

A Theoretical Study of Anion and Cation Radicals of Ethynethiol and Ethynedithiol

J.H. Ali

Physics Dept., Science College, Karbala Univ., Karbala-IRAQ.

Jaafar1951@yahoo.com

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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 spin densities for radical anions and cations of the ethynethiol and ethynedithiol molecules were evaluated theoretically .The calculation method was the semi-empirical MINDO/3-FORCES MO method. It was found that the anion of the ethynedithiol molecule is the more stable than the corresponding neutral one in opposite to the situation of the other molecule. Also , it is difficult to oxidize both of molecules but the ethynedithiol molecule is the easier one

Introduction

The ethynethiol is formed, among other products, from the photolysis of 1,2,3-thiadiazol⁽¹⁾. The ethynedithiol oligomers were synthesized, also, and they

are used as cathode components of lithium-sulfur batteries⁽²⁾. The molecular structure and the numbering of atoms of studied molecules are shown in Fig.1

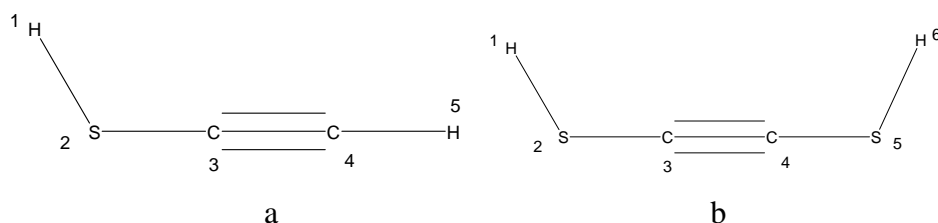


Fig.1: a and b are the ethynethiol and ethynedithiol molecules respectively

In a previous paper⁽³⁾, the neutral ethynethiol and ethynedithiol molecules have been studied theoretically. However, there is no reported experimental and or theoretical study concerning the ethynethiol and ethynedithiol radical anions and cations. We now report the calculated equilibrium geometries, heat of formations, dipole moments, ionization energies, HOMO- LUMO orbital energies, charge and electron densities, and the spin densities for radical anions and cations of these two molecules by calculation based on the MINDO/3-FORCES MO⁽⁴⁻⁶⁾ model. The molecular

energy of each species, obtained from the semi empirical MINDO/3 method⁽⁷⁾, was completely minimized according to the Murtagh-Sargent minimization technique⁽⁸⁾. The derivative of the energy was calculated, analytically, according to Pulay's Force method⁽⁹⁾. The applications the MINDO/3-FORCES method are well known^(3,10-18).

Results and Discussions

The optimized geometries parameters along with the heat of formations, dipole moments, ionization energies, HOMO- LUMO orbital energies, for each one of the ethynethiol and ethynedithiol molecules and their corresponding radical anions and cations, obtained with MINDO/3-FORCES model⁽⁴⁻⁶⁾, were listed in Table 1.

The charges and electron densities for each atom of the neutral, anions and cations of the two molecules were also shown, Tables 2 and 3. Table 4 shows the spin densities for each atom of these radical anions and cations

From Table 1, it is obvious that the conversion of the neutral molecule to the corresponding ion increases the dipole moment. The more increment was found for the radicals anions and the ethynedithiol anion has the higher value, 13.207 against 9.248 Debye for the other anion, Table 1. Also, the low energy value of the Lower Unoccupied Molecular Orbital, LUMO, of the ethynedithiol molecule, indicates that this molecule has high tendency for reduction. This fact is supported by the low heat of formation of its corresponding anion, 27.978 against 32.970 kcal mol⁻¹ for neutral molecule, Table 1. Moreover, both the molecules

are difficult to be oxidized and forming the corresponding cation. However, the ethynethiol molecule is the more difficult one due to the higher heat of formation of its cation, Table 1. The instability of resulting cations is supported by the very low energy values of their LUMO. This refers to the high tendency of these cations to accept an electron and convert to the corresponding neutral molecules. From Table 1, it is obvious that the ethynethiol cation has the higher of this tendency because of it has the lowest LUMO energy value, -5.4702 against -4.8527 eV for the ethynedithiol cation, Table 1.

For the ethynethiol, the C-H bond length increases in the order: anion > neutral > cation, Table 1. The increment or shrinkage of the bond length is depended on the magnitude of the electron-electron repulsion and the electronic-nuclear attraction. As the electron and the spin densities, at each one of the two atoms forming the bond, are increased, the repulsion between these electron densities is increased and the attraction with the two nuclei is increased. So, the bond becomes weak and, consequently, the bond length is increased. For C-H bond, the electron densities at the C and H atoms have their higher values (4.417 and 1.030 respectively) for anion

and the lower ones (3.831 and 0.816 respectively) for cation, Table 3. Therefore the attraction with nuclei is increased and in turn the C-H bond length has its the maximum value, 1.0792 Å in anion and the minimum one, 1.0531 Å, in cation, Table 1. For the same reason, the ethynethiol anion has the higher values of the geometrical parameters: C≡C, S-C, and H-S bond lengths, and the ∠HSC bond angle, Table 1. The increment of the angle may be attributed to the present of higher electron density along with the higher spin densities at each of the H and C atoms in this anion, Tables 3,4. This leads to increase the repulsion between these two atoms and, consequently, the angle is opened to extent more than that

for the neutral and cation ethynethiol, Table 1.

For ethynedithiol, the increment of the H-S and C-C bond lengths show the different order, i.e.: cation > anion > neutral, Table 1. The reason also may be attributed to the fact that the cation has the higher values of both of electron and spin densities at the H and S atoms, Tables 3 and 4. So, the electronic nuclear attraction is increased and, in turn, the length of this bond is increased. The C-S bond length increases in the order: anion > neutral > cation. The reason of this order is that the anion here has the higher values of both of electron and spin densities at the C and S atoms, Tables 3 and 4, and, as explained before, the bond length is increased.

Table 1* The bond lengths and bond angles along with some physical properties for ethynethiol and ethynedithiol molecules. For atoms numbering, see Fig.1

Geometric parameter ^{§,**}	Ethynethiol (ethynedithiol)		
	Neutral***	anion	cation
ΔH_f , kcal mol ⁻¹	45.11(32.97)	54.093(27.978)	252.286(223.136)
μ , Debye	2.577(0.141)	9.284(13.207)	8.922(11.696)
HOMO, eV	-9.1104(-8.511)	7.4035(6.3824)	-6.1525(-5.6836)
LUMO, eV	0.6207(0.0193)	9.7916(6.6956)	-5.4702(-4.8527)
Ionization energy, eV	9.1104(8.511)	7.4035(-6.3824)	6.1525(5.6836)
H-S	1.3445(1.3299)	1.3634(1.3392)	1.3299(1.3580)
S-C	1.6696(1.7050)	1.7258(1.7339)	1.7050(1.6053)
CC	1.2112(1.1963)	1.2250(1.2097)	1.1963(1.3229)
C-H	1.0740(-----)	1.0792(-----)	1.0531(-----)
HSC \angle	95.26°(97.39)	99.27(96.38)	97.36(99.29)

* calculated in this work, [§] Bond length in Å and bond angle in degrees., **The values in parenthesis are for ethynedithiol molecule.***Data from ref.3.

Table 2* The charge densities of ethynethiol and ethynedithiol molecules .For atoms numbering, see Fig.1

Atom**	Neutral***	anion	cation
H ₁	0.115(0.114)	-0.061(0.058)	0.165(0.158)
S ₂	-0.081(-0.082)	-0.471(-0.420)	0.450(0.262)
C ₃	0.062(-0.032)	-0.021(-0.138)	0.032(0.080)
C ₄	-0.218(-0.033)	-0.417(-0.139)	0.169(0.080)
H ₅ (S ₅)	0.122(-0.081)	-0.030(-0.419)	0.184(0.262)
H ₆	----- (0.114)	----- (0.058)	----- (0.158)

For symbols , see Table .1

Table 3* The electron densities of ethynethiol and ethynedithiol molecules. For atoms numbering, see Fig-1 .

Atom**	Neutral***	anion	cation
H ₁	0.885(0.886)	1.061(0.942)	0.835(0.842)
S ₂	6.081(6.082)	6.471(6.420)	5.550(5.738)
C ₃	3.938(4.032)	4.021(4.138)	3.968(3.920)
C ₄	4.218(4.033)	4.417(4.139)	3.831(3.920)
H ₅ (S ₅)	0.878(6.081)	1.030(6.419)	0.816(5.738)
H ₆	----- (0.886)	----- (0.942)	----- (0.842)

For symbols , see Table .1

Table 4* The spin densities of ethynethiol and ethynedithiol anions and cations radicals.
For atoms numbering, see Fig.1 .

Atom**	anion	cation
H ₁	0.1400(0.0030)	0.0000(0.0000)
S ₂	0.4239(0.3025)	0.5477(0.2370)
C ₃	0.2763(0.1955)	0.1580(0.2629)
C ₄	0.0789(0.1964)	0.2943(0.2629)
H ₅ (S ₅)	0.0000(0.3011)	0.0000(0.2370)
H ₆	------(0.0014)	------(0.0000)

For symbols , see Table .1

Conclusion:-Compared with the ethynethiol molecule, the ethynedithiol is the easier one for reduction and oxidation.

References

- O.P. Strausz. *Pure Appl. Chem.*, 1971, **4**, 165
- B.A.Trofimov, A.G. Mal'kina, I.A.Dorofeev, G.F.Myachina, I.V.Rodionova, T.I. Vakul'skaya , L.M. Sinegovskaya , T.A.Skotheim , *Doklady chemistry*, 2007, **414(1)**,125.
- J.H .Ali , A.M. Bashi and S.M. Haddawal, *National Journal of Chemistry*, 2009, **33**, 60.
- S. M. Khalil and M. Shanshal. *Theor. Chem.. Acta.*, 1977, **46**, 23.
- S. M. Khalil and M. Shanshal , *Z. Naturforsch*, 1978, **33a**, 722.
- J. H. Ali and M. Shanshal, *Z. Naturforsch.*, 2003, **58a**, 1
- R.C.Bingham, M.J.S.Dewar, and D.H.Lo, *J..Am. Chem , Soc.*, 1975, **97**, 1285.
- B.A.Murtagh and R.W.H. Sargent. *Comput. J.*13 ,185, 1970.
- P.Pulay., *Mol. Phys.*, 1969, **17**.
- S.M.Khalil, *Z.Naturforsch.*, 1988, **43a**, 485.
- D. H. Abed, S. f. Al- Saidi and M. Shanshal, *Chim. Acta Turc*, **1995**, **23**, 7.
- R. M .Kubba, S.H.Rida and A.H. Hanoon, *National Journal of chemistry*, 2005, **17**, 60.
- J.H .Ali, A.M. Bashi and S.M. Haddawal , *Journal of the University of Karbala*, 2007, **5(1)**, 90.
- J.H. Ali , S.M. Haddawi, A.Bashi, and R. T. Haiwal, *National Journal of Chemistry*, 2008, **31**, 439.
- J.H. Ali , *Journal of the University of Karbala*, 2009, **7(2)** , 166,
- J.H. Ali ,CSASC En.,Vol.4 College of Science ^{4th}Scientific Conference, 193, 2009.
- J.H. Ali , *Journal of the University of Karbala* , 2010, **8(1)** , 421.
- J.H. Ali , *National Journal of Chemistry*, 2010, **39**.