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Conformational analysis of extracted natural dithiins from garlic and onion: a computational study

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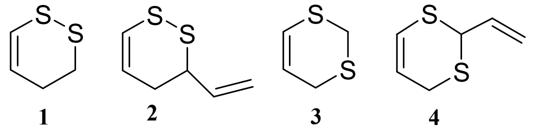
Abstract: Optimized geometries and energies for conformations of 4*H*-1,2-dithiin, 3-vinyl-4*H*-1,2-dithiin, 4*H*-1,3-dithiin, and 2-vinyl-4*H*-1,3-dithiin were calculated using the HF/6-31+G*, B3LYP/6-31+G*, and MP2/6-31+G* levels of theory. In each of them, three energy minima and two transition states were found. The results indicated that twisted forms corresponded to all the above molecules were the most stable conformers than their other conformers. The boat forms related to each of them were observed as local minimum. The results showed that the twisted forms had more stability than the related boat forms. The half-chair conformers for each molecule were attributed to the transition state forms. The half-chair forms were calculated to be 12.4-23.9 kJ mol^{-1} less stable than their twisted conformations.

Keywords: Ab initio; Conformational analysis; Dithiins; Onion; Garlic.

Introduction

Onion (*Allium cepa*) and garlic (*Allium sativum*), among two of the oldest cultivated plants are both used for medicinal purposes to treat a wide variety of diseases [1-5]. For example, they are applied in heart disease, headaches, insect bites, tumors and worm control [6-8]. Furthermore, onion and garlic have important biological properties including: antimicrobial, antioxidant, anticarcinogenic, antimutagenic, antiasthmatic, immunomodulatory, and prebiotic properties [5, 7, 8]. 3-vinyl-4*H*-1,2-dithiin (**2**) and 2-vinyl-4*H*-1,3-dithiin (**4**) are hetereocyclic compounds containing two sulfur atoms which are extracted from onion and garlic [1-8, 9] (Scheme **1**). 3-vinyl-4*H*-1,2-dithiin (**2**) and 2-vinyl-4*H*-1,3-dithiin (**4**) exhibit antithrombotic activity [10]. Moreover, it has been proved that 2-vinyl-4*H*-1,3-dithiin (**4**) has a beneficial effect on cardiovascular variables [6].

Dithiins are compounds with similar molecular structure to cyclohexene that two methylenes of it are substituted by two sulfur atoms. The replacement of carbon by another element in cycloalkenes will generate changes in several structural parameters and will affect the conformational properties of the molecules [11]. For example, replacement of an oxygen and/or a nitrogen in place of carbon in cyclohexene will lead to a change in bond lengths and bond angles (C=C 1.34 Aº, C=O 1.23 Aº, C=N 1.38 Aº). The most stable structure of cyclohexene has been investigated by electron diffraction [12] and microwave spectroscopy [13, 14]. Various studies have established that the lowest energy in the cyclohexene conformations correspond to a half-chair form (twisted form) with C_2 symmetry and with a twist angle of 60° [15]. In cyclohexene ring, interconversion from one twisted form to another can be done through passing of boat conformation (bent form) with C_s symmetry [16–19].



Scheme 1. Structures of the studied dithiins

In line with the calculational studies on cyclohexene rings in the literatures [15-20] and their derivatives [11, 21], this manuscript introduces the results of similar calculations from different points of view such as structural optimization and conformational interconversion of 4*H*-1,2-dithiin (**1**), 3-vinyl-4H-1,2-dithiin (**2**), 4*H*-1,3-dithiin (**3**), and 2-vinyl-4H-1,3-dithiin (**4**) (Scheme **1**) using the HF/6-31+G*,

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B3LYP/6-31+G*, and MP2/6-31+G* levels of theory. It is noteworthy that compounds of **2** and **4** are as extracted natural compounds from garlic and onion, but in the present research, the structures of **1** and **3** conform to the simulated projection. Optimized geometries and energies of the half-chair and boat conformers of **1** and **3** structures had been calculated in advance [11]. The results indicated that half-chair conformers (twisted forms) of **1** and **3** structures had more stability than boat forms [11].

Results and discussion

The results obtained of the MP2/6-31+G* calculations are used in the discussions of conformational energies bellow. Among the factors that will affect the relative stability of the conformers of six-membered unsaturated heterocyclic including: 4*H*-1,2-dithiin (**1**), 3-vinyl-4H-1,2-dithiin (**2**), 4*H*-1,3-dithiin (**3**), and 2-vinyl-4H-1,3-dithiin (**4**) (Scheme **1**) are angle strain, lone pair-lone pair repulsion, π electron-lone pair repulsion, hyperconjugation (anomeric effect), and torsional strain resulting from eclipsing of adjacent methylene groups.

4H-1, 2-dithiin (1) and 3-vinyl-4H-1, 2-dithiin (2)

The results in Tables **1** and **2** are data collected from the *ab initio* methods corresponding to different conformers of molecules **1** and **2**. Three potential energy minima and two transition states were obtained for description of the conformational features of **1** and **2** (Figs. **1** and **2**).

4H-1, 2-dithiin (1)

In 4*H*-1, 2-dithiin (**1**) was observed the most stability in twisted forms with Φ_{1234}= -68.0 (**1-twist)** and 68.0° (**1-twist**'), (Table **1** and Fig. **1**). Existence twisting of the ring in **1-twist** and **1-twist**' conformers reduced both the angle strain and torsional strain by decreasing the inner angles and staggering the methylene groups [11]. Although, an interaction between the sulfur nonbonded electrons and the *π*-bond electrons of the double bond led to instability, an interaction between the sulfur nonbonded electrons and *π** in these conformers was a stabilizer factor [11]. Moreover, hyperconjugation effect (anomeric effect) was important in **1-twist** and **1-twist**' conformers ($n_{S(2)} \rightarrow \sigma^*_{C(3)-Hax}$). According to the results, the obtained torsional angles of **1-twist** and **1-twist**' (as the most stable forms) were -68º and 68°, respectively, while the torsional angle in the half-chair structure (twisted form) of cyclohexene was 60°. Replacement of two sulfur atoms instead of two carbon atoms in cyclohexene led to a change in torsional angle of the most stable form, about 8 degrees. When the S-S-C-C torsion was rotated to -33.6°, **1-half-chair** was obtained as a transition state conformer with C_1 symmetry (Fig. **1**). The energy of **1-half-chair** conformer was calculated to be 23.9 kJ mol^{-1} more than the related twisted forms (Table **1**). In **1-half-chair**, lone pair-lone pair repulsions increased on adjacent sulfur atoms at the eclipse conformation of their lone pairs, when the sulfur atoms were coplanar. In addition, eclipsing of lone pairs of the S_1 atom and *π*-bond electrons of the double bond could lead to increase instability in this conformer. Therefore, the lowest stability was attributed to **1-half-chair** form. By fixing the dihedral angle at -9.4°, a conformational change occurred that led to the other minimum-energy, **1-boat** conformation, with C_1 symmetry (Fig. **1**) which had 11.0 kJ mol^{-1} more energy than **1-twist** (Table **1**). Energy reduction in **1-boat** compared to **1-half-chair** was due to twisting of the =$C_{(6)}$-$S_{(1)}$-$S_{(2)}$-$C_{(3)}$ torsional angle (49.8°) that it led to decrease the lone pairs interactions of adjacent sulfur atoms to the preferred gauche conformation adopted by HSSH (89.9°) [11]. Followed by the rotation of the S-S-C-C torsion to 38.3°, **1-half-chair'** was formed as the second transition state conformer that had 18.0 kJ mol^{-1} more energy than **1-twist** (Table **1** and Fig. **1**). The probable reason for instability of **1-half-chair'** conformer than **1-twist** may be due to a repulsive transannular *π* electrons-lone pair interaction between the double bond and S_2 atom; and eclipsing of adjacent methylene groups between C_3 and C_4. Furthermore, the sulfur atoms of **1-half-chair'** conformer were not coplanar (S_1-S_2-C_3= 98°) that this led to more stability **1-half-chair'** than **1-half-chair** form. Finally, by rotating Φ_{1234} from 38.3° to 68.0°, **1-twist**′ conformer was obtained which had the same energy surface compared to **1-twist** conformer.

In the literature [11], energy difference between half-chair (twisted form) and boat conformers of molecule **1** was about 12.1 kJ mol^{-1}, as it was obtained 11 kJ mol^{-1} in the current study. The structural parameters obtained in this paper from **1-twist**, **1-twist**′, and **1-boat** conformers were also in consistency with the findings of Freeman quest [11]. For example, the calculated C_3-S_2-S_1 and =C_6-S_1-S_2 bond angles for the twisted conformer of structure **1** were 98° and 100.8°, respectively (see Table **1** and [11]). The calculated C_3-S_2, C_6-S_1, S_1-S_2 and C_5=C_6 bond lengths for **1-twist** were 1.816 A°, 1.770 A°, 2.064 A° and 1.323 A°, respectively (see Table **1** and [11]).

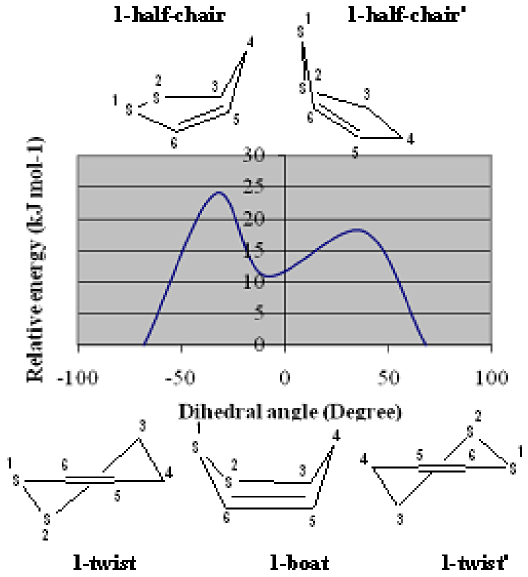

Fig. 1 The plot of the variation of MP2/6-31+G* relative energy (kJ mol^{-1}) vs Φ_{1234} of 4*H*-1,2-dithiine (1)

3-vinyl-4H-1,2-dithiin (2)

The variations of conformational energy of 3-vinyl-4*H*-1,2-dithiin (**2**) conformers are shown in Fig. **2** and Table 2. In the case of 3-vinyl-4*H*-1,2-dithiin (**2**), two twisted forms were obtained at Φ_{1234}= -69.2° (**2-twist**) and 65.2° (**2-twist'**) with C_1 symmetry, which were located at minimum energy surfaces (Fig. **2**). The **2-twist** form had the most stability comparing to other conformers related to the structure **2**. The calculated energy of **2-twist'** conformer was 3.4 kJ mol^{-1} higher than **2-twist** conformer (Table **2**). Other minimum energy was observed in the boat form with Φ_{1234}= -6.9° (**2-boat**), which was 10.3 kJ mol^{-1} unstable than **2-twist** conformer (Table **2**). In fact, the ring of molecule **2** could be interconvert from one twisted form to another through passing the related boat conformation. The transition state forms energy with Φ_{1234}= -39.3° (**2-half-chair**) and 32.7° (**2-half-chair'**) were respectively obtained 19.4 and 21.1 kJ mol^{-1} more than **2-twist** form (Table **2** and Fig. **2**).

The more stability of twisted forms in compound **2** was attributable to twisting of the ring that it led to reduction in both the torsional strain and lone pair-lone pair interactions of the S_1-S_2 atoms. The other reason for the stability of **2-twist** form was due to position the vinyl substitution at equatorial arrangement (Fig. **2**) that led to deduction possible repulsions π electrons-π electrons between the two double bonds. Moreover, the hyper conjugative orbital interaction ($n_{S(2)} \rightarrow \sigma^*_{C(3)\text{-}H_{ax}}$) was also observed as a stabilizer factor in **2-twist** form. But in **2-twist'** form, interactions between the π-bond electrons of the double bond of the ring and the π-bond electrons of the vinyl substitution increased. Because, the vinyl substitution took the axial arrangement. In addition, the hyper conjugative orbital interaction had not in **2-twist'** form. It was generally obtained that the conformation with the smaller dipole moment had the lower electrostatic energy and a reduced overall energy [22, 23]. Moreover, instability in **2-twist** form could be result of a transannular π electron-lone pair interaction between the double bond of the ring and -S_2 atom. In **2-half-chair** conformer, the C_3-H_{ax} and C_4-H_{ax} bonds were in eclipsed form; and there was also a repulsive transannular π electron-lone pair interaction between the double bond of the ring and -S_2 atom. These causes in **2-half-chair** led to instability and energy increase about 19.4 kJ mol^{-1} than **2-twist** conformer. In **2-half-chair'** form, the S_1 and S_2 atoms were coplanar and the lone pairs arranged in eclipsed form. It was reason of increased lone pair-lone pair interactions in the S_1 and S_2 atoms, and more instability **2-half-chair'** than **2-twist**.

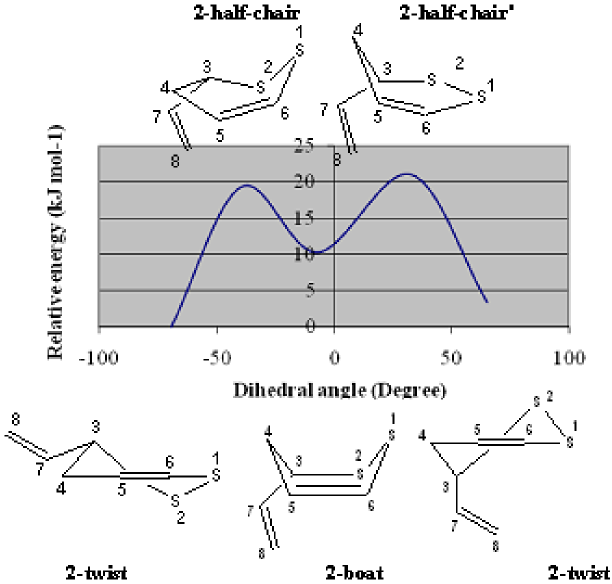

Fig. 2 The plot of the variation of MP2/6-31+G* relative energy (kJ mol^{-1}) vs Φ_{1234} of 3-vinyl-4*H*-1,2-dithiin (2)

Analysis of conformational changes between 4H-1, 2-dithiin (1) and 3-vinyl-4H-1, 2-dithiin (2)

According to the obtained results general trend of conformational changes in both molecules **1** and **2** were the same. Both molecules had the twisted and boat conformers as minima energy forms; and the half-chair conformers were as transition states (Figs. **1** and **2**). But, the difference between energy levels in the same forms of each molecule was different than the

Table 1 Calculated total energies (hartree), ZPVE, relative energy (kJ mol^{-1}), and structural parameters (obtained at the HF/6-31+G* level) for various conformations of 4*H*-1,2-dithiine (**1**)

Feature	**1-twist**	**1-half-chair**	**1-boat**	**1-half-chair'**
HF/6-31+G*	-949.96798	-949.95832	-949.96158	-949.95993
B3LYP/6-31+G*	-952.40284	-952.39509	-952.39784	-952.39576
MP2/6-31+G*	-950.73185	-950.72276	-950.72767	-950.72501
ZPVE[a]	57.8701	57.6502	57.7783	57.6285
E_{rel}[b]	0.0	25.4	16.8	21.1
E_{rel}[c]	0.0	19.5	12.8	17.6
E_{rel}[d]	0.0	23.9	11.0	18.0
r_{16}/A^{o}	1.770	1.765	1.772	1.773
r_{12}/A^{o}	2.064	2.109	2.080	2.066
r_{23}/A^{o}	1.816	1.822	1.833	1.818
r_{34}/A^{o}	1.527	1.532	1.542	1.555
r_{45}/A^{o}	1.510	1.505	1.507	1.513
r_{56}/A^{o}	1.323	1.322	1.324	1.321
$\theta_{123}/^{o}$	98.0	104.3	102.4	100.1
$\theta_{234}/^{o}$	112.0	114.4	114.7	116.4
$\theta_{345}/^{o}$	115.8	111.6	114.7	119.0
$\theta_{612}/^{o}$	100.8	104.7	99.0	97.8
$\theta_{165}/^{o}$	127.4	126.0	119.7	121.7
$\theta_{456}/^{o}$	128.3	123.7	121.6	125.3
$\Phi_{1234}/^{o}$	-68.0	-33.6	-9.4	38.3

[a] ZPVE was obtained with B3LYP/6-31+G* level.

[b] Relative energy was obtained with HF/6-31+G* calculations.

[c] Relative energy was obtained with B3LYP/6-31+G* calculations.

[d] Relative energy was obtained with MP2/6-31+G* calculations.

same conformers in other molecule (Tables **1** and **2**). This was the result of the present and absence of the vinyl substitution in different conformers of the molecules **1** and **2**.

For example in molecule **1**, that there was not a vinyl substitution, level energy of the twisted conformers (**1-twist** and **1-twist'**) as the most stable conformers of **1** were the same. But, energy difference between the twisted conformers **2** (**2-twist** and **2-twist'**) was about 3.4 kJ mol^{-1} (Table **2**). This was due to different position of the vinyl substitution in the each twisted conformer **2**. In **2-twist** conformer, the vinyl substitution was at the equatorial arrangement; and in **2-twist'** conformer was at the axial position.

Another example is the difference between energy level transition states in molecules **1** and **2**. The **1-half-chair** and **1-half-chair'** forms (as transition states of molecule **1**) had energy difference about 5.9 kJ mol^{-1} and the energy difference between **2-half-chair** and **2-half-chair'** was 1.7 kJ mol^{-1} (Tables **1** and **2**). Energy difference between transition states of molecule **1** was the result of interactions between the non-bonded electrons of the sulfur atom and the π bond electrons of the double bond. But, energy difference in **2-half-chair** and **2-half-chair'** was the result of amount the interactions of the vinyl substitution and the π bond electrons of the double bond.

4H-1,3-dithiin (3) and 2-vinyl-4H-1,3-dithiin (4)

Relative energies, geometrical parameters and zero-point vibrational energy (ZPVE) of **3** and **4** are provided in Tables **3** and **4**. Conformational energy curves for **3** and **4** structures showed three energy minima and two transition state geometries (Figs. **3** and **4**).

Table 2 Calculated total energies (hartree), ZPVE, relative energy (kJ mol^{-1}), and structural parameters (obtained at the HF/6-31+G* level) for various conformations of 3-vinyl-4*H*-1,2-dithiin (**2**)

Feature	**2-twist**	**2-half-chair**	**2-boat**	**2-half-chair'**	**2-twist'**
HF/6-31+G*	-1026.84531	-1026.83537	-1026.83836	-1026.83493	-1026.84236
B3LYP/6-31+G*	-1029.79872	-1029.78657	-1029.79001	-1029.78730	-1029.79329
MP2/6-31+G*	-1027.86781	-1027.86044	-1027.86390	-1027.85979	-1027.86650
ZPVE[a]	78.4156	78.2228	78.3995	78.1110	78.3824
E_{rel}[b]	0.0	26.1	18.3	27.3	7.8
E_{rel}[c]	0.0	31.1	22.8	28.7	14.1
E_{rel}[d]	0.0	19.4	10.3	21.1	3.4
r_{16}/A°	1.769	1.771	1.772	1.763	1.764
r_{12}/A°	2.061	2.063	2.082	2.110	2.067
r_{23}/A°	1.830	1.829	1.841	1.828	1.829
r_{34}/A°	1.534	1.568	1.551	1.534	1.536
r_{45}/A°	1.509	1.512	1.506	1.505	1.510
r_{56}/A°	1.323	1.321	1.324	1.321	1.323
θ_{123}/°	97.8	99.9	103.1	105.5	100.8
θ_{234}/°	110.0	115.1	112.9	112.3	109.9
θ_{345}/°	116.4	119.6	114.8	112.8	116.3
θ_{612}/°	100.5	97.9	99.2	104.9	101.5
θ_{165}/°	126.8	121.4	119.3	125.7	128.0
θ_{456}/°	128.4	125.2	121.2	123.5	128.4
Φ_{1234}/°	-69.2	-39.3	-6.9	32.7	65.2

[a] ZPVE was obtained with B3LYP/6-31+G* level.

[b] Relative energy was obtained with HF/6-31+G* calculations.

[c] Relative energy was obtained with B3LYP/6-31+G* calculations.

[d] Relative energy was obtained with MP2/6-31+G* calculations.

4H-1,3-dithiin (3)

In 4*H*-1,3-dithiin (**3**) was obtained the lowest energy in twisted forms with Φ_{1234}= -64.9° (**3-twist**) and 64.9° (**3-twist'**) (Table **3** and Fig. **3**). The relative stability of the twisted forms of **3** (**3-twist** and **3-twist'**) was attributed to the absence of lone pair-lone pair repulsion and decrease in torsional strain owing to twisting of the ring; and separation of two sulfur atoms by one methylene groups [11]. Moreover, the axial and equatorial C-H bonds in **3-twist** and **3-twist'** conformers had the same length (1.081 A°). Therefore, in these conformers were not observed hyperconjugation effects [11]. The torsional angle in the most stable conformer of 4*H*-1,3-dithiin (**3**) was different with the dihedral angle in cyclohexene about 5 degrees. Upon rotation of the dihedral angle to -23.3°, the transition state conformer (**3-half-chair**) was resulted with C_1 symmetry (Fig. **3**). The transition state energy was 12.4 kJ mol^{-1} higher than **3-twist** form (Table **3**). In **3-half-chair** and **3-half-chair'** forms, the S_1 atom and the double bond (C_5=C_6) were coplanar (Fig. **3**). Thus, an interaction between the S_1 nonbonded electrons and the π-bond electrons of the double bond was destabilizing in **3-half-chair** and **3-**

half-chair' forms. With fixing the torsional angle about -17.5°, a conformational change occurred. This change led to a boat form (**3-boat**) as the other minimum-energy. This conformer (**3-boat**) was 7 kJ mol^{-1} more in energy than **3-twist** form (Table **3**). Relatively stability of the boat conformer to transition states may be due mainly to the structure's ability to lower the sulfur lone pair-lone pair repulsions by twisting along the six-membered ring and separation of the two sulfur atoms by one methylene group. Relative instability of **3-boat** to **3-twist** is probably the result of a transannular π electrons-lone pair interaction between the double bond and -S$_3$ atom.

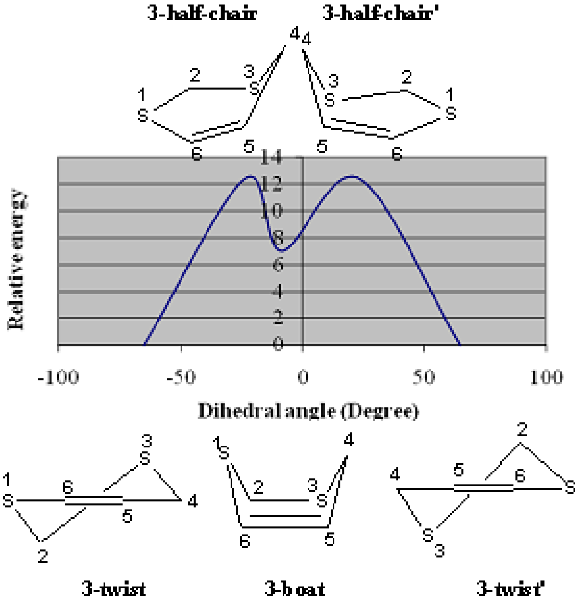

Fig. 3 The plot of the variation of MP2/6-31+G* relative energy (kJ mol^{-1}) vs Φ_{1234} of 4*H*-1,3-dithiine (3)

The obtained results of the calculated conformations of structure **3** in Freeman researches [11] were comparable to the obtained data in this paper. For example, the calculated bond angles of the C$_2$-S$_3$-C$_4$ and =C$_6$-S$_1$-C$_2$ for the twisted conformer **3** were 98.2° and 101.0°, respectively (see Table **3** and [11]). In the present study, the calculated S$_1$-C$_2$-S$_3$-C$_4$ torsional angle in twisted forms **3** were obtained -64.9° (**3-twist**) and 64.9° (**3-twist'**) (Table **3** and Fig. **3**). The same torsional angle in the half-chair form (twisted form) of Freeman researches [11] had been determined 64.8°. The calculated C$_2$-S$_1$, C$_2$-S$_3$ and C$_5$=C$_6$ bond lengths in **3-twist** were 1.809 A°, 1.806 A° and 1.323 A°, respectively (see Table **3** and [11]). In Freeman researches [11], energy difference between half-chair (twisted form) and boat conformers related to molecule **3** was about 8.4 kJ mol^{-1} while it was obtained 7.0 kJ mol^{-1} in this study.

2-vinyl-4H-1,3-dithiin (4)

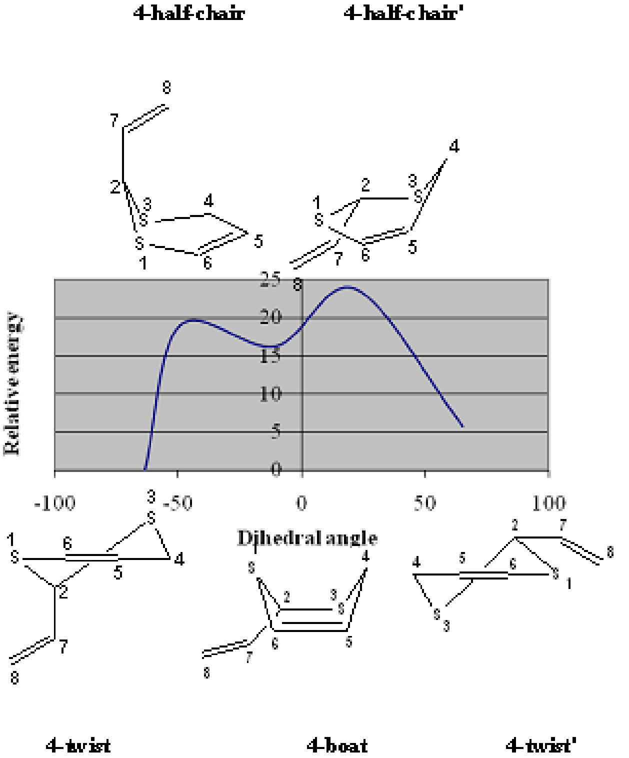

Fig. 4 The plot of the variation of MP2/6-31+G* relative energy (kJ mol^{-1}) vs Φ_{1234} of 2-vinyl-4*H*-1,3-dithiin (4)

In 2-vinyl-4H-1,3-dithiin (**4**), twisted forms with Φ_{1234}= -63.4 (**4-twist**) and 65.4° (**4-twist'**) were calculated to be in the low-energy region. **4-twist'** form had 5.8 kJ mol^{-1} greater energy relative to **4-twist** form (Table **4**). The other minimum-energy was corresponded to the boat form (**4-boat**) with Φ_{1234}= -10.4°. The boat conformer had 16.3 and 10.5 kJ mol^{-1} more energy than **4-twist** and **4-twist'** forms, respectively (Table **4**). Transition state forms with Φ_{1234}= -58.9° (**4-half-chair**) and 22.0° (**4-half-chair'**) were about 16.9 and 23.8 kJ mol^{-1} higher in energy than **4-twist** conformer (Table **4**). In order to decrease interactions between lone pairs of sulfur atoms and π electrons of vinyl substitution, **4-twist** adopted a torsional angle -63.4° at gauche form between the sulfur atoms and vinyl substitution (Fig. **4**), while the vinyl substitution took at axial arrangement. This factor was stabilizer for **4-twist**. In **4-twist',** there was eclipsed form between the vinyl substitution and lone pair of the S$_1$ atom as a factor its instability to **4-twist** (Fig. **4**). The lower stability of **4-half-chair** compared with **4-twist** may be due to the transannular lone pair-

Table 3 Calculated total energies (hartree), ZPVE, relative energy (kJ mol^{-1}), and structural parameters (obtained at the HF/6-31+G* level) for various conformations of 4*H*-1,3-dithiine (**3**)

Feature	3-twist	3-half-chair	3-boat
HF/6-31+G*	-949.96340	-949.95711	-949.95870
B3LYP/6-31+G*	-952.39697	-952.39175	-952.39238
MP2/6-31+G*	-950.73017	-950.72545	-950.72752
ZPVE[a]	57.4448	57.2648	57.4314
E_{rel}[b]	0.0	16.5	12.3
E_{rel}[c]	0.0	13.0	12.0
E_{rel}[d]	0.0	12.4	7.0
r_{16}/A°	1.762	1.766	1.772
r_{12}/A°	1.809	1.838	1.818
r_{23}/A°	1.806	1.814	1.823
r_{34}/A°	1.813	1.825	1.832
r_{45}/A°	1.506	1.499	1.501
r_{56}/A°	1.323	1.322	1.324
$\theta_{123}/^{o}$	114.4	118.2	116.0
$\theta_{234}/^{o}$	98.2	100.9	101.7
$\theta_{612}/^{o}$	101.0	105.0	98.2
$\theta_{165}/^{o}$	128.9	123.8	120.9
$\theta_{456}/^{o}$	128.2	122.1	122.0
$\Phi_{1234}/^{o}$	-64.9	-23.3	-17.5

[a] ZPVE was obtained with B3LYP/6-31+G* level.
[b] Relative energy was obtained with HF/6-31+G* calculations.
[c] Relative energy was obtained with B3LYP/6-31+G* calculations.
[d] Relative energy was obtained with MP2/6-31+G* calculations.

lone pair interactions between the S_1 and S_3 atoms in this conformer. Interactions between the S_1 nonbonded electrons and the π-bond electrons of the vinyl substitution and the same time with the π-bond electrons of the $-C_5=C_6-$ double bond were led to unstable **4-half-chair'** conformer compared with **4-twist** form (Fig. **4**).

Analysis of conformational changes between 4H-1,3-dithiin (3) and 2-vinyl-4H-1,3-dithiin (4)

At first glance, general trend of conformational changes in both molecules **3** and **4** were the same**.** Both molecules had the twist and boat conformers as minima energy forms; and the half-chair conformers were as transition states (Figs. **3** and **4**). But, the difference between energy levels in the same forms of each molecule was different than the same conformers in other molecule (Tables **3** and **4**). This was the result of the present and absence of the vinyl substitution in different conformers of the molecules **3** and **4**. For example, the molecule **3** had the twisted conformers with the same energy level, as well as the half-chair conformers had the same energy level (Fig. **3**). But, energy surfaces between the twisted conformers (**4-twist** and **4-twist'**) and the half-chair forms (**4-half-chair** and **4-half-chair'**) in the molecule **4** were different. The difference of energy surface in the **4-twist** and **4-twist'** was 5.8 kJ mol^{-1} which was resulted of position equatorial from the vinyl substitution in **4-twist'** form. Energy difference in **4-half-chair** and **4-half-chair'** were 6.9 kJ mol^{-1} (Table **4**) which was reflected to the interactions of the π-bond electrons of the vinyl substitution and the non-bonded electrons of the sulfur atoms (Fig. **4**). Therefore, the vinyl substitution affects on the energy surfaces of the molecule **4**.

Table 4 Calculated total energies (hartree), ZPVE, relative energy (kJ mol^{-1}), and structural parameters (obtained at the HF/6-31+G* level) for various conformations of 2-vinyl-4*H*-1,3-dithiin (**4**)

Feature	**4-twist**	**4-half-chair**	**4-boat**	**4-half-chair'**	**4-twist'**
HF/6-31+G*	-1026.84105	-1026.83232	-1026.83378	-1026.83257	-1026.84070
B3LYP/6-31+G*	-1029.79102	-1029.78589	-1029.78374	-1029.78328	-1029.79045
MP2/6-31+G*	-1027.86920	-1027.86277	-1027.86299	-1027.86014	-1027.86700
ZPVE[a]	78.0718	77.7363	78.0090	77.8603	77.9989
E_{rel}[b]	0.0	22.9	19.1	22.3	0.9
E_{rel}[c]	0.0	12.1	18.9	19.5	1.2
E_{rel}[d]	0.0	16.9	16.3	23.8	5.8
r_{16}/A°	1.762	1.760	1.772	1.768	1.762
r_{12}/A°	1.819	1.827	1.827	1.843	1.818
r_{23}/A°	1.823	1.820	1.845	1.835	1.822
r_{34}/A°	1.813	1.813	1.828	1.822	1.813
r_{45}/A°	1.504	1.502	1.500	1.500	1.505
r_{56}/A°	1.322	1.323	1.322	1.321	1.323
θ_{123}/°	112.4	112.5	114.0	116.2	113.0
θ_{234}/°	99.3	102.9	103.0	101.6	98.6
θ_{345}/°	114.3	116.1	113.5	111.1	114.8
θ_{612}/°	103.2	102.7	100.4	105.6	70.9
θ_{165}/°	129.3	129.4	120.6	123.3	129.4
θ_{456}/°	127.2	128.5	121.4	121.6	127.3
Φ_{1234}/°	-63.4	-58.9	-10.4	22.0	65.4

[a] ZPVE was obtained with B3LYP/6-31+G* level.

[b] Relative energy was obtained with HF/6-31+G* calculations.

[c] Relative energy was obtained with B3LYP/6-31+G* calculations.

[d] Relative energy was obtained with MP2/6-31+G* calculations.

Conclusions

In summary, from structural and energy perspectives, *ab initio* calculations provided a picture of the conformations of **1-4** structures. The twisted conformations from each of them were the most stable forms than the other related conformers. Other stable forms were found in the boat forms. The boat forms of **1-4** had 7-16.3 kJ mol^{-1} less stable than the twist conformers. Half-chair forms were determined as transition state conformations. Energy of half-chair forms of **1**, **2**, **3**, and **4** were obtained 12.4-23.93 kJ mol^{-1} higher than twisted conformers. Dithiin rings for all of molecules (**1-4**) could interconvert from one twisted form to another through passing the related boat conformations.

Computational methods

The energies and optimized geometries for conformers of 4*H*-1,2-dithiin (**1**), 3-vinyl-4H-1,2-dithiin (**2**), 4*H*-1,3-dithiin (**3**), and 2-vinyl-4H-1,3-dithiin (**4**) were calculated with the Gaussian 98 program [24] using HF, B3LYP, and MP2 methods with 6-31+G* basis set. Initially, the geometries of all stationary points with different torsional angles for each molecule of **1-4** were fully optimized. As well as, calculations on the same geometries for each molecule of **1-4** were performed to obtain the relevant transition structures using keyword "OPT=TS". The frequency calculations at the B3LYP/6-31+G* level on each optimized structure were done to confirm the characters of optimized structures and to obtain zero-point energy corrections. For minimum state structures, only real frequency values and for transition state structures one imaginary frequency values were accepted [25]. The frequencies were scaled by a factor of 0.98 [26] and were used to compute the zero-point vibrational energies. The structural parameters were obtained by HF/6-31+G* level of theory.

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