

Importance of steric effect on the hydrogen bond strength of malondialdehyde and acetylacetone 3-substituted derivatives. An *ab initio* study

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SUMMARY

The molecular geometries of various 3-substituted malondialdehyde and acetylacetone derivatives, in their chelate, open and H-centred conformations, were optimized and the hydrogen bond energies evaluated, in order to estimate the effect of 3-substitution steric hindrance on the hydrogen bond strength. Calculations were performed at the *ab initio* 3–21G and 6–31G** level, with and without correlation energy inclusion, using the Møller–Plesset approach (where possible) and the B3LYP functional. The frequencies of the O–H stretching mode were evaluated, too. The obtained results indicate that the C_s chelate conformations are the most stable structures. The O...O distances are rather longer than the values typical of the H-centred conformers, at least in gas phase. The strengthening of the hydrogen bridge, on passing from the parent to the 3-substituted derivatives, is not so relevant as expected on the ground of literature data, the maximum increase being about 21 kJ mol^{−1} (in 3-*t*-butyl-acetylacetone). An increase of the steric effect to stress the O...O distance caused the breaking of the hydrogen bridge instead of strengthening, so indicating that the literature X-ray geometries (in particular the O...O distances) are governed, at least partially, by crystalline forces. ©1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Malondialdehyde (MDA) and acetylacetone (pentane-2,4-dione, here labelled as ACAC) are the simplest compounds with strong intramolecular hydrogen bonding [1,2]. Several experimental data suggest that the strength of such a bridge is enhanced when the H atom in position 3 (see Figure 1) is substituted by electron-withdrawing groups [3], and it increases strongly when very cumbersome substituents are involved [4–8] because steric interactions push the two oxygen atoms closer to each other. In particular, X-ray diffraction and NMR studies on several acetylacetone derivatives with a variously substituted benzene ring as the 3-substituent group [4–8], indicate that the benzene ring is rotated by about 80–90° with respect to the chelate ring and that $r_{O...O}$ is about 2.41–2.42 Å, i.e. remarkably shorter than 2.512 Å [9] or 2.535 Å [10], the values found for ACAC from electron diffraction and X-ray structure determinations, respectively.

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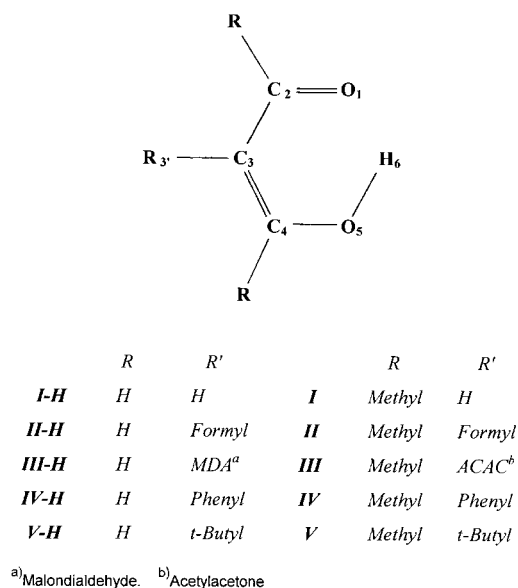


Figure 1. Molecules studied and the adopted numbering system

Following the semi-empirical relationship of Bellamy and Owen [11], which correlates the experimental $r_{O...O}$ values with the hydrogen bond strength and with the shift of the OH stretching mode, a reassignment of the IR spectra of the above cited compounds was proposed. In particular, the band of the OH stretching mode was located in the range of $1400\text{--}1600\text{ cm}^{-1}$, rather than in the range of $2500\text{--}2700\text{ cm}^{-1}$, which is the region characteristic of the most common hydrogen bonds [5]. Moreover, a hydrogen bond energy of at least 110 kJ mol^{-1} was suggested for 3-(2,4,6-trimethylbenzene)-acetylacetone [8].

Indeed, these conclusions do not seem to be in line with expectation since, as the 3-substituent ring is rotated by about 90° , one expects that conjugation and steric effects would not be very relevant, and, in any case, not sufficient to justify very remarkable $r_{O...O}$ shortening and very strong hydrogen bond energy variations. Results in line with such expectation, showing only a moderate increase of the hydrogen bond energy (E_{HB}) with respect to that of ACAC, were obtained by AM1 and PM3 calculations recently carried out on some of the compounds reported in References 4–8 [12]. Since semi-empirical methods suffer when evaluating correctly the repulsive interactions at very short O...O distances, the above results were not considered conclusive and a further *ab initio* study was performed on malondialdehyde [13] in order to inspect the shape of the potential energy well of the O–H...O bridge on varying the O...O distance and consequently to estimate which effects its evolution can induce on the energy of the bridge. Absolute values of the hydrogen bridge energy cannot be obtained because it is bound to the definition adopted for its estimate as well as to the sophistication of the method adopted for geometry optimization and correlation energy evaluation; here we will discuss the hydrogen bond strengthening as a variation of E_{HB} with respect to that of the parent compound. Our study on the potential energy well of malondialdehyde [13] gave the following conclusions:

1. the shift of the frequency of the OH group involved in a hydrogen bridge towards lower values with respect to that of an hydrogen bonding free OH groups stops when the potential well reaches a single minimum shape;

2. the low value of ν_{OH} is a consequence of the modification of the potential energy curve, i.e. it is bound to the molecular symmetry rather than to the O \cdots O distance;
3. the energetic cost of moving the two oxygen atoms close to each other until the single minimum potential well is reached is not relevant (10–15 kJ mol $^{-1}$);
4. a very rough estimate of the hydrogen bridge strengthening on passing from the C_s to the C_{2v} minimum energy conformation indicates that it should not be higher than 30 kJ mol $^{-1}$, at the most.

So, it could be possible that the very short O \cdots O distance in the above cited compounds is governed by crystalline forces rather than by an excessive steric effect and/or by the hydrogen bond strengthening.

In order to check the reliability of the above conclusion and to rationalize the literature experimental data, *ab initio* calculations were extended to some acetylacetone and malondialdehyde derivatives characterized by progressive increasing of the 3-substituent group dimensions (see Figure 1), including also the *t*-butyl group, which cannot decrease steric interactions through rotation as benzene can do. The results are discussed in this paper.

CALCULATIONS

All calculations were performed on a Digital ALPHA-3400 and a SUN Ultra1 workstations, by means of GAUSSIAN 92 and GAUSSIAN 94 programs [14,15]. The geometry of each molecule was fully optimized. The only restrictions were limited to the hydrogen atoms of the methyl groups, to which a dihedral angle of 120° with respect to each other was imposed. Moreover, in the H-centred structures (C_{2v} symmetry in the chelate ring), all the C–H bond lengths and the H–C–C bond angles of the methyl groups, with exclusion of the *t*-butyl group, were assumed to be equal to each other. However, test calculations carried out on acetylacetone (6–31G** basis) and on the H-centred structures of 3,3'-bis acetylacetone (3-21G basis) pointed out that when the equality of all of the CH bond lengths and HCC bond angles of methyl groups is imposed, the energy increases by only 0.66 kJ mol $^{-1}$ in the former (0.46 kJ mol $^{-1}$ in the open conformation) and 1.4 kJ mol $^{-1}$ in the latter case.

The 3–21G and 6–31G** bases, with and without correlation energy inclusion at the MP2 level, were selected for calculations, but owing to the relevant dimensions of the acetylacetone derivatives **III**, **IV** and **V** and the limited hard disk capacity, we were obliged to limit the calculations to the B3LYP [16–19] approximation when the latter basis was considered.

RESULTS AND DISCUSSION

Molecular geometry

In Tables 1 and 2, the C_s and C_{2v} optimized geometries of the parent malondialdehyde and acetylacetone are compared with those of the analogous conformations of their most hindered derivatives, obtained by the 6–31G** basis. Geometries coming from the less extended 3–21G basis, or without correlation energy inclusion, are omitted for space saving. Geometrical parameters for **II-H** and **II**, calculated at the same previous level are available in Reference 20, whilst results obtained by the semi-empirical PM3 method are reported in Reference 21.

Analysis of the geometrical parameters indicates that the main effect of 3-substitution is a lengthening of r_{2-3} , r_{3-4} and r_{5-6} , and a shortening of r_{4-5} , showing an increased conjugative effect (which appears more substantial within the B3LYP results) in the C=C–O–H framework. The O–H \cdots O angles are in

Table 1. Calculated and experimental molecular geometries of malondialdehyde and its 3-substituted derivatives (distances in Å, angles in degrees). Figures in parentheses refer to the geometrical parameters of the H-centred conformation

	I-H ^a MP2/6-31G**	I-H ^a B3LYP 6-31G**	I-H Exper. ^b	III-H MP2/6-31G**	III-H B3LYP 6-31G**	III-HP MP2/6-31G**	III-HP B3LYP 6-31G**	V-H MP2/6-31G**	V-H B3LYP 6-31G**
r ₁₋₂	1.249 (1.286)	1.245 (1.281)	1.234	1.247 (1.253)	1.244 (1.279)	1.250 (1.286)	1.247 (1.280)	1.250 (1.288)	1.247 (1.283)
r ₂₋₃	1.440 (1.397)	1.437 (1.400)	1.454	1.450 (1.402)	1.448 (1.410)	1.452 (1.409)	1.447 (1.411)	1.449 (1.405)	1.445 (1.407)
r ₃₋₄	1.363 (1.397)	1.368 (1.400)	1.348	1.371 (1.402)	1.377 (1.410)	1.377 (1.409)	1.382 (1.411)	1.370 (1.405)	1.374 (1.407)
r ₄₋₅	1.329 (1.286)	1.319 (1.281)	1.320	1.327 (1.253)	1.316 (1.279)	1.328 (1.286)	1.315 (1.280)	1.332 (1.288)	1.321 (1.283)
r ₅₋₆	0.994 (1.204)	1.007 (1.210)	0.969	0.995 (1.186)	1.009 (1.208)	0.997 (1.197)	1.016 (1.202)	0.995 (1.199)	1.009 (1.204)
r _{O1...O5}	2.592 (2.363)	2.555 (2.370)	2.553	2.583 (2.318)	2.533 (2.352)	2.524 (2.348)	2.480 (2.532)	2.553 (2.352)	2.514 (2.356)
r _{O1...H6}	1.697 (1.204)	1.643 (1.210)	1.68	1.688 (1.186)	1.617 (1.208)	1.622 (1.197)	1.551 (1.202)	1.653 (1.199)	1.594 (1.204)
δ ₁₋₂₋₃	123.5 (121.9)	123.4 (121.9)	123.0	123.9 (122.5)	123.9 (122.5)	124.2 (122.8)	123.9 (122.9)	124.6 (122.9)	124.5 (123.0)
δ ₂₋₃₋₄	119.5 (116.0)	118.9 (116.0)	119.4	118.3 (113.7)	117.2 (114.7)	116.1 (113.9)	115.3 (113.7)	116.9 (114.0)	116.2 (113.9)
δ ₃₋₄₋₅	124.5 (121.9)	123.9 (121.9)	124.5	124.9 (122.5)	124.5 (122.5)	125.2 (122.8)	124.8 (122.9)	125.1 (122.9)	124.7 (123.0)
δ ₄₋₅₋₆	105.4	105.5	106.3	105.6	105.6	105.7	105.4	105.5	105.5
δ _{O-H...O}	147.5 (157.9)	150.0 (156.7)	147.6	147.6 (155.4)	148.6 (156.4)	148.2 (157.4)	149.4 (156.2)	148.2 (157.6)	148.9 (156.4)
ω _{3-3'}				115.0 (90.0)	119.3 (90.0)	0.0	0.0	119.9 (59.9)	119.8 (60.0)

^aFor compound II-H see Reference 20. For the numbering system see Figure 1.

^bReference 22.

Table 2. Calculated and experimental molecular geometries of acetylacetone and its 3-substituted derivatives (distances in Å, angles in degrees). Figures in parentheses refer to the H-centred conformations

	I ^a MP2/6–31G**	I ^a B3LYP 6–31G**	I ^a Exper. ^b	III ^a B3LYP 6–31G**	III ^a Exper. ^c	V ^{a,d} B3LYP 6–31G**
r_{1-2}	1.254 (1.291)	1.252 (1.287)	1.243	1.254 (1.286)	1.295	1.267 (1.290)
r_{2-3}	1.446 (1.402)	1.442 (1.406)	1.430	1.457 (1.419)	1.411	1.461 (1.435)
r_{3-4}	1.367 (1.402)	1.374 (1.406)	1.382	1.390 (1.419)	1.395	1.411 (1.435)
r_{4-5}	1.335 (1.291)	1.325 (1.287)	1.319	1.321 (1.286)	1.310	1.315 (1.290)
r_{5-6}	0.999 (1.201)	1.013 (1.206)	1.049	1.022 (1.201)	–	1.050 (1.180)
$r_{O1...O5}$	2.559 (2.361)	2.519 (2.365)	2.512	2.464 (2.355)	2.424	2.360 (2.311)
$r_{O1...H6}$	1.646 (1.201)	1.586 (1.206)	–	1.516 (1.201)	–	1.371 (1.180)
δ_{1-2-3}	121.9 (120.5)	121.6 (120.3)	123.0	121.9 (120.9)	121.2	121.2 (121.3)
δ_{2-3-4}	120.6 (117.4)	120.0 (117.6)	119.7	117.4 (116.0)	117.9	114.1 (113.5)
δ_{3-4-5}	122.6 (120.5)	121.9 (120.3)	121.0	122.0 (120.9)	121.6	122.4 (121.3)
δ_{4-5-6}	105.2	105.2	81.0	105.4	–	104.8
$\delta_{O-H...O}$	150.8 (158.5)	150.8 (157.4)	137.0±7	151.8 (157.4)	–	153.9 (156.7)
$\omega_{3-3'}$				89.4 (90.0)	89.0	70.9 (101.2)

^aFor compound **II** see Reference 20. For the numbering system see Figure 1.

^bReference 9. According to this study H₆ lies out of the molecular plane ($\omega_{6-5-4-3} = 26^\circ$). The value of 81° for δ_{4-5-6} in our opinion is unreliable.

^cReference 23.

^d $\omega_{6-5-4-3} = -3.3$; $\omega_{1-2-3-4} = 4.7$.

the range of 148 – 154° in the chelate and 156 – 158° in the H-centred forms. Calculations, at any level of approximation, predict the chelate C_s structure as the most stable conformation for all of the compounds studied here.

Correction for the zero point vibration energy does not change the obtained stability order when correlation energy is evaluated at MP2 level. On the contrary, when the B3LYP functional is adopted, the above correction makes the energy of the H-centred structure lower than that of the chelate and open forms. This fact is not expected and does not appear to be justifiable because it occurs also for the parent compounds **I-H** and **I**, for which the C_s , chelate, form is indicated as the most stable conformation by all of the most recent theoretical and experimental findings. Since a trend opposite to that of the Møller–Plesset second order was noted also when correlation energy effects were analysed in a conformational analysis study of **II** and **II-H** [20], we suspect that the error, if any, is to be attributed to the B3LYP approach; therefore the zero point energy correction is neglected here. As discussed in Reference 20, the most stable conformation of compound **II-H** was predicted to be that with the C=O group *trans* with respect to the double bond of the chelate ring (see Figure 2), whilst for **II** the *cis* structure was found to be the preferred one.

Compounds **III-H**, and **III** differ from **II-H** and **II** by having a malondialdehyde or an acetylacetone framework as a 3-substituent group, instead of the formyl group; therefore the possibility that the C=C double bonds of the two component moieties are *cis* or *trans* to each other was taken into account. Whilst for **III** all calculations converge towards a single conformation characterized by a torsion angle around the C₃–C_{3'} bond ($\omega_{3-3'}$) in the range of 90° , for **III-H**, different results, depending on the adopted basis, were obtained. In particular, 3–21G, MP2/3–21G, B3LYP/3–21G and 6–31G** results, predicted $\omega_{3-3'}$ near 90° , whilst a torsion angle of about 60° or 120° between the C=C double bonds of the two malondialdehyde moieties were found according to MP2/6–31G** and B3LYP/6–31G** approaches, i.e. both *cis* and *trans* conformations are predicted. Inspection of the related energies indicates that the *cis* accommodation is slightly more stable than the *trans* one ($\Delta E_{cis-trans} = -0.87$

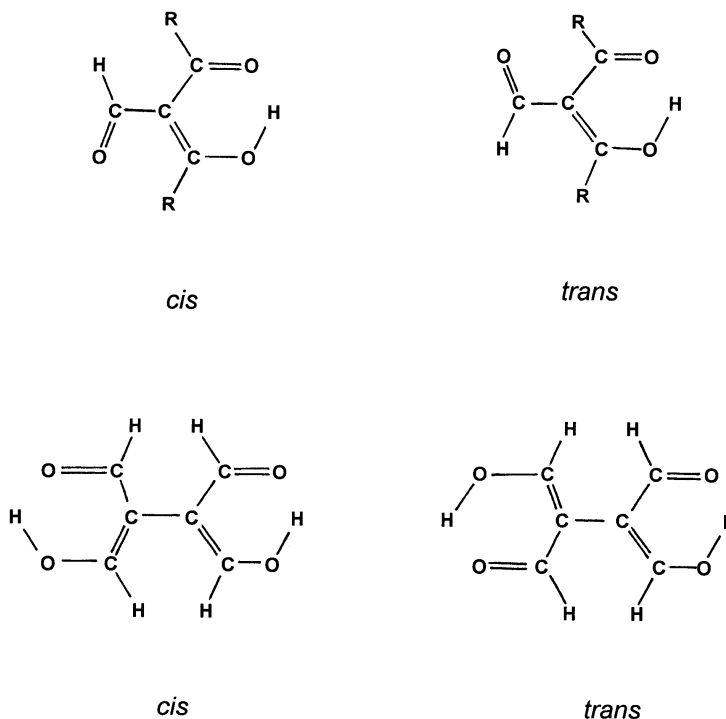


Figure 2. *cis* and *trans* Conformations of 3-formyl-malondialdehyde ($R = H$), 3-formyl-acetylacetone ($R = \text{methyl}$) and 3-3'-bis-malondialdehyde

and $-0.27 \text{ kJ mol}^{-1}$ according to MP2 and B3LYP, respectively), whilst the opposite is true for the open structures according to B3LYP ($\Delta E_{\text{cis-trans}} = +1.57 \text{ kJ mol}^{-1}$). The very low energy difference indicates that the stabilization due to conjugation is negligible or absent. When the molecular planarity is imposed, and therefore conjugation increases, the conformations with the $\text{C}=\text{C}$ double bond in the *trans* position become more stable than the *cis* ones ($\Delta E_{\text{cis-trans}} = 3.56$ and 2.51 kJ mol^{-1} , according to MP2 and B3LYP, respectively). This analogy with the results concerning **II-H** [20] confirms that the *trans* form is favoured by a better conjugation. The $\Delta E_{\text{cis-trans}}$ between the planar open structures (12.05 and $10.66 \text{ kJ mol}^{-1}$, according to MP2 and B3LYP) is rather higher than that between the chelate forms. This higher energy difference is due mainly to the greater steric effect occurring in the *cis* conformation between the H atom pairs bonded to C_2 and $\text{C}_{2'}$ and to C_4 and $\text{C}_{4'}$, which causes also a modest departure from planarity of the $\text{C}=\text{O}$ and $\text{O}-\text{H}$ groups ($\omega_{1-2-3-4} = \omega_{1'-2'-3'-4'} = 24.7^\circ$, $\omega_{6-5-4-3} = \omega_{6'-5'-4'-3'} = 173.0^\circ$ at the B3LYP level; lower values according to MP2).

The preferred H-centred conformation has the two malondialdehyde moieties perpendicular to each other (D_{2d} symmetry); the energy gain due to the increased conjugation when planarity is imposed (D_{2h} symmetry) is not sufficient for stability order inversion ($\Delta E_{D_{2h}-D_{2d}}$ is 23.95 and $17.65 \text{ kJ mol}^{-1}$ according to MP2 and B3LYP approaches).

Returning to the geometrical peculiarities, comparison between theoretical and experimental data also points out that the $\text{O} \cdots \text{O}$ distances of malondialdehyde and acetylacetone, coming from microwave [22] and gas phase electron diffraction [9] studies, respectively, were reproduced very well when the correlation energy is evaluated at the B3LYP level [20]. A less good agreement is found for **III**: here,

indeed, the experimental bond lengths are closer to those calculated for the H-centred conformations than to those of the minimum energy, C_s , geometry, and also the theoretical O \cdots O distance is rather different from the experimental 2.424 Å [23] value. Very likely, such disagreement depends on the fact that experimental data come from X-ray diffraction in the solid state, whilst the calculated ones refer to the gas phase. Support for this interpretation is given by the above cited good agreement between the B3LYP calculated O \cdots O distance of acetylacetone (2.519 Å) and the experimental one deduced by electron diffraction spectra (2.512 Å [9]), but also by the bad agreement with the datum coming from X-ray diffraction studies (2.535 Å [10]). So we conclude that in gas phase the acetylacetone moieties of **III** are rotated by about 90° with respect to each other: in such a condition they have nearly cancelled the steric effects between the methyl groups (which cannot be sufficiently reduced by the increase in the conjugation in a hypothetical planar structure) and each of them preserves the less stressed C_s symmetry typical of the parent compound **I**.

Hydrogen bonding

In contrast to the intermolecular hydrogen bonding, which is generally linear and whose strength is easily evaluable as the difference between the hydrogen-bonded adduct and the energy of the two separate molecule (preferably corrected for the basis set superposition error [24,25]), the intramolecular hydrogen bridge is non-linear (also in the H-centred conformations) and not easily quantitatively evaluable.

In studying the intramolecular hydrogen bridge strength of the title compounds we will use the term E_{HB} , defined as the stabilization of the chelate conformation with respect to the open one, which is usually identified with the *hydrogen bond energy*. In previous papers we have pointed out that this definition can be incorrect for defining the absolute energy of the bridge because it is affected by energy terms extraneous to the hydrogen bond (e.g. the different strain in the two conformations). Such datum can be used with confidence to compare different stabilities of the O–H \cdots O bridges within the same class of compounds, as in the present case. Moreover, it is important to bear in mind that the hydrogen bond energy as defined above cannot be taken as the real hydrogen bond strength because its values are strictly dependent on the method and the basis set adopted for calculating geometries, and the energies of the chelate and open conformations.

This is clearly evident from the data of Table 3 and it is confirmed also by the rather different value (53.4 kJ mol^{−1}) found by Gilli *et al.* [26] on the grounds of his resonance assisted hydrogen bonding (RAHB) model. Therefore the best way to compare the data obtained for the title compounds is to see the variation of E_{HB} with respect to the parent compounds **I** and **I-H**, respectively, because such difference can be associated with the strengthening of the hydrogen bridge.

Looking at the data reported in Table 3 one notes that (at the MP2/6–31G** level) E_{HB} values increase by about 10 kJ mol^{−1} on passing from malondialdehyde to acetylacetone, and this increase is accompanied by a shortening of 0.033 Å of the O \cdots O distance. The situation does not change appreciably when the correlation energy is calculated by the B3LYP functional. An analogous trend is noted at the MP2/3–21G level, but the E_{HB} increase and the $r_{O\cdots O}$ decrease are lower than those obtained by using the MP2/6–31G** approach.

From data concerning **III**, **IV**, **III-H** and **IV-H** (see Table 3), it can be seen that 3-substitution involving planar cumbersome groups causes only moderate $r_{O\cdots O}$ shortening, because the strong steric effect is decreased by the rotation around the C₃–C_{3'} bond. When steric hindrance cannot be decreased by rotation, as for the *t*-butyl group (**V** and **V-H**), the hydrogen bridge shows the shortest O \cdots O distance, independently of the calculation approach. Excluding the forced planar forms, the shortening ranges from a minimum of 0.14 Å (MP2/3–21G) to a maximum of 0.21 Å (6–31G**), on going from **I** to **V**. In

Table 3. O...O distances (Å) and E_{HB} values (kJ mol⁻¹) obtained for the studied compounds at various levels of *ab initio* calculations. For comparison purposes, the reported energies of **III-H** and **III** refer to a single hydrogen bridge

Comp.	3-21G		MP2/3-21G		6-31G**		MP2/6-31G**		B3LYP/6-31G**	
	$r_{\text{O...O}}$	E_{HB}	$r_{\text{O...O}}$	E_{HB}	$r_{\text{O...O}}$	E_{HB}	$r_{\text{O...O}}$	E_{HB}	$r_{\text{O...O}}$	E_{HB}
I-H	2.606	66.41	2.606	70.46	2.680	52.08	2.592	58.61	2.555	62.84
II-H^a	2.583	64.09	2.592	65.68	2.649	50.93	2.574	55.50	2.531	60.39
II-H^b	2.579	71.24	2.595	71.53	2.649	55.75	2.581	59.19	2.536	64.27
III-H^c	2.585	67.17	2.594	69.58	2.645	53.08	2.583	57.52	2.533	63.41
III-HP^c	2.565	69.68	2.554	72.84	2.586	55.03	2.510	65.40	2.480	70.51
III-H^d	—	—	—	—	—	—	2.579	57.30	2.531	62.49
III-HP^d	—	—	—	—	—	—	2.524	61.15	2.493	66.43
IV-H	2.587	67.10	2.595	69.83	2.645	53.26	—	—	2.526	64.64
IV-HP	2.530	74.28	2.546	75.88	2.578	58.96	—	—	2.480	70.70
V-H	2.564	70.81	2.577	73.61	2.614	56.28	2.553	61.89	2.514	67.43
I	2.563	70.50	2.583	77.09	2.627	63.09	2.559	67.94	2.519	72.86
II^a	2.479	87.59	2.511	85.30	2.514	71.50	2.469	75.19	2.439	81.21
II^b	2.464	93.10	2.501	88.40	2.503	80.66	2.459	83.55	2.423	90.55
III^c	2.508	82.35	2.552	78.30	2.543	68.05	—	—	2.465	78.03
IV	2.517	82.11	2.556	79.28	2.554	67.86	—	—	—	—
IV-P	2.368	109.45	2.410	103.60	2.383	87.03	—	—	—	—
V	2.397	99.41	2.443	97.49	2.417	79.71	—	—	2.360	94.37

^aFormyl C=O in *cis* position with respect to the C=C double bond of the chelate ring.

^bFormyl C=O in *trans* position with respect to the C=C double bond of the chelate ring.

^cC=C double bonds in *cis* position.

^dC=C double bonds in *trans* position.

^eExperimental $r_{\text{O...O}}$ value of 2.424 Å [13].

P indicates a forced planar conformation.

the corresponding malondialdehyde derivatives (**I-H-V-H**), where much lower repulsive interactions are present, the $r_{\text{O...O}}$ shortening is also much lower (from a minimum of 0.029 Å (MP2/3-21G) to a maximum of 0.066 Å (6-31G**)). In this series of compounds, E_{HB} undergoes negligible changes with respect to **I-H**. On the contrary, in the acetylacetone series more remarkable E_{HB} variations are evident, but the maximum predicted hydrogen bridge strengthening with respect to **I** is found for **V** and ranges from 17.57 to 21.51 kJ mol⁻¹, depending on the adopted basis set. In other words, the E_{HB} increase is not so relevant as argued from the geometrical experimental findings: this conclusion is in line with the results of our previous study on the potential energy well of malondialdehyde and confirms that part of the steric strain can be dampened by the hydrogen bridge without dramatic geometrical and/or energetic changes. Support for the present findings comes from literature data concerning eight 1,3-diaryl-1,3-propanedione enols [27], where steric hindrance causes $r_{\text{O...O}}$ to decrease from 2.502 to 2.432 Å accompanied by hydrogen bond strengthening much lower than the present ones (maximum strengthening of about 7 kJ mol⁻¹).

It is also noteworthy that E_{HB} concerning **III** is only 11.8 kJ mol⁻¹ higher than that of **I** according to 3-21G results, which scales to 5-6 kJ mol⁻¹ according to the 6-31G** and B3LYP/6-31G** level. It is lower than the E_{HB} found for **II**, where the steric effects are scarce, due to the modest dimension of the formyl group, and the hydrogen bridge strengthening is attributed nearly exclusively to the inductive effect and the increase in conjugation. Since in **III** the two molecular moieties are perpendicular to each other, the increase of conjugation with respect to **I** is excluded; the modest E_{HB} increase is attributed

to presence of a modest steric effect.

Compound **V** shows the shortest calculated O...O distance but its geometry still belongs to the C_s symmetry group. In compound **IV** $r_{O...O}$ is 2.517 Å according to 3-21G, and 2.55 Å according to MP2/3-21G and 6-31G** results. These distances are still far from the limit distance of 2.30 Å, characteristic of the H-centred structure. In order to obtain a shift of $r_{O...O}$ towards such a value, steric repulsions were artificially increased by progressively forcing a reduction in the phenyl group rotation in compound **IV** until complete coplanarity with the chelate acetylacetone ring is reached. The first interesting result obtained in such calculations was the impossibility of reaching such a planar minimum energy conformation without loosing the hydrogen bridge. In fact, for $\omega_{3-3'}$ lower than 60° the molecule tends to rotate the C=O and/or O-H groups to diminish its energy, whilst $r_{O...O}$ is still in the range of 2.5 Å. This fact seems to indicate that there is a limit to the hydrogen bridge stabilization, i.e. when $r_{O...O}$ is forced to diminish owing to steric hindrance, the related increase of the conjugation and the electrostatic attractive contributions are still not sufficient to balance the simultaneous increase of the repulsion terms. However in **V** a distance of about 2.4 Å, or lower if the B3LYP functional is used, is reached without significant planarity loss of the chelate ring. When full planarity to **IV** was imposed, $r_{O...O}$ shortens until 2.41 (MP2/3-21G), 2.383 (6-31G**) and 2.368 Å (3-21G) whilst E_{HB} increase up to more than 100 kJ mol⁻¹ (see Table 3). But such a forced situation is not reliable since in the planar open conformation $r_{O...O}$ is shorter (2.374 Å in MP2/3-21G; 2.372 Å in 6-31G**) than in the H-bonded one. Comparison of the geometrical parameters of **IV** and **V** allows the rationalization of the entire situation. In **V** there is a cumbersome group whose interaction with the methyl groups of the acetylacetone framework pushes the oxygen atoms towards each other. The strain is partially damped by the hydrogen bridge and by an adequate deformation of bond angles as well as by the stretching of the bond lengths of the *t*-butyl group (e.g. the C-C bond reaches 1.552 Å) with negligible rotation of the O-H and C=O groups involved in the hydrogen bridge. In **IV** the benzene ring cannot undergo relevant deformations and the increased strain originating from the forced planarity causes the breaking of the hydrogen bridge. When full planarity is imposed the molecule tries to diminish its remarkable strain by lengthening the bond lengths and by widening all of the bond angles, except for δ_{2-3-4} bond angle which is narrowed; this implies $r_{O...O}$ shortening and E_{HB} increase. But such a E_{HB} increase is only apparent and it is due mainly to the different strain in the H-bonded and open conformations, respectively. In other words, in the chelate structure the repulsive terms between the H and O atoms are far greater than those between the two oxygen atoms in the open structure. This fact confirms once again that in very stressed systems the stability difference between chelate and open conformations is no longer a measurement of the hydrogen bond energy.

Proton transfer barrier

For each compound studied here, optimization was extended also to its H-centred conformation, characterized by a C_{2v} symmetry imposed limitedly to the chelate ring: the energy difference between this and the minimum energy form represents the barrier to the proton transfer, i.e. the barrier to be overcome by the hydrogen atom involved in the hydrogen bridge when it passes from one to the other oxygen atom. Looking at Table 4, where such barriers are collected, one notes that the barrier decreases progressively following the shortening of the O...O distance. Since on shortening $r_{O...O}$, the potential energy well evolves from a double to a single minimum with consequent barrier disappearance, the barrier value is a probe for evaluating how distant the bridge is from the H-centred accommodation. Data in Table 4 indicate that **III** and **III-H** are more distant than the other compounds from a symmetric situation; this is also seen when the B3LYP results are considered.

Table 4. O...O distances (Å) and barriers to the proton transfer (kJ mol⁻¹) obtained for the studied compounds at various levels of *ab initio* calculations (*r*_{O...O} is that of the H-centred structures). For **III-H** and **III** the reported energies refer to a single hydrogen bridge

	3-21G		MP2/3-21G		6-31G**		MP2/6-31G**		B3LYP/6-31G**	
	<i>r</i> _{O...O}	Δ <i>E</i>	<i>r</i> _{O...O}	Δ <i>E</i>	<i>r</i> _{O...O}	Δ <i>E</i>	<i>r</i> _{O...O}	Δ <i>E</i>	<i>r</i> _{O...O}	Δ <i>E</i>
I-H	2.342	32.67	2.604	17.07	2.323	42.99	2.363	15.20	2.370	9.93
II-H^a	2.344	27.80	2.421	13.64	2.325	35.63	2.367	11.37	2.372	7.58
II-H^b	2.344	28.22	2.421	15.98	2.325	38.17	2.367	14.69	2.372	8.82
III-H^c	2.338	30.95	2.414	16.42	2.318	40.19	2.362	15.14	2.365	9.61
III-HP^c	2.324	32.96	2.400	15.82	2.305	40.88	2.348	14.70	2.352	9.48
III-H^d	—	—	—	—	—	—	2.362	11.28	2.365	7.25
III-HP^d	—	—	—	—	—	—	2.348	13.06	2.352	8.51
IV-H	2.337	32.21	2.413	16.77	2.317	41.32	—	—	2.363	8.95
IV-HP	2.325	27.95	2.400	13.97	2.307	35.52	—	—	2.353	6.91
V-H	2.329	35.52	2.404	19.23	2.310	43.72	2.352	16.47	2.356	10.92
I	2.340	22.23	2.413	16.60	2.319	32.26	2.361	13.52	2.365	8.12
II^a	2.325	19.84	2.400	10.62	2.307	24.84	2.351	8.14	2.352	5.90
II^b	2.325	15.82	2.400	9.24	2.307	22.45	2.351	7.39	2.352	4.10
III^c	2.329	24.70	2.409	12.45	2.308	31.92	—	—	2.355	7.14
IV	2.332	25.28	2.411	13.99	2.310	32.76	—	—	—	—
IV-P	2.276	11.69	2.347	5.23	2.261	14.76	—	—	—	—
V	2.284	19.78	2.356	11.86	2.266	23.57	—	—	2.311	6.47

^aFormyl C=O in *cis* position with respect to the C=C double bond of the chelate ring.

^bFormyl C=O in *trans* position with respect to the C=C double bond of the chelate ring.

^cC=C double bonds in *cis* position.

^dC=C double bonds in *trans* position.

^eExperimental *r*_{O...O} value of 2.424 Å [13].

P indicates a forced planar conformation.

O–H stretching frequency

Since the frequency of the O–H stretching mode is bound to the strength of the hydrogen bridge (which, in turn, depends on the O...O distance), calculation of the vibration spectra can give a very important contribution to the rationalization of the hydrogen bond energies. Owing to the relevant dimensions of the studied molecules and the limited hard disk capacity of the available computers, it was not possible to perform calculations at the MP2/6-31G** level, which were limited to the parent malondialdehyde and to the **II-H** molecules. So, to have homogeneous results, it was decided to perform such calculations using the B3LYP/6-31G** approach, for which very limited disk space is necessary. The most significant results coming from these calculations are collected in Table 5.

Notwithstanding numerous experimental and theoretical studies, the assignment of the IR spectrum of malondialdehyde and acetylacetone is still a debated problem. The frequency of the OH stretching mode of the former compound should be in the range of 2850–3100 cm⁻¹, but its most probable value is about 2860 cm⁻¹ [28,29]. The same band in the spectrum of acetylacetone should be at 2750–2800 cm⁻¹ [30–32].

For **I-H** our calculations predict the OH stretching frequency at 3319 and 3053 cm⁻¹ at the MP2 and B3LYP level, respectively, when the 6-31G** basis is used. When corrected by means of the scaling factor suggested for such methods (0.9434 for the former and 0.9613 for the latter [19]) the above values become 3131 and 2935 cm⁻¹. This last figure shows better agreement with the experimental data. The unscaled values for the open and H-centred conformations are also reported in Table 5. It is interesting

Table 5. Calculated vibrational frequencies (B3LYP/6–31G**) of the O–H stretching mode of the studied compounds (ν in cm^{-1})

Compound	Conformer		
	Chelate ^a ν	Open ^a ν	H-centred ^a ν
I-H	3053 (3319)	3834 (3897)	1894 (1721)
II-H (<i>cis</i>)	2913 (3204)	3812 (3870)	1886 (1898)
II-H (<i>trans</i>)	2938 (3266+3221) ^b	3818 (3878)	1885 (1898)
III-H (<i>cis</i>)	3015	3831	1886–1891
III-H (<i>planar</i>) ^c	2956; 2960	3828	1889–1894
V-H	3009 + 2983 ^b	3831	1895
I	2932	3808	1899
II (<i>cis</i>)	2553	3781	1885
II (<i>trans</i>)	2426	3792	1885
III	2778	3801	1891
V	2349	3781	1893

^aValues in parentheses are MP2/6–31G** results.^bCoupled with C₄–H stretching mode.^c*Trans* form.

to note that the value of 1721 cm^{-1} (MP2/6–31G**) concerning the H-centred form of **I-H** is about 200 cm^{-1} lower than that obtained for the same compound when $r_{\text{O}\cdots\text{O}}$ was fixed to 2.3 \AA (1915 cm^{-1} [13]) but no symmetry was imposed. Such a difference can be attributed to different anharmonicity of the energy well, which at this $\text{O}\cdots\text{O}$ distance is rather flattened).

For **I-H**, the calculated $\Delta\nu$, on passing from the chelate to the H-centred conformation, is about 1600 cm^{-1} ; it lowers to about 1160 cm^{-1} at the B3LYP level. On going from **I-H** to **II-H** the frequency does not change appreciably in the open and H-centred forms, whilst the shift between the OH frequency of the chelate forms of **I-H** and **II-H** is about $120\text{--}140\text{ cm}^{-1}$. These low values reflect the very low change of the hydrogen bond energies obtained with all the adopted basis sets when formyl is the 3-substituent group, independently of the correlation energy inclusion. Lower shifts are evidenced when the O–H frequency of **I-H** is compared with that of **III-H** and **V-H**, so suggesting that in these compounds also no relevant hydrogen bond energy variation occurs.

In the chelate isomer of acetylacetone, **I**, the calculated ν_{OH} value is 2932 cm^{-1} , which becomes 2815 cm^{-1} when scaled: it fits very well the experimental datum (2800 cm^{-1}) [30–32]. Also in this series, the O–H vibration frequency of the H-centred and open conformers remain nearly constant and independent of the nature and/or bulkiness of the 3-substituent group; moreover they are practically equal to those found for the corresponding malondialdehyde derivatives. As far as the chelate conformers are concerned the maximum frequency shift with respect to the open structures is found for the most hindered (**V**, $\Delta\nu = 1432\text{ cm}^{-1}$) and the most conjugated (**II-H**_{*trans*}, $\Delta\nu = 1366\text{ cm}^{-1}$) compounds, for which the highest hydrogen bond energies are also found (see Table 3). The lowest $\Delta\nu_{\text{OH}}$ (1023 cm^{-1}) was calculated for **III**; it is a consequence of the modest steric effect previously predicted for this compound.

In the assignment of the experimental IR spectra of **III** and **IV** and other derivatives, the band associated with the O–H stretching mode was located in the range $1400\text{--}1600\text{ cm}^{-1}$ [4–8]. Our calculated values appear to be about 1000 cm^{-1} higher than the experimental ones, notwithstanding the good agreement found for the parent compounds **I** and **I-H**. On the other hand, the theoretical shifts are in line with the calculated geometries and proton transfer barriers, which indicate that, in

the gas phase minimum energy conformations, the studied molecules are still far from the H-centred accommodation. Bearing in mind that the experimental geometries deduced from X-ray diffraction spectra are closer to the H-centred structure and that in such a situation the ν_{OH} values calculated in this paper are approaching the experimental ones, being in the range of 1890 cm^{-1} (Table 5), two conclusions can be deduced: (i) the localization of the band originating from the OH stretching mode in the $1400\text{--}1600\text{ cm}^{-1}$ region of the IR spectrum is realistic; (ii) the low O...O distances reported in the literature are very likely to have been produced by crystalline and/or packing forces typical of the solid state rather than by exceptional hydrogen bond strengthening.

CONCLUSION

The results obtained in the present study allow some interesting remarks. The first of these is that the steric effect cannot increase the hydrogen bridge strength so remarkably as the literature O...O distances suggest, since the 3-substituting group can diminish the repulsions through rotation (III, IV), when possible; when it is not possible (V) no exceptional E_{HB} increase was found, or the hydrogen bond bridge was broken (IV-P). In agreement with a previous estimate [13], our values indicate that, when correlation energy is taken into account, E_{HB} increases are in the range of 20 kJ mol^{-1} , at the most. An E_{HB} increase of 26.5 kJ mol^{-1} was artificially obtained for IV-P (according to the MP2/3-31G approach) only when the molecule was forced to full planarity and simultaneously constrained to maintain the hydrogen bridge.

Another remark is that (if the B3LYP/6-31G** datum concerning V is excluded) $r_{\text{O...O}}$ is longer than the available experimental values and the optimized geometry of the chelate ring is still far from the C_{2v} symmetry. Moreover, the fact that molecule IV prefers to break the hydrogen bridge rather than to shorten the O...O distance when the steric effect is increased by forcing the 3-substituent phenyl group towards coplanarity with the chelate ring, suggests that the experimental data from X-ray diffraction are most likely affected by interactions and/or constrictions peculiar to the solid state rather than to an actual increase in the hydrogen bridge stability. That the intramolecular hydrogen bond strengthening due to the strong steric effect is not exceptional, notwithstanding the $r_{\text{O...O}}$ shortening, is also confirmed by the previously cited literature data concerning 1,3-diaryl-1,3-propanedione enols [27].

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