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Combined Vibrational Spectroscopic and Quantum Chemical Investigations of 1,8-diaminooctane

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Abstract

This paper contains the molecular parameters, vibrational properties and some theoretical calculations of 1,8-diaminooctane. Bond angles, bond lengths, vibrational properties, dipole moments, frontier molecular orbitals and molecular electrostatic potential of 1,8-diaminooctane were performed with using density functional theory calculations with B3LYP/6-311++G(d,p) level of theory. Vibrational properties were interpreted with the by using scaled quantum mechanical force field. This study enables us to figure out the vibrational and structural properties and some electronic properties of the 1,8-diaminooctane by means of the theoretical and experimental studied methods.

Keywords: 1,8-diaminooctane, density functional theory, theoretical calculations, molecular electrostatic potential.

1. Introduction

This molecule concerns of the monoalkylamines which are organic compounds including a primary aliphatic amine group. An alkane-α and ω-diamine in which the two amino groups are separated by eight methylene groups [1]. The 1,8-diaminooctane is used as cross link effects while the synthesis of various molecular carbon nanotubes and macrocycle molecules [2]. Aliphatic diamines are important compounds that are widely used in coordination chemistry, biochemistry and polymer chemistry. This molecule has a fundamental carbon chain structure. So, it is used like synthesis molecule. This molecule is used as the ligand in the formation of Hofmann type host-guest compounds. Molecular formula of 1,8-diaminooctane is $C_8H_{20}N_2$ and be found in solid phase.

FT-IR spectra of 1,8-diaminooctane was reported by Kasap and Özbay [3]. In that study, this molecule had been purchased from Sigma-Aldrich and used without further purification. IR spectra of 1,8-diaminooctane had been recorded 400-4000 cm^{-1} with Perkin-Elmer Spectrum One FT-IR spectrometer.

In our study, the molecular structure (bond angles, bond lengths, dipole moments) and vibrational frequencies of 1,8-diaminooctane have been calculated by density functional theory (DFT) with B3LYP method and 6-311++G(d,p) level of theory.

2. Materials and Methods

In this study, 1,8-diaminooctane molecule was drawn in three dimensions using the molecular drawing program GaussView 3.0 [4]. The geometrical parameters of this structure were automatically entered as input data in the Gaussian 03W package program [5]. Then, 1,8-diaminooctane molecule were optimized by means of the B3LYP/6-311++G(d,p) level of theory. Bond angles, bond lengths and vibrational frequencies of 1,8-diaminooctane molecule have been calculated DFT/B3LYP with 6-311++G(d,p). The vibrational frequencies of the optimized geometry were corrected by multiplying with scaling factors [6] for comparing the experimental values. The optimized geometrical structure of the title molecule is shown in Figure 1.

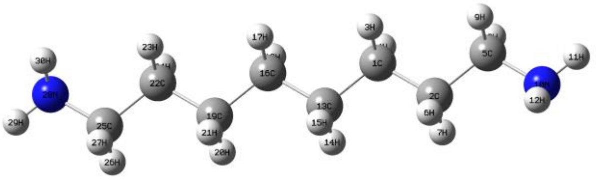

Figure 1. Molecular structure and atomic numbering of 1,8-diaminooctane.

Since there is not published experimental data on the bond lengths and bond angles of the 1,8-diaminooctane, the calculated geometrical parameters of this molecule were compared with the experimental values of the geometrical parameters of the 1,6-diaminohexane molecule as similar molecule performed by Meng and

Lin [7].

The potential energy distribution (PED) was calculated via using the scaled quantum mechanics (SQM) program [8] and the fundamental vibrational modes were assigned with their PED values.

Addition to these properties, HOMO-LUMO energy gap and MEP have been calculated by DFT/B3LYP with same basis set.

3. Results and Discussion

Geometrical parameters

The experimental values and the calculated geometrical parameters of 1,8-diaminooctane were compared in Table 1.

In the B3LYP/6-311++G(d,p) level of theory, the N-C-C (116.49°) bond angle is greater than the C-C-C (113.65°), H-N-H (104.78°) and H-C-H (106.21°). In general, the N-C-C bond angles are greater than the C-C-C, H-C-H and H-N-H bond angles. This is also consistent with the experimental results.

In the B3LYP/6-311++G(d,p) level of theory, the C-C (1.54 Å) bond length is greater than the N-C (1.48 Å), C-H (1.10 Å) and N-H (1.03 Å). In general, the C-C bond lengths are greater than the N-C, C-H and N-H bond lengths. This is also consistent with the experimental results.

Our calculated the geometrical parameters were found to be very compatible with compared experimental the geometrical parameters.

Table 1. Experimental and calculated parameters of 1,8-diaminooctane.

Bond Lengths (Å)	B3LYP/6-311++G(d,p)	Experimental [7]
N-H	1.03	0.90
C-H	1.10	0.97
N-C	1.48	1.48
C-C	1.54	1.51
Bond Angles (°)		
H-C-H	106.21	107.59
H-N-H	104.78	107.69
N-C-C	116.49	114.71
C-C-C	113.65	112.01

1,8-diaminooctane molecule has 30 atoms in which the C and N atoms are planar and the H atoms are out of plane. This molecule belongs to the point group C_{2h}. Since this molecule is a non-linear molecule, it has 84 normal vibrational modes.

Vibrational Assignment

The vibrational frequencies and IR vibrational intensity are given in Table 2. The experimental and calculated FT-IR and FT-Raman spectra for 1,8-diaminooctane are given in Figures 2-4. Also, the corresponding data are given in Table 2.

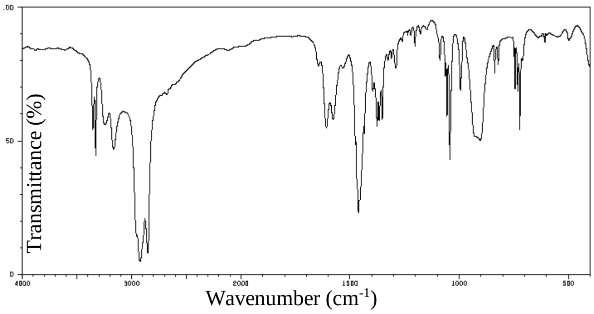

Figure 2. Experimental FT-IR spectra of 1,8-diaminooctane.

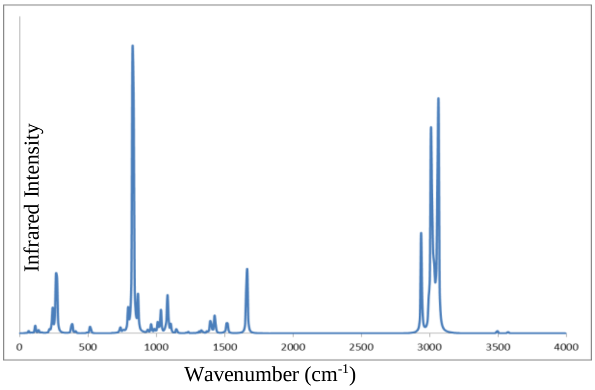

Figure 3. Theoretical FT-IR spectra of 1,8-diaminooctane.

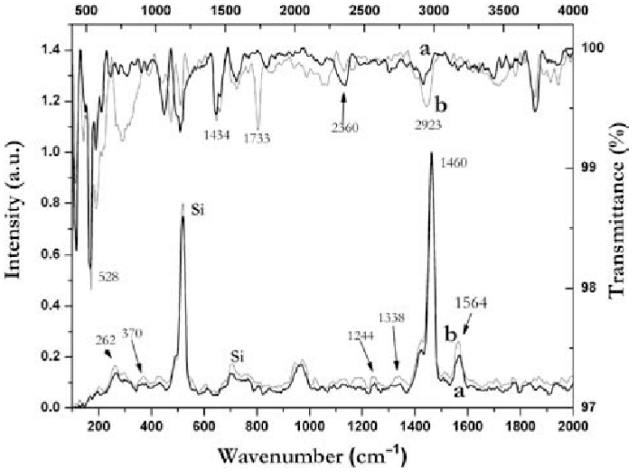

Figure 4. Experimental and theoretical FT-Raman spectra of 1,8-diaminooctane.

Table 2. The vibration frequencies of 1,8-diaminooctane molecule.

	Freq^a.	I_{IR}^b	FT-IR [3]	PED (%)
ν_1	34	0.137		
ν_2	49	0.081		
ν_3	62	0.658		
ν_4	82	0.281		
ν_5	108	2.070		
ν_6	130	0.528		
ν_7	134	0.485		
ν_8	152	0.304		
ν_9	165	0.071		
ν_{10}	210	0.854		
ν_{11}	230	7.822		
ν_{12}	254	9.932		
ν_{13}	260	19.49		

ν_{14}	368	4.383		
ν_{15}	393	0.601		
ν_{16}	475	0.247		
ν_{17}	498	2.918		
ν_{18}	515	6.845		
ν_{19}	709	1.826		
ν_{20}	715	0.027		
ν_{21}	732	0.715		
ν_{22}	765	5.648		
ν_{23}	797	47.03		
ν_{24}	802	81.22		
ν_{25}	836	9.548	860 m, br	δ_{HCH}(37%)
ν_{26}	904	0.755		
ν_{27}	930	2.610		
ν_{28}	954	1.229	951 vw	δ_{HCH}(53%)
ν_{29}	975	2.719		
ν_{30}	987	1.514		
ν_{31}	998	6.143	1005 vw	δ_{CCC}(27%)+δ_{HNH}(10%)+δ_{HCH}(10%)
ν_{32}	1023	0.280		
ν_{33}	1028	0.515		
ν_{34}	1031	0.283		
ν_{35}	1040	3.126		
ν_{36}	1047	11.54	1052 vw	δ_{CCH}(13%)+δ_{HNH}(13%)
ν_{37}	1068	2.193	1075 vw	δ_{CCH}(20%)+δ_{HNH}(18%)
ν_{38}	1109	1.554	1089 vw	δ_{CCC}(40%)+δ_{HNH}(13%)+δ_{HCH}(10%)
ν_{39}	1174	0.160		
ν_{40}	1190	0.432		
ν_{41}	1212	0.101	1218 vw	δ_{CCH}(48%)
ν_{42}	1231	0.105		
ν_{43}	1252	0.181		
ν_{44}	1270	0.519		
ν_{45}	1282	0.233		
ν_{46}	1291	0.122		
ν_{47}	1296	0.042		
ν_{48}	1299	0.242	1305 vw	δ_{HCH}(30%)+δ_{HNH}(18%)
ν_{49}	1325	0.572	1338 vw	δ_{HCH}(26%)+δ_{HNH}(21%)
ν_{50}	1342	0.229		
ν_{51}	1348	3.970		
ν_{52}	1353	0.379		
ν_{53}	1356	1.059	1367 vw	δ_{HCH}(25%)+δ_{HNH}(18/%)
ν_{54}	1380	6.998	1390 w, sh	δ_{HCH}(36%)
ν_{55}	1434	0.107		
ν_{56}	1437	0.020	1440 vw	δ_{HCH}(40%)
ν_{57}	1439	0.005		
ν_{58}	1442	0.048		
ν_{59}	1449	0.272		
ν_{60}	1457	0.083		
ν_{61}	1464	3.048	1466 s	δ_{HCH}(32%)+δ_{HNH}(28%)
ν_{62}	1471	1.840	1487 m	δ_{HCH}(42%)+δ_{HNH}(21%)
ν_{63}	1604	14.86	1584 s	δ_{HCH}(57%)
ν_{64}	1609	11.58		
ν_{65}	2841	31.22	2856 vs	ν_{CH}(65%)
ν_{66}	2892	1.911		
ν_{67}	2893	0.368		
ν_{68}	2896	4.347		
ν_{69}	2897	0.423		
ν_{70}	2901	0.201		
ν_{71}	2908	39.41		
ν_{72}	2910	9.590		
ν_{73}	2913	3.190		
ν_{74}	2919	35.355		
ν_{75}	2920	3.950	2926 vs	ν_{CH}(87%)
ν_{76}	2932	5.181		
ν_{77}	2936	12.24		
ν_{78}	2947	5.435		
ν_{79}	2958	0.661		
ν_{80}	2960	100.0		
ν_{81}	3376	0.627		
ν_{82}	3380	0.365		
ν_{83}	3452	0.231	3321 s	ν_{NH}(79%)
ν_{84}	3456	0.309	3381 s	ν_{NH}(79%)

vs:very strong, m: medium, s:strong, w:weak, vw:very weak,ν: stretching, δ: in plane bending

[a] Obtained from the wavenumbers calculated at DFT using scaling factor 0.967.

[b] Relative absorption intensities normalized with the highest peak absorption equal to 100,

[c] FT-IR values were taken Ref. [3]

[d] Potential energy distribution (PED) calculated at the B3LYP/6-311++G(d,p) level of theory, Only contributions ≥10% are listed,

The NH stretching vibrations appear at 3500-3300 cm^{-1} [9,10]. For 1,8-diaminooctane N-H stretching vibrations are observed at 3381 cm^{-1} and 3321 cm^{-1} experimentally (FT-IR spectra) [3] and assigned at 3456 cm^{-1} and 3452 cm^{-1} (DFT/B3LYP with 6-311++G(d,p)) according to our calculation. It can be seen that in Table 2, experimental and theoretical results are very consistent with each other.

The asymmetric and symmetric stretching modes of the CH$_2$ group usually occur in the region from 2800 to 3000 cm^{-1}[11]. In FT-IR spectra for 1,8-diaminooctane C-H stretching vibrations are observed at 2856 cm^{-1} and 2926 cm^{-1} experimentally [3]. These vibrations calculated at 2841 cm^{-1} and 2920 cm^{-1} by B3LYP/6-311++G(d,p) calculation (Table 2). The theoretical results are very good agreement with experimental ones.

The H-C-H in-plane bending vibrations characterize in the region 1300-1500 cm^{-1}[12]. Experimentally, the in-plane H-C-H bending modes were measured at 1305, 1338, 1367, 1390, 1440, 1466, 1487 and 1584 cm^{-1} in FT-IR spectra [3]. These vibrations calculated at 1299, 1325, 1356, 1380, 1437, 1464, 1471 and 1604 cm^{-1} by means of B3LYP/6-311++G (d,p) (Table 2). It can be seen that in Table 2, experimental and theoretical results are very consistent with each other.

The C-C-H in-plane bending vibrations appear in the region 1300-1000 cm^{-1} [12]. Experimentally, the in-plane C-C-H bending modes were measured at 1052, 1075, 1089 and 1218 cm^{-1} in FT-IR spectra [3]. These vibrations calculated at 1047, 1068, 1109 and 1212 cm^{-1} by means of B3LYP/6-311++G (d,p) (Table 2). It can be seen that in Table 2, experimental and theoretical results are very compatible.

All aromatic C-H stretching vibrations were found to be weak. This reason may be attributed to decrease in the dipole moment because of decrease the negative charge on the C atom [13]. This decrease is due to the withdrawing of electrons from the carbon atom of the molecule due to the reduction of inductive effect, resulting in an increase in the chain length of the molecule [13].

HOMO-LUMO analysis

The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and HOMO-LUMO energy gaps have been performed with using DFT at B3LYP/6-311++G(d,p) level. They are very important parameters in quantum chemistry. HOMO defines the ability to donate an electron and LUMO defines the ability to obtain an electron. The plots of HOMO, HOMO-1, LUMO, LUMO+1 for 1,8-diaminooctane were given in Figure 5. The HOMO-LUMO energy gap (ΔE) value of 1,8-diaminooctane calculated as 6.18 eV. This value for Urea 6.72 eV in the literature [14]. So, 1,8-diaminooctane is very soft molecule and very stable than Urea molecule.

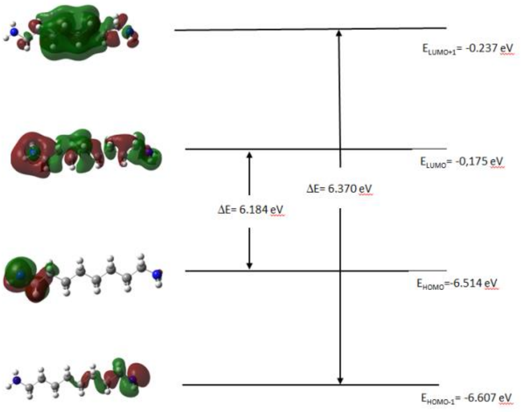

Figure 5. Frontier molecular orbitals of 1,8-diaminooctane.

Besides, dipole moment values of 1,8-diaminooctane calculated by DFT and these values are given in Table 3.

Table 3. The dipole moment (field-independent basis, Debye) values of 1,8-diaminooctane.

μ_x	μ_y	μ_z	μ_{tot}
-1.21	1.62	1.07	2.29

MEPS of 1,8-diaminooctane

The molecular electrostatic potential (MEP) maps of 1,8-diaminooctane's ground state are shown in Figure 6. Using the B3LYP/6-311++G(d,p) level of theory, the MEP maps were drawn. The MEP can be seen as reactivity maps on organic molecules, showing the most likely regions where point charges can approach the molecule. The MEP is used for researching reactivity regions. In MEP maps, red color shows negative, blue color shows positive areas. In Figure 6 right side picture, MEP in 1,8-diaminooctane is mainly over Nitrogen atoms.

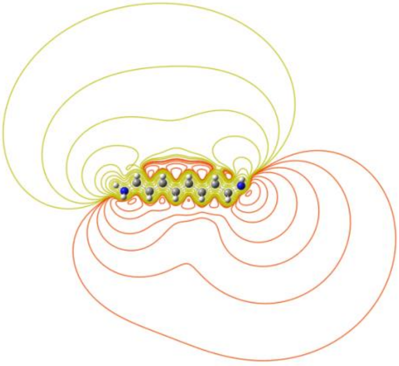

Figure 6. The MEP maps of 1,8-diaminooctane

4. Conclusion

In this work, the geometrical parameters, vibrational frequencies, dipole moments, HOMO-LUMO and MEP of 1,8-diaminooctane were performed with using Gaussian 03W program. In that all theoretical calculations, we used B3LYP/6-311++G(d,p) level of theory. The calculated geometrical structural and vibrational spectral data of 1,8-diaminooctane with DFT methods are good consistent with available experimental data.

Author's Contributions

Akif Özbay: Drafted and wrote the manuscript, performed the experiment and result analysis.

Aysun Gözütok: Assisted in analytical analysis on the structure, supervised the experiment's progress, result interpretation and helped in manuscript preparation.

Ethics

There are no ethical issues after the publication of this manuscript.

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