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Vibrational analysis of dibenzo-18-crown-6. Effect of dispersion correction on the calculated vibrational spectra

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ABSTRACT

We report for the first time a detailed vibrational analysis of dibenzo-18-crown-6, db18c6. The experimental IR and Raman spectra of db18c6 were measured. The assignment of the fundamental vibrational frequencies of db18c6 was aided by using scaled quantum mechanical force fields calculated at the B3LYP/6-311G** and CAM-B3LYP/6-311G** levels. Comparison between the experimental and calculated spectra of some of the important conformations of db18c6 led to the conclusion that db18c6 in the solid phase exists in a C_2 conformation that is similar to that predicted by X-ray, for also the solid phase. The effect of inclusion of the atom pair-wise dispersion correction to the B3LYP method, known as the B3LYP-D3 method, on the calculated IR and Raman spectra of db18c6 at the B3LYP level was also investigated. It was concluded that the effect of inclusion of the dispersion correction on the calculated vibrational frequencies and intensities is negligible.

1. Introduction

Crown ethers play a major role in the field of host-guest complexes. This major role is due to the ability of crown ethers to bind to various ions with high selectivity. Consequently, there have been a large number of applications of crown ethers as a reflection of these studies. For instance, crown ethers are used in treatment of nuclear waste [1–7], cancer treatment [8–10], biomedical diagnosis [11,12] and photochemistry [13]. Two of the most important crown ethers are 18-crown-6 (18c6) and dibenzo-18-corwn-6 (db18c6), Fig. 1.

An important and interesting issue of crown ethers is that they are large ring flexible molecules with large number of possible conformations. The larger the ring size, the larger the number of possible combinations of the ring dihedral angles and the consequent larger number of possible conformations. A problem arises, is that in what conformation, or conformations, the specific crown ether exists and how to predict the possible conformations of a given crown ether. Recently, we used the efficient CONFLEX [14,15] conformational search method of cyclic molecules to predict the possible conformations of different crown ethers [16–23] including 18c6 [17] and db18c6 [23]. In a previous publication, the vibrational analysis of free 18c6 was reported [21]. The aim of the current study is to use the vibrational spectroscopy to predict in what conformation free db18c6 exists. This is achieved through the measurement of the vibrational, IR and Raman, spectra of db18c6 and by comparison between the experimental and calculated vibrational spectra of some of the important predicted conformations of db18c6, to predict in what conformation free db18c6 exists.

In a previous publication, we reported a detailed conformational analysis of db18c6 [23]. It is probably the first time to report a detailed conformational analysis of a molecule of this size. The conformational search predicted about 14,000 conformations. To predict the lowest-lying conformations of db18c6, computations were performed at different levels of theory from the HF/STO-3G level for the 9000 lowest MMFF94s energy conformations and up to the G3MP2 level for a limited number of selected conformations. Due to the large number of predicted conformations and it is known that the conformation determined experimentally of db8c6 by X-ray is of C_2 symmetry [24], computations at the highest G3MP2 level were performed only for selected conformations of C_2 symmetry. At the G3MP2 level, the predicted ground state conformation was more stable than the experimental solid state conformation by only 1.60 kcal/mol. Similar to 18c6 [17], it was concluded that the intramolecular hydrogen bonding is the major factor that determines the conformational stability of db18c6.

Recently, the dispersion correction to the DFT functionals was introduced by Grimme [25–27]. The method showed great success in the prediction of many molecular properties [28]. There is only one publication that compares between the calculated vibrational frequencies at the B3LYP and B3LYP-D3 levels [29]. In this report, comparison was made for both the harmonic and anharmonic vibrational frequencies and using the B3LYP functional of the DFT method. This publication predicted that the dispersion correction has only a quite small effect, within only few wave numbers, on the calculated vibrational frequencies. A second aim of the current manuscript is then to study the effect of the

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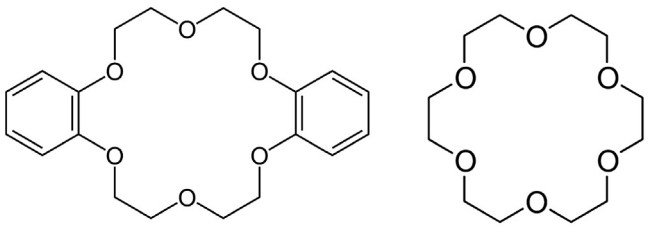

Dibenzo-18-crown-6 18-crown-6

Fig. 1. Dibenzo-18-crown-6 and 18-crown-6.

dispersion correction to the B3LYP functional on the calculated vibrational spectrum, vibrational frequencies and intensities, of db18c6, as an example molecule.

There are only two previous studies of the vibrational spectrum of db18c6 [30,31]. Both studies were confined to quite limited number of bands. In the first study in Ref. [30], the Raman spectrum of free db18c6 and its Na^+ complex was reported in the 100–700 cm^{-1} region. In the second study in Ref. [31], the IR and Raman spectra of free db18c6 and its H_2O and H_3O^+ complexes have been reported [31]. In the first study in Ref. [30], no force field calculations were performed and in the second study in Ref. [31], the assignment of the limited number of bands was not dependent on scaled force field.

2. Experimental Details

Db18c6 purchased from Sigma-Aldrich was used after recrystallized from chloroform. The IR spectrum was measured for the solid sample as KBr pellet. The IR spectrum was recorded on a Thermo Nicolet Nexus 870 FT-IR spectrometer. The spectrometer is equipped with KBr beam splitter and DTGS detector. Between 128 and 516 scans were collected depending on the resolution. Resolutions between 1 and 0.25 cm^{-1} were tried without any significant effect on the resolution of the spectrum. The Raman spectrum was measured for the solid sample using dispersive Horiba LabRAM spectrometer. The spectrometer is equipped with 532, 633 and 785 nm laser sources. The spectrometer utilizes a multichannel air-cooled CCD camera as a detector.

3. Computational Details

At the optimized geometries, force fields were calculated for some selected conformations of db18c6 predicted in a previous conformational search reported in Ref. [23]. The force fields were calculated at the B3LYP/6-311G** and CAM-B3LYP/6-311G** levels. Since the vibrational frequencies calculated at the B3LYP and CAM-B3LYP levels are always overestimated, the computed Cartesian coordinate force fields were converted to internal coordinate force fields. The internal coordinate force fields were scaled using a set of scale factors. To minimize the difference between the experimental and calculated vibrational frequencies, the selected set of scale factors was varied. We used the scale2 program [32] to convert the Cartesian to internal coordinate force fields and in the scaling and refinement of the scale factors. The set of internal coordinates used in the conversion of the Cartesian to internal coordinate force fields is as described in Refs. [33,34]. The internal coordinate force fields were scaled using the equation: [35–37]

$$F_{ij}^{scaled} = \sqrt{C_i C_j}\, F_{ij}^{unscaled}$$

In the above equation, F_{ij}^{scaled} and $F_{ij}^{unscaled}$ refer to the scaled and unscaled force constants and C_i and C_i are scale factors of internal coordinates i and j, respectively.

Two scaling schemes were tried. In the first, a single scale factor scaling was used. This is considered as the most commonly used scaling scheme since it simply means to multiply the calculated vibrational frequencies by a single scale factor. This is because it is not required in this case to use the internal coordinates, and to use a program to convert the Cartesian to internal coordinate force field and to scale the internal coordinate force field. There is a large number of publications that report an estimate of the value of this scale factor at different levels of theory [38–47]. The second scaling scheme we tried in the current study, is to use a unique scale factor for each group of similar internal coordinates. This second choice requires the use of special programs for the selection of the internal coordinates and scaling of the corresponding force field. However, the later scaling scheme produces scaled vibrational frequencies closer to the experimental vibrational frequencies. Compared to single scale factor scaling, there is a less number of publications that report an estimate of these internal coordinate force field scale factors [45–47].

To investigate the effect of the atom pair-wise dispersion correction on the calculated vibrational frequencies and intensities, the vibrational spectrum was calculated at the B3LYP-D3/6-311G** level. The damped option of the DFT-D3 method was used [25–27]. Conformation **88** of db18c6 was used in these calculations since, as will be detailed shortly, it is the predicted conformation of free db18c6 in the solid phase by vibrational spectroscopy in the current study and is the conformation determined experimentally by X-ray [24].

All the computations at the DFT level were performed using the Gaussian program [48]. The Gaussian program default parameters were used in these computations.

4. Results and Discussion

Fig. S1 depicts the IR and Raman spectra of db18c6 in the solid phase. The observed vibrational frequencies are listed in Table S1. The vibrational bands reported in the Raman spectrum in Fig. 2 in Ref. [30] are included in Table S1. Only six bands were assigned in Fig. 2 in Ref. [30]. These six bands were assigned to the closest bands in the current study in Table S1 based on the same Raman spectrum. There is a good correspondence, within 3 cm^{-1}, between the bands reported in the current study in Table S1 and those reported in Ref. [30], of the same Raman spectrum. This is with the exception of the two bands at 764 and 947 cm^{-1} in Ref. [30], where the difference is as high as 14 cm^{-1}.

The vibrational assignment reported in Ref. [31] is also included in Table S1. This assignment reported in Ref. [31] is based on the measured IR and Raman spectrum. In Ref. [31] also a limited number of bands were assigned and those assigned were mainly for intense bands. Consequently, in Table S1, bands assigned in Ref. [31] were assigned to the closest intense bands in the current study. The difference between the frequencies of the bands reported in the current study and those reported in Ref. [31] is 4 cm^{-1} or less. This is with the exception of the bands reported in Ref. [31] at 738, 777 and 1256 cm^{-1}, where the difference is as high as 9 cm^{-1}. Only 18 bands were assigned in Ref. [31] with four bands assigned at the same position, at 1256 cm^{-1}. In the current study, it was not feasible to assign four bands at the same 1256 cm^{-1} frequency and only two of which were included in Table S1.

In the current study, force fields were calculated at the B3LYP/6-311G** level for conformations of db18c6 of C_2 symmetry that were considered for computation at the MP2 level in Ref. [23]. This is with the exception of five conformations. The conformations that were considered for computation at the MP2 level in Ref. [23] are conformations **88**, **448**, **474**, **479**, **499**, **639**, **2803**, **3575**, **4070**, **4083**, **4840**, **6824**, **7378**, **8889** and **11,919**. Conformations **499**, **639**, **4070**, **4083** and **11,919** were excluded from the force field calculations. This is because conformations **499**, **639**, **4070**, **4083** and **11,919** had the same energy as conformations **479**, **479**, **88**, **4840** and **8889**, respectively, at many levels of theory used in Ref. [23], including the B3LYP level. Consequently, force field calculations were performed for conformations **88**, **448**, **474**, **479**, **2803**, **3575**, **4840**, **6824**, **7378** and **8889** only for a total of ten conformations. Conformation **448** represents the gas phase ground