondary orbital interaction in the *exo/endo* stereoselectivity estimated with the s-type probe orbital (□) and the p-type probe orbital (■), and those of the orbital distortion estimated with the s-type probe orbital (○) and the p-type probe orbital (●) at the AM1 level. R is the distance between the centroid of each probe orbital and the reaction center.

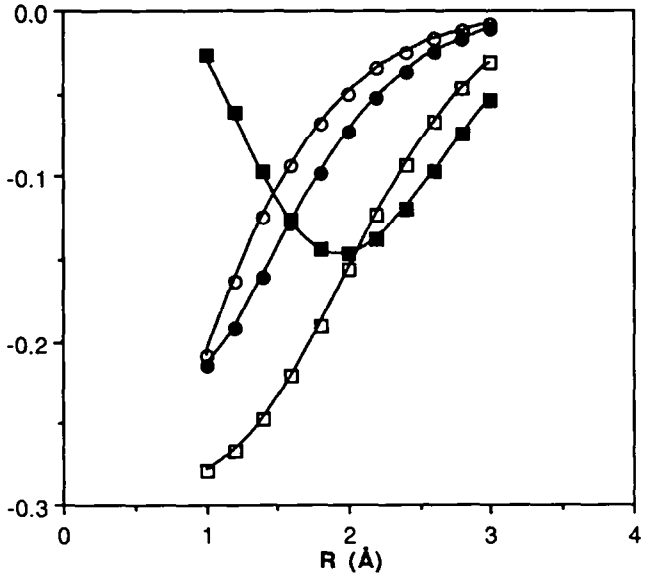


Figure 4. Effects of the secondary orbital interaction in the *exo/endo* stereo-

selectivity estimated with the s-type probe orbital (□) and the p-type probe orbital (■), and those of the orbital distortion estimated with the s-type probe orbital (○) and the p-type probe orbital (●) at the HF/STO-3G level. R is the distance between the centroid of each probe orbital and the reaction center.

Electrophilic additions to 1-methoxycyclohexene-2

In the electrophilic reaction of 1-methoxycyclohexene-2 with NBS[12] or NCS,[13] the addition occurs preferentially from the direction syn to oxygen at C_2 (Figure 5). Kahn *et al.* pointed out that the orbital distortion was too small to cause the stereoselectivity. They tried to interpret the selectivity by the electrostatic potential.[4]

Six conformers were found for 1-methoxycyclohexene-2 (Table II). Conformer 1 is the most stable at the AM1 level. Moreover, the dipole moment of conformer 1 is the largest among all conformers at the AM1 level. Therefore, the population of conformer 1 is predicted to be very high in water, which is the solvent in the electrophilic reaction of 1-methoxycyclohexene-2 with NBS or NCS, and the discussion below is given for conformer 1.

At the AM1 level, HOMO slightly distorts in the direction anti to oxygen at C_2, which is considered to be the reaction center. The 2s coefficient of HOMO at C_2 is 0.002, while the $2p_z$ coefficient is 0.617. This is in conflict with the stereoselectivity. Although HOMO distorts in the direction syn to oxygen at C_2 at the HF/STO-3G level, the distortion is small. The 2s coefficient of HOMO at C_2 is -0.025, while the $2p_z$ coefficient is 0.608. In Table III, $h^X_{H,HOMOS}$ absolute values that are above 0.05 ev are listed. It is concluded that the effects of the orbital distortion on the stereoselectivity are smaller than those of the secondary orbital interaction between the LUMO of the reagent and the HOMO distribution at H_1, H_4, and H_4' (Figure 5). For example, the effect of the orbital distortion on the stereoselectivity at C_2 is estimated to be -0.072 (-0.758+0.686) ev, while that of the secondary orbital interaction is estimated to be -0.134 ev at the HF/STO-3G level. Experimentally, the ratios of products (A:B:C:D ; see Figure 5) in the electrophilic reaction of 1-methoxycyclohexene-2 are 10:4:1:0 with NBS[12] and 5:3.8:1:0 with NCS,[13] respectively. At the AM1 level, $h_{H,HOMOS}$ are -0.897, -0.792, -0.799, and -0.815 ev for the attacks from A, B, C, and D, respectively. Although details of the selectivity are not reproduced, the main product can be predicted. At the HF/STO-3G level, $h_{H,HOMOS}$ are -0.893, -0.850, -0.850 , and -0.840 ev for the attacks from A, B, C, and D, respectively. This order is consistent with the selectivity.

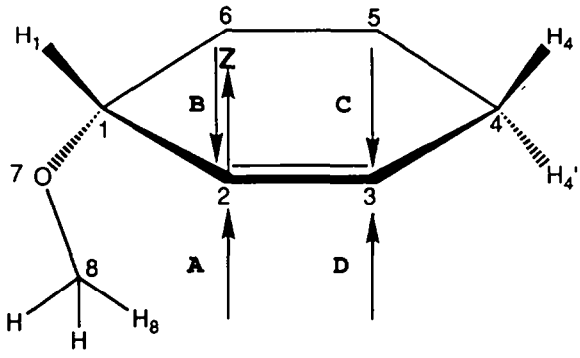


Figure 5. Numbering of atoms in 1-methoxycyclohexene-2, definition of z axis, and direction of attacks (A, B, C, and D).

Table II. Conformers of 1-methoxycyclohexene-2.

/ conformer	1	2	3	4	5	6
ΔE (kcal/mol)	0.00	0.75	0.99	1.03	1.60	2.24
μ (Debye)	1.63	1.29	1.47	1.63	1.16	1.36
$\tau_{6\text{-}1\text{-}2\text{-}3}$ (deg.)	22	21	21	2	-11	-9
$\tau_{5\text{-}4\text{-}3\text{-}2}$	13	13	14	-24	-16	-18
$\tau_{8\text{-}7\text{-}1\text{-}2}$	-61	80	162	-61	65	152

ΔE, relative energy; μ, dipole moment; τ, torsional angle at the AM1 level.

Table III. $h^{X}_{H,HOMO}$ (ev) for conformer 1 of 1-methoxycyclohexene-2.

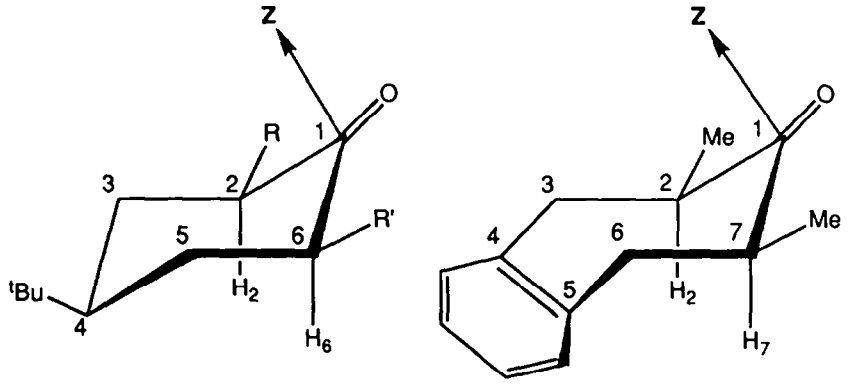
/ X	C_1	C_2	C_3	C_4	H_1	H_4	H_4'	H_8
AM1								
A	0.061	-0.728	-0.336					
B	0.081	-0.733	-0.288		0.163			
C		-0.299	-0.700	0.094		0.093		
D		-0.352	-0.705	0.094			0.148	
HF/STO-3G								
A	0.061	-0.758	-0.293					-0.060
B	0.056	-0.686	-0.334		0.134			
C		-0.302	-0.720	0.062		0.078		
D		-0.336	-0.698	0.068			0.136	

: $h_{H,HOMO}$
-0.897
-0.792
-0.799
-0.815
-0.893
-0.850
-0.850
-0.840

Numbering and the direction of attacks (A, B, C, and D) are shown in Figure 5.

Reductions of cyclohexanone derivatives and a benzocycloheptenone one

As generalized by Barton, axial attack of nucleophiles on cyclohexanone is favored when the steric hindrance is negligible.[14] Klein,[15] Ahn *et al.*,[16] and Ashby *et al.*[17] tried to interpret the selectivity by the distortion of LUMO at the carbonyl carbon, the reaction center. In compounds 1-3 (Figure 6), however, the distortion is very small and points in the equatorial direction at the AM1 level. For compounds 1-3, the 2s coefficients of LUMO at the carbonyl carbon are -0.009, -0.010, -0.012, respectively, while the $2p_z$ coefficients are 0.760, 0.760, and 0.760, respectively. This is in conflict with the selectivity. At the HF/STO-3G level, although the distortion points in the axial direction, it is also very small. For compounds 1-3, the 2s coefficients of LUMO at the carbonyl carbon are 0.003, 0.003, and 0.002, respectively, while the $2p_z$ coefficients are 0.680, 0.681, and 0.682, respectively. In Tables IV-VI, $h^X{}_{H,LUMO}$s absolute values that are above 0.05 ev are listed. From these results, we concluded that the secondary orbital interaction between the HOMO of the reagent and the LUMO distribution at α-axial hydrogens has larger effects on the selectivity than the orbital distortion at the carbonyl carbon. The differences in $h_{H,LUMO}$ between axial and equatorial attacks are -0.109 (-0.549+0.440), -0.095 (-0.542+0.447), and -0.074 (-0.533 +0.459) ev for compounds 1-3, respectively, at the AM1 level. At the HF/STO-3G level, these are -0.109 (-0.401+0.292), -0.089 (-0.392+0.303), and -0.062 (-0.380+ 0.318) ev for compounds 1-3, respectively. The decrease in the difference from compounds 1 to 3 is caused mainly by the decrease of the LUMO distribution at α-axial hydrogens and the increase of the LUMO distribution at C_3 and C_5.



	R	R'
1	H	H
2	Me	H
3	Me	Me

4

Figure 6. Numbering of atoms in cyclohexanone derivatives and a benzocycloheptenone one, and definition of z axis.

Table IV. $h^{X}_{H,LUMO}$ (ev) for compound 1.

/ X	C_1	O	C_3	C_5	H_2	H_6	: $h_{H,LUMO}$
ax. (AM1)	-0.885	0.281					-0.549
ax. (HF/STO-3G)	-0.808	0.314	0.065	0.065			-0.401
eq. (AM1)	-0.910	0.276			0.132	0.132	-0.440
eq. (HF/STO-3G)	-0.798	0.316			0.145	0.145	-0.292

Numbering is shown in Figure 6.

Table V. $h^{X}_{H,LUMO}$ (ev) for compound 2.

/ X	C_1	O	C_3	C_5	H_2	H_6	: $h_{H,LUMO}$
ax. (AM1)	-0.884	0.282	0.057	0.051			-0.542
ax. (HF/STO-3G)	-0.809	0.314	0.077	0.067			-0.392
eq. (AM1)	-0.913	0.276			0.125	0.131	-0.447
eq. (HF/STO-3G)	-0.801	0.315			0.137	0.144	-0.303

Numbering is shown in Figure 6.

Table VI. $h^{X}_{H,LUMO}$ (ev) for compound 3.

/ X	C_1	O	C_3	C_5	H_2	H_6	: $h_{H,LUMO}$
ax. (AM1)	-0.882	0.282	0.059	0.059			-0.533
ax. (HF/STO-3G)	-0.808	0.314	0.080	0.080			-0.380
eq. (AM1)	-0.915	0.275			0.120	0.120	-0.459
eq. (HF/STO-3G)	-0.804	0.314			0.132	0.132	-0.318

Numbering is shown in Figure 6.

Table VII. $h^{X}_{H,LUMO}$ (ev) for compound 4.

/ X	C_1	O	C_3	C_6	H_2	H_7	$h_{H,LUMO}$
ax. (AM1)	-0.877	0.282	0.102	0.102			-0.477
ax. (HF/STO-3G)	-0.785	0.305	0.155	0.155			-0.276
eq. (AM1)	-0.909	0.272			0.065	0.065	-0.537
eq. (HF/STO-3G)	-0.795	0.306			0.071	0.071	-0.397

Numbering is shown in Figure 6.

Ratios of axial/equatorial attacks in reactions between compounds 1-3 and LAH were experimentally obtained as 93:7, 83:17, and 53:47, respectively.[18] In Figure 7, their logarithmic value is plotted against the difference in $(h_{H,LUMO})^2$ between axial and equatorial attacks (Δh). Although the lines do not pass through the origin because of other interactions, the correlation is good. By extrapolating this correlation line, equatorial attack preference is predicted for compound 4 (Figure 6 and Table VII). The predicted ratios of axial/equatorial attacks are 0.0:100.0 at both the AM1 and HF/STO-3G levels. This is consistent with the stereoselectivity.[5] Houk *et al.* noted that the equatorial attack preference in the nucleophilic reaction of compound 4 with LAH could be interpreted only by the steric hindrance in the transition state.[5] However, it can also be interpreted by frontier orbital theory.

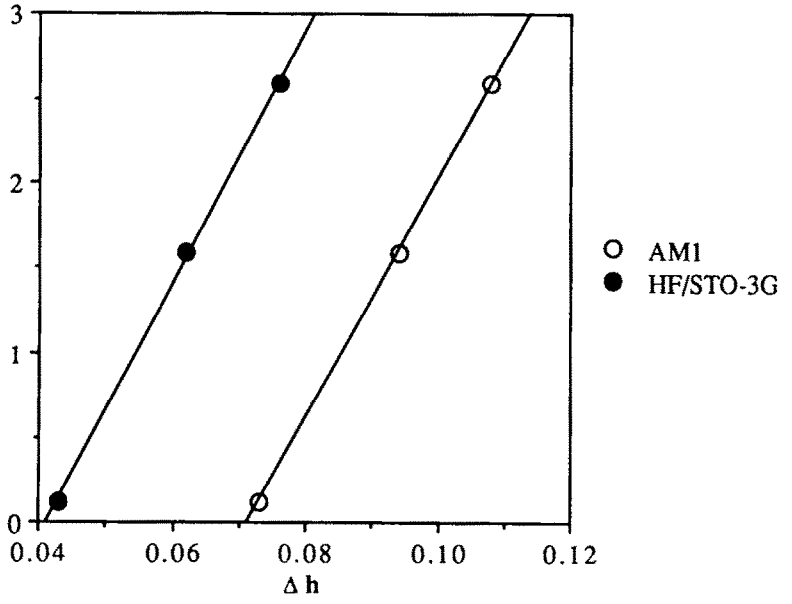


Figure 7. Relationship between ln(axial/equatorial) and Δh at the AM1 and HF/STO-3G levels.

Electrostatic potential

Kahn *et al.* proposed the importance of electrostatic interactions in stereoselectivities.[4] Electrostatic potential was calculated at the same point where the s-type probe orbital was put using the HF/STO-3G wave function (Figure 1 - (a) and (b)).

In the case of norbornene, electrostatic potentials are -6.25 and -2.95 kcal/mol for *exo* and *endo* attacks, respectively. This is consistent with the stereoselectivity.

In the case of 1-methoxycyclohexene-2, electrostatic potentials are 7.14, -4.47, -2.70, and -0.36 kcal/mol for attacks from A, B, C, and D (Figure 5), respectively. Although the order is consistent with the selectivity for attacks from B, C, and D, the main product generated by the attack from A can not be predicted.

For cyclohexanone derivatives and a benzocycloheptenone one (Figure 6), electrostatic potentials are listed in Table VIII.

Table VIII. Electrostatic potentials for cyclohexanone derivatives and a benzocycloheptenone one (kcal/mol).

\ compound	1	2	3	4
axial	8.51	9.18	9.62	17.29
equatorial	6.94	6.99	7.06	7.77
ESP(ax. - eq.)	1.57	2.19	2.56	9.52

For compounds 1 - 3, the axial attack preference is reproduced (The reaction center of LAH has minus charge.). However, the sign of the regression coefficient for the relationship between ln(ax./eq.) and the difference in electrostatic potentials (ESP (ax. - eq.) in Table VIII) is minus (Figure 8). This is unreasonable. Moreover, the equatorial attack preference can not be reproduced for compound 4.

From these results, we concluded that the orbital interaction model is superior to the electrostatic interaction model for the interpretaion of the stereoselectivities.

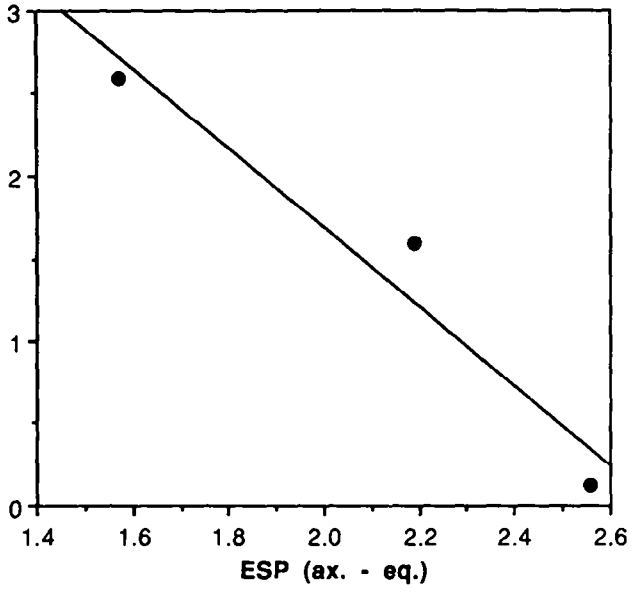


Figure 8. Relationship between ln(axial/equatorial) and ESP(ax. - eq.).

Conclusion

Generally, stereoselectivities in chemical reactions have been interpreted by the orbital distortion at the reaction center when frontier orbital theory is considered. However, we concluded in this paper that the secondary orbital interaction is more important than the orbital distortion in some reactions.

Effects of the electrostatic interaction were also examined for the reactions. We concluded that the orbital interaction model is superior to the electrostatic interaction model for the interpretation of the stereoselectivities.

The stereoselectivity in the reduction of the benzocycloheptenone derivative which Houk *et al.* [5] thought could be interpreted only by steric interaction could be elucidated by frontier orbital theory. It is not easy to compare the effects of steric interaction on stereoselectivities with those of the other interactions. One way to estimate the effects of the steric interaction may be obtaining the energy difference between the initial and transition states for each reactant separately and adding sum of the exchange and dispersion interaction energies between reactants at the transition state to the energy differences. However, the energy difference is diminished by perturbations such as charge transfer and electrostatic field. In other words, steric interaction is not separable from the other interactions. Although the effects of orbital interaction were not compared with those of steric interaction in

this paper, our results may be a motive for reexaminations of factors in stereoselectivities which could not be interpreted by the orbital distortion at the reaction center.

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