Comparative Study of Molecular Mechanics and Theoretical Conformational Analysis of a New 16-Crown-5 Ether via X-ray Crystallography and NMR Spectroscopy

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A molecular comparative study and a conformational analysis of a new 16-crown-5 ether were conducted using X-ray crystallography and NMR spectroscopy. The resulting X-ray crystal structure of the cyanoethyl *sym*-dibenzo-16-crown-5 ether showed three important conformational isomers, which are stable conformations not commonly seen in X-ray crystallography. The B3LYP/6-31G* method of the Gaussian 98 package program was also applied to study the new cyanoethyl *sym*-dibenzo-16-crown-5 ether. Theoretical conformation analysis was conducted using molecular mechanics and density functions to determine the relative stabilities of the three isomers of the cyanoethyl *sym*-dibenzo-16-crown-5 ether. The optimal geometric structure of the compound was determined. Reasonable agreement between the calculated values of the molecule mechanics and those obtained from the X-ray crystal structure was found. The ionization potentials, higest occupied molecular orbital and lowest unoccupied molecular orbital energies, energy gaps, heat of formation, atomization energies, and vibration frequencies of the compound were also calculated. The results of this study allow researchers to better understand the structure and properties of the new cyanoethyl *sym*-dibenzo-16-crown-5 ether.

Introduction

Information on the behavior of molecular conformation can help explain biologically important phenomena such as molecular recognition.[1] The exploration of conformation space is in general not easy, and the issue is especially difficult for cyclic molecules because of the interdependence of torsion angle.[2] However, considerable progress has been made in the area over the years that has allowed the production of many significantly populated conformers.

Over the past several decades, many studies of the crown ethers have been conducted using semiempirical, ab initio, and DFT calculation methods.[3−12] Oxygen-bearing crown ethers have received a lot of interest because of their remarkable ability to selectively bind specific complex solutions contaminated with chemically similar cations. Crown ether molecules have been employed as prototypes for this kind of weak interaction, as studied in the supramolecular chemistry.

Many theoretical studies in this area have focused on 18-crown-6 (18c6) in gases,[13−15] in solutions,[16−22] or in complexes formed with metal.[21−34] On the other hand, little effort has been spent on the research of lariat crown ether (LCE). Because the sidearm LCEs are key components of the metal-crown ether

complexes, studying the cooperativeness of LCE molecules is important in understanding the structures and properties of biological systems. Such understanding would be useful for rational design of drugs and host molecules.

The purpose of this research is to investigate the geometric structures, molecular orbital energy, and other thermodynamic properties of the conformation isomers. The B3LYP method of the Gaussian 98 package program[35] and the 6-31G* base set function (BSF)[36−40] of the density function theory (DFT) were used to study the properties of LCEs. The coordinates obtained from the X-ray structural analysis were first used as input data to conduct a geometric optimization analysis (GOA). A series of systematic theoretical calculations was then conducted using the results of the GOA on three important conformational isomers of cyanoethyl *sym*-dibenzo-16-crown-5 ethers.

Experimental Section

Reagents and Chemicals. Only analytical reagent grade chemicals were used in the preparation of cyanoethyl *sym*-dibenzo-16-crown-5 ether. The hydroxy-*sym*-dibenzo-16-crown-5 ethers were synthesized and used after recrystallization from chloroform-hexane (1:5, V:V).

Synthesis of Cyanoethyl *sym*-Dibenzo-16-crown-5 Ether. Cyanoethyl *sym*-dibenzo-16-crown-5 ether was prepared as follows. First, 1.73 g (5 mmol) of hydroxy-*sym*-dibenzo-16-

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crown-5 ether[41] was dissolved in 50 mL of anhydrous THF. Then, 1.12 g (10 mmol) of potassium butyl oxide (t-BuOK) was added to the solution under nitrogen. Reaction of the mixture was continued for 5 h at room temperature. The mixture was then cooled to 0 °C. A double equivalent of 3-bromopropionitrile (1.08 g, 10 mmol) was then added to the mixture, and the reaction was continued for another 3 h. Then, deionized water was slowly added to the mixture to destroy the excess *t*-BuOK and terminate the reaction. After purification by column chromatography (silica gel, 70−230 mesh, CHCl$_3$ as eluent), the desired product was obtained at 15% (0.29 g) yield, mp 114.0 ∼ 115.0 °C. Elemental analysis Calcd (found) for C$_{22}$H$_{25}$-NO$_6$: C, 66.42 (66.15); H, 6.17 (6.31); N, 3.71(3.51). MS (EI): m/Z 399.0 (M$^+$, 56.3%), 136.0 (76.3%), 121.0 (100%), 110.0 (63.0%), 80.0 (34.1%).

^{1}H NMR (CDCl$_3$): δ 2.71 (t, 2H, OCH$_2$CH_2CN), 3.97(m, 4H, OCH$_2$CH_2OCH_2CH$_2$O), 4.09 (t, 2H, OCH_2CH$_2$CN), 4.16 (m, 3H, OC*H*H′*CH*C*H*H′O, 4H, OCH_2CH$_2$OCH$_2$CH_2O), 4.34 (m, 2H, OCH*H*′CHCH*H*′O), 6.84 ∼ 7.00 (m, 8H, benzo group).

Single Crystal of Cyanoethyl *sym*-Dibenzo-16-crown-5 Ether. The single-crystal cyanoethyl *sym*-dibenzo-16-crown-5 ether was produced by a recrystallization followed by a crystal-growing process. First, the recrystallized cyanoethyl *sym*-dibenzo-16-crown-5 ether was heated together with a proper amount of *n*-hexane. Chloroform was then slowly added to the mixture until it dissolved. Magnesium sulfate was then added, and the mixture was filtered while still hot. The filtered product was then put into a crystal-growing bottle. *n*-Hexane vapor was used to slowly diffuse the product until a perfect crystal was produced. The structure of the resulting single crystals was analyzed by X-ray. Data were collected using a Nonius CAD-4 diffractometer with graphite-monochromate Mo Kα radiation at 25 °C. Atomic scattering factors were taken from the International Tables for X-ray Crystallography,[42] and data reduction and structural refinement were performed using NRCVAX packages.[43] Cell parameters were obtained from 25 reflections with a 2θ of 19.54−24.12°.

Calculation of Molecular Orbital Fields

A. Method of Calculation and Input. As described above, this calculation was conducted using the B3LYP method and the 6-31G* BSF. The Gaussian 98 software provides many DFT models such as the MP2, MP4, and B3LYP methods. Each of these DFT methods can provide accurate calculations and analyses of molecular energy and frequency. The exact energy in the single matrix of these DFT is replaced by a more general formula, the so-called "exchange-correlation function" (ECF). This function can contain the electron exchange and correlation energies not included in the Hartree−Fock theory.

The name of each DFT is composed of the names of the exchange and correlation functions. In some situations, the standard synonym used in this field can also be used as key words. For example, the LYP key word is from the Lee, Yang, and Parr function. The key words of correlation functions can also be combined with the exchange function, e.g., the term BLYP indicates the use of the Becke exchange function and the LYP correlation function. Similarly, the B3LYP method involves the use of Beck's three-parameter function and the LYP correlation function.

The 6-31G* BSF involves the use of Gaussian-type orbital (GTO) equation by Boys (1950) instead of the Slater-type orbital (STO) equation. The wave function of STO is $\chi_{nlm} = \gamma^{n-1}e^{-\zeta r}Y^l_m(\theta, \phi)$, where ξ is an adjustable exponent parameter. The STO equation can provide reasonable and accurate descrip-

tion of the electron distribution in the near and far fields of the nuclear. However, the twin-electron integral of this orbital field is more complicate and difficult.

To simplify the calculation of this integral, Boys replaced STO by GTO. The format of GTO is $x^l y^m z^n e^{-\alpha r2}$, where α is an adjustable exponent parameter. The advantage of this GTO is that the product of two functions can be another GTO allowing $\langle \chi_i \chi_k | 1/r_{12} | \chi_m \chi_n \rangle$ to be simplified to $\langle \chi_s | 1/r_{12} | \chi_t \rangle$. However, GTO cannot describe the electron behavior as reasonably and accurately as the STO. One way to overcome this is to use *n* GTOs with different exponents to simulate one STO-*n*G. For example, STO-3G indicates the use of three GTOs to simulate one STO:

$$STO \cong c_1 GTO(\alpha_1) + c_2 GTO(\alpha_2) + c_3 GTO(\alpha_3) \quad (1)$$

The coefficients c_1, c_2, and c_3 and exponents α_1, α_2, and α_3 in eq 1 are constants during the calculation of molecular orbital field. This equation is called the contracted Gaussian-type orbital (CGTO) equation.

The "6" in 6-31G* indicates that, when using a Slater orbital field containing a single exponent ζ (single-ζ) to represent an atomic orbital field, the Slater field is composed of six CGTOs. The "31" indicates that, among the Valence atomic orbital field, each atomic orbit is split into two STOs, i.e., having two orbital exponents (double-ζ). One of the two STOs is composed of "three" CGTOs and the other is represented by "one" CGTO, resulting in the "31" term. The "G" in "6-31G*" represents GTO and the "*" indicates that six polarized d functions (d$_{x^2}$, d$_{y^2}$, d$_{z^2}$, d$_{xy}$, d$_{yz}$, d$_{xz}$) were added to the non-hydrogen atoms such as carbon, nitrogen, and oxygen to increase the accuracy of calculations. Thus, the B3LYP/6-31G* method indicates the selection of the 6-31G* BSF and the use of B3LYP method to conduct calculations.

The values obtained from the X-ray structural analysis were used in the input of the theoretical calculation program as initial coordinates. The standard bond length, bond angle, and related atomic van del Wall radius were selected as starting point to conduct geometric optimization calculations.

B. Geometric Optimization. The results of the calculations were used to verify the reasonableness of the input coordinate data. If unreasonable data were used, either the geometric symmetry of the molecule would be destroyed or an unusual bond length or bond angle would be produced. Any of these errors would result in the termination of the calculations. Based on past experience, the calculations can achieve convergence much easier if the input data is closer to the experimental values of the minimal energy point of the molecule. By starting the calculations using the standard bond length and bond angle, the completion and convergence of the SCF calculations can be achieved in fewer steps. The converged calculations can then provide the optimal geometric bond length, bond angle, and two-face angle of the three conformational isomers.

C. Orbital Field Energy, Vibration Frequency, and Thermodynamic Properties. Using the optimal solutions of the geometric calculations, thermodynamic calculations of orbital energy, vibration frequency, ionization energy, energy gap between HOMO−LUMO, atomic heat, enthalpy and Gibbs energy, etc., of each conformal isomer were conducted. The results were then used to determine the relative stability of the conformational isomers. The resulting molecular stability and conductivity are of special importance and value.

Results and Discussion

Geometric Structure. The obtained geometric structure of cyanoethyl *sym*-dibenzo-16-crown-5 ether is shown in Figure

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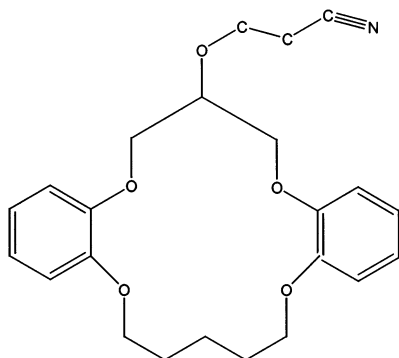*J. Phys. Chem. A, Vol. 107, No. 22, 2003* **4565**

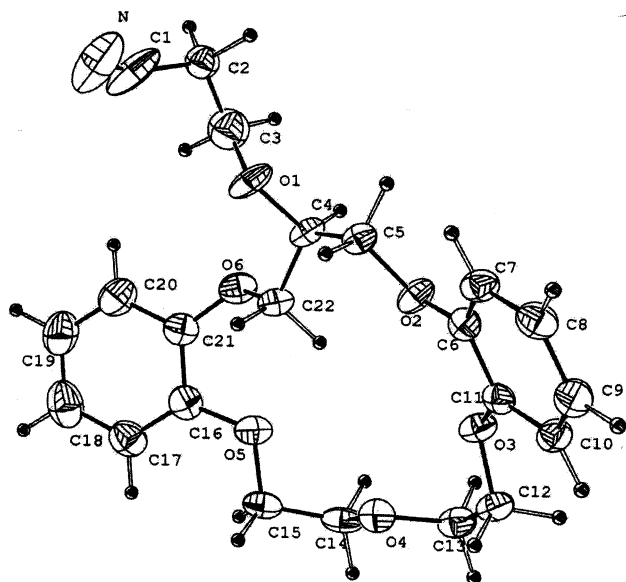**Figure 1.** Structure of cyanoethyl *sym*-dibenzo-16-crown-5 ether.

Figure 2. ORTEP diagram of conformational isomer 1 of cyanoethyl *sym*-dibenzo-16-crown-5 ether.

Figure 3. ORTEP diagram of conformational isomer 2 of cyanoethyl *sym*-dibenzo-16-crown-5 ether.

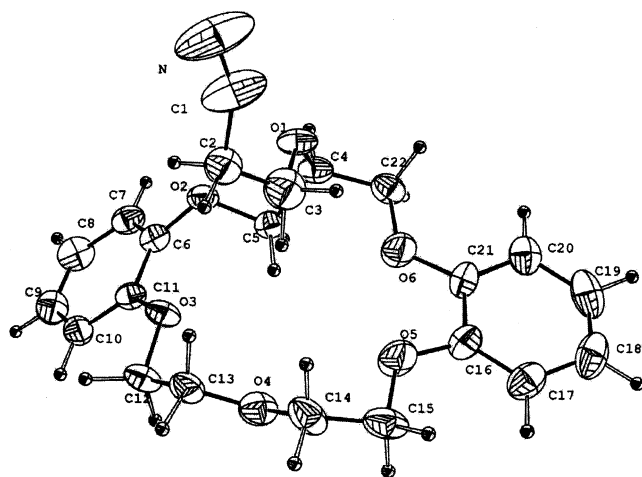**Figure 4.** ORTEP diagram of conformational isomer 3 of cyanoethyl *sym*-dibenzo-16-crown-5 ether.

TABLE 1: Experimental and Theoretical Atomic Bond Lengths (Å)

atomic bond lengths (Å)	experimental results			theoretical results		
	isomer 1	isomer 2	isomer 3	isomer 1	isomer 2	isomer 3
N–C1	1.094	1.066	1.079	1.161	1.161	1.161
O1–C3	1.387	1.413	1.514	1.419	1.421	1.420
O1–C4	1.418	1.443	1.442	1.428	1.422	1.428
O2–C5	1.433	1.421	1.430	1.430	1.434	1.422
O2–C6	1.372	1.376	1.382	1.370	1.378	1.371
O3–C11	1.340	1.359	1.357	1.367	1.368	1.367
O3–C12	1.427	1.435	1.425	1.424	1.424	1.424
O4–C13	1.434	1.393	1.429	1.415	1.413	1.416
O4–C14	1.417	1.408	1.390	1.423	1.417	1.423
O5–C15	1.444	1.401	1.450	1.425	1.433	1.426
O5–C16	1.381	1.376	1.370	1.366	1.378	1.364
O6–C21	1.364	1.365	1.368	1.382	1.371	1.380
O6–C22	1.442	1.419	1.435	1.433	1.427	1.434
C1–C2	1.600	1.490	1.670	1.467	1.465	1.464
C2–C3	1.408	1.440	1.430	1.534	1.542	1.546
C4–C5	1.531	1.512	1.533	1.531	1.531	1.532
C4–C22	1.490	1.468	1.473	1.523	1.532	1.524
C6–C7	1.372	1.374	1.343	1.394	1.392	1.394
C6–C11	1.411	1.399	1.392	1.418	1.412	1.418
C7–C8	1.404	1.406	1.422	1.401	1.397	1.401
C8–C9	1.383	1.356	1.401	1.388	1.392	1.388
C9–C10	1.401	1.403	1.351	1.401	1.399	1.401
C10–C11	1.386	1.385	1.385	1.393	1.398	1.393
C12–C13	1.475	1.481	1.474	1.524	1.516	1.525
C14–C15	1.508	1.501	1.508	1.523	1.525	1.522
C16–C17	1.345	1.326	1.372	1.396	1.391	1.396
C16–C21	1.405	1.383	1.395	1.411	1.414	1.412
C17–C18	1.383	1.440	1.388	1.399	1.398	1.399
C18–C19	1.379	1.346	1.413	1.393	1.392	1.393
C19–C20	1.341	1.386	1.342	1.399	1.399	1.399
C20–C21	1.389	1.373	1.370	1.391	1.397	1.390

bond lengths and torsion angles of the three major conformational isomers obtained from the X-ray crystallography structural analysis were provided in Tables 1 and 2, respectively. The crystallographic data collected are listed in Table 3. The bond lengths and torsion angles obtained using the theoretical calculations are also listed in Tables 1 and 2, respectively. These tables show that the experimental and theoretical results are almost identical, except for conformational isomer **3** in which the theoretical and experimental C1–C2–C3 torsion angles (112.2° and 93.1°, respectively) are significantly different. An effort had been spent to fix this torsion angle at 93.1°, but the geometric optimization process still yielded the original angle

1. Through structural analysis using X-ray crystallography, the ORTEP diagrams of the three major conformational isomers were identified, as shown in Figures 2–4. As described above, the coordinates obtained from the X-ray structural analysis were used as input to the theoretical calculations. The Am 1 semiempirical method was first used to conduct calculations and achieve convergence. The geometric optimization was then conducted using the 6-31G* BSF and the B3LYP method. The
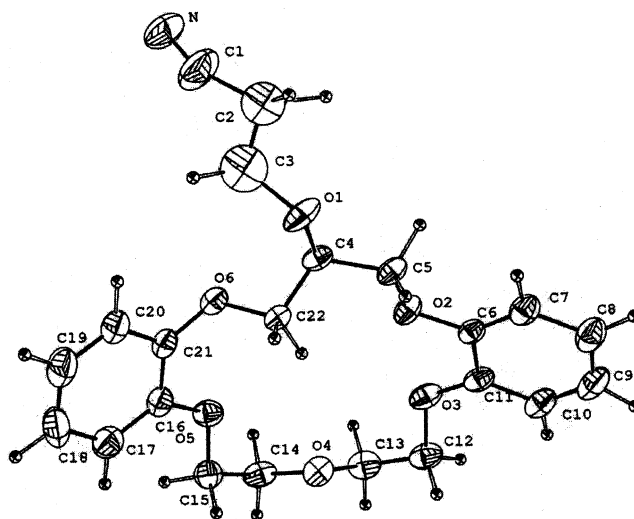
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TABLE 2: Experimental and Theoretical Atomic Torsion Angle (°)

atomic torsion angle (°)	experimental results			theoretical results		
	isomer 1	isomer 2	isomer 3	isomer 1	isomer 2	isomer 3
C3−O1−C4	119.3	118.3	113.1	115.8	119.5	116.2
C5−O2−C6	116.4	115.6	117.3	118.1	117.0	118.1
C11−O3−C12	117.8	117.8	117.8	118.8	118.9	119.0
C13−O4−C14	112.3	113.2	111.7	113.7	114.7	113.7
C15−O4−C16	115.4	121.2	116.5	119.6	115.4	119.7
C21−O6−C22	116.5	123.0	115.8	114.5	118.7	115.1
N−C1−C2	156.9	152.6	150.5	179.2	178.9	178.5
C1−C2−C3	110.6	112.1	93.1	112.5	112.7	112.2
O1−C3−C2	117.3	111.4	106.5	107.7	111.2	110.2
O1−C4−C5	103.3	113.3	102.4	105.1	115.3	105.2
O1−C4−C22	112.2	110.5	112.6	111.3	112.3	111.4
C5−C4−C22	114.3	113.7	113.6	111.4	112.7	111.3
O2−C5−C4	106.7	106.8	104.4	108.3	107.2	108.5
O2−C6−C7	124.4	118.6	124.5	124.7	118.5	124.7
O2−C6−C11	114.2	121.1	114.3	115.9	121.6	115.9
C7−C6−C11	121.3	120.1	121.1	119.4	119.7	119.4
C6−C7−C8	120.7	120.9	121.5	120.5	120.7	120.5
C7−C8−C9	118.1	118.8	115.6	120.0	119.5	120.1
C8−C9−C10	121.6	121.2	122.8	120.0	120.4	120.0
C9−C10−C11	120.2	120.0	120.1	120.5	120.2	120.5
O3−C11−C6	116.4	115.8	117.0	115.8	116.0	115.7
O3−C11−C10	125.5	125.3	124.3	124.7	124.6	124.7
C6−C11−C10	118.1	118.9	118.7	119.5	119.4	119.5
O3−C12−C13	107.3	107.1	108.1	109.0	107.3	108.9
O4−C13−C12	109.5	111.1	110.2	114.1	107.9	114.0
O4−C14−C15	111.4	110.4	111.2	108.2	106.8	108.1
O5−C15−C14	106.5	105.5	107.6	104.7	107.4	104.7
O5−C16−C17	126.8	125.6	124.3	124.8	119.4	125.0
O5−C16−C21	113.2	112.7	116.1	115.6	120.7	115.5
C17−C16−C21	120.0	121.7	119.6	119.6	119.8	119.5
C16−C17−C18	120.9	119.6	121.4	119.8	120.7	119.9
C17−C18−C19	119.7	117.5	117.6	120.6	119.5	120.5
C18−C19−C20	119.5	123.0	120.3	119.8	120.5	119.6
C19−C20−C21	122.1	118.1	122.1	120.0	120.1	120.4
O6−C21−C16	123.3	114.4	121.6	119.6	116.0	120.0
O6−C21−C20	118.7	125.4	119.5	120.1	124.6	120.0
C16−C21−C20	117.6	120.1	118.9	120.3	119.3	120.0
O6−C22−C4	108.9	108.0	108.7	108.9	110.0	109.0

of 112.2°. The cause of this difference might be the vibration of the triple bonds between the carbon and nitrogen molecules regardless of whether they are in solution or in solid phase. This can be verified by the fact that the experimental values of C1−C2−C3 torsion angles of conformational isomers **1** and **2** (110.6° and 112.1°, respectively) are significantly different from the value of conformational isomer **3**.

Molecular First Ionization Potentials, HOMO and LUMO Energies, and Energy Gaps. Table 4 lists the calculated values of the first ionization potentials (FIP), HOMO, LUMO, and energy gap ($\Delta\epsilon_{HOMO-LUMO}$) of the three major conformational isomers. Conformational isomer **1** was found to have the lowest FIP. Conformational isomer **3** was found to have the lowest energy gap, indicating higher conductivity. On the other hand, conformational isomer **2** was found to have both the highest FIP and the highest energy gap.

Thermal Properties. Table 5 provides the calculated thermal properties of the three conformational isomers, including enthalpy of formation (ΔH_f), Gibbs energy of formation (ΔG_f), enthalpy of atomization (ΔH_a), and Gibbs energy of atomization (ΔG_a). The results show that all three conformational isomers are all very stable and easy-to-form molecules, with conformational isomer **1** being the most easy-forming and stable one.

Vibration Frequencies. All calculated vibration frequencies of the three conformational isomers are positive. The results indicate that the molecules are located at a stable, minimal point

TABLE 3: Crystallographic Data

cyanoethyl *sym*-dibenzo-16-crown-5 ether	
empirical formula	$C_{22}H_{25}NO_6$
formula weight	399.44
crystal system	monoclinic
space group	P2(1)/c
unit cell dimensions (Å)	a = 14.844(0)
	b = 17.418(0)
	c = 24.003(0)
β (°)	97.5(0)
volume (Å³)	6152.37(0)
Z (atoms/unit cell)	12
DcalcMgm⁻³	1.294
$M_u$mm⁻¹	0.09
F(000)	2544
range of 2θ/deg	49.8
crystal size	0.50 × 0.45 × 0.35 mm
octants measured	h(−17 to 17)
	k(0 to 20)
	l(0 to 28)
number of unique reflection	10811
number of reflections measured	11092
number of reflections with I>2σ (I)	5561
number of variables	767
R_f	0.089
R_w	0.098
GoF	1.678

TABLE 4: Comparison of HOMO, LUMO, Energy Gaps ($\Delta\epsilon_{HOMO-LUMO}$), and First Ionization Potentials of Cyanoethyl *sym*-Dibenzo-16-crown-5 Ethers of Three Conformational Isomers (eV)

molecule parameters	isomer **1**	isomer **2**	isomer **3**
ϵ_{HOMO}	−5.6872	−6.0300	−5.7848
ϵ_{LUMO}	0.1521	−0.1056	0.0163
I_{first}	5.6872	6.0301	5.7848
$\Delta\epsilon_{HOMO-LUMO}$	5.8393	6.1356	5.7643

TABLE 5: Comparison of Calculated Thermal Properties of Cyanoethyl *sym*-Dibenzo-16-crown-5 Ethers of Three Conformational Isomers (298 K, kcal mol⁻¹)

thermal properties	isomer **1**	isomer **2**	isomer **3**
ΔH_f	−2677.9183	−2674.1462	−2676.8777
ΔG_f	−2418.4606	−2414.5631	−2417.9783
ΔH_a	6671.7466	6667.9727	6670.7055
ΔG_a	6227.3057	6223.4064	6226.8231

of the potential energy surface and are therefore very stable molecules. The calculated maximum frequencies were between 3227.363 and 3232.125 cm⁻¹, and conformational isomer **1** was found to have the lowest frequency (22.106 cm⁻¹). Therefore, conformational isomer **1** was found to be the most stable isomer.

Conclusions

In the field of X-ray structural analysis, the finding of this research that three different conformational isomers coexist stably in a new lariat crown ether is hardly seen. Using the B3LYP/6-31G* method, theoretical data of the three conformational isomers of cyanoethyl *sym*-dibenzo-16-crown-5 ether were successfully established.

The following conclusions can be drawn from this research:

The calculated bond lengths, torsion angles, and other geometric structures of the three conformational isomers are almost identical to the experimental values indicating reasonable results. The only exception was the C1−C2−C3 torsion angle of conformational isomer **3**, but the difference can be reasonably explained. These results show that the geometric structural calculations of these molecules were successful.

The calculations of FIP, HOMO, LUMO, and energy gaps show that the three conformational isomers have low energy

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gaps between the FIP and HOMO. The electrons on the most outer orbit are therefore easy to escape, indicating higher conductivity.

The results of thermal property and vibration frequency calculations show that the three conformational isomers are all located at a stable, minimal point of the potential energy surface. They are all therefore stable conformational isomers.

The calculations conducted using the B3LYP/6-31G* method have yielded satisfactory results in both accuracy and execution time. Good agreement between theoretical and experimental results was also found.

This research has identified the conformational preferences of the cyanoethyl *sym*-dibenzo-16-crown-5 ether that can be used as building blocks for the lariat crown ether macrocycles. This kind of high-density, high-energy lariat crown ether has not yet been widely researched, and the results of this research should contribute to the material science and other related fields.

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