On Hydrogen Bonding in the Intramolecularly Chelated Tautomers of Enolic Malondialdehyde and its Mono- and Dithio-analogues

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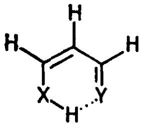
The intramolecular hydrogen bondings in enolic malondialdehyde and its mono- and dithio-analogues have been evaluated by a semiempiricial SCF–MO–CNDO method. The calculations predict that the hydrogen bonds play an important part in the stabilities of malondialdehyde and monothiomalondialdehyde,† whereas dithiomalondialdehyde‡ hardly exists as a hydrogen-chelated tautomeric form.

IN recent years a considerable amount of work has been devoted to studies, experimental [1-3] as well as theoretical,[4,5] of the structure of the planar intramolecularly chelated enolic tautomers of diacylmethanes. The parent compound, enolic malondialdehyde (1),[1-5] has been specially studied with the intention of establishing a possible asymmetric (C_s) or symmetric (C_{2v}) structure for the molecule. However, the available data about the structure of (1) are not definitive and, sometimes, apparently contradictory.[5]

Recently a theoretical contribution of major importance on the hydrogen bonding in enolic malondialdehyde (1) has appeared,[5] reporting on the structure of (1) as a function of the intramolecular O–O distance. The authors conclude that at O–O distances up to *ca.* 2.3 Å (1) exhibits C_{2v} symmetry, whereas C_s symmetry is preferred for r(O–O) above *ca.* 2.3 Å. In agreement with these results we have found that a complete geometry–energy optimization of (1) by the CNDO/B procedure [6] predicts r(O–O) 2.289 Å and affords a potential energy minimum corresponding to the C_{2v} structure. The OH bond lengths are calculated to be 1.154 Å.



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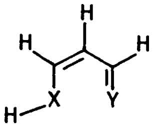

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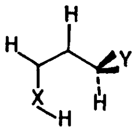

C

(1) X = Y = O
(2) X = O, Y = S
(3) X = S, Y = O
(4) X = Y = S

We have previously shown that the monothio-analogues of β-diketones, the β-thioxoketones, as well as the parent monothiomalondialdehyde, exist as rapidly interconverting intramolecularly chelated (*Z*)-enol and (*Z*)-enethiol tautomers.[7-9] No evidence was found for the presence of only one intermediary structure.[9] This is probably a reflection of the rather long S–O distances found for these compounds.[8] For the enol (2A) and enethiol (3A) tautomers of monothiomalondidehyde the SO distances were calculated to be 3.081 and 2.857 Å, respectively. Thus, both distances are considerably longer than the sum of standard OH and SH distances.[10] The enol (2A) was calculated to be the thermodynamically more stable tautomer by 40.1 kJ mol^{-1} relative to (3A),[9] in excellent agreement with experimentally obtained results.[7,8] The activation barrier for the enol to enethiol conversion was found to be *ca.* 45 kJ mol^{-1}.[9] This value is very close to previously reported activation barriers calculated for the enol–enol conversion in β-diketone systems.[5,10]

Although the dithio-analogues, β-dithioketones, have still not been reported synthesized, we have studied theoretically the enethiol tautomer (4A) of the parent dithiomalondialdehyde for comparison. A very long distance between the two sulphur atoms in (4A) is predicted, leading us preliminarily to the assumption that only a very weak hydrogen bond, if any at all, can exist in this compound. Furthermore, the enethiol–enethiol conversion is calculated to require an activation energy of 333 kJ mol^{-1}; this is more than seven times the activation energy for the above mentioned (2A) to (3A) conversion, suggesting an almost complete loss of the proton during the reaction.

Geometries and bonding energies for the structures under consideration were calculated by the Boyd–Whitehead CNDO/B procedure,[6] the bonding energies being minimized with respect to all internal valence coordinates. Relevant geometric data for structures (1A)—(4A) are given in Table 1. The structure of the asymmetrical C_s structure (1A) (hypothetical [10] according to our calculations) has, however, been minimized only with respect to $\mathrm{C\hat{O}H}$, the remainder being adapted from the HOC=CC skeleton in (2A) complementary with an experimentally obtained C=O distance.

TABLE 1

Geometric data for the tautomers (1A)—(4A)

	(1A)	(2A)	(3A)	(4A)
r(XH) (Å)	0.994 [a]	0.994	1.468	1.335
r(H · · · Y) (Å)	2.090 [a]	2.149	1.434	3.205
r(XY) (Å)	2.964 [a]	3.081	2.857	4.074
$\mathrm{C\hat{X}H}$ (°)	107.2	109.0	85.2	107.0

[a] These values are not geometry–energy optimized.

In order to obtain information about the relative

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† Systematic name 3-thioformylpropanal.

‡ Systematic name malondicarbothialdehyde.

magnitudes of the intramolecular hydrogen bonds in the tautomers (1A)—(4A) we have studied variations in bond energies, as well as variations in r(XH), r(XY), and $C\hat{X}H$, as functions of two different structural changes: (1) rotation (θ) 0—180° around the C–X bond, leading to the *exo*-structures (1B)—(4B), and (2) rotation (ω) 0—90° around the C–C bond, leading to structures (1C)—(4C).* Relevant geometric data for the structures B and C are given in Tables 2 and 3.

The changes in bonding energies brought about by the above mentioned structural changes (Table 4) are assumed to reflect mainly the ruptures of the hydrogen bonds. However, the transformations are believed also to effect energy changes owing to release in steric strain. An estimation of the relative energy changes connected with hydrogen bond rupture and strain release, respectively, is rather speculative, although our results (Table 4) nevertheless seems to indicate that strain energy release plays more important parts in compounds (3) and (4) than in (1) and (2). This is most clearly demonstrated by the transformation (4A) to (4C), where the rotation results in an energy gain of 8 kJ mol^{-1}. Here, the energy gain arising from the release of steric strain (originating from the two adjacent bulky sulphur atoms) in the *Z*-enethiol (4A) is greater than the small energy increase due to the rupture of the very weak hydrogen bond.

TABLE 2

Geometric data for the tautomers (1B)—(4B)

	(1B)	(2B)	(3B)	(4B)
r(XH) (Å)	0.994 [a]	0.962	1.335	1.333
r(XY) (Å)	2.964 [a]	2.547	3.592	4.024
$C\hat{X}H$ (°)	235.2	234.3	252.7	253.7

[a] These values are not geometry–energy optimized.

TABLE 3

Geometric data for the tautomers (1C)—(4C)

	(1C)	(2C)	(3C)	(4C)
r(XH) (Å)	0.976	0.976	1.336	1.335
$C\hat{X}H$ (°)	113.2	113.0	108.1	108.4

TABLE 4

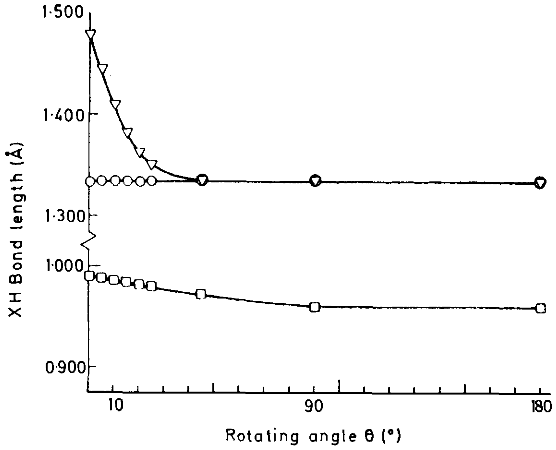
Bonding energy gains as results of rotations A→B and A→C for componds (1)—(4) (kJ mol^{-1})

Compound	$E^{A}_{bond} - E^{B}_{bond}$	$E^{A}_{bond} - E^{C}_{bond}$
(1)	−33.1	−23.2
(2)	−22.6	−23.8
(3)	−12.5	−8.9
(4)	−6.2	+8.0

The results given in Table 4 for compound (1A) should be regarded with some reserve owing to the incomplete minimization procedure carried out for this compound. Most probably the calculated ΔE values are too high. In spite of this, it is nevertheless noteworthy that the calculated hydrogen bond strength in (1A) is comparable with those in (2A) and (3A), and otherwise consistent with generally accepted OH · · · O hydrogen bond strengths.[12] Furthermore, the calculations predicts only a very weak hydrogen bond in (4A), which is also confirmed by the calculated values of r(SH) and $C\hat{S}H$ (Tables 1—3); these are both close to experimentally determined values [for methanethiol r(SH) 1.329 Å, $C\hat{S}H$ 100.3°).[13]

More interesting, however, is the study of the enol (2A) and enethiol (3A) tautomeric structures of the unsymmetrical β-thioxoketone system. Most striking are the calculated energy differences, predicting the OH · · · S hydrogen bond to be 2—3 times stronger than the O · · · HS hydrogen bond (Table 4). This is in excellent agreement with results reported by Snyder *et al.*,[14] who used the Schroeder–Lippincott potential function model of the hydrogen bond [15] to study properties of intramolecular OH · · · S and O · · · HS hydrogen bonds. Their results strongly indicate that sulphur may be a much better acceptor than oxygen in intramolecular hydrogen bonds. Furthermore, our predictions are in agreement with experimental results obtained from parallel studies,[8] where a negative reaction entropy for the enethiol to enol conversion in aromatic β-thioxoketones was determined.

The release of hydrogen bonds of considerable strength by the transformation A to B and A to C is further demonstrated by the changes predicted for r(XH), r(XY), and $C\hat{X}H$ (comparing Tables 1 and 2, and 1 and 3). However, it is important to note that the relative elongations of the XH bonds in XH · · · Y cannot be taken as direct measures for the respective hydrogen bond strengths. Hence, the OH bond in (2A) is elongated by *ca.* 3% relative to that in (2B), whereas the SH bond in (3A) is found to be *ca.* 10% longer than the SH bond in (3B). The XH bond lengths in the structures B and C are found to correspond to reported values.[13] The variations in the XH bond lengths as functions of



XH Bond lengths as functions of the rotating θ for the conversions (2A)→(2B) (□), (3A)→(3B) (▽), and (4A)→(4B) (○)

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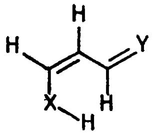
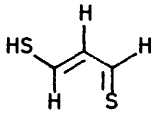
* The reliability of the CNDO/B estimates of hydrogen bond strengths was tested by calculating the potential-energy surface for the FHF$^-$ → FH + F$^-$ reaction. The hydrogen bond strength was determined to be 247 kJ mol^{-1}, which is in excellent agreement with previously reported experimental and theoretical (SCF–CI) data.[11]

the rotation angle θ, as depicted in the Figure, simply reflect the relative bond strength of the SH and OH bonds, the latter being *ca.* 125 kJ mol^{-1} stronger than the former, and consequently much less sensitive toward weak attractive forces such as hydrogen bonds. The changes in the XH bond lengths relative to the values calculated for the non-hydrogen-bonded tautomers B can be taken as reasonable measures of the extents of hydrogen bondings as functions of the rotation angle θ. It is seen (Figure) that the intramolecular hydrogen bonds in (2A) and (3A) are almost totally released upon rotation about the C–X bonds by 75 and 45°, respectively.

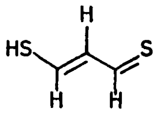
Our calculations predict that intramolecular hydrogen bonding plays a part as a stabilizing factor in (1)—(3), but hardly for (4). However, conjugation must necessarily also influence the choice of structure. Calculations on the planar rotamers D thus shown enhanced stabilization of this rotameric form of A compared with structures B and C. However, in the case of (4) the structure (4D) is even more energetically favourable than (4A) (ΔE 22.8 kJ mol^{-1}). This allows us to predict that β-dithioketones, whenever they appear as real substances, probably will exist in the D form, or, alternatively, in the *trans*-forms (4E and F), or, perhaps, even in the dithioxo-form (4G).



D



(4E)



(4F)

$HC(S)CH_2C(S)H$

(4G)

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