

BLYP and mPW1PW91 Calculated Structures and IR Spectra of the Stereoisomers of Tetra-*O*-methylsulfinylcalix[4]arene

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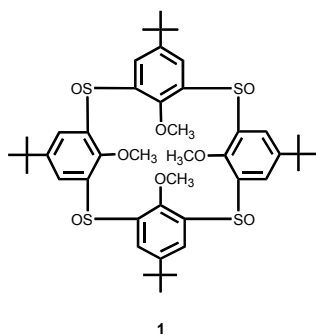
Molecular structures of the various conformers for the four stereoisomers of tetra-*t*-butyl-tetra-*O*-methylsulfinylcalix[4]arene (**1**) were optimized using *DFT*BLYP and *mPW1PW91/6-31G(d,p)* (hybrid HF-DF) calculation methods. We have analyzed the total electronic and Gibbs free energies and normal vibrational frequencies of 16 different structures from four major conformations (cone (CONE), partial cone (PC), 1,2-alternate (1,2-A), 1,3-alternate (1,3-A)) of the four stereoisomers [**1**(*rccc*), **1**(*rcct*), **1**(*rctt*), **1**(*rtct*)]. The *mPW1PW91/6-31G(d,p)* calculations suggested that the **1**(*rccc*)_{CONE}, **1**(*rcct*)_{PC}, **1**(*rctt*)_{PC}, and **1**(*rtct*)_{1,3-A} were the most stable conformations of the respective stereoisomers. These outcomes are in accordance with the experimental structures obtained from X-ray crystallography. The electrostatic repulsion between the sulfinyl and methoxy groups is a primary factor for the relative stabilities of the four different conformations. The IR spectra of the most stable conformers [**1**(*rccc*)_{CONE}, **1**(*rcct*)_{PC}, **1**(*rctt*)_{PC}, **1**(*rtct*)_{1,3-A}] of each stereoisomer were compared to each other.

Key Words: mPW1PW91, Conformer, Stereoisomer, Infrared, Sulfinylcalix[4]arene

Introduction

Thiacalix[4]arenes in the presence of sulfur atoms, instead of methylene groups, exhibit novel structural and functional features, including facile oxidation of sulfur bridges and extra binding sites. 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.¹⁻³ The oxidation of sulphur bridges to the corresponding sulfoxide⁴ or sulfone⁵ derivative, reactions unknown in the chemistry of 'classical' calixarenes, have been reported.⁶ These novel features, together with substantially different conformational preferences⁷ and unusual complexation abilities,⁸ make thiacalixarenes good candidates for the role of building blocks and molecular scaffolds.

Recently, the conformational behaviors of all four stereoisomers [**1**(*rcct*), **1**(*rcct*), **1**(*rtct*), **1**(*rccc*)] of tetra-*t*-butyl-tetra-*O*-methylsulfinylcalix[4]arene (**1**) were studied by ¹H-NMR spectroscopic methods.⁹



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Scheme 1. Chemical structure of tetra-*t*-butyl-tetra-*O*-methylsulfinylcalix[4]arene (**1**)

In this study, we have optimized the conformers (cone, partial-cone, 1,2-alternate, 1,3-alternate) of the four stereoisomers of **1** using BLYP and *mPW1PW91* (hybrid HF-DF) calculation methods. The primary objective of this research is to determine the structures and relative stability of the 16 different conformational stereoisomers for **1** using the *mPW1PW91/6-31G(d,p)* calculation method. The secondary objective is to compare the calculated IR spectra of the most stable conformers of four stereoisomers of **1** obtained from the *DFT*BLYP/6-31G(d) method.

Computational Methods

The initial 16 conformational stereoisomers of **1** were constructed using the molecular mechanics (MM), molecular dynamics (MD), and semi-empirical calculations of HyperChem.¹⁰ Optimized structures were found by conformational searches using a previously described, simulated annealing method.¹¹ The stereoisomers of **1** obtained from the MM/MD and AM1 calculations were fully re-optimized using an *DFT* method to determine both the relative energies and structures of 16 distinct conformational stereoisomers. The *DFT* BLYP/6-31G(d) method was used to calculate the normal mode frequencies of the final structures. Each vibrational spectrum shows no negative frequencies, confirming that the optimized structures exist in energy minima. For direct comparison with experimental data, the calculated 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 (*mPW1*) calculation methods,^{12,13} such as *mPW1PW91*, are new hybrid Hartree-Fock-density functional (HF-DF) models that obtain remarkable results both for covalent and non-covalent interactions.¹⁴ Additional *mPW1PW91/6-31G(d,p)* optimizations were performed using Gaussian 03 to obtain more accurate total electronic energies and structures for conformational stereoisomers of **1**.

Result and Discussion

The structures of the four main conformations (CONE, PC, 1,2-A, 1,3-A) of the four stereoisomers [**1**(*rccc*), **1**(*rcct*), **1**(*rcct*), **1**(*rtct*)] (refer to Fig. 7 of reference 1(b) and Fig. 1 of reference 9 for the configurational notations of sulfinylcalixarenes) were obtained with the 6-31G(d) basis set by complete optimization without any constraints 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 shows the BLYP optimized total electronic and Gibbs free energies for the 16 compounds. The BLYP/6-31G(d) calculated Gibbs free energies in Table 1 suggest that the CONE conformation was the most stable of the four conformers of the **1**(*rccc*) stereoisomer, that the PC was the most stable conformer of the **1**(*rcct*) and **1**(*rcct*) stereoisomers, and that the 1,3-A conformation was the most stable of the **1**(*rtct*) stereoisomer. And the PC conformer of the **1**(*rcct*) stereoisomer is the global minimum among the 16 conformational stereoisomers. However, the BLYP/6-31G(d,p) calculated total electronic energies tell that the 1,3-A conformation of the **1**(*rtct*) stereoisomer has

Table 1. BLYP calculated relative energies (in kcal/mol)^a of the conformational stereoisomers of tetra-*O*-methylsulfinylcalix[4]arene (**1**)

Stereoisomer ^b	Basis set		/6-31G(d)		/6-31G(d,p)
	Conformer		ΔG^c	ΔE^d	ΔE^e
1 (<i>rccc</i>)	CONE		0.93	1.11	1.07
	PC		1.17	1.40	1.29
	1,2-A		12.99	12.36	12.15
	1,3-A		3.73	2.93	2.74
1 (<i>rcct</i>)	CONE		3.26	4.38	4.27
	PC	most stable	0.00	0.00	0.00
	1,2-A		6.61	6.24	5.91
	1,3-A		3.84	1.32	0.95
1 (<i>rcct</i>)	CONE		9.58	8.86	8.65
	PC	most stable	0.99	0.47	0.34
	1,2-A		6.33	6.12	5.91
	1,3-A		3.03	1.16	0.95
1 (<i>rtct</i>)	CONE		8.84	7.79	7.56
	PC		4.44	2.99	2.77
	1,2-A		10.86	9.84	9.56
	1,3-A		1.73	0.01	-0.20

^aThe relative energy (in kcal/mol) compared to the [**1**(*rcct*)_{PC}]. ^bThe dispositions of the sulfinyl oxygen atoms are denoted by the term *cis* (*c*) or *trans* (*t*) relative to the reference sulfinyl oxygen atom (*r*) with respect to the mean plane defined by the macrocycle as suggested by Bohmer.^{1a} The notation proceeds around the system in a direction from the reference oxygen, which is chosen in order to prioritize *cis* over *trans* and maximize the number of *cis*. ^cThe relative energy (in kcal/mol) compared to the most stable conformational stereoisomer [**1**(*rcct*)_{PC}], of which Gibbs free energy at 298 K is -3902.85129 Hartree. ^dThe relative energy (in kcal/mol) compared to the [**1**(*rcct*)_{PC}], of which BLYP/6-31G(d) calculated total electronic energy is -3903.64579 Hartree. ^eThe relative energy (in kcal/mol) compared to the [**1**(*rcct*)_{PC}], of which BLYP/6-31G(d,p) calculated total electronic energy is -3903.72442 Hartree.

a comparable stability with the **1**(*rcct*)_{PC}.

The electronic energies of these structures were additionally minimized by the *m*PW1PW91 method with the 6-31G(d) and 6-31G(d,p) basis sets, consecutively. Table 2 reports the *m*PW1PW91 optimized total electronic energies and dipole moments of the 16 conformational stereoisomers of **1**.

In the crystals,^{1b} **1**(*rccc*) adopts a CONE conformation in which all the methoxy groups are in the direction opposite that of the sulfinyl oxygen atoms, with respect to the mean plane defined by the macrocycle. However, **1**(*rcct*) and **1**(*rcct*) adopted a PC conformation in which the methoxy group(s) between the two adjacent sulfinyl groups of the *cis* conformation were in the direction opposite that of sulfinyl oxygen atoms, with **1**(*rtct*) adopting an univocally defined 1,3-A conformation. These X-ray structures obey the following two rules attributable to the minimization of the electrostatic repulsion between the sulfinyl and methoxy groups: (a) at least one of the two methoxy groups adjacent to a sulfinyl group is in a direction opposite that of the sulfinyl oxygen atom; (b) the methoxy group on the benzene ring between the two adjacent sulfinyl groups of the *cis* conformation is in a direction opposite that of the sulfinyl oxygen atoms. Therefore, it is concluded that the conformations of sulfinylcalix[4]arenes like **1** are strongly controlled by the electrostatic repulsion between the sulfinyl and methoxy groups.

The *m*PW1PW91/6-31G(d,p) calculations in Table 2 also suggest that the CONE conformation was the most stable of

Table 2. *m*PW1PW91 calculated relative energies (in kcal/mol)^a and dipole moments (in Debye) of the conformational stereoisomers of tetra-*O*-methylsulfinylcalix[4]arene (**1**)

Stereoisomer ^b	Basis set		/6-31G(d)		/6-31G(d,p)	
	Conformer		ΔE^c	ΔE^d	$\Delta \Delta E^e$	Dipole moment
1 (<i>rccc</i>)	CONE		0.84	1.02	0.00	0.46
	PC		1.32	1.34	0.32	2.94
	1,2-A		14.15	14.05	13.03	5.92
	1,3-A		3.68	3.54	2.52	5.98
1 (<i>rcct</i>)	CONE		5.14	5.15	5.15	3.72
	PC	most stable	0.00	0.00	0.00	0.97
	1,2-A		7.38	7.28	7.28	3.36
	1,3-A		2.16	1.94	1.94	3.30
1 (<i>rcct</i>)	CONE		10.71	10.61	10.16	6.72
	PC	most stable	0.45	0.45	0.00	3.49
	1,2-A		7.18	7.09	6.64	0.18
	1,3-A		1.86	1.67	1.22	1.84
1 (<i>rtct</i>)	CONE		9.55	9.42	8.71	6.07
	PC		3.81	3.67	2.96	3.79
	1,2-A		11.84	11.62	10.91	2.80
	1,3-A		0.99	0.71	0.00	0.08

^{a,b}See footnotes in Table 1. ^cThe relative energy (in kcal/mol) compared to the most stable conformational stereoisomer [**1**(*rcct*)_{PC}], of which *m*PW1PW91/6-31G(d) calculated total electronic energy is -3904.21083 Hartree. ^dThe relative energy (in kcal/mol) compared to the most stable conformational stereoisomer [**1**(*rcct*)_{PC}], of which *m*PW1PW91/6-31G(d,p) calculated total electronic energy is -3904.28637 Hartree. ^e $\Delta \Delta E$ is the relative energy (in kcal/mol) compared to the most stable conformer of the respective stereoisomer.

the four conformers of the **1**(*rccc*) stereoisomer, that the PC was the most stable conformer of the **1**(*rcct*) and **1**(*rtct*) stereoisomers, and that the 1,3-A conformation was the most stable of the **1**(*rtct*) stereoisomer. These calculated results for the four stereoisomers accord with the above experimental observations of tetra-*t*-butyl-tetra-*O*-methylsulfinylcalix[4]arene **1**. Specifically, the orderings of the relative stabilities (in kcal/mol) of the four conformers of the respective stereoisomers listed as $\Delta\Delta E$ in Table 2 are the following:

1(*rccc*) - CONE (the most stable): PC(+0.32): 1,3-A(+2.52): 1,2-A (+13.03 the least stable);

1(*rcct*) - PC (most stable): 1,3-A (+1.94): CONE (+5.15): 1,2-

A (+7.28);

1(*rtt*) - PC (most stable): 1,3-A (+1.22): 1,2-A (+6.64): CONE (+10.16);

1(*rtct*) - 1,3-A (most stable): PC (+2.96): CONE (+8.71): 1,2-A (+10.91).

Figures 1-4 show the *mPW1PW91/6-31G(d,p)* calculated structures of all four conformers (CONE, PC, 1,2-A, 1,3-A) of the respective stereoisomers [**1**(*rccc*), **1**(*rcct*), **1**(*rtt*), **1**(*rtct*)]. Visualization of the optimized structures in Fig. 1 - 4 was performed with PosMol.¹⁶

The *mPW1PW91/6-31G(d,p)* calculated average bond distance (1.509 Å) between the bridging sulfur and oxygen atoms

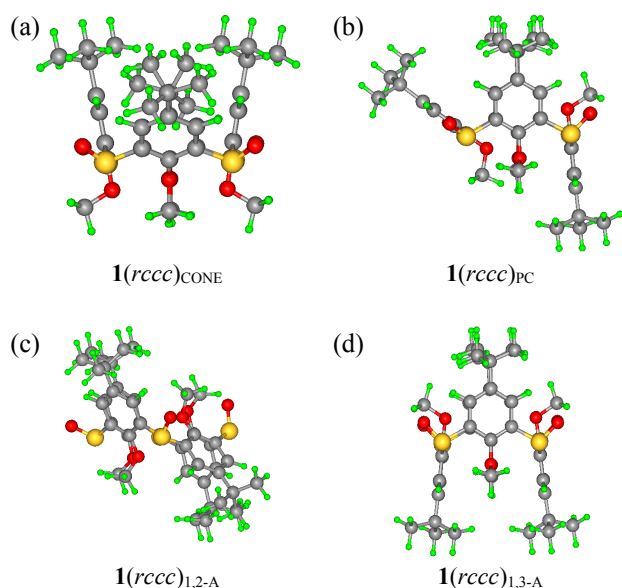


Figure 1. *mPW1PW91/6-31G(d,p)* calculated structures of four conformers (CONE, PC, 1,2-A, 1,3-A) of **1**(*rccc*). The visualization of the optimized structures in Fig. 1 - 4 was performed with PosMol.¹⁶

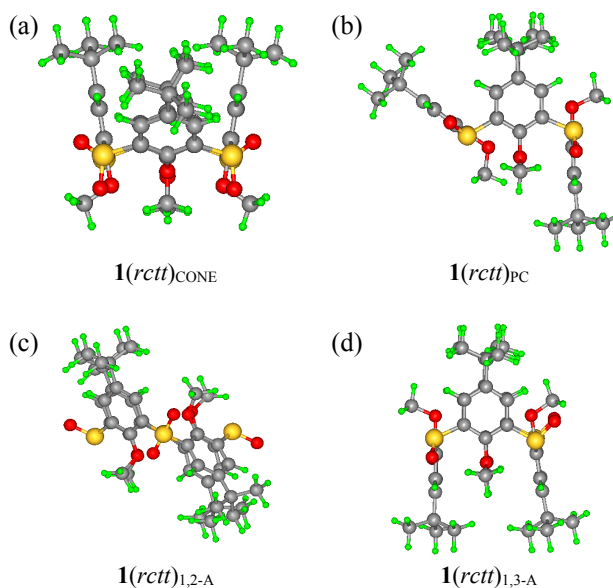


Figure 3. *mPW1PW91/6-31G(d,p)* calculated structures of four conformers (CONE, PC, 1,2-A, 1,3-A) of **1**(*rtt*).

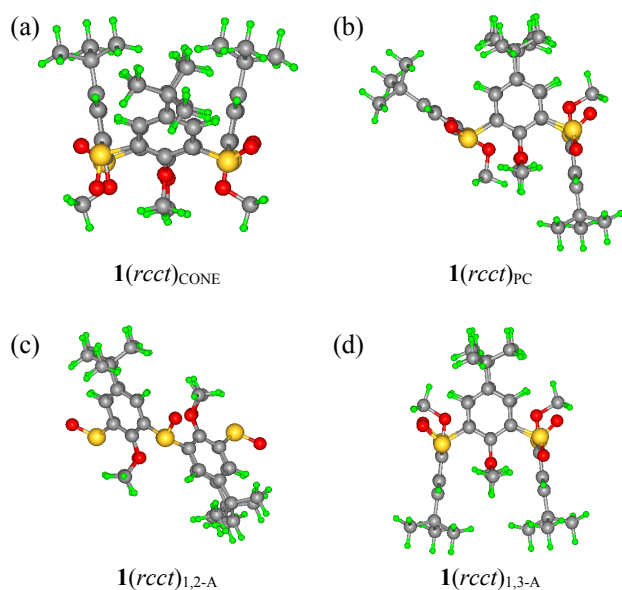


Figure 2. *mPW1PW91/6-31G(d,p)* calculated structures of four conformers (CONE, PC, 1,2-A, 1,3-A) of **1**(*rcct*).

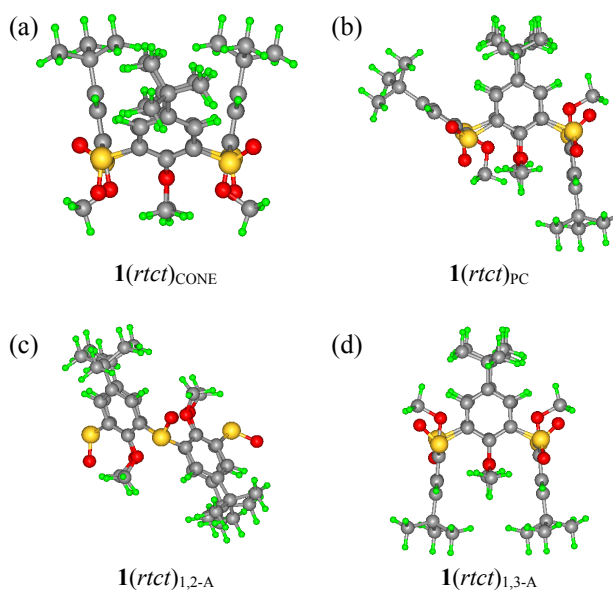
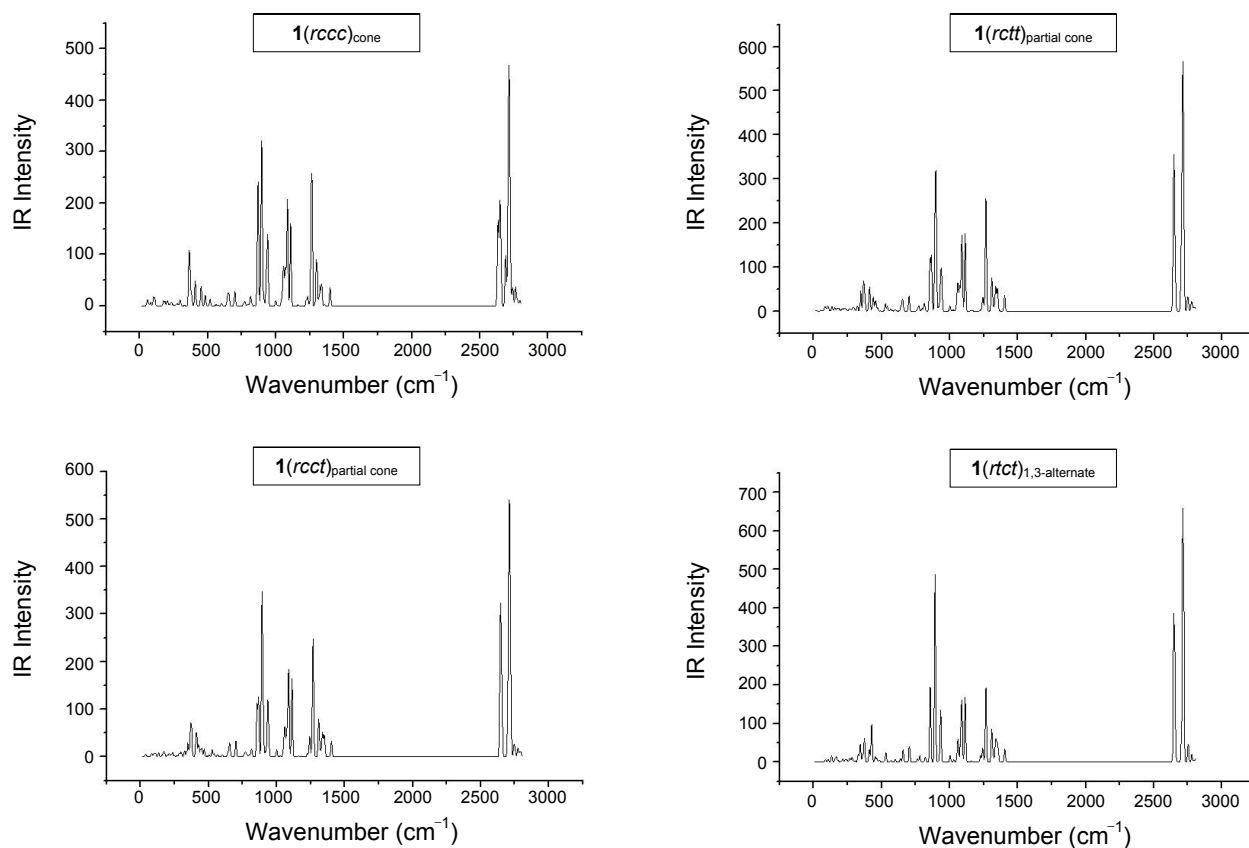


Figure 4. *mPW1PW91/6-31G(d,p)* calculated structures of four conformers (CONE, PC, 1,2-A, 1,3-A) of **1**(*rtct*).

Table 3. Main features of BLYP calculated vibrational modes of the most stable conformer of the respective stereoisomer of **1**

1(Stereoisomer) _{conformer}									
Peak No.	1(<i>rccc</i>) _{CONE}		Vibrational modes Description	1(<i>rcct</i>) _{PC}		1(<i>rcct</i>) _{PC}		1(<i>rtct</i>) _{1,3-A}	
	Energy/cm ⁻¹	Broadened Intensity ^a		Energy/cm ⁻¹	Int. ^a	Energy/cm ⁻¹	Int. ^a	Energy/cm ⁻¹	Int. ^a
1	364	107	out-of-plane + in-plane bending vibrations of molecular skeleton	370	71	370	68	427	96
2	870	241	C _{me} -O _{ether} stretching	868	126	865	127	856	196
3	895	320 ^b	S=O stretching	893	348 ^b	898	318 ^b	891	487 ^b
4	939	138	C-S stretching	935	120	937	97	932	134
5	1085	208	C-O _{ar} stretching + C-C _{ar} stretching + CCC _{ar} bending	1089	185	1088	172	1089	161
6	1107	159	C _{ar} -C _{tb} stretching + CCC _{tb} bending	1114	165	1114	175	1113	169
7	1263	257	CCC _{ar} bending	1268	247	1267	247	1267	193
8	2649	206 ^c	C _{me} -H stretching in methoxy group	2646	322 ^c	2648	355 ^c	2646	386 ^c
9	2715	467 ^d	C _{me} -H stretching in <i>t</i> -butyl group	2710	540 ^d	2712	566 ^d	2715	658 ^d

^aCalculated infrared intensity from BLYP/6-31G(d) method by the broadened IR spectra assuming a Lorentzian line width of 10 cm⁻¹. ^bThis big peak is made by the broadened IR spectra of four peaks of S=O stretching vibrations. ^cThis peak is created by fifteen small peaks from the C_{me}-H stretching vibrations in methoxy and *t*-butyl groups. ^dThis big intensity is composed of five medium peaks from the C_{me}-H stretching vibrations in *t*-butyl groups.

**Figure 5.** The BLYP/6-31G(d) calculated IR spectra of the most stable conformers [**1**(*rccc*)_{CONE}, **1**(*rcct*)_{PC}, **1**(*rcct*)_{PC}, **1**(*rtct*)_{1,3-A}] of four stereoisomers of **1**.

of **1** was slightly longer than the experimental value (1.493 Å)^{1b} of **1**. The mPW1PW91/6-31G(d,p) calculated average bond distance (1.811 Å) between the bridging sulfur and carbon atoms of **1** was closer to the experimental value (1.802 Å)^{1b} of **1**.

The BLYP/6-31G(d) calculated IR spectra of the most stable conformers [**1**(rccc)_{CONE}, **1**(rcct)_{PC}, **1**(rctt)_{PC}, **1**(rtct)_{1,3-A}] of the respective stereoisomers of **1** are compared in Table 3 and Fig. 5. The main features (frequencies and intensities) of the four conformational stereoisomers differ little between each other. However, detailed vibrations have a variety of concerted motions of different bond stretchings and bendings. Table 3 lists the common features of the four different conformational stereoisomers. The first peak (364 ~ 427 cm⁻¹) arises from the concerted motions of out-of-plane and in-plane bending vibrations of the molecular skeleton. The different conformational stereoisomers show distinct vibrational characteristics at low frequencies. The second peak (856 ~ 870 cm⁻¹) is caused by C_{me}-O_{ether} (the bond between the methoxy carbon and ether oxygen) stretching vibrations. The third peak (891 ~ 895 cm⁻¹) is composed of four kinds of S=O bond stretching vibrations, collectively drawn as a big peak due to the Lorentzian line broadening of 10 cm⁻¹. The fourth peak (932 ~ 939 cm⁻¹) comes from C-S bond stretching vibrations. The fifth peak (1085 ~ 1089 cm⁻¹) arises from the concerted vibrations of C_{ar}-O bond stretching, C-C_{ar} bond stretching, and CCC_{ar} angle bending. The sixth peak (1107 ~ 1114 cm⁻¹) comes from C_{ar}-C_{tb} (the bond between the aromatic carbon and the *t*-butyl quaternary carbon atom) stretching vibrations. The seventh peak (1263 ~ 1267 cm⁻¹) arises from the vibrations of CCC_{ar} angle bending. The eighth peak (2646 ~ 2649 cm⁻¹) is composed of 15 small-intensity lines of C_{me}-H (the bond between the methoxy carbon and hydrogen atom) stretching vibrations. The ninth peak (2710 ~ 2715 cm⁻¹) comes from five medium-intensity lines of C_{tb}-H (the bond between the *t*-butyl carbon and hydrogen atom) stretching vibrations.

Conclusion

The total electronic and Gibbs free energies and normal vibrational frequencies of 16 different structures from four major conformations (CONE, PC, 1,2-A, 1,3-A) of the four stereoisomers [**1**(rccc), **1**(rcct), **1**(rctt), **1**(rtct)] were optimized using DFT BLYP and mPW1PW91/6-31G(d,p) (hybrid HF-DF) calculation methods. The **1**(rccc)_{CONE}, **1**(rcct)_{PC}, **1**(rctt)_{PC}, and **1**(rtct)_{1,3-A} were the most stable conformations of the respective stereoisomers. These calculated results correlate very well with the experimental structures obtained from X-ray crystallography. The electrostatic repulsion between the sulfinyl and methoxy groups is a primary factor for the relative stabilities of the four different conformations.

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