View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by Crossref

http://www.e-journals.net

ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
Vol. 5, No.4, pp. 884-893, October 2008

Tautomerism of 5-Methyl Imidazolidine Thio Derivatives in the Gas Phase: A Density Functional Study

ZAKI S SAFI[#] and FAKHR M ABU-AWWAD[*]

[#]Department of Chemistry, Al Azhar University-Gaza, Gaza City, Palestine.
[*]Department of Chemistry, The Islamic University of Gaza, Gaza City, Palestine.
fmacm@mail.iugaza.edu

Received 11 December 2007; Revised 29 January 2008; Accepted 13 February 2008

Abstract: Relative tautomerisation energies, enthalpies, entropies, Gibbs free energies, and dipole moments for 5-methyl-2,4-dioxo-imidazolidine and its thio analogous have been studied in the gas phase using hybrid density functional at the B3LYP level of theory using 6-31(d) and 6-311+(2df,2p) basis sets with full geometry optimization. A comparative investigation of their energies revealed that the keto form of the compound is the predominant tautomer with a very high tautomeric energy barrier. The findings conclude that the intramolecular prototropic tautomerisation process is thermodynamically unfavored.

Keywords: Imidazolidine, B3LYP, Tautomerism, Dipole moment.

Introduction

The prototropic tautomerisation and intramolecular proton transfer of the keto-enol reactions of heterocyclic systems with several basic centers, O, N and S atoms, are of great interest to medicinal and biochemical applications. Also, understanding of the relative stabilities of heterocyclic tautomers and any subsequent conversions between tautomeric forms is very vital for both structural chemists and biologists[1,2]. Along this line, relative stabilities of various tautomeric structures of five-, six- (oxo and thioxo groups in positions 2 and 4 respectively) and seven-membered heterocyclic rings (oxo and thioxo groups in positions 3 and 5 respectively) were investigated using both theoretical and experimental tools[3-11]. Both tools indicate that in these compounds the thioxo, dioxo or dithio tautomer is most stable.

Particularly important are hydantoins for having different therapeutic activities including anticonvulsants, antiarrhythmic, bactericides, fungicides, and anticancers. Their anticonvulsant activity has been investigated for tens of years[12-17]. Hydantoins molecules

form two chains linked by N-H . . . O hydrogen bonds, from which inversion centers create a chain of rings. The chemical reactivities of hydantoins are primarily determined by the stability of their corresponding tautomers[18].

The common studies of tautomerisation of carbonylic and thiocarbonylic compounds such as uracil, thiouracil, 1,2,4-triazepines, oxazolidine and thiazolidine, can anticipate that 5-methyl-2,4-dioxo-imidazolidine and its thio analogous may exhibit five different tautomeric structures with different conformations. These tautomers have been covered extensively in the literature. However, this study employs density functional theory (DFT) on the corresponding potential energy surface (PES) aiming at further investigation of those structures and to present a complete analysis of their relative stabilities in the gas phase. This work includes exploring the energetic barrier and consequently the thermodynamic feasibility of every possible tautomerisation. Also, the impact of substitution on the optimized geometric parameters including bond lengths, bond angles and bond densities is analyzed.

Computational methods

The B3LYP hybrid density functional was employed to fully optimize molecular geometries of four imidazolidine derivatives in the gas phase, namely: 5-methyl-2,4-dioxo imidazolidine (1), 5-methyl-2-thio-4-oxo-imidazolidine (2), 5-methyl-2-oxo-4-thio-imidazolidine (3), and 5-methyl-2,4-dithio-imidazolidine (4), respectively[19,20]. A total of thirty six different forms were optimized using the 6-31G(d) basis set and then to obtain structural, electronic and energetic information. The harmonic vibrational frequencies were also calculated at the same level of theory to ensure that each stationary point corresponds to a true local minimum on the potential energy surface (PES) and transition state (TS), and to estimate the zero-point energy (ZPE) corrections. A similar procedure was adapted to locate the transition states (TSs) associated with prototropic tautomerisation processes. The TSs have been named by indicating the two minima that they connect.

Subsequent calculations of the single point energies of all the systems included in this study have been performed using B3LYP\ 6-311+(2df,2p) level of theory to obtain more reliable energies of both local minima and the transition states. Also, relative energies were computed by subtracting the most stable energy after including the corresponding ZPE corrections scaled by an empirical factor[21] of 0.9806. Enthalpies ΔH, and Gibbs free energies ΔG, were calculated by considering the thermal corrections at 298.15 K and the values obtained for the entropy by using the harmonic vibrational frequencies.

The basis set superposition error (BSSE) is not taken into consideration in this study because for the employed DFT and DFT/HF hybrid methods, this error is usually small when the basis set expansion is sufficiently flexible[22]. Finally, the charge densities and electron densities were mapped by means of the atoms in molecules (AIM) theory of Bader through locating the relevant bond critical points[23,24]. All DFT calculations were carried out using the Gaussian 03 software package while AIM calculations used AIMPAC program.

Results and Discussion

Tautomerisation

Figure 1 displays the 9 different conformers for each of the five different tautomeric compounds 1-4 which are under investigation in this work. Therefore, a total of 36 structures have been optimized, local minima of the PES have been assured, positive harmonic frequencies have been checked-out, and a single-point runs at the B3LYB/6-311+(2df,2p) level of theory have been computed for the most stable conformers of each tautomer. The optimized geometries of the 36 structures and another 16 transition states are available from the authors upon request.

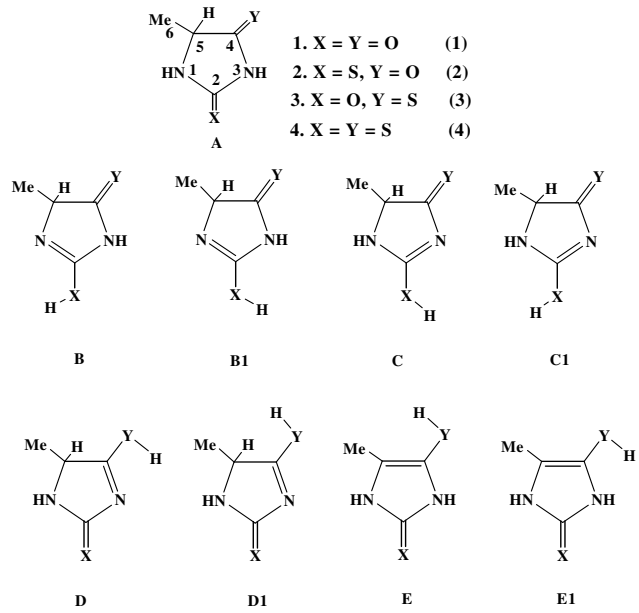


Figure 1. Different tautomeric forms of 5-methyl-2,4-oxo / thio-imidazolidine.

The calculated values of dipole moments μ, and the corresponding relative energies ΔE, ΔH, ΔG, and entropies ΔS, in kcal/ mol for all the systems including transition states considered in this study are listed in Table 1.

For 2,4-dioxohydantoin, several experimental techniques and high level computations have revealed that the tautomer A is predominant in both gas and solution phases[25]. Along this line, our current DFT calculations agree with these previous findings, where for all compounds and in all cases probed, the tautomer A is the lowest energy structure with energy preference of 2.5 kcal/mol compared to tautomer 4E of 5-methyl-imidazolidine-2,4-dithione compounds.

For dioxo derivatives (1), the computed order of stability of tautomers in gas phase was rated as A > B ≈ D > C > E. These findings agree with published theoretical and experimental studies for hydantoin which also concluded that the dione tautomer, A is the most stable one[25]. Contrary to Kleinpeter *et al*, tautomers B and D are almost degenerate while the relative stabilities of tautomers C and E are reversed[25]. However, tautomers B and D are the most stable tautomers amongst all the enolic structures where they are 17.4 kcal/mol less stable than tautomer A. Though tautomers B and D are degenerate, conformer B1 is favorable than conformer D1 by 0.3 kcal/mol of stability.

The disparity in the stability order can be attributed to the presence of the electron-donating CH_3 group, substituted at position 5 within the hydantoin ring. It should be noted that the two carbonyl groups on positions 2 and 4 are competitors.

For 5-methyl-2-thio-oxo-imidazolidine system (2), the stability revealed from data in Table 1 comes in the order of A > D > C > E > B. The energy difference between gas phase tautomer A, the most stable tautomer of (2), and tautomer D, as the second most stable one, is about 13.8 kcal/mol. Therefore, a negligible expected amount of gas phase tautomer D would be in equilibrium with tautomer A. Evidently, the calculations here concluded that the gas-phase tautomerisation process of the O atom at position 4 is favored over the S atom at position 2.

Table 1. Relative energies (kcal/mol), Enthalpies (298 K, kcal/mol), Gibbs free energies (298 K, kcal/mol), and Dipole moments (in Debye) for the different 5-methyl-2,4-oxo/thio-imidazolidine compounds studies.

	(1)				(2)				(3)				(4)			
	ΔE	ΔH	ΔG°	μ	ΔE	ΔH	ΔG°	μ	ΔE	ΔH	ΔG°	μ	ΔE	ΔH	ΔG°	μ
A	0.0	0.0	0.0	2.6	0.0	0.0	0.0	3.5	0.0	0.0	0.0	2.9	0.0	0.0	0.0	3.4
B	17.4	17.1	17.4	2.5	18.9	18.8	18.9	1.9	14.3	14.5	14.4	3.4	13.5	13.7	13.6	2.9
B1	23.5	23.5	23.5	3.1	24.7	24.8	24.6	2.2	15.7	15.9	15.8	3.5	14.9	15.2	15.1	2.7
C	19.0	19.0	19.0	5.0	16.8	17.0	17.0	5.0	19.7	19.7	19.8	6.0	17.1	17.4	17.3	5.9
C1	25.6	25.6	25.6	7.1	18.3	18.5	18.5	6.6	26.5	26.4	26.6	8.0	18.8	19.0	19.0	7.4
D	17.4	17.4	17.4	7.5	13.8	14.0	14.1	6.2	17.3	17.2	17.3	5.0	15.3	15.5	15.4	6.0
D1	23.8	24.0	24.0	7.5	15.4	15.7	15.9	8.5	23.5	23.7	23.6	6.6	16.6	16.9	16.8	7.6
E	21.5	22.2	20.8	5.0	17.5	18.0	17.7	7.2	6.0	6.4	6.3	3.5	2.6	2.9	2.8	5.5
E1	21.6	22.1	21.9	3.8	17.6	17.9	17.9	6.1	6.0	6.4	6.3	3.5	2.6	2.9	2.8	5.5
TS (A-B)	53.5	53.4	53.5	0.5	55.3	55.3	54.7	0.9	42.6	42.5	42.5	0.8	43.2	43.2	43.2	0.8
TS (A-C)	51.4	51.4	51.4	4.5	40.2	40.1	39.5	4.7	52.1	52.0	52.2	5.1	40.2	40.2	40.2	5.2
TS (A-D)	54.3	54.2	54.2	4.3	41.0	40.9	40.3	5.3	55.2	55.2	55.5	4.4	42.0	41.8	41.9	5.2
TS (A-E)	78.0	78.1	78.1	3.6	75.6	75.4	74.7	3.0	44.7	44.6	44.7	3.0	44.6	44.5	44.68	5.5

For 5-methyl-2-oxo-4-thio-imidazolidine (3), the data listed in Table 1 show that the most stable conformers in the gas phase are following the trend A > E > B > D > C. The most stable diketo tautomer A, is about 6.0 kcal/mol more stable than the most stable enolic structure, E. Noticeably, the same trend remains valid when the dithio system (4) is being investigated where the most stable enolic conformer, E is less stable than A tautomer by about 2.6 kcal/mol.

Prototropic tautomerisation

A possible prototropic tautomerisation in the gas phase is being explored by analyzing the energy profiles of the transition states connecting the keto form of A, the most stable tautomer from one side, and at the other side one of the two most stable enolic structures of each of our systems. Energy profiles computed at B3LYP/6-311+G(2df,2p)//B3LYP/6-31(d) level of theory are shown in Figure 2(a-d). Activation energy barriers of all possible transition states involved in the mechanisms are also depicted in the same figure, as well as the relative energy values corresponding to the most stable tautomers as listed in Table 1.

For 5-methyl-2,4-dioxo-imidazolidine system (1), as illustrated in Figure 2a, the tautomers B and D are degenerate. However, the transition state TS(A-B) is 0.8 kcal/mole more stable than the transition state connecting between A and D, TS(A-D). In other words, the 1,3 hydrogen shift from tautomer A to tautomer B through the TS(A-B) is favored over the 1,3 hydrogen shift from tautomer A to tautomer D through TS(A-D) by 0.8 kcal/mol. This indicates that the intramolecular prototropic tautomerisation at the oxygen atom attached to position 2 is energetically favored over the corresponding oxygen atom attached to position 4. Obviously, because of the high energy barrier, the intramolecular prototropic tautomerisation is thermodynamically unfavored.

For 5-methyl-2-thio-4-oxo-imidazolidine (2), as shown in Figure 2b, though the enol form D, is more stable than the enol form C by 3 kcal/mol, the activation barriers of their tautomerisation processes are about 41.0 and 40.2 kcal/mol respectively. These findings may suggest that formation of enol form C through the transition state TS(A-C) is energetically favored over formation of enol form D through the transition state TS(A-D) by about 0.8 kcal/mol. Therefore, the intramolecular 1,3 hydrogen shift at the heteroatom (S atom) attached to position 2 is energetically favored over the corresponding heteroatom (O atom) attached to position 4.

Similarly, for 5-methyl-2-oxo-4-thio-imidazolidine, (3), and 5-methyl-2,4-dithio-imidazolidine (4), E is the most stable tautomer among all the enolic forms and tautomer B comes second most stable. However, the computed activation barriers of a possible tautomerisation from A-B through the transition state TS(A-B) is lower than that of A-E through the transition state TS(A-E).

It is worth mentioning that contrary to what have been concluded about uracil, thiouracil, and oxo/thio triazepines that their tautomerisation are favored at any S atom regardless of its position; tautomerisation here is thermodynamically favored at position 2, regardless of the type of the heteroatom attached to it.

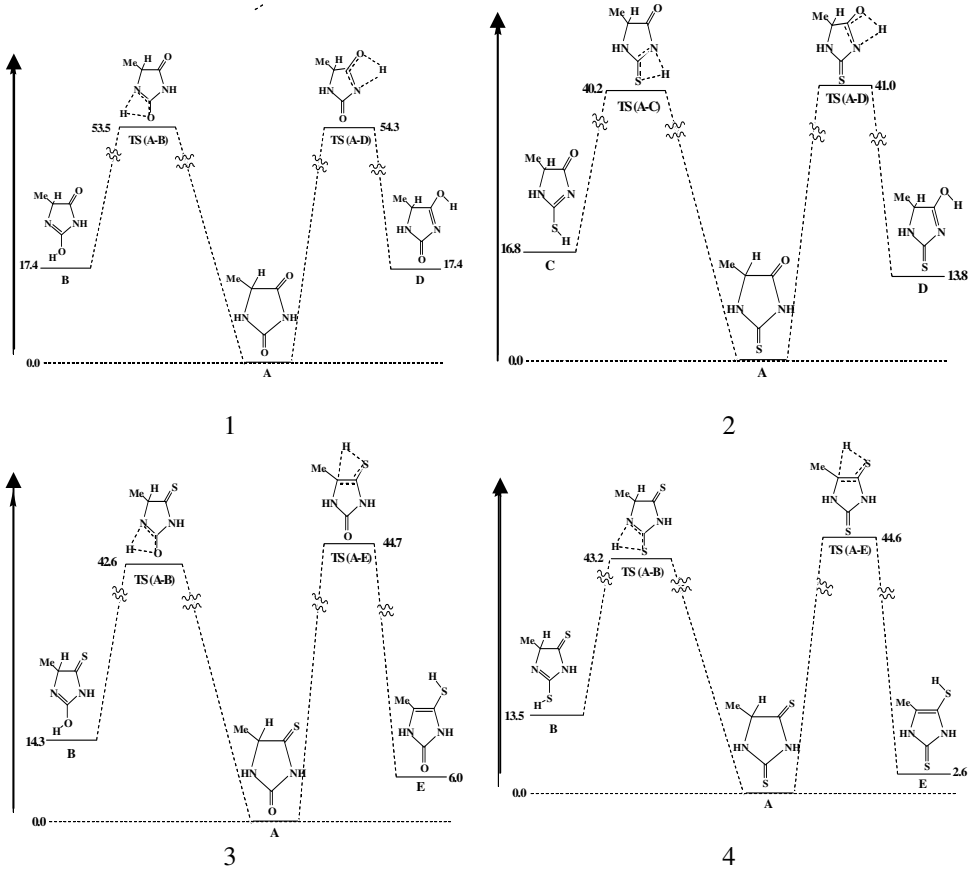


Figure 2. Energy profiles corresponding to the unimolecular tautomerization processes of 5-methyl-2,4-oxo/thio-imidazolidine

Structure and bonding

The optimized geometry parameters (bond lengths R, bond angles A) for all the studied compounds 1-4, and their gas phase tautomeric forms were computed at the B3LYP method using 6-31G(d) basis set. Some geometric parameters of the tautomers A, D and E of the compounds 1-4 are listed in Table 2, while the other structural parameters are available from the authors upon request.

A systematic inspection of the most stable tautomers A, of all the species under investigation concludes that [Me-C5-N1] fragment has roughly the same geometrical parameters (Table 2). Also, the bonds C6-C5 and C5-N1 have about the same charge densities as well as electron densities at the bond critical points (Table 3). This may reveal that the impact of carbonyl and thiocarbonyl substituent is local and limited to the positions directly attached to the substituents, which are in a good agreement with the results obtained for the seven-membered triazepine ring[4].

Both Table 2 and Table 3 show that the structural features of N1-C2(O)-N2 or [N1-C2(S)-N2] and [N3-C4(O)-C5] or [N3-C4(S)-C5] fragments are dependant on the type of the substituent at position C2 or C4.

Table 2. Optimized geometrical parameter (bond lengths in Å), the values between brackets is for hydantoin adapted from Ref.

	1			2			3			4		
	A	D	E	A	D	E	A	D	E	A	D	E
N1-C2	1.374 (1.371)	1.387	1.383	1.356	1.369	1.366	1.367	1.384	1.397	1.351	1.364	1.378
C2-N3	1.413 (1.393)	1.441	1.398	1.392	1.418	1.378	1.424	1.448	1.387	1.400	1.423	1.368
N3-C4	1.379 (1.367)	1.280	1.387	1.385	1.286	1.383	1.356	1.281	1.406	1.362	1.288	1.401
C4-C5	1.541 (1.460)	1.515	1.355	1.539	1.511	1.360	1.535	1.528	1.362	1.532	1.523	1.365
C5-N1	1.458 (1.457)	1.447	1.417	1.458	1.451	1.408	1.459	1.446	1.394	1.462	1.450	1.389
C5-C6 (Me)	1.529	1.531	1.490	1.530	1.535	1.491	1.530	1.536	1.490	1.532	1.536	1.490
C2=X (O, S)	1.212 (1.222)	1.210	1.222	1.657	1.653	1.676	1.211	1.209	1.221	1.655	1.652	1.673
C4=Y (O, S)	1.212 (1.225)	1.335	1.359	1.210	1.331	1.355	1.646	1.761	1.757	1.644	1.755	1.758
N1-C2-N3	105.2 (107.4)	107.8	102.9	105.7	108.4	103.3	104.3	107.7	111.4	104.9	108.3	103.1
C2-N3-C4	113.5 (111.67)	106.1	110.8	113.7	106.4	111.2	114.5	106.7	107.3	114.7	107.1	111.7
N3-C4-C5	105.7 (106.8)	116.5	109.0	105.3	115.8	108.3	105.6	115.3	106.4	105.3	114.7	106.7
C4-C5-N1	101.7 (104.7)	97.2	105.1	101.2	96.8	104.6	101.9	97.7	112.2	101.3	97.2	105.9
C5-N1-C2	113.4 (109.4)	112.4	112.2	114.1	112.5	112.6	113.6	112.2	99.1	113.9	112.7	112.5

In the fragments [N1-C2(O)-N2] or [N1-C2(S)-N2], the calculations show that the bond distances of N1-C2 and C2-N3 in (1) and (3) respectively are longer than their counterparts in (2) and (4). Similarly, the same was observed for [N3-C4(O)-C5] and [N3-C4(S)-C5] fragments in (1) and (2) (or (3) and (4)). It is evident, from Table 2, that the bond lengths of N3-C4 and C4-C5 are longer for the 4-oxo than for the 4-thio derivatives. These findings are in good agreement with previously published findings of Lamsabhi *et al.*[4].

Table 3. Charge density (ρ), electron density (∇ (ρ), and energy density at the bond critical points (bcp) of tautomer A of 5-methyl-imidazolidine.

	(1)			(2)			(3)			(4)		
	ρ / a.u	∇ (ρ)	H(ρ) / a.u	ρ / a.u	∇ (ρ)	H(ρ) / a.u	ρ / a.u .	∇ (ρ)	H(ρ) / a.u	ρ / a.u	∇ (ρ)	H(ρ) / a.u
N1-C2	0.323	0.274	-0.476	0.330	0.261	-0.522	0.327	0.274	-0.495	0.333	0.257	-0.532
C2-N3	0.297	0.241	-0.402	0.308	0.252	-0.450	0.291	0.230	-0.382	0.304	0.246	-0.436
N3-C4	0.313	0.242	-0.477	0.309	0.241	-0.463	0.324	0.212	-0.522	0.320	0.213	-0.510
C4-C5	0.252	0.151	-0.206	0.253	0.152	-0.207	0.252	0.148	-0.205	0.253	0.150	-0.207
C5-N1	0.265	0.322	-0.187	0.264	0.185	-0.325	0.263	0.185	-0.321	0.262	0.182	-0.318
C5-C6 (Me)	0.246	0.141	-0.197	0.244	0.140	-0.196	0.244	0.139	-0.194	0.244	0.139	-0.195
C2=X (O, S)	0.416	0.003	-0.722	0.214	-0.022	-0.251	0.417	-0.002	-0.723	0.215	-0.024	-0.252
C4=Y (O, S)	0.412	-0.031	-0.706	0.414	-0.036	-0.709	0.220	-0.015	-0.263	0.221	-0.018	-0.264

In addition, charge densities of the bonds lengths of N1-C2 and C2-N3 are smaller for 2-oxo derivatives than their counterparts in the 2-thio-derivatives. The same trend is also true when the bond lengths of N3-C4 and C4-C5 of the 4-oxo derivatives are compared with their counterparts in the 4-thio derivatives (Table 4).

Table 4. Harmonic vibrational frequencies (ν=cm^{-1}) and infrared intensities (I) of the different 5-methyl-2,4-oxo/thio-imidazolidine compounds studies.

Assignment	(1)		(2)		(3)		(4)	
	ν	I	ν	I	ν	I	ν	I
C2=O stretch	1891	240.2			1887.0	660.0	-	-
C4=O stretch	1853	742.2	1863	420.0	-	-	-	-
C2=S stretch	-	-	1176	133.9	-	-	1147.0	142.1
C4=S stretch	-	-	-	-	1125.0	31.8	1280.0	101.6
N1-H stretch	3653	41.8	3656	50.1	3662.0	57.9	3658.0	68.9
N3-H stretch	3645	72.4	3643	86.9	3631.0	69.3	3625.0	73.4
N1-H bending	1438	16.7	1386	-	1492	-	1566	-
N3-H bending	1367	77.3	1409	-	1423	-	1566	-

Obviously, the tabulated results show that the geometrical parameters and charge densities are dependent on the substituents at positions 2 and 4. Also, the S atom is less electronegative than the O atom where C=O group depopulates the bonds to which it is attached to a greater degree.

The C2=O in N1-C2(O)-N3 fragment in the (3) (or (1)) compound appears redshifted in comparison with the counterpart C4=O in (2) (or (1)). Also, the stretching frequency band of the C=O bond is dependent on the relative position of the carbonyl group within the ring. Actually, the C2=O stretching band of (1) and (3) compounds appears at 1891 and 1887 cm^{-1}, respectively, whereas the C4=O stretching mode of the (2) and (1) has frequencies of 1853 and 1863 cm^{-1}, respectively (Table 4). This disparity in the frequency values can be explained in terms of the resonance between the C2=O and the two adjacent two nitrogen atoms. The C2=O linkage forms two resonances due to the conjugation of the lone pairs of the two adjacent nitrogen atoms with the carbonyl groups, while the C4=O is only involved in one resonance with the adjacent nitrogen lone pair. These predictions can be reached when the C=S stretching mode is considered, but in this case, and as it is well known, the C=S stretching mode appears usually coupled with other vibrational displacements.

Evidently, the intrinsic characteristics of the carbonyl and the thiocarbonyl groups change slightly depending on their relative positions within the ring. It is found that the carbonyl group attached to position 4 within the ring is stronger than the similar carbonyl group attached to position 2, as reflected in a smaller charge density at the bond critical point (Table 3), however they have almost the same bond length.

Our computed results indicate that the C2=S bond is longer than the corresponding C4=S bond by about 1.1 pm (Table 2). However, the former bond has a smaller charge density at the bond critical point than the later (Table 3).

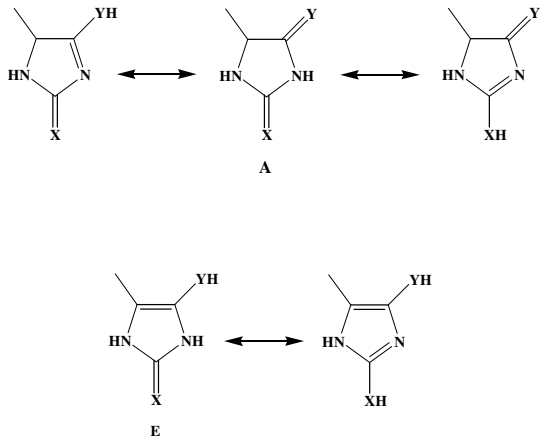
Another interesting example of the harmonic vibrational frequencies is shown in Table 4 that relates to the N-H stretching modes. The data indicates that in case of (1) compound, the N3-H stretching mode appears at 3646 cm^{-1}, while it is redshifted in all the systems when O atom is replaced by sulfur, except in the case of 5-methyl-2-oxo-4-thio-imidazolidine compound (3), which is blue-shifted by 16 cm^{-1}. The redshifted is maximum for the dithione derivatives, (4). These findings are in good agreement with previous experimental work of Rostkowska *et al* for 2-thio, 4-thio and 2,4-dithio uracil derivatives, and theoretical work of Lamsabhi *et al* for 3,5-oxo/thio 3,7-dimethyl-1,2,4-triazepines[26,4].

The C=O (or C=S) groups attached to positions 2 and 4 of the hydantoin ring are used here as an example to explore the effect of the intramolecular 1, 3-dydrogen shift on the geometrical parameters. This effect can be investigated through the alteration in the bond lengths of the C=O and the C=S groups. The ring nitrogen lone pair electrons is conjugated with the C=O group in amides or with C=S in thioamides.

For 5-methyl-2,4-dithio-imidazolidine- derivatives (4), it is evident from Table 2 that the C2=S bond in tautomer D is 0.3 pm shorter than that in tautomer A. It shows more double bond character because of lack of conjugation of the sigma lone pair in D. On the other hand, the C2=S bond length of the tautomer E has more single bond character and has a longer bond length than A by 1.8 pm. This inconsistency in the bond length of the C2=S can be explained in terms of the resonance available between C2=S and the adjacent –N3-H group. In this case, the nitrogen lone pair of electrons is more involved in resonance with the two C2=S groups attached to positions 2 and 4 (Scheme 1), which is reflected by the shorter bond lengths. The same trends were also observed when the C2=S bond of the (2) derivatives are explored.

For 5-methyl-2-oxo-4-thio-imidazolidine derivatives (3), the C2=O bond of tautomer D has more double bond character and shorter bond length than the same bond in tautomer A. However, the C2=O bond of tautomer E has more single bond character and longer bond

length than the same bond of tautomers A and B by 0.10 pm and 0.12 pm, respectively. The disparity in the length of C2=O bond could be attributed from one hand, to the involvement of the N3 lone pair in tautomer A in the resonance together with both C2=O and C4=S groups (see Scheme 1), while in tautomer E, on the other hand, the same N3 lone pair is involved with C2=O only in the resonance. Consistently, the C2=O has more single bond character than the corresponding bonds of tautomers A and D. The same trends were also observed when comparing the C2=O bond lengths of (1) derivatives.



Scheme 1.

Conclusion

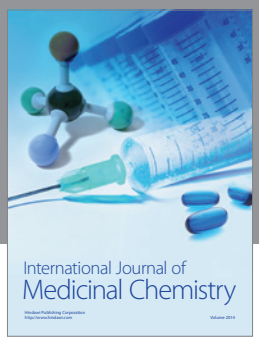
In summary, we may conclude that among all the investigated 9 tautomeric structures, diketo/dithione forms are predominant in gas phase and are thermodynamically more stable than enol/thiol forms, with a high energy barrier. On the other hand, contrary to previous findings for uracil, thiourcail and oxo/thio triazepines, the tautomerisation process was always favored at the hetero atom (sulfur or oxygen) attached to position 4 within the five-membered ring, though a competitiveness is clearly observed when the compound (1) is the system of concern.. Hence, the two oxygen atoms of the carbonyl groups attached to positions 2 and 4 have the same possibility to undergo the tautomerisation process.

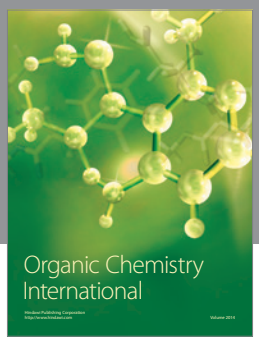
The computed relative energies of the enol/thiol forms with respect to its keto/thione forms are inversely proportional to the electronegativity, where the difference in the relative energies between those of dithione and thiol forms is smaller than those of diketo and enol forms. The tautomers' stability order is impacted by the electron donating group, CH_3 attached to position five in the hydantoin ring. The bond lengths, charge densities and the harmonic vibrations of the C=X (X=O and S) were investigated and showed small changes in their magnitudes as a result for tautomerisation.

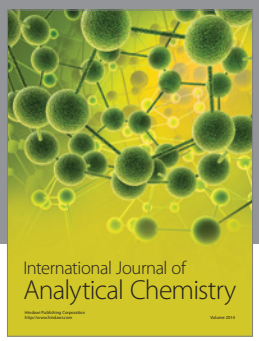
References

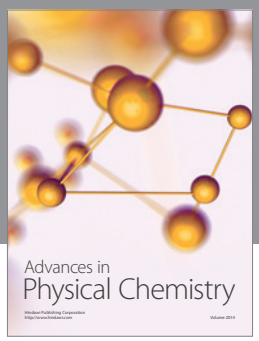
1. Elguero J, Katritzky A R, and Denisko O, *Adv Heterocycl Chem.,* 2000,**76**,1.
2. Minkin V I, Garnovski A D, Elguero J, Katritzky A R, and Denisko O, *Adv Heterocycl Chem.*, 2002, **38**, 1110.
3. Tahmassebi D, *J Mol Struct.,* (THEOCHEM), 2003, **638,** 11
4. Agelova S, Enchev V, Markova N, Denkova P and Kostova K, *J Mol Struct***.,** (THEOCHEM), 2004 **711**, 201.

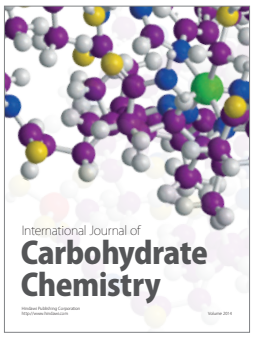
5. Santos M, Junior M, Oliviera S, da Silva J, Lima M, Lima M, Galdino S and Pitta I*, J Mol Struct*., (THEOCHEM), 2005, **715,** 191.
6. Lamsabhi M, Alcami M, Mo O, Bouab W, Esseffar M, Abboud J L M, and Yanez M, *J Phys Chem., A*, 2000, **104**, 5122.
7. Lamsabhi M, Esseffar M, Bouab W, El Messaoudi T, Abboud J L M, Alcami M, and Yanez M, *J Phys Chem., A*., 2002, **106,** 7383.
8. Allegretti P, Labadier G, Sierra M, and Furing J, *Afinidad LVII*, Enero-Febrero 2000**, 485**, 41.
9. Lamsabhi M, El Messaoudi T, Esseffar M, Esseffar, Alcami M, and Yanez M, *New J Chem.,* 2002*,* **26,** 711.
10. Yu F-L, Schwalbe C H, and Watkin D, *Acta Cryst.*, 2004, C**60,** 714.
11. K. Sabih and K. Sabih; *Anal Chem.*, 1969**, 41**, 1452.
12. Locock R A and Coutts R T, *Org Mass Spectrom*, 1970, **3(6)**, 735.
13. Camerman K and Camerman N, *Acta Cryst.,* 1971, **B27**, 2205.
14. Simig Gy, Lemport K, Tamas J, and Czria G, *Tetrahedron*, 1975, **31**, 1195.
15. Schmidt M W, Baldridge K K, Boatz J A, Jenesen J H, Koseki S, Gordon M S, Yadav A, and Yadav V K, *J Mol Struct.,* (THEOCHEM), 1994, **315**, 245.
16. Keinpeter E, *Struct. Chem.*, 1997, **8**, 161.
17. Nguyen K A, Windus T L and Albert S T, *QCPE Bull.,* 1990, **10**, 52.
18. Bovamick N and Clarke H T, *J Am Chem Soc.*, 1938, **60**, 2426; Piasek Z, Urbanski T *Tetrahedron Lett.,*, 1962, **16**, 723.
19. Becke A D, *J Chem Phys.*, 1993, **98**, 5648.
20. Lee C, Yang W, and Parr R G, *Phys Rev., B***, 1988, 37**, 785.
21. Scott A P and Radom L, *J Phys Chem.*, 1996, **100**, 16502.
22. Hertwig R H, Koch W, Schroder D, Schwarz H, Hrusak J and Schwerdtfeger P, *J Phys Chem.*, 1996, **100**, 12253.
23. Bader R F W, "Atoms in Molecules: A Quantum Theory", Clarendon Press Oxford Univ. Oxford, 1990.
24. Cheeseman J and Bader R F W have provided the AIMPAC package; 2000 Ed.
25. Kleinpeter E, Heydenreich M, Kalder L, Koch A, Hennig D, Kempter D, Benassi R, and Taddei F, *J Mol Struct,* 1997**, 403,** 111.
26. Rostkowska H, Szezepaniak K, Nowak M J, Leszezynski J, Kubulat K and Person W B, *J Am Chem Soc.*, 1990, **112**, 2147.

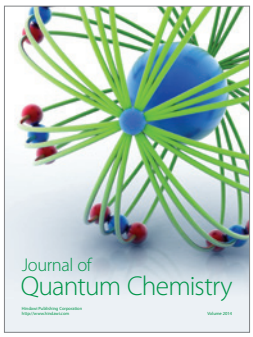


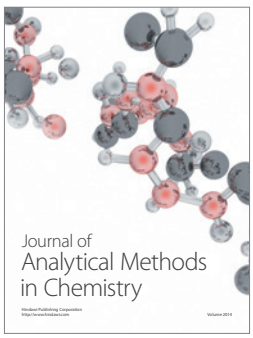


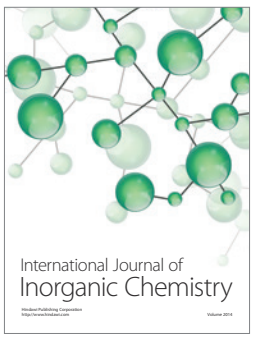


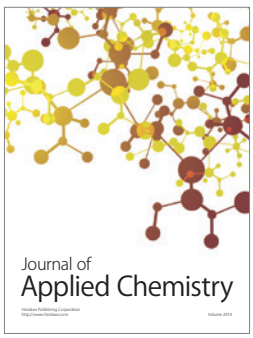


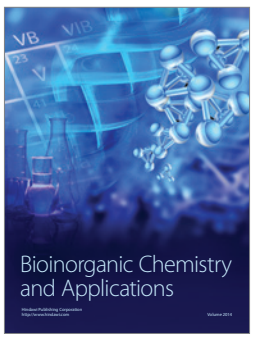


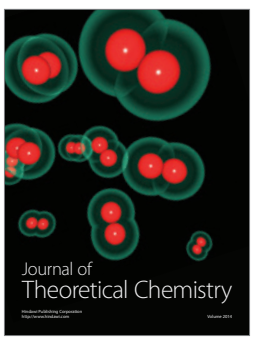


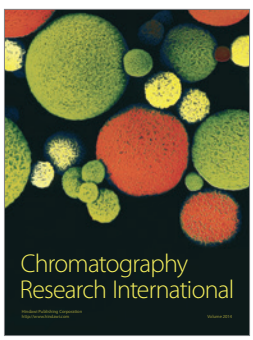


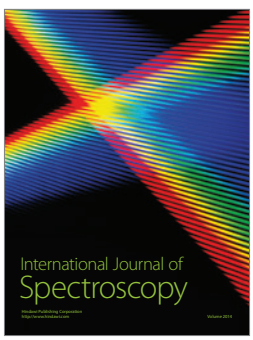












Hindawi

Submit your manuscripts at
http://www.hindawi.com