



A DFT STUDY OF THE EFFECT OF HALOGENATION ON THE CONFORMATION OF 1,4-DITHIIN AND ITS S-OXIDE DERIVATIVES

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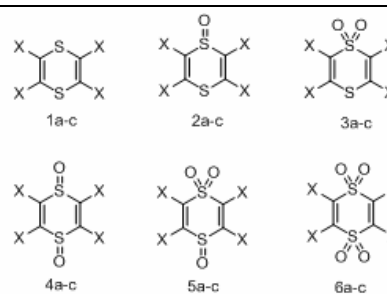
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The molecular structure conformations of perfluoro, perchloro, and perbromo-1,4-dithiin derivatives were studied using DFT at the B3LYP/6-311+G** level of theory. The anti-aromatic parent compound (8 π -electron) has a non-planar cyclic structure with the boat conformation. Our calculations show that fluoridation and increasing oxidation of the sulfur heteroatoms drive the geometry towards a planar ring by drawing away electronic density and decreasing antiaromaticity.



X a=F, b=Cl, c=Br

INTRODUCTION

It is clear that the energy landscape of organic molecules is very shallow, and even within a pure chemical species the crystalline polymorph can depend on molecular conformation.¹ It then becomes of great interest to understand how molecular conformation can be chemically controlled. Here, we study how different substituents control the conformation of a six-membered heterocycle. An earlier ¹H-NMR and single crystal X-ray study of 1,4-cyclohexadiene has shown that the boat conformation of the ring can be converted to planar conformation upon substitution in some cases.^{2,3} 1,4-cyclohexadiene derivatives were investigated using *ab-initio* and DFT methods and found to have 6 π -electrons and homoaromatic character, which contribute to stabilizing the planar or shallow boat conformations. Moreover, the substitution has

affected the molecular structure. The sulfur analogues of 1,4-cyclohexadiene have attracted attention, as the thiopyran ring has a shallow boat conformation,⁴ which has been confirmed via single crystal X-ray diffraction.^{5,6} Among cyclohexadiene, the dithiin and its derivatives have been extensively investigated.⁷ Parham *et al.* synthesized 1,4-dithiins and their oxides.⁸ The fastest conformational change caused by the one-electron oxidation of 3,6-diphenyl-1,2-dithiin has been analyzed by UV-Vis and EPR spectro-electro-chemical methods.⁹ The molecular structure and conformational flexibility of antiaromatic six-membered 1,4-diheterocycles have been computed using *ab-initio* quantum-chemical methods and reported that molecules without the sulfur atom have shown a planar equilibrium conformation, whereas molecule containing sulfur atoms have shown a boat conformation.¹⁰ The 6 π electronic systems of non-planar boat conformers for thiabenzene, 1-thianaph

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thalene, 2-thianaphthalene, and 9-thiaanthracene have been theoretically studied and found to be more stable than the corresponding planar conformers with 8π -electrons in the ring.¹¹ Kassae *et al.* have carried out geometry optimization for heterocyclic benzenes including oxabenzene, thiabenzene, selenabenzene, tellurabenzene, 1,1-dihydropyridinium, 1,1-dihydrophosphonium, 1,1-dihydroarsinium, and 1,1-dihydrostybinium using quantum mechanics methods. Boat conformers were global minima for oxabenzene, thiabenzene, selenabenzene, and tellurabenzene, while in contrast, planar conformers were the most stable for 1,1-dihydropyridinium, 1,1-dihydrophosphonium, 1,1-dihydroarsinium, and 1,1-dihydrostybinium.¹² The conformational analysis of 1,4-dithiin and S-oxygenated derivatives were investigated by Vessally using DFT. 1,4-dithiin, 1,4-dithiin-1-oxide, 1,4-dithiin-1,4-dioxide, and 1,4-dithiin-1,1,4-trioxide were shown to take the boat conformation, while 1,4-dithiin-1,1-dioxide took a shadow boat conformation. On the other hand, 1,4-dithiin-1,1,4,4-tetraoxide took a planar conformation.¹³

In the attempt to extend the work of Vessally,¹³ in the present work we study the energetic and structural properties of halogenated 1,4-dithiins and their S-oxygenated derivatives. We are particularly interested in the effect replacing the hydrogen atoms by halogen atoms have on their molecular geometry. This paper reveals quantitative chemical knowledge and detailed insight about the molecular structure of these compounds.

COMPUTATIONAL DETAILS

Full geometric optimizations were carried out using density functional theory DFT, followed by frequency calculations at the same level of theory. All structures were found to be minima with no imaginary frequencies noted. All calculations were performed using the Gaussian 09 program package.¹⁴ The B3LYP method is formed through a combination of Becke's three parameter hybrid functional¹⁵ and the LYP semi local correlation function.¹⁶ The 6-311++G** basis set was used with the B3LYP method. Thermochemical parameters such as thermal energy (E), thermal enthalpy (H) and Gibbs free energy (G), were also calculated. The zero point energy (ZPE) was scaled by 0.9804.¹⁷

RESULTS AND DISCUSSION

The series of perhalo-1,4-dithiin (1_{a-c}, 2_{a-c}, 3_{a-c}, 4_{a-c}, 5_{a-c}, 6_{a-c}) compounds are shown in Figure 1.

The replacement of the hydrogen atoms of 1,4-dithiin and their S-oxygenated derivatives with halogen atoms (fluorine, chlorine and bromine) leads to perhalo-1,4-dithiins and their S-oxygenated derivatives.

The heterocyclic compounds C₄H₄SS, C₄H₄SOS, C₄H₄SOSO, which have 8 π -electrons in the ring and have anti-aromatic character are reported to have the boat conformer as the most stable conformer. The overlap between the lone pair atomic orbital(AO) of the heteroatoms and the p_z AOs of the carbon atoms of double bonds (p- π overlap) increase the anti-aromatic character in these 8 π -electron systems.¹³ However, the fluoro-derivatives give different conformations, C₄F₄SS has the boat conformation as the most stable conformer, while C₄F₄SOS and C₄F₄SOSO have half-chair and planar conformations respectively. The most stable conformations of the perhalo-1,4-dithiin and its oxides are presented in Figure 2. The stable structures of the 1,4-dithiin and its oxides are also presented therein for comparison. In general, the substitutions of the hydrogen atoms with Cl, or Br in 1,4-dithiin and its oxides do not significantly affect their conformational stability, while F is sufficiently electronegative to shift the conformation in many cases. The most stable conformer of heterocyclic molecules 1a-c, 2a-c, 3a-c, 4b-c, and 5b-c was found to be the boat conformation. These molecules adopt a non-planar geometry to avoid the destabilization that results from anti-aromaticity. The non-planar 1a-c, 2a-c, and 4b-c have 8 π -electrons in the ring which is a characteristic of anti-aromatic compounds. The overlap between the lone pair AO of heteroatoms and p_z double bonds (p- π overlap) increase the anti-aromatic character in these 8 π -electron systems. If these molecules were planar, they would have a single eight-electron π system around the ring, but they instead adopt the boat conformation with two individual π bonds. Figure 2 shows the optimized structures of perfluoro-1,4-dithiine and its oxygenated derivatives. Compounds 4a, 5a and 6a have a planar conformation.

The molecules 5 b-c have 6 π -electrons and are not aromatic. The cyclic electron delocalization in the 1,4-dithiin rings of these molecules is discontinuous, as the lone-pair electrons at the sulfur atoms as donors and the C=C bonds as acceptors are alternatively arranged to diminish the consequences of Huckel's rule of $[4n+2]\pi$ electrons. Thus, the molecules assume the boat conformation because their 6 π -electrons are not delocalized Figure 3.

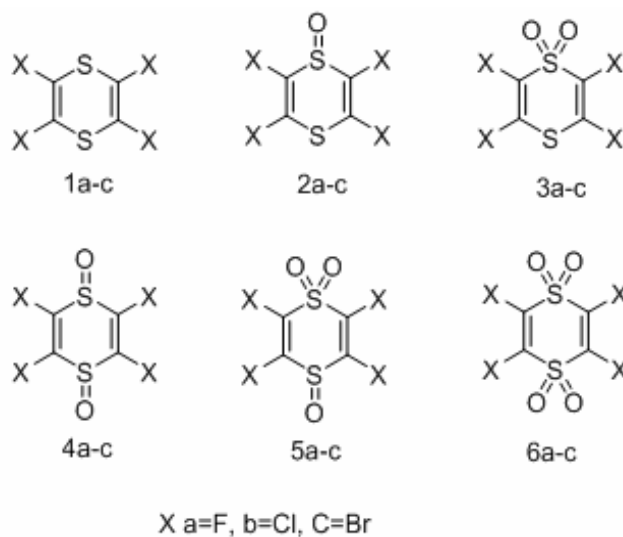


Fig. 1 – Structures of perhalo-1,4-dithiins and their S-oxygenated derivatives.

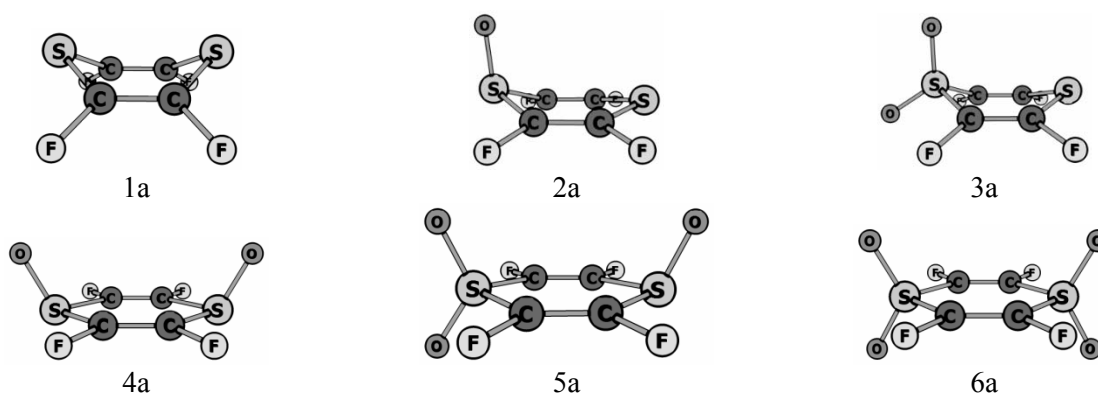
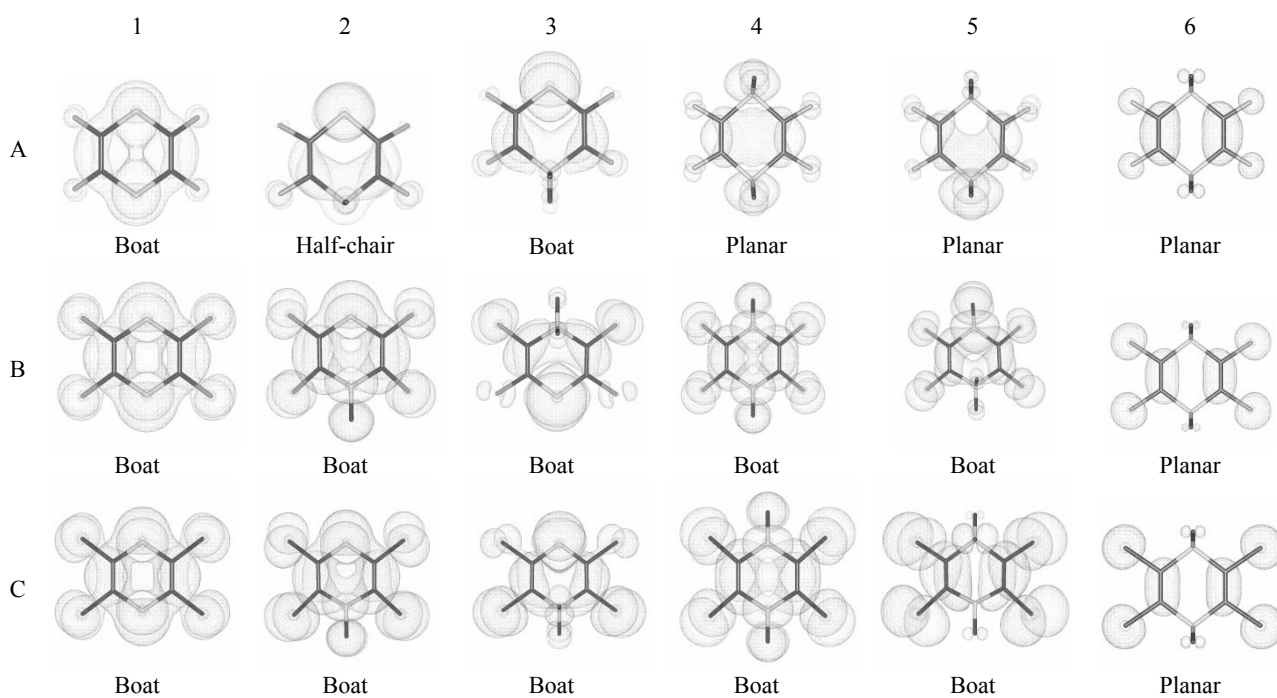


Fig. 2 – Optimized structure of 1-6a at the B3LYP/6-311+G**level of theory.

Fig. 3 – HOMO of compounds A₁₋₆, B₁₋₆, and C₁₋₆.

The equilibrium conformation of 4a, 5a, and 6a-c which have 8, 6, and 4 π -electron systems respectively is planar or nearly planar. In this case, it is probable that p- π overlap prevails over the energetically unfavorable conjugation in the π -electron system. Our results for 6a-c agree well with results obtained for non-halogenated 1,4-dithiins[13]. In general, the equilibrium structures of these heterocyclic systems were determined by the balance between the steric and conjugative effects. The conjugative effect involves π -electron interaction between the π -systems of the two ethylenic moieties and the lone pair of sulfur atom, which favors the planar arrangement of the ring. The steric effect is the

strain about the heteroatoms caused by diffuse lone-pairs of heteroatoms which force the ring to deviate from planarity in order to relieve strain. The interaction which destabilizes the planar ring is absent for 6a-c because the lone pairs of the heteroatoms are instead bonded to oxygen atoms. The presence of halogen atom has no notable effects on the bond length of the compounds, but has a great effect on the dihedral angles; Table 1 shows the dihedral angle of all molecules.

The calculated energies and structural parameters of all molecules are given in Tables 2 and 3 respectively.

Table 1

Dihedral angles of perhalo-1,4-dithiin and their S-oxygenated derivatives

Compound	Dihedral angle (°)			Compound	Dihedral angle (°)		
	C=C-S-C	C=C-SO-C	C=C-SO ₂ -C		C=C-S-C	C=C-SO-C	C=C-SO ₂ -C
1a	41.667	-	-	4a	-	0.00	-
1b	42.737	-	-	4b	-	51.549	-
1c	42.486	-	-	4c	-	54.265	-
2a	14.344	31.335	-	5a	-	3.78	6.211
2b	43.69	58.49	-	5b	-	49.52	45.639
2c	42.988	59.463	-	5c	-	50.931	46.508
3a	25.047	-	35.361	6a	-	-	0.00
3b	23.819	-	41.151	6b	-	-	0.00
3c	22.83	-	41.762	6c	-	-	0.00

Table 2

The thermal energies (E), thermal enthalpies (H), and thermal free energies (G), energies calculated in Hartree

Compound	E (a.u)	H (a.u)	G (a.u)
1a	-1348.30913	-1348.26341	-1348.30782
1b	-2789.74054	-2789.69940	-2789.74889
1c	-11245.39767	-11245.35805	-11245.41298
2a	-1423.50968	-1423.45922	-1423.50710
2b	-2864.94009	-2864.89425	-2864.94697
2c	-11320.59853	-11320.55422	-11320.61219
3a	-1498.74203	-1498.685461	-1498.73503
3b	-2940.17937	-2940.12749	-2940.18157
3c	-11395.83736	-11395.78702	-11395.84635
4a	-1498.69678	-1498.64167	-1498.69308
4b	-2940.13277	-2940.08243	-2940.13726
4c	-11395.79230	-11395.74351	-11395.80340
5a	-1573.93010	-1573.86889	-1573.92204
5b	-3015.37042	-3015.31407	-3015.37077
5c	-11471.02908	-11470.97433	-11471.03618
6a	-1649.16219	-1649.09490	-1649.14883
6b	-3090.60393	-3090.54143	-3090.59985
6c	-11546.26278	-11546.20187	-11546.26522

Table 3

Bond length Å, bond angle, and dihedral angle of perhalo-1,4-dithiin and their S-oxygenated derivatives

perhalo-1,4-dithiine					
	C-C	C-S	C-S-C	C-C-S	C-S-C=C
Experimental ¹⁸	1.29	1.78	100	124	
Vessally	-	1.78	100	-	35.46
1a	1.322	1.768	98.380	122.825	41.667
1b	1.337	1.774	100.578	121.384	42.737
1c	1.335	1.773	100.998	121.296	42.486

perhalo-1,4-dithiine 1-oxide							
	C-C	C-S	C-SO	C-S-C	C-SO-C	C-SO-C=C	C-S-C=C
Vessally	-	1.77	1.82	100.66	96.41	39.18	25.18
2a	1.333	1.749	1.803	100.137	94.578	31.335	14.344
2b	1.331	1.781	1.858	100.749	93.914	58.497	43.690
2c	1.329	1.779	1.857	101.095	94.060	59.463	42.988

perhalo-1,4-dithiine 1,1-dioxide							
	C-C	C-S	C-SO ₂	C-S-C	C-SO-C	C-SO ₂ -C=C	C-S-C=C
Vessally	-	1.75	1.77	103.55	103.92	8.68	3.98
3a	1.331	1.759	1.795	101.063	99.870	35.361	25.047
3b	1.337	1.759	1.803	103.774	101.795	41.151	23.819
3c	1.335	1.757	1.804	104.168	102.183	41.762	22.830

perhalo-1,4-dithiine 1,4-dioxide				
	C-C	C-SO	C-SO-C	C-SO-C=C
Vessally	-	1.81	97.26	36.75
4a	1.324	1.817	96.773	0.036
4b	1.325	1.870	94.219	51.549
4c	1.324	1.871	94.042	54.265

perhalo-1,4-dithiine 1,1,4-trioxide							
	C-C	C-SO	C-SO ₂	C-SO-C	C-SO ₂ -C	C-SO-C=C	C-SO ₂ -C=C
Vessally	-	2.01	1.96	93.55	94.91	52.33	44.62
5a	1.324	1.824	1.799	97.761	101.912	3.780	6.211
5b	1.328	1.882	1.822	94.750	100.999	49.520	45.639
5c	1.327	1.884	1.823	94.951	101.011	50.931	46.508

perhalo-1,4-dithiine 1,1,4,4-tetraoxide				
	C-C	C-SO ₂	C-SO ₂ -C	C-SO ₂ -C=C
Vessally	-	1.79	105.45	0
6a	1.324	1.806	102.914	0
6b	1.328	1.809	105.871	0.011
6c	1.326	1.809	106.32	0.018

CONCLUSION

The presence of halogen atoms on 1,4-dithiin molecules has no great effect on the bond angle or the bond length but strongly affects the dihedral angles within the molecule. Non-oxygenated

molecules have the boat conformation due to the antaromatic 8- π electron system. Increasing the number of oxygens present on the system reduces the unfavorable π -p interaction as the sulfur p-electrons become occupied in bonding orbitals. The presence of fluorine atoms draws more

electrons from the π system and also reduces the π -p interaction, favoring the planar conformation even with less oxygen present.

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