



mPW1PW91 study for conformational isomers of methylene bridge-monosubstituted tetramethoxycalix[4]arenes



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ABSTRACT

Structures of ten conformational isomers of methylene bridge-monosubstituted tetramethoxycalix[4]arenes, 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetramethoxy-2-ethylcalix[4]arene (1), and methyl 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetramethoxycalix[4]arene-2-carboxylate (2) were optimized by quantum mechanical mPW1PW91/6-31G(d,p) (hybrid Hartree–Fock density functional) calculations. The total electronic and Gibbs free energies of the various conformations (cone, partial cone, 1,2-alternate, and 1,3-alternate) of 1 and 2 were analyzed. The cone (equatorial) and partial cone (equatorial) conformers were disclosed to be the most stable among all the isomers of 1 and 2. The calculated structures agreed well with the experimental results. The IR spectra were calculated at the mPW1PW91/6-31G(d,p) level for the most stable conformer of each methylene bridge-monosubstituted tetramethoxycalix[4]arene.

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1. Introduction

Calix[4]arenes are macrocyclic molecules consisting of four phenolic rings interconnected by methylene groups [1–4]. The derivatization reactions of calix[4]arenes usually involve the phenolic hydroxyl groups, *p*-positions, or phenolic units as a whole. Homocalixarenes [5] and thiacalixarenes [6], in which the bridging methylene units of the conventional calixarene framework are completely replaced by organic groups or heteroatoms, represent well-known structural modifications of the calixarene family [7,8]. In contrast, calixarenes with monosubstituted methylene bridges (meso positions) are rare [9–12]. The laterally monosubstituted calixarenes may open interesting aspects of calixarene chemistry such as the preparation of oligotopic receptors [13–17] as well as calixarenes attached to a specific target or support [18–21].

The methylene bridge-monosubstituted calixarenes are important [22–28], because in the cone conformation, for example, the methylene protons of the derivative are not equivalent [29]. Thus, there is a possibility of (at least partial) locking the conformation of the monosubstituted calixarenes because of the energy differences between the equatorial and axial orientations of the substituent. In

the simplest instance of the monosubstitution on one of the four methylene bridges of the calix[4]arene, an equatorial disposition of the lateral substituent appears to be strongly preferred, even though this does not necessarily inhibit the associated conformational changes; e.g., rotation of the phenolic units through the annulus. The relative stabilities of their conformations have been both experimentally and theoretically studied [22–27]. In general, the conformations of calix[4]arenes are analyzed in terms of four basic arrangements resulting from the “up” or “down” orientation of the phenol rings relative to the average macrocyclic plane passing through the four methylene carbons. These arrangements are usually designated as “cone,” “partial cone (PC),” “1,3-alternate (1,3-A),” and “1,2-alternate (1,2-A)” [1] (Scheme 1). In the cone conformation, the four methylene groups are equivalent; however, the two protons of a given methylene group are diastereotopic. By analogy with the chair conformation of cyclohexane derivatives, these protons are usually labeled as “equatorial” and “axial” [30].

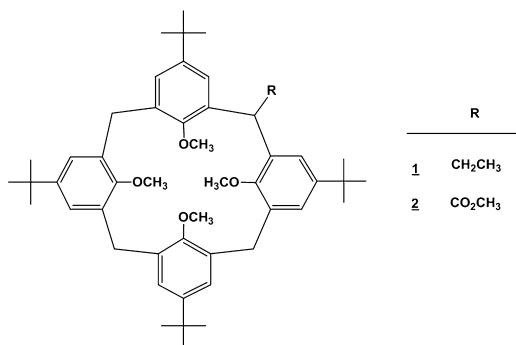
Several conformations are possible for a calix[4]arene derivative with a single monosubstituted methylene bridge or two opposite, each monosubstituted, methylene bridges [31,32]. These conformations result from the possible up–down orientations of the aryl groups and the axial/equatorial/isoclinal disposition of the substituent(s). The ideal conformers for each substitution pattern are shown in Scheme 2.

The conformational effects of the formal introduction of substituents on the methylene bridges have not been studied well, most probably because of the lack of synthetic methods for

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Scheme 1. Methylene bridge-monosubstituted tetramethoxycalix[4]arenes **1**, (5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetramethoxy-2-ethylcalix[4]arene), and **2** (methyl 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetramethoxycalix[4]arene-2-carboxylate).

the preparation of such compounds. The cone, PC, 1,2-A, and 1,3-A conformers of methylene bridge-monosubstituted calix[4]arenes **1** and **2** (Scheme 1) were optimized by means of mPW1PW91 calculations, and their relative stabilities were compared. The IR spectra for the most stable conformers of **1** and **2** were also generated from mPW1PW91/6-31G(d,p) calculations.

2. Computational methods

The initial conformations of the axial and equatorial isomers of **1** and **2** were constructed by means of molecular mechanics (MM), molecular dynamics (MD), and semi-empirical AM1 calculations of HyperChem [33]. Further optimization performed by conformational searches using simulated annealing has been described elsewhere [34]. The cone, PC, 1,2-A, and 1,3-A conformers of the isomers of **1** and **2** obtained from the MM/MD and AM1 calculations were fully re-optimized by a Hartree–Fock density functional (HF–DF) method to determine the relative energy and structure of each distinct conformer. The

modified Perdew–Wang 1-parameter (mPW1) calculations [35,36] such as mPW1PW91 are hybrid HF–DF models that provide good results both for the covalent and non-covalent interactions [37]. The mPW1PW91/6-31G(d),/6-31G(d,p), and/6-311 + G(d,p) optimizations were performed using Gaussian 09 [38] to obtain more accurate total electronic energies, Gibbs free energies, and structures of the conformational stereoisomers of **1** and **2**.

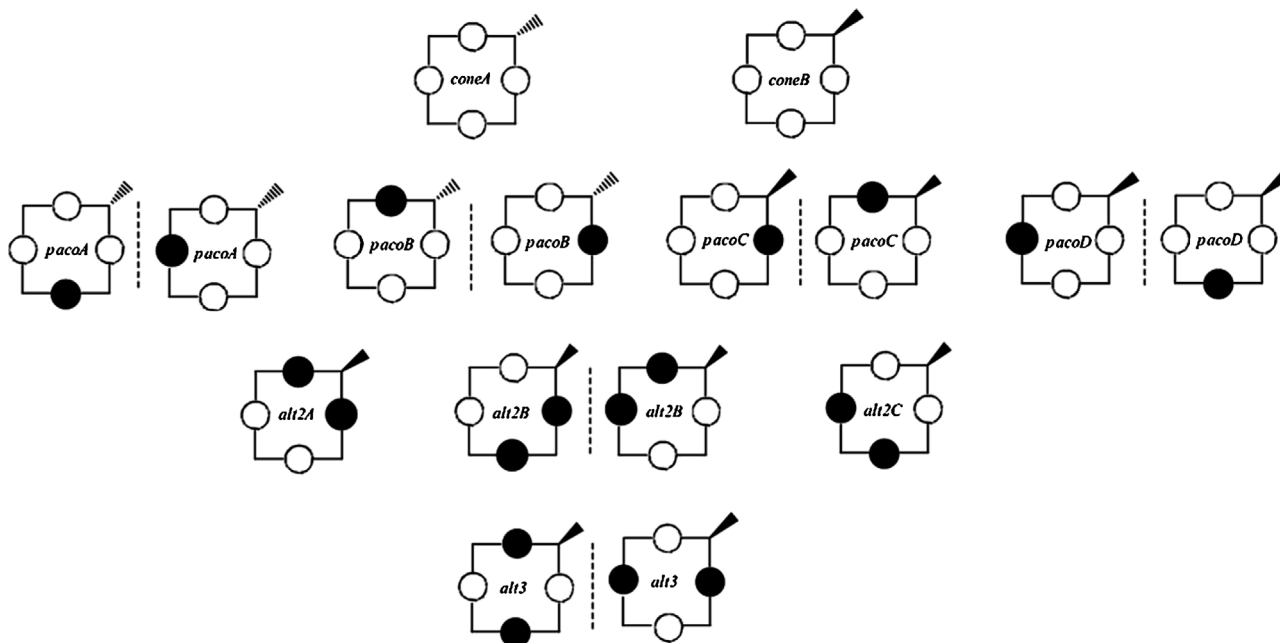
The mPW1PW91 calculations were also used to generate the normal mode frequencies of the final structures. None of the vibrational spectrum showed negative frequency, confirming that the optimized structures exist at the energy minima. For the direct comparison with the experimental data, the calculated vibrational frequencies were scaled by the recommended scale factor (0.893) [39]. The broadened IR spectra were obtained assuming a Lorentzian line width of 10 cm⁻¹.

3. Results and discussion

3.1. Configurational and conformational considerations

Because the derivatives of **1** and **2** possess a monosubstituted methylene bridge, the substituent at the bridge may be located at the axial, equatorial, or isoclinal position. The different possible dispositions of the substituents on the selected conformations of the macrocycles are shown in Scheme 2.

The steric considerations indicate that the equatorial or isoclinal dispositions of the substituents at the monosubstituted methylene bridges would be favored over the more sterically crowded axial dispositions. In some substitution patterns, this may subsequently influence the preferred conformation of the macrocycle resulting from different “up” or “down” orientations of the ring. The major conformations in the solution of **1** and **2** have been experimentally determined to be a mixture of cone and PC forms of the equatorial isomer [22–27]. The crystal conformation of **2** has been experimentally determined to be the PC conformation of the equatorial isomer [26].



Scheme 2. Possible conformers of methylene bridge-monosubstituted tetramethoxycalix[4]arenes (**1** and **2**). Filled and unfilled circles represent the “up” and “down” orientation of the methoxy groups, respectively. Mirror images are separated by a broken line. Notations such as coneA are adopted from reference [23] and listed in Table 1.

Table 1
mPW1PW91-Calculated energies^a of conformational isomers of **1** and **2**.

| Compound Conformation: notation ^b | 1 | | 2 | |
|---|-------------|--------------|-------------|--------------|
| | <i>E</i> | ΔE^c | <i>E</i> | ΔE^c |
| Cone (equatorial): coneA | -2246.66184 | 0.00 | -2395.95790 | 0.00 |
| Cone (axial): coneB | -2246.65287 | 5.63 | -2395.94915 | 5.49 |
| PC (axial): pacoA | -2246.65034 | 7.21 | -2395.94610 | 7.40 |
| PC (isoclinal1): pacoB | -2246.65742 | 2.78 | -2395.95235 | 3.48 |
| PC (isoclinal2): pacoC | -2246.65745 | 2.75 | -2395.95144 | 4.05 |
| PC (equatorial): pacoD | -2246.66019 | 1.04 | -2395.95590 | 1.26 |
| 1,2-A (axial): alt2A | -2246.64432 | 11.00 | -2395.93906 | 11.82 |
| 1,2-A (isoclinal): alt2B | -2246.65216 | 6.07 | -2395.94508 | 8.04 |
| 1,2-A (equatorial): alt2C | -2246.65503 | 4.27 | -2395.95123 | 4.19 |
| 1,3-A (isoclinal): alt3 | -2246.65160 | 6.43 | -2395.94594 | 7.51 |

^a Error limits of total electronic energies are 0.00001 Ha (A.U.); basis sets of the mPW1PW91 calculations are 6-31G(d) and 6-31G(d,p) for **1** and **2**, respectively.

^b Notation from Fig. 4 of reference [23].

^c Relative energy (kcal/mol) of the conformational isomer relative to the respective lowest energy conformer (cone).

Table 2
mPW1PW91-Calculated Gibb free energies^a of conformational isomers of **1** and **2**.

| Conformation: notation | 1 | | 2 | |
|----------------------------|-------------|--------------|-------------|--------------|
| | <i>G</i> | ΔG^b | <i>G</i> | ΔG^b |
| Cone (equatorial): coneA | -2245.66809 | 0.00 | -2394.98472 | 0.00 |
| Cone (axial): coneB | -2245.65799 | 6.34 | -2394.97284 | 7.45 |
| PC (axial): pacoA | -2245.65527 | 8.05 | -2394.97044 | 8.96 |
| PC (isoclinal 1): pacoB | -2245.66085 | 4.55 | -2394.97990 | 3.02 |
| PC (isoclinal 2): pacoC | -2245.66169 | 4.02 | -2394.97508 | 6.05 |
| PC (equatorial): pacoD | -2245.66525 | 1.79 | -2394.98213 | 1.62 |
| 1,2-A (axial): alt 2A | -2245.65083 | 10.83 | -2394.96451 | 12.68 |
| 1,2-A (isoclinal): alt 2B | -2245.65834 | 6.12 | -2394.97021 | 9.10 |
| 1,2-A (equatorial): alt 2C | -2245.66251 | 3.51 | -2394.98105 | 2.30 |
| 1,3-A (isoclinal): alt 3 | -2245.65799 | 6.34 | -2394.97439 | 6.48 |

^a Error limits of Gibbs free energies are 0.00001 Ha (A.U.); basis sets of the mPW1PW91 calculations are 6-31G(d) and 6-31G(d,p) for **1** and **2**, respectively.

^b Relative Gibbs free energy (kcal/mol) of the isomer relative to their respective lowest energy conformer (cone).

3.2. Quantum mechanical calculation results

The above discussions on the structural preferences were computationally verified in the selected conformations of the tetramethoxy-*p-tert*-butylcalix[4]arenes with a monosubstituted methylene group. The structures of the various conformers of tetramethoxy-*p-tert*-butylcalix[4]arenes **1** and **2** were optimized by mPW1PW91 (hybrid HF–DF) calculations.

The total electronic and Gibbs free (Tables 1 and 2) energies of the various conformations were calculated using mPW1PW91/6-31G(d) and mPW1PW91/6-31G(d,p) for **1** and **2**, respectively.

The relative Gibbs free energies (ΔG) at 298 K indicate that the cone and PC conformations of the equatorial isomers showed the highest stability among all the conformational stereoisomers of **1** and **2**.

Table 3
mPW1PW91/6-311+G(d,p)-Calculated energies^a of conformational isomers of **1** and **2**.

| Compound Conformation: notation | 1 | | | 2 | |
|------------------------------------|-------------|--------------|--------------|-------------|--------------|
| | <i>E</i> | ΔE^b | ΔE^c | <i>E</i> | ΔE^d |
| Cone (equatorial): coneA | -2247.11133 | 0.00 | 0.01 | -2396.45180 | 0.00 |
| Cone (axial): coneB | -2247.10284 | 5.33 | 7.40 | -2396.44350 | 5.21 |
| PC (axial): pacoA | -2247.10057 | 6.75 | 8.24 | -2396.44131 | 6.58 |
| PC (isoclinal 1): pacoB | -2247.10778 | 2.23 | 2.02 | -2396.44753 | 2.68 |
| PC (isoclinal 2): pacoC | -2247.10794 | 2.13 | 1.83 | -2396.44641 | 3.38 |
| PC (equatorial): pacoD | -2247.11040 | 0.59 | 0.00 | -2396.45049 | 0.82 |
| 1,2-A (axial): alt 2A | -2247.09476 | 10.40 | 11.27 | -2396.43407 | 11.13 |
| 1,2-A (isoclinal): alt 2B | -2247.10303 | 5.21 | 7.25 | -2396.44137 | 6.54 |
| 1,2-A (equatorial): alt 2C | -2247.10585 | 3.44 | 3.75 | -2396.44646 | 3.35 |
| 1,3-A (isoclinal): alt 3 | -2247.10304 | 5.20 | 2.23 | -2396.44253 | 5.82 |

^a Error limits of total electronic energies are 0.00001 Ha (A.U.); basis sets of the mPW1PW91 calculations are 6-311+G(d) and 6-311+G(d,p) for **1** and **2**, respectively.

^b Relative energy (in kcal/mol) for possible conformers of **1** (with an ethyl substituent) obtained using the mPW1PW91 method to the respective lowest energy conformer (cone).

^c Relative energy (in kcal/mol) for possible conformers of **1** (with an ethyl substituent) obtained using the MMFF94 force field (SYBYL) to the respective lowest energy conformer (paco D)^(b).

^d Relative energy (in kcal/mol) for possible conformers of **2** (with a methyl ester substituent) obtained using the mPW1PW91 method to the respective lowest energy conformer (cone).

The total electronic energies of the various conformations of **1** and **2** were also calculated using mPW1PW91/6-311 + G(d) and mPW1PW91/6-311 + G(d,p), respectively. The results of Table 3 were calculated using bigger basis sets than those of Table 1. The relative energies [23] of the possible conformers of ethyl-substituted **1** obtained by the MMFF94 force field (SYBYL) to their respective lowest energy conformer (pacoD) are also listed in Table 3. These values, which were obtained by the MM method, are comparable to the mPW1PW91-calculated data.

The mPW1PW91-calculated relative stabilities of the various conformers of **1** and **2** ranked as follows:

1: cone (equatorial) ~ PC (equatorial) > 1,2-A (equatorial) > PC (isoclinal 2) > PA (isoclinal 1) > 1,2-A (isoclinal) ~ 1,3-A (isoclinal) ~ cone (axial) > PC (axial) > 1,2-A (axial).

2: cone (equatorial) ~ PC (equatorial) > 1,2-A (equatorial) > PC (isoclinal 1) > PC (isoclinal 2) > 1,3-A (isoclinal) > cone (axial) > 1,2-A (isoclinal) ~ PC (axial) > 1,2-A (axial).

The different conformers of **1** (with an ethyl substituent) and **2** (with a methoxycarbonyl substituent) show similar relative stabilities. The predominance of the cone and PC conformations may be explained by avoiding the repulsion between the α -C-atom of the lateral ethyl or carboxylate substituent and the neighboring methoxy substituents (Fig. 1).

The most stable equatorial isomers (cone and PC) of **2** calculated using mPW1PW91 method agree well with the experimental structures in the solution [18–20].

The 1,2-A-type conformers of the axial isomers of **1** and **2** are very unstable; therefore, they are the least probable conformers because of the steric hindrance described above.

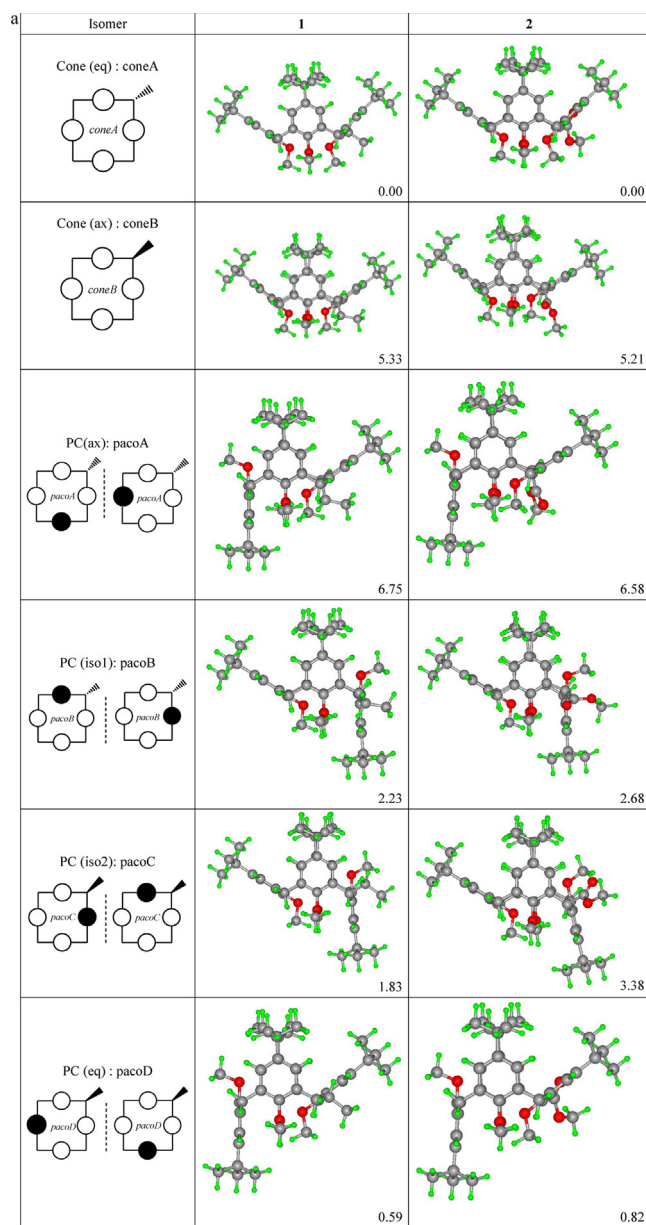


Fig. 1. Optimized structures of various conformers of **1** and **2** with relative energy differences (in kcal/mol) by mPW1PW91 and 6-31G(d,p) calculation methods, respectively; visualizations of optimized structures in Figs 1 and 2 were performed with PosMol [40]. Red balls indicate oxygen atoms. In drawings shown in left column, filled and unfilled circles represent “up” and “down” orientation of methoxy groups, respectively. Mirror images are separated by a broken line.

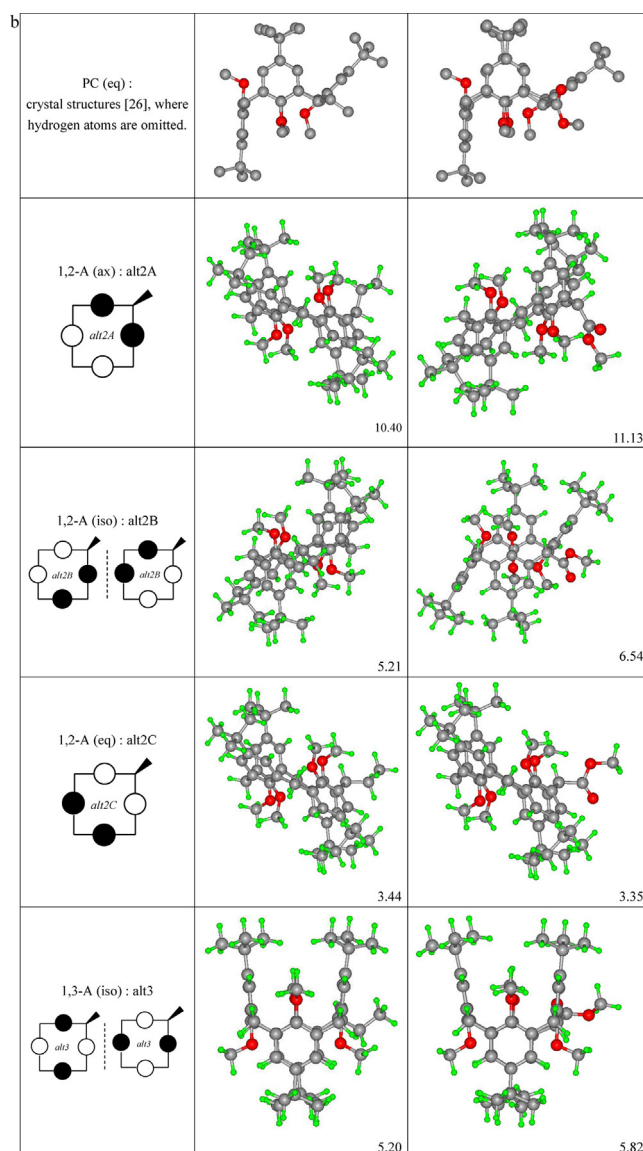


Fig. 1. (Continued).

The dipole moments of the various conformational isomers of **1** and **2** were calculated (Table 4). The dipole moments of the cone conformers of **1** and **2** were of larger magnitude owing to the four methoxy groups being in the same direction in the lower rim of the calix[4]arenes.

Table 4
mPW1PW91-Calculated dipole moments^a of conformers of **1** and **2**.

| Compound | 1 | 2 |
|----------------------------|----------|----------|
| Cone(equatorial): coneA | 1.4636 | 2.6602 |
| Cone (axial): coneB | 1.6471 | 2.7552 |
| PC (axial): pacoA | 1.1882 | 1.5014 |
| PC (isoclinal 1): pacoB | 0.8204 | 1.9517 |
| PC (isoclinal 2): pacoC | 0.9345 | 1.8261 |
| PC (equatorial): pacoD | 0.9337 | 2.1391 |
| 1,2-A (axial): alt 2A | 0.6549 | 2.1072 |
| 1,2-A (isoclinal): alt 2B | 0.5628 | 1.3417 |
| 1,2-A (equatorial): alt 2C | 0.1434 | 1.3026 |
| 1,3-A (isoclinal): alt 3 | 0.3651 | 1.3917 |

^a Error limits of dipole moments are 0.0001 D; basis sets of the mPW1PW91 calculations are 6-31G(d) and 6-31G(d,p) for **1** and **2**, respectively.

3.3. Calculated infrared spectra

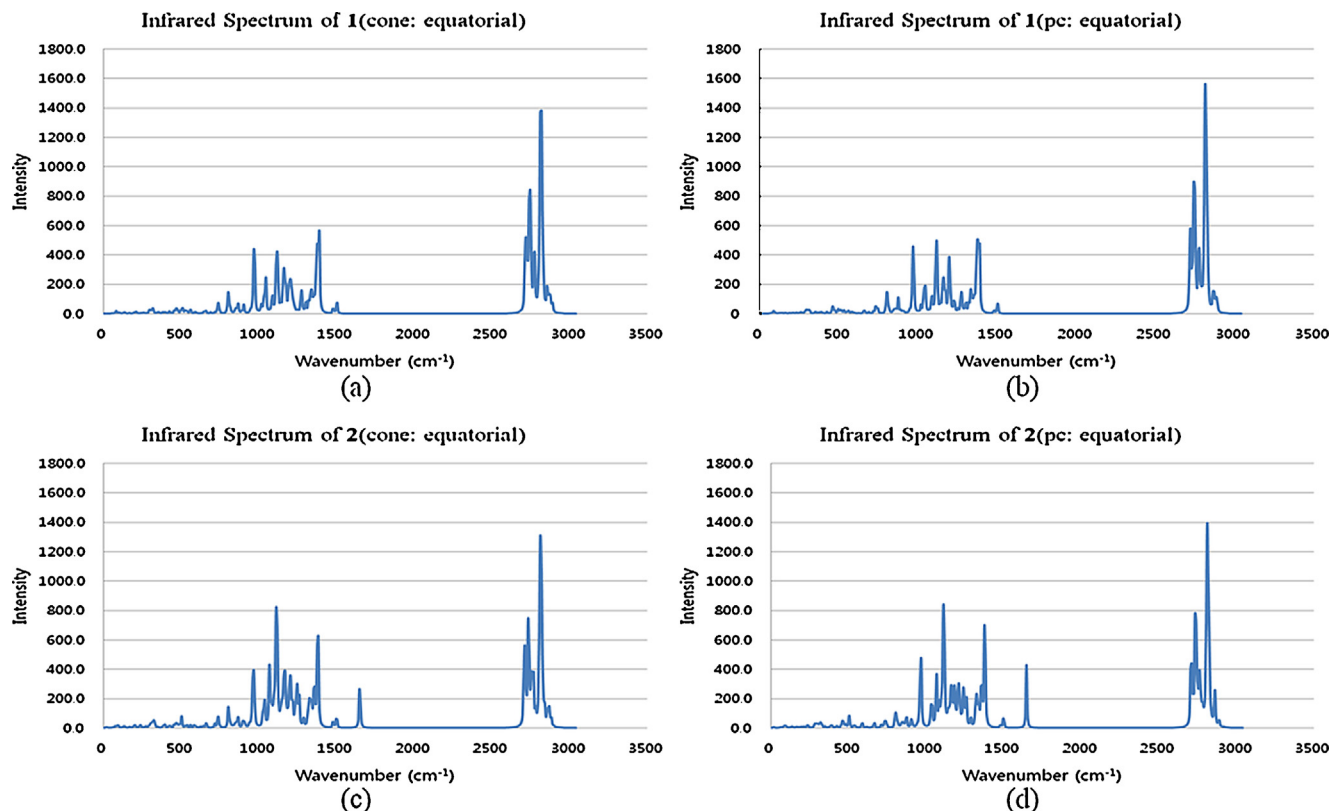
The IR spectra of the stable conformers (cone and PC) of the equatorial isomers of **1** and **2** were calculated at the mPW1PW91/6-31G(d,p) level (Table 5 and Fig. 2). The main spectral features (frequencies and intensities) of the two conformers were approximately same (Table 4). The peaks around 968 cm⁻¹ were attributed to the C_{methoxy}-O bond stretching vibrations of **1** and **2**, and the peaks around 1068 cm⁻¹ were attributed to the C_{ester}-O bond stretching vibrations of **2**. The peaks at 1132–1390 cm⁻¹ were attributed to the various C_{aromatic}-O bond stretching vibrations. The peaks around 1647 cm⁻¹ were attributed to two C=O stretching vibrations of **2**.

The peaks at 2718–2818 cm⁻¹ were attributed to the various C-H stretching vibrations as follows:

2718 cm⁻¹: C_{methoxy}-H (the bond between the methoxy carbon and hydrogen atom) stretching vibration; 2740 cm⁻¹: C_{t-butyl}-H (the bond between the *t*-butyl carbon and hydrogen atom) symmetric stretching vibration; and 2811–2818 cm⁻¹: C_{t-butyl}-H antisymmetric stretching vibration.

Table 5Main characteristic features (energy/cm⁻¹) of mPW1PW91-calculated vibrational modes^a of stable conformational isomers of **1** and **2**.

| 1 (equatorial) | | Vibrational modes description | 2 (equatorial) | |
|-----------------------|------------|--|------------------------|------------------------|
| Cone | PC | | Cone | PC |
| 968 | 968 | C _{methoxy} -O stretching | 968 | 968 |
| | | C _{ester} -O stretching | 1068 | 1068 |
| 1118 | 1118 | C _{aromatic} -O stretching | 1111 | 1111 |
| 1197 | 1204 | | 1168, 1204 | 1161, 1214 |
| 1375, 1390 | 1375, 1390 | | 1375, 1382 | 1375, 1382 |
| | | C=O stretching | 1647 | 1647 |
| 2718 | 2718 | C _{methoxy} -H stretching | 2718 | 2718 |
| 2740 | 2740 | C _{t-butyl} -H symmetric stretching | 2740 | 2740 |
| 2818 | 2818 | C _{t-butyl} -H antisymmetric stretching | 2811–2818 ^b | 2811–2818 ^b |

^a mPW1PW91/6-31G(d,p)-calculated infrared intensities of the broadened IR signals assuming a Lorentzian line width of 10 cm⁻¹.^b This large peak formed in the broadened IR spectra was attributed to numerous peaks for C_{t-butyl}-H antisymmetric stretching vibrations.**Fig. 2.** mPW1PW91/6-31G(d,p)-calculated IR spectra of more stable conformations of **1** and **2**: (a) **1** (cone (equatorial): coneA), (b) **1** (PC (equatorial): pacoA), (c) **2** (cone (equatorial): coneA), and (d) **2** (PA (equatorial): pacoA). For direct comparison with experimental data, calculated vibrational frequencies were scaled by recommended scale factor (0.893) [31,32]. Broadened IR spectra are shown assuming a Lorentzian line width of 10 cm⁻¹.

4. Conclusion

The total electronic and Gibbs free energies were calculated and optimized at the mPW1PW91/6-31G(d,p) and/6-311 + G(d,p) (hybrid HF-DF) level for the various conformational (cone, PC, 1,2-A, and 1,3-A) stereoisomers of **1** and **2**. The cone and PC conformers were the most stable conformational isomers of **1** and **2**. The calculated structures of the most stable conformational isomers agree well with the experimental results.

The mPW1PW91-calculated relative stabilities of the various conformers of **1** and **2** were ranked as follows:

1: cone (equatorial) ~ PC (equatorial) > 1,2-A (equatorial) > PA (isoclinal 2) > PA (isoclinal 1) > 1,2-A (isoclinal) ~ 1,3-A (isoclinal) ~ cone (axial) > PC (axial) > 1,2-A (axial).

2: cone (equatorial) ~ PC (equatorial) > 1,2-A (equatorial) > PC (isoclinal 1) > PC (isoclinal 2) > 1,3-A (isoclinal) > cone (axial) > 1,2-A (isoclinal) ~ PC (axial) > 1,2-A (axial).

The IR spectra of the most stable conformers of **1** and **2** were compared with the help of mPW1PW91/6-31G(d,p) calculations.

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