

and

$$\xi_c = -2\Theta_c/(\Theta_c^2 + 4). \quad (\text{A5})$$

Eq. (A4) is a trivial solution with no external input. If Eq. (A5) is substituted into Eq. (A2), we obtain

$$[(1 + \xi_c \Theta_c)^2 + 4\xi_c^2]^{1/2} = -1. \quad (\text{A6})$$

Since ξ_c and Θ_c are both real, Eq. (A6) is physically meaningless. Therefore, we conclude that Eq. (A5) is not a physically acceptable solution. Hence, there is no Hopf bifurcation curve in the parameter plane because $\text{tr}(J)=0$ is not satisfied physically. Since $\text{tr}(J) \neq 0$ is a continuous function with respect to ξ and Θ , $\text{tr}(J)$ has the same sign on the whole plane of physically acceptable parameter values. Therefore, we can easily determine the sign of $\text{tr}(J)$ by arbitrarily taking the parameter values. For example, $\text{tr}(J) < 0$ when $\Theta = 0$ and $\xi = 1.0$. It is, therefore, concluded that the steady state attained under a constant input is locally stable.

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Theoretical Studies of 1,5-Sigmatropic Rearrangements Involving Group Transfer¹

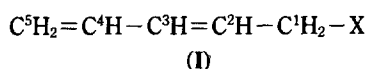
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The 1,5-sigmatropic rearrangements involving group (X) migration in ω -(X)-substituted 1,3-pentadiene, $\text{C}^1\text{H}_2=\text{C}^2\text{H}-\text{C}^3\text{H}=\text{C}^4\text{H}-\text{C}^5\text{H}_2-\text{X}$, where $\text{X}=\text{H}$, CH_3 , BH_2 , NH_2 , OH or F , are investigated MO theoretically using the AM1 method. For the migrating groups without lone pair electrons, $\text{X}=\text{H}$, CH_3 , or BH_2 , the suprafacial pathway is favored, whereas for the migrating groups with lone pair electrons participating in the TS, $\text{X}=\text{NH}_2$, OH , or F , the antarafacial pathway is favored electronically. However excessive steric inhibition in the antarafacial TS for $\text{X}=\text{NH}_2$ leads to subjacent orbital controlled suprafacial process. The antarafacial shift of F is relatively disfavored compared to that of OH due to smaller orbital overlap and larger interfrontier energy gap in the TS.

Introduction

The $[i, j]$ sigmatropic rearrangements² involve variety of processes and have been widely studied experimentally and theoretically. The unifying features of all these reactions are that they are concerted, uncatalyzed and involve a bond migration through a cyclic transition state (TS) in which an atom or a group is simultaneously joined to both termini of a π electron system.³ In the 1,5-sigmatropic rearrangement involving group transfer, a terminal group, X , at C_1 shifts to C_5 in a neutral 1,3-pentadiene system, (I), with σ - π bond interchanges occurring at the both termini, C_1 and C_5 .



However the number of electrons, not the number of atoms, participating in the cyclic TS determines the selection

rules⁴; when $4n+2$ electrons participate, suprafacial migration in thermally allowed, whereas for $4n$ electron systems antarafacial migration is allowed. For example, suprafacial migration of a group X is normally allowed for 6 electron systems involving [1,5]-neutral, [1,6]-cation and [1,4]-anionic rearrangements. In a previous work on the role of lone pairs in 1,3-sigmatropic group rearrangements^{5,6}, however, we have shown that for a migrating group with lone pair electrons (X), the participation of lone pairs in the TS causes an alteration of the selection rule; normally antarafacial-allowed [1,3]-group shift becomes suprafacially allowed [1,5]-group shift when lone pair electrons on the migrating group participate in the TS. In this work, we report on the AM1-MO^{7,8} theoretical studies of sigmatropic rearrangements involving group (X) migrations in the 1,3-pentadiene system, I, using various migrating groups without ($\text{X}=\text{H}$, BH_2 or CH_3) and with ($\text{X}=\text{NH}_2$, OH , or F) lone pair electrons. Here

Table 1. The Heat of Formation, ΔH_f , of Ground (GS) and Transition States (TS) and $\Delta H_f^\ddagger$ in kcal/mol^a

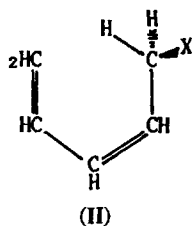
X	GS	TS		$\Delta H_f^\ddagger$	
		A	S	A	S
BH ₂	33.9	52.2	47.7	18.4	13.8
H	22.0	—	60.4	—	37.8
CH ₃	15.0	118.2	98.0	103.2	83.9
NH ₃	25.8	—	57.7	—	31.9
OH	-23.3	22.6	28.8	45.9	52.2
F _v	-26.8	22.2	27.9	49.0	54.9

^aA and S denotes antarafacial and suprafacial processes, respectively.

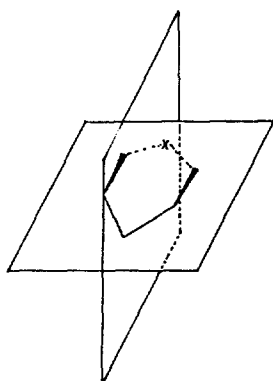
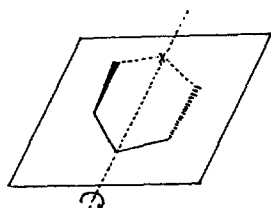
again we confirm that participation of the lone pair on X in the TS alters the selection rule from that for 6 ($4n+2$) electron systems to that for 8 ($4n$) electron systems involving [1,7]-type sigmatropic shifts.

Calculations

The semiempirical AM1 MO method⁷ was used throughout in this work. The reactant structure in which a gauche CH₂X fragment is attached to the *cis*-1,3-butadiene fragment, II, was adopted after full geometry optimization. Two TS struc-



tures corresponding to suprafacial and antarafacial pathways were considered. The suprafacial TS has a C_s symmetry, (III), whereas the antarafacial TS has a C₂ symmetry, (IV). The TS was characterized by confirming only one negative eigenvalue in the Hessian matrix.⁹

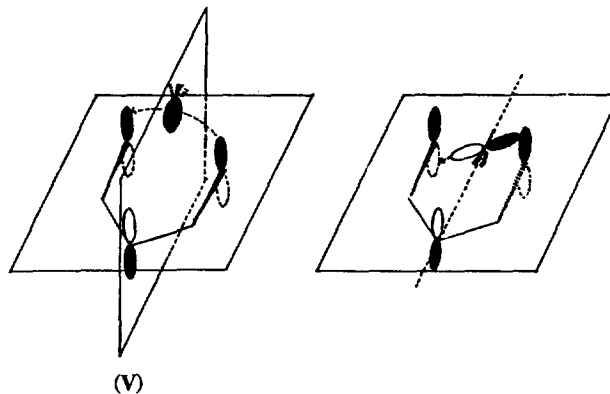
C_s symmetry TSC₂ symmetry TS

Results and Discussions

X=H. Sigmatropic [1,5]-hydrogen shift has been studied extensively both experimentally and theoretically.^{3,10} Since

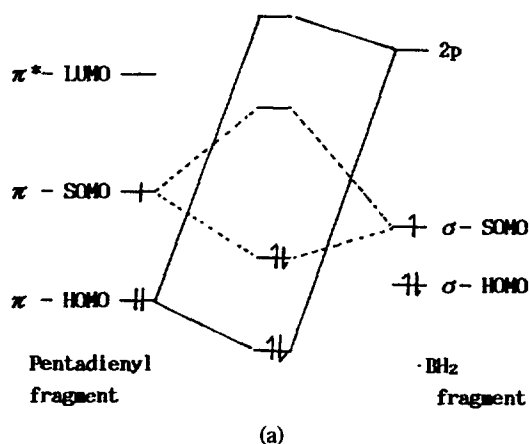
the hydrogen atom has only 1s valence orbital the frontier MO (FMO) pattern¹¹ for the TS is relatively simple. In accordance with the selection rules for thermal reactions, MINDO/3 as well as *ab initio* at MP2/6-31G* level calculations gave suprafacially allowed TS with C_s symmetry.^{12,13} In this work, we therefore determined the energy and structure of the suprafacial TS only. The activation enthalpy, $\Delta H^\ddagger$, of 37.8 kcal/mol for this reaction by AM1 (Table 1) is thus in good agreement with the experimental results of $\Delta H^\ddagger = 35.2 \pm 2.2$ kcal/mol (at $T=200^\circ\text{C}$).¹⁴ In fact our $\Delta H^\ddagger$ value is in better agreement with experiment than the low level *ab initio* results of 43.6 kcal/mol at 3-21G level and 62 kcal/mol at STO-3G level as well as the MINDO/3 result of 48.1 kcal/mol.¹⁵ The $\Delta H^\ddagger$ value within experimental uncertainty was reported by Jensen and Houk¹³ using higher level basis sets including correlation energy, RMP4(SDTQ)/6-31G**/RMP2/6-31G*.

X=CH₃. For this migrating group, the activation enthalpy is higher by ca. 20 kcal/mol compared with the hydrogen shift (X=H). Direct comparison with the experimental value is not possible due to paucity of experimental data, but the methyl group migration has considerably higher activation barrier than other group shifts in Table 1. For the methyl group shift the suprafacial pathway with C_s symmetry is again more favorable (by ca. 19.3 kcal/mol) than the antarafacial process with C₂ symmetry. This is in accord with the selection rule for thermal [1,5]-neutral sigmatropic shifts. According to the FMO theory, in the suprafacial TS, the singly occupied MO (SOMO) of the pentadienyl radical interacts with an sp³-hybridized (CH₃) σ -orbital, (V), whereas in the antarafacial TS the SOMO interacts with an sp²-hybridized (CH₃) 2p-orbital, (VI). Obviously, in the former process configuration is retained, while in the latter it is inverted.

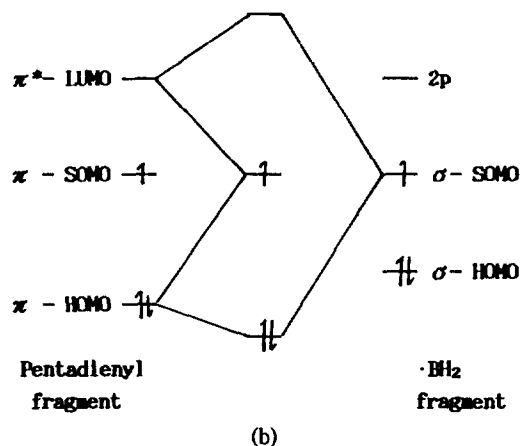


Since the sp³- σ orbital lies lower than the 2p orbital, the suprafacial TS becomes more stabilized in the orbital interaction with the pentadienyl system. Moreover, in the suprafacial TS with C_s symmetry, three hydrogen atoms in the CH₃ group point away from the pentadienyl frame, while in the antarafacial TS with C₂ symmetry one hydrogen atom points toward the pentadienyl frame; thus steric repulsion is relatively large in the coplanar (heavy atoms) antarafacial TS compared with the non-coplanar (heavy atoms) suprafacial process. The suprafacial process therefore has more favorable orbital as well as steric interaction.

X=BH₂. For this migrating group, X=BH₂, the activation barrier is relatively lower than that for X=H or CH₃



The lines — and — are for interactions leading to the TS (VII) and (VIII), respectively.

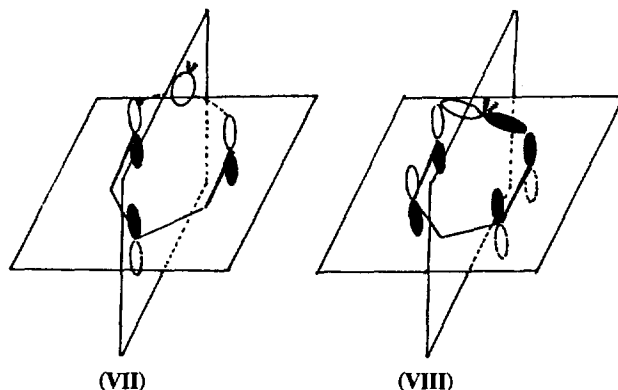


This interaction leads to the TSs (IX).

Figure 1. FMO interaction schemes in supra- (a) and antarafacial (b) 1,5- BH_2 shifts.

due to a low lying vacant $2p$ orbital in the B atom. In the thermally allowed suprafacial TS, (VII), the two singly occupied MOs(SOMOs) of the pentadienyl (π) and BH_2 (sp^2 hy-

bridized σ on B) fragments overlap in-phase with C_s symmetry, which is quite similar to the corresponding for TS for $\text{X}=\text{CH}_3$, (V). However, the empty $2p$ orbital of the B atom can also interact with the highest occupied MO(HOMO) of the pentadienyl fragment in the TS again with C_s symmetry, (VIII). This secondary interaction is particularly effective in rendering additional stabilization to the suprafacial TS owing to large orbital overlap, (VIII), (Figure 1a). On the



other hand, in the thermally forbidden antarafacial TS, the interaction between sp^2 - σ of BH_2 and bonding π pentadienyl orbital, which overlap in-phase, restabilizes one electron in the former and stabilizes two electrons in the latter. In this so-called "subjacent orbital control"¹⁶ interaction, (IX), the odd electron is restabilized in a compensating manner and the energy of the atomic σ orbital of B remains unchanged

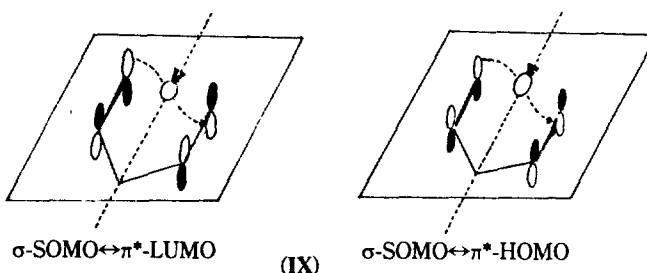


Table 2. Geometries of the Ground States (GS) and Transition state (TS) (Bond Lengths and Angles are in Å and Degrees Respectively)^a

X	BH_2			CH_3			H	
	GS	A-TS	S-TS	GS	A-TS	S-TS	GS	S-TS
$d(\text{C}^1\text{-C}^2)$	1.336	1.443	1.437	1.335	1.392	1.389	1.335	1.408
$d(\text{C}^2\text{-C}^3)$	1.449	1.390	1.392	1.450	1.394	1.388	1.444	1.392
$d(\text{C}^3\text{-C}^4)$	1.340	1.390	1.392	1.338	1.394	1.388	1.341	1.392
$d(\text{C}^4\text{-C}^5)$	1.475	1.443	1.437	1.482	1.392	1.389	1.472	1.408
$d(\text{C}^5\text{-X})$	1.538	1.636	1.658	1.510	2.175	2.416	1.119	1.417
$\angle \text{C}^1\text{C}^2\text{C}^3$	123.2	121.3	122.5	123.2	126.9	124.3	128.2	121.6
$\angle \text{C}^2\text{C}^3\text{C}^4$	126.1	119.9	119.6	125.9	130.1	122.1	129.6	119.8
$\angle \text{C}^3\text{C}^4\text{C}^5$	126.7	121.3	122.5	126.4	126.9	124.3	127.5	121.6
$\angle \text{C}^4\text{C}^5\text{X}$	116.3	113.1	109.5	111.5	99.9	103.0	110.8	101.5
$\angle \text{C}^1\text{C}^2\text{C}^3\text{C}^4$	-167.7	22.1	14.2	-153.2	-28.8	-12.4	0.0	15.6
$\angle \text{C}^2\text{C}^3\text{C}^4\text{C}^5$	-0.3	22.1	-14.2	0.4	36.3	12.4	0.0	-15.6
$\angle \text{C}^3\text{C}^4\text{C}^5\text{X}$	-110.6	-40.0	39.9	-113.3	-49.9	-19.4	59.9	30.8

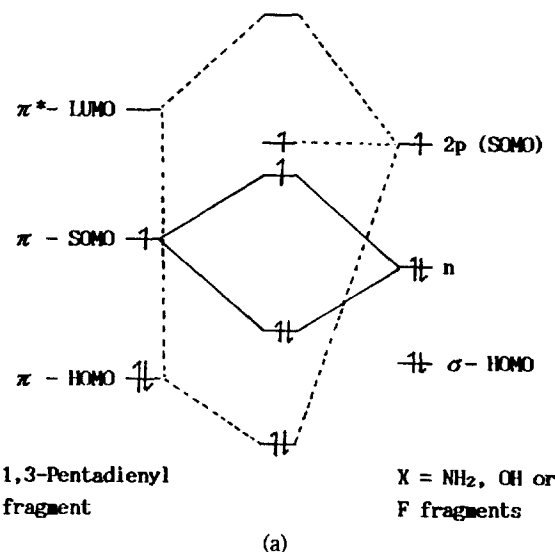
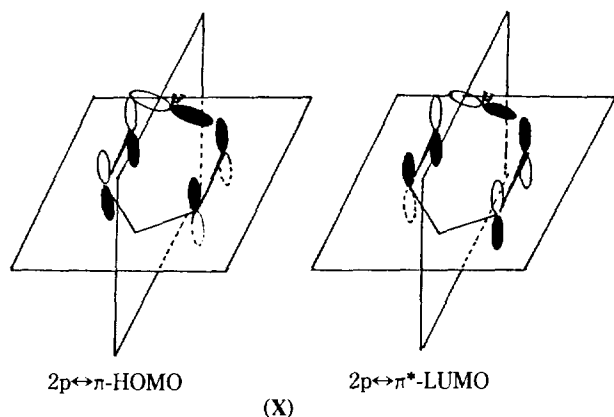
^aA and S represent antarafacial and suprafacial processes, respectively.

Table 3. Charge Densities for Reactants and Transition States (in electron unit)^a

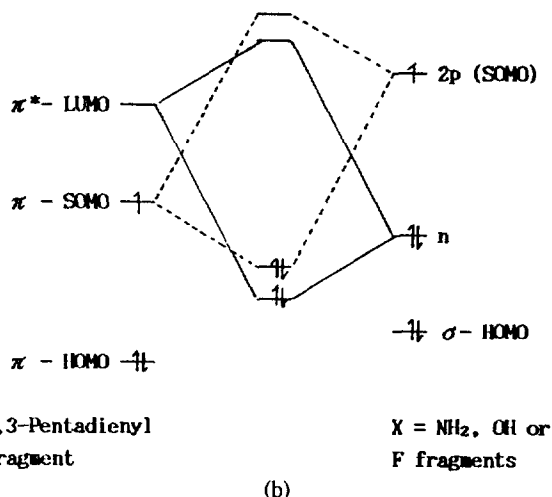
X	Suprafacial					
	C ¹	C ²	C ³	C ⁴	C ⁵	X
BH ₂	GS +0.011	-0.012	-0.031	-0.010	-0.003	+0.045
	A-TS -0.005	+0.286	-0.189	+0.286	-0.005	-0.373
	S-TS -0.023	+0.281	-0.173	+0.281	-0.023	-0.343
CH ₃	GS +0.011	-0.010	-0.023	-0.030	+0.026	+0.016
	A-TS +0.025	-0.056	-0.026	-0.056	+0.025	+0.087
	S-TS +0.052	-0.060	+0.004	-0.060	+0.025	+0.013
H	GS +0.012	-0.013	-0.029	-0.029	-0.017	+0.077
	A-TS —	—	—	—	—	—
	S-TS -0.037	-0.022	-0.031	-0.022	-0.037	+0.150

^aA and S represent antarafacial and supra-facial processes, respectively.

(Figure 1b), while there occurs a net stabilization of a bonding electron pair in the π -HOMO. This effect is often sufficient to make the symmetry-forbidden pathway predominate over the symmetry-allowed path which is sterically hindered, e.g., 1,3-sigmatropic shift of a CH₃ group. However in the present case of 1,5-sigmatropic BH₂ shift, the allowed, supra-facial, pathway is much more stabilizing compared to the forbidden, antarafacial, subadjacent orbital control pathway as the results of $\Delta H^\ddagger$ in Table 1 indicate; although the latter is forbidden and unfavorable compared to the former it also has a relatively low activation barrier due to relatively small steric hindrance by two hydrogen atoms attached to boron. In the antarafacial TS, there is another type of symmetry allowed secondary interaction involving the empty $2p$ in B and the π -SOMO of pentadienyl. This is a two orbital-one-electron interaction, and hence the stabilizing effect is again relatively small. In Tables 2 and 3, we have collected geometrical parameters and positional group charge densities, respectively, of the reactants and TSs for X=H, CH₃ and BH₂. We note in Table 3 that for X=BH₂ the electron density increases from the ground state to the TS in the migrating BH₂ group due to the charge transfer into the vacant $2p$ in B. This is in contrast to the charge density decrease in the migrating H and CH₃ groups, in which no low lying vacant symmetry allowed orbitals are available.



The lines — and — are for interactions leading to the TS (X) and (XI), respectively.



The lines — and — are for interactions leading to the TS (XII) and (XIII), respectively.

Figure 2. FMO interaction schemes in supra- (a) and antarafacial (b) 1,5-group (X) shifts for X=NH₂, OH or F.

X=NH₂, OH and F. In these three migrating groups, 1-3 lone pairs are present in addition to a singly occupied $2p$ AO in heavy atom; consequently the FMO interaction schemes. Figure 2, are very similar except that orbitals in the migrating groups lie at somewhat different levels and the number of nonbonding orbitals (n) increases from one to three as the heavy atom changes from the group V element (N) to the group VII element (F). In the supra-facial orbital interactions, Figure 2a, there are two major stabilizing contribution: (i) A 'subadjacent orbital control' type between the SOMOs, (X), and (ii) a two-orbital-three-electron type interaction between the SOMO of the 1,3-pentadienyl fragment and the lone pair orbital (n) of the migrating group (XI). Both of these interactions have a relatively low stabilizing effect; in the former the interfrontier level gap, $\Delta\epsilon$, is large so that charge transfer stabilization E_{ct} in Eq. (1),¹⁷ is small, whereas in the latter one electron occupies antibonding level

Table 4. The FMO levels and interfrontier energy gaps, $\Delta\epsilon$, in eV

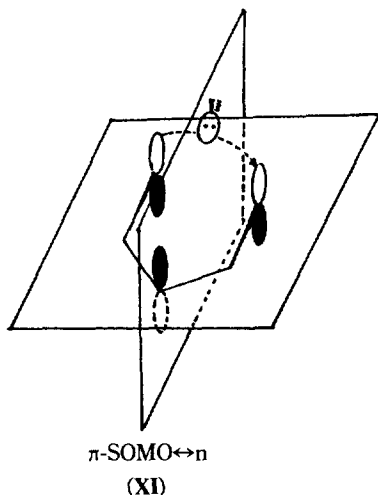
X	L ^a	2p	π -HOMO	π^* -LUMO	$\Delta\epsilon_1^b$	$\delta\epsilon_2^c$
NH ₂	-9.8945	3.4875	-9.0981	0.3396	10.2341	12.5856
OH	-11.1197	3.4030	-9.2106	0.3295	11.4492	12.6136
F	-12.6963	3.3890	-9.4003	0.1653	12.8616	12.7893

^a Lone pair orbital (n). ^b $\Delta\epsilon_1 = \pi^*\text{-LUMO} - n(X)$. ^c $\Delta\epsilon_2 = 2p(X) - \pi\text{-HOMO}$.

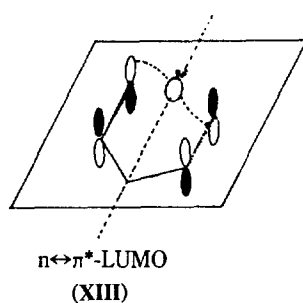
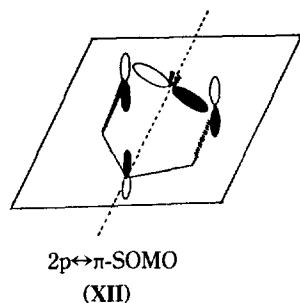
so that it is destabilizing.

$$E_{\alpha} \approx \frac{H_{ij}^2}{\Delta\epsilon} \quad (1)$$

where H_{ij} is an orbital interaction matrix element between MOs i and j , the size of which is proportional to the overlap between the two MOs.



On the other hand, in the antarafacial orbital interactions, Figure 2b, there are two types of two-orbital-two-electron interaction, both of which are strongly stabilizing; (i) A SOMO-SOMO interaction between the two fragments, (XII), and (ii) an interaction between the lone pair (n) of the migrating group and the π^* -LUMO of the 1,3-pentadienyl fragment, (XIII). Thus for these migrating groups with lone pair



orbitals, (X=NH₂, OH or F), the orbital interactions in the TS favor antarafacial shifts. This conclusion is in agreement with our previous MO theoretical results on the 1,3-sigmatropic shifts of migrating groups with lone pairs (n). In effect, the involvement of a lone pair in the [1, n]-X shifts causes to alter [1, $n+2$]-X shifts when a lone pair electrons in

Table 5. Charge Densities for Reactants (GS) and Transition States (TS) (in Electron unit)^a

X		C ¹	C ²	C ³	C ⁴	C ⁵	X
NH ₂	GS	+0.018	-0.016	-0.024	-0.016	+0.095	-0.057
	A-TS	—	—	—	—	—	—
	S-TS	+0.173	-0.441	+0.179	-0.441	+0.173	+0.359
OH	GS	+0.021	-0.021	-0.018	-0.003	+0.148	-0.127
	A-TS	+0.200	-0.223	+0.090	-0.223	+0.200	-0.045
	S-TS	+0.298	-0.454	+0.200	-0.454	+0.200	+0.113
F	GS	+0.032	-0.025	+0.002	-0.052	+0.217	-0.174
	A-TS	+0.287	-0.367	+0.160	+0.287	-0.367	+0.003
	S-TS	+0.322	-0.442	+0.204	-0.442	+0.322	+0.035

^a A and S represent antarafacial and suprafacial processes, respectively.

the non-bonding orbital of the migrating group, X, participate in the TS. Thus the thermally allowed selection rule for these systems with X=NH₂, OH or F belongs to a [1, 7]-sigmatropic shift type for which the antarafacial pathway is allowed. However we have so far considered only the orbital interaction aspect. There are an additional factor to be considered in determining the actual reaction pathway, i.e., the steric effect in the TS. As it has been noted before, in the antarafacial TS, the steric congestion does become important due to the coplanar C₂ symmetry, especially when there are hydrogen atoms present in the migrating group, X. The X=NH₂ group is indeed an example of such cases, and as a result for this group the normally forbidden (for 1,7-sigmatropic thermal shift) suprafacial pathway (a subjacent orbital control) becomes more favored. In fact we failed to determine the antarafacial TS for this migrating group. Out of the two groups (X=OH and F) which proceed by the antarafacially allowed pathways, the migrating group OH has lower activation enthalpy, $\Delta H^\ddagger$, by ca. 3 kcal/mol than the migrating group F, probably due to (i) a smaller size of the atom F resulting in an ineffective orbital overlap, i.e., smaller H_{ij} , value in Eq. (1), and (ii) a large interfrontier level gap, $\Delta\epsilon$ in Eq. (1), as shown in Table 4. Geometrical parameters and positional group charge densities of the reactants and TSs for X=NH₂, OH and F are given in Tables 5 and 6, respectively.

We conclude that for the migrating groups, H, CH₃ and BH₂ the suprafacial 1,5-shift is favored in accordance with the selection rule for thermal sigmatropic rearrangement, but for the migrating groups with lone pair electrons, NH₂, OH and F, the antarafacial shift is favored electronically indicating that these groups follow thermally allowed 1,7-shift due to participation of a lone pair electrons in the TS. For the NH₂ group, however, excessive steric inhibition in the allowed antarafacial TS leads to subjacent orbital controlled suprafacial process. The TS for F shift has lower stabilization energy, and hence higher activation barrier, than that for migration of OH due to smaller orbital overlap and larger interfrontier energy gap, both factors leading to unfavorable charge transfer stabilization, (Eq. (1)).

Table 6. Geometries of the Ground States (GS) and Transition State (TS) (Bond Lengths and Angles are in Å and Degrees Respectively)^a

X	NH ₂		OH			F		
	GS	S-TS	GS	A-TS	S-TS	GS	A-TS	S-TS
d(C ¹ -C ²)	1.335	1.468	1.335	1.436	1.449	1.335	1.452	1.458
d(C ² -C ³)	1.449	1.380	1.450	1.389	1.382	1.451	1.383	1.378
d(C ³ -C ⁴)	1.340	1.380	1.339	1.389	1.382	1.338	1.383	1.378
d(C ⁴ -C ⁵)	1.494	1.468	1.487	1.436	1.449	1.495	1.452	1.458
d(C ⁵ -X)	1.446	1.515	1.422	1.552	1.544	1.383	1.481	1.467
<C ¹ C ² C ³	123.3	119.8	123.4	118.3	120.0	123.4	120.0	116.9
<C ² C ³ C ⁴	125.4	122.4	124.8	117.9	122.4	124.6	120.6	122.6
<C ³ C ⁴ C ⁵	124.0	119.8	124.2	118.3	120.0	123.8	120.0	116.9
<C ⁴ C ⁵ X	113.9	110.6	107.6	108.2	108.6	112.3	108.7	110.9
<C ¹ C ² C ³ C ⁴	179.4	-5.1	163.4	27.1	-6.5	-157.2	18.1	-21.9
<C ² C ³ C ⁴ C ⁵	0.5	5.1	-0.3	27.1	6.5	-0.5	18.1	4.2
<C ³ C ⁴ C ⁵ X	-170.8	-30.9	179.8	-47.2	-33.8	178.6	-26.4	-4.2

^aA and S denotes antara- and supra-facial processes, respectively.

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