

## Ab initio study and NBO analysis Study of structures and relative stability of the cyclic allenes obtained from cyclohepta-1,3,5-triene

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### Abstract

NBO analysis, density functional theory (DFT: B3LYP/6-31G\*\*// B3LYP/6-31G\*) and ab initio molecular (MO: MP2/6-31G\*\*//B3LYP/6-31G\*) based method were used to investigate the structural optimization and configurational properties of cycloocta-1,3,4,6-tetraene (**1**), cycloocta-1,2,4,6-tetraene (**2**), cyclonona-1,2,4,6,7-pentaene (**3**), cyclonona-1,2,4,5,7-pentaene (**4**) and cyclodeca-1,2,4,5,7,8-hexaene (**5**), which could be obtained by adding C<sub>sp</sub> atoms into C=C double bonds of cyclohepta-1,3,5-triene.

The NBO analysis of donor-acceptor (bond-antibond) interactions revealed that there is no any correlation between the  $\Sigma(\pi \rightarrow \pi^*)$  resonance energies and the order of the stability of the various configurations of compounds **1-5**, however, NBO results revealed that the sum of  $\pi$  and  $\sigma$  bonding orbital deviations ( $\Sigma\pi_{Dev} + \Sigma\sigma_{Dev}$ ) increase from the most stable form of compound **1-5** to their relative unstable forms.

The relative stability of various configurations of compounds **1-5** could fairly be explained by the  $\Sigma\sigma_{dev}$  and  $\Sigma\pi_{dev}$  values.

**Key words:** cyclic allenes, NBO analysis, ab initio calculations, cyclohepta-1,3,5-triene

### Introduction

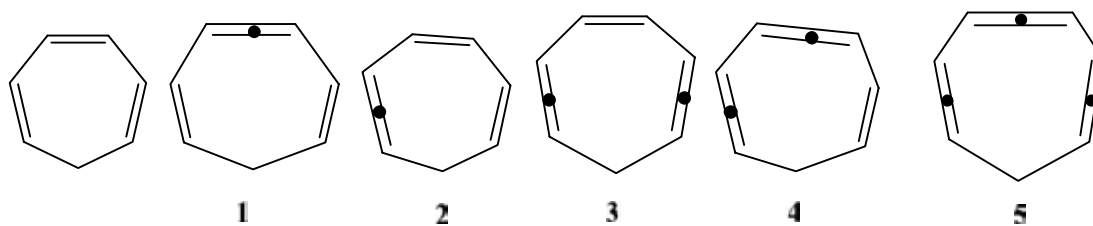
The ring constraint and steric impact of the presence of two double bonds in an orthogonal geometry in the unsaturated allenes could be considered responsible for the bending and twisting of the normally linear perpendicular allene, as well as for their resultant electronic effect and kinetic reactivity.<sup>(1-4)</sup>

Cyclic allenes, with allenic moiety, could experience some electron cyclic interactions of the out-of-plane  $\pi$  bonds and also electrons in plane.<sup>(5-7)</sup> Recently, we have reported the structural and energetic features of cyclodeca-1,2,4,6,7,9-hexaene(**2**),<sup>(8)</sup> cyclodeca-1,2,4,6,8,9-hexaene (**3**),<sup>(8)</sup> cycloundeca-1,2,4,5,7,8,10-heptaene (**4**),<sup>(9)</sup> cyclododeca-1,2,4,5,7,8,10,11-octaene (**5**).<sup>(10,11)</sup>

It seems one can obtain the cycloocta-1,3,4,6-tetraene (**1**), cycloocta-1,2,4,6-tetraene (**2**), cyclonona-1,2,4,6,7-pentaene(**3**),cyclonona-1,2,4,5,7-pentaene(**4**)and cyclodeca-1,2,4,5,7,8-hexaene (**5**) using both carbenes addition and then elimination reactions on the cyclohepta-1,3,5-triene. However, our library survey showed that there are no published experimental or

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theoretical data on the structure or configurational features of compounds **1-5** (see scheme 1).



see scheme 1

In this work, we have investigated computationally the structural, configurational properties of compounds **1-5**, by both ab initio and DFT methods, using the GAUSSIAN 98 package of programs.<sup>(12-16)</sup> In addition, the nature of the allenic bonds (population and bonding orbital deviation) in compounds **1-5** were systematically and quantitatively investigated by the NBO (Natural Bond Orbital) analysis.<sup>(17-20)</sup>

Although, there is no experimental or theoretical data about compounds **1-5**, it is possible to learn something about it by using theoretical methods that have proved to be reliable in other applications. Effectively, 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.<sup>(12,13,15)</sup> Also, the B3LYP functional method combines Becke's three-parameter exchange function with the correlation function of Lee *et al.*<sup>(12,13)</sup>

### Computational details

Ab initio density functional theory (DFT) and molecular orbital (MO) calculations were carried out using MP2/6-31G\*\*/B3LYP/6-31G\* and B3LYP/6-31G\*\*/B3LYP/6-31G\* levels of theory with the GAUSSIAN 98 package of programs<sup>16</sup> implemented on a Pentium-PC computer with 1.7 GHz processor.

Initial estimation of the structural geometries of the compounds **1-5** was obtained by a molecular mechanic program PCMODEL(88.0)<sup>(21)</sup> and for further optimization of geometries, PM3 method of MOPAC 7.0 computer program was used.<sup>(22,23)</sup> GAUSSIAN 98 program was 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 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.<sup>(24,25)</sup> 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).<sup>(26)</sup> These geometry structures were reoptimized by QST3 subroutine at the B3LYP/6-31G\* level. The vibrational frequencies of ground states and transition states were calculated by FREQ subroutine. Finally, NBO analysis was performed based on the HF/6-31G\* optimized geometries, by the NBO 3.1 program<sup>(17,18)</sup> included in GAUSSIAN 98 package of programs.

### Results and Discussion

Corrected zero point ( $ZPE^C$ ) and total electronic ( $E_{el}$ ) energies ( $E_0 = E_{el} + ZPE^C$ ) for possible configurations of compounds **1-5**, as calculated by the density functional theory (B3LYP/6-31G\*\*/B3LYP/6-31G\*) and ab initio molecular orbital (MP2/6-31G\*\*/B3LYP/6-31G\*) methods, are given in Tables **1-5**. In addition, the resonance energies ( $E_{\pi}$ ) associated with  $\pi \rightarrow \pi^*$  delocalizations,  $\sigma$  and  $\pi$  hybridized orbital deviations from their normal values,

and also  $\sigma$  and  $\pi$  bonding and antibonding orbital occupancies in the most stable configurations of compounds **1-5**, was systematically and quantitatively investigated by the NBO (Natural Bond Orbital) analysis.

The unsymmetrical configuration constructed by a combination of one allenic unit with two *cis*  $\pi$  bond (ZRZ or ZSZ,  $C_1$  symmetry), was found to be the most stable geometry of compound **1**, as calculated by MP2/6-31G\*\*/B3LYP/6-31G\* and B3LYP/6-31G\*\*/B3LYP/6-31G\* levels of theory.

Based on the MP2/6-31G\*\*/B3LYP/6-31G\* results, the unsymmetrical configuration of compound **1**, constructed by a combination of one allenic unit with a *cis*  $\pi$  bond and a *trans*  $\pi$  bond (ZRE or ZSE,  $C_1$  symmetry) is found to be 29.96 kcal mol<sup>-1</sup> above the energy of ZRZ (or ZSZ) diastereoisomer. Also, 1-ZRZ configuration is 52.99 and 56.38 kcal mol<sup>-1</sup> more stable than 1-ERE(parallel,  $C_1$  symmetry) and 1-ERE(perpendicular,  $C_2$  symmetry) configurations, respectively, as calculated by MP2/6-31G\*\*/B3LYP/6-31G\* level of theory. In addition, the calculated energy barrier for interconversion of unsymmetrical 1-ZRZ and 1-ZRZ' configurations *via* axial symmetrical 1-ZRZ ( $C_2$  symmetry) form is 1.80 and 2.28 kcal mol<sup>-1</sup>, as calculated by MP2/6-31G\*\*/B3LYP/6-31G\* and BELYP/6-31G\*\*/B3LYP/6-31G\* levels of theory, respectively.

In addition, MP2/6-31G\*\*/B3LYP/6-31G\* results revealed that the unsymmetrical RZZ configuration of compound **2** is 17.84, 29.52 and 58.62 kcal mol<sup>-1</sup> more stable than unsymmetrical 2-RZE, 2-REZ and 2-REE forms, respectively.

On the other hand, the axial symmetrical RZR configuration of compound **3** is 1.30, 28.49 and 33.41 kcal mol<sup>-1</sup> more stable than 3-RZS ( $C_s$  symmetry), 3-RES ( $C_1$  symmetry) and 3-RER ( $C_2$  symmetry), respectively, as calculated by MP2/6-31G\*\*/B3LYP/6-31G\* level of theory.

Further, MP2/6-31G\*\*/B3LYP/6-31G\* results revealed that the unsymmetrical RRZ configuration of compound **4** is 2.64, 17.76 and 28.04 kcal mol<sup>-1</sup> more stable than the unsymmetrical 4-RSZ, 4-RRE and 4-RSE forms, respectively. Finally, MP2/6-31G\*\*/B3LYP/6-31G\* results showed that the unsymmetrical RSS configuration of compound **5** is 0.68 and 1.06 kcal mol<sup>-1</sup> more stable than the axial symmetrical 5-RSR and 5-RRR forms, respectively.

Table 1. Calculated total electronic energies ( $E_{el}$ ), zero-point energies (ZPE) and relative energies  $\Delta E_0$  ( $E_0$ , in hartree), for the energy-minimum configurations of compound **1**.

method Geometry	ZPE <sup>a</sup>	B3LYP/6-31G**/B3LYP/6-31G*			MP2/6-31G**/B3LYP/6-31G*		
		$E_{el}$	$E_0$	$\Delta E_0^b$	$E_{el}$	$E_0$	$\Delta E_0^b$
1-ZRZ, $C_1$	0.129880	-309.545924	-309.416044	0.000000 (0.000000) <sup>c</sup>	-308.483767	-308.353887	0.000000 (0.000000) <sup>c</sup>
1-ZRZ, $C_2$	0.129435	-309.541846	-309.412411	0.003633 (2.279744)	-308.480455	-308.351102	0.002867 (1.799071)
1-ZRE, $C_1$	0.128549	-309.493825	-309.365276	0.050768 (31.857428)	-308.434696	-308.306147	0.04774 (29.957327)
1-ERE ( $\parallel$ ), $C_2$	0.128213	-309.455321	-309.327108	0.088936 (55.808229)	-308.397658	-308.269445	0.084442 (52.988199)
1-ERE ( $\perp$ ), $C_2$	0.127727	-309.448325	-309.320598	0.095446 (59.893319)	-308.391760	-308.264033	0.089854 (56.384284)

<sup>a</sup> Relative to the most stable form.

<sup>b</sup> Numbers in parenthesis are the corresponding  $\Delta E_0$  values in kcal mol<sup>-1</sup>.

<sup>c</sup> Corrected by multiplying by a scaling factor (0.9804).

Table 2. Calculated total electronic energies ( $E_{el}$ ), zero-point energies ( $ZPE$ ) and relative energies  $\Delta E_s$  ( $E_s$ , in hartree), for the energy-minimum configurations of compound 2.

method \ Geometry	$ZPE^a$	B3LYP/6-31G*/B3LYP/6-31G*			MP2/6-31G*/B3LYP/6-31G*		
		$E_{el}$	$E_0$	$\Delta E_0^c$	$E_{el}$	$E_0$	$\Delta E_0^c$
2-RZZ, $C_1$	0.130507	-309553414	-309.422907	0.000000 (0.000000) <sup>b</sup>	-308.487430	-308.356923	0.000000 (0.000000) <sup>b</sup>
2-RZE, $C_1$	0.128930	-309.514286	-309.385356	0.037551 (23.563628)	-308.457426	-308.328496	0.028427 (17.838227)
2-REZ, $C_1$	0.129218	-309.496837	-309.367619	0.055288 (34.693772)	-308.439104	-308.309886	0.047037 (29.516188)
2-REE, $C_1$	0.128249	-309.437836	-309.309587	0.11332 (71.109433)	-308.391760	-308.263511	0.093412 (58.616964)

<sup>a</sup> Relative to the most stable form.<sup>b</sup> Numbers in parenthesis are the corresponding  $\Delta E_0$  values in kcal mol<sup>-1</sup>.<sup>c</sup> Corrected by multiplying by a scaling factor (0.9804).Table 3. Calculated total electronic energies ( $E_{el}$ ), zero-point energies ( $ZPE$ ) and relative energies  $\Delta E_s$  ( $E_s$ , in hartree), for the energy-minimum configurations of compound 3.

method \ Geometry	$ZPE^a$	B3LYP/6-31G*/B3LYP/6-31G*			MP2/6-31G*/B3LYP/6-31G*		
		$E_{el}$	$E_0$	$\Delta E_0^c$	$E_{el}$	$E_0$	$\Delta E_0^c$
3-RZR, $C_2$	0.134410	-347.625992	-347.491582	0.000000 (0.000000) <sup>b</sup>	-346.445352	-346.310942	0.000000 (0.000000) <sup>b</sup>
3-RZS, $C_8$	0.134205	-347.622400	-347.488195	0.003387 (2.125376)	-346.443070	-346.308865	0.002077 (1.303338)
3-RRS, $C_1$	0.124275	-347.566957	-347.433581	0.058001 (36.396207)	-346.389816	-346.265541	0.045401 (28.489582)
3-RER, $C_2$	0.133251	-347.568135	-347.434884	0.056698 (35.578562)	-346.390951	-346.257700	0.053242 (33.409887)

<sup>a</sup> Relative to the most stable form.<sup>b</sup> Numbers in parenthesis are the corresponding  $\Delta E_0$  values in kcal mol<sup>-1</sup>.<sup>c</sup> Corrected by multiplying by a scaling factor (0.9804).Table 4. Calculated total electronic energies ( $E_{el}$ ), zero-point energies ( $ZPE$ ) and relative energies  $\Delta E_s$  ( $E_s$ , in hartree), for the energy-minimum configurations of compound 4.

method \ Geometry	$ZPE^a$	B3LYP/6-31G*/B3LYP/6-31G*			MP2/6-31G*/B3LYP/6-31G*		
		$E_{el}$	$E_0$	$\Delta E_0^c$	$E_{el}$	$E_0$	$\Delta E_0^c$
4-RRZ, $C_1$	0.134141	-347.613977	-347.479836	0.000000 (0.000000) <sup>b</sup>	-346.436562	-346.302421	0.000000 (0.000000) <sup>b</sup>
4-RSZ, $C_1$	0.134111	-347.611743	-347.477632	0.002204 (1.383032)	-346.432328	-346.298217	0.004204 (2.638052)
4-RRE, $C_1$	0.133232	-347.582468	-347.449236	0.030600 (19.201806)	-346.407348	-346.274116	0.028305 (17.761671)
4-RSE, $C_1$	0.133550	-347.570475	-347.436925	0.042911 (26.927082)	-346.391293	-346.257743	0.044678 (28.035892)

<sup>a</sup> Relative to the most stable form.<sup>b</sup> Numbers in parenthesis are the corresponding  $\Delta E_0$  values in kcal mol<sup>-1</sup>.<sup>c</sup> Corrected by multiplying by a scaling factor (0.9804).

Table 5. Calculated total electronic energies ( $E_{el}$ ), zero-point energies (ZPE) and relative energies  $\Delta E_0$  ( $E_0$ , in hartree), for the energy-minimum configurations of compound **5**.

method Geometry	ZPE <sup>a</sup>	B3LYP/6-31G**//B3LYP/6-31G*			MP2/6-31G**//B3LYP/6-31G*		
		$E_{el}$	$E_0$	$\Delta E_0^z$	$E_{el}$	$E_0$	$\Delta E_0^z$
5-RSS, $C_1$	0.138550	-385.683045	-385.54495	0.000000 (0.000000) <sup>c</sup>	-384.384836	-384.246286	0.000000 (0.000000)
5-RSR, $C_2$	0.138427	-385.683287	-385.54486	0.000090 (0.056476)	-384.383622	-384.245195	0.001091 (0.684613)
5-RRR, $C_2$	0.137993	-385.68053	-385.542537	0.002413 (1.514182)	-384.382594	-384.244601	0.001685 (1.057354) <sup>c</sup>

<sup>a</sup> Relative to the most stable form.<sup>b</sup> Numbers in parenthesis are the corresponding  $\Delta E_0$  values in kcal mol<sup>-1</sup>.<sup>c</sup> Corrected by multiplying by a scaling factor (0.9)

At this point it seems useful to remind some interesting concepts concerning the NBO analysis, which was effectively used in this work. In the NBO analysis<sup>(17,18)</sup> the electronic wavefunctions are interpreted, in terms of a set of occupied Lewis and a set of unoccupied non-Lewis localized orbitals. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydberg) non-Lewis NBO orbitals, corresponds to a stabilizing donor-acceptor interaction, which is taken into consideration by examining all possible interactions between filled (donor) and empty (acceptor) orbitals, and then evaluating their energies by second order perturbation theory. Accordingly, 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. NBOs closely correspond to the picture of localized bonds and lone pairs as basic units of molecular structure, so that is possible to conveniently interpret ab initio wavefunctions in terms of the classical Lewis structure concepts by transforming these functions to NBO form. The interactions due to electron delocalization are generally analyzed by selecting a number of bonding and antibonding NBOs, namely, those relevant to the analysis of donor and acceptor properties. As a result, 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. However, these orbitals suffer from small departures from the idealized Lewis structure, caused by interactions among them, known as hyperconjugative or stereoelectronic interactions. 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. For each donor NBO (i) and acceptor NBO (j), the stabilization energy ( $E_2$ ) associated with i→j delocalization, is explicitly estimated by following equation:

$$E_2 = \Delta E_{ij} = q_i \frac{F^2(i, j)}{\varepsilon_j - \varepsilon_i} \quad (1)$$

where  $q_i$  is the  $i$ th donor orbital occupancy,  $\varepsilon_i$ ,  $\varepsilon_j$  are diagonal elements (orbital energies) and  $F(i, j)$  off-diagonal elements, respectively associated with NBO Fock matrix.

The NBO analysis of donor-acceptor (bond-antibond) interactions revealed that there is no any correlation between the  $\sum(\pi \rightarrow \pi^*)$  resonance energies and the order of the stability of the various configurations of compound **1**, however, NBO results revealed that the sum of  $\pi$  and  $\sigma$  bonding orbital deviations,  $\sum_{Dev}$  and  $\sum_{\sigma Dev}$ , increase from the most stable form of compound **1** to its unstable form. The calculated values of the  $\pi$  bonding orbital deviation summations,  $\sum \pi_{Dev}$ , for **1-ZRZ**, **1-ZRE**, **1-ERE** (parallel,  $C_1$  symmetry) and **1-ERE** (perpendicular,  $C_2$  symmetry) configurations are 46.9°, 59.6°, 142.5° and 155.0°, respectively. Also, NBO results showed that

the  $\sum \sigma_{Dev}$  values for **1-ZRZ**, **1-ZRE**, **1-ERE** (parallel,  $C_1$  symmetry) and **1-ERE** (perpendicular,  $C_2$  symmetry) are 95.5°, 137.1°, 161.3° and 267.0°, respectively (see Tables 6-8).

On the other hand, the  $\sum \pi_{Dev}$  and  $\sum \sigma_{Dev}$  values increase from RZZ configuration of compound **2** to **2-RZE**, **2-REZ** and **2-REE** configuration. Based on the B3LYP/6-31G\* optimized ground state geometries, the NBO analysis showed that the  $\sum \pi_{Dev}$  values in **2-RZZ**, **2-RZE**, **2-REZ** and **2-REE** configurations are 43.0°, 79.7°, 110.4 and 220.8° kcal mol<sup>-1</sup>, respectively. Also, the  $\sum \sigma_{Dev}$  values for **2-RZZ**, **2-RZE**, **2-REZ** and **2-REE** configurations are 75.6°, 157.0°, 166.3° and 253.3°, respectively. These facts could fairly explain the more stability of **2-RZZ** configuration, compared to **2-RZE**, **2-REZ** and **2-REE** stereoisomers (see Tables 9-11).

Based on the optimized ground state geometries using B3LYP/6-31G\* method, the NBO analysis of donor-acceptor (bond-antibond) interactions revealed that there is no any correlation between the  $\sum(\pi \rightarrow \pi^*)$  resonance energies and the order of the stability of the various configurations of compound **3**, however, NBO results revealed that the sum of  $\pi$  and  $\sigma$  bonding orbital deviations,  $\sum \pi_{Dev}$  and  $\sum \sigma_{Dev}$ , increase from the most stable form of compound **3** to its unstable form. The  $\sum \pi_{Dev}$  values for **3-RZR**, **3-RZS**, **3-RES** and **3-RER** configurations are 39.0°, 94.3°, 160.0° and 196.5°, respectively (see Tables 12-14).

Further, NBO results revealed that the  $\sum \pi_{Dev}$  values in **4-RRZ**, **4-RSZ**, **4-RRE** and **4-RSE** configurations are 45.3°, 56.2°, 28.5° and 81.9°, respectively. Also, the  $\sum \sigma_{Dev}$  values for **4-RRZ**, **4-RSZ**, **4-RRE** and **4-RSE** configurations are 109.5°, 98.7°, 123.9° and 155.8°, respectively. Based on the optimized ground state geometries using B3LYP/6-31G\* method, the NBO analysis of donor-acceptor (bond-antibond) interactions revealed that there is no any correlation between the  $\sum(\pi \rightarrow \pi^*)$  resonance energies and the order of the stability of the various configurations of compound **4**. The  $\sum(\pi \rightarrow \pi^*)$  resonance energies for **4-RRZ**, **4-RSZ**, **4-RRE** and **4-RSE** configurations are 23.83, 32.87, 11.6 and 47.23 kcal mol<sup>-1</sup>, respectively (see Tables 15-17).

Finally, NBO results revealed that the  $\sum \pi_{Dev}$  values in **5-RRR** ( $C_2$  symmetry), **5-RSS** ( $C_1$  symmetry) and **5-RSR** ( $C_2$  symmetry) configurations, are 78.2°, 81.8° and 84.1°, respectively. Also, NBO results indicate that the deviations of  $\pi$  bonding orbitals ( $\sum \pi_{dev}$ ) in the above forms are 29.0°, 42.9° and 21.1°, respectively. In addition, NBO results show that the sum of  $\pi \rightarrow \pi^*$  electronic delocalization in the above configurations are 41.96°, 25.67° and 13.09° kcal mol<sup>-1</sup>, respectively (see Tables 18-20).

In conclusion, NBO results show that the deviations of  $\pi$  and  $\sigma$  bonding orbitals ( $\sum(\sigma_{dev} + \pi_{Dev})$ ) could fairly explain the relative stability of configurations of all above compounds.

Altogether, B3LYP/6-31G\* method predicted that the MP2/6-31G\*\*/B3LYP/6-31G\* and BELYP/6-31G\*\*/B3LYP/6-31G\* results revealed that **1-ZRE** ( $C_1$  symmetry), **2-RZZ** ( $C_1$  symmetry), **3-RZR** ( $C_2$  symmetry), **4-RRZ** ( $C_1$  symmetry) and **5-RSS** ( $C_1$  symmetry) configurations are particularly important because they are expected to be significantly populated at room temperature.

Table 6. NBO analysis results of  $\pi$  bonding orbital deviations from their normal values (normal values:  $\pi=90.0^\circ$ ); and also, the  $\pi$  bonding and  $\pi^*$  anti-bonding occupancies of compound **1**, based on the B3LYP/6-31G\* calculated geometries

Geometry	1-ZRZ, $C_1$		1-ZRE, $C_1$		1-ERE ( $\parallel$ ), $C_2$		1-ERE ( $\perp$ ), $C_2$	
	Occup.	Dev.	Occup.	Dev.	Occup.	Dev.	Occup.	Dev.
Orbitals								
$\pi_{C1-C2}$	1.91115	1.5 7.6	1.93448	1.4 8.2	1.91489	12.5 18.9	1.78939	8.6 16.4
$\pi_{C2-C3}$	1.92541	3.3 0.1	1.90706	5.6 4.5	1.91541	12.4 18.7	1.91048	16.3 19.9
$\pi_{C4-C5}$	1.92796	9.7 8.6	1.90562	4.3 2.9	1.91712	20.0 19.9	1.85951	13.3 14.1
$\pi_{C7-C8}$	1.91808	2.8 4.2	1.93948	10.7 12.4	1.91634	20.1 20.0	1.84910	4.1 2.9
$\pi^*_{C1-C2}$	0.10481	-	0.10533	-	0.07703	-	0.16374	-
$\pi^*_{C2-C3}$	0.08147	-	0.09313	-	0.07628	-	0.07141	-
$\pi^*_{C4-C5}$	0.06439	-	0.08869	-	0.08659	-	0.15790	-
$\pi^*_{C7-C8}$	0.08459	-	0.07118	-	0.08665	-	0.21500	-
$\sum \pi_{Dev}$		46.9		59.6		142.5		155.0

Table 7. NBO calculated stabilization energies ( $E_2$ ), based on the calculated geometries using B3LYP/6-31G\* level of theory, for  $\pi \rightarrow \pi^*$ , in the ground state structure of compound **1**.

Electron Transfers (Donor $\rightarrow$ Acceptor)	Resonance Energy (Stablization Energy)			
	1-ZRZ, $C_1$	1-ZRE, $C_1$	1-ERE ( $\parallel$ ), $C_2$	1-ERE ( $\perp$ ), $C_2$
$\pi_{1-2} \rightarrow \pi^*_{7-8}$	11.66	7.02	18.94	3.86
$\pi_{7-8} \rightarrow \pi^*_{1-2}$	10.72	8.10	11.27	5.34
$\pi_{2-3} \rightarrow \pi^*_{4-5}$	6.77	8.59	8.00	3.76
$\pi_{4-5} \rightarrow \pi^*_{2-3}$	6.20	5.98	5.87	5.23
$\pi_{4-5} \rightarrow \pi^*_{1-2}$	0.53	2.07	0.65	-
$\pi_{4-5} \rightarrow \pi^*_{7-8}$	-	-	6.05	0.98
$\pi_{7-8} \rightarrow \pi^*_{4-5}$	-	-	1.26	1.01
$\pi_{2-3} \rightarrow \pi^*_{7-8}$	-	-	-	1.69
$\pi_{1-2} \rightarrow \pi^*_{4-5}$	-	-	2.18	1.70
$\sum (\pi \rightarrow \pi^*)$	35.88	31.76	54.22	23.57

Table 8. NBO analysis results of  $\sigma$  bonding orbital deviations from their normal values (normal values:  $\sigma=0.0^\circ$ ) of various configurations of compound **1**, based on the B3LYP/6-31G\* calculated geometries.

Geometry	<b>1</b> -ZRZ, C <sub>1</sub>		<b>1</b> -ZRE, C <sub>1</sub>		<b>1</b> -ERE (II), C <sub>2</sub>		<b>1</b> -ERE (I), C <sub>2</sub>	
	Dev.		Dev.		Dev.		Dev.	
Orbitals								
$\sigma_{C1-C2}$	3.0	-	-	-	12.5	-	17.5	-
	3.8	1.4	1.4	1.4	14.5	1.4	20.0	1.4
$\sigma_{C2-C3}$	8.4	13.5	13.5	13.5	21.8	21.8	17.4	17.4
	8.7	13.9	13.9	13.9	24.3	24.3	19.8	19.8
$\sigma_{C3-C4}$	6.1	16.5	16.5	16.5	1.5	1.5	16.5	16.5
	7.5	14.0	14.0	14.0	-	-	14.0	14.0
$\sigma_{C4-C5}$	13.0	4.8	4.8	4.8	13.1	13.1	21.8	21.8
	12.6	5.2	5.2	5.2	13.1	13.1	21.7	21.7
$\sigma_{C5-C6}$	3.4	6.7	6.7	6.7	10.8	10.8	7.7	7.7
	3.0	12.3	12.3	12.3	16.6	16.6	14.3	14.3
$\sigma_{C6-C7}$	3.1	1.4	1.4	1.4	11.3	11.3	7.7	7.7
	2.0	1.4	1.4	1.4	17.2	17.2	14.3	14.3
$\sigma_{C7-C8}$	5.2	15.5	15.5	15.5	1.2	1.2	21.9	21.9
	5.7	16.2	16.2	16.2	-	-	21.9	21.9
$\sigma_{C8-C1}$	4.1	5.8	5.8	5.8	3.4	3.4	16.5	16.5
	5.9	8.5	8.5	8.5	-	-	14.0	14.0
$\sum \sigma_{dev}$	95.5		137.1		161.3		267	

Table 9. NBO analysis results of  $\pi$  bonding orbital deviations from their normal values (normal values:  $\pi=90.0^\circ$ ); and also, the  $\pi$  bonding and  $\pi^*$  anti-bonding occupancies of compound **1**, based on the B3LYP/6-31G\* calculated geometries.

Geometry	RZZ, C <sub>1</sub>		RZE, C <sub>1</sub>		REZ, C <sub>1</sub>		REE, C <sub>1</sub>	
	Occup.	Dev.	Occup.	Dev.	Occup.	Dev.	Occup.	Dev.
Orbitals								
$\pi_{C1-C2}$	1.95371	5.6	1.94162	4.1	1.95645	4.9	1.93397	3.1
		10.2		6.5		10.4		8.7
$\pi_{C2-C3}$	1.87086	5.9	1.92496	7.5	1.87743	3.9	1.93655	8.0
		1.5		0.7		6.6		6.6
$\pi_{C4-C5}$	1.83824	1.9	1.93876	11.4	1.83702	12.5	1.80207	24.1
		1.9		12.0		9.2		26.2
$\pi_{C6-C7}$	1.87249	1.1	1.94988	18.7	1.90623	15.3	1.80478	24.4
		1.3		18.8		15.4		22.5
$\pi^*_{C1-C2}$	0.06762		0.05893		0.09316		0.09369	
$\pi^*_{C2-C3}$	0.13276		0.08424		0.11321		0.05317	
$\pi^*_{C4-C5}$	0.16799		0.05517		0.13459		0.19735	
$\pi^*_{C6-C7}$	0.12729		0.6641		0.09025		0.15553	
$\sum \pi^*$		29.4		79.7		78.2		123.6



Table 10. NBO calculated stabilization energies ( $E_2$ ), based on the calculated geometries using B3LYP/6-31G\* level of theory, for  $\pi \rightarrow \pi^*$ , in the ground state structure of compound **2**.

Electron Transfers (Donor $\rightarrow$ Acceptor)	Resonance Energy (Stabilization Energy)			
	2-RZZ, $C_1$	RZE, $C_1$	REZ, $C_1$	REE (1), $C_1$
$\pi_{2-3} \rightarrow \pi_{4-5}^*$	13.82	6.22	0.78	1.13
$\pi_{4-5} \rightarrow \pi_{2-3}^*$	10.5	6.92	6.81	-
$\pi_{4-5} \rightarrow \pi_{6-7}^*$	14.65	-	9.96	20.48
$\pi_{1-2} \rightarrow \pi_{6-7}^*$	-	2.15	-	-
$\pi_{2-3} \rightarrow \pi_{6-7}^*$	-	0.70	-	-
$\pi_{6-7} \rightarrow \pi_{1-2}^*$	-	-	0.99	-
$\pi_{6-7} \rightarrow \pi_{4-5}^*$	-	-	10.78	25.3
$\pi_{4-5} \rightarrow \pi_{1-2}^*$	-	-	2.28	2.29
$\pi_{1-2} \rightarrow \pi_{4-5}^*$	-	-	-	0.67
$\Sigma(\pi \rightarrow \pi^*)$	38.97	15.99	31.6	49.87

Table 11. NBO analysis results of  $\sigma$  bonding orbital deviations from their normal values (normal values:  $\sigma=0.0^\circ$ ) of various configurations of compound **2**, based on the B3LYP/6-31G\* calculated geometries.

Geometry	RZZ, $C_1$	RZE, $C_1$	REZ, $C_1$	REE, $C_1$
	Dev.	Dev.	Dev.	Dev.
Orbitals				
$\sigma_{C1-C2}$	8.5	5.5	4.7	3.1
	9.5	6.2	5.9	3.7
$\sigma_{C2-C3}$	6.1	3.8	13.4	14.2
	5.2	2.6	13.1	16.1
$\sigma_{C3-C4}$	3.8	5.9	11.1	12.6
	1.6	4.3	13.1	19.2
$\sigma_{C4-C5}$	4.5	15.6	12.6	27.5
	3.5	16.3	10.7	26.2
$\sigma_{C5-C6}$	4.8	11.9	10.4	24.0
	4.4	8.4	14.4	25.0
$\sigma_{C6-C7}$	3.5	20.8	20.1	25.6
	5.0	20.9	20.5	26.6
$\sigma_{C7-C8}$	1.4	7.9	1.6	4.0
	1.1	13.5	2.8	4.3
$\sigma_{C8-C1}$	4.7	5.3	3.6	5.4
	8.0	8.1	8.3	12.8
$\Sigma \sigma_{Dev}$	75.6	157.0	166.3	253.3

Table 12. NBO analysis results of  $\pi$  bonding orbital deviations from their normal values (normal values:  $\pi=90.0^\circ$ ); and also, the  $\pi$  bonding and  $\pi^*$  anti-bonding occupancies of compound **3**, based on the B3LYP/6-31G\* calculated geometries.

Geometry	<b>3</b> -RZR, $C_2$		<b>3</b> -RZS, $C_6$		<b>3</b> -RER, $C_2$		<b>3</b> -RES, $C_1$	
	Occup.	Dev.	Occup.	Dev.	Occup.	Dev.	Occup.	Dev.
$\pi_{C1-C2}$	1.95450	0.9 2.8	1.95596	2.8 3.2	1.95390	1.7 6.2	1.92619	2.9 8.9
$\pi_{C2-C3}$	1.90844	1.2 2.6	1.90806	1.2 3.4	1.89108	13.0 12.8	1.91990	17.4 15.6
$\pi_{C4-C5}$	1.89775	0.3 0.3 1.2	1.89540	12.8 12.8	1.91563	7.0 7.0	1.90897	15.9 13.8
$\pi_{C6-C7}$	1.90849	1.2 2.6	1.90806	1.2 3.4	1.89109	13 12.8	1.89551	10.1 9.4
$\pi_{C7-C8}$	1.95449	0.9 2.8	1.95596	2.8 3.2	1.95390	1.7 6.2	1.94307	3.2 7.9
$\pi^*_{C1-C2}$	0.06024	-	0.06490	-	0.06864	-	0.06518	-
$\pi^*_{C2-C3}$	0.09364	-	0.09609	-	0.07751	-	0.08670	-
$\pi^*_{C4-C5}$	0.11827	-	0.10665	-	0.14225	-	0.12278	-
$\pi^*_{C6-C7}$	0.09363	-	0.09609	-	0.07752	-	0.09216	-
$\pi^*_{C7-C8}$	0.06025	-	0.06490	-	0.06863	-	0.07643	-
$\sum \pi_{Dev}$		<b>15.6</b>		<b>61.8</b>		<b>81.4</b>		<b>105.1</b>

Table 13. NBO calculated stabilization energies ( $E_2$ ), based on the calculated geometries using B3LYP/6-31G\* level of theory, for  $\pi \rightarrow \pi^*$ , in the ground state structure of compound **3**.

Electron Transfers (Donor $\rightarrow$ Acceptor)	Resonance Energy (Stabilization Energy)			
	<b>3</b> -RZR, $C_2$	<b>3</b> -RZS, $C_6$	<b>3</b> -RER, $C_2$	<b>3</b> -RES, $C_1$
$\pi_{2-3} \rightarrow \pi^*_{4-5}$	10.98	8.75	13.07	9.63
$\pi_{4-5} \rightarrow \pi^*_{2-3}$	9.29	7.45	3.71	7.50
$\pi_{6-7} \rightarrow \pi^*_{4-5}$	10.97	8.75	13.06	10.89
$\pi_{4-5} \rightarrow \pi^*_{6-7}$	9.29	7.45	3.71	6.03
$\pi_{1-2} \rightarrow \pi^*_{7-8}$	-	-	-	1.73
$\pi_{1-2} \rightarrow \pi^*_{4-5}$	-	-	-	1.22
$\pi_{7-8} \rightarrow \pi^*_{1-2}$	-	-	-	0.78
$\sum (\pi \rightarrow \pi^*)$	40.53	32.4	33.55	37.78

Table 14. NBO analysis results of  $\sigma$  bonding orbital deviations from their normal values (normal values:  $\sigma=0.0^\circ$ ) of various configurations of compound **3**, based on the B3LYP/6-31G\* calculated geometries.

Geometry	<b>3-RZR, C<sub>2</sub></b>	<b>3-RZS, C<sub>5</sub></b>	<b>3-RER, C<sub>2</sub></b>	<b>3-RES, C<sub>1</sub></b>
	Dev.	Dev.	Dev.	Dev.
Orbitals				
$\sigma_{C1-C2}$	2.9 3.3	3.0 3.0	2.3 3.4	3.9 5.6
$\sigma_{C2-C3}$	3.9 3.5	5.5 4.9	18.5 16.9	23.4 20.9
$\sigma_{C3-C4}$	1.7 -	2.6 2.0	12.8 15.2	13.6 16.2
$\sigma_{C4-C5}$	1.2 1.2	17.0 17.0	4.8 4.8	15.8 15.0
$\sigma_{C5-C6}$	1.7 -	2.7 2.0	12.8 15.2	11.3 14.2
$\sigma_{C6-C7}$	3.9 3.5	5.5 4.9	18.5 16.9	14.4 12.9
$\sigma_{C7-C8}$	2.9 3.3	3.0 3.0	2.3 3.4	2.6 3.6
$\sigma_{C8-C5}$	- 3.0	3.4 5.7	1.6 4.5	4.8 7.9
$\sigma_{C9-C1}$	- 3.0	3.4 5.7	1.6 4.5	4.0 6.4
$\sum\sigma_{Dev}$	<b>39.0</b>	<b>94.3</b>	<b>160.0</b>	<b>196.5</b>

Table 15. NBO analysis results of  $\pi$  bonding orbital deviations from their normal values (normal values:  $\pi=90.0^\circ$ ); and also, the  $\pi$  bonding and  $\pi^*$  anti-bonding occupancies of compound **4**, based on the B3LYP/6-31G\* calculated geometries.

Geometry	<b>4-RRZ, C<sub>1</sub></b>		<b>4-RSZ, C<sub>1</sub></b>		<b>4-RRE, C<sub>1</sub></b>		<b>4-RSE, C<sub>1</sub></b>	
	Occup.	Dev.	Occup.	Dev.	Occup.	Dev.	Occup.	Dev.
Orbitals								
$\pi_{C1-C2}$	1.92633	3.2 1.2	1.91895	1.2 3.4	1.93932	0.1 5.0	1.91617	4.4 16.2
$\pi_{C2-C3}$	1.93715	5.1 0.8	1.92994	2.9 3.5	1.93902	4.7 1.5	1.89116	8.6 11.3
$\pi_{C4-C5}$	1.93327	9.7 10.1	1.94367	8.4 9.1	1.93815	0.2 1.7	1.93103	9.1 7.1
$\pi_{C7-C8}$	1.95080	3.4 8.3	1.94877	4.8 12.4	1.94183	3.0 6.5	1.95026	3.6 5.4
$\pi_{C8-C5}$	1.91925	0.0 3.5	1.90986	6.9 3.6	1.94143	1.1 4.7	1.89621	9.1 7.1
$\pi^*_{C1-C2}$	0.07972	-	0.10060	-	0.07859	-	0.11176	-
$\pi^*_{C2-C3}$	0.07690	-	0.07699	-	0.07006	-	0.08972	-
$\pi^*_{C4-C5}$	0.05792	-	0.06440	-	0.05903	-	1.91617	-
$\pi^*_{C7-C8}$	0.07224	-	0.06304	-	0.07000	-	0.05579	-
$\pi^*_{C8-C5}$	0.08195	-	0.09638	-	0.06171	-	1.89116	-
$\sum\pi_{Dev}$		<b>45.3</b>		<b>56.2</b>		<b>28.5</b>		<b>81.9</b>

Table 16. NBO calculated stabilization energies ( $E_2$ ), based on the calculated geometries using B3LYP/6-31G\* level of theory, for  $\pi \rightarrow \pi^*$ , in the ground state structure of compound **4**.

Electron Transfers (Donor $\rightarrow$ Acceptor)	Resonance Energy (Stabilization Energy)			
	<b>4</b> -RRZ, $C_1$	<b>4</b> -RSZ, $C_1$	<b>4</b> -RRE, $C_1$	<b>4</b> -RSE, $C_1$
$\pi_{2-3} \rightarrow \pi^*_{4-5}$	4.77	6.63	3.44	14.65
$\pi_{1-2} \rightarrow \pi^*_{8-9}$	5.86	9.44	1.15	9.79
$\pi_{4-5} \rightarrow \pi^*_{2-3}$	4.23	5.84	2.38	8.46
$\pi_{8-9} \rightarrow \pi^*_{1-2}$	6.27	10.96	1.75	13.31
$\pi_{4-5} \rightarrow \pi^*_{7-8}$	0.80	-	-	-
$\pi_{7-8} \rightarrow \pi^*_{4-5}$	0.53	-	-	0.51
$\pi_{8-9} \rightarrow \pi^*_{2-3}$	0.77	-	0.57	-
$\pi_{1-2} \rightarrow \pi^*_{7-8}$	0.60	-	0.93	-
$\pi_{4-5} \rightarrow \pi^*_{1-2}$	-	-	1.38	-
$\pi_{8-9} \rightarrow \pi^*_{4-5}$	-	-	-	0.51
$\Sigma(\pi \rightarrow \pi^*)$	23.83	32.87	11.6	47.23

Table 17. NBO analysis results of  $\sigma$  bonding orbital deviations from their normal values (normal values:  $\sigma=0.0^0$ ) of various configurations of compound **4**, based on the B3LYP/6-31G\* calculated geometries.

Geometry	<b>4</b> -RRZ, $C_1$	<b>4</b> -RSZ, $C_1$	<b>4</b> -RRE, $C_1$	<b>4</b> -RSE, $C_1$
	Dev.	Dev.	Dev.	Dev.
<b>Orbitals</b>				
$\sigma_{C1-C2}$	6.7 7.2	4.0 4.8	3.1 3.2	5.0 6.0
$\sigma_{C2-C3}$	7.0 7.6	3.6 3.9	10.1 10.5	11.3 12.9
$\sigma_{C3-C4}$	2.3 3.3	- 2.6	10.2 10.0	13.7 12.6
$\sigma_{C4-C5}$	13.8 14.0	12.7 12.7	5.0 5.8	6.8 6.4
$\sigma_{C5-C6}$	-	2.2 2.3	6.1 10.2	6.6 12.4
$\sigma_{C6-C7}$	3.3 6.0	1.5 4.6	4.0 5.4	7.1 6.8
$\sigma_{C7-C8}$	4.4 5.4	6.8 8.4	3.8 4.5	4.2 4.9
$\sigma_{C8-C9}$	8.3 7.7	9.2 7.6	8.6 8.0	9.7 8.8
$\sigma_{C9-C1}$	6.3 6.2	6.0 5.8	7.1 8.3	9.8 10.8
$\Sigma\sigma_{Dev}$	109.5	98.7	123.9	155.8

Table 18. NBO analysis results of  $\pi$  bonding orbital deviations from their normal values (normal values:  $\pi=90.0^\circ$ ); and also, the  $\pi$  bonding and  $\pi^*$  anti-bonding occupancies of compound **5**, based on the B3LYP/6-31G\* calculated geometries.

Geometry	<b>5</b> -RSR, $C_2$		<b>5</b> -RSS, $C_1$		<b>5</b> -RRR, $C_2$	
	Occup.	Dev.	Occup.	Dev.	Occup.	Dev.
Orbitals						
$\pi_{C2-C3}$	1.90855	6.5 4.5	1.89842	4.8 2.9	1.93219	6.1 6.6
$\pi_{C1-C2}$	1.95389	1.5 4.6	1.95169	2.6 4.6	1.95339	0.6 2.3
$\pi_{C4-C3}$	1.91757	1.2 4.7	1.90323	1.6 5.2	1.93964	2.2 0.3
$\pi_{C8-C5}$	1.95391	1.4 4.6	1.93866	2.2 4.5	1.95286	0.5 2.5
$\pi^*_{C1-C2}$	0.05544	-	0.06003	-	0.06168	-
$\pi^*_{C2-C3}$	0.09509	-	0.10956	-	0.06627	-
$\pi^*_{C4-C3}$	0.09615	-	0.11421	-	0.07347	-
$\pi^*_{C8-C5}$	0.05552	-	0.07147	-	0.06300	-
$\sum\pi_{Dev}$		<b>29</b>		<b>28.4</b>		<b>21.1</b>

Table 19. NBO calculated stabilization energies ( $E_2$ ), based on the calculated geometries using B3LYP/6-31G\* level of theory, for  $\pi \rightarrow \pi^*$ , in the ground state structure of compound **5**.

Electron Transfers (Donor $\rightarrow$ Acceptor)	Resonance Energy (Stablization Energy)		
	<b>5</b> -RSR, $C_2$	<b>5</b> -RSS, $C_1$	<b>5</b> -RRR, $C_2$
$\pi_{2-3} \rightarrow \pi^*_{4-5}$	11.34	11.96	4.64
$\pi_{5-6} \rightarrow \pi^*_{7-8}$	9.65	0.66	3.03
$\pi_{4-5} \rightarrow \pi^*_{2-3}$	9.62	10.90	3.43
$\pi_{7-8} \rightarrow \pi^*_{5-6}$	11.35	0.79	0.58
$\pi_{5-6} \rightarrow \pi^*_{8-9}$	-	0.7	0.83
$\pi_{7-8} \rightarrow \pi^*_{4-5}$	-	0.66	0.58
$\sum(\pi \rightarrow \pi^*)$	<b>41.96</b>	<b>25.67</b>	<b>13.09</b>

Table 20. NBO analysis results of  $\sigma$  bonding orbital deviations from their normal values (normal values:  $\sigma=0.0^0$ ) of various configurations of compound **5**, based on the B3LYP/6-31G\* calculated geometries.

Geometry	5-RSR, $C_2$ Dev.	5-RSS, $C_1$ Dev.	5-RRR, $C_2$ Dev.
<b>Orbitals</b>			
$\sigma_{C1-C2}$	2.4 2.8	1.3 -	-
$\sigma_{C2-C3}$	7.0 6.3	5.0 4.3	11.0 9.7
$\sigma_{C3-C4}$	5.3 5.7	4.8 5.1	4.8 5.8
$\sigma_{C4-C5}$	2.5 3.3	2.5 3.1	5.0 5.6
$\sigma_{C5-C6}$	2.5 3.4	4.7 5.1	5.0 5.6
$\sigma_{C6-C7}$	5.3 5.7	5.6 6.0	5.0 5.9
$\sigma_{C7-C8}$	7.0 6.3	6.8 6.1	11.0 9.7
$\sigma_{C8-C9}$	2.3 2.8	2.1 2.4	-
$\sigma_{C9-C10}$	1.0 3.3	3.2 5.2	-
$\sigma_{C10-C1}$	- 3.3	3.2 5.3	-
$\Sigma\sigma_{Dev}$	<b>78.2</b>	<b>81.8</b>	<b>84.1</b>

Representative structural parameters for various configurations of compounds **1-5**, are given in Figs. 1-5, respectively. Theoretical calculations provide structural parameters for isolated molecule at 0K, therefore, theoretical calculations are not reported, in principal, to reproduce the experimental values quantitatively.<sup>26</sup> Nevertheless, it is possible to carry out ab initio calculations, for instance at the Hartree-Fock level, from which many properties and structures can be obtained with an accuracy that is competitive with experiments.<sup>27-30</sup> The  $C_{sp^2}-C_{sp^2}-C_{sp^2}-C_{sp^2}$  arrangement in the allenic moieties of the unstable configurations of compounds 1-5 are twisted from their minimum energy states (with a corresponding angle of  $90^\circ$ ), as a result of ring strain.

In addition, the  $C=C=C$  fragments are bent in various configurations of compound **1** and contracted from the normal value of  $180^\circ$  (see Fig.5). The angles of the  $C=C=C$  fragments in the **1-ZRZ**, **1-ZRE**, **1-ERE** (parallel,  $C_1$  symmetry) and **1-ERE** (perpendicular,  $C_2$  symmetry) configurations are  $159.1^\circ$ ,  $155.2^\circ$ ,  $146.4^\circ$  and  $143.6^\circ$ , respectively (see Fig. 1). These results show that the  $C=C=C$  fragment twisting in the **1-ZRZ** configuration is smaller than that the other configurations.

The  $C=C=C$  fragment and also  $C_{sp^2}-C_{sp^2}-C_{sp^2}-C_{sp^2}$  dihedral angle deviations can be seen in the various configurations of compounds **2-5** (see Figs. 2-5).

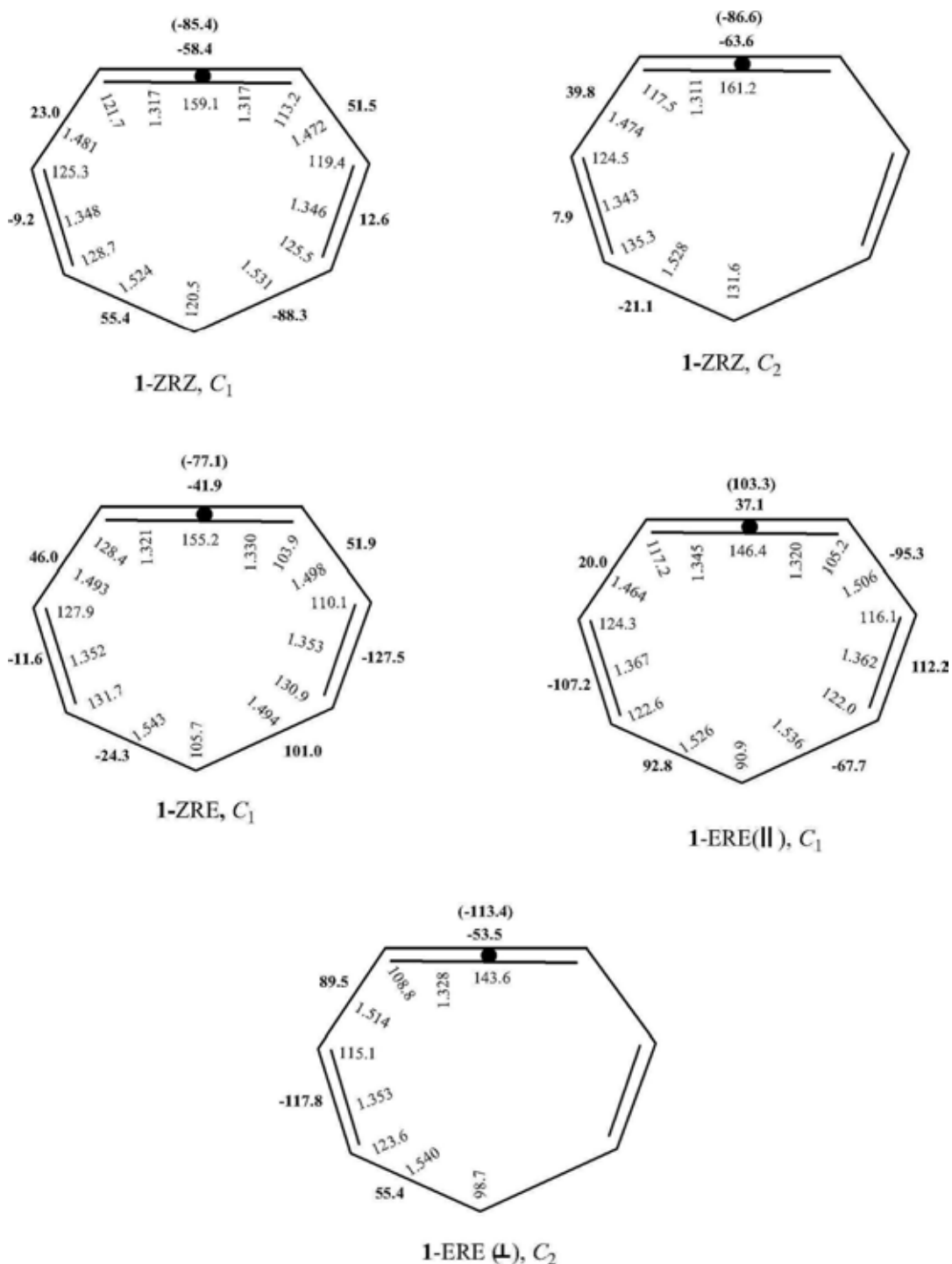


Fig. 1. B3LYP/6-31G\* calculated structural parameters for the energy-minimum and energy-minimum configurations of compound **I**. Bond lengths are in angström (Å) unit and angles in degrees (°).

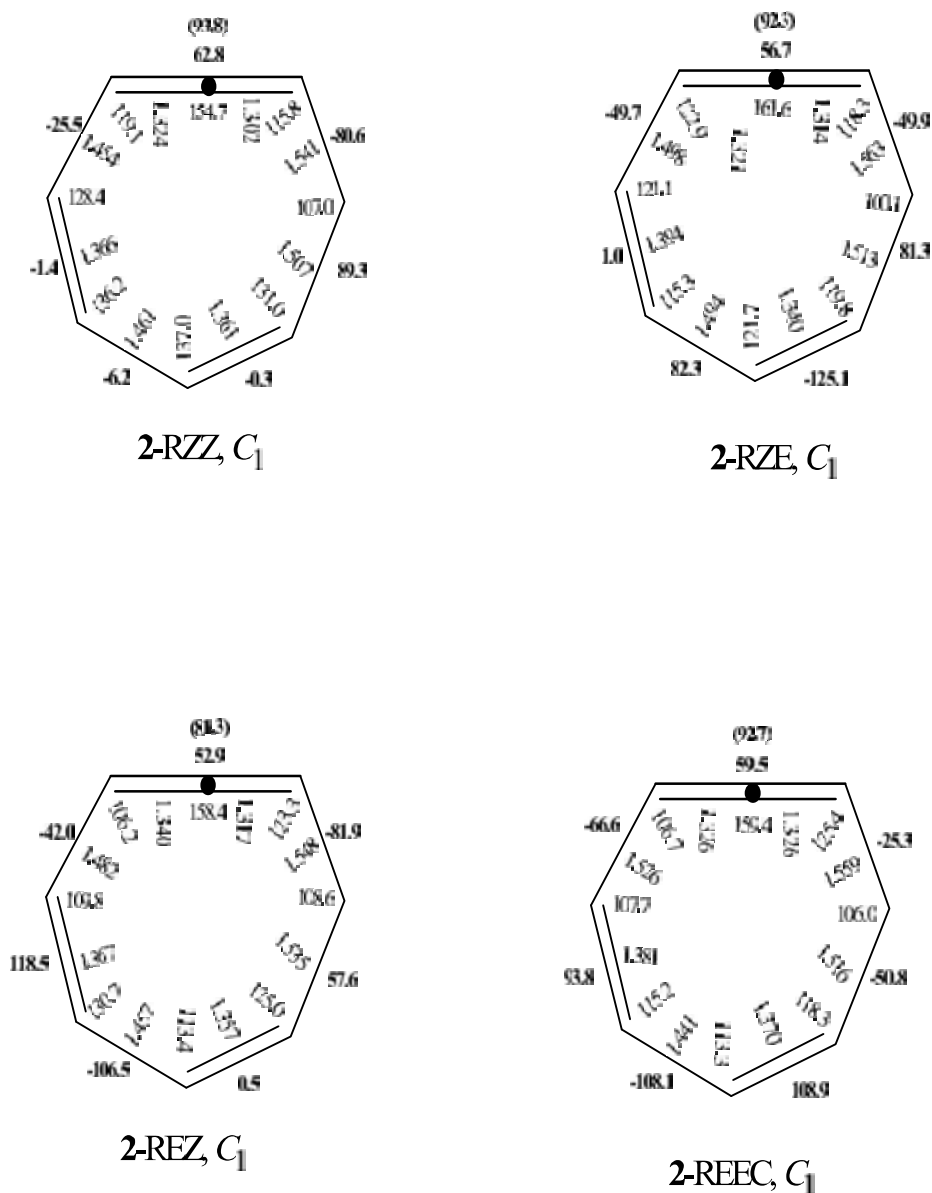


Fig. 2. B3LYP/6-31G\* calculated structural parameters for the energy-minimum and energy-minimum configurations of compound **2**. Bond lengths are in angstrom ( $\text{\AA}$ ) unit and angles in degrees ( $^\circ$ ).



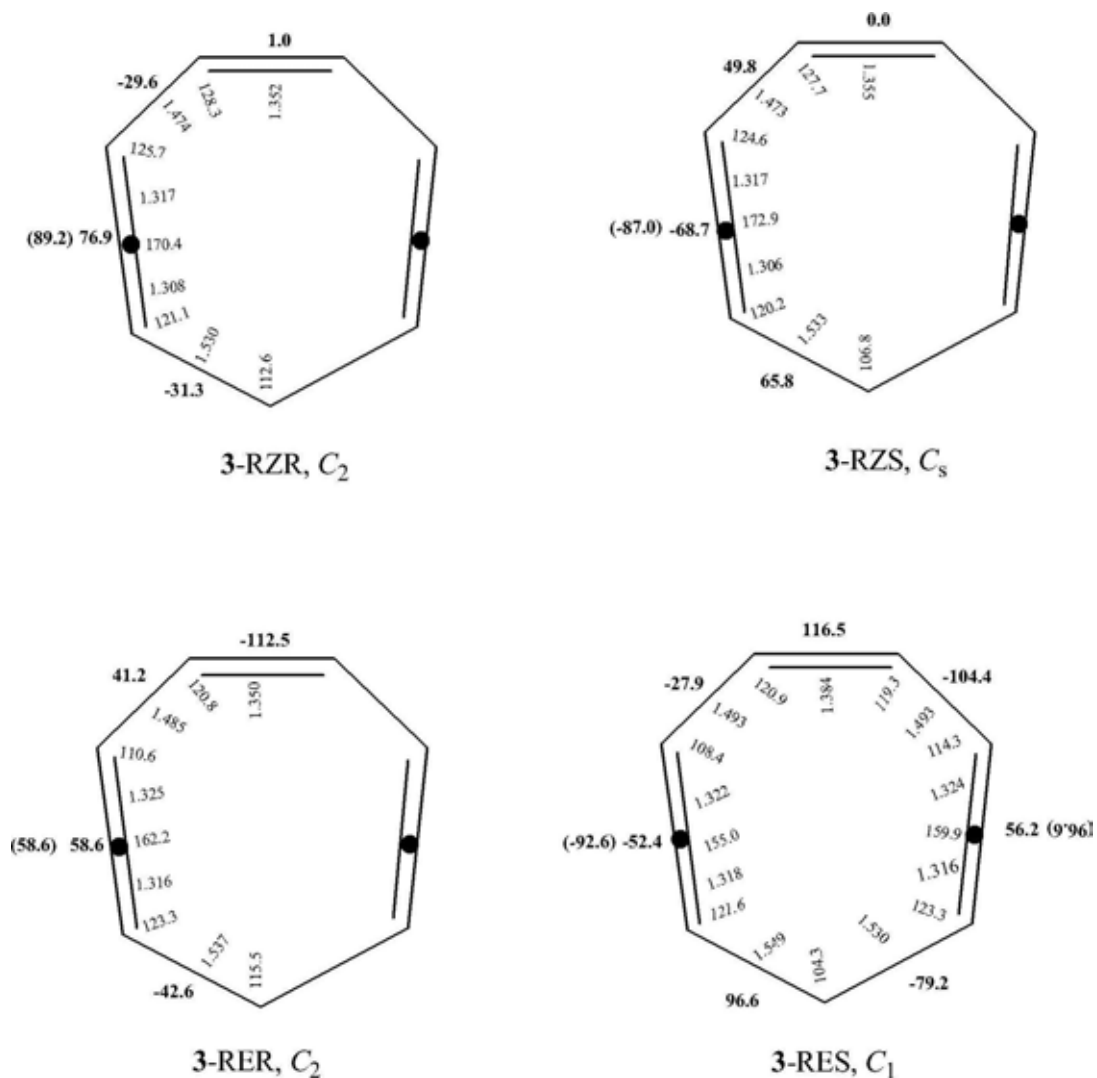


Fig. 3. B3LYP/6-31G\* calculated structural parameters for the energy-minimum and energy-minimum configurations of compound **3**. Bond lengths are in angström (Å) unit and angles in degrees (°).

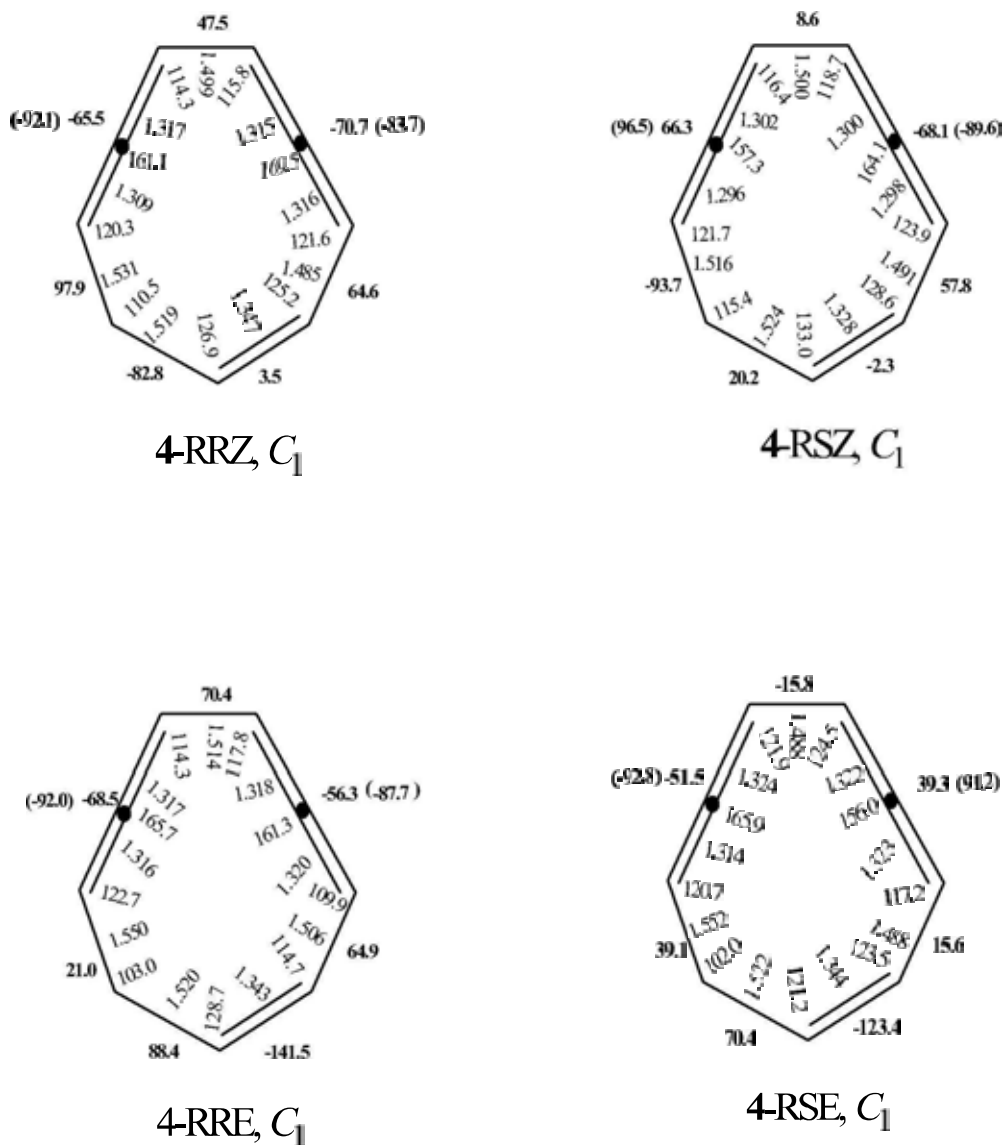


Fig. 4. B3LYP/6-31G\* calculated structural parameters for the energy-minimum and energy-minimum configurations of compound **4**. Bond lengths are in angström (Å) unit and angles in degrees (°).

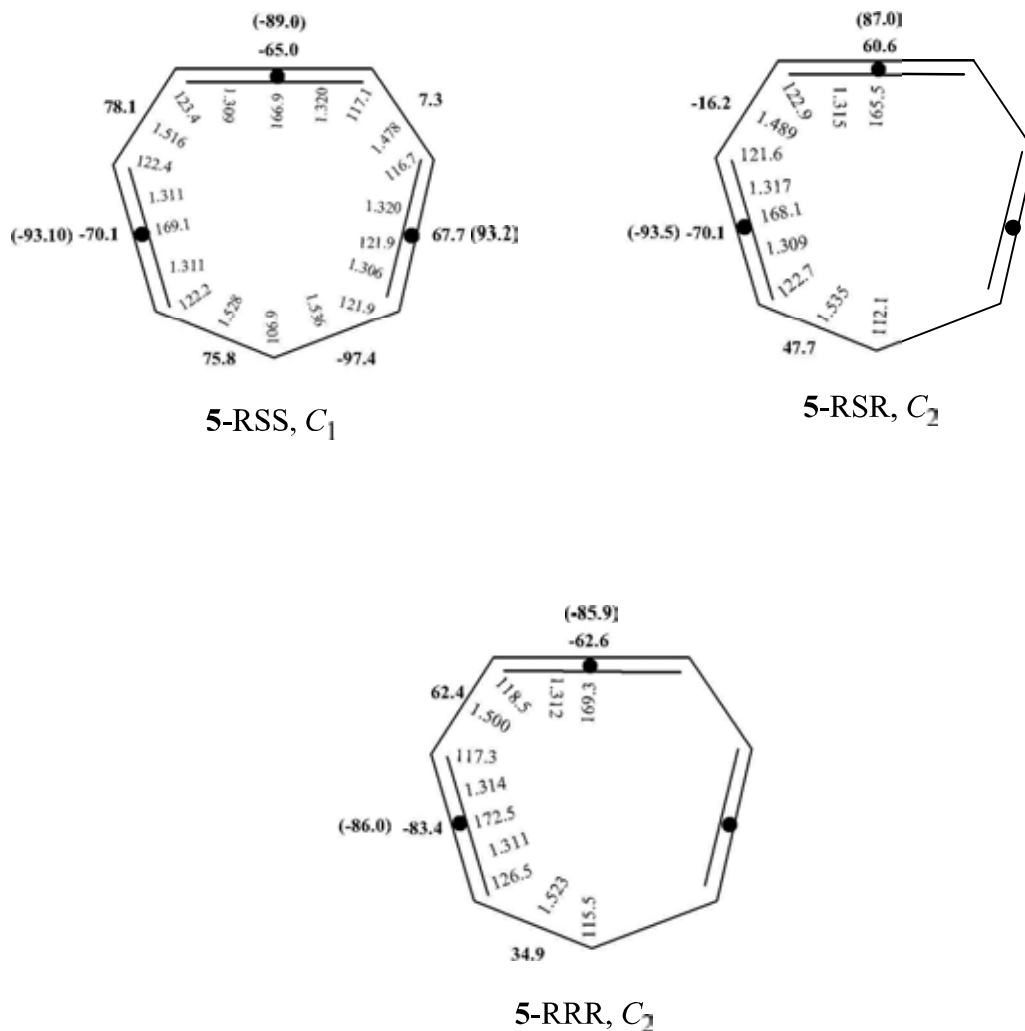


Fig. 5. B3LYP/6-31G\* calculated structural parameters for the energy-minimum and energy-minimum configurations of compound **5**. Bond lengths are in angström (Å) unit and angles in degrees (°).

## Conclusion

NBO analysis, density functional theory (DFT: B3LYP/6-31G\*\*/B3LYP/6-31G\*) and ab initio molecular (MO: MP2/6-31G\*\*/B3LYP/6-31G\*) based methods provided a useful picture both from bonding, energetic and also structural properties for possible configurations of compounds **1-5**. MP2/6-31G\*\*/B3LYP/6-31G\* and B3LYP/6-31G\*\*/B3LYP/6-31G\* results revealed that **1-ZRE** ( $C_1$  symmetry), **2-RZZ** ( $C_1$  symmetry), **3-RZR** ( $C_2$  symmetry), **4-RRZ** ( $C_1$  symmetry) and **5-RSS** ( $C_1$  symmetry) configurations are the most stable forms of compounds **1-5**, respectively. These configurations are expected to be significantly populated at room temperature.

In conclusion, NBO results show that the deviations of  $\pi$  and  $\sigma$  bonding orbitals ( $\Sigma(\sigma_{dev} + \pi_{Dev})$ ) could fairly explain the relative stability of configurations of all above compounds

It would be valuable, of course, to have direct experimental data on the configurations of compound **1** for comparison with the results of ab initio calculations and NBO analysis.

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