Substituent effects on keto–enol tautomerization of β-diketones from X-ray structural data and DFT calculations†‡§

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Single crystal X-ray structure determinations of six crystals **1–6** of β-diketones, the related DFT calculations as well as a systematic investigation, on the CSD (Cambridge Structural Database) files, of all acyclic β-diketones having at least one α-hydrogen, in both β-diketo and β-keto–enol tautomeric forms, are reported. In spite of the stabilization energy gained by the formation of strong intramolecular O–H···O resonace assisted hydrogen bonds (RAHB) a certain number of non-enolized structures were retrieved. The structural data show that the steric and electronic properties of the substituents play a definite role in tuning the hydrogen bond strength and determining the enolic site but the driving force able to shift from the more common β-keto–enol tautomer to the β-diketo one can be only the steric hindrance of bulky groups. In this context the substituents in position 2 play a crucial role in establishing the tautomeric form. In fact, while the 2-unsubstituted β-diketones (or 2-substitued by a group linked by a sp^2 carbon) assume almost exclusively the β-keto–enol form with some exceptions for very bulky substituents, β-diketones carrying 2-alkyl substituents, in general, display the β-diketo tautomeric form. The only exceptions are the 2-alkyl curcumin derivatives where the planar β-keto–enol group is stabilized by extended π-conjugation within the whole molecule and by the absence of short contacts between the alkyl R_2 groups and R_1 or R_3 substituents. DFT calculations on the six compounds, **1–6**, show that in the four more overcrowded structures, **3–6**, the *trans*-β-diketo tautomer is more stable than the *Z*-β-keto–enol isomer unlike what happens for **1** and **2** where the *Z*-β-keto–enol isomer is the most stable by a few kcal mol^{-1}. Thereby, the occurrence of the *trans*-β-diketo tautomer for all compounds, in the crystal, can be interpreted in terms of the existence of a large activation energy in the mechanism to attain the *Z*-β-keto–enol isomer containing an intramolecular O–H···O hydrogen bond.

Introduction

β-Diketones are compounds extensively studied for their prototropic tautomerism[1–3] (Scheme 1) and have been the subject of several experimental[4–8] and theoretical investigations[9–13] in order to understand the tautomeric equilibrium mechanism and the nature of the strong intramolecular O–H···O hydrogen bond.

These studies have been mainly addressed to assess the H-bond single or double well potential, its dynamic or static nature and its energetic characteristics.[14–18] The stabilization of the β-keto–enol (or β-enol–keto) tautomeric form has been explained in term of the resonance assisted hydrogen bond (RAHB) model, which is a synergistic interplay between π-delocalization and H-bond strengthening.[19–23] The O–H···O H-bond energies have been calculated to be about 12–15 kcal mol^{-1} in acetylacetone (R_1 = R_3 = Me, R_2 = H),[10,24] 16 kcal mol^{-1} in benzoylacetone (R_1 = Ph, R_3 = Me, R_2 = H)[14] and 19 kcal mol^{-1} in dibenzoylmethane (R_1 = Ph, R_3 = Ph, R_2 = H),[17] much higher than the usual H-bond energies of 4–6 kcal mol^{-1}. Accordingly, simple β-diketones, that is β-diketones carrying small substituents, display in solution only a few percent of the β-diketo tautomer, often supported by the polarity of the solvent, and in the solid state assume almost exclusively the β-keto–enol form. Conversely, the presence of bulkier substituents seems to be the driving force able to shift the tautomeric equilibrium toward the β-diketo form.

Although many structural determinations of β-diketones have been reported, no systematic investigations of the occurrence of β-diketo tautomeric structures with respect to the more common β-keto–enol ones have been performed. Since, in general, the great majority of molecular crystals of acyclic β-diketones having at least one α-hydrogen are built up by enol tautomers, all crystal structures of β-diketones are worth systematically analysing in the light of the structural peculiarities of their substituents. In order to better clarify the reason for the stability of the less common β-diketo tautomer, this

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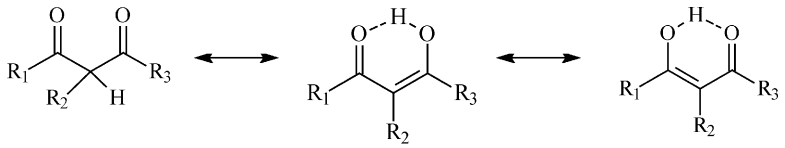


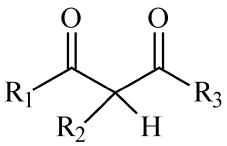
β-Diketo β-Keto-enol β-Enol-keto

Scheme 1

paper is devoted to discovering which substituents are able to switch the tautomeric equilibrium toward the β-diketo form, losing in this way the energetic contribution of the very strong intramolecular resonance assisted hydrogen bond. For this purpose, a structural search has been performed on the CSD files[25] and six new structures of non-enolized β-diketones are reported. DFT calculations on these last six compounds have been carried out to establish the relative stabilities, in the gas phase, of β-diketone tautomers with respect to both the *E*-β-keto–enol and *Z*-β-keto–enol isomers.

Experimental

This paper reports the crystal structure of the following six compounds (Scheme 2): **1** = 3-[1-(4-chlorophenyl)ethyl]pentane-2,4-dione; **2** = 2-[1-(4-chlorophenyl)ethyl]-1-phenylbutane-1,3-dione; **3** = 2-[1-(2-chlorophenyl)ethyl]-1-phenylbutane-1,3-dione; **4** = 1,3-diphenyl-2-(1-phenylethyl)propane-1,3-dione; **5** = 2-[1-(2-chlorophenyl)ethyl]-1,3-diphenylpropane-1,3-dione; **6** = 1,3-diphenyl-2-(1-phenylpropyl)propane-1,3-dione. They were synthesized by addition of the activated methylene of the appropriate β-diketone to alkenes catalyzed by gold and silver. The synthesis procedure has been reported elsewhere.[26] The crystals were obtained by slow evaporation:



1: $R_1 = R_3 = Me$; R_2 = 1-(4-chlorophenyl)ethyl
2: $R_1 = Ph$; $R_3 = Me$; R_2 = 1-(4-chlorophenyl)ethyl
3: $R_1 = Ph$; $R_3 = Me$; R_2 = 1-(2-chlorophenyl)ethyl
4: $R_1 = R_3 = Ph$; R_2 = 1-phenylethyl
5: $R_1 = R_3 = Ph$; R_2 = 1-(2-chlorophenyl)ethyl
6: $R_1 = R_3 = Ph$; R_2 = 1-phenylpropyl

Scheme 2

1, **3**, **5** and **6** from ethanol; **2** from acetonitrile and **4** from methanol.

The diffraction data for all compounds were collected at room temperature, 295 K, using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Data sets were integrated using t he DENZO-SMN package[27] and corrected for Lorentz and polarization effects. The structures were solved by direct methods (SIR97)[28] and refined using full-matrix least-squares. All non-H atoms were refined anisotropically and

Table 1 Crystal data and structure refinement

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Chemical formula	$C_{13}H_{15}ClO_2$	$C_{18}H_{17}ClO_2$	$C_{18}H_{17}ClO_2$	$C_{23}H_{20}O_2$	$C_{23}H_{19}ClO_2$	$C_{24}H_{22}O_2$
M_r	238.70	300.77	300.77	328.39	362.83	342.42
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1/a$	*Pbca*	*Pbca*	$P2_1/a$	*Pbca*
a/Å	5.3281 (2)	15.3369 (7)	7.1662 (2)	16.9980 (2)	11.1539 (3)	17.0267 (4)
b/Å	8.3677 (3)	5.5988 (2)	11.4546 (3)	9.9242 (3)	16.3314 (6)	9.9384 (2)
c/Å	28.9434 (13)	19.0061 (11)	38.4210 (12)	21.5231 (5)	11.4618 (3)	22.3568 (7)
α/°	90.00	90.00	90.00	90.00	90.00	90.00
β/°	90.00	109.104 (2)	90.00	90.00	114.694 (1)	90.00
γ/°	90.00	90.00	90.00	90.00	90.00	90.00
V/Å^3	1290.41 (9)	1542.1 (1)	3153.8 (2)	3630.8 (1)	1896.9 (1)	3783.2 (2)
Z	4	4	8	8	4	8
D_x/Mg m^{-3}	1.229	1.295	1.267	1.202	1.270	1.202
μ/mm^{-1}	0.28	0.25	0.24	0.08	0.22	0.08
Crystal size/mm	0.44 × 0.24 × 0.21	0.35 × 0.31 × 0.24	0.42 × 0.31 × 0.13	0.55 × 0.17 × 0.12	0.43 × 0.35 × 0.21	0.52 × 0.28 × 0.08
Measured reflections	7896	5343	5340	7329	7619	6855
Independent reflections	2459	3025	3009	3938	4126	3704
Observed reflections	1484	1716	1506	2709	2652	2146
R_{int}	0.062	0.039	0.054	0.023	0.027	0.041
θ_{max}/°	26.0	26.0	26.0	27.0	27.0	26.0
Refinement on	F^2	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.052	0.049	0.051	0.049	0.051	0.049
$wR(F^2)$	0.141	0.133	0.124	0.135	0.140	0.125
S	1.02	1.01	1.03	1.01	1.01	1.00
No. of parameters	172	258	247	306	311	323
$\Delta\rho_{max}/e$ Å^{-3}	0.14	0.25	0.16	0.20	0.18	0.13
$\Delta\rho_{min}/e$ Å^{-3}	−0.22	−0.22	−0.16	−0.18	−0.33	−0.15

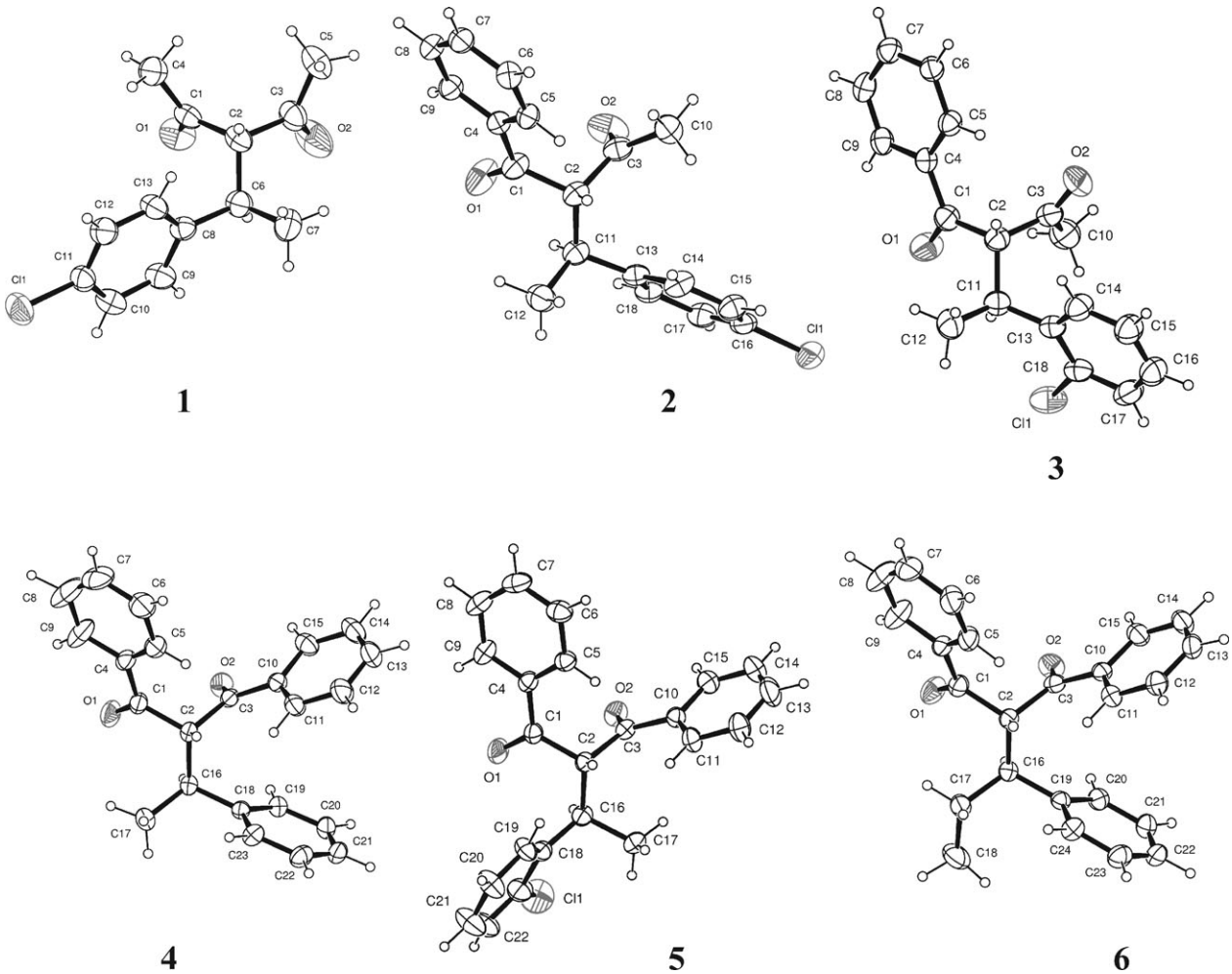


Fig. 1 ORTEP views of compounds **1–6**, showing displacement ellipsoids at the 30% probability level.

the hydrogens isotropically, with the exception of the hydrogens of some methyl groups of compounds **1** and **3** which were included on calculated positions riding on their carrier atoms. All calculations were performed using SHELXL97[29] and PARST[30] as implemented in the WINGX[31] system of programs. The crystal data and refinement parameters are summarized in Table 1.

Results and discussion

ORTEP[32] views of the six structures are shown in Fig. 1. Selected geometric parameters are reported in Table 2. All the six molecules are characterized by bulky 2-alkyl substituents, which, probably for steric reasons, do not allow the formation of the intramolecular O–H···O hydrogen bond. The six compounds minimize the intramolecular interactions by

Table 2 Selected distances (Å), angles, torsion angles and dihedral angles (°)

	1	2	3	4	5	6
C1–O1	1.198(4)	1.220(4)	1.217(3)	1.217(2)	1.211(3)	1.218(2)
C3–O2	1.200(5)	1.194(3)	1.205(4)	1.219(2)	1.220(3)	1.220(2)
C1–C2	1.528(5)	1.529(3)	1.529(4)	1.527(2)	1.530(3)	1.532(3)
C2–C3	1.518(4)	1.538(4)	1.525(4)	1.540(2)	1.533(3)	1.542(2)
O1···O2	3.216(4)	3.190(3)	4.275(3)	3.788(2)	3.378(2)	3.070(2)
C1–C2–C3	108.4(3)	106.2(2)	108.3(2)	105.1(1)	107.3(2)	105.6(1)
O1–C1–C2–C3	71.9(4)	96.6(3)	96.5(3)	95.0(2)	113.7(2)	92.2(2)
O2–C3–C2–C1	−82.3(4)	−54.2(3)	112.4(3)	−52.8(2)	−49.3(2)	−53.9(2)
O1–C1–C2–C6	−51.7(4)					
O2–C3–C2–C6	41.5(5)					
O1–C1–C2–C11		−26.0(3)	−28.6(3)			
O2–C3–C2–C11		67.2(3)	−124.1(3)			
O1–C1–C2–C16				−23.1(2)	−5.2(3)	−26.5(2)
O2–C3–C2–C16				67.9(2)	71.9(2)	67.2(2)
O1,C1,C2^O2,C3,C2	70.2(4)	80.9(3)	75.8(2)	81.1(2)	86.8(2)	78.8(2)

Table 3 Intermolecular C–H···O interactions (Å, °)

	C–H	C···O	H···O	C–H···O
1				
C2–H2···O1^{I}	0.96(3)	3.480(4)	2.54(3)	165(3)
C13–H13···O1^{I}	0.92(3)	3.601(4)	2.68(3)	176(2)
C5–H53···O2^{II}	0.96	3.469(6)	2.59	153
Symmetry: I = $x-1, y, z$; II = $2-x, 1/2+y, 3/2-z$.				
2				
C14–H14···O2^{I}	0.95(3)	3.412(4)	2.49(3)	166(2)
Symmetry: I = $x, y+1, z$.				
3				
C14–H14···O1^{I}	0.85(2)	3.569(4)	2.75(2)	171(2)
C7–H7···O2^{II}	0.93(2)	3.412(4)	2.69(2)	134(2)
Symmetry: I = $3/2-x, y-1/2, z$; II = $1-x, -y, 1-z$.				
4				
C11–H11···O1^{I}	1.00(2)	3.407(2)	2.52(2)	149(2)
C20–H20···O1^{II}	0.94(2)	3.443(2)	2.68(2)	140(2)
C21–H21···O2^{III}	0.93(2)	3.532(2)	2.66(2)	156(2)
Symmetry: I = $3/2-x, y+1/2, z$; II = $x-1/2, -y, 1/2-z$; III = $1-x, 1/2+y, 1/2-z$.				
5				
C20–H20···O1^{I}	1.00(4)	3.288(4)	2.38(4)	151(3)
C13–H13···O1^{II}	0.96(3)	3.454(3)	2.66(3)	140(2)
C2–H2···O2^{I}	0.94(2)	3.615(3)	2.72(2)	158(2)
C7–H7···O2^{III}	0.95(3)	3.393(3)	2.72(3)	129(2)
Symmetry: I = $x-1/2, 1/2-y, z$; II = $1/2+x, 1/2-y, z+1$; III = $1-x, 1-y, 2-z$.				
6				
C11–H11···O1^{I}	0.96(2)	3.389(2)	2.48(2)	158(1)
C22–H22···O2^{II}	0.97(2)	3.586(3)	2.70(2)	152(2)
Symmetry: I = $1/2-x, 1/2+y, z$; II = $-x, 1/2+y, 1/2-z$.				

adopting suitable conformations where the planes containing the carbonyl moieties are almost perpendicular to each other, forming dihedral angles in the range 70.2–86.8°. Because of the absence of classical hydrogen bond donors, the crystal packing is dominated by C–H···O short contacts[33] involving the carbonyl oxygens (Table 3). The presence of the β-diketo tautomers in the solid state is in agreement with the fact that in β-diketones the 2-alkyl substituents cause, in solution, a dramatic decrease in the enol content which becomes very low for bulky groups.[34] This is usually ascribed to non-bonding interactions ;between R_2 and R_1 and/or R_2 and R_3. These considerations, however, cannot be general because sometimes the compression determined by the substituents makes the oxygen atoms closer and the hydrogen bond shorter and stronger. On the other hand, when the intramolecular repulsions become remarkable, the formation of the O–H···O resonance assisted hydrogen bond is hindered. Thus, the steric effects of the substituents are rather complicated due to competition between factors stabilizing or destabilizing the tautomeric forms.

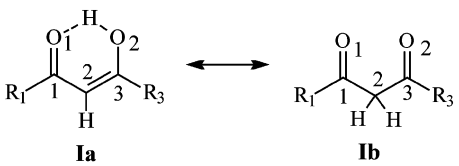
In order to discover which steric or electronic factors are able to influence the relative stability of both the tautomers in crystal, the structures of acyclic β-diketones retrieved from the CSD files were divided into several classes according to the chemical features of the R_2 substituents which seem to be the most important structural factors able to stabilize the β-diketo or β-keto–enol form. In order to simplify the discussion, only acyclic β-diketones having R_1, R_2 and R_3 groups linked to the β-diketo moiety by means of C–C bonds have been taken into account.

Crystal structure analysis

2-Unsubstituted β-diketones (Class I). Class **I** contains a great number of compounds (93 different molecules and 148 structural data, Table S1 of ESI‡) which exhibit almost exclusively the β-keto–enol tautomeric form **Ia** (Scheme 3). Only two peculiar compounds adopt the β-diketo form **Ib**.

All the β-keto–enols display strong intramolecular O–H···O H-bonds assisted by resonance with O···O distances in the range 2.43–2.56 Å. The shortest H-bonds have been observed in compounds having two aromatic R_1 and R_3 substituents which, probably, are involved in enhancing the π-delocalization within the heterodienic system.[17] These effects can be appreciated by comparing the structures of three typical β-keto–enols: acetylacetone ($R_1 = R_3 = Me$), benzoylacetone ($R_1 = Me$, $R_3 = Ph$) and dibenzoylmethane ($R_1 = R_3 = Ph$). The structures of acetylacetone (LIWPIQ, Fig. 2a),[16] determined at two different temperatures, display the longest O···O distances of 2.541(2) and 2.547(1) Å, while the structures of benzoylacetone (BZOYAC, Fig. 2b)[15,35] show intermediate distances, in the range 2.485(5)–2.502(4) Å, and the several structural determinations of dibenzoylmethane (DBEZLM, Fig. 2c)[36] exhibit the shortest distances, in the range 2.452(4)–2.461(4) Å.

Furthermore, it is well known that some substituents at the phenyl rings can shorten the O···O distance down to 2.43 Å, but it is not clear which electron attracting or electron releasing groups and which position on the phenyl ring promote the



Ia **Ib**

R_1, R_3 = any substituent linked by a Carbon atom

Scheme 3

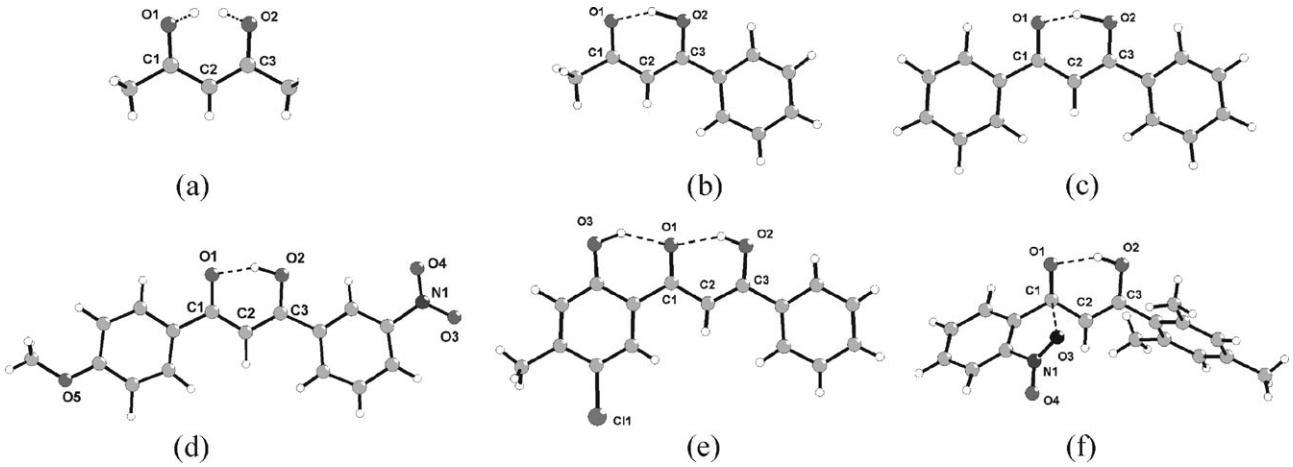


Fig. 2 (a) Structure of acetylacetone (LIWPIQ/01)[16] showing both the disordered tautomeric hydrogens, O1···O2 = 2.541, 2.547 Å; (b) structure of benzoylacetone (BZOYAC/01/02/03/04/05/06),[15,35] O1···O2 = 2.485–2.502 Å; (c) structure of dibenzoylmethane (DBEZLM/01/02/03/04/05),[36] O1···O2 = 2.452–2.461 Å; (d) structure of 1-(4-methoxyphenyl)-3-(3-nitrophenyl)-1,3-propanedione enol (JITXAL, EVEXAE/01/02),[5,17] O1···O2 = 2.434–2.448 Å; (e) structure of 1-(2-hydroxy-4-methyl-5-chlorophenyl)-3-phenyl-1,3-propanedione enol (LEPLUO),[38] O1···O2 = 2.552 Å; (f) structure of 3-hydroxy-3-mesityl-1-(2-nitrophenyl)-2-propen-1-one (JITWUE/01/02/03/04),[5,17] O1···O2 = 2.554–2.559 Å.

H-bond shortening. The shortest O1···O2 H-bond distances were, in fact, retrieved in 1,3-diaryl-1,3-propanedione enols containing, on the aryl groups, substituents with different electronic properties, such as: JITXAL[5] and EVEXAE[17] (two polymorphs) [R_1 = *p*-OMe-Ph, R_3 = *m*-NO_2-Ph; O1···O2 = 2.434(1)–2.448(2) Å] (Fig. 2d); DBEZLM[36] (three polymorphs) [R_1 = R_3 = Ph; O1···O2 = 2.452(4)–2.461(4) Å] (Fig. 2c); TOLACP10[37a] [R_1 = *p*-Me-Ph, R_3 = Ph; O1···O2 = 2.455(4) Å], FAXWAD[37b] [R_1 = R_3 = *p*-Me-Ph; O1···O2 = 2.436(1) Å], NENLOI[37c] [R_1 = *p*-*t*Bu-Ph, R_3 = Naphth; O1···O2 = 2.444(2) Å]. Conversely, it is well known that some specific factors are able to weaken the intramolecular O–H···O H-bonds, such as donor–acceptor interactions and further hydrogen bonds involving the carbonylic oxygen, because probably they influence the synergy between the hydrogen bonding strength and the π-conjugation within the heterodienic system. For instance, the intramolecular H-bond at the ketonic oxygen, as shown in LEPLUO (Fig. 2e),[38] or donor–acceptor interactions such as O3···C1=O1, as observed in JITWUE (Fig. 2f),[5–17] cause a lengthening of the O···O hydrogen bond up to 2.56 Å, not being able, however, to shift the equilibrium toward the β-diketo form.

Only rarely do very bulky R_1 and R_3 substituents prevent a close approach of the oxygens and the β-diketone moiety from attaining the planar conformation necessary to obtain the β-keto–enol tautomer. This situation has been observed only in two compounds, YECKOG (Fig. 3a)[39a] and ZOVDET (Fig. 3b),[39b] being very strained molecules which assume the β-diketo tautomeric form where the enolization brings no advantage. It is worthy of note that the presence of only one bulky substituent is unable to produce the β-diketo form as shown in the β-keto–enol HECGIF (Fig. 3c)[40] which undergoes only a slight lengthening to an O1···O2 intramolecular H-bond distance of 2.536 Å.

β-Diketones with R_2 substituents linked by a sp^2 or sp carbon (Class II). Table 4 reports the compounds of Class **II** (Scheme

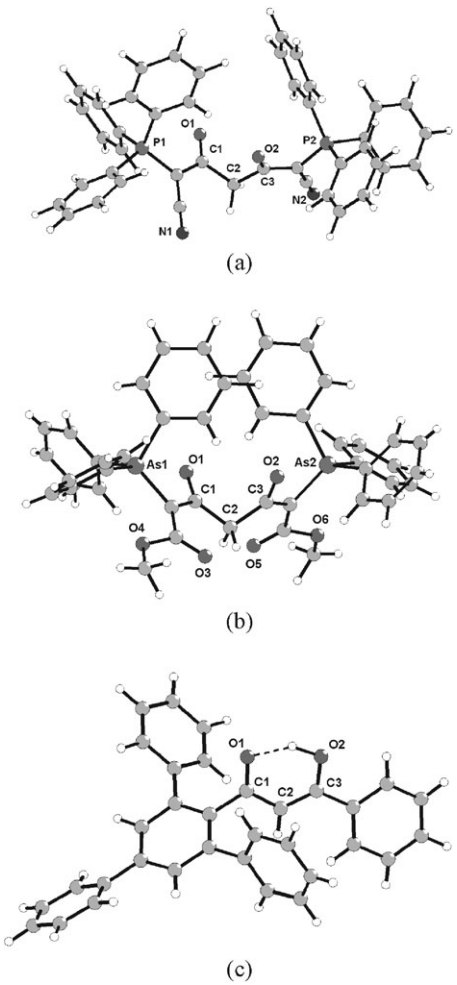


Fig. 3 Structure of 2,6-bis(triphenylphosphoranylidene)-1,7-heptanedinitrile-3,5-dione (YECKOG),[39a] O1···O2 = 3.337 Å; (b) structure of dimethyl 2,6-bis(triphenylarsorane-3,5-dioxopimelate (ZOVDET),[39b] O1···O2 = 3.298 Å; (c) structure of 3-phenyl-1-(2,4,6-triphenylphenyl)-propane-1,3-dione (HECGIF),[40] O1···O2 = 2.536 Å.

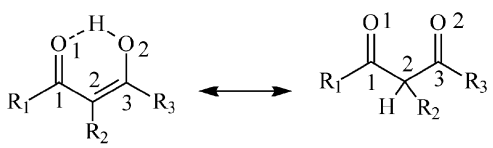
Table 4 Structural data for β-diketones of Class **II**

REFCODE	R_1	R_3	R_2	O···O/Å	Ref.
β-Diketo–enols (Class **IIa**)					
GASKIU	Me	Me	4-Ome–Ph	2.449	41*a*
ISUHIN	Me	Me	4-CN–Ph	2.456	41*b*
JIRKAW	Me	Me	3,4,5-Me–Ph	2.460	41*c*
SAPYAJ	Me	Me	4-OPh–Ph	2.442	41*d*
SAPYEN	Me	Me	4-NO_2–Ph	2.445	41*d*
SAPYIR	Me	Me	4-*i*-Pr–Ph	2.418	41*d*
SEYLUD	Me	Me	2,4-OMe–Ph	2.444 2.475	41*e*
TUFQOA	Me	Me	Ph	2.444	41*f*
QEJFOA	Me	Me	8-(Benzoyloxy)-quinolin-5-yl	2.459	41*g*
PUXNIF	Me	Me	9,10-Anthrylene	2.452	41*h*
PUXNOL	Me	Me	2-OMe-1-Naphthalenyl	2.460	41*h*
DODHAF	Me	Me	Vinyl-4-Br-benzoate	2.438	41*i*
LUVSOK	Me	Me	[a]	2.445	41*j*
LUVTAK	Me	Me	[b]	2.469	41*j*
VOXGOE	Me	Me	[c]	2.442	41*k*
COXXOC	Me	Me	[d]	2.438	41*l*
NELQAW	C(H)═C(H)–Ph	Me	C(═O)–OEt	2.427	41*m*
ZOLJAL	C(H)═C(H)–Ph	Me	C(═O)–Ph	2.446	41*n*
MEYNAF	Me	Me	CN	2.465	41*o*
HAKTIX	*t*-Bu	*t*-Bu	CN	2.394	41*p*
β-Diketones (Class **IIb**)					
OCIQOG	*t*-Bu	*t*-Bu	C(═O)–Me	3.189	41*q*
GINXUV	Ph	Ph	4-OMe–Ph	3.391	41*r*
OHUVAO	4-OMe–Ph	4-OMe–Ph	[e]	3.138	41*s*

[a] 3-Acetyl-4-(4-methoxyphenyl)-2-methyl-5-furyl. [b] 3-Acetyl-2-methyl-4-phenyl-5-furyl. [c] 5-Methylenefuran-2(5*H*)-one. [d] 4-Methyldienyl-1,3,5-triphenylpenta-2-dien-1-one. [e] *N*′-(4-Methylbenzylidene)-*N*-phenylcarbohydrazide.

4) retrieved from the CSD files. The great majority of these molecules include small R_1 and R_3 substituents (often methyl groups) and adopt the β-keto–enol form **IIa**. The R_2 substituents cause a remarkable shortening of the O···O distance, in the range 2.394 to 2.475 Å, irrespective of their electronic properties. For instance, in the structures of SAPYEN[41d] (R_1 = R_3 = Me, R_2 = *p*-nitro-phenyl) (Fig. 4a) and GASKIU[41a] (R_1 = R_3 = Me, R_2 = *p*-methoxy-phenyl) (Fig. 4b), in spite of *para*-phenyl substituents having opposite electronic properties, the O···O H-bond distances of 2.445 (3) and 2.449(3) Å are practically identical. Thus, it is reasonable to conclude that the O···O distance shortening could be mainly due to steric interactions between the R_1···R_2 and R_3···R_2 moieties. An enhancement of these interactions is probably due to the smaller covalent radii of the sp^2 and sp hybridized carbons of the R_2 groups causing a shortening of the C_2–C(R_2) bond distances.

Other interesting examples of compounds of Class **IIa** are given by MEYNAF (Fig. 4c)[41o] and HAKTIX (Fig. 4d)[41p] having R_2 = CN but different R_1 = R_3 substituents: in MEYNAF (R_1 = R_3 = Me) $d_{O\cdots O}$ = 2.465(2) Å, while in HAKTIX (R_1 = R_3 = *t*-Bu) $d_{O\cdots O}$ = 2.394(2) Å. The rather shorter distance in the latter structure is probably due to the



R_1, R_3 = any substituent linked by a Carbon atom
R_2 = any substituent linked by a sp^2 or *sp* Carbon

Scheme 4

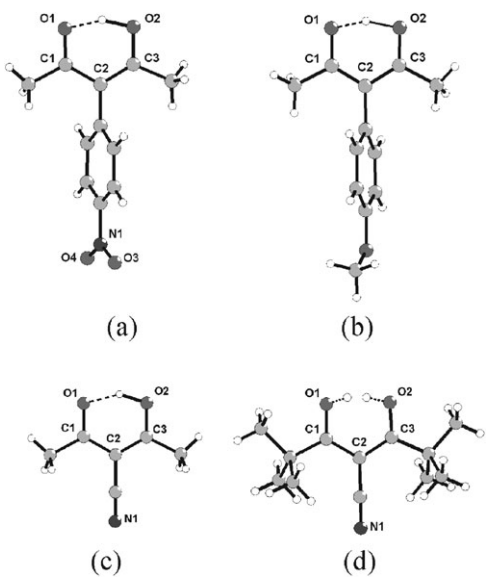


Fig. 4 (a) Structure of 3-(4-nitrophenyl)pentane-2,4-dione (SAPYEN),[41d] O1···O2 = 2.445 Å; (b) structure of 3-(4-methoxyphenyl)-pentane-2,4-dione (GASKIU),[41a] O1···O2 = 2.449 Å; (c) structure of 3-cyano-4-hydroxypent-3-en-2-one (MEYNAF),[41o] O1···O2 = 2.465 Å; (d) structure of 4-cyano-2,2,6,6-tetramethyl-3,5-heptanedione (HAKTIX),[41p] O1···O2 = 2.394 Å; both the disordered tautomeric protons are shown.

Table 5 Structural data for bis-β-diketones of Class **III**

REFCODE	R_1, R_1'	R_3, R_3'	O···O/Å	Ref.
Bis-β-keto–enols (Class **IIIa**)				
TACETA02	Me	Me	2.437	42*a*
DACEDO	Me	2-Methylpropyl	2.440	42*b*
WIRJIQ	Me	Ph	2.446	42*c*
Bis-β-diketones (Class **IIIb**)				
FAMJAE	Me	Ph	3.480	42*d*
FAMHUW	Ph	Ph	3.270	42*d*

greater steric compression exerted by the *t*-Bu groups with respect to Me ones.

The very short $d_{O1\cdots O2}$ of 2.394(2) Å, in HAKTIX, seems to be a limit situation, because when a bulkier substituent replaces the CN group, forcing the oxygens to come very close to each other, the repulsion prevails over the H-bond attractive forces. In such structures, the β-diketo form turns out to be the more stable tautomer as shown in OCIQOG[41q] (R_1 = R_3 = *t*-Bu, R_2 = acetyl) (Fig. 5a). Moreover, when R_1, R_3 are phenyl derivatives and R_2 is a bulky group the β-diketo form is predominant as observed, for instance, in crystals of OHUVAO[41s] (Fig. 5b) and GINXUV,[41r] which are β,β′-triketones unable to enolize for steric reasons.

2,2′-Bis-β-diketones (Class III). Table 5 reports the retrieved structures of 2,2′-bis-β-diketones (Class **III**) (Scheme 5).

These compounds include the bis-β-diketo (**IIIb**) and bis-β-keto–enol (**IIIa**) systems linked through a C2–C2′ bond. Here,

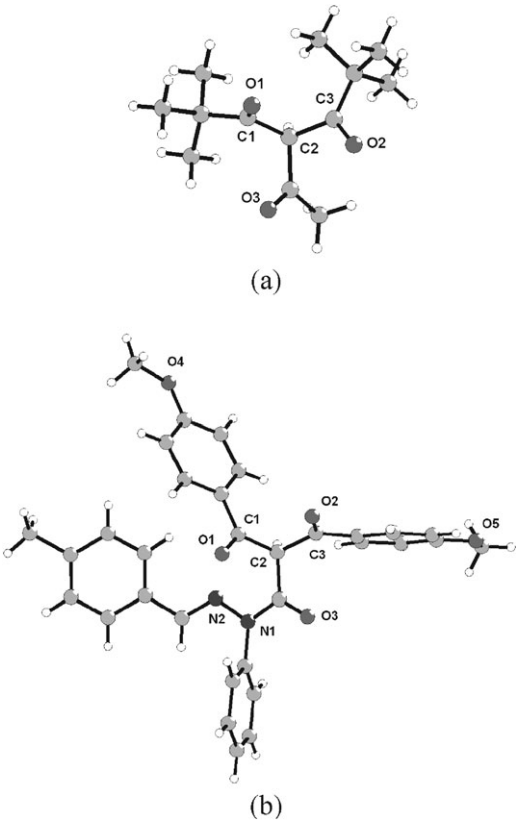
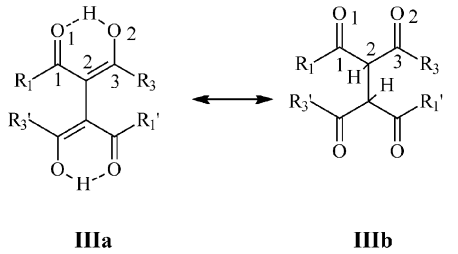


Fig. 5 (a) Structure of 4-acetyl-2,2,6,6-tetramethyl-3,5-heptanedione (OCIQOG);[41q] (b) structure of 2,2-bis(4-methoxybenzoyl)-*N*′-(4-methylbenzylidene)-*N*-phenylacetohydrazide (OHUVAO).[41s]



R_1, R_1', R_3, R_3' = any substituent linked by a Carbon atom

Scheme 5

the steric effects involve the substituents on both β-diketone moieties and determine both the molecular conformation and the stability of the tautomeric forms. In structures such as TACETA02[42a] (R_1 = $R_{1'}$ = R_3 = $R_{3'}$ = Me) (Fig. 6a) and DACEDO[42b] (R_1 = $R_{1'}$ = Me; R_3 = $R_{3'}$ = 2-methylpropyl), which carry small substituents, the steric interactions are minimized by mutual rotation of the β-keto–enol groups.

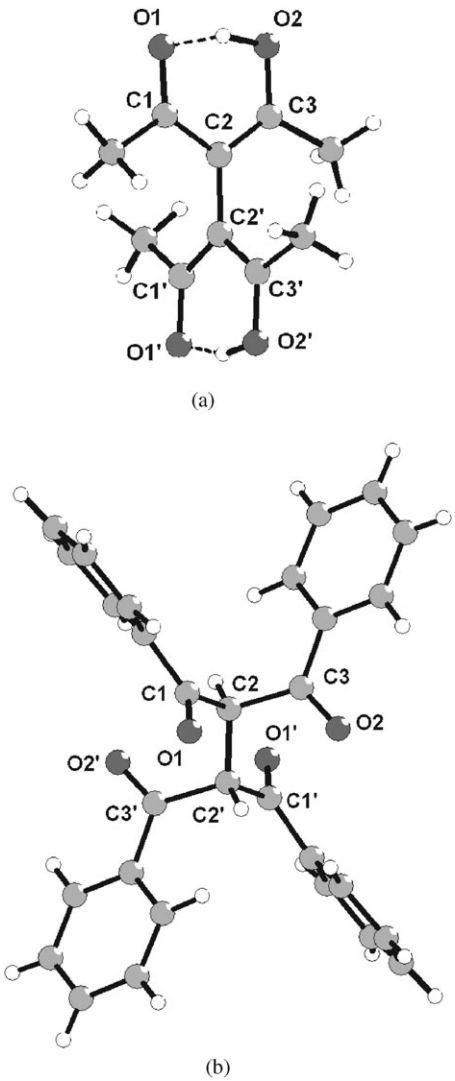
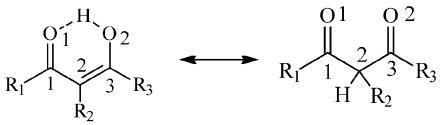


Fig. 6 (a) Structure of tetra-acetylethane (TACETA02),[42a] O1···O2 = 2.437 Å; (b) Structure of 1,1,2,2-tetra-benzoylethane (FAMHUW).[42d]



IVa **IVb**

R_1, R_3 = any substituent linked by a Carbon atom
R_2 = any substituent linked by a sp^3 Carbon

Scheme 6

Therefore, these compounds do not undergo strong intramolecular compression and adopt the more stable β-keto–enol form. Conversely, when the substituents are phenyl groups as in FAMHUV[42d] (Fig. 6b), the rotation around the C2–C2′ bond probably is not enough to avoid the intramolecular short contacts, leading the molecules to assume the β-diketo form. Surprisingly, when the substituents are both Me and Ph groups the compounds can crystallize in both the tautomeric forms as observed in WIRJIQ[42c] and FAMJAE[42d] which crystallize as bis-β-keto–enol and bis-β-diketo, respectively. This suggests that the two tautomeric forms should be energetically almost equivalent and the driving force determining the formation of one tautomeric form rather than the other could be the nature of the crystallization solvent.

β-Diketones with the R_2 substituent linked by an sp^3 carbon (Class IV). Class **IV** (Scheme 6) contains the greatest number of structures in the β-diketo form (**IVb**) and includes also the six molecules whose structures are reported in this paper. The data in Table 6 show that the presence of a 2-alkyl group is essential for obtaining the β-diketo tautomer irrespective of the R_1 and R_3 substituents, see for instance the structures of IGAGOM[43e] (R_1 = R_3 = Me) (Fig. 7a), and ACEZEO[43k] (R_1 = R_3 = Ph) (Fig. 7b). It is evident that, even when R_1 and R_3 are small groups, the intramolecular strain exerted by the bulky R_2 alkyl groups does not favour the approach of the oxygen necessary to form the intramolecular O–H···O H-bond.

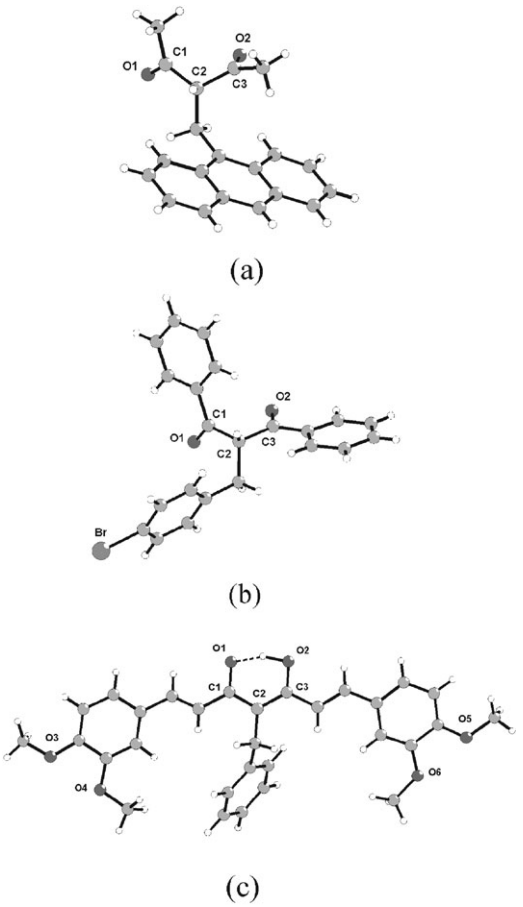


Fig. 7 (a) Structure of 3-(9-anthrylmethyl)pentane-2,4-dione (IGAGOM);[43e] (b) structure of 2-(4-bromobenzyl)-1,3-diphenylpropane-1,3-dione (ACEZEO);[43k] (c) structure of 1,7-bis(3,4-dimethoxyphenyl)4-benzylhepta-1,6-diene-3,5-dione (FAPLEN),[43d] O1···O2 = 2.444 Å.

Among these compounds there are only a few exceptions, belonging to the chemical class of curcumin derivatives, which adopt exclusively the β-keto–enol tautomeric form. An example is given by the structure of FAPLEN[43d] (Fig. 7c) where its

Table 6 Structural data for β-diketones of Class **IV**

REF CODE	R_1	R_3	R_2	O···O	Ref.
β-Diketo–enols (Class **IVa**)					
COGWAW	C(H)═C(H)–Ph	C(H)═C(H)–Ph	*n*-Butyl	2.441	42*b*
YAPGUR	C(H)═C(H)–Ph	C(H)═C(H)–Ph	2-Propenyl	2.423	43*b*
PINHOJ	C(H)═C(H)–Ph	C(H)═C(H)–Ph	$C(H_2)$–Ph	2.389	43*c*
FAPLIR	Vinyl-(4-OH-3-OMe-Ph)	Vinyl-(4-OH-3-OMe-Ph)	2-Oxo-2-ethoxyethyl	2.431	43*d*
FAPLEN	Vinyl-(3,4-OMe-Ph)	Vinyl-(3,4-OMe-Ph)	$C(H_2)$–Ph	2.444	43*d*
β-Diketones (Class **IVb**)					
IGAGOM	Me	Me	9-Anthrylmethyl	3.320	43*e*
WAQLUW	Me	Me	[a]	3.111	43*f*
WOGDUR	Me	Me	[b]	3.591	43*g*
FEFBEY	Me	Me	[c]	3.475	43*h*
YODKOR	Me	4-Me-Ph	[d]	4.381	43*i*
GINXOQ	Ph	Ph	Me	3.190	43*r*
FETXIL	Ph	Ph	Ethyl	3.169	43*j*
ACEZEO	Ph	Ph	4-Br-benzyl	3.173	43*k*
BIDVIU	Ph	Ph	[e]	3.319	43*l*

[a] Quinoxaline-2,3-diyldimethylene. [b] 8-Nitratotricyclo(5.2.1.$0^{2,6}$)dec-3-en-10-yl. [c] 1-Ethyl-6-methoxy-2,3-dicyano-1,4,5,6-tetrahydropyrazin-2-yl. [d] 1,2,3-Triphenylcyclopropen-3-yl. [e] Diethyl-3-(triphenylphosphoranylidene)succinat-2-yl.

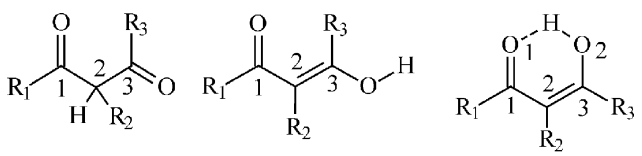
stabilization is probably related to the crucial role played by the R_1 and R_3 vinylbenzene moieties. The peculiar properties of these molecules have been evidenced by DFT calculations[44] on the parent molecule of curcumin, in the gas phase, displaying a considerable delocalization over the whole framework and a stabilization energy of 6.7 kcal mol^{-1} of the β-keto–enol tautomer with respect to the β-diketo one. Furthermore, it can be observed that in these curcumin derivatives the intramolecular interactions of R_2 with R_1 and R_3, in the tautomeric form **IVa**, are minimized by the extended configurations and conformations of the vinylbenzene groups.

DFT calculations

In order to establish the relative stabilities of β-diketone tautomers of the six compounds **1–6** in the gas phase, quantum-mechanical calculations have been performed optimizing the geometry of the three isomers shown in Scheme 7: β-diketo in the *trans* conformation as found in the crystal structures, β-keto–enol in the *E* configuration and β-keto–enol in the *Z* configuration forming an intramolecular O–H···O hydrogen bond.

The problem of choosing an appropriate level of theory for this kind of molecules has been widely investigated by several authors.[45] It is generally recognized that the H-bond geometry cannot be reproduced at the Hartree–Fock level and that electron correlation can be satisfactorily accounted for both by *ab initio* MP2 (or higher) methods and by density functional theory (DFT) methods with an appropriate functional. In view of these considerations and of the fact that DFT methods are faster, all calculations were accomplished by using the Dmol$^{(3)}$ code of the MaterialStudio system of programs,[46] in the framework of the Perdew-Wang generalized-gradient approximation (PW91).[47] The geometry optimization has been accomplished by using the numeric DNP basis set, which, though comparable to 6-31G** Gaussian basis set, is believed to be more accurate.

The differences in energy (kcal mol^{-1}) between both *E* and *Z* isomers of the β-keto–enol form and the *trans*-β-diketo one (Scheme 7), for compounds **1–6**, are reported in Table 7. The data show that for all structures the *E*-β-keto–enol isomer is less stable than the *trans*-β-diketo one, while the results are controversial for compounds in the *Z* form displaying an intramolecular hydrogen bond. For structures **3–6** the *Z* isomer is still less stable than the *trans*-β-diketo one, but for the less crowded compounds **1** and **2**, the *Z* isomer exhibits an over stability of a few kcal mol^{-1}. These results can be explained in the light of the recently proposed tautomerization mechanism for simple model molecules such as acetylacetone[48] ($R_1 = R_3 = Me$, $R_2 = H$) and malonaldehyde[48,49] ($R_1 = R_2 = R_3 = H$). Since the direct tautomerization is very unlikely, owing to the difficulty of cleaving the C–H methylene bond whose energy has been calculated to be 87.6 kcal mol^{-1}, the proton transfer can be obtained by means of auxiliary molecules, such as water or other solvent molecules, which attain the tautomerism *via* a low activation energy. It is evident that β-diketones should be conformationally flexible enough to include solvent molecules and to put the oxygens closer and closer to form the intramolecular hydrogen bond of the *Z*-β-keto–enol tautomer. These conditions are, of course, more easily obtained in β-diketone molecules without bulky substituents which, on the other hand, can cause strong intra- and inter-molecular repulsive interactions responsible for the formation of the β-diketo tautomers. Thereby it is reasonable to suppose that not only in compounds **3–6** but also in **1–2** the steric hindrance of the substituents should play an essential role in increasing the activation energies of the tautomerization process, even in the presence of auxiliary solvent molecules, and thus preventing the formation of the *Z*-β-keto–enol tautomer.



trans-β-Diketo **Va** | *E*-β-Keto-enol **Vb** | *Z*-β-Keto-enol **Vc**

Scheme 7

Table 7 Calculated ΔE (kcal mol^{-1}) between *E*/*Z*-β-keto–enol and *trans*-β-diketo tautomers

Compound	E [Vb] − E [Va]	E [Vc] − E [Va]
1	+8.80	−1.15
2	+13.83	−4.17
3	+10.28	+4.47
4	+12.56	+3.44
5	+11.27	+0.49
6	+11.01	+1.54

Conclusions

The structural considerations reported so far suggest that β-diketones can exist in the solid state both in the tautomeric β-diketo or β-keto–enol forms, but the number of β-keto–enol structures is far greater than the number of β-diketo ones owing to the stabilization energy gained by the formation of the strong intramolecular O–H···O resonance assisted hydrogen bond. The steric and electronic properties of the substituents play a definite role in tuning the hydrogen bond strength and the choice between the β-keto–enol or β-enol–keto tautomers, but the driving force able to shift from the β-keto–enol (or β-enol–keto) form to the β-diketo one can only be the steric hindrance of particular substituents. Almost all 2-unsubstituted β-diketones display the β-keto–enol form and only in rare cases is the compression due to very bulky R_1 and R_3 groups on the oxygens responsible for the β-diketo tautomer formation. In compounds where R_2 is an aryl group, or a generic substituent linked by means of a sp^2 or sp hybridized carbon atom, the β-keto–enol form is still prevalent and O···O distances are systematically very short, but when the steric hindrance of the substituents is remarkable the β-diketo form becomes more stable. If the R_2 substituent is an alkyl group, the compounds display almost universally the β-diketo form, with the single exception of the curcumin derivatives where the planar β-keto–enol group is stabilized by an extended π-conjugation and by the absence of short contacts between the alkyl R_2 groups and R_1 or R_3 substituents.

These considerations are supported by the results of DFT calculations which show that in molecules **3–6** the β-diketo form is the most stable. As for compounds **1** and **2**, for which, conversely, the *Z*-β-keto–enol tautomer turns out to be the most stable, it seems that the gain in energy due to the formation of the intramolecular O–H···O hydrogen bond is not enough to overcome the high activation energy barrier of the enolization process.

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