

Conformational analysis of perhalo-1,4-dithiin

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Abstract

The molecular structure and conformational transformation of Perhalo-1,4-dithiin **I, II and III** with different halogen atoms (fluorine, chlorine, and bromine), studied using density functional theory at 6-31G* level. The boat conformations were found to be minimum in all compounds, where the planar structure represents a transition state, the potential barrier for rotation was also estimated and found to be varied between 3.9 and 6.5 Kcal/mol, HOMO and LUMO molecular orbitals calculation were carried to improve that the π 8 electronic system was non-favorable.

Keywords: DFT, Heterocyclic, Halogenation, conformation.

Introduction

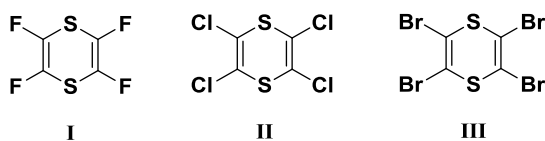
X-ray diffraction¹ and theoretical studies found that 1,4-dithiine and its derivatives prefer boat conformation² due to the antiaromatic character of these compounds, whereas the conformations of its oxides depend on the oxidation state of the sulfur atom³, high oxidation state leads to planar conformation. The x-ray diffraction has shown that C=C-S-C dihedral angle for 1,4-dithiine was 34°. Borbulevych² at el. Obtain this results using an ab initio method with a 6-31G basis set. The effect of the halogen substituent on the conformation of 1,4-dithiine is the aim of this study.

Method of calculations

Full geometry optimization was conducted using DFT, followed by frequency calculations at the same levels of theory. Calculations were performed using the Gaussian 09⁴ program package. The B3LYP method is formed through a combination of Becke's three parameters hybrid functional and the LYP semi-local correlation function. 6-31G* basis set was used. The conformational flexibility of the rings was studied by scanning of the C - S - C = C dihedral angle in the range of $\pm 45^\circ$ with a 10° step. A different scan range is used to make comparable energy changes at the deviation of the ring from equilibrium conformation.

Results and Discussion

The molecular structures of halogenated 1,4-dithiin were studied using B3LYP/6-31G* level of theory. DFT calculations show that the molecules have boat conformation as minima and the planar conformation is a transition state. The 1,4-dithiine molecules have 8π electrons in the ring and have antiaromatic character. The overlap between the lone pair AO of sulfur atom and the P_z AOs of the carbon atoms of the π bonds improve antiaromatic character. According to Hückel's rule for aromaticity $[4n+2]$ an 8π electronic system is unfavorable. Therefore, 1,4-dithiin favored the boat conformation to avoid the 8π system. Besides this, there are some other factors that explain the boat conformation of the 1,4-dithiines. The Van Der Waal's radius of sulfur is greater than carbon which principally leads to weak π -p overlap. Bending strain rings with sulfur caused by increasing of endocyclic bond angle at the sulfur atom in planar conformation. Halogen atoms are known to withdraw electrons by both mesomeric and inductive effect, such a withdrawn effect attracts attention as they may increase the aromaticity of 1,4-dithiin and predominate the planar conformation. A series of perhalo-1,4-dithiin with fluoro (**I**), chloro (**II**) and bromo (**III**) substituent scheme 1 were studied.



Scheme 1: series of perhalo-1,4-dithiin

The most stable conformer of perhalo-1,4-dithiine **I**, **II** and **III** on the potential energy surface Figure 1 was found to be the boat. The rotation barrier of these compounds was reported in table 1, rotation takes place through the planar conformer which is a transition state.

Table 1: relative activation energies of perhalo-1,4-dithiin compounds

compound	Boat conformer ΔE (Kcal/mol)	Planar conformer ΔE (Kcal/mol)
I	0.0	6.5
II	0.0	6.0
III	0.0	3.9

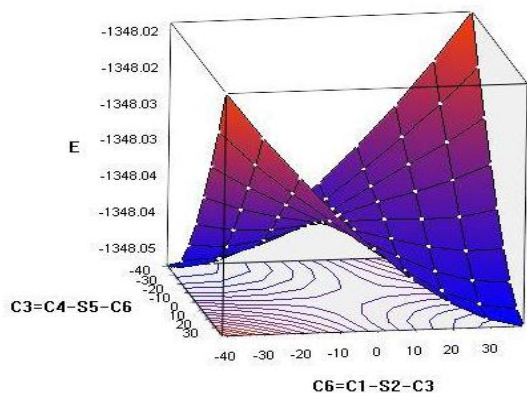
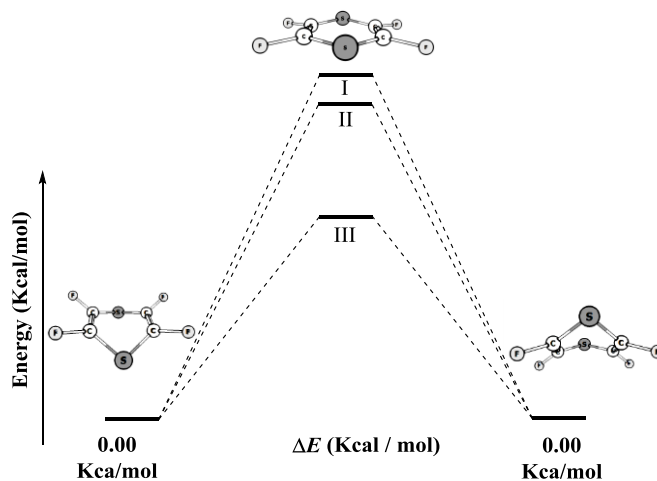


Figure 1: potential energy surface for dihedral angel of perhalo-1,4-dithiin compounds.

The fluorine **I** and chlorine **II** derivative required almost one and half the energy required by the bromine derivative **III** for rotation scheme 2.



Scheme 2: relative energy for I possible conformers.

The type of substituent has an impact on the dihedral angles, Table 2. Shows the dihedral angle of each compound compared with 1,4-dithiin.

Table 2: The dihedral angle of boat conformer perhalo-1,4-dithiin compounds

compound	C-S-S-C	C-S-C=C
1,4-dithiin (experimental)	137°	-
1,4-dithiin (B3LYP/6-311++G**)	-	35.46°
I	128.8°	41.18°
II	129.22°	42.63°
III	130.98°	40.72°

The C-S-C=C and C-S=S-C dihedrals are shown in Figure 2, and Figure 3 respectively.

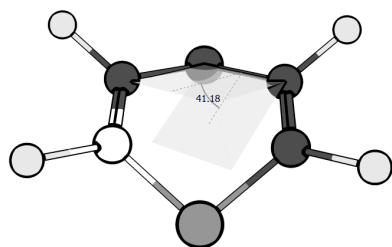


Figure 2: C-S-C=C dihedral

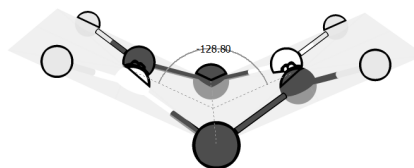


Figure 3: C-S-S-C dihedral

Frontier molecular orbitals were calculated, the HOMO and LUMO for compound I are shown in Figure 4. Analyzing the frontier orbitals show no sight of aromaticity, the boat conformation with C_{2v} point group shows small interaction between the π bond of the ethylene moiety with p^* AO of the sulfur atom, planar conformation with D_{2h} point group appear to have 8 nodes, shows antiaromatic character, Other atomic orbitals have been examined as well, and no evidence on conjugation in planar conformer were found.

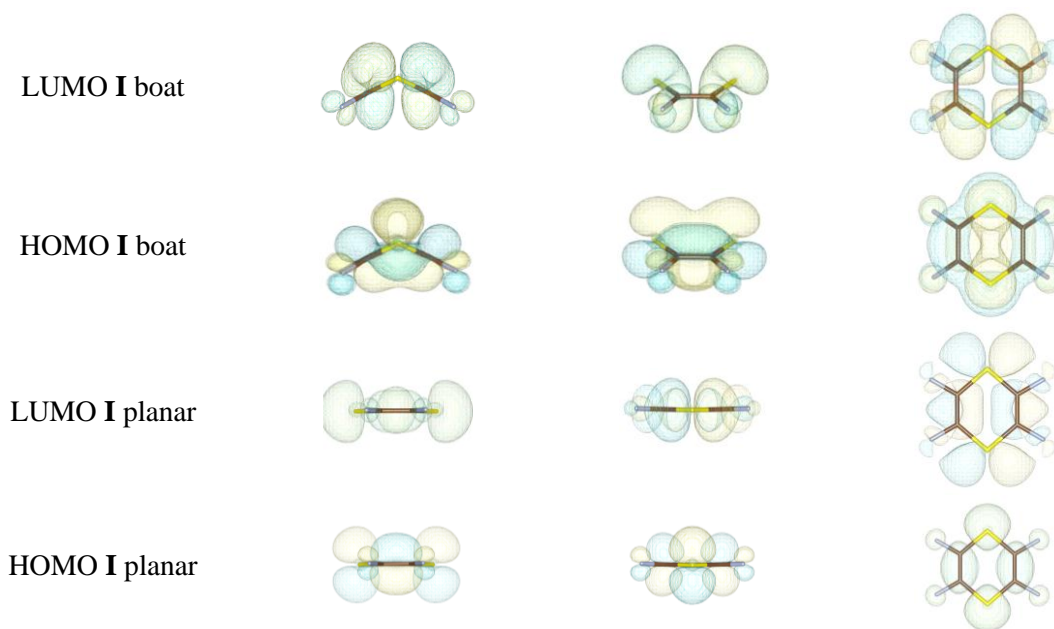


Figure 4: atomic orbitals of compound I

Conclusion

The favored conformer of perhalo-1,4-dithiin ($C_4F_4X_2$) **I**, **II** and **III** were found to be the boat, the same as non-halogenated 1,4-dithiine. The most stable boat conformers have $C_1=C_6-S_5-C_4$ dihedral angle of 41.18° , 42.63° , and 40.72° respectively. The energy barrier for transformation from a boat into planar were 6.5, 6.0 and 3.9 Kcal/mol respectively, examination of the molecular orbitals supported that 8 π electronic system are not favorable.

References

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