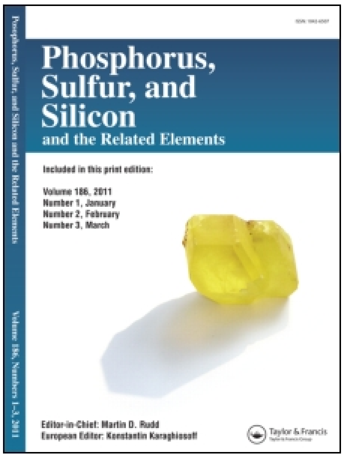

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Stereoelectronic Effects on the Conformational Properties of 1,3-Dioxane, 1,3-Dithiane, and 1,3-Diselenane: An Ab Initio Study and NBO Analysis

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Stereoelectronic Effects on the Conformational Properties of 1,3-Dioxane, 1,3-Dithiane, and 1,3-Diselenane: An Ab Initio Study and NBO Analysis

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NBO analysis, density functional theory (DFT: B3LYP/6-31G//B3LYP/6-31G*) and ab initio molecular orbital (MO: MP2/6-31G*//B3LYP/6-31G*) based methods were used to study the stereoeletronic effects on the conformational properties of 1,3-dioxane (**1**), 1,3-dithiane (**2**) and 1,3-diselenane (**3**). The obtained B3LYP/6-31G*//B3LYP/6-31G* and MP2/6-31G*//B3LYP/6-31G* results show that the ring flipping barrier heights [via rotation about C—M bond, (M = O (**1**), M = S (**2**) and M = Se (**3**))] decrease from compound **1** to compound **3**.*

*Based on the optimized ground state geometries using B3LYP/6-31G** method, the NBO analysis of donor-acceptor (bond-antibond) interactions revealed that the stabilization energies associated with the electronic delocalization from the equatorial non-bonding Lone Pair orbitals [LP(e)$_{M1}$] to σ^*_{C2-M3} antibonding orbitals, decrease form **1** to **3**. The LP(e)$_{M1}$ → σ^*_{C2-M3} resonance energies for compounds **1–3** are 12.66, 6.73 and 5.33 kcal mol^{-1}, respectively. The LP(e)$_{M1}$ → σ^*_{C2-M3} delocalizations could fairly explain the decrease of occupancies of LP(e)$_{M1}$ non-bonding orbitals and the increase of occupancies of σ^*_{C2-M3} anti-bonding orbitals, from compound **1** to **3**. The electronic delocalization from LP(e)$_{M1}$ non-bonding orbitals to σ^*_{C2-M3} anti-bonding orbitals increase the ground state structure stability, therefore, the decrease of LP(e)$_{M1}$ → σ^*_{C2-M3} delocalizations could fairly explain the easiness of ring flipping processes from compound **1** to **3**.*

Keywords Ab initio; molecular modeling; NBO; 1,3-dioxane; 1,3-dithiane; 1,3-diselenane

INTRODUCTION

Conformational equilibria in alicyclic molecules have been studied in the past several years. Theoretical treatments of cycloalkanes have also

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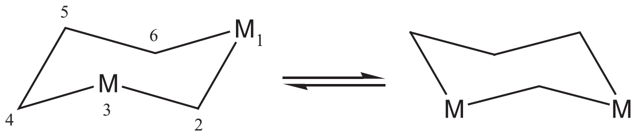

[Numbering used for compounds **1**–**3** (**1**: M=O; **2**: M=S and **3**: M=Se)]

SCHEME 1 Schematic representation of ring flipping process for compounds 1–3. [Numbering used for compounds **1–3 (1:** M = **O; 2:** M = S and **3**: M = Se).]

provided values in reasonable agreement with experimental.[1–5] Contrary to the abundance of information in the cyclohexane area, there has been a paucity of data concerned with conformational properties in heterocyclic systems.[6–8] The knowledge about conformational properties of heterocyclic compounds should be of very general interest since saturated heterocyclic compounds comprise a large segment of organic and inorganic chemistry and are quite widespread in nature, e.g., in alkaloids, carbohydrates, and plant growth regulators, among other compounds.

Microwave spectroscopy,[9] gas electron diffraction data[10] and vibrational spectroscopic studies[11] were consistent with the chair conformation of 1,3-dioxane. Although, there are very few detailed experimental and theoretical studies in mono hetero systems; however, it has been estimated from experimental studies on substituted 1,3-dioxanes that the twist form of 1,3-dioxane is of higher energy relative to its chair than in cyclohexane.[12–18] A wide range of ΔG°_{c-t} values (2-9 kcal mol^{1}) derived from studies on substituted 1,3-dioxanes has been reported for 1,3-dioxane.[13–19]

There is no experimental or theoretical published data about the donor-acceptor delocalization effects on the conformational properties of compounds **1–3**. In this work, the structural properties and the dynamic behaviors of compounds **1–3** were investigated computationally using both ab initio MO and DFT methods (see Scheme 1).[20–24]

Also, the stabilization energies (E_2) associated with $\mathrm{LP(e)}_{\mathrm{M1}} \rightarrow \sigma^*_{\mathrm{C2-M3}}$ delocalizations (see Figures 1–3) and their influences on the dynamic behavior of compounds **1–3** were quantitatively investigated by the NBO (Natural Bond Orbital) analysis.[25,26] The successful application of density functional theory (DFT) based methods broadened the applicability of the computational methods and now represents an interesting approach for determining activation barrier and molecular energies.[21–24] On the other hand, the B3LYP method combines Becke's three-parameter exchange function with the

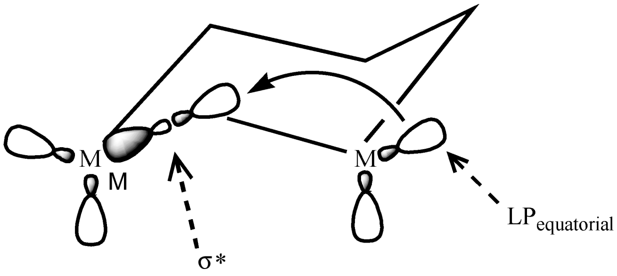

FIGURE 1 Schematic representation of delocalization from LP$_{\text{equatorial}}$ non bonding to σ^* antibonding orbitals in compounds **1–3**.

correlation function of Lee et al.[21,22] Also, NBO (natural bond orbital) analysis was used to investigate the nature of the bonds and resonance energies in compounds 1–3.[25,26]

Computational Details

Ab initio calculations were carried out using MP2/3-21G*//B3LYP/6-31G* and B3LYP/6-31G*//B3LYP/6-31G* levels of theory with the GAUSSIAN 98 package of programs[13] implemented on a Pentium–PC computer with 1.7 GHz processor.

Initial estimation of the structural geometries of the compounds **1–3** was obtained by a molecular mechanic program PCMODEL (88.0)[27] and for further optimization of geometries, PM3 method of MOPAC 7.0 computer program was used.[28,29] GAUSSIAN 98 program was

$$\mathbf{1}:\Delta E^{\ddagger}\ (\text{kcal mol}^{-1}) = \begin{cases} 9.30\ (\text{B3LYP}) \\ 10.57\ (\text{MP2}) \end{cases} \qquad \mathbf{1}:\Delta E\ (\text{kcal mol}^{-1}) = \begin{cases} 5.86\ (\text{B3LYP}) \\ 6.06\ (\text{MP2}) \end{cases}$$

$$\mathbf{2}:\Delta E^{\ddagger}\ (\text{kcal mol}^{-1}) = \begin{cases} 9.28\ (\text{B3LYP}) \\ 9.76\ (\text{MP2}) \end{cases} \qquad \mathbf{2}:\Delta E\ (\text{kcal mol}^{-1}) = \begin{cases} 4.61\ (\text{B3LYP}) \\ 3.28\ (\text{MP2}) \end{cases}$$

$$\mathbf{3}:\Delta E^{\ddagger}\ (\text{kcal mol}^{-1}) = \begin{cases} 8.19\ (\text{B3LYP}) \\ 9.28\ (\text{MP2}) \end{cases} \qquad \mathbf{3}:\Delta E\ (\text{kcal mol}^{-1}) = \begin{cases} 3.35\ (\text{B3LYP}) \\ 3.02\ (\text{MP2}) \end{cases}$$

FIGURE 2 Schematic representation of stabilization energy (resonance energy) (E_2) from donor (LP$_{\text{equatorial}}$) to acceptor (σ^*) for bonding and antibonding orbitals.

finally used to perform ab initio calculations at the B3LYP/6-31G** level. Energy minimum molecular geometries were located by minimizing energy, with respect to all geometrical coordinates without imposing any symmetrical constraints. The nature of the stationary points for compounds **1–3** has been fixed by means of the number of imaginary frequencies. For minimum state structures, only real frequency values, and in the transition-state, only single imaginary frequency value was accepted.[30,31] The structures of the molecular transition state geometries were located using the optimized geometries of the equilibrium molecular structures according to the Dewar et al procedure (keyword SADDLE).[32] These geometry structures were reoptimized by TS subroutine at the B3LYP/6-31G** level. The vibrational frequencies of ground states and transition states were calculated by FREQ subroutine.

NBO analysis was then performed using B3LYP/3-21G* level by the NBO 3.1 program[25,26] included in GAUSSIAN 98 package of programs.

The bonding and antibonding orbital occupancies in the ground state structures of compounds **1–3**, and also the stabilization energies associated with $\mathrm{LP(e)_{M1}} \rightarrow \sigma^*_{\mathrm{C2-M3}}$ delocalizations were calculated using NBO analysis. In the NBO analysis[25,26] the electronic wavefunctions are interpreted in terms of a set of occupied Lewis and a set of unoccupied non-Lewis localized orbitals. The delocalization effects (or donor–acceptor charge transfers) can be estimated from the presence of off-diagonal elements of the Fock matrix in the NBO basis. The NBO program searches for an optimal natural Lewis structure,which has the maximum occupancy of its occupied NBOs, and in general agrees with the pattern of bonds and lone pairs of the standard structural Lewis formula. Therefore, the new orbitals are more stable than pure Lewis orbitals, stabilizing the wave function and giving a set of molecular orbitals equivalent to canonical molecular orbitals.

RESULTS AND DISCUSSION

Corrected zero point (ZPE^c) and total electronic (E_{el}) energies ($E_o = E_{\mathrm{el}} + ZPE$) for ground and transition state geometries of compounds **1** and **4**, as calculated by the density functional theory B3LYP/6-31G* level of theory are given in Table I. For single-point energy calculations, ab initio molecular orbital (MP2/6-31G*//B3LYP/6-31G*) method was used (see Table I).

MP2/6-31G*//B3LYP/6-31G* results showed that the energy barriers of ring flipping (Chair→Twist-Boat) processes in compounds **1–3** are 10.57, 9.76, and 9.28 kcal mol^{-1}, respectively. Also, the energy barrier

TABLE I B3LYP/6-31G*//B3LYP/6-31G* and MP2/6-31G*//B3LYP/6-31G* Calculated Total Energies *E*, Zero-Point Energies *ZPE* (from HF/6-31G* level), and Relative Energies Δ*E* (E_h, in Hartree), for the Energy-Minimum and Energy-Maximum Geometries of Compounds 1–3

Method	B3LYP/6-31G*// B3LYP/6-31G*				MP2/6-31G*//B3LYP/6-31G*		
Geometry	ZPE^c	E_{el}	E_0	ΔE_0^a	E_{ele}	E_0	ΔE_0
1-C	0.121076	–307.666288	–307.545212	0.000000 (0.000000)[b]	–306.702483	–306.581407	0.000000 (0.000000)[b]
1-TB	0.120652	–307.656522	–307.535870	0.009342 (5.862198)[b]	–306.692409	–306.571757	0.009650 (6.0554715)[b]
[**1**-C→**1**-TB]‡	0.120225	–307.650617	–307.530392	0.014820 (9.299698)[b]	–306.684789	–306.564564	0.016843 (10.569150)[b] (9.9 ± 0.2)[d]
2-C	0.113801	–953.621624	–953.507823	0.000000 (0.000000)[b]	–951.917146	–951.801069	0.000000 (0.000000)[b]
2-TB	0.113786	–953.614262	–953.500476	0.007347 (4.610315)[b]	–951.909618	–951.795832	0.005237 (3.286269)[b]
[**2**-C→**2**-TB]‡	0.113530	–953.606564	–953.493034	0.014789 (9.280245)[b]	–951.899040	–951.785510	0.015559 (9.763428)[b]
3-C	0.110949	–4956.003804	–4955.892855	0.000000 (0.000000)[b]	–4952.030614	–4951.919665	0.000000 (0.000000)[b]
3-TB	0.110998	–4955.998509	–4955.887511	0.005344 (3.353413)[b]	–4952.025849	–4951.914851	0.004814 (3.020833)[b]
[**3**-C→**3**-TB]‡	0.110930	–4955.990712	–4955.879809	0.013046 (8.186495)[b]	–4952.015803	–4951.9048873	0.014792 (9.282127)[b]

[a] Relative to the ground state; [b] numbers in parenthesis are the corresponding Δ*E* values in kcal mol^{-1}. [c] corrected by multiplying by a scaling factor (0.9804); and [d] experimental value [see Refs. 19,33]

TABLE II NBO Calculated σ Bonding Orbitals, σ^* Anti-Bonding Orbitals, Lone Pairs Occupancies, and the Stabilization Energies Associated with the LP(e) $_{\mathrm{M1}} \rightarrow \sigma^*_{\mathrm{C2-M3}}$ Delocalization, Based on B3LYP/6-31G* Optimized Energy-Minimum Geometries of Compounds 1–3

Compound	**1**	**2**	**3**
State	C	C	C
Occupancies			
$\sigma^*_{\mathrm{C2-M1}}$	0.04947	0.04145	0.03515
$\sigma^*_{\mathrm{C2-M3}}$	0.04947	0.04145	0.03815
LP(e) $_{\mathrm{M1}}$	1.90479	1.92481	1.93714
LP(e) $_{\mathrm{M3}}$	1.90479	1.92481	1.93713
Stabilization energies (donor→acceptor)			
LP(e) $_{\mathrm{M1}} \rightarrow \sigma^*_{\mathrm{C2-M3}}$	12.66	6.73	5.33
LP(e) $_{\mathrm{M3}} \rightarrow \sigma^*_{\mathrm{M1-C2}}$	12.66	6.73	5.33

of ring flipping (Chair→Twist-Boat) processes in compounds **1–3** are 9.30, 9.28, and 8.15 kcal mol^{-1}, respectively, as calculated by B3LYP/6-31G*//B3LYP/6-31G* level of theory. These results revealed that the ring flipping (Chair→Twist-Boat) processes energy barriers decrease from **1** to **3**.

It has to be noted that the MP2/6-31G*//B3LYP/6-31G* and B3LYP/6-31G*//B3LYP/6-31G* calculated energy barriers of ring flipping (Chair→Twist-Boat) processes for compound 1 is in excellent agreement with the experimentally determined value of 9.9 ± 0.2 kcal mol^{-1}.[33]

Based on the B3LYP/6-31G* optimized ground state geometries, the NBO analysis of donor-acceptor interactions showed that in compounds **1–3**, the stabilization energies associated with the electronic delocalization from the equatorial non-bonding Lone Pair orbitals (LP(e)$_{\mathrm{M1}}$) to $\sigma^*_{\mathrm{C2-M3}}$ antibonding orbitals decreased from compound **1** to compound **3** (see Table II). NBO results show that the LP(e)$_{\mathrm{M1}} \rightarrow \sigma^*_{\mathrm{C2-M3}}$ resonance energies for compounds **1–3** are 12.66, 6.73, and 5.33 kcal mol^{-1}, respectively. As we expected, the NBO results show that the LP(e)$_{\mathrm{M1}} \rightarrow \sigma^*_{\mathrm{C2-M3}}$ resonance energies in the ground state structures of compounds **1–3** were more than the LP(a)$_{\mathrm{M1}} \rightarrow \sigma^*_{\mathrm{C2-M3}}$ delocalizations.

Also, the LP(e)$_{\mathrm{M1}} \rightarrow \sigma^*_{\mathrm{C2-M3}}$ delocalizations could fairly explain the decrease of LP(e)$_{\mathrm{M1}}$ non-bonding orbitals occupancies, as well as the increase of the $\sigma^*_{\mathrm{C2-M3}}$ anti-bonding orbitals occupancies, from **1** to **3**. NBO results show that in compounds **1–3**, the occupancies of LP(e)$_{\mathrm{M1}}$

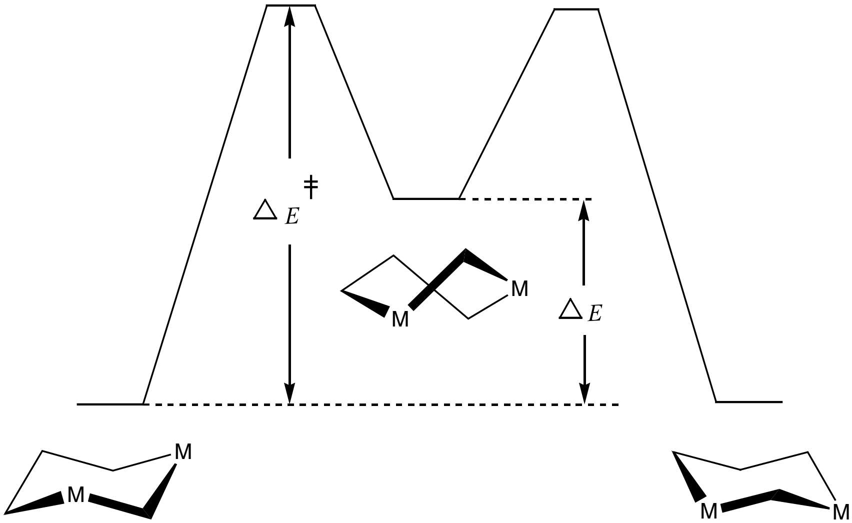

FIGURE 3 Calculated energy profile of ring-flipping process for compounds **1–3** (**1**: M = O; **2**: M = S and **3**: M = Se).

non-bonding orbitals are 1.90479, 1.92481, and 1.93714, and also the occupancies of $\sigma^*{}_{\mathrm{C2-M3}}$ anti-bonding orbitals are 0.04947, 0.04145, and 0.03815, respectively (see Table II).

The more $\mathrm{LP(e)_{M1}} \rightarrow \sigma^*{}_{\mathrm{C2-M3}}$ stabilization energy could increase the ground state structure stability. Based on this argument, it could be expected that the ring flipping (Chair→Twist-Boat) processes energy barriers (ΔE_o) should be decreased from compound **1** to compound **3**. (see Figure 3 and Tables I–II). Therefore, it can be concluded that in compounds **1–3**, the ring flipping (Chair→Twist-Boat) processes barrier heights are controlled by $\mathrm{LP(e)_{M1}} \rightarrow \sigma^*{}_{\mathrm{C2-M3}}$ resonance energies.

Representative structural parameters for the ground and transition state structures of compounds **1–3**, as calculated by B3LYP/6-31G** level of theory, are shown in Table III.

Although, due to the nature of the various approximations involved in theoretical calculations, it is not expected, in principal, to obtain exactly the experimental values.[34] However, it is possible to carry out theoretical calculations, from which many properties and structures can be obtained with an accuracy that is competitive with experiments.[35–38]

The lengthier C—M bond could increase the torsional and bond angle strains in transition state structures, which could increase the TS structure energies (e.g., ring flipping [Chair→Twist-Boat) processes barrier heights). For example, B3LYP/6-31G* results show that ϕ_{3456}

TABLE III B3LYP/6-31G* Calculated Structural Parameters for the Energy-Minimum and Energy-Maximum Geometries of Compounds 1–3

Compound	**1**			**2**			**3**		
State	C	TB	$[C\to TB]^{\ddagger}$	C	TB	$[C\to TB]^{\ddagger}$	C	TB	$[C\to TB]^{\ddagger}$
Bond lengths (Å)									
$r_{1\text{-}2}$	1.407	1.419	1.400	1.830	1.844	1.850	1.963	1.981	1.974
$r_{2\text{-}3}$	1.407	1.401	1.416	1.830	1.824	1.849	1.963	1.956	1.981
$r_{3\text{-}4}$	1.427	1.434	1.430	1.838	1.851	1.834	1.978	1.988	1.999
$r_{4\text{-}5}$	1.532	1.544	1.548	1.533	1.540	1.527	1.531	1.540	1.524
$r_{5\text{-}6}$	1.532	1.530	1.522	1.533	1.532	1.526	1.531	1.532	1.529
$r_{6\text{-}1}$	1.427	1.429	1.426	1.838	1.846	1.850	1.978	1.984	1.971
Bond angles (°)									
$\theta_{1\text{-}2\text{-}3}$	113.3	112.8	115.7	115.5	114.8	122.5	113.5	112.6	120.5
$\theta_{2\text{-}3\text{-}4}$	110.9	111.6	121.9	98.4	99.5	105.3	95.4	96.9	108.3
$\theta_{3\text{-}4\text{-}5}$	110.3	110.0	115.9	114.4	114.9	113.0	113.5	114.8	118.2
$\theta_{4\text{-}5\text{-}6}$	108.7	108.7	109.0	114.0	114.1	112.3	116.2	114.4	113.7
$\theta_{5\text{-}6\text{-}1}$	110.3	111.3	107.1	114.4	113.1	116.9	113.5	112.3	112.3
$\theta_{6\text{-}1\text{-}2}$	110.9	113.0	110.7	98.4	99.8	108.7	95.4	97.4	101.6
Torsion angels (°)									
$\phi_{1\text{-}2\text{-}3\text{-}4}$	60.0	−68.7	1.2	59.6	−66.5	0.4	60.1	−67.2	4.1
$\phi_{2\text{-}3\text{-}4\text{-}5}$	−56.5	38.7	−45.6	−57.9	28.5	−42.8	−59.7	36.7	−52.3
$\phi_{3\text{-}4\text{-}5\text{-}6}$	52.7	20.9	72.3	65.8	38.3	77.0	69.9	33.5	84.8
$\phi_{4\text{-}5\text{-}6\text{-}1}$	−52.7	−58.0	−53.6	−65.8	−77.1	−60.0	−71.4	−82.4	−57.2
$\phi_{5\text{-}6\text{-}1\text{-}2}$	56.5	34.2	14.0	57.9	32.0	15.6	59.6	40.8	11.2
$\phi_{6\text{-}1\text{-}2\text{-}3}$	−60.0	27.9	12.8	−59.6	36.8	11.6	−60.8	32.2	10.3

Bond lengths are in Angström (Å) and angles are in degree (°).

dihedral angles in the transition state structures of compounds **1–3** are 72.3°, 77.0° and 84.8°, respectively. Also, the θ_{612} bond angle in the transition state structures of compounds **1–3** are 110.7°, 108.7°, and 101.6°, respectively. Based on these structural parameters, it can be concluded that the lengthier C-M bond could increase the torsional and bond-angle strains in transition state structures, from **1** to **3**. The obtained results revealed that the energy barriers of the ring flipping processes decrease from **1** to **3**. Therefore, the increase of the torsional and bond-angle strains in transition state structures, is confronted to the decrease of the $\text{LP(e)}_{\text{M1}} \rightarrow \sigma^*{}_{\text{C2-M3}}$ resonance energies. Consequently, the lengthier C-M bond is not only responsible to the ring flipping (Chair→Twist-Boat) processes in compound **1–3**, and it seems that the $\text{LP(e)}_{\text{M1}} \rightarrow \sigma^*{}_{\text{C2-M3}}$ delocalizations play a more important role in these processes.

CONCLUSION

The above reported DFT calculations and NBO analysis provided a reasonable picture from structural, energetic and bonding points of view for the ring-flipping process in compounds **1–3**. Effectively, the results of DFT level of theory showed that the ring-flipping process barrier heights decreased, from compounds **1–3**.

In addition, NBO results revealed the following, as well:

- the resonance energy associated from the electronic delocalization from LP(e)_{M1} non-bonding orbitals to $\sigma^*{}_{\text{C2-M3}}$ anti-bonding orbitals ($\text{LP(e)}_{\text{M1}} \rightarrow \sigma^*{}_{\text{C2-M3}}$) decreased from compound **1** to **3**; and
- the $\sigma^*{}_{\text{C2-M3}}$ bonding orbitals occupancies decreased via $\text{LP(e)}_{\text{M1}} \rightarrow \sigma^*{}_{\text{C2-M3}}$ delocalizations from compound **1** to **3**.

It can be concluded that the ground state structure stability increase by the increase of the electronic delocalization from LP(e)_{M1} non-bonding orbitals to $\sigma^*{}_{\text{C2-M3}}$ anti-bonding orbitals. Therefore, the decrease of $\text{LP(e)}_{\text{M1}} \rightarrow \sigma^*{}_{\text{C2-M3}}$ delocalization from compound **1** to **3**, could fairly explain the easiness of ring flipping processes from compound **1** to **3**.

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