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SHORT COMMUNICATION

DFT CALCULATIONS ON 1,4-DITHIINE AND S-OXYGENATED DERIVATIVES

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ABSTRACT. The molecular structures of 1,4-dithiine and S-oxygenated derivatives are studied using B3LYP/6-311++G** level of theory. These compounds have 8π-electrons in the ring. This led to stabilization of non-planar conformation. DFT calculations show that 1,4-dithiine, C_4H_4SS, 1,4-dithiine-1-oxide, C_4H_4SOS, 1,4-dithiine-1,4-dioxide, C_4H_4SOSO and 1,4-dithiine-1,1,4-trioxide, $C_4H_4SO_2SO$; have boat conformation. 1,4-dithiine-1,1-dioxide, $C_4H_4SO_2S$, have a shadow boat conformation. 1,4-dithiine-1,1,4,4-tetraoxide, $C_4H_4SO_2SO_2$, have a planar conformation.

KEY WORDS: DFT calculation, 1,4-Dithiine, S-Oxygenated, Molecular structure

INTRODUCTION

1,4-Cyclohexadienes and some of its heterocyclic analogues have been studied for the conformational point of view [1]. ^{1}H-NMR studies show 1,4-cyclohexadiene ring has a boat conformation [2]. Among the heterocycles, 1,4-dihydropyridine derivatives have been studied more than the other analogues. A boat conformation has been observed for 1,4-dihydropyridine [3]. There are a few reports on the structure of 1,4-cyclohexadiene sulfur analogues. In thioxathene, the thiopyran ring has a shallow boat conformation [4]. This conformation is consistent to the later studies *via* single crystal X-ray diffraction method [5]. It has been found that various types of six membered 1,4-dihydroheterocycles posses a high conformational flexibility using *ab initio* calculation [6]. Among cyclohexadiene, the dithiine and its derivatives have extensively been studied [7-10]. In follow up on our works [11-13], we are especially interested to study of optimized conformations of 1,4-dithiine and S-oxygenated derivatives.

EXPERIMENTAL

The Gaussian 98 system of programs are employed for the full geometry optimizations on 1,4-dithiine and S-oxygenated derivatives at HF/6-311++G** and B3LYP/6-311++G** levels of theory [14-16]. The former optimized geometrical outputs are used as inputs for the B3LYB/6-311++G** calculations; obtaining more accurate values of activation electronic energies (E), enthalpies (H) and Gibbs free energies (G). In order to find thermochemistry parameters including thermal energy (E), thermal enthalpy (H) and Gibbs free energy (G), keyword "Freq" was used. For the sake of brivaty, the data of HF/6-311++G** level is excluded. In order to find energy minima, the geometry will be adjusted until a stationary point on the potential surface is found. All calculations are done through full optimization. Here, the Berny algorithm is employed for all full minimizations, using redundant internal coordinates [17]. For minimum state structures, only real frequency values are accepted. The calculations exhibit systematic errors and thus benefit from scaling. Thermodynamic functions obtained through frequency calculations are multiplied by the scaling factor of 0.89 suggested by Hehre *et al.* [18] for HF; and by 0.99 scaling factor of Rauhut and Pulay [19] for B3LYP level.

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RESULTS AND DISCUSSION

The molecular structure of 1,4-dithiine, C_4H_4SS; 1,4-dithiine-1-oxide, C_4H_4SOS; 1,4-dithiine-1,4-dioxide, C_4H_4SOSO; 1,4-dithiine-1,1,4-trioxide, $C_4H_4SO_2SO$; 1,4-dithiine-1,1-dioxide, $C_4H_4SO_2S$; and 1,4-dithiine-1,1,4,4-sulfotetraoxide, $C_4H_4SO_2SO_2$, are studied using B3LYP/6-311++G** level of theory. DFT calculations show that the molecules C_4H_4SS, C_4H_4SOS, C_4H_4SOSO, $C_4H_4SO_2SO$ have boat conformation and the molecule $C_4H_4SO_2S$ have a shadow boat conformation. Molecule $C_4H_4SO_2SO_2$ have a planar conformation (Figure 1).

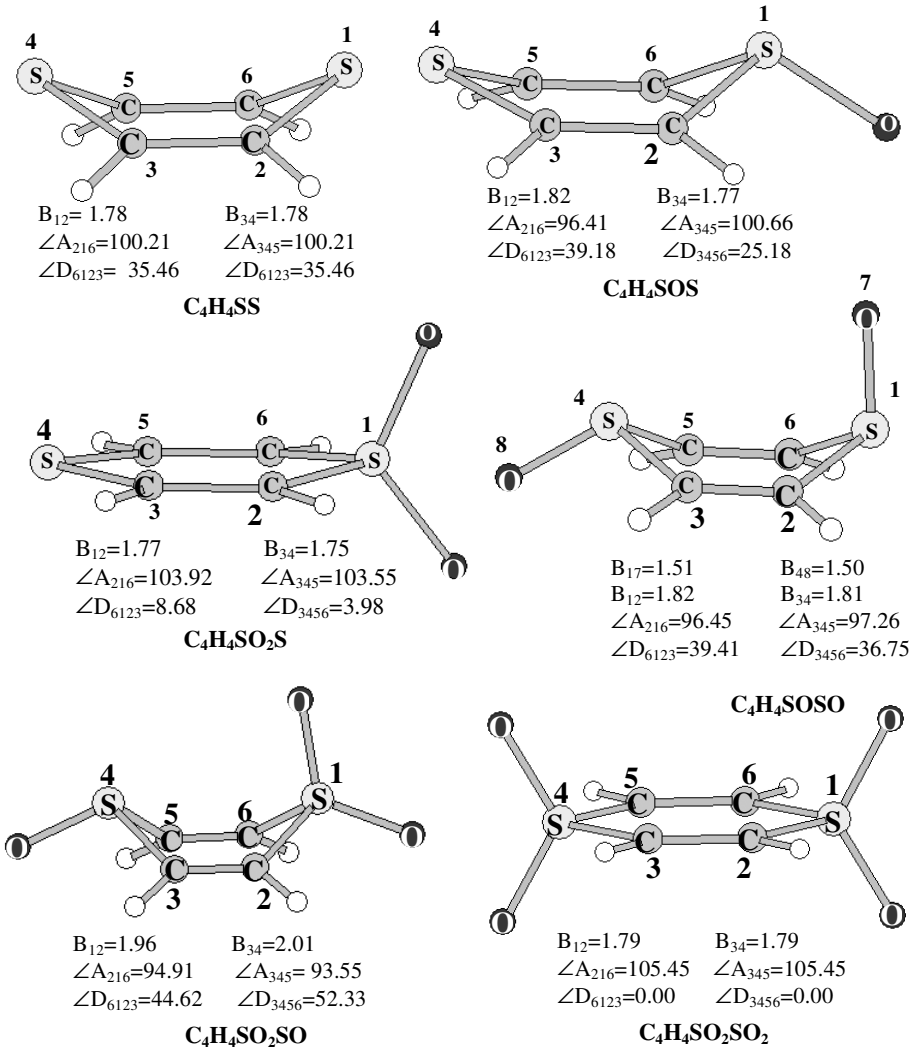

Figure 1. Full optimized conformations for 1,4-dithiine and S-oxygenated derivatives at B3LYP/6-311++G**.

Planar heterocyclic C_4H_4SS, C_4H_4SOS, C_4H_4SOSO, $C_4H_4SO_2SO$ have 8π-electrons in the ring and have antiaromatic character. The overlap between the lone pair AO of hereoatoms and P_z AOs of the carbon atoms of double bonds (p-π overlap) improve antiaromatic character. Such a 8π-electrons system is unfavorable from an energetic viewpoint. Therefore, the most stable conform of C_4H_4SS, C_4H_4SOS, C_4H_4SOSO, $C_4H_4SO_2SO$ is boat form. However, planar heterocyclic $C_4H_4SO_2S$ and $C_4H_4SO_2SO_2$ have not 8π-electrons in the ring and do not show antiaromatic character. Thus the most stable conforms of $C_4H_4SO_2S$ and $C_4H_4SO_2SO_2$ are shadow boat and planar form, respectively.

Two molecules $C_4H_4SO_2S$ and C_4H_4SOSO are compared through their total energies or Gibbs free energies. The B3LYP/6-311++G** calculations of total energies on $C_4H_4SO_2S$ and C_4H_4SOSO indicate that the molecule $C_4H_4SO_2S$ is more stable respect to C_4H_4SOSO. The molecule $C_4H_4SO_2S$ is 33.9 kcal/mol more stable than C_4H_4SOSO. Thus, it could be concluded that a molecule containing two oxygen atoms attached to a sulfur atom ($C_4H_4SO_2S$) is stablized more than a molecule that have two oxygen atoms attached to two separate sulfur atoms (C_4H_4SOSO).

The geometrical parameters, bond lengths, bond angles and dihedral angles are presented in Figure 1. The oxygen on sulfur atoms tends to have an equatorial position rather than axial position. However, for C_4H_4SOSO, one of the oxygen on sulfur atom is placed on equatorial position and another oxygen is placed on axial position. Generally, the bond length C-S is shorter than C-SO for all of compounds. Sharing of nonbonding electrons of sulfur atom with adjacent double bond may describe the shorter bond length of C-S respect to C-SO. The bond angle C-S-C is generally more than C-SO-C. Also, the dihedral angle C-S-C-C is more than C-SO-C-C.

For C_4H_4SOSO, the bond length C-SO_{axial} is larger than C-$SO_{equatorial}$. The bond angle C-SO_{axial}-C is larger for C-$SO_{equatorial}$-C. The dihedral angle C-SO_{axial}-C-C is larger for C-$SO_{equatorial}$-C-C. The equatorial oxygen reasonably contains high *s* character with respect to axial oxygen. High *s* character of equatorial oxygen atom leads to decrease the bond lengths of S=$O_{equatorial}$ and C-$SO_{equatorial}$ with respect to S=O_{axial} and C-SO_{axial}, respectively.

CONCLUSION

DFT calculations show that the molecules C_4H_4SS, C_4H_4SOS, C_4H_4SOSO, $C_4H_4SO_2SO$ have boat conformation and molecule $C_4H_4SO_2S$ have a shadow boat conformation. Molecule $C_4H_4SO_2SO_2$ have a planar conformation. For C_4H_4SOSO, the bond length C-SO_{axial}, the bond angle C-SO_{axial}-C and dihedral angle C-SO_{axial}-C-C are larger than C-$SO_{equatorial}$, C-$SO_{equatorial}$-C and C-SO_{axial}-C-C, respectively.

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