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*m*PW1PW91 Conformational Study of Di-*t*-butyl-dinitro-tetramethoxysulfonylcalix[4]arene

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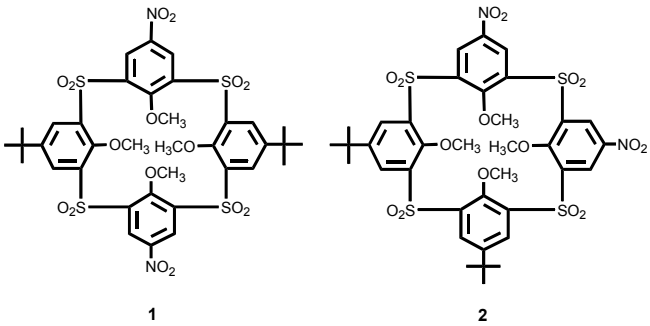
The structures of the conformers for 1,3-di-*t*-butyl-2,4-dinitro-tetramethoxysulfonylcalix[4]arene (**1**) and 1,2-di-*t*-butyl-3,4-dinitro-tetramethoxysulfonylcalix[4]arene (**2**) were optimized using *DFT* BLYP and mPW1PW91/6-31G(d,p) (hybrid HF-DF) calculation methods. We have analyzed the total electronic and Gibbs free energies and the differences between the various conformations (cone, partial-cone (PC), 1,2-alternate, and 1,3-alternate) of **1** and **2**. For both compounds, the 1,3-alternate (1,3-A) conformers were calculated to be the most stable, which correlate very well with the experimental results**.** The orderings of the relative stability of **1** and **2** that resulted from the *m*PW1PW91/6-31G(d,p) calculations are the following: **1**: 1,3-A (*syn*) > PC (*syn*) > PC (*anti*) > 1,2-A (*anti*) > CONE (*syn*); **2**: 1,3-A (*anti*) > PC (*anti*) > PC (*syn*) > 1,2-A (*anti*) > 1,2-A (*syn*) > CONE (*syn*). The BLYP/6-31G(d) calculated IR spectra of the most stable 1,3-A conformers of **1** and **2** are compared.

Key Words: *m*PW1PW91, BLYP, Conformer, 1,3-Alternate, Thiacalix[4]arene

Introduction

Thiacalix[4]arenes represent a very promising group of macrocyclic compounds with many applications in supramolecular chemistry.[1] The presence of the four sulfur atoms instead of the methylene bridges imposes many novel, interesting features in thiacalixarenes[2] when compared to classical calixarenes.[3] This makes such compounds of particular interest, especially with potential applications such as inclusion of a variety of guest molecules, recognition of metal ions, chiral recognition, novel anion receptors, and novel dendritic-shelled molecular receptors.[4] Oxidation of the sulphur bridges to the corresponding sulfoxide or sulfone derivative, reactions unknown in the chemistry of 'classical' calixarenes, have been reported.[5,6] These novel features, together with substantially different conformational preferences[7] and unusual complexation abilities,[8] make thiacalixarenes prime candidates for the role of building blocks and molecular scaffolds. Lhoták *et al.* have extensively studied the direct nitration of the thiacalix[4]arene upper rim, synthesizing 1,3-di-*t*-butyl-2,4-dinitro-tetramethoxysulfonylcalix[4]arene (**1**) and 1,2-di-*t*-butyl-3,4-dinitro- tetramethoxysulfonylcalix[4]arene (**2**).[9]



Scheme 1. Chemical structure of the 1,3-di-*t*-butyl-2,4-dinitro-tetramethoxysulfonylcalix[4]arene (**1**) and 1,2-di-*t*-butyl-3,4-dinitro-tetramethoxysulfonylcalix[4]arene (**2**)

In this study, the conformers (cone, partial-cone, 1,2-alternate, 1,3-alternate) of **1** and **2** were optimized using BLYP and *m*PW1PW91 (hybrid HF-DF) calculation methods. The primary objective of this research was to determine the structures and relative stability of the different conformers for **1** and **2** using the *m*PW1PW91/6-31G(d,p) calculation method. The secondary objective was to compare the calculated IR spectra of the most stable conformers of **1** and **2** obtained from the *DFT* BLYP/6-31G(d) method.

Computational Methods

The initial conformations of the 1,3-di-*t*-butyl-2,4-dinitro-tetramethoxysulfonylcalix[4]arene (**1**) and 1,2-di-*t*-butyl-3,4-dinitro-tetramethoxysulfonylcalix[4]arene (**2**) were constructed using the molecular mechanics (MM), molecular dynamics (MD), and semi-empirical calculations of HyperChem.[10] Optimized structures were found by conformational searches by a previously described simulated annealing method.[11] The conformers (CONE, PC, 1,2-A, 1,3-A) of **1** and **2** obtained from the MM/MD and AM1 calculations were fully re-optimized using a *DFT* method to determine both the relative energies and structures of the distinct conformers. The *DFT* BLYP/6-31G(d) method was used to calculate the normal mode frequencies of the final structures. Each vibrational spectrum showed no negative frequencies, confirming that the optimized structures exist at an energy minimum. For direct comparison with experimental data, the calculated vibrational frequencies were scaled by the recommended scale factor (0.893).[12] Furthermore, broadened IR spectra are presented assuming a Lorentzian line width of 10 cm^{-1}.

Modified Perdew-Wang 1-parameter (*m*PW1) calculation methods,[12,13] such as *m*PW1PW91, are new hybrid Hartree-Fock-density functional (HF-DF) models that obtain remarkable results both for covalent and non-covalent interactions.[14]

Additional *m*PW1PW91/6-31G(d,p) optimizations were performed using Gaussian 03[15] to obtain more accurate total electronic energies and structures for conformational stereoisomers of **1**.

Results and Discussion

The structures of the conformers for 1,3-di-*t*-butyl-2,4-dinitro-tetramethoxysulfonylcalix[4]arene (**1**) and 1,2-di-*t*-butyl-3,4-dinitro-tetramethoxysulfonylcalix[4]arene (**2**) were optimized using *DFT* BLYP and mPW1PW91/6-31G(d,p) (hybrid HF- DF) calculation methods.

Since only two out of the four *t*-butyl groups in the *p-tert*-butyltetramethoxysulfonylcalix[4] arene are substituted, two kinds (*syn* and *anti*) of partial-cone (PC) conformers of **1** and **2** were possible. Furthermore, the 1,2-alternate (1,2-A) of **2** can also possess *syn* and *anti* conformations. The structures of the five conformations [CONE (syn), PC (syn), PC (anti), 1,2-A (*anti*), 1,3-A (*syn*)] of **1** and the six conformations [CONE (syn), PC (syn), PC (anti), 1,2-A (*syn*), 1,2-A (*anti*), 1,3-A (*anti*)] of **2** were obtained by complete optimization without any constraints with the 6-31G(d) basis set at the restricted BLYP level. The normal vibrational frequencies and Gibbs free energies were calculated using the optimized structures. These geometries were then used as input for additional optimizations with the 6-31G(d,p) basis set.

Table 1 reports the BLYP/6-31(d,p) optimized total electronic energies and the differences between the various conformations (cone, partial-cone (PC), 1,2-alternate, and 1,3-alternate) of **1** and **2**. Table 2 reports the BLYP/6-31(d) optimized Gibbs free energies and the differences between the various conformations of **1** and **2**. The relative stabilities (ΔE and ΔG) of the various conformers obtained from the BLYP calculations in Tables 1 and 2 show a similar trend, and suggest that there is no entropy effect between different conformers. These BLYP calculations report that the 1,3-alternate conformers are the most stable for both compounds of **1** and **2**, respectively.

The total electronic energies of these structures were additionally optimized by the *m*PW1PW91 method with the 6-31G (d,p) basis set.

Table 3 reports the *m*PW1PW91/6-31G(d,p) optimized total electronic energies and their differences and the dipole moments of the distinct conformers of **1** and **2**. The *m*PW1PW91/6-31G (d,p) calculations in Table 3 also suggest that the 1,3-alternate conformers are the most stable for both compounds of **1** and **2**, respectively. These calculated results accord very well with the experimental results.[9] The orderings of relative stability obtained from the mPW1PW91/6-31G(d,p) calculations are the following: **1**: 1,3-A (*syn*) > PC (*syn*) > PC (*anti*) > 1,2-A (*anti*) > CONE (*syn*); **2**: 1,3-A (*anti*) > PC (*anti*) > PC (*syn*) > 1,2-A (*anti*) > 1,2-A (*syn*) > CONE (*syn*).

These relative stabilities of the conformers of **1** and **2** are very similar to the trend of the calculated results obtained from tetra-*t*-butyl-tetramethoxysulfonylcalix[4]arene.[16a] However, the orderings of the conformers of **1** and **2** are different from the calculated outcomes of the stereoisomers of tetra-*t*-butyl-tetra-*O*-methylsulfinylcalix[4]arene.[16b]

The dipole moments of the various conformers of **1** and **2** in Table 3 show that the magnitude (11.00 Debye) of the most stable 1,3-A (*syn*) conformer of **1** was substantial due to the *syn*-position of the 1,3-nitro groups and, that the value (0.97 Debye) of the most stable 1,3-A (*anti*) conformer of **2** was very small due to the *anti*-position of the 1,2-nitro groups.

The *m*PW1PW91/6-31G(d,p) calculated average bond distance (1.79 Å) between the bridging sulfur and carbon atoms of **1** was slightly longer than the experimental[9] C-S distance (1.77 Å). The calculated average bond distances (1.46 Å) between the bridging sulfur and oxygen atoms of **1** were also

Table 1. BLYP/6-31G(d,p) calculated energies of the various conformers of **1** and **2**

	1	**2**
Conformer	ΔE^a	ΔE^a
CONE (*syn*)	10.70	12.20
PC (*syn*)	3.67	5.21
PC (*anti*)	4.40	4.22
1,2-A (*syn*)	not applicable	10.93
1,2-A (*anti*)	8.96	9.78
1,3-A (*syn*)	−4299.21184[b]	not applicable
1,3-A (*anti*)	not applicable	−4299.21262[b]

[a]The relative energy (kcal/mol) compared to the most stable 1,3-A conformer. [b]Total electronic energy written in Hartree.

Table 2. BLYP/6-31G(d) calculated Gibb free energies of the various conformers of **1** and **2**

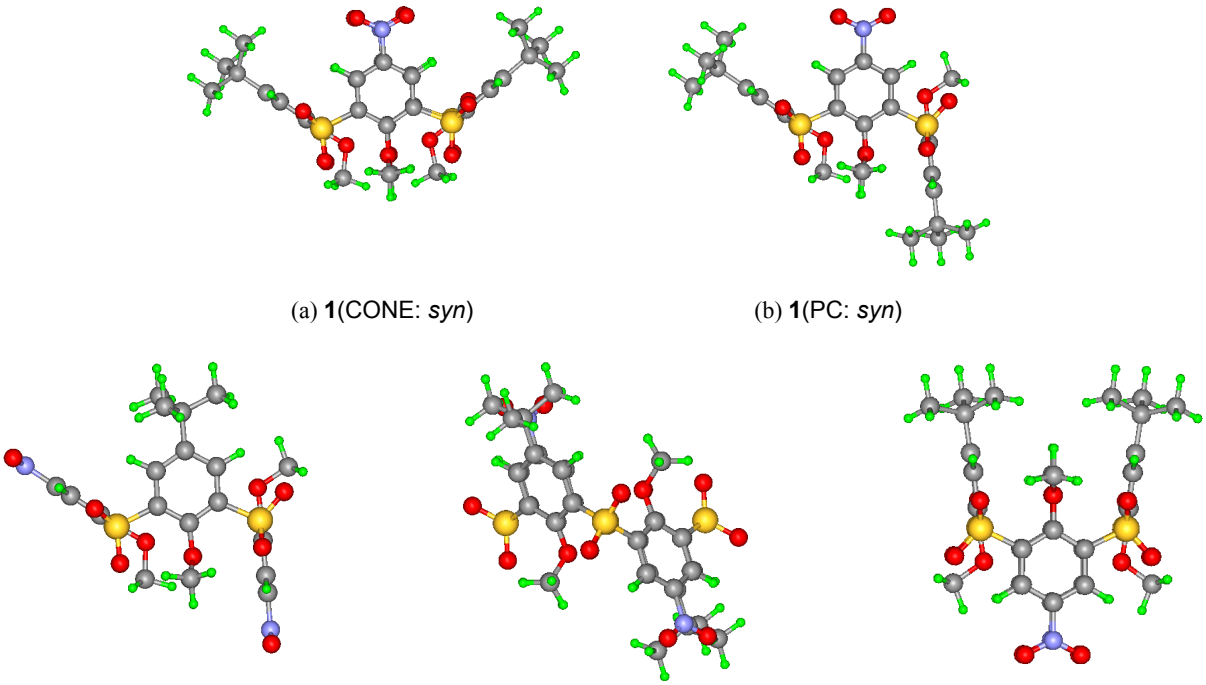
	1	**2**
Conformer	ΔG^a	ΔG^a
CONE (*syn*)	9.32	10.44
PC (*syn*)	3.64	4.44
PC (*anti*)	4.44	3.90
1,2-A (*syn*)	not applicable	
1,2-A (*anti*)	7.99	8.43
1,3-A (*syn*)	−4298.60873[b]	not applicable
1,3-A (*anti*)	not applicable	−4298.60949[b]

[a]The relative Gibbs free energy (kcal/mol) compared to the most stable 1,3-A conformer. [b]Total Gibbs free energy at 298 K written in Hartree.

Table 3. mPW1PW91/6-31G(d,p) calculated energies and dipole moment (Debye) of the various conformers of **1** and **2**

	1		**2**	
Conformer	ΔG^a	Dipole moment	ΔG^a	Dipole moment
CONE (*syn*)	12.15	1.52	13.89	5.78
PC (*syn*)	4.23	6.33	6.06	5.33
PC (*anti*)	4.93	7.20	4.89	6.14
1,2-A (*syn*)	not applicable		12.97	11.12
1,2-A (*anti*)	10.38	0.04	11.50	3.96
1,3-A (*syn*)	−4299.48667[b]	11.00	not applicable	
1,3-A (*anti*)	not applicable		−4299.48799[b]	0.97

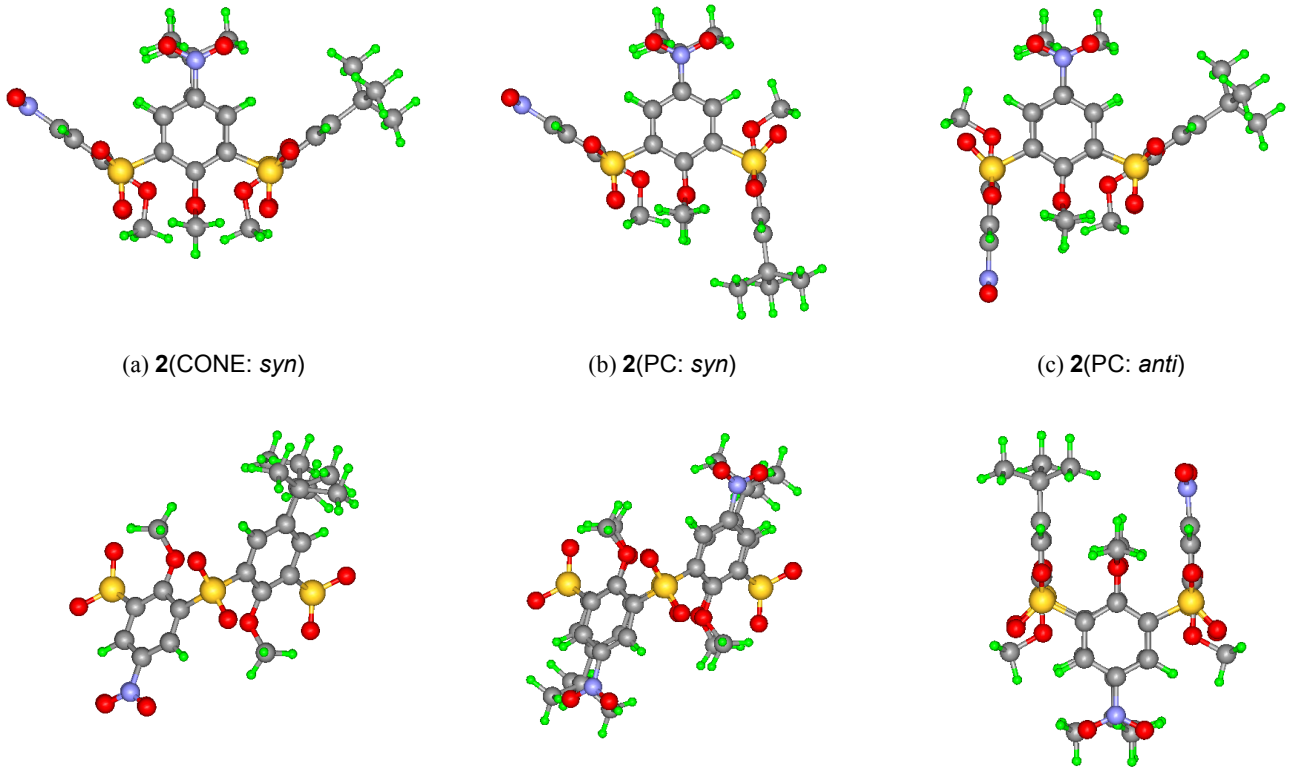
[a]The relative energy (kcal/mol) compared to the most stable 1,3-A conformer. [b]Total electronic energy written in Hartree.



(a) **1**(CONE: *syn*) (b) **1**(PC: *syn*)

(c) **1**(PC: *anti*) (d) **1**(1,2-A: *anti*) (e) **1**(1,3-A: *syn*)

Figure 1. *m*PW1PW91/6-31G(d,p) calculated structures of five conformers (CONE (*syn*), PC (*syn*), PC (*anti*), 1,2-A (*anti*), 1,3-A (*syn*)) of **1**. Visualizations of the optimized structures in Fig. 1 and 2 were performed with PosMol.[17]



(a) **2**(CONE: *syn*) (b) **2**(PC: *syn*) (c) **2**(PC: *anti*)

(d) **2**(1,2-A: *syn*) (e) **2**(1,2-A: *anti*) (f) **2**(1,3-A: *anti*)

Figure 2. *m*PW1PW91/6-31G(d,p) calculated structures of six conformers (CONE (*syn*), PC (*syn*), PC (*anti*), 1,2-A (*syn*), 1,2-A (*anti*), 1,3-A (*anti*)) of **2**.

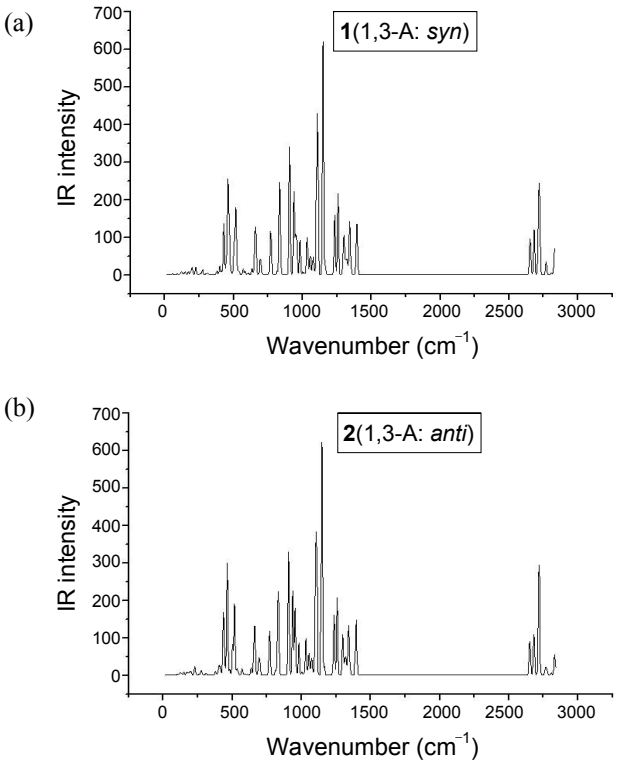


Figure 3. The BLYP/6-31G(d) calculated IR spectra of the most stable 1,3-A conformers of **1** and **2**, respectively. (a) **1**(1,3-A: *syn*); (b) **2**(1,3-A: *anti*).

longer than the experimental[9] value (1.43 Å) of S=O. The average calculated distances between the two adjacent and two opposite sulphur atoms of 1,3-A of **1** were 5.61 and 7.93 Å (experimental[9] 5.54 and 7.84 Å), respectively, while the typical distances between corresponding CH_2 groups in the 1,3-A of calix[4]arene (**3**) were 5.0 and 7.1 Å. This demonstrates the larger cavity of the thiacalix[4]arenes in comparison to classical calix[4]arenes.

The BLYP/6-31G(d) calculated IR spectra of the most stable conformers of **1** and **2** are compared in Table 4 and Fig. 3. The main features (frequencies and intensities) of the most stable 1,3-A conformers of **1** and **2** differ very little between each other. However, detailed vibrations have a variety of concerted motions of molecular skeletons. Table 4 lists the common features of the 1,3-A conformers of **1** and **2**. The first series of five peaks (427 ~ 770 cm^{-1}) arose from the concerted motions of the various (C-C, C-S, C-O, C-N) stretching vibrations and out-of-plane and in-plane bending vibrations of the molecular skeleton. The IR spectra of **1** and **2** showed distinct vibrational characteristics in low frequencies. The sixth peak (833 or 835 cm^{-1}) was caused by C_{me}-O_{ether} (the bond between the methoxy carbon and ether oxygen) stretching vibrations. The seventh peak (906 or 905cm^{-1}) was composed of S=O bond stretching vibrations. The eighth peak (937 cm^{-1}) arose from C-S bond stretching vibrations. The ninth peak (1109 cm^{-1}) was due to the concerted vibrations of C_{ar}-O bond stretching and anti-symmetric S=O stretchings. The tenth peak (1149 cm^{-1}) came from two C-N stretching vibrations, which appeared as a single, large peak

Table 4. Main characteristic features of BLYP calculated vibrational modes of the most stable 1,3-A conformers of **1** and **2**

	1(1,3-A: *syn*)			**2** (1,3-A: *anti*)	
Peak No.	Energy/cm^{-1}	Intensity[a]	Vibrational modes: Description	Energy/cm^{-1}	Intensity[a]
1-5	427 458 514 658 768	136 255 178 127 116	out-of-plane + in-plane bending and stretching vibrations of molecular skeleton	436 464 515 662 770	167 298 189 131 117
6	833	245	C_{me}-O stretching	835	223
7	906	340	S=O stretching	905	328
8	937	222	C-S stretching	937	225
9	1109	428	C_{ar}-O stretching + anti-symmetric S=O stretching	1109	383
10	1149	620[b]	C-N stretching	1149	599[b]
11-14	1234 1259 1301 1344	159 216 104 142	CCH and OCH bendings + C-C and C_{ar}-O stretching (anti-symmetric)	1237 1259 1299 1341	160 206 109 133
15	1397	135	N=O stretching	1398	137
16-19[c]	2652 2682 2717 2830	91 119 244 69	C-H stretchings[c] in benzyl, methyl and *t*-butyl group	2651 2682 2719 2830	91 109 293 54

[a]Calculated infrared intensity from BLYP/6-31G(d) method by the broadened IR spectra assuming a Lorentzian line width of 10 cm^{-1}. [b]This large peak is made by the broadened IR spectra of four peaks of S=O stretching vibrations. [c]Various peaks from the C-H stretching vibrations from the methoxy and *t*-butyl groups and benzyl rings.

due to the Lorentzian line broadening of 10 cm^{-1}. The next series of four peaks (1234 ~ 1344 cm^{-1}) arose from vibrations of CCH and OCH angle bending and anti-symmetric C-C and C_{ar}-O stretching. The fifteenth peak (1397 or 1398 cm^{-1}) came from N=O stretching vibrations.

The final series of four peaks (2651 ~ 2830 cm^{-1}) are composed of various C-H stretching vibrations: 16th (2652 cm^{-1}): C_{tb}-H (the bond between the *t*-butyl carbon and hydrogen atom) stretching; 17th (2682 cm^{-1}): C_{me}-H (the bond between the methoxy carbon and hydrogen atom) stretching; 18th (2717 cm^{-1}): C_{tb}-H (the bond between the *t*-butyl carbon and hydrogen atom) stretching; 19th (2830 cm^{-1}): C_{ar}-H (the bond between the aromatic carbon and hydrogen atom) stretching.

Conclusion

The total electronic and Gibbs free energies and the differences between the various conformations (cone, partial-cone (PC), 1,2-alternate, and 1,3-alternate) of **1** and **2** were calculated using *DFT* BLYP and *m*PW1PW91/6-31G(d,p) (hybrid HF-DF) calculation methods. For both compounds, the 1,3-alternate conformers were calculated to be the most stable, which correlate very well with the experimental results**.** The orderings of the relative stability of **1** and **2** that resulted from the *m*PW1PW91/6-31G(d,p) calculations are the following: **1**: 1,3-A (*syn*) > PC (*syn*) > PC (*anti*) > 1,2-A (*anti*) > CONE (*syn*); **2**: 1,3-A (*anti*) > PC (*anti*) > PC (*syn*) > 1,2-A (*anti*) > 1,2-A (*syn*) > CONE (*syn*).

The main features (frequencies and intensities) of the BLYP/6-31G(d) calculated IR spectra of the most stable 1,3-A conformers of **1** and **2** differ very little between each other. However, detailed vibrations in low frequencies (427 ~ 770 cm^{-1}) have different concerted-motions of molecular skeletons.

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