*m*PW1PW91 Calculated Structures and IR Spectra of the Conformational Stereoisomers of C-Cyanophenyl Pyrogallol[4]arene

Sangdoo Ahn,* Tae Jung Park, and Jong-In Choe*

Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea

*E-mail: sangdoo@cau.ac.kr (S. Ahn); choeji@cau.ac.kr (J.-I. Choe)

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Molecular structures of the various conformational stereoisomers of 2,8,14,20-cyanophenyl pyrogallol[4]arenes **1** were optimized using the *m*PW1PW91 (hybrid Hartree-Fock density functional) calculation method. The total electronic and Gibbs free energies and the normal vibrational frequencies of the different structures from three major conformations (CHAIR, TABLE, and 1,2-Alternate) of the four stereoisomers [**1**(*rccc*), **1**(*rcct*), **1**(*rcft*), and **1**(*rtct*)] were analyzed. The *m*PW1PW91/6-31G(d,p) calculations suggested that **1**(*rcct*)_{1,2-A}, **1**(*rcft*)_{CHAIR}, and **1**(*rtct*)_{CHAIR} were the more stable conformations of the respective stereoisomers. Hydrogen bonding is the primary factor for the relative stabilities of the various conformational isomers, and maximizing the π - π interaction between the cyanophenyl rings is the secondary factor. The calculated IR spectra of the more stable conformers [**1**(*rcft*)_{CHAIR}, **1**(*rcct*)_{1,2-A}, **1**(*rtct*)_{CHAIR}] were compared with the experimental IR spectrum of **1**(*rcft*)_{CHAIR}.

Key Words : *m*PW1PW91, Conformer, Stereoisomer, IR spectrum, Cyanophenyl pyrogallol[4]arene

Introduction

Calixarenes, which are a class of synthetic macrocycles, have been extensively explored.¹⁻⁵ Resorcinarenes⁶ and pyrogallolarenes⁷ are structurally analogous to calixarenes. Till date, many variants and hybrids of calixarenes, including calixcrowns,⁸ calix[4]resorcinarenes,⁹ and cavitands,¹⁰⁻¹² have been synthesized.

Molecular capsules, self-assembled from calix[4]arenes, resorcin[4]arenes, cavitands, and pyrogallol[4]arenes, have received increasing interest in recent years.¹³⁻²⁴ In particular, pyrogallol[4]arenes have drawn much attention since their emergence as new hydrogen-bonded dimeric and hexameric molecular receptors.²⁴⁻²⁸ Many of the dimers are comprised of monomers seamed together, either directly or *via* hydrogen bond donor/acceptor solvent molecules.²⁹⁻³³ The hexameric pyrogallol[4]arene spheroidal structures are held together by hydrogen bonding between the monomers.³⁶⁻³⁸ Pyrogallol[4]arenes have been shown to self-assemble into remarkable multicomponent assemblies, including nanocapsules, nanotubes, and bilayer networks.³⁷ The formation of large self-assembled nanocapsules by hydrogen bonding of the upper-rim hydroxyls prompted researchers to attempt encapsulation of target molecules and thus obtain a variety of interesting cocrystals.³⁸⁻⁴¹ The synthesis, crystal structure, and IR spectroscopic investigation of C-cyanophenyl pyrogallol[4]arene **1** without any modification of the hydroxyl groups of pyrogallols have been reported.⁴² In this study, we have optimized the conformers (CHAIR, TABLE, 1,2-Alternate) of the four stereoisomers [**1**(*rccc*), **1**(*rcct*), **1**(*rcft*), and **1**(*rtct*)] of **1** using *m*PW1PW91 (hybrid HF-DF) calculation methods. The primary objective of this research was to determine the structures and relative stability of the different

Scheme 1. Chemical structure of 2,8,14,20-cyanophenylpyrogallol[4]arene **1** with three stable conformations (TABLE, CHAIR, and 1,2-A) of the calix[4]arene backbone of **1**.

conformational stereoisomers for **1** using the *m*PW1PW91/6-311+G(d,p) calculation method. The secondary objective was to compare the calculated IR spectra of the more stable conformers of the four stereoisomers of **1** obtained from the *m*PW1PW91 method. These findings might be useful for the design of receptors based on pyrogallol[4]arenes, and in turn, for the construction of superstructures derived from hydrogen bonds or metal coordination.

Computational Methods

Three major conformations (CHAIR, TABLE, and 1,2-Alternate) of the four stereoisomers [**1**(*rccc*), **1**(*rcct*), **1**(*rcft*), **1**(*rtct*)] were constructed using the molecular mechanics (MM), molecular dynamics (MD), and semi-empirical cal-

culations of HyperChem.⁴³ Optimized structures were found by conformational searches using a previously described, simulated annealing method.⁴⁴ The stereoisomers of **1** obtained from the MM/MD and AM1 calculations were fully re-optimized using the mPW1PW91/6-31G(d) (hybrid HF-DF) calculation method to determine both the relative energies and structures of distinct conformational stereoisomers. Modified Perdew-Wang 1-parameter (mPW1) calculation methods^{45,46} such as mPW1PW91 are new hybrid Hartree-Fock density functional (HF-DF) models that help in obtaining remarkable results for both covalent and non-covalent interactions.⁴⁷ Additional mPW1PW91/6-311+G(d,p) optimizations were performed using Gaussian 09⁴⁸ to obtain more accurate total electronic energies and structures for the conformational stereoisomers of **1**.

The mPW1PW91/6-31G(d) method was also used to calculate the normal mode frequencies of the final structures. None of the vibrational spectra showed 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 (0.950).⁴⁹ Furthermore, broadened IR spectra were presented assuming a Lorentzian line width of 10 cm⁻¹.

Results and Discussion

The dispositions of the cyanobenzoyl groups are denoted as *cis* (*c*) or *trans* (*t*) relative to the reference cyanobenzoyl group (*r*) with respect to the mean plane defined by the macrocycle. The notation proceeds around the system in a direction from the reference group, which is chosen to prioritize *cis* over *trans* and maximize the number of *cis*. The structures of the three main conformations (CHAIR, TABLE, and 1,2-Alternate) of the four stereoisomers [**1**(*recc*), **1**(*rectt*), **1**(*rcct*), and **1**(*rtct*)] were optimized using the mPW1PW91/6-31G(d) (hybrid HF-DF) calculation method to determine both the relative energies and structures of various distinct conformational stereoisomers.

Table 1 shows the total electronic and Gibbs free energies minimized by the mPW1PW91 method with the 6-31G(d)

basis set for the distinct conformational isomers. The calculated Gibbs free energies in Table 1 suggest the following: (1) the 1,2-A conformation is the most stable of the **1**(*rcct*) isomers, (2) the CHAIR conformer is also the most stable of the **1**(*rtct*) stereoisomers, and (3) the CHAIR conformer is the most stable of the **1**(*rectt*) stereoisomers, which agrees with the conformation (**1**(*rectt*)_{CHAIR}) of the experimental crystal structure.⁴²

The electronic energies of these structures were also optimized with the 6-311+G(d,p) basis set to obtain more accurate total electronic energies and structures for the stereoisomers of **1**. Table 2 reports the additional mPW1PW91 calculated total electronic energies and the dipole moments of the seven conformational stereoisomers of **1**.

Figure 1 shows three most stable structures (**1**(*rcct*)_{1,2-A}, **1**(*rectt*)_{CHAIR}, and **1**(*rtct*)_{CHAIR}) calculated by the mPW1PW91/6-311+G(d,p) method. Visualization of the optimized structures in Figure 1 was performed with PosMol.⁵⁰ (Figure S1 in "Supplementary Material" shows the calculated structures of three conformers (CHAIR, TABLE, and 1,2-Alternate) of the respective stereoisomers [**1**(*recc*), **1**(*rcct*), **1**(*rectt*), and **1**(*rtct*)] including the less stable conformers.) The frontier orbitals (HOMO and LUMO) for the more stable confor-

Table 2. mPW1PW91/6-311+G(d,p) calculated energies and dipole moments of **1**

Disposition	Conformation	<i>E</i> (a. u.)	ΔE^a	Dipole moment ^b (Debye)
1 (<i>recc</i>)	CHAIR	-3277.3548	11.69	17.83
	TABLE	-3277.3647	5.50	11.53
1 (<i>rcct</i>)	CHAIR	-3277.3593	8.87	13.49
	TABLE	-3277.3583	9.50	10.99
	1,2-Alternate	-3277.3692	2.66	16.98
1 (<i>rectt</i>)	CHAIR	-3277.3690	2.81	4.28
	TABLE	-3277.3649	5.37	8.68
1 (<i>rtct</i>)	CHAIR	-3277.3735	0.00	3.54
	TABLE	-3277.3533	12.64	8.88

^aThe relative energy (in kcal/mol) compared to [**1**(*rtct*)_{CHAIR}]. ^bError limits of the dipole moments are 0.01 Debye.

Table 1. mPW1PW91/6-31G(d) calculated total electronic and Gibbs free energies^a of **1**

Disposition ^b	Conformation	<i>E</i> (a. u.)	ΔE^c	<i>G</i> (a. u.)	ΔG^d
1 (<i>recc</i>)	CHAIR	-3276.4677	12.56	-3275.7538	10.54
	TABLE	-3276.4780	6.12	-3275.7636	4.38
1 (<i>rcct</i>)	CHAIR	-3276.4713	10.34	-3275.7589	7.35
	TABLE	-3276.4695	11.48	-3275.7566	8.74
	1,2-Alternate	-3276.4877	0.00	-3275.7673	2.02
1 (<i>rectt</i>)	CHAIR	-3276.4795	5.17	-3275.7684	1.36
	TABLE	-3276.4800	4.86	-3275.7652	3.39
1 (<i>rtct</i>)	CHAIR	-3276.4850	1.69	-3275.7706	0.00
	TABLE	-3276.4672	12.89	-3275.7514	12.02

^aError limits of total electronic and Gibbs free energies are 0.00001 Hartree (a. u.). ^bThe dispositions of the cyanobenzoyl groups are denoted by *cis* (*c*) or *trans* (*t*) relative to the reference cyanobenzoyl group (*r*) with respect to the mean plane defined by the macrocycle, as suggested by Bohmer.¹ The notation proceeds around the system in a direction from the reference group, which is chosen in order to prioritize *cis* over *trans* and maximize the number of *cis*. ^cThe relative energy (in kcal/mol) compared to [**1**(*rcct*)_{1,2-A}]. ^dThe relative Gibbs free energy (in kcal/mol) compared to [**1**(*rtct*)_{CHAIR}].

Figure 1. *mPW1PW91/6-311+G(d,p)* calculated structures of **1**. Visualization of the optimized structures was performed with PosMol.⁵⁰ The frontier orbitals (HOMO and LUMO) for the more stable conformations of **1** ($1(rcct)_{CHAIR}$, $1(rtct)_{CHAIR}$, and $1(rcct)_{1,2-A}$) are drawn by GaussView.⁵¹

mations of **1** ($1(rcct)_{1,2-A}$, $1(rcct)_{CHAIR}$, and $1(rtct)_{CHAIR}$) were drawn using GaussView.⁵¹ The HOMO orbitals of these three conformers are mainly located at the pyrogallolarene moieties. However, the LUMO orbital in each conformer is located at one of the cyanophenyl groups.

It is well established that the substitution of aryls for alkyls on methine units connecting the pyrogallols of pyrogallol[4]arene yields a chair conformation.^{52,53} The CHAIR conformer of **1**(*rcct*) exhibits C₂ symmetry around the centroid of pyrogallol[4]arene (Fig. 1). Two 4-cyanophenyl substituents pointing along the same direction face each other so that the π - π interaction between the cyanophenyl rings is maximized. At the terminal of the cyanophenyl rings, the calculated

distances between two nitrogen atoms are 4.954 Å and 5.028 Å, which are larger than the observed distance (3.588 Å) in the crystal structure⁴² and the typically required distance (3.400 Å)⁵⁴ for π - π interaction in phenyl rings.

The experimental IR spectrum⁴² and *mPW1PW91/6-31G(d)* calculated IR spectra (Fig. 2) of the more stable conformers [$1(rcct)_{CHAIR}$, $1(rtct)_{CHAIR}$, and $1(rcct)_{1,2-A}$] of the respective stereoisomers of **1** are compared in Table 3. The main features (frequencies and intensities) of the conformational stereoisomers differ only slightly in the low-frequency range. However, the high-frequency vibrations of free and restricted O-H bond stretching correspond to a wide wavenumber range, between 3300 and 3600 cm⁻¹, depend-

Table 3. Experimental and calculated vibrational frequencies of the more stable conformational isomers of **1**

Experimental ⁴²			Calculated			
1 (<i>rcct</i>) _{CHAIR}		1 (Stereoisomer)	1 (<i>rcct</i>) _{CHAIR} Fig. 2(a)		1 (<i>rtct</i>) _{CHAIR} Fig. 2(b)	1 (<i>rcct</i>) _{1,2-A} Fig. 2(c)
Energy/cm ⁻¹	Intensity	Vibrational modes	Energy/cm ⁻¹	Int. ^a	Energy/cm ⁻¹	Energy/cm ⁻¹
500	weak	O-H wagging	390, 517	medium	390	525
610	medium	Ring breathing, C-H wagging	560	weak	577	551, 555
820, 875	medium	OH wagging + C-O stretching	810	weak	773, 842	805
1050	medium	C-O stretching	1000, 1066	medium	996, 1073	974
1120	medium	C-O stretching	1192	medium	1201	1186
1220, 1280	medium	C-O stretching	1280	strong	1278, 1321	1252, 1303
1470, 1520	medium	C-O _{ar} stretching + C-C _{ar} stretching + CCC _{ar} bending	1466	strong	1466–1501	1457–1487
1630	medium	C-C stretching	1625	medium	1628	1600–1628
2248	strong	C-N stretching	2262	medium	2261	2230, 2261
~3100	medium, broad	C-H stretching	3082	weak	3056–3090	3065–3099
3300–3500	medium, broad,	H-bonded O-H stretching	3529	medium	3407	3385, 3407, 3484
3500–3580	strong	Unrestricted O-H stretching	3582	strong	3578	~3589

^aCalculated infrared intensity from mPW1PW91/6-31G(d,p) method by the broadened IR spectra assuming a Lorentzian line width of 10 cm⁻¹.

Figure 2. mPW1PW91/6-31G(d) calculated IR spectra (in cm⁻¹) of the more stable conformers (a) **1**(*rcct*)_{CHAIR}, (b) **1**(*rtct*)_{CHAIR}, and (c) **1**(*rcct*)_{1,2-A} of **1**.

ing on the presence of hydrogen bonds. Table 3 lists the common features of the three calculated conformational stereoisomers and an experimental IR spectrum. The first peak (390–517 cm⁻¹) is due to the O-H wagging motion. The second peak (560–610 cm⁻¹) is attributed to the C-H wagging motion and the out-of-plane bending vibrations of the four cyanophenyl rings. The third peak (773–875 cm⁻¹) is attributed to the concerted motion of the C-O stretching and O-H wagging vibrations. The next three peaks (974–1520

cm⁻¹) are due to the numerous concerted vibrations of C_{ar}-O bond stretching, C-C_{ar} bond stretching, and CCC_{ar} angle bending. The peaks at 2230–2262 cm⁻¹ are assigned to CN triple stretching vibrations. **1**(*rcct*)_{1,2-A} shows two CN bond stretching vibrations (2230 and 2261 cm⁻¹), as opposed to the single CN stretching peak of the **1**(*rcct*)_{CHAIR} or **1**(*rtct*)_{CHAIR} isomer, the intensity of which is weaker than that of the experimental peak of **1**(*rcct*)_{CHAIR}. The peaks (3050–3100 cm⁻¹) are composed of low-intensity lines corresponding to C-H stretching vibrations.

From the last two rows of Table 3, it is seen that the peaks (3300–3500 cm⁻¹) due to the restricted O-H bond stretchings are shifted to the lower-frequency range as compared to the free O-H vibrational frequencies (3500–3600 cm⁻¹). The extent of shift depends on the relative strength of the hydrogen bond between the hydroxyl hydrogen atom and the hydroxyl oxygen and/or the nitrogen atom of the cyanophenyl group. As listed in Table 3, **1**(*rcct*)_{1,2-A} shows three extra H-bonded O-H bond stretching vibrations (3385, 3407, and 3484 cm⁻¹) as compared to **1**(*rcct*)_{CHAIR}, which proves that hydrogen bonding plays the primary role in the stability of the conformational stereoisomers of **1**.

Conclusion

The total electronic and Gibbs free energies and normal vibrational frequencies of the different structures from four major conformations (CHAIR, TABLE, and 1,2-A) of the four stereoisomers [**1**(*recc*), **1**(*rcct*), **1**(*rcct*), and **1**(*rtct*)] were optimized using mPW1PW91 (hybrid HF-DF) calculation methods. **1**(*rcct*)_{1,2-A}, **1**(*rcct*)_{CHAIR}, and **1**(*rtct*)_{CHAIR} were the more stable conformations of the respective stereoisomers. The calculated results correlated well with the experimental structures obtained from X-ray crystallography. Hydrogen bonding is the primary factor for the relative stabilities of the

various conformational stereoisomers, and maximizing the π - π interaction between the cyanophenyl rings is the secondary factor. The calculated IR spectra of the more stable conformers [**1**(*rcct*)_{CHAIR}, **1**(*rcct*)_{1,2-A}, and **1**(*rtct*)_{CHAIR}] were compared with the experimental IR spectrum of **1**(*rcct*)_{CHAIR}.

Supplementary Material. All calculated structures of three conformers (CHAIR, TABLE, and 1,2-Alternate) of the respective stereoisomers [**1**(*rcct*), **1**(*rcct*), **1**(*rcct*), and **1**(*rtct*)] are reported.

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