

AM1 Study of Intramolecular Hydrogen Bonding in the Dithio Analogues of Malondialdehyde and Acetylacetone

Giuseppe Buemi

*Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6,
95125 Catania, Italy*

All the molecular structures of the dithioanalogues of malondialdehyde and acetylacetone were fully optimized by the AM1 method in order to study the thioketo-enethiol tautomerism and to evaluate the hydrogen-bond strength. Whilst the hydrogen-bonded tautomer of the dithioacetylacetone is still predicted to be the most stable conformer, an enethiol *trans* structure of dithiomalondialdehyde is calculated to be slightly more stable than the hydrogen-bonded one. In any case an equilibrium between more than two enethiol conformers is to be expected, with an insignificant percentage of the diketo tautomer. The hydrogen-bond strengths are 18.06 and 15.66 kJ mol⁻¹ in dithiomalondialdehyde and dithioacetylacetone, respectively. The H-centred structure is the most probable transition state in the proton-transfer process and a barrier lower than that in the corresponding oxygenated compounds is predicted.

The keto-enol tautomerism of malondialdehyde and acetylacetone has been widely studied from the experimental as well as from the theoretical point of view.^{1,2} The most recent results indicate the two equivalent asymmetrical enol structures as the most stable, while the symmetrical C_{2v} enol conformation is the transition state in the proton-transfer process.^{2,3} The strong hydrogen bond present in the enolic malondialdehyde and acetylacetone is the main factor in determining the stabilization of these forms, together with the conjugation of the double bonds, which is absent in the keto conformers. When the oxygen atoms of these molecules are substituted by sulphur to obtain the dithio analogues, rather different stabilization and hydrogen-bonding energies are expected. This is principally due to the increased size of sulphur with respect to oxygen (which implies longer bond lengths) and its lower electronegativity.

Although β -dithioketones have still not been synthesized, to the best of our knowledge, the role of hydrogen bonding in the dithiomalondialdehyde enethiol conformers has been investigated⁴ by means of the Boyd-Whitehead CNDO/B procedure:⁵ a very weak hydrogen bond and a very high activation energy to the enethiol-enethiol conversion were predicted, but no complete geometry was reported. Indeed, the knowledge of the behaviour of sulphur in the intramolecular H-bonds is an interesting and fascinating problem and deserves to be investigated thoroughly and compared with the H-bond between oxygen atoms.

In a previous paper² we studied malondialdehyde and acetylacetone by using the most recent semiempirical method AM1,⁶ which was shown to evaluate in a reliable way both molecular geometries and hydrogen bond strength.^{2,7-10} In the present paper we discuss the molecular structures and hydrogen bonds of the simplest β -dithioketones, dithiomalondialdehyde (I) and dithioacetylacetone, or pentane-2,4-dithione, (II). Since all calculations were performed by the same method and by adopting the same options, the present results are directly comparable with those previously obtained for malondialdehyde and acetylacetone.²

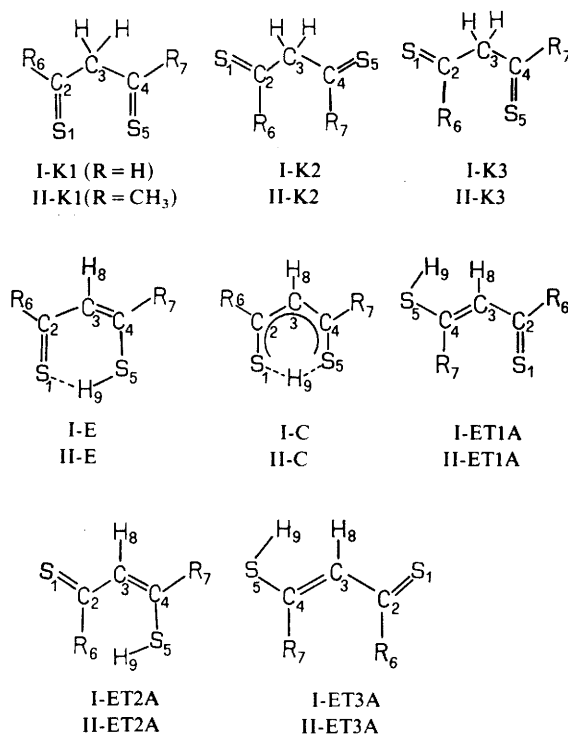


Fig. 1. Possible isomers of dithiomalondialdehyde (R = H) and dithioacetylacetone (R = CH₃), and related numbering system.

Calculations

All the possible conformers of dithiomalondialdehyde (I) and dithioacetylacetone (II) were fully optimized at AM1 level, taking into account also the correlation energy by inserting in the calculations all the configurations arising from the two highest occupied and the two lowest virtual molecular orbitals. Calculations were carried out on a VAX-STATION-2000 computer using the AMPAC package furnished by QCPE.^{6b} No geometrical restriction was imposed except the equality of all the C-H bond lengths and the H-C-C bond angles of the methyl groups. These were always free to rotate in order to reach the most favoured conformation.

Results and Discussion

Molecular Structure

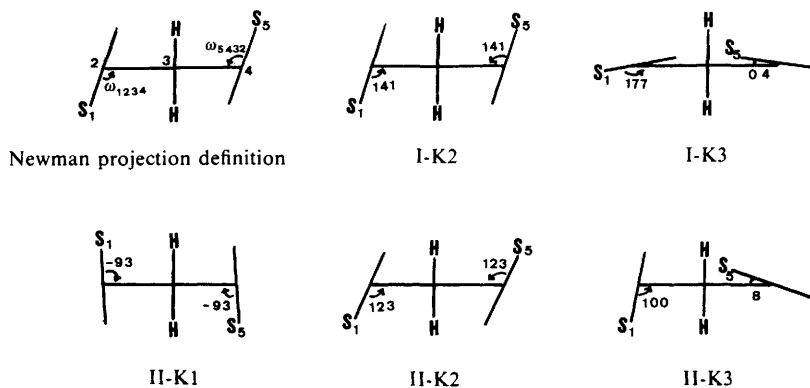
Fig. 1 shows the three thio-keto and the five enethiol conformers of the dithiomalondialdehyde and dithioacetylacetone, together with the adopted numbering system. The geometries obtained for the thio-keto tautomers of I and II are reported in table 1. Since optimization leads to non-planar forms, a Newman-type projection is given in fig. 2 for a better pictorial representation.

Analogous to what was found for malondialdehyde,² the repulsion between the two hetero-atoms in the *cis* position (S₁ and S₅ in this case) does not allow the existence of the *cis* diketo I-K1 conformer, which, through rotation of the S=C-H framework around the single C₂-C₃ and/or C₃-C₄ bonds, reaches the symmetrical, *trans* I-K2 and I-K2' structures. The latter differs from I-K2 in having the torsional angles $\omega_{1234} =$

Table 1. Optimized geometries of dithiomalondialdehyde (**I**) and dithioacetylacetone (**II**) keto conformations

	I-K2	I-K2'	I-K3	II-K1	II-K2	II-K3
r_{12}	1.5316	1.5328	1.5328 ($r_{4-5} = 1.5322$)	1.5419	1.5421	1.5411 ($r_{4-5} = 1.5414$)
r_{23}	1.4846	1.4833	1.4823 ($r_{3-4} = 1.4826$)	1.4976	1.4946	1.4940 ($r_{3-4} = 1.4934$)
r_{26}	1.1050	1.1054	1.1073	1.4818	1.4821	1.4823 ($r_{4-7} = 1.4864$)
r_{3H}	1.1228	1.1297	1.1304	1.1262	1.1278	1.1285
$r_{CH(CH_3)}$	—	—	—	1.1200	1.1199	1.1196
δ_{123}	125.2	124.9	124.7 ($\delta_{3-4-5} = 128.3$)	122.5	122.0	122.1 ($\delta_{3-4-5} = 125.6$)
δ_{234}	112.3	113.9	116.0	112.1	113.8	115.8
δ_{326}	114.1	115.0	114.6 ($\delta_{3-4-7} = 112.0$)	114.6	115.2	115.0 ($\delta_{3-4-7} = 112.6$)
δ_{HC3H}	106.5	105.9	106.0	107.2	107.0	106.7
$\delta_{HCC(CH_3)}$	—	—	—	110.7	110.7	110.7
ω_{1234}	141.5	180.0	177.4	-93.3	122.7	100.3
ω_{5432}	141.5	180.0	0.4	-93.3	122.7	8.2
μ	0.373	0.877	2.156	1.062	0.570	3.580
ΔH_f	248.51	249.64	251.42	194.52	194.27	197.48

Bond lengths in Å, angles in degrees, dipoles in D, energies in kJ mol⁻¹.

**Fig. 2.** Newman-type projection of the non-planar dithioketo tautomers.

141.5° = ω_{5432} . I-K2 is 19.65 kJ mol⁻¹ more stable than the hypothetical planar *cis* form and only 1.1 kJ mol⁻¹ more stable than the IK2' form. Both of them can oscillate widely without appreciable changes in bond lengths and bond angles as their minima are in a very shallow potential-energy well. The substitution of H₂ and H₆ by CH₃ mainly causes a decrease of δ_{123} and a stretching of *ca.* 0.01 Å in r_{12} and r_{23} .

The minimum-energy geometries of dithioacetylacetone differ from those of **I** principally in the value of the torsional angle ω_{1234} . Here also we find two minima (for $\omega_{1234} = 93.3^\circ$ and $\omega_{1234} = 122.7^\circ$) separated by a very small maximum so that it can be argued that the R—C=S framework can oscillate freely from *ca.* 90° to *ca.* 140°. The planar structures of II-K₂ and II-K₃ are obstructed by the steric effects between the methyl groups in the former and between the methyl group and S atom in the latter.

More interesting than the diketo forms are the enethiol conformations, whose minimum-energy geometries are reported in tables 2 and 3. In all of them H₉ is constantly coplanar to the heavy-atom ring plane, deviations being negligible. In contrast to

Table 2. Optimized geometries of dithiomalondialdehyde (I) enol conformations

	I-E		I-C	I-ET1 ^a		I-ET2 ^a		I-ET3 ^a	
	H-bonded	open	H-centred	A	B	A	B	A	B
r_{12}	1.5490	1.5427	1.5934	1.5434	1.5438	1.5431	1.5428	1.5421	1.5420
r_{23}	1.4259	1.4308	1.3923	1.4334	1.4342	1.4312	1.4343	1.4341	1.4350
r_{34}	1.3612	1.3578	1.3923	1.3569	1.3572	1.3565	1.3563	1.3564	1.3570
r_{45}	1.6368	1.6497	1.5934	1.6458	1.6525	1.6459	1.6561	1.6419	1.6542
r_{26}	1.1086	1.1089	1.1053	1.1074	1.1075	1.1053	1.1066	1.1063	1.1066
r_{47}	1.1055	1.1030	1.1053	1.1040	1.1020	1.1051	1.1013	1.1023	1.1004
r_{38}	1.1083	1.1085	1.1049	1.1053	1.1053	1.1079	1.1068	1.1054	1.1057
r_{59}	1.3399	1.3264	1.5846	1.3253	1.3244	1.3238	1.3239	1.3249	1.3241
$r_{S1...S5}$	3.2854	3.1929	3.0277	—	—	—	—	—	—
$r_{S1...H9}$	2.2073	—	1.5846	—	—	—	—	—	—
δ_{123}	128.5	128.8	126.8	127.3	127.3	124.1	124.0	124.3	124.4
δ_{234}	128.9	129.0	126.0	124.4	124.1	126.7	125.1	122.6	122.4
δ_{345}	130.5	126.8	126.8	126.2	122.3	130.6	124.8	126.2	122.2
δ_{459}	103.0	100.5	97.5	102.8	101.4	103.9	101.2	102.8	101.3
$\delta_{S...H9...S}$	134.2	—	145.6	—	—	—	—	—	—
δ_{623}	113.5	112.9	117.1	113.7	113.7	116.9	115.9	115.7	115.7
δ_{743}	118.3	117.8	117.1	121.3	120.5	118.9	119.1	121.5	120.8
δ_{834}	116.5	116.6	117.0	113.7	113.7	117.5	118.3	120.7	120.5
μ	1.972	3.564	2.200	2.915	4.811	1.671	3.911	1.957	3.672
ΔH_f	196.78	214.85	216.64	196.87	202.10	198.69	203.43	192.54	199.46
barrier	32.06			31.62		30.14		32.15	
H-bond	18.06								

Bond lengths in Å, angles in degrees, dipoles in D, energies in kJ mol⁻¹. ^a In the conformers labelled B, H₉ is rotated by 180° with respect to the position shown in fig. 1.

malondialdehyde, where I-E was the most stable tautomer followed by the nearly isoenergetic I-ET1A and I-ET3A forms ($\Delta E \approx 8.4$ kJ mol⁻¹), I-ET3A is the most stable tautomer of dithiomalondialdehyde, followed by I-E, whose energy is comparable with that of I-ET1A ($\Delta E = 4.2$ kJ mol⁻¹). This different stability order is probably due to the dimensions of sulphur, which produces a steric effect and a deformation energy higher than oxygen does, as can be argued from the increased values of δ_{123} , δ_{234} and δ_{345} in the I-E tautomer of dithiomalondialdehyde with respect to the analogous tautomer of malondialdehyde. The enethiol form I-ET3A is 55.97 kJ mol⁻¹ more stable than the dithioketo form I-K2; this figure is lowered to 42.86 kJ mol⁻¹ if the correlation energy is omitted. Partitioning of the total energy shows that I-ET3A is favoured, with respect to I-K2, by the one-centre electron-electron repulsion, the two-centre core-electron resonance, the two-centre electron-electron repulsion and the two-centre core-core repulsion energy terms.

The S...S distance in I-E (3.2854 Å) is *ca.* 0.8 Å shorter than predicted by CNDO/B⁴ and shorter than the sum of the S atom van der Waals radii (3.70 Å). This occurs also in II, but substituting H₆ and H₇ by CH₃ groups changes the stability order, making the planar hydrogen-bonded II-E conformer of dithioacetylacetone the most stable structure, as in the parent acetylacetone. The calculated C=S bond lengths (*ca.* 1.54 Å in I and *ca.* 1.56 Å in II) are practically equal to the experimental bond length of carbon disulphide (1.553 Å¹¹) and 0.11–0.15 Å shorter than that in thiourea (1.71 Å¹¹), thioacetamide (1.713 Å¹¹) and 1-(1-methylcyclopropyl)-3-thioxobutan-1-one

Table 3. Optimized geometries of dithioacetylacetone (I) enol conformations

	II-E		II-C	II-ET1 ^a		II-ET2 ^a		II-ET3 ^a	
	H-bonded	open	H-centred	A	B	A	B	A	B
r_{12}	1.5603	1.5526	1.6049	1.5547	1.5550	1.5613	1.5593	1.5592	1.5587
r_{23}	1.4317	1.4382	1.3986	1.4376	1.4379	1.4343	1.4385	1.4373	1.4377
r_{34}	1.3684	1.3634	1.3986	1.3630	1.3638	1.3619	1.3603	1.3603	1.3613
r_{45}	1.6509	1.6651	1.6049	1.6705	1.6746	1.6621	1.6715	1.6738	1.6783
r_{26}	1.4905	1.4907	1.4866	1.4907	1.4899	1.4817	1.4805	1.4813	1.4812
r_{47}	1.4866	1.4853	1.4866	1.4758	1.4758	1.4908	1.4852	1.4768	1.4766
r_{38}	1.1097	1.1089	1.1058	1.1086	1.1093	1.1155	1.1114	1.1116	1.1128
r_{59}	1.3460	1.3294	1.5778	1.3240	1.3237	1.3198	1.3250	1.3239	1.3233
$r_{\text{CH}(\text{CH}_3)}$	1.1192	1.1194	1.1194	1.1200	1.1202	1.1198	1.1201	1.1200	1.1199
$r_{\text{S1}\cdots\text{S5}}$	3.2180	3.0540	3.0223	—	—	—	—	—	—
$r_{\text{S1}\cdots\text{H9}}$	2.0981	—	1.5778	—	—	—	—	—	—
δ_{123}	126.2	126.0	125.4	126.1	126.1	118.3	119.1	119.0	119.1
δ_{234}	130.1	128.9	127.6	128.0	128.1	134.0	130.0	130.0	130.1
δ_{345}	128.1	123.9	125.4	121.3	116.7	131.5	124.4	120.8	116.0
δ_{459}	102.3	100.5	97.5	102.6	102.2	105.0	101.1	102.7	102.3
$\delta_{\text{S-H9-S}}$	137.2	—	146.6	—	—	—	—	—	—
δ_{623}	114.1	113.7	116.9	113.9	113.8	122.7	120.2	120.8	120.9
δ_{743}	118.4	119.7	116.9	125.1	124.5	117.7	119.8	126.7	126.1
δ_{834}	115.8	116.8	116.2	117.9	117.4	114.2	116.5	117.2	116.6
$\delta_{\text{HCC}(\text{CH}_3)}$	110.6	110.7	110.6	110.7	110.8	110.7	110.8	110.8	111.0
ω_{1234}	-0.1	0.	0	0	0	180.0	180.0	178.6	178.3
ω_{5432}	0.	0.	0	180.0	180.0	0	0.	180.0	180.0
$\omega_{\text{H}745}$	-0.5	-59.9	0	0	0	7.8	60.4	-0.8	-1.6
$\omega_{\text{H}621}$	0.2	0.	0	0	0.6	0.7	0.	0.	-0.5
μ	2.764	3.879	3.093	2.701	1.817	2.103	4.236	2.269	4.483
ΔH_f	144.29	159.95	160.06	151.67	154.30	164.52	158.44	153.30	158.67
barrier		26.18	—		12.18		11.17		11.41
H-bond		15.66							

Bond lengths in Å, angles in degrees, dipoles in Debyes, energies in kJ mol⁻¹. ^a In the B-conformers H₉ is rotated by 180° with respect to the position shown in fig. 1.

(1.679 Å¹²). Also the C—S single bond (1.64–1.67 Å, according to AM1) is predicted to be *ca.* 0.15 Å shorter than that in methanethiol (1.819 Å¹¹), but very close to the values calculated by the same method in cyclic compounds, such as 1,4-dithiin, 1,4-dithiino[2,3-*c*;6,5-*c'*]disothiazole (1.67–1.69 Å¹³) and thieno[3,4-*b*]thiophene-2-carboxylic acid (1.67–1.71 Å¹⁴).

The S—H bond (1.339 Å in I-E, 1.3460 Å in II-E) is longer than that in the open structure of the same conformers (1.3264 Å in I-E, 1.3294 in II-E), indicating the presence of the hydrogen bond. On the other hand, a study carried out using the Schroeder-Lippincott potential function model¹⁵ predicted a minimum in the potential energy curve of the S—H ⋯ S bridge.¹⁶ The above S—H bond lengths agree well with those calculated by CNDO/B,⁴ as well as with the experimental data found for methanethiol and hydrogen sulphide (1.336 and 1.328 Å, respectively¹¹), and with the S—H bond lengths of 2-aminoethanethiol (1.371 Å¹⁷) from electron diffraction investigation.

The rotation barrier of H₉ (ΔE_{0-90}) is nearly constant in I (30–32 kJ mol⁻¹) and is comparable with the analogous barrier found for II-E (26.18 kJ mol⁻¹). On the contrary,

lower values (11–12 kJ mol⁻¹) were calculated for II-ET1, II-ET2 and II-ET3. This difference is attributed to the —CH₃ groups, whose interactions with neighbouring atoms increase the energies of the planar structures, thus decreasing the barrier values. In fact in II-E, where they are far enough from each other and from other atoms, the barrier is of the same order as that found in I.

From the I-E tautomer it is possible to obtain I-ET2A through rotation of the S₁=C₂—R₆ framework; in the same way it is possible to obtain I-ET1A starting from I-ET3A, and *vice versa*. The related torsional barriers, calculated as the difference between the energy of the conformation having the S₁=C₂—R₆ moiety rotated by 90° and the most stable planar conformer (ΔE_{0-90}) are 16.95 kJ mol⁻¹ for the I-E → I-ET2A (24.3 kJ mol⁻¹ in malondialdehyde) and 17.64 kJ mol⁻¹ for the I-ET3A → I-ET1A transformations (12.72 kJ mol⁻¹ for I-ET1A → I-ET3A in malondialdehyde). The analogous barriers for II are 15.78 and 4.75 kJ mol⁻¹ in the two cases, respectively. The barriers concerning the chelated I-E and II-E tautomers are higher because of the presence of the H-bond. The nearly equal barriers concerning the I-E → I-ET2A and I-ET3A → I-ET1A pathways at first sight seem to be anomalous, as there is no H-bonding involvement. However, in our opinion, these can be justified bearing in mind the remarkable difference in the bond angles of I-ET3A and I-E, which suggests a minor deformation energy contribution in the former tautomer and is likely to be responsible for the total energy of I-ET3A being lower than that of the chelated I-E form.

Finally it is noteworthy that the two most stable tautomers of I (I-ET3A and I-E) and II (II-E and II-ET1A) are predicted to show comparable dipole moments (*ca.* 2 and *ca.* 2.7 D,[†] respectively).

Hydrogen Bonding

The hydrogen bond between two atoms, A and B, originates mainly from electrostatic interactions, and its strength is relevant when A and B are strongly electronegative (*i.e.* for oxygen, nitrogen and fluorine). The Pauling electronegativity for sulphur is 2.5, *i.e.* higher than that for hydrogen (2.1), but much lower than that for oxygen (3.5), therefore the intramolecular hydrogen bonding in β -dithioketones, if any, must be less strong than in β -diketones.

The existence of an intramolecular hydrogen bond in the I-E and II-E chelated tautomers of dithiomalondialdehyde and dithioacetylacetone can be inferred from the following considerations, deduced by analysing both the geometrical parameters (tables 2 and 3) and the net charge densities: (i) the S—H bond in the chelated structures is longer than in the open ones; (ii) the S...S distance (3.2854 Å in I-E, 3.2180 Å in II-E) is shorter than the sum of the S atom van der Waals radii; (iii) only in I-E and II-E does the S₁ atom show a small negative charge, thus making possible a weak attractive S...H interaction; in all the other isomers S₁ and S₅ are both positively charged.

The attribution of a numerical value to the strength of intramolecular hydrogen bond is not simple because it is affected by energy contributions (*e.g.* strain energy and/or interaction between non-bonded atoms) which cannot easily be quantified. By assuming the energy difference between the H-bonded and the open structures of I-E and II-E as the most reliable estimation of the hydrogen-bond energy, values of 18.06 kJ mol⁻¹ for dithiomalondialdehyde and 15.66 kJ mol⁻¹ for dithioacetylacetone were obtained. These figures are about half of those found for malondialdehyde and acetylacetone (37.4 and 32.8 kJ mol⁻¹, respectively), thus indicating a weaker hydrogen bond, as expected. In both cases we found a non-linear hydrogen bond; the S—H...S angles being 134.2° in I-E and 137.2° in II-E, *i.e.* not far from the values of 134.6° and 136.3° calculated for the corresponding conformers of malondialdehyde and acetylacetone.²

[†] 1 D = 3.335 64 × 10⁻³⁰ C m.

The above H-bond strengths are stronger than those predicted by CNDO/B (6.2 kJ mol^{-1} ⁴) and by the potential function model (from 0.4 to 4.2 kJ mol^{-1} ¹⁶). However, it is noteworthy that the S...S distances reported in ref. (4) and (16) range from *ca.* 4 to 4.3 \AA , *i.e.* they are longer than the sum of the S atom van der Waals radii (3.70 \AA). Moreover the S...S distance and the hydrogen-bond energies from the potential-function model are highly dependent on the molecular geometry and on $\theta_{\text{H-S...S}}$ (bent angle). The H-bond energies of ref. (16) were calculated for θ ranging from 40 to 50° , which is larger than the θ values obtained by us for I-E (28.8°) and II-E (26.3°).

It is interesting to note that the S...O distance in non H-bonded molecules containing the open conjugated five-membered 'ring' typical of thioxoaldehydes has been found¹⁸ to range from *ca.* 2.4 to 2.9 \AA by *ab initio* calculations (STO-3G and 3-21G basis sets), in agreement with X-ray diffraction data.¹⁹ These distances are shorter than the sum of S and O van der Waals radii (3.25 \AA) as a consequence of not yet fully understood non-bonded S...O interactions. Similar interactions could also occur between O...O and S...S pairs to give O...O and S...S distances close to those predicted by AM1 in the open I-E and II-E structures of dithiomalondialdehyde and dithioacetylacetone and in the corresponding oxygenated analogues.

The energies of the H-centred conformations I-C and II-C are higher than those of I-E and II-E, so that they represent the transition state in the proton-transfer pathway from one enethiol form to the other: the activation energies ($19.86 \text{ kJ mol}^{-1}$ in I and $15.77 \text{ kJ mol}^{-1}$ in II) are far lower than those calculated for the corresponding oxygenated parents (99.08 and $94.22 \text{ kJ mol}^{-1}$ for malondialdehyde and acetylacetone, respectively²).

The analysis of the total energies of the various tautomers suggests that dithiomalondialdehyde may exist as a mixture of more than two enethiol conformers and the percentage of the dithio keto forms would be very low. An analogous conclusion can be drawn for the dithioacetylacetone.

Conclusions

The AM1 results concerning dithiomalondialdehyde and dithioacetylacetone predict molecular structures very similar to those found for the oxygen analogues,² but the I-ET3A tautomer of dithiomalondialdehyde is slightly more stable than the H-bonded I-E, probably because its bond angles are less deformed with respect to the standard values. However, on the grounds of the total energies, an equilibrium among more than two tautomers is to be expected in both molecules.

The hydrogen-bond strengths are weaker than in malondialdehyde and acetylacetone, but stronger than predicted by CNDO/B and by the potential function model. The transition states in the proton-transfer process are the H-centred structures I-C and II-C, which imply a barrier of $19.86 \text{ kJ mol}^{-1}$ in I and $15.77 \text{ kJ mol}^{-1}$ in II.

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References

- 1 J. Emsley, *Struct. Bonding* (Berlin), 1984, **57**, 147.
- 2 G. Buemi and C. Gandolfo, *J. Chem. Soc. Faraday Trans. 2*, 1989, **85**, 215.
- 3 K. Iijima, A. Ohnogi and S. Shibata, *J. Mol. Struct.*, 1987, **156**, 111.
- 4 L. Carlsen and F. Duus, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1080.
- 5 R. J. Boyd and M. A. Whitehead, *J. Chem. Soc., Dalton Trans.*, 1972, 73; 78; 81.
- 6 (a) M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902; (b) Q.C.P.E. program no. 506.
- 7 G. Buemi, F. Zuccarello and A. Raudino, *J. Mol. Struct. (Theochem.)*, 1988, **164**, 379.

- 8 F. Zuccarello and G. Buemi, *Gazz. Chim. Ital.*, 1988, **118**, 359.
- 9 M. Masamura, *J. Mol. Struct. (Theochem.)*, 1988, **164**, 299.
- 10 M. Masamura, *J. Mol. Struct. (Theochem.)*, 1988, **168**, 227.
- 11 *Tables of Interatomic Distances and Configurations in Molecules and Ions*, Special Publication No. 18 (The Chemical Society, London, 1965).
- 12 L. Norskov-Lauritsen, L. Carlsen and F. Duus, *J. Chem. Soc., Chem. Commun.*, 1983, **496**.
- 13 G. Buemi and C. Gandolfo, *J. Mol. Struct. (Theochem.)*, 1989, **187**, 325.
- 14 G. Buemi, *Bull Chem. Soc. Jpn*, 1989, **62**, 1262.
- 15 R. Schroeder and E. R. Lippincott, *J. Phys. Chem.*, 1957, **61**, 921.
- 16 W. R. Snyder, H. D. Schreiber and J. N. Spencer, *Spectrochim. Acta, Part A*, 1973, **29a**, 1225.
- 17 S. L. Barkowski and K. Heldberg, *J. Am. Chem. Soc.*, 1987, **109**, 6989.
- 18 J. G. Ángyán, R. A. Poirier, Á. Kucsman and I. G. Csizmadia, *J. Am. Chem. Soc.*, 1987, **109**, 2237.
- 19 (a) A. Hordvik, E. Sletten and J. Sletten, *Acta Chem. Scand.*, 1969, **23**, 1377; (b) J. A. Kapecki, J. E. Baldwin and I. C. Paul, *J. Am. Chem. Soc.*, 1968, **90**, 5800; (c) C. Cohen-Addad, M. S. Lehmann, P. Becker, I. Parkanyi and A. Kálmán, *J. Chem. Soc., Perkin Trans. 2*, 1984, 191; (d) J. G. Ángyán, Á. Kucsman, R. A. Poirier and I. G. Csizmadia, *J. Mol. Struct. (Theochem.)*, 1985, **123**, 189. (f) J. P. De Barbeyrac, D. Gonbeau and G. Pfister-Guillozo, *J. Mol. Struct.*, 1973, **16**, 103.

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