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Origin of π-Facial Stereoselectivity of Hydride Reduction of Cyclohexanones. A New Interpretation Based on Quantitative Analysis of Exterior Frontier Orbital Extension.[§]

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Abstract: A new theoretical interpretation for π-facial stereoselectivity of hydride reduction of cyclohexanones has been proposed based on the simple assumption that the lowest unoccupied molecular orbital (LUMO) of the substrates should play an essential role in the reaction: π-Facial stereoselectivity is described by relative magnitude of exterior frontier orbital extension (EFOE) of the LUMO above or below the carbonyl plane, which is defined by integrated "hole density" of the LUMO at the carbonyl carbon over three-dimensional spatial points outside repulsive molecular surface, where the absolute total value of the gaussian functions belonging to the carbonyl carbon makes the maximum contribution to the total value of the LUMO wave function so that the driving force vector on hydride is maximally directed toward the carbonyl carbon. A good linear correlation is observed for ten alkyl-substituted cyclohexanones ($NaBH_4$ in 2-propanol) between the difference in the square of EFOE densities for the axial (EFOE(ax)) and equatorial (EFOE(eq)) areas ($\lambda = \mathrm{EFOE(ax)}^2 - \mathrm{EFOE(eq)}^2$) and the difference in activation enthalpy for equatorial ($\Delta H^{\ddagger}_{eq}$) and axial ($\Delta H^{\ddagger}_{ax}$) attack ($\Delta\Delta H^{\ddagger} = \Delta H^{\ddagger}_{eq} - \Delta H^{\ddagger}_{ax}$). © 1997 Elsevier Science Ltd.

INTRODUCTION

The origin of π-facial stereoselectivity of hydride reduction of ketones has been a subject of intense investigation for over four decades and numerous theoretical interpretation models have been proposed.[1] Two transition-state models have appeared to date; the Cieplak model[2,3] and the Felkin-Anh model,[4] both of which refer to the importance of *anti*-periplanar vicinal bond conjugation in the transition state. Recently a revival qualitative explanation based on unsymmetrical extension of the lowest unoccupied molecular orbital, i.e. LUMO ($\pi^*_{C=O}$), with respect to the carbonyl plane (the orbital distortion model[5]) has been reported by several groups.[6] More recently, a strong view against this model has been offered by Houk, who emphasized the importance of the electrostatic interactions between substrate ketones and incoming hydride.[7b] In 1993, Boyd reported by using the AIM (Atoms in Molecules) theory that the transition state effects are less important than the electrostatic field difference between the two sides of the carbonyl plane.[8]

In our recent communication,[9] we reported that the major conventional transition state models for hydride reduction, namely the Felkin-Anh model and the Cieplak model, refer to only marginal side effects (*anti*-periplanar effects and torsional strain effect) in the case of cyclohexanone reduction. Quantitative evaluation of the Cieplak vs. Felkin-Anh effects in the transition states of cyclohexanone reduction with LiH by Natural Bond Orbital (NBO) analysis (B3LYP/6-31G*) has revealed that (a) Almost no Felkin-Anh conjugation (*anti*-periplanar-effect) was found in either (axial or equatorial) transition state, (b) Cieplak conjugation effects always predominate over the corresponding Felkin-Anh effects, (c) Equatorial Cieplak effect is greater than axial Cieplak effect but the difference is marginal, and (d) Torsional strain effect is less than one half of the energy difference between axial and equatorial transition states. These results were entirely inconsistent with the claims of both theoretical models.

Herein we report a new quantitative analysis for the origin of π-facial stereoselectivity of hydride reduction of cyclic ketones based on the assumption that the lowest unoccupied molecular orbital (LUMO) of substrate ketones should play an important role in determining the π-facial stereoselectivity and propose a new interpretation based on Exterior Frontier Orbital Extension model (hereafter abbreviated as the EFOE model), which simply focuses on spatial extension of the LUMO *in the exterior of a molecule.* We shall show that the observed stereochemistry of metal hydride reduction of cyclohexanones can be explained successfully by the EFOE model in which the EFOE densities of the LUMO are integrated over the three-dimensional exterior points satisfying such a criterion that the driving force vector of the reaction is maximally oriented toward the carbonyl carbon.

RESULTS AND DISCUSSION

The new model is based on the experimental observation that the enthalpy of activation of this reaction is generally very low ($\Delta H^{\ddagger}$ = 7.6 kcal mol^{-1} for cyclohexanone),[10] which implies possible occurrence of very early transition state in the reduction process. This strongly suggests that π-facial stereoselectivity of the reaction should be determined at an early stage and that a substrate ketone in its ground state should contain sufficiently essential information as to π-facial stereoselectivity. It is therefore assumed that stereochemical origin may arise from the properties of the LUMO of a starting ketone.

1. Quantitative Analysis of Cyclohexanone LUMO

We show how the frontier orbital effects are important in dictating π-facial stereoselectivity by analyzing *quantitatively* the LUMO of cyclohexanone (**1**) as an example. A close inspection of the LUMO of **1**, calculated with the geometry optimized at the RHF/6-31G* level, clearly shows two notable features (Figure 1).

First the LUMO possesses significant *anti*-bonding nature in the region between the π*-orbital of the carbonyl carbon and the 1s orbitals of the two axial hydrogens at C-2 and 6 (i.e. the equatorial area). As noted previously by Kurita et al.,[11] this should create a barrier or "blocking wall" when hydride approaches the carbonyl carbon (C-1) from the equatorial side. Indeed computation of the change in "hole density" of the LUMO[12] along hypothetical linear equatorial hydride approach within the plane (*x*-*y* plane) normal to the carbonyl plane (*y*-*z* plane) toward C-1 at an angle between 90° and 120° with respect to the C=O bond clearly indicates the points where "hole densities"[12] suddenly vanish along the linear path. Figure 2 shows a plot of the points where the hole density vanishes upon linear equatorial hydride approach at an approaching angle θ. The blocking wall against hydride approach is located at 2.0 Å (θ = 120°) – 3.0 Å (θ =

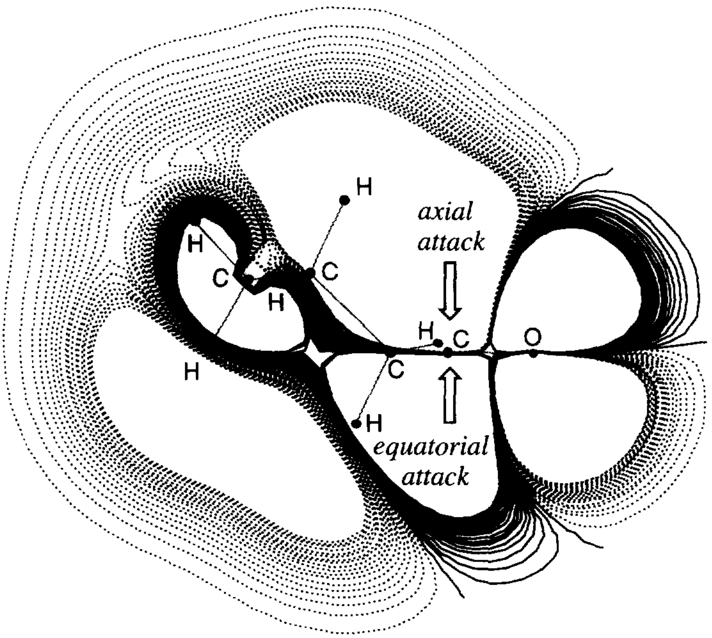


Figure 1. Contour diagram of the LUMO of cyclohexanone (**1**) (cross section with respect to the symmetry plane containing C-1, C-4 and O) calculated using 6-31G* basis set with the geometry optimized at the same level. (Contour lines correspond values between 0.0090 and –0.0030).

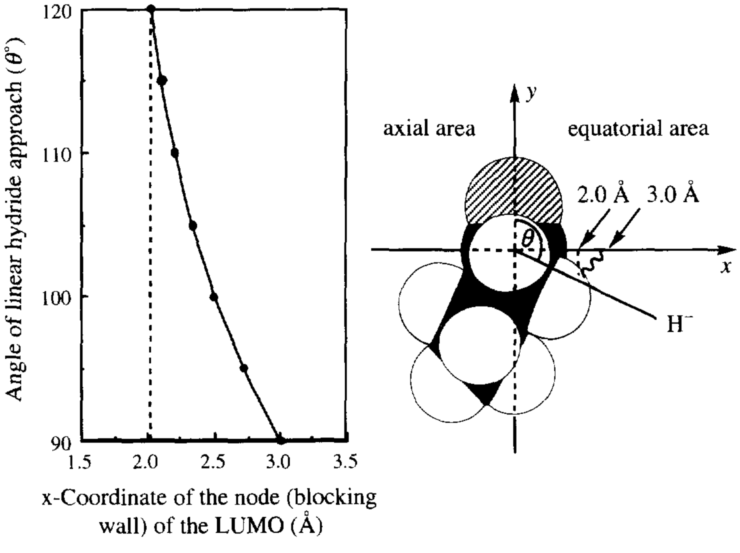


Figure 2. A plot of the position of node of the LUMO (blocking wall) in the equatorial area vs. angle(θ) of linear hydride approach to the carbonyl carbon of cyclohexanone (**1**), the space-filling side view of which is shown on the right (See text for details).

90°) from C-1 along the axis (x) normal to the carbonyl plane (y–z plane). It should be difficult for hydride to approach the carbonyl from the equatorial side ($x > 0$) beyond this wall. On the other hand the corresponding axial approach ($x < 0$) shows no sign of such a trend: the "hole density" of the LUMO monotonously increases along the linear path toward C-1.[13] *The location of the blocking wall in the equatorial area suggests that the stereochemistry of hydride reduction of 1 is determined at an early stage in the exterior region of the molecule.*

Secondly the LUMO contains a small contribution of carbon s orbital to the π*-orbital ($\pi^*_{C=O}$) at the carbonyl carbon, causing some orbital distortion toward the axial direction with respect to the carbonyl plane as pointed out previously.[6a,7a] There have been some controversies as to the mechanism and the magnitude of the LUMO distortion,[6b,7a] both of which will be analyzed here considering the extension of the LUMO at the neighboring atoms, which has not been considered before, to emphasize again the importance of the LUMO distortion for **1**.

Contrary to the prediction of Klein,[5b] it has recently been suggested that the direction of the LUMO distortion at the carbonyl carbon is attributed to the effect of the two axial hydrogens at C-2 and 6, which is inconsistent with the general rule of orbital mixing. We show here by using the perturbation theory that the

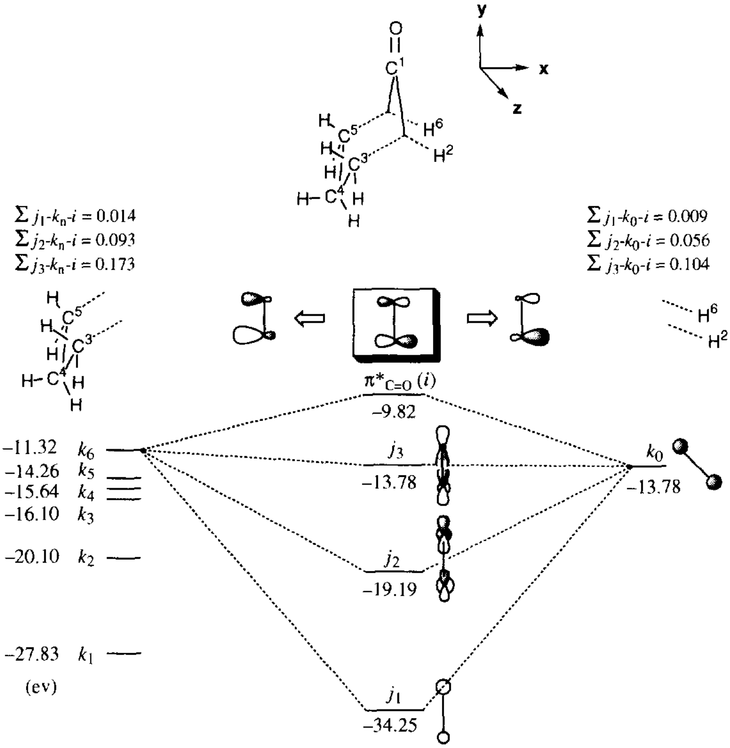
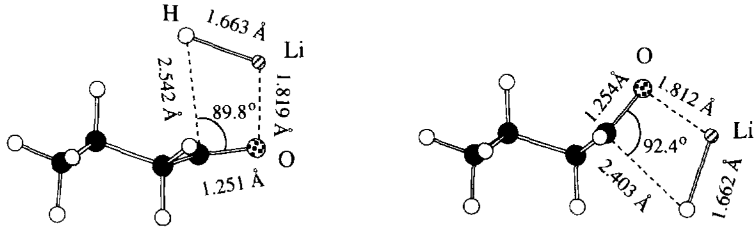


Figure 3. Mechanism of orbital distortion of $\pi^*_{C=O}$. Secondary perturbation coefficients of mixing of MO j (σ_{C-O}) into MO i ($\pi^*_{C=O}$) through MO k (C^3H_2-C^4H_2-C^5H_2 or H^2-H^6) were obtained at the extended Hückel level.[15] Total mixing coefficients for MO j, which contains 2s AO contribution at the carbonyl carbon, are denoted as $\Sigma\ j_m$–k_n–i (m=1,2,3; n=0,1,2,3,4,5,6). Major interactions $\Sigma\ j_m$–k_n–i (m=1,2,3; n=0 or 6), all of which are out-of-phase mixing, are indicated by dotted lines.

LUMO distortion toward axial direction is caused *by the three methylene unit (C-3, 4 and 5) rather than by the axial hydrogens at C-2 and 6.*[14] As shown in Figure 3, second-order perturbational coefficients (c_{ji}'') for the LUMO of **1** using the equation derived by Imamura[14a] at the extended Hückel level[15,16] suggest that *the 2s orbital mixing into the LUMO at the carbonyl carbon through the three methylene unit (C-3, 4, and 5) is greater than that through the two axial hydrogens at C-2 and 6*: namely, second order mixing coefficients (c_{ji}'') of the three occupied orthogonal MO's of C=O containing 2s orbital of the carbonyl carbon (−13.78, −19.19 and −34.25 eV) into the LUMO (−9.82 eV) through the three methylene unit (C-3, 4 and 5) are 0.173, 0.093 and 0.014, respectively, while the corresponding mixing coefficients through the two axial hydrogens at C-2 and 6 are 0.104, 0.056 and 0.009, respectively.

A consequence for the above orbital distortion mechanism is significant. First the direction and the magnitude of the LUMO distortion should depend on the conformational environment near the carbonyl carbon. Secondly this effect should significantly depend on the precision of the basis set for ab initio calculation. It is expected that the higher the basis set precision, the greater the LUMO distortion. Indeed calculations of orbital distortion index (δ) at carbonyl carbon (C-1) for the LUMO, which is defined by the following equation; $\delta = 100 \times (d_A - d_E) / (d_A + d_E)$, where d_A and d_E are integrated "electron densities" due to the carbonyl carbon wave functions of the LUMO for above (the axial region) and below (the equatorial region) the carbonyl plane, respectively, at the 3-21G and 6-31G* levels show significant s orbital mixing with the latter (δ = 55.1%) being greater than the former (δ = 31.4%). However, STO-3G, whose wave function tails are considerably neglected,[17] exhibits marginal and inverse orbital distortion (δ = −2.2%). It is hence understandable why the Felkin-Anh model, which employed the STO-3G basis set, ignored orbital distortion effects.[4b] Significant increase of the LUMO distortion of **1** at high levels of ab initio calculations strongly suggests that this effect must again be emphasized as an important factor for nucleophilic π-facial stereoselectivity.

Importance of the two frontier orbital effects is augmented by an early transition state optimized at high levels which takes into account electron correlation effect. At the B3LYP/6-31G* and MP2/6-31G* levels, the transition state structures are quite different from the previous results obtained by RHF calculations.[4d,6a] Figure 4 shows the structures obtained with the B3LYP method.[9] The distance between the incoming hydride and the carbonyl carbon ($r_{\text{C}\cdots\text{H}}$ = 2.403 Å) and the angle of hydride approach (θ = 92.4°) clearly show much earlier transition state, which occurs soon after passing the blocking wall, than that



(a) (b)

Figure 4. Side views of the transition state structures of the reaction of cyclohexanone (**1**) with lithium hydride obtained at the B3LYP/6-31G* level. (a) axial approach. (b) equatorial approach.

predicted previously. An MP2 calculation gives similar results ($r_{C\cdots H}$ = 2.25 Å ; θ = 96.4°). Considerable importance of the LUMO in hydride reduction of **1** may also be found in the theoretical observation that the distortion of the LUMO tends to be magnified by structural deformation toward the incoming hydride along the coordinate leading to the transition states so that the electron transfer from hydride can take place more easily from either face of the π-plane. Thus the distortion indices of the hypothetical LUMO's for the axial and equatorial transition states calculated at the B3LYP/6-31G* level are δ = 66.6% and −16.0%, respectively. The direction of the latter distortion is surprising in that *inverse* LUMO distortion (distortion toward the equatorial area) occurs in the process toward the transition state of equatorial hydride approach. The substrate is apparently making out the shortage of the driving force for bond formation with hydride by intolerable conformational change (Figure 4b).

2. Description of the EFOE Model

The two features of the LUMO described above strongly indicate its essential role in determining the π-facial stereochemistry of cyclohexanone reduction. This is more explicitly demonstrated by defining a new quantity called "Exterior Frontier Orbital Electron density" (EFOE density), which simply represents the magnitude of spatial expanse of a frontier orbital outside repulsive molecular surface integrated under specific conditions. Namely, the EFOE density for hydride reduction is defined by *integrated "hole density" of the LUMO*[12] *of the carbonyl carbon above or below the carbonyl plane over the three-dimensional spatial points which satisfy the following criteria*: (1) They must exist outside repulsive molecular surface (exterior region) defined by an assembly of spherical atoms having the van der Waals radii.[18] Only points located within 5 au (2.65 Å) from the molecular surface, where hole density of an MO virtually becomes null, are considered. (2) They are assigned to the carbonyl carbon *only if the absolute total value of the wave functions belonging to the carbonyl carbon makes the maximum contribution to the total value of the LUMO wave function at the point.* This condition is essential since the stereoselectivity should depend on the magnitude of overlap between hydride and the LUMO wave functions due to the carbonyl carbon. *The driving force vector located on the hydride should be maximally directed toward the carbonyl carbon when this condition is satisfied.* It should be noted here that since only spatial points outside molecular surface are taken into account, steric effects upon hydride approach at an early stage of the reaction are implicitly considered to some degree in the EFOE model.

3. Cyclohexanone

The EFOE density values of the LUMO of cyclohexanone (**1**) for the two faces of the carbonyl plane, calculated at various ab initio levels, show that the axial hydride approach is indeed much more favored in agreement with experimental observation (Table 1).

The results obtained at all levels of calculation are consistent and calculation at the RHF/6-31G* level seems satisfactory both in terms of accuracy and the time required for computation. It should be noted here that relative magnitude of the axial and equatorial EFOE density values is independent of the sign of the orbital distortion index (δ) as clearly shown by the calculation at the STO-3G level. An especially notable tendency seen in Table 1 is that the higher the calculation level employed, the higher the axial and equatorial ratio of EFOE values. Thus the highest ax/eq ratio (1.94 / 0.25 = 7.78) or the largest ax/eq difference (1.94 − 0.25 = 1.69) is attained with the RHF/6-31G* level using the structure optimized at the same level. This suggests that some correlation may exist between selectivity of reduction and EFOE density values.

Table 1. EFOE densities for the LUMO of cyclohexanone (**1**) at various ab initio levels of MO calculation.

Basis Sets RHF/	Levels of Structure Optimization : RHF/					
	STO-3G		3-21G		6-31G*	
	EFOE Densities of Cyclohexanone LUMO (%)[a]					
	ax	eq	ax	eq	ax	eq
STO-3G	0.15	0.14	0.14	0.13	0.15	0.11
3-21G	1.35	0.63	1.27	0.57	1.42	0.46
4-31G	1.45	0.44	1.35	0.39	1.54	0.27
6-31G*	1.83	0.45	1.68	0.39	1.94	0.25

[a] ax = axial face of the carbonyl plane; eq = equatorial face of the carbonyl plane. Values of EFOE densities are expressed in % unit.[12]

4. Alkyl-substituted Cyclohexanones

To test whether or not the EFOE density values are correlated with the kinetic parameters of the reduction of the cyclohexanone system, those for various alkyl-substituted cyclohexanones, the activation enthalpies of which have been known, were calculated at the RHF/6-31G*//RHF/6-31G* level and the relationship of these experimental and theoretical parameters were examined. Since it can be assumed based on the frontier orbital theory[5a] that within a series of compounds of similar structure the activation enthalpy for the axial and equatorial attack ($\Delta H^{\ddagger}_{ax}$ and $\Delta H^{\ddagger}_{eq}$, respectively)[10c] should be roughly proportional to the square of the overlap integral between the HOMO of hydride and the LUMO of a ketone (early transition state assumption), one can assume that the square of an EFOE density value on one side of the carbonyl plane should be correlated with the corresponding activation enthalpy. The larger the square of the overlap integral between the frontier orbitals, the lower the activation enthalpy. This suggests that the EFOE density in principle should show some correlation with the experimentally determined enthalpy difference ($\Delta\Delta H^{\ddagger} = \Delta H^{\ddagger}_{eq} - \Delta H^{\ddagger}_{ax}$). It is therefore expected that $\Delta\Delta H^{\ddagger}$ should be proportional to the difference in the square of EFOE density values (EFOE(ax) for axial attack and EFOE(eq) for equatorial one) between the two faces of the carbonyl plane ($\lambda = \mathrm{EFOE(ax)}^2 - \mathrm{EFOE(eq)}^2$). Figure 5 shows a plot of $\Delta\Delta H^{\ddagger}$vs. λ for ten alkyl-substituted cyclohexanones including three sterically highly crowded cyclohexanones, such as 3,3,5-trimethylcyclohexanone ($NaBH_4$ in 2-propanol).[10c] One may recognize a good linear correlation between these two parameters ($r^2 = 0.940$). The observed linear correlation between the EFOE values and the $\Delta\Delta H^{\ddagger}$'s strongly indicates that the stereochemistry of carbonyl reduction in conformationally rigid systems may most probably be dictated chiefly by the spatial extension of the LUMO on two sides of the carbonyl plane of a starting ketone. It is remarkable that the sterically hindered ketone, 3,3,5-trimethylcyclohexanone, shows only marginal deviation, strongly indicating that the EFOE density should contain some steric information as well.

In conclusion, we have shown that the π-facial stereoselectivity of hydride reduction of cyclohexanones can be explained by quantitative analysis of the substrate LUMO. We will show shortly that this new model, the parameter (the EFOE density) of which apparently contains steric information, can also be successfully applied to a variety of other conformationally rigid ketones.

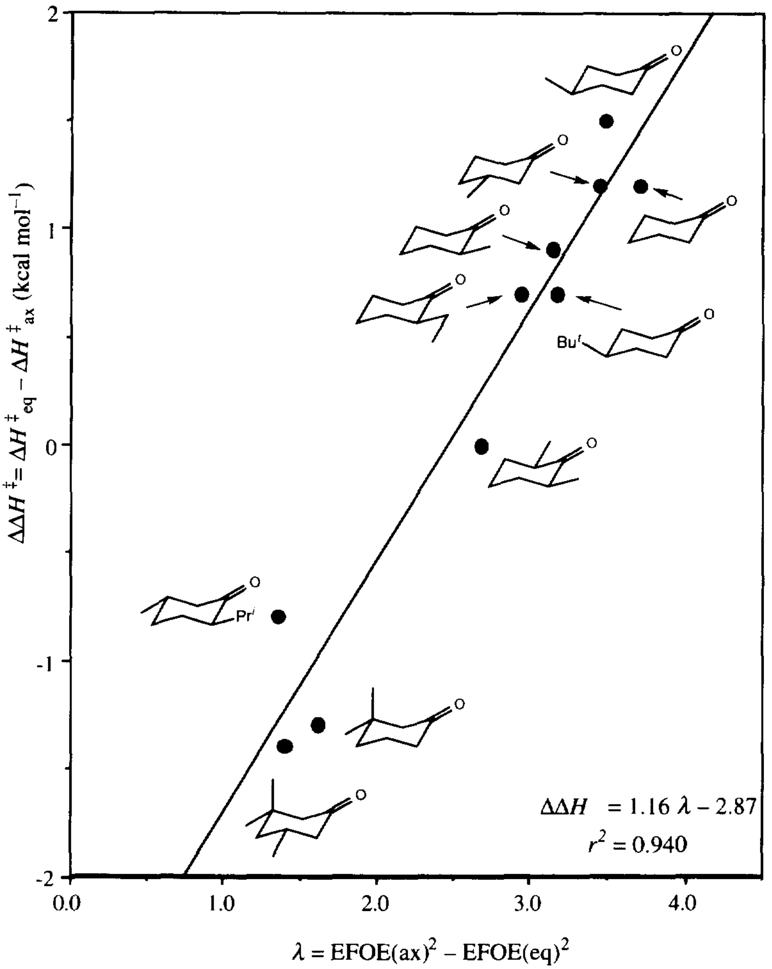


Figure 5. A plot of the difference in square of EFOE densities for axial (EFOE(ax)) and equatorial (EFOE(eq)) areas (λ = EFOE(ax)^2 − EFOE(eq)^2) vs. the difference in the activation enthalpy ($\Delta\Delta H^{\ddagger}$) between those of equatorial ($\Delta H^{\ddagger}_{eq}$) and axial attack ($\Delta H^{\ddagger}_{ax}$) for the reduction of alkyl-substituted cyclohexanones ($NaBH_4$ in 2-propanol).[10c]

Computational Methods

Structure data of molecules were generated with MOMOCON[19] or SPARTAN Ver. 3.0.[20] These were optimized with SPARTAN Ver 3.0 or 4.1, Gaussian 92[21] or 94[22] using the RHF/6-31G* level with Sun SPARCstation 2, Silicon Graphics Indigo, Silicon Graphics Power Indigo2 or HP9000/715. The IBM SP2 computer at the Computer Center of the Institute for Molecular Science was used for computation of transition states.

EFOE densities were computed at the RHF/6-31G* level using our original program based on the three-dimensional lattice method at 0.2 au (0.106 Å) mesh. The carbonyl plane is taken as the plane which include the C=O bond and which is parallel with the line connecting the two α-carbons. The conventional data of Bondi's van der Waals radii were employed for definition of molecular surface: 1.70 Å (C); 1.20 Å (H); 1.52 Å (O).[18]

Perturbational coefficients[14a] were calculated by our original program based on extended Hückel MO method.[15] The extended Hückel parameters employed here are the usual ones. Coulomb integrals and exponents for Slater orbitals are: C-2s (−21.4 eV, 1.625); C-2p (−11.42 eV, 1.625); H-1s (−13.6 eV, 1.3); O-2s (−32.3 eV, 2.275); O-2p (−14.8 eV, 2.275). Resonance integrals were evaluated by the Wolfsburg-Helmholz equation and overlap integrals were computed according to Mulliken's formulae.[16]

MO contour diagram (Figure 1) was produced with MOLDEN 3.1.[23]

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