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Journal of Sulfur Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926081>

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Online publication date: 12 August 2010

To cite this Article Nadim, Emad Saleh , Raissi, Heidar , Yoosefian, Mehdi , Farzad, Farzaneh and Nowroozi, Ali Reza(2010) '*Ab initio* and DFT computational studies on molecular conformations and intramolecular hydrogen bonding in 3-mercapto-but-2-enethial', Journal of Sulfur Chemistry, 31: 4, 275 – 285

To link to this Article: DOI: 10.1080/17415993.2010.492871

URL: <http://dx.doi.org/10.1080/17415993.2010.492871>

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***Ab initio* and DFT computational studies on molecular conformations and intramolecular hydrogen bonding in 3-mercapto-but-2-enethial**

Emad Saleh Nadim^{a*}, Heidar Raissi^b, Mehdi Yoosefian^b, Farzaneh Farzad^b and Ali Reza Nowroozi^c

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(Received 12 April 2010; final version received 10 May 2010)

The molecular structure and intramolecular hydrogen bond energies of 20 conformers of 3-mercapto-but-2-enethial were investigated at MP2/6-311 + +G**, B3LYP/6-311 + +G**, and G2MP2 levels of theory. Furthermore, calculations for all the possible conformations of the title compound in water and CCl₄ solutions were also carried out at the B3LYP/6-311 + +G** level of theory. The calculated geometrical parameters and conformational analysis in gas phase, water, and in CCl₄ solutions showed that the 4-mercapto-but-3-ene-2-thione conformers of this compound are more stable than the others. This stability is mainly due to the formation of an S–H...S intramolecular hydrogen bond, which is assisted by π -electrons resonance. Hydrogen bond energies for all conformers of 3-mercapto-but-2-enethial were obtained from the related rotamers method (RRM). The “atoms in molecules” theory of Bader which is based on topological properties of the electron density (ρ) was used to analyze critical points and to study the nature of hydrogen bond in these systems. Natural bond orbital (NBO) analysis was also performed for better understanding the nature of intramolecular interactions in 3-mercapto-but-2-enethial. The results of these calculations were in agreement with data obtained by the RRM.

Keywords: 3-mercapto-but-2-enethial; molecular conformations; related rotamers method; *ab initio*; AIM calculation

1. Introduction

Intermolecular and intramolecular hydrogen-bonding interactions exist widely in chemical and biological systems and play a fundamental role not only in molecular properties and structures but also in chemical and biological processes. A wealth of information on hydrogen bonds can be found in the literature (1, 2), and hydrogen bonds can be probed experimentally using NMR (3), IR (4), Compton profile anisotropies (5), and other techniques. However, there have been controversies over the essence of hydrogen bonds, notably those of either the pure electrostatic (2, 6) or partial covalent nature (5, 7, 8). Generally, hydrogen-bonding interactions are close to or

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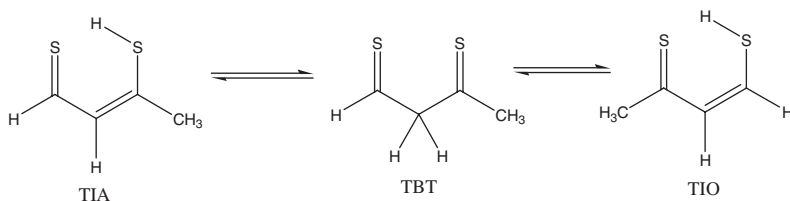


Figure 1. Tautomery equilibria in MBE.

slightly stronger than van der Waals interactions, but still fall into the category of weak interactions with a strength ranging from 2 to 10 kcal/mol, depending on the bond length and linearity (6, 8).

This view has been challenged recently as more and more strong and unconventional hydrogen bonds have been recognized (9–12). As a matter of fact, several types of strong hydrogen bonds have been investigated, for example, charge-assisted hydrogen bonds (CAHBs) (12, 13), low-barrier hydrogen bonds (LBHBs) (14, 15), dihydrogen bonds (DHBs) (8, 16), and resonance-assisted hydrogen bonds (RAHBs) (10–12). In a CAHB, a positive or negative charge on the proton donating or accepting group remarkably enhances the strength of the hydrogen bond, while LBHBs are a class of hydrogen bonds that have a low energy barrier for the proton shift from the proton donor to proton acceptor. The low barrier is usually accompanied by a very short hydrogen bond length. LBHBs are particularly important in enzymatic catalysis where there is a weak hydrogen bond in the initial enzyme–substrate complex and can be converted to an LBHB in the transition state (15, 17). LBHBs are assumed to be largely covalent in character (18).

DHBs are designated as X–H...H–M where X is an electronegative atom such as O or N, and M is a transition metal or boron. On the other hand, RAHB highlights the cooperativity between the π -electron delocalization and hydrogen bonds; the term was coined by Gilli and co-workers in the late 1980s, who have continued to refine their theory by publishing a series of papers (10–12). In RAHB, the hydrogen bond donor and acceptor atoms are connected through π -conjugated double bonds, which were utilized in this work.

As a typical example of RAHB, we used 3-mercapto-but-2-enethial (MBE) which forms intramolecular ... S=C–C=C–S–H ... hydrogen bond enhanced by the resonance. MBE is an interesting molecule due to its involvement only in the intramolecular hydrogen bond. It possesses the S ... H–S intramolecular hydrogen bond and has a relatively simple structure. Theoretically, three classes of tautomers namely Thial (TIA), Thione (TIO), and Thioxo (TBT) can be expected for it (Figure 1). The results of theoretical calculations demonstrate that this compound exists predominantly in the 4-mercapto-but-3-ene-2-thione form. Our theoretical calculations emphasize that the hydrogen bond strength increases from TIO to TIA conformers. MBE has two intramolecular hydrogen bond conformers and both of them are stabilized by π -electron delocalization.

The main goals of this work were to determine the order of stability of the various MBE conformations, to predict the most stable structure in the gas phase and in solution, and to evaluate the intramolecular hydrogen bond strength in more stable conformers. For this purpose, we obtained the exact value of the intramolecular hydrogen bond energies by the related rotamers method (RRM) (19).

2. Method of analysis

The calculations have been performed using the Gaussian 98 program (20). The reliably accurate description of weak interaction like HBs generally requires an electron correlation treatment.

Density functional theory offers an electron correlation correction frequently comparable to the second-order Moller–Plesset theory (MP2) or in certain cases, and for certain purposes, even superior to MP2, but at considerably lower computational cost (21, 22).

The geometry optimization for all the possible conformations of MBE was carried out by B3LYP (23), MP2 methods with 6-311 + +G** (190 basis functions, 298 primitive Gaussians) basis set, and G2MP2 theoretical level. The topological properties of the electron density contribution for various kind of intramolecular hydrogen bond have been analyzed in terms of the Bader theory of atoms in molecules (AIM) by means of AIM2000 (24–26) software analysis. Furthermore, harmonic vibration frequencies were calculated at B3LYP/6-311 + +G** and MP2/6-311 + +G** levels of theory in order to confirm the nature of stationary points found and to account for the zero-point vibrational energy (ZPVE) correction.

3. Results and discussion

From the theoretical point of view, MBE has 20 different possible conformers. On the basis of functional groups, these conformers can be classified into three tautomeric classes: 3-mercapto-but-2-enethial (TIA), 4-mercapto-but-3-ene-2-thione (TIO), and 3-thioxo-butanethial (TBT), which have 8, 8, and 4 rotamers, respectively. Our theoretical calculations on MBE show that the 4-mercapto-but-3-ene-2-thione conformers of the MBE are more stable than the other conformers. Comparison of all hydrogen-bonded and non-hydrogen-bonded systems in all conformers using mean energies illustrates the following stability order for MBE conformers at B3LYP/6-311 + +G** level (The first and second values in parentheses refer to calculations at MP2/6-311 + +G** and G2MP2 levels of theory, respectively. The first and second values in brackets refer to mean energies with considering ZPVE correction at B3LYP/6-311 + +G** and MP2/6-311 + +G** levels of theory, respectively. * show that there is not H-bond in TBT conformers).

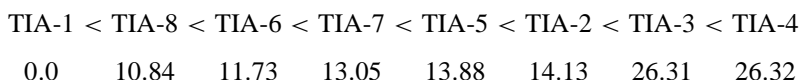
	TIO	<	TIA	<	TBT
	14.27		16.61		58.66
Non-H-bonded	(8.93, 9.11)		(9.93, 10.60)		(40.88, 41.99)
<i>E</i> (KJ/mol)	[15.14, 24.44]		[16.67, 33.96]		[62.42, 44.76]
	TIA	<	TIO	<	TBT
	0		0.128		*
H-bonded	(0.72, 1.09)		(0.0, 0.0)		(* , *)
<i>E</i> (KJ/mol)	[0.0, 0.0]		[0.22, 3.52]		[* , *]

Therefore in non-hydrogen-bonded systems, TIO conformers are about 2.34 and 44.39 KJ/mol more stable than TIA and TBT conformers, respectively. Furthermore the TIA conformers are about 42.05 KJ/mol more stable than the TBT conformers but in hydrogen-bonded systems, the thial conformers are more stable than the others. The values of this energy gap reveals that the TBT and non-H-bonded conformers have less stability with respect to H-bonded conformers and the Boltzmann distribution function predicts that their presence in the conformational equilibrium is unlikely. Finally, from above results, it can be concluded that the energy order in non-H-bonded conformers is independent of computational level and also correlation energy, while the energy order in H-bonded conformers somewhat depends on theoretical level and electron correlation. Moreover, we can also estimate the correlation energy terms $E_{\text{corr}} = E_{\text{MP2}} - E_{\text{HF}}$, where E_{corr} designates the correlation energy term. The result of our theoretical calculations

show that for the TIA-1 ($E_{\text{corr}} = 2216.55$ KJ/mol) with the strongest H-bond, there is substantial energy contribution coming from electron correlation. This is also typically due to partly covalent interaction (the correlation energy estimated for other conformers, available upon request as a supplementary table). The extra stability of TIO conformers is due to the hyper-conjugation of CH_3 in the π -electron resonance and formation of intramolecular hydrogen bonds.

3.1. The thial group

The structures of possible conformations and their relative energies with respect to the most stable conformer in thial tautomer are given in Figure 2. Their structural parameters and relative energies are listed in the Table 1. The stability order of the different TIA conformers (in KJ/mol) calculated at B3LYP/6-311++G** level shows the following stability order:



Additionally, we calculated the zero-point energy at the B3LYP/6-311 + +G** level and the MP2/6-311 + +G** level and the results including ZPVE show the same stability order. The present results predict that the heavy atom skeletons of the eight conformations of the TIA tautomer (Figure 2) are fully planar. The comparison of the relative energies of the different TIA conformers shows that TIA-1 is more stable than all the other conformers (TIA-2–TIA-8). This stability is due to the formation of a relatively strong S...H–S intramolecular hydrogen bond, which is assisted by π -electron resonance. Here the strength of the intramolecular hydrogen bond was calculated by means of the RRM method (19). It is worth mentioning that the RRM (19) is a method for calculations of hydrogen bond energies. By using this method, we applied hydrogen-bonded conformer TIA-1 and three related non-hydrogen-bonded rotamers (TIA-2–TIA-4). We obtained the energy differences between particular conformers of thial using a thermodynamic cycle which is presented in Figure 3. The rotation about the C–S bond converts the TIA-1 and TIA-3 to TIA-2 and TIA-4, respectively. Theoretical calculations show that the hydrogen bond and the resonance of π -electrons strongly affect the stability order of conformers. Our theoretical results show that there is the resonance of π -electrons in the TIA-1 conformers. Geometrical parameters presented in Table 1 showed that the C=S, C–C, C=C, and C–S bond distances in TIA conformers were very similar. This means that the energy function is not sensitive to bond distance changes. In TIA-1 conformer both C=C and C=S bond lengths have increased, whereas C–C and C–S bond lengths have decreased with regard to the other thial conformers. These behaviors are caused by hydrogen bond formation, which in fact increase the π -electron resonance in the chelated ring. Analysis of geometrical parameters provides evidence that bond angles in the TIA-1 chelate ring

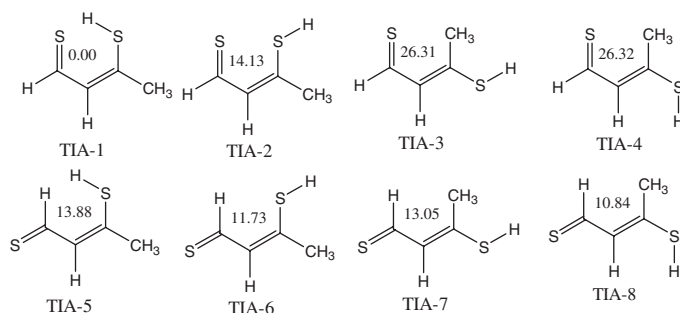


Figure 2. Possible thial conformers in MBT.

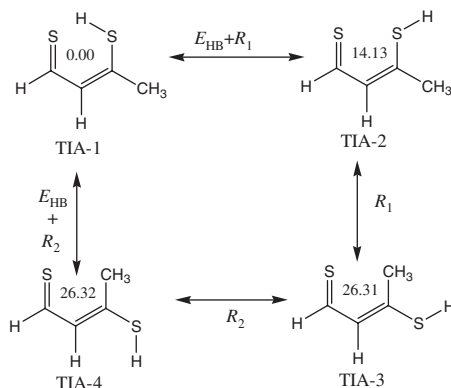


Figure 3. Thermodynamic cycle describing the energy of intramolecular hydrogen bond in thial conformers (S...H–S hydrogen bond). Path 1: $E_{\text{HB}} = \Delta E_{1,2} - \Delta E_{3,4} = 14.13 - (-0.01) = 14.14$ KJ/mol, $R_1 = -0.01$ KJ/mol. Path 2: $E_{\text{HB}} = \Delta E_{1,4} - \Delta E_{2,3} = 26.32 - (12.18) = 14.14$ KJ/mol, $R_2 = 12.18$ KJ/mol.

Table 1. Geometrical parameters of MBE conformers and relative energy calculated at the B3LYP/6–311++G** level.

	C=S	C–C	C=C	C–S	S–H	S...H	S...S	Erel (KJ/mol)
TIA-1	1.665	1.421	1.377	1.736	1.395	2.072	3.360	0.00 (0.72) [1.09]
TIA-2	1.650	1.428	1.367	1.756	1.360	4.463	3.107	14.13 (8.34) [5.72]
TIA-3	1.651	1.440	1.363	1.772	1.348	5.700	5.201	26.31 (18.84) [19.43]
TIA-4	1.650	1.441	1.364	1.768	1.349	5.470	5.219	26.32 (16.93) [16.47]
TIA-5	1.645	1.429	1.362	1.767	1.347	4.252	4.975	13.89 (7.47) [10.39]
TIA-6	1.643	1.432	1.360	1.773	1.348	5.984	4.775	11.73 (3.35) [4.47]
TIA-7	1.646	1.431	1.361	1.771	1.348	6.329	5.380	13.05 (7.96) [8.38]
TIA-8	1.646	1.431	1.361	1.768	1.349	5.119	5.458	10.85 (6.65) [9.34]
TIO-1	1.672	1.435	1.367	1.724	1.389	2.114	3.369	0.13 (0.00) [0.00]
TIO-2	1.658	1.441	1.358	1.743	1.360	4.441	3.093	10.45 (5.19) [2.48]
TIO-3	1.654	1.457	1.347	1.748	1.347	5.180	4.905	11.37 (5.67) [7.39]
TIO-4	1.653	1.457	1.348	1.741	1.351	5.369	4.895	10.84 (7.45) [7.01]
TIO-5	1.656	1.451	1.357	1.750	1.344	4.779	5.246	28.31 (21.17) [23.71]
TIO-6	1.655	1.455	1.354	1.762	1.347	6.160	5.076	20.80 (12.73) [13.90]
TIO-7	1.653	1.450	1.350	1.757	1.347	6.288	5.405	10.67 (5.18) [5.67]
TIO-8	1.654	1.350	1.361	1.749	1.350	5.198	5.465	7.43 (2.11) [3.60]
TBT-1	1.629	1.510	–	–	–	–	4.780	42.85 (26.10) [26.60]
TBT-2	1.630	1.515	–	–	–	–	5.504	54.81 (37.66) [40.22]
TBT-3	1.632	1.515	–	–	–	–	5.157	63.36 (46.98) [47.44]
TBT-4	1.625	1.511	–	–	–	–	3.477	73.62 (52.79) [53.71]

Note: Values in parentheses refer to calculation at the MP2/6–311++G** level and values in brackets refer to calculation at G2MP2.

are closer to the standard sp^2 hybridization (27) values compared with other conformers. Due to the presence of a relatively strong S...H–S hydrogen bond and by considering the relative energies, the TIA-1 conformer is the most stable. Therefore, it seems that the TIA-1 conformer is a global minimum.

3.2. The thione group

MBE has eight possible thione conformers (Figure 4), all of which on average are more stable than the thial conformer. The stability is related to the existence of the S...H–S hydrogen bond and π -electron resonance in the chelated ring. Because of π -electron delocalization, all thione conformers have planar structures. The geometrical parameters and relative energies of TIO

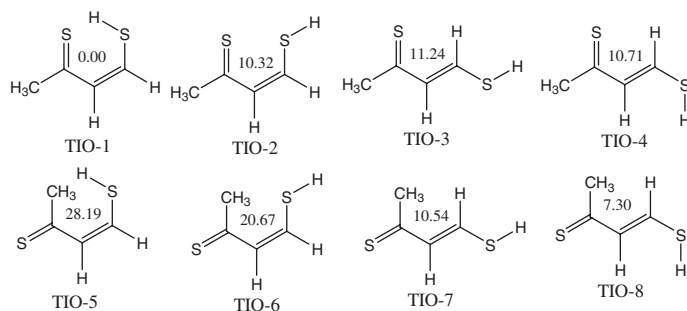
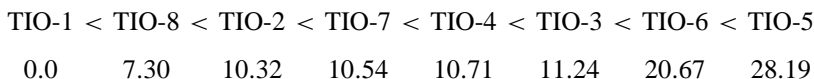


Figure 4. Possible thione conformers in MBT.

conformers are given in Table 1. The absence of imaginary frequency proved that all of these planar forms which have particular local minima on PES are stable. Additionally, the stability order of the different TIO conformers (in KJ/mol) calculated at the B3LYP/6-311++G** level showed the following stability order:



Furthermore, the ZPVE correction does not considerably change the energy orders and is not a sensitive parameter. According to Shuster's method (28), the energy difference between the TIO-1 and TIO-2 is equal to the hydrogen bond energy (10.32, 5.19, and 2.48 KJ/mol at B3LYP, MP2, and G2MP2, respectively), while the RRM method (19) gives different results. The hydrogen bond energy in the TIO-1 conformer was calculated by the RRM method and the results are shown in Figure 5. This method (19) suggests that the value of intramolecular hydrogen bond energy of TIO-1 conformer is ~ 9.79 KJ/mol (Figure 5). The comparison between the S...H-S hydrogen bond in TIO-1 and TIA-1 conformers showed that the S...H-S hydrogen bond in TIA-1 conformer was stronger than TIO-1 conformer. Furthermore, the values of S...H distances in TIA-1 and TIO-1 conformer are about 3.360 and 3.369 Å, respectively, which supports the above results.

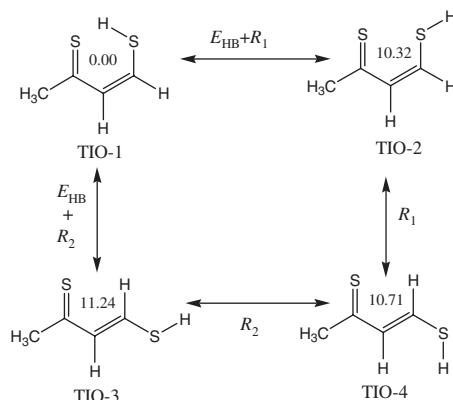


Figure 5. Thermodynamic cycle describing the energy of intramolecular hydrogen bond in thione conformers (S-H...S hydrogen bond). Path 1: $E_{\text{HB}} = \Delta E_{1,2} - \Delta E_{3,4} = 10.32 - (0.53) = 9.79$ KJ/mol, $R_1 = 0.53$ KJ/mol. Path 2: $E_{\text{HB}} = \Delta E_{1,4} - \Delta E_{2,3} = 10.71 - (0.92) = 9.79$ KJ/mol, $R_2 = 0.92$ KJ/mol.

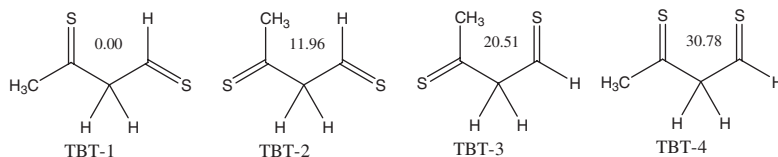
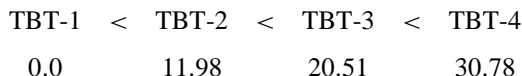


Figure 6. Possible thioxo-butaneethial conformers in MBT.

3.3. The thioxo group

The possible conformations of thioxo tautomers are shown in Figure 6. Although MBE has four possible thioxo conformers, the existence of imaginary frequencies at all the computational levels showed that all of them were unstable. It looks as though the electronic repulsion between the sulfur lone pairs of electrons lowers the stability of conformers. The geometrical parameters and relative energies of TBT conformers are listed in Table 1. The stability order of the different TBT conformers (in KJ/mol) calculated at the B3LYP/6-311 + +G** level shows the following stability order:



It is necessary to mention that the thioxo-butaneethial conformers cannot form hydrogen bonds. The absence of π -delocalization and the proton in the ring of TBT conformers causes the hydrogen bond not to be formed. The results of theoretical calculations also showed that the TBT forms are less stable than the TIA and TIO forms. This is mainly due to the breaking of the conjugation between two double bonds due to the existence of a CH_3 group. Additionally, the ZPVE correction does not change the energy orders.

3.4. Water and CCl_4 solutions

To study the geometry and the intramolecular hydrogen bond energy changes in the various MBE conformers, B3LYP/6-311 + +G** optimization in water and CCl_4 solutions was carried out. The solvent effect was calculated using the self-consistent reaction field (SCRF) model. For the Onsager model (SCRF = dipole), the solute radius in Angstroms and the dielectric constant of the solvent are read as two free-format real numbers on one line from the input stream (29). A suitable solute radius is computed by a gas-phase molecular volume calculation. The relative energies and geometrical parameters of TIA, TIO, and TBT conformers are presented in Table 2. The results obtained from this table showed that the order of stability among the most stable TIO-1 and TIA-1 tautomers does not change considerably. It is worth mentioning that the hydrogen bond strength in TIA-1 and TIO-1 conformers in CCl_4 solution is weaker than the gas phase. For example, the hydrogen bond energy value for the $\text{S} \cdots \text{H-S}$ bridge in TIO-1 reduces to 5.66 KJ/mol (in gas phase is 9.79 KJ/mol), whereas E_{HB} for the $\text{S} \cdots \text{H-S}$ bridge in TIA-1 conformer in CCl_4 solution is 11.34 KJ/mol, which is close to the gas phase (14.14 KJ/mol) and increases to 24.56 KJ/mol in water solution.

A comparison of the total energies in the gas phase and in solution is also interesting because it points out that full optimization in a solvent is often not necessary since only modest changes are noted with respect to the geometrical parameters obtained in the gas phase. The maximum different energy gain is obtained on passing from the gas phase to water solution in the molecules considered here are about 36.67, 26.20, and 9.11 KJ/mol and were found for the TIA-7, TIO-5, and TBT-4, respectively. The maximum different energy gain is obtained on passing from the gas phase to CCl_4 solution for the molecules considered here were about 9.56, 4.63, and 21.30 KJ/mol

Table 2. Geometrical parameters of MBE conformers and relative energy calculated at the B3LYP/6-311++G** level in water solution.

	C=S	C-C	C=C	C-S	S-H	S...H	S...S	Erel (KJ/mol)
TIO-1	1.675 (1.673)	1.434 (1.434)	1.367 (1.367)	1.725 (1.724)	1.388 (1.388)	2.115 (2.115)	3.371 (3.370)	20.39 (0.69)
TIO-2	1.664 (1.660)	1.437 (1.439)	1.359 (1.358)	1.740 (1.742)	1.358 (1.359)	4.480 (4.454)	3.134 (3.107)	24.95 (8.90)
TIO-3	1.659 (1.656)	1.451 (1.455)	1.351 (1.349)	1.742 (1.738)	1.348 (1.347)	5.198 (5.186)	4.913 (4.908)	30.81 (11.75)
TIO-4	1.663 (1.657)	1.450 (1.455)	1.352 (1.349)	1.733 (1.738)	1.352 (1.351)	5.384 (5.374)	4.894 (4.894)	24.78 (9.19)
TIO-5	1.664 (1.658)	1.444 (1.448)	1.361 (1.358)	1.741 (1.747)	1.344 (1.344)	4.800 (4.787)	5.257 (5.250)	25.73 (27.98)
TIO-6	1.666 (1.658)	1.443 (1.449)	1.360 (1.356)	1.749 (1.757)	1.348 (1.347)	6.171 (6.162)	5.078 (5.075)	32.23 (18.40)
TIO-7	1.665 (1.657)	1.441 (1.447)	1.356 (1.351)	1.744 (1.752)	1.348 (1.347)	6.298 (6.291)	5.404 (5.403)	21.42 (7.29)
TIO-8	1.661 (1.656)	1.444 (1.448)	1.354 (1.352)	1.740 (1.746)	1.351 (1.351)	5.213 (5.203)	5.472 (5.467)	25.73 (7.42)
TIA-1	1.670 (1.667)	1.418 (1.420)	1.379 (1.377)	1.736 (1.736)	1.390 (1.393)	2.090 (2.076)	3.372 (3.363)	18.72 (0.00)
TIA-2	1.658 (1.653)	1.422 (1.426)	1.371 (1.368)	1.751 (1.754)	1.358 (1.359)	4.507 (4.478)	3.155 (3.124)	25.89 (11.61)
TIA-3	1.661 (1.654)	1.430 (1.437)	1.371 (1.366)	1.758 (1.768)	1.348 (1.348)	5.725 (5.708)	5.207 (5.203)	41.36 (25.35)
TIA-4	1.662 (1.654)	1.422 (1.437)	1.373 (1.366)	1.748 (1.763)	1.350 (1.349)	5.443 (5.475)	5.147 (5.221)	40.03 (25.08)
TIA-5	1.653 (1.648)	1.422 (1.427)	1.369 (1.364)	1.758 (1.764)	1.347 (1.347)	4.258 (4.253)	4.983 (4.977)	29.96 (13.13)
TIA-6	1.660 (1.648)	1.418 (1.427)	1.373 (1.364)	1.758 (1.769)	1.348 (1.348)	6.005 (5.989)	4.786 (4.776)	14.79 (6.79)
TIA-7	1.687 (1.653)	1.401 (1.425)	1.392 (1.366)	1.735 (1.764)	1.352 (1.348)	6.379 (6.336)	5.389 (5.377)	0.00 (5.42)
TIA-8	1.663 (1.651)	1.417 (1.427)	1.374 (1.364)	1.749 (1.762)	1.350 (1.349)	5.139 (5.122)	5.472 (5.461)	20.55 (8.60)
TBT-1	1.631 (1.630)	1.510 (1.510)	-	-	-	-	4.767 (4.775)	60.99 (38.06)
TBT-2	1.631 (1.631)	1.516 (1.515)	-	-	-	-	5.500 (5.502)	76.58 (55.98)
TBT-3	1.632 (1.627)	1.515 (1.511)	-	-	-	-	5.154 (4.139)	86.23 (43.99)
TBT-4	1.625 (1.626)	1.511 (1.510)	-	-	-	-	3.477 (3.479)	88.13 (71.91)

Note: Values in parentheses refer to CCl₄ solution.

and were found for the TIA-7, TIO-3, and TBT-4, respectively. Since cavitation and dispersion energy terms nearly balance each other, being of the same order but having opposite signs, the main contribution to the stabilization of the molecules in solution comes from the solute-solvent polarization energy (30).

3.5. AIM analysis

The precise mapping of the distribution of charge density in hydrogen-bonded systems is a classical topic in structural chemistry (31), with a large number of individual studies reported (32). Currently, Bader's quantum theory of AIM is the most frequently used formalism in theoretical analyses of charge density (33). Here each point in space is characterized by a charge density $\rho(r)$, and further quantities such as the gradient of $\rho(r)$, the Laplacian function of $\rho(r)$, and the matrix of the second derivatives of $\rho(r)$ (Hessian matrix). The property of the Laplacian of the electron density, which is used to determine regions of concentration and depletion of the electron charge density, forms a basis for the classification of the atomic interactions (34). The atomic interactions were classified into two general classes, shared interactions and closed-shell interactions. The shared interactions (as covalent and polar bonds) are caused by a contraction of the charge density toward the line of interaction linking the nuclei. For these interactions the electronic charge is concentrated in the internuclear region and $\nabla^2\rho < 0$. The closed-shell interactions are governed by the contraction of the charge density toward each of interacting nuclei. In this case, the electronic charge is depleted in the interatomic surface and $\nabla^2\rho > 0$.

Two conformers which were involved in intramolecular hydrogen bond were selected (TIA-1 and TIO-1 conformers); the corresponding values of ρ_{BCP} and $\nabla^2\rho_{\text{BCP}}$ for these conformers are presented in Table 3. Comparison between the electron density of TIA-1 and TIO-1 (for the S...H bonding) showed that ρ_{BCP} for the TIA-1 conformer is higher than the corresponding value for TIO-1. As a consequence, the strength of the hydrogen bond in TIA-1 is greater than the TIO-1. These results are consistent with the results obtained by the RRM method. Furthermore, the calculated electron density properties of TIA-1 and TIO-1 conformers showed that S...H bondings have low ρ_{BCP} (about 0.0433 and 0.0401, respectively) and negative $\nabla^2\rho_{\text{BCP}}$ values. These properties are typical for shared interactions. Compared with TIA-1, in TIO-1 the electron density at the C=S and C-C bond critical points have lower values and are correlated with the lengthening of these bonds.

3.6. NBO analysis

The results of our natural bond orbital (NBO) analysis (occupation number (ON) for the assignments and their orbital energies) for MBE conformers are provided in Table 4. In this table, the

Table 3. Topological parameters of chelated ring and hydrogen bond energy (E_{HB}) for TIO-1 and TIA-1.

	TIO-1			TIA-1		
	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	ε	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	ε
S...H	0.0401	-0.0142	0.0351	0.0433	-0.0140	0.0341
C=S	0.2232	0.0942	0.1235	0.2247	0.0865	0.1034
C=C	0.3190	0.2243	0.2727	0.2924	0.1947	0.1561
C-C	0.2873	0.1884	0.1390	0.3154	0.2197	0.2583
C-S	0.2097	0.1044	0.2169	0.2065	0.0990	0.2138
RING	0.0115	-0.0155	-1.2293	0.0121	-0.0165	-1.2817
E_{HB} (KJ/mol)	9.79			14.14		

Table 4. NBO analysis of the chelated ring of MBT conformers.

Conformer	TIA-1	TIO-1
ON (n_{2s})	1.984	1.980
$E(n_{2s})$	-0.695	-0.700
ON (n_{2s})	1.795	1.811
$E(n_{2s})$	-0.238	-0.244
ON (σ S-H)	1.984	1.986
$E(\sigma$ S-H)	-0.564	-0.564
ON (σ S-H)	0.149	0.136
$E(\sigma$ S-H)	0.156	0.156
π S=C \rightarrow π^* C-C	8.570	1.270
π C=C \rightarrow π^* S-C	32.250	-
$n_{2s} \rightarrow \sigma^*$ C-C	5.110	4.970
$n_{2s} \rightarrow \sigma^*$ S-H	35.700	32.190

NBO occupation numbers for $\sigma^*(\text{S-H})$ antibonds, the sulfur lone pairs electrons, n_s , and their respective orbital energies, E , are shown. Furthermore, the donor-acceptor interaction and their second-order perturbation stabilization energies $E^{(2)}$ (calculated at B3LYP/6-311++G** level of theory) for the chelated rings of TIO-1 and TIA-1 are presented in Table 4. In the NBO analysis of the hydrogen-bonded systems, the charge transfer between the lone pairs of electrons of the proton acceptor and antibonds of proton donors is the most important interaction. The results of NBO analysis showed that in the chelated structures of the MBE conformers, two lone pairs of electrons of sulfur atoms (n_{2s}) participate as donor and $\sigma^*(\text{S-H})$ antibonds as acceptors. The NBO order again supports the strength of intramolecular hydrogen bond in MBE conformers.

4. Conclusions

This study of hydrogen-bonding strength was based on the geometric parameters which may be known from the experiment or derived from *ab initio* or DFT calculations. Since the geometrical criteria for the existence of hydrogen bonding are controversial, the AIM theory was applied to analyze this type of interaction. To avoid ambiguity, our studies were restricted only to geometrical, topological parameters derived from the Bader's theory and population analysis. The main findings that have been obtained from this work are given below.

According to all of the theoretical calculations, the stability orders (ΔE in KJ/mol) for the 4-mercapto-but-3-ene-2-thione conformers in gas phase are as follows:

$$\begin{aligned} & \text{TIA-1} < \text{TIO-1} < \text{TIO-8} < \text{TIO-2} < \text{TIO-7} < \text{TIO-4} < \text{TIA-8} < \text{TIO-3} < \text{TIA-6} < \text{TIA-7} < \\ & 0.0 \quad 0.13 \quad 7.43 \quad 10.45 \quad 10.67 \quad 10.84 \quad 10.85 \quad 11.37 \quad 11.73 \quad 13.05 \\ & \text{TIA-5} < \text{TIA-2} < \text{TIO-6} < \text{TIA-3} < \text{TIA-4} < \text{TIO-5} < \text{TBT-1} < \text{TBT-2} < \text{TBT-3} < \text{TBT-4} \\ & 13.89 \quad 14.13 \quad 20.80 \quad 26.31 \quad 26.32 \quad 28.31 \quad 42.85 \quad 54.81 \quad 63.36 \quad 73.62 \end{aligned}$$

Theoretical calculations showed that the TIA-1 is the most stable conformer of MBE both in the gas phase and in CCl_4 solution, while TIA-7 is the most stable conformer in water solution. The extra stability of TIO conformers is due to the hyper-conjugation of CH_3 in the π -electron resonance and intramolecular hydrogen bond formation. We concluded that the hydrogen bond strength in the TIA conformer ($\text{S}\dots\text{H-S}$) in CCl_4 solution is weaker than in the gas phase, while in water solution it becomes stronger. Our results also showed that ZPVE correction does not have any significant effect on stability order of these conformers.

References

- (1) (a) Scheiner, S. *Ann. Rev. Phys. Chem.* **1994**, *45*, 23–56; (b) Scheiner, S. *Hydrogen Bonding A Theoretical Perspective*; Oxford University Press: New York, 1997.
- (2) (a) Jeffrey, G.A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997; (b) Desiraju, G.R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: New York, 2001.
- (3) Tuttle, T.; Graefenstein, J.E.; Kraka, A.Wu.; Cremer, D. *J. Phys. Chem. B* **2004**, *108*, 1115–1129.
- (4) Brauer, B.; Gerber, R.B.; Kabelac, M.; Hobza, P.; Bakker, J.M.; Riziq, A.G.A.; de Vries, M.S. *J. Phys. Chem. A* **2005**, *109*, 6974–6984.
- (5) Isaacs, E.D.; Shukla, A.; Platzman, P.M.; Hamann, D.R.; Barbiellini, B.; Tulk, C.A. *Phys. Rev. Lett.* **1999**, *82*, 600–603.
- (6) Pauling, L.C. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
- (7) (a) Tapan, K.G.; Viktor, N.S.; Patrick, R.K.; Ernest, R.D. *J. Am. Chem. Soc.* **2000**, *122*, 1199–1205; (b) Pakiari, A.H.; Eskandari, K. *J. Mol. Struct.* **2006**, *759*, 51–60.
- (8) Grabowski, S.J.; Sokalski, W.A.; Leszczynski, J. *J. Phys. Chem. A* **2005**, *109*, 4331–4341.
- (9) Raissi, H.; Jalbout, A.F.; Nasseria, M.A.; Yoosefian, M.; Ghiassi, H.; Hameed, A.J. *Int. J. Quant. Chem.* **2008**, *108*, 1444–1451.
- (10) (a) Gilli, G.; Bellucci, F.; Ferretti, V.; Bertolasi, V. *J. Am. Chem. Soc.* **1989**, *111*, 1023–1028; (b) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **2000**, *122*, 10405–10417; (c) Gilli, P.; Bertolasi, V.; Pretto, L.; Lyëka, A.; Gilli, G.; *J. Am. Chem. Soc.* **2002**, *124*, 13554–13567.
- (11) Raissi, H.; Jalbout, A.F.; Fazli, M.; Yoosefian, M.; Ghiassi, H.; Wang, Z.; Leon, A. *De Int. J. Quant. Chem.* **2009**, *109*, 1497–1504.
- (12) Fazli, M.; Jalbout, A.F.; Raissi, H.; Ghiassi, H.; Yoosefian, M. *J. Theor. Comput. Chem.* **2009**, *8*, 713–732.
- (13) Gora, R.W.; Grabowski, S.J.; Leszczynski, J. *J. Phys. Chem. A* **2005**, *109*, 6397–6405.
- (14) (a) Cleland, W.W.; Kreevoy, M.M. *Science* **1994**, *264*, 1887–1890; (b) Frey, P.A.; Whitt, S.A.; Tobin, J.B. *Science* **1994**, *264*, 1927–1930; (c) Warshel, A.; Papazyan, A.; Kollman, P.A. *Science* **1995**, *269*, 102–106.
- (15) Cleland, W.W.; Frey, P.A.; Gerlt, J.A. *J. Biol. Chem.* **1998**, *273*, 25529–25532.
- (16) (a) Lough, A.J.; Park, S.; Ramachandran, R.; Morris, R.H. *J. Am. Chem. Soc.* **1994**, *116*, 8356–8357; (b) Lee, J.C.; Peris, E.; Rheingold, A.L. *J. Am. Chem. Soc.* **1994**, *116*, 11014–11019; (c) Richardson, T.B.; Gala, R.H.; Crabtree, R.H.; Siegbahn, P.E.M. *J. Am. Chem. Soc.* **1995**, *117*, 12875–12876; (d) Custelcean, R.; Jackson, J.E. *Chem. Rev.* **2001**, *101*, 1963–1980.
- (17) Gerlt, J.A.; Gassman, P.G. *Biochemistry* **1993**, *32*, 11934–11952.
- (18) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **1994**, *116*, 909–915.
- (19) Nowroozi, A.; Raissi, H.; Farzad, F. *J. Mol. Struct.* **2005**, *730*, 161–170.
- (20) Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Zakrzewski, G.; Montgomery, J.A.; Stratmann, R.E.; Burant, J.C.; Dapprich, S.; Millam, J.M.; Daniels, A.D.; Kudin, K.N.; Strain, M.C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G.A.; Ayala, P.Y.; Cui, Q.; Morokuma, K.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Cioslowski, J.; Ortiz, J.V.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, L.R.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Gonzalez, G.; Challacombe, M.; Gill, P.M.W.; Johnson, B.; Chen, W.; Wong, M.W.; Andres, J.L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E.S.; Pople, J.A. *GAUSSIAN98 Revision A.6*; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (21) Rablen, R.P.; Lockman, J.W.; Jorgensen, W.L. *J. Phys. Chem. A* **1998**, *102*, 3782–3797.
- (22) Novoa, J.J.; Sosa, C.J. *J. Phys. Chem.* **1995**, *99*, 15837–15845.
- (23) Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (24) Beigler-Koenig, F.W.; Schonbohm, J.; Bsyales, D. *J. Comput. Chem.* **2001**, *22*, 545–559.
- (25) Beigler-Koenig, F.W.; Bader, R.F.W.; Tang, Y.H. *J. Comput. Chem.* **1982**, *3*, 317–328.
- (26) Bader, R.F.W.; Tang, Y.H.; Tal, Y.; Beigler-Koenig, F.W. *J. Am. Chem. Soc.* **1984**, *104*, 946–952.
- (27) Desiraju, G.R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: New York, 1999.
- (28) Shuster, P.; Zundel, G.; Sandorfy, C. *Hydrogen Bonding*; North Holland: Amsterdam, 1976.
- (29) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486–1493.
- (30) Buemi, G.; Zuccarello, F.; Venuvanalinam, P.; Ramalingam, M. *Theor. Chem. Acc.* **2000**, *104*, 226–234.
- (31) Coppens, P. *X-Ray Charge Densities and Chemical Bonding*; Oxford University Press: Oxford, 1997.
- (32) Nothing like a complete literature survey of charge density studies in the field of hydrogen bonds can be given here. For a small selection of recent examples, see (a) Mallison, P.R.; Wozniak, K.; Wilson, C.C.; McCormack, K.L.; Yufit, D.S. *J. Am. Chem. Soc.* **1999**, *121*, 4640–4646; (b) Arnold, W.D.; Sanders, L.K.; McMahon, M.T.; Volkov, A.V.; Wu, G.; Coppens, P.; Wilson, S.R.; Godbout, N.; Oldfield, E. *J. Am. Chem. Soc.* **2000**, *122*, 4708–4717; (c) Macchi, P.; Iversen, B.; Sironi, A.; Chakoumakos, B.C.; Larsen, F.K. *Angew. Chem.* **2000**, *112*, 2831–2834; (d) Gopalan, R.S.; Kumaradhas, P.; Kulkarni, G.U.; Rao, C.R.N. *J. Mol. Struct.* **2000**, *521*, 97–106.
- (33) (a) Bader, R.F.W. *Atoms in Molecules A Quantum Theory*; Oxford University Press: Oxford, 1990; (b) Bader, R.F.W.; Popelier, P.L.A.; Keith, T.A. *Angew. Chem.* **1994**, *106*, 647–659; (c) Bone, R.G.A.; Bader, R.F.W. *J. Phys. Chem.* **1996**, *100*, 10892–10911; (d) Bader, R.F.W. *J. Phys. Chem. A* **2000**, *102*, 7314–7323.
- (34) Bader, R.F.W.; MacDougall, P.J.; Lau, C.D.H. *J. Am. Chem. Soc.* **1984**, *106*, 1594–1605.