FT-IR, RAMAN AND DFT STUDIES ON THE VIBRATIONAL SPECTRA OF 2,2-BIS(AMINOETHOXY)PROPANE

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ABSTRACT. Various structural forms and molecular structures of 2,2-bis(aminoethoxy)propane (baep) were examined both experimentally and theoretically including FT-IR and Raman spectroscopic methods. Among the possible structural configurations, 30 of them were handled in the framework of this study. The structural optimizations and calculations of vibrational frequencies of baep ($C_7H_{18}N_2O_2$) were performed using Becke-3-Lee–Yang–Parr (B3LYP) density functional methods with 6-311++G(d,p) basis set. In order to support the reliability of the vibrational assignments, total energy distributions (TED) calculations were done with scaled quantum mechanical (SQM) method. Comparison between the experimental and theoretical results regarding the mean absolute error calculations shows that the results of B3LYP method is able to give satisfactory results for the prediction of vibrational frequencies for the studied molecule.

KEY WORDS: 2,2-Bis(aminoethoxy)propane, IR spectra, Raman spectra, Molecular structure, DFT

INTRODUCTION

Ketal based linkages have recently been investigated for the development of novel acid-cleavable polymers those are formulated into the particles to produce potential pH-sensitive drug delivery systems. Besides the stability at physiological pH 7.4, ketal based linages are more sensitive to the acidic environment of tumors and phagosomes than acetal, hyrozone and esters [1, 2]. Molecules containing primary amines have been paid attention for a wide range of applications such as separation of tungsten from sodium molybdate solution and selective extraction [3].

In order to support and to make the interpretation of vibrational frequencies easier those obtained with infrared and Raman spectroscopic methods, DFT (density functional theory) method is widely used and shows acceptable results for different types of molecules [4-8].

In this study FT-IR and Raman spectroscopic properties, optimized molecular structures of a homobifunctionalized amino ketal, 2,2-bis(aminoethoxy)propane were investigated with experimental and theoretical level. Theoretically obtained vibrational and structural data for the most stable conformer of the title molecule were also compared to the experimentally obtained data and all the findings were also identified and presented in this study.

EXPERIMENTAL

Materials and methods

A commercial sample of baep (98%) was purchased and used without further purification. FT-IR spectrum was recorded using Bruker Optics IFS66v/s FTIR spectrometer at a resolution of 2 cm^{-1}. The Raman spectrum was obtained using a Bruker Senterra Dispersive Raman microscope spectrometer with 532 nm excitation from a 3B diode laser having 3 cm^{-1} resolution in the spectral region of 3700–400 cm^{-1}.

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Computational procedure

For the search of stable conformers, many different possible structures were created and 30 of them were examined. During the creation of possible geometric conformers the previously reported studies were taken into account [9-11]. For the search of the stable conformers, 30 forms of baep were first optimized by B3LYP with 6-311G++(d,p) basis set in the gas phase. Following the optimization, it was found that some of them (C1, C2, C4, C12, C20) had negative frequencies so they belonged to transition states and they were no longer considered and some of them were found positive frequencies and henceforth, none of them belonged to a transition state. Among the optimized structures C25 (conformer 25) was found more stable than other conformers. The optimized structures of C25 and C23 are given in Figure 1 in which oxygen, nitrogen, carbon and hydrogen atoms were indicated with red, blue, grey and white colors, respectively. Therefore, all the experimental results were compared to C25 conformer. The vibrational wavenumbers of baep were calculated including the same method and the basis set. TED calculations were performed with the scaled quantum mechanical (SQM) program [12, 13]. During the assignments and the matching of the experimental and theoretical vibrational wavenumbers of the title molecule several factors were considered, such as: animation option of the GaussView package program, relative intensities of the vibrational bands and previously reported data in the literature. All the related calculations were conducted with Gaussian 09 program on a personal computer [14].
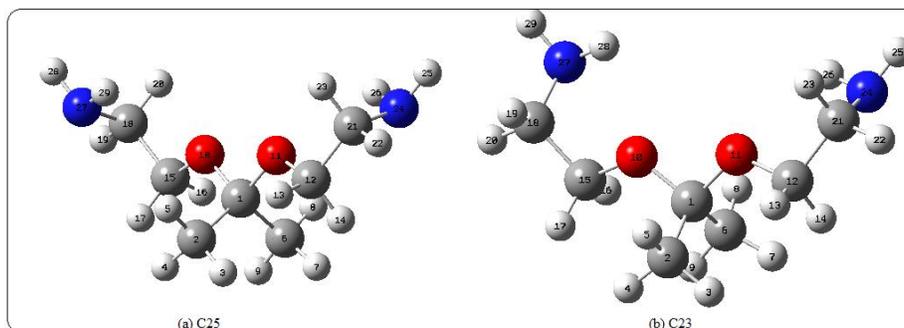

(a) C25   (b) C23

Figure 1. Possible stable conformers of baep optimized with B3LYP/6-311++G(d,p) level of theory.

RESULTS AND DISCUSSION

Geometrical structures

The lowest energy configuration in the gas phase was found as C25. Furthermore, the optimized energy difference between conformer C25 and C23 (Figure 1) is around 0.2 kcal, which suggests an abundance of 71% for C25 and 29% for C23. The rest of the conformers were ignored due to their high optimization energy when compared to C25. Input structures chosen before the optimization and the optimized structures at the end of the calculation using Gaussian program and related level of calculations show that the resultant structure is closely related to how the initial geometry of the molecule was chosen. Indeed some preferred input geometries led to negative or imaginary frequencies at the end of frequency calculations. Several important geometric parameters were mentioned here. For example, for both conformers, N-H and C-O bond lengths were calculated around 1.01 Å and 1.42 Å. Dihedral angles of D(5;2;1;6) and D(8;6;1;2) for both C25 and C23 suggest almost a planar structure with an angle around 177°.

The most obvious difference between both conformers is that NH$_2$ groups are on the same side of the plane constructed by (15;10;1;11 or 12;11;1;10) atoms for C23 and are on the opposite sides of the mentioned planes for C25. Some important torsional angles were summarized in Table 1.

Table 1. The magnitude of some important torsional angles of conformer C25 and C23.

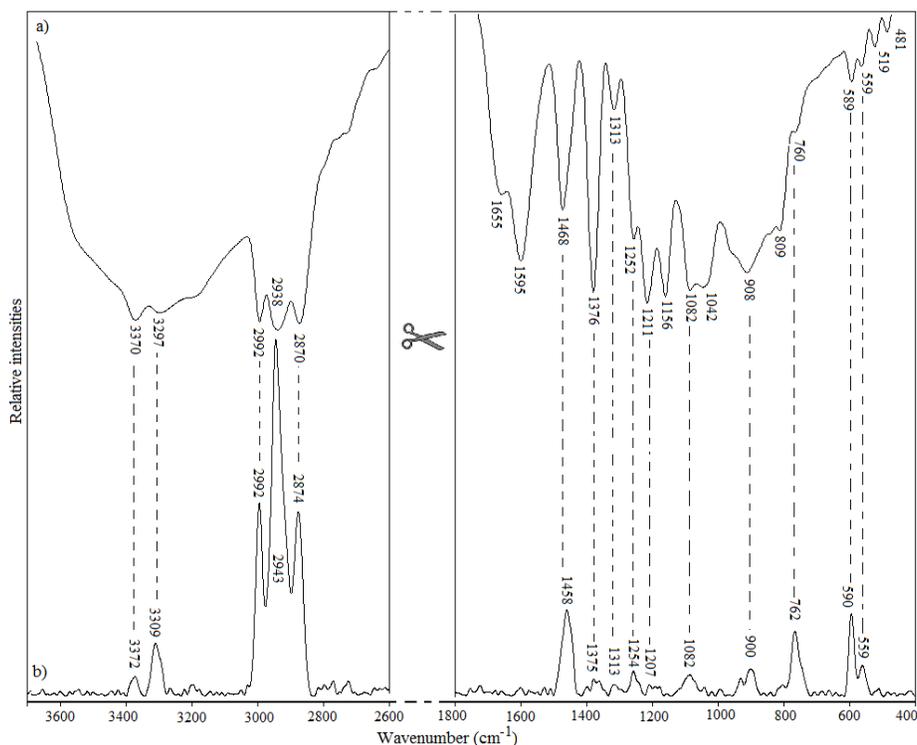| Torsion angles (º)	B3LYP/6-311++G(d, p)	
	C25	C23
C15-C18-N27-H28	179.6	60.4
C15-C18-C27-H29	61.9	179.0
H16-C15-C18-N27	175.2	55.9
O10-C15-C18-N27	64.4	64.3
C1-O10-C15-C18	170.3	179.0
C15-O10-C1-C6	52.1	51.0
C15-O10-C1-C2	73.8	74.8
C15-O10-C1-O11	168.7	167.5
O10-C1-O11-C12	168.7	166.0
C1-O11-C12-C21	170.3	169.0
O11-C12-C21-N24	64.4	64.8
O11-C12-C21-H22	176.9	176.6
C12-C21-C24-H25	179.6	179.7
C12-C21-N24-H26	61.9	61.8

Figure 2. FT-IR (a) and Raman (b) spectra of baep.

Vibrational studies of baep

The title molecule baep contains 29 atoms, therefore, it shows 81 normal vibrational modes and it is a member of C_1 point group with identity (E) symmetry operation. Within the 30 conformers, from C1 to C30, C25 was found as having the lowest optimization energy showing no negative or imaginary frequencies. As a result, all the experimental results were compared to the theoretical results of C25 conformer. Theoretical findings for infrared and Raman wavenumbers together with experimental results of the title molecule were shown in Table 2. Experimental (FT-IR and Raman) spectra of baep were presented in Figure 2.

In the high wavenumber region bands appeared at around 3372 cm^{-1} (R), 3370 cm^{-1} (IR) are the antisymmetric NH_2 vibrations while those appeared at 3309 cm^{-1} (R) and 3297 cm^{-1} (IR) are due to symmetric NH_2 vibrations. The broadened shape of the band at this region could be attributed to the indication of residue of moisture in the sample and intra and intermolecular interactions. The theoretically calculated results for these bands are 3370 cm^{-1} and 3297 cm^{-1} and the related TED values are given in Table 2. As seen in Figure 2, antisymmetric NH_2 vibration possess higher intensity than symmetric NH_2 vibration in IR spectrum and reverse occurs in Raman spectrum. Similar observations were also reported in previous works [9, 15]. Molecular electronic polarizability of symmetric vibrational form of NH_2 changes more when compared to the antisymmetric stretching of NH_2. This could explain the differences in band intensities.

Table 2. Comparison of the experimental and calculated vibrational wavenumbers (cm^{-1}) of baep in gas phase.

Assignments (C25)	Experimental		B3LYP/6–311++G(d,p)		
			Gas phase		
TED	IR	Raman	ν^{β}	I_{IR}	I_R
ν27-28(54)+ν27-29(45)	3370	3372	3370	4.85	63.85
ν24-26(53)+ν24-25(44)	3297	3309	3297	2.53	122.67
ν6-8(32)+ν2-5(32)+ν6-7(12)+ν2-4(11)	2992	2992	2998	23.41	67.29
ν2-3(18)+ν6-9(18)+ν2-5(17)+ν6-8(16)+ν2-4(13)	2938	2943	2926	6.79	227.57
ν15-16(31)+ν12-13(30)+ν15-17(19)+ν12-14(18)	2870	2874	2876	32.41	134.66
	1655	-	-	-	-
δ28-27-29(27)+δ25-24-26(25)+δ18-27-29(10)+δ21-24-26(9)	1595	-	1619	63.86	-
δ3-2-5(12)+δ4-2-5(12)+δ7-6-8(12)+δ8-6-9(12)	1468	1458	1465	12.96	10.15
ν15-18(5)+ν12-21(5)	1376	1375	1372	26.05	0.26
δ15-18-20(10)+δ12-21-23(10)+δ20-18-27(6)+δ24-21-23(6)	1313	1313	1295	6.99	0.32
	1252	1254	-	-	-
δ10-15-17(9)+δ11-12-14(9)+δ20-18-27(5)+δ10-15-16(5)	1211	1207	1217	13.43	9.01
ν11-12(7)+ν10-15(7)+δ12-21-22(6)+δ15-18-19(6)	1156	-	1162	4.65	0.91
ν15-18(14)+ν12-21(14)+ν21-24(12)+ν18-27(12)	1082	1082	1082	34.68	1.15
ν18-27(18)+ν21-24(17)	1042	-	1041	8.85	-
ν1-10(18)+ν1-11(18)	908	900	897	61.93	0.16
δ21-24-26(9)+δ18-27-29(9)+δ21-24-25(6)+τ19-18-27-29(6)	809	-	803	38.50	2.76
ν1-10(10)+ν1-11(10)+ν10-15(7)+ν11-12(7)	760	762	772	34.02	5.94
δ1-11-12(13)+δ1-10-15(13)+δ10-15-18(5)+δ11-12-21(5)	589	590	590	8.86	1.20
	559	559	-	-	-
	519	-	-	-	-
δ6-1-10(7)+δ2-1-11(7)+ν1-2(7)+ν1-6(7)	481	-	484	5.25	0.37

IR: Infrared; ν^{β}: Wavenumbers scaled with SQM methodology; I_{IR}: Infrared intensities (km/mol); I_R: Raman activities (Å^4/amu).

CH stretching vibrations experimentally/theoretically appeared at 2992 cm^{-1} (IR, R)/2998 cm^{-1}, 2943 cm^{-1} (R) and 2938 cm^{-1} (IR)/2926 cm^{-1}, 2874 cm^{-1} (R) and 2870 cm^{-1} (IR)/2876 cm^{-1}.

Related TED values can be seen in Table 2 for all vibrations. While NH_2 bending vibrations or more precisely scissoring vibrations of baep seem Raman inactive or its intensity is too low to describe it meaningfully (Figure 2), its IR band appears at 1595 cm^{-1} as a strong band which is theoretically calculated as 1619 cm^{-1}. The band appeared at 1468 cm^{-1} (IR) and 1458 cm^{-1} (R) are due to stretching modes of CH_3. This band is theoretically predicted as 1465 cm^{-1}. The band at 1313 cm^{-1} (IR, R) which is theoretically calculated as 1295 cm^{-1} is due to CC stretching vibrations (Table 2). Measurements made under 1313 cm^{-1} have revealed mixed type of vibrations as can be seen in Table 2.

CONCLUSIONS

Experimental and theoretical vibrational IR and Raman spectra and structural properties of baep were analyzed with B3LYP/6-31++G(d,p) level of theory. In brief, following results can be summed up: (i) B3LYP/6-31++G(d,p) level of theory came up with acceptable results in the calculation of vibrational frequencies for the title molecule following the application of SQM method. (ii) Among the examined conformers, C25 conformer was found having the lowest optimized energy in the gasphase. (iii) It was seen that the optimized output structure with Gaussian program strongly depends on the input configuration of the investigated molecule. Therefore, it is important to identify a various range of possible structures before optimization procedure. Observation of no negative frequencies does not always mean that the obtained structure has the lowest optimization energy.

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