Theoretical Study on the Ethynethiol and Ethynedithiol Molecules

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Abstract

The equilibrium geometries , heat of formations, dipole moments , ionization energies, HOMO- LUMO orbital energies, charge and electron densities , and the ir spectra for ethynethiol and ethynedithiol molecules were evaluated theoretically .The calculation method was based on the semi-empirical MINDO/3-FORCES MO method. In comparison with ethynethiol , the second molecule has the lower values for both frequency and ir intensity values of the fundamental vibration localized at the CC bond and , also, it has the higher value for the frequency of the other fundamental concentrated at the CS bond. This effect may be due to the resonance effect caused by the S atom

الخلاصة

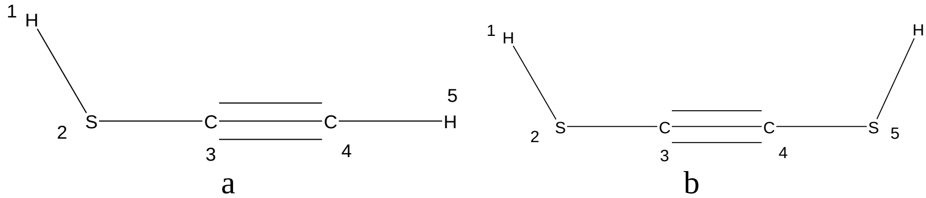
تم حساب الشكل الهندسي المستقر، حرارة التكوين ، عزم ثنائي القطب، طاقة التاين ، الطاقة لأعلى مدار ممتلئ وكذلك لأوطأ مدار فارغ ، الشحنات والكثافات الالكترونية وكذلك طيف الأشعة تحت الحمراء للجزيئتين اثينايل ثايول و الأثينايل دایاثا يول. ووجد إن المط الاهتزازي CC في اثينايل ثايول له اعلي تردد واعلي شدة امتصاص في منطقة الأشعة تحت الحمراء مما في الجريئة الثانية بينما تنعكس الوضعية في حالة المط الاهتزازي CS الذي له اعلي تردد في جزيئه الأثينايل داياثايول . واعزي ذلك إلى تاثيرالرنين في جزيئة الأثينايل داياثا يول الناتج من منح ذرة S لمزدوجها الالكتروني مما يؤدي إلى أضعاف ألآصرة CCالثلاثية والى تقوية ألآصرة C-S ألأمر الذي تسبب في تقليل الرتبة للأصره CC وبالتالي تقليل التردد لنمط المط ألأهتزازي الأساسي المتمركزعليها وادى ايضا الى زيادة الرتبة وبالتالي زيادة التردد للمط المتمركز على اللآصرة CS.

Introduction

The ethynethiol is formed, along among other products, from the photolysis of 1,2,3-thiadiazol[1]. The ethynethiol-based polysulfide polymers$[C_2H_2S_x]$(x=1-6) have been synthesized by the reaction of acetylides and elemental sulfur in liquid ammonia[2].Recently , the ethynedithiol oligomers were also synthesized and they used as cathode components of lithium-sulfur batteries[3].

Although the optimized geometry of ethynethiol , using different basis sets; STO-3G, 6-31G*…etc. were reported [4] but there was incomplete study concerned the vibration spectrum of this molecule; However, only six over nine fundamental vibration modes were experimentally determined[5] On others hand, there are no reported study whether it is experimental or theoretical concerns the evaluation of the equilibrium geometry of ethynedithiol and its vibration spectrum

The aim of this study is to give a complete theoretical treatment includes the evaluation of the equilibrium geometries, heats of formation, dipole moments, ionization energies, HOMO-LUMO orbital energies, charge and electron densities, and the IR spectra for ethynethiol and ethynedithiol molecules . The molecular structure and the numbering of atoms of studied molecules are shown in Fig.1



a b

Fig1:- a and b are the ethynethiol and ethynedithiol molecules respectively

The present study is based on MINDO/3-FORCES model [6,7] which was developed and applied to the treatment of organic molecules[8-11]. Such treatment yields the equilibrium geometry and energy values of the molecules in addition to their fundamental vibration frequencies (3N-6) and ir absorption intensities.

MINDO/3-FORCES model adopts the pulay forces method[12] to evaluate the force constants of molecules that are introduced then to the Wilson Secular equation of the following form[13].

$$\sum_j L_j (F_{ij} - M_{ij}\lambda) = 0$$

Solution of this equation yields vibration frequencies ($\lambda = 4\pi^2 \nu^2 C^2$) and vibration mode eigen vector coefficients, L_j.These coefficients are utilized in evaluating the atomic partial participation values (APP) (the partial contribution of each atom to the molecular vibration), the ir absorption intensities and in doing the graphical representation of each of vibration mode[8-11].

Results and Discussion

The geometric parameters , taken from ab initio method [4], were used as a starting point in this study .The equilibrium geometries, heats of formation, dipole moments , ionization energies, HOMO- LUMO orbital energies , for ethynethiol and ethynedithiol molecules , were listed in Table-1 .Also, the charge and electron atomic densities , for both the molecules, were calculated , Table 2. Tables-3 and 4 show our 3N-6 calculated fundamental vibration frequencies along with their assignments and the corresponding IR absorption intensities for the ethynethiol and ethynedithiol molecules respectively. The comparison of the available experimental fundamental vibration frequencies [5] with our scaled calculated frequencies [14], for the ethynethiol molecule, were, also, shown, Table-3. The comparison is being good

The ethynethiol and ethynedithiol molecules are belonged to C_s and C_{2v} symmetry point groups respectively. According to the C_s character table, the ethynethiol has nine fundamental vibration modes which are distributed among the following irreducible representation ,$\Gamma_9 = 7a^{-} + 2a^{=}$,Table-3. On the other hand, the irreducible representation, $\Gamma_{12} = 5a_1 + 2a_2 + b_1 + 4b_2$, is belonging to the ethynedithiol molecule, which has the C_{2v} symmetry and posses twelve fundamental vibration modes ,Table-4 .The a^{-} , a_1, b_2 are in-plane modes while the others are out of plane. In addition, all the modes are ir and Raman active except those having the a_2 symmetry that are Raman active only.

From Table-1, it is obvious that ethynedithiol has the lower heat of formation, ΛH_f, than the ethynethiol ; 32.97 against 45.11kcal.mol^{-1} . This means that the replacement of the acidic hydrogen, in the ethynethiol molecule, by the SH group, leads to stabilize the ethynedithiol molecule via the resonance effect. This resonance results from donation of the S atom, Fig.1-b, its lone pair electron so that a resonance conjugation is occurred within the ethynedithiol molecule. The stability of etynedithiol molecule is supported by its low dipole moment , Table-1. This Table , also , shown our calculated. bond lengths and bond angles. These are in fair agreement with those calculated by the other methods [4].

Comparing Tables-3 and 4 shows that , in the ethynethiol molecule, the CC stretch fundamental vibration has the higher frequency and the higher IR absorption intensity values compared to that for ethynedithiol .On contrast , the C-S stretch fundamental vibration has its lower frequency value This may be attributed , as we mentioned, above, to the resonance effect caused by the S atom in the ethynedithiol The S atom denotes its lone pair electron via the resonance effect so that the CC triple bond, in the ethynedithiol molecule, becomes weaker and the C-S bond becomes stronger ones. The weak bond means a low bond order and, in turn, a low vibration frequency value associated with this bond. The reduction of the IR absorption intensity of the CC stretch fundamental vibration in the ethynedithiol may be attributed to the low polarity of the CC bond. This low polarity is due to the similar and small charge densities of the two C atom.;-0.032 against -0.033, Table-2. Moreover, the polarization in the S-C bond is, also, low due to the similar and small charge densities of S and C atoms in the both molecules , Table-2 .However, this may be the reason of the low ir intensity of the C-S stretch mode in both molecules.

Table-1*: The bond lengths and bond angles along with some physical properties for ethynethiol and ethynedithiol.

Geometric parameter**	ethynethiol	ethynedithiol
ΛH_f, kcal mol^{-1}	45.11	32.97
μ, Debye	2.577	0.141
HOMO, eV	-9.1104	-8.511
LUMO, eV	0.6207	0.0193
Ionization energy, eV	9.1104	8.511
H-S	1.3445(1.3299)	1.3299
S-C	1.6696(1.705)	1.7050
CC	1.2852(1.1963)	1.1963
C-H	1.0740(1.0531)	-------
$\angle$HSC	95.26^o(97.36^o)	97.39^o

* calculated in this work, **Bond length in A^o and bond angle in degrees. The values in parenthesis are the geometric parameters calculated with 6-31G* basis set[4]

Table-2* The charge and electron densities of ethynethiol and ethynedithiol molecules calculated in this work. The values in parenthesis are for ethynedithiol molecule. For atoms numbering, see Fig-1 .

atom	Charge densities	Electron densities
H_1	0.115(0.114)	0.885(0.886)
S_2	-0.081(-0.082)	6.081(6.082)
C_3	0.062(-032)	3.938(4.032)
C_4	-0.218(-0.033)	4.218(4.033)
H_5(S_5)	0.122(-0.081)	0.878(6.081)
H_6	-------(0.114)	-------(0.886)

* calculated in this work

Table (3):-The computed nine fundamental vibration frequency values along with their corresponding ir absorption intensities for the ethynethiol molecule. The available experimental frequencies are, also, shown.

Mode No.	Sym* .	Frequency (cm^{-1})		ir absorption intensity, $km.mol^{-1}$, (calculated this work)		Description
		Calcd.$ This work.	Exptl.[5]	**	***	
ν_1	a^-	3654(3164)	3315	0.71	0.66	C-H st.
ν_2		2594(2573)	2575	22.25	21.58	S-H st..
ν_3		2414(2156)	2065	3.24	3.53	CC st.
ν_4		821 (821)	1112	3.68	6.19	δ C-H+.δ S-H
ν_5		717(802)	959	0.1	0.05	C-S st.
ν_6		693(693)	-----	3.03	2.9	δ S-H+δ C-H
ν_7		145(145)	-----	0.43	0.67	δ S-H
ν_8	$a^=$	773(773)	٥٥٨	3.59	3.59	γ_{C-H}
ν_9		175(175)	----.	8.22	8.22	γ C-S+γ S-H

* under C_s symmetry; $: the values in parenthesis are the scaled frequencies[15]; abbreviations used st ,stretch; δ , in-plane bending; ; γ , out of plane bending; ** and *** The derivative of the dipole moment with respect to the parallel coordinate only and with respect to all coordinates respectively.

Table(4):-The computed twelve fundamental vibration frequency values along with their corresponding ir absorption intensities for the ethynedithiol molecule.

Mode No.	Sym*.	Calculated in this work Freq., cm^{-1}	absorption intensity, Km mol^{-1} **	***	Description
ν_1	a_1	2611	16.89	16.35	S-H st..
ν_2		2148	0.0	0 .01	CC st.
ν_3		709	3.3	5.97	δ S-H
ν_4		481	0.0	0.01	δ C-S
ν_5		111	0.59	5.19	δ C-S
ν_6	a_2	459	0.0	0.0	γ CC
ν_7		32	0.01	0.01	γ SS
ν_8	b_1	149	6.12	6.12	γ C-S
ν_9	b_2	2604	35.92	35.25	S-H st.
ν_{10}		957	0.0	0.19	C-S st.
ν_{11}		689	0.21	0.20	δ S-H+ δ CC
ν_{12}		439	0.01	0.01	δ CC

* under C_{2v} symmetry. For symbols and abbreviations, see Table 3

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