

Valerio Bertolasi,* Loretta
Pretto, Valeria Ferretti, Paola
Gilli and Gastone Gilli

Dipartimento di Chimica and Centro di Strutturalistica
Diffraattometrica, Università di Ferrara,
Via L. Borsari 46, I-44100 Ferrara, Italy

Correspondence e-mail: m38@unife.it

Interplay between steric and electronic factors in determining the strength of intramolecular N—H...O resonance-assisted hydrogen bonds in β -enaminones

The crystal structures of five β -enaminones are reported: (2*Z*)-3-(benzylamino)-1,3-diphenyl-prop-2-en-1-one, (2*Z*)-3-(benzylamino)-3-(2-hydroxyphenyl)-1-phenyl-prop-2-en-1-one, (2*Z*)-3-(benzylamino)-3-(4-methoxyphenyl)-1-(3-nitrophenyl)-prop-2-en-1-one, 2-{1-[(4-methoxyphenyl)amino]ethylidene}-cyclohexene-1,3-dione and 2-{1-[(3-methoxyphenyl)amino]ethylidene}cyclohexene-1,3-dione. The structures were analysed and compared with those of similar compounds in order to establish which factors determine the range (2.53–2.72 Å) of N...O hydrogen-bond distances in intramolecularly hydrogen-bonded β -enaminones. It has been shown that, beyond electronic resonance-assisted hydrogen-bond effects modulated by substituents, the necessary requirements to produce very short N—H...O hydrogen bonding are steric intramolecular repulsions, including the embedding of an enaminonic C—C or C—N bond in an aliphatic six-membered ring. By considering the structural features it is possible to expect the strength of N—H...O hydrogen bonds adopted by specific β -enaminones.

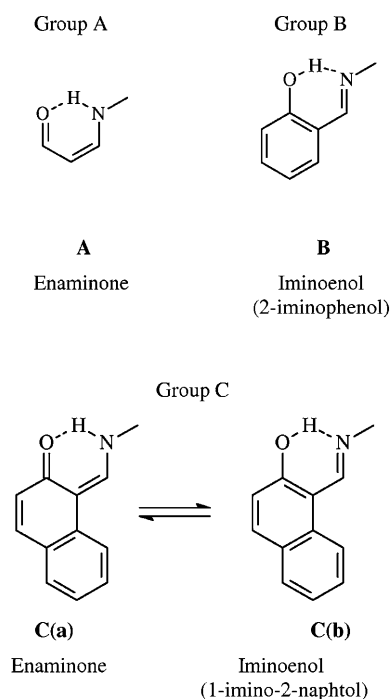
Received 10 July 2006

Accepted 21 September 2006

1. Introduction

β -Enaminones, $\cdots\text{O}=\text{C}-\text{C}=\text{C}-\text{NH}\cdots$, are well known for their ability to form intramolecular resonance-assisted hydrogen bonds (RAHBs; Gilli *et al.*, 2000; Gilli & Gilli, 2000; Cindrić *et al.*, 2005), which are strictly similar to those formed by the homologous series of $\cdots\text{O}=\text{C}-\text{C}=\text{N}-\text{NH}\cdots$ keto-hydrazones (Bertolasi *et al.*, 1993, 1994, 1999; Gilli *et al.*, 2002, 2005, 2006). Their most attractive feature is that they can display $\cdots\text{O}=\text{C}-\text{C}=\text{C}-\text{NH}\cdots \leftrightarrow \cdots\text{HO}-\text{C}=\text{C}-\text{C}=\text{N}\cdots$ enaminone–iminoenol tautomerism and can then form, according to their substituents, both N—H...O and O—H...N RAHBs. In a previous detailed analysis (Gilli *et al.*, 2000) it has been shown that β -enaminones can be classified in three different groups (Scheme 1).

(i) Group A: β -Enaminones (also called simple β -enaminones). They can form only N—H...O hydrogen bonds which are significantly weaker than the corresponding homonuclear O—H...O bonds in β -diketone enols $\cdots\text{O}=\text{C}-\text{C}=\text{C}-\text{OH}\cdots$ [$2.39 \leq d(\text{O}\cdots\text{O}) \leq 2.44$ Å] (Emsley, 1984; Gilli *et al.*, 1989; Gilli & Bertolasi, 1990; Bertolasi *et al.*, 1991), a fact that has been accounted for by the much higher proton affinity (PA) of nitrogen with respect to oxygen, which substantially hinders any valence bond N—H...O $\leftrightarrow$ N...H—O resonance mixing. Observed N...O distances are found to be scattered in the range 2.53–2.72 Å and to display strong dependence on the chemical nature of the substituents.



Scheme 1

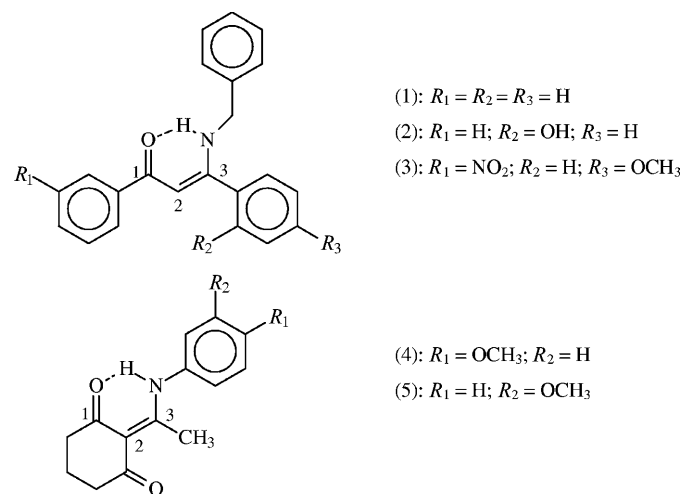
(ii) Group B: β -Enaminones characterized by the fusion of the RAHB ring with a phenyl group. A number of chemical variations have been investigated, such as *N*-salicylidene-anilines (Inabe, 1991; Wozniak *et al.*, 1995; Ogawa *et al.*, 1998; Burgess *et al.*, 1999; Fukuda *et al.*, 2003; Arod *et al.*, 2005) and 2-iminophenols (Filarowski *et al.*, 2002, 2005; Filarowski, 2005). Although few compounds are present in both tautomeric forms, these molecules prefer to form rather short O—H $\cdots$ N (instead of N—H $\cdots$ O) hydrogen bonds [$2.46 \leq d(\text{N}\cdots\text{O}) \leq 2.57 \text{ \AA}$] whose formation is to be imputed (Gilli *et al.*, 2000) to the large resonant energy of the phenyl ring, which stabilizes the iminoenol (2-iminophenol) form against the N/O PA difference; this energy would be lost in forming the enaminone tautomer.

(iii) Group C: Probably the most interesting enaminones. Here the RAHB ring is fused with a naphthalene group and, because of the smaller resonance energy of this molecule, the two N—H $\cdots$ O and N $\cdots$ H—O tautomers become nearly isoenergetic, so as to be easily shifted from one state to the other by the effect of properly chosen N-substituents. This situation results in the formation of tautomeric N—H $\cdots$ O/N $\cdots$ H—O bonds in a double-well potential with substituent-modulated proton populations. Accordingly, their crystal structures become dynamically or statically disordered according to the lower or higher value of the proton transfer energy barrier (Inabe *et al.*, 1994; Kaitner *et al.*, 1998; Nazir *et al.*, 2000; Popović *et al.*, 2001).

The classification into three groups is strongly supported by the density functional theory calculations carried out at the B3LYP/6-31+G(*d,p*) level on the three sample molecules of

Scheme 1. Defining $\Delta E = E(\text{O—H}\cdots\text{N}) - E(\text{N—H}\cdots\text{O})$ as the energy difference between the two hydrogen-bond minima, the calculated values of ΔE and $d(\text{O}\cdots\text{N})$ are $33.49 \text{ kJ mol}^{-1}$ and $2.713 \text{ \AA}$ for A, $-14.95 \text{ kJ mol}^{-1}$ and $2.614 \text{ \AA}$ for B, and 1.88 kJ mol^{-1} and $2.571 \text{ \AA}$ for C (Gilli *et al.*, 2000).

Since the three groups have been studied in uneven detail, we have undertaken a series of investigations on the less studied groups A and C, generally aimed at establishing the role played by the steric and electronic properties of the substituents in determining both the strength of the intramolecular RAHBs formed and the shape of the proton-transfer energy profile. In this first paper, these criteria are applied to group A compounds carrying different substituents and, for this purpose, we report here the crystal structures of three simple β -enaminones, (1) (2*Z*)-3-(benzylamino)-1,3-diphenyl-prop-2-en-1-one, (2) (2*Z*)-3-(benzylamino)-3-(2-hydroxyphenyl)-1-phenyl-prop-2-en-1-one and (3) (2*Z*)-3-(benzylamino)-3-(4-methoxyphenyl)-1-(3-nitrophenyl)-prop-2-en-1-one, which are derived from diaryl β -diketones, and two β,β' -diketo enamines, (4) 2-[1-[(4-methoxyphenyl)amino]ethylidene]cyclohexene-1,3-dione and (5) 2-[1-[(3-methoxyphenyl)amino]ethylidene]cyclohexene-1,3-dione, which are derived from 2-acetyl-1,3-cyclohexanedione (Scheme 2). Experimental geometries will be compared with those of other similar compounds endowed with a variety of substituents retrieved from the Cambridge Structural Database (CSD; Allen *et al.*, 1979).



Scheme 2

2. Experimental

2.1. Synthesis

Compounds (1), (2) and (3) were synthesized by the condensation reaction, in a benzene solution, of a suitable 1,3-diaryl β -diketone derivative with benzylamine. The reaction mixture was refluxed and stirred for some hours. The slurry was reduced in volume on a rotatory evaporator and allowed

Table 1
Experimental details.

	(1)	(2)	(3)	(4)	(5)
Crystal data					
Chemical formula	C ₂₂ H ₁₉ NO	C ₂₂ H ₁₉ NO ₂	C ₂₃ H ₂₀ N ₂ O ₄	C ₁₅ H ₁₇ NO ₃	C ₁₅ H ₁₇ NO ₃
<i>M_r</i>	313.38	329.38	388.41	259.30	259.30
Cell setting, space group	Triclinic, <i>P</i> $\bar{1}$	Orthorhombic, <i>Pbca</i>	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P2₁/n</i>
Temperature (K)	150	150	150	150	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.9727 (2), 9.7552 (2), 10.0208 (2)	14.2380 (3), 14.3109 (3), 16.8047 (3)	6.9599 (2), 8.4786 (3), 17.1616 (6)	7.7200 (2), 8.9566 (3), 9.5777 (3)	14.0608 (3), 6.6407 (1), 14.4581 (3)
α , β , γ (°)	89.081 (1), 71.002 (1), 85.786 (1)	90.00, 90.00, 90.00	82.282 (2), 78.773 (2), 75.599 (2)	93.830 (2), 92.083 (2), 105.755 (2)	90.00, 107.312 (1), 90.00
<i>V</i> (Å ³)	827.08 (3)	3424.1 (1)	958.18 (6)	634.92 (3)	1288.85 (4)
<i>Z</i>	2	8	2	2	4
<i>D_x</i> (Mg m ⁻³)	1.258	1.278	1.346	1.356	1.336
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.08	0.08	0.09	0.10	0.09
Crystal form, colour	Prism, colourless	Prism, colourless	Plate, colourless	Prism, colourless	Irregular, colourless
Crystal size (mm)	0.44 × 0.24 × 0.21	0.32 × 0.31 × 0.25	0.35 × 0.33 × 0.09	0.50 × 0.38 × 0.17	0.43 × 0.32 × 0.24
Data collection					
Diffractometer	Nonius Kappa CCD	Nonius Kappa CCD	Nonius Kappa CCD	Nonius Kappa CCD	Nonius Kappa CCD
Data collection method	φ and ω scans	φ and ω scans	φ and ω scans	φ and ω scans	φ and ω scans
Absorption correction	None	None	None	None	None
No. of measured, independent and observed reflections	8302, 4703, 3866	10 220, 4138, 3631	8934, 4331, 3563	5780, 2862, 2554	11 215, 3749, 3285
Criterion for observed reflections	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)
<i>R</i> _{int}	0.020	0.024	0.031	0.028	0.028
$\theta_{\max}$ (°)	30.0	28.0	27.5	27.6	30.0
Refinement					
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.049, 0.120, 1.06	0.056, 0.132, 1.35	0.056, 0.123, 1.19	0.052, 0.145, 1.08	0.053, 0.123, 1.15
No. of reflections	4703	4138	4331	2862	3749
No. of parameters	293	303	342	232	240
H-atom treatment	Refined independently	Mixture of independent and constrained refinement	Refined independently	Mixture of independent and constrained refinement	Refined independently
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.3404P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 2.1857P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.5384P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0714P)^2 + 0.3622P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 0.7763P]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	<0.0001	<0.0001	<0.0001	0.001	<0.0001
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.24, -0.30	0.29, -0.25	0.21, -0.27	0.46, -0.47	0.31, -0.22

Computer programs used: *Kappa CCD Server Software* (Nonius, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *SIR97* (Altomare *et al.*, 1999), *SHELXL97* (Sheldrick, 1997), *ORTEPIII* (Burnett & Johnson, 1996), *PARST* (Nardelli, 1995), *PLATON* (Spek, 2003).

to stand overnight. The colourless products were isolated by filtration and recrystallized from a mixture of methanol/ethyl acetate.

The procedure for the synthesis of compounds (4) and (5) was analogous, using, in a toluene solution, 2-acetyl-1,3-cyclohexanedione and 4-methoxyaniline or 3-methoxyaniline. The products were recrystallized from ethanol.

2.2. Crystal structure determination

The diffraction data for all compounds were collected at 150 K using a Nonius KappaCCD diffractometer with graphite-monochromated Mo *K*α radiation ($\lambda = 0.7107$ Å). Data sets were integrated using the *DENZO-SMN* package (Otwinowski & Minor, 1997) and corrected for Lorentz and

polarization effects. The structures were solved by direct methods (Altomare *et al.*, 1999) and refined using full-matrix least squares. All non-H atoms were refined anisotropically and the H atoms isotropically. In structure (2) the *ortho* hydroxy group of the phenyl ring in position 3 is disordered over both *ortho*, *ortho'* positions. This O atom was refined over both positions with partial occupancies of 0.8 and 0.2, respectively. The O—H and C—H H atoms involved in this disorder were included in calculated positions, riding on their attached atoms. In structure (4) the C5(H₂) group of the cyclohexanedione ring was found to be disordered and was refined over two positions with occupancies of 0.61 and 0.39, respectively. Both the H atoms were included in calculated positions, riding on their attached atoms. All calculations were performed using *SHELXL97* (Sheldrick, 1997) and *PARST*

Table 2Selected bond distances (Å), bond numbers (*in italic>*) and angles (°).

	(1)	(2)	(3)	(4)	(5)
O1—C1	1.254 (1) <i>1.62</i>	1.272 (1) <i>1.52</i>	1.256 (2) <i>1.61</i>	1.252 (2) <i>1.64</i>	1.248 (2) <i>1.66</i>
C1—C2	1.426 (2) <i>1.32</i>	1.412 (2) <i>1.40</i>	1.418 (3) <i>1.37</i>	1.445 (2) <i>1.21</i>	1.446 (2) <i>1.21</i>
C2—C3	1.386 (2) <i>1.57</i>	1.388 (2) <i>1.56</i>	1.388 (2) <i>1.56</i>	1.429 (2) <i>1.30</i>	1.424 (2) <i>1.35</i>
N1—C3	1.337 (2) <i>1.44</i>	1.330 (2) <i>1.39</i>	1.338 (3) <i>1.43</i>	1.328 (2) <i>1.50</i>	1.328 (2) <i>1.50</i>
λ	0.39	0.43	0.41	0.44	0.42
Del%	78	86	82	88	84
C1—C10	1.506 (1)	1.496 (2)	1.503 (2)		
C3—C4	1.492 (2)	1.493 (2)	1.492 (3)		
N1—C16	1.454 (1)	1.455 (2)	1.458 (2)		
C2—C7				1.465 (2)	1.465 (2)
O2—C7				1.230 (2)	1.229 (2)
N1—C9				1.433 (2)	1.430 (2)
O1—C1—C2	123.1 (1)	122.2 (2)	123.2 (2)	123.1 (1)	123.0 (1)
C1—C2—C3	124.0 (1)	124.4 (2)	122.9 (2)	120.1 (1)	120.3 (1)
N1—C3—C2	122.2 (1)	122.8 (2)	122.1 (2)	119.0 (1)	119.5 (1)
$\Sigma\alpha$	369.3	369.4	368.2	362.2	362.8
C3—N1—C16	126.8 (1)	125.5 (2)	126.5 (2)		
C3—N1—C9				127.4 (2)	127.2 (1)

(Nardelli, 1995) as implemented in the *WinGX* (Farrugia, 1999) system of programs. The crystal data and refinement parameters are summarized in Table 1.¹

2.3. Hydrogen-bond strength and π -delocalization indices

Resonance-assisted hydrogen bonding can be defined as a positive synergism between hydrogen-bond strengthening and π -delocalization of the interleaving resonant fragment, two quantities that need to be precisely defined. In this paper, hydrogen-bond strengths are evaluated through the N $\cdots$ O contact distances and the π -delocalization through the indices λ ($0 \leq \lambda \leq 1$) and Del% = $100(1 - |2\lambda - 1|)$ ($0 \leq \text{Del}\% \leq 100$) (Gilli *et al.*, 2004; Bertolasi *et al.*, 2006), which have the following meaning. With reference to the extreme $\cdots\text{HN}=\text{C}=\text{C}=\text{O}\cdots$ (EO = enaminone) and $\cdots\text{N}=\text{C}=\text{C}=\text{OH}$ (IE = iminoenol) forms, the two extreme geometries are characterized by the same Del% = 0 and by $\lambda = 0$ and 1 for EO and IE, respectively, while the fully π -delocalized structure has Del% = 100 for $\lambda = 0.5$. The π -delocalization parameter, λ , has been evaluated from the Pauling bond numbers, n , of the bonds involved as $\lambda = (1/4)[(2 - n_1) + (n_2 - 1) + (2 - n_3) + (n_4 - 1)]$, where n_1, n_2, n_3 and n_4 are the bond orders of the C1=O, C1—C2, C2=C3 and C3—N bonds, respectively. Bond numbers are calculated from the Pauling (1960) equation $d(1) - d(n) = c \log_{10} n$, where the pure single ($n = 1$) and double ($n = 2$) bond distances are 1.49 and 1.33 Å, 1.38 and 1.20 Å, and 1.41 and 1.27 Å for $\text{Csp}^2\text{—Csp}^2$, $\text{Csp}^2\text{—O}$ (Allen *et al.*, 1987) and $\text{Csp}^2\text{—Nsp}^2$ (Ferretti *et al.*, 1993) bonds, respectively.

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK5040). Services for accessing these data are described at the back of the journal.

Table 3

Structural and spectroscopic parameters of hydrogen bonds.

	D—H (Å)	H $\cdots$ A (Å)	D $\cdots$ A (Å)	D—H $\cdots$ A (°)	δ_{NH} (p.p.m.)	ν_{NH} (cm ⁻¹)
(1)						
N1—H1 $\cdots$ O1	0.92 (2)	1.94 (2)	2.693 (1)	137 (1)	11.56	3175
(2)						
N1—H1 $\cdots$ O1	0.94 (2)	1.95 (2)	2.694 (2)	134 (2)	11.73	3288
O2—H20 $\cdots$ O1 ⁱ	0.82†	1.86	2.670 (2)	168	—	—
O2'—H20' $\cdots$ O1 ⁱⁱ	0.82†	2.07	2.730 (8)	138	—	—
(3)						
N1—H1 $\cdots$ O1	0.93 (3)	1.88 (2)	2.650 (2)	139 (2)	11.87	3261
(4)						
N1—H1 $\cdots$ O1	0.94 (2)	1.73 (2)	2.544 (2)	143 (2)	14.87	2862
(5)						
N1—H1 $\cdots$ O1	0.90 (2)	1.79 (2)	2.554 (2)	141 (2)	15.03	2880

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $x - \frac{1}{2}, y, \frac{3}{2} - z$. † Calculated H atoms.

3. Results and discussion

3.1. Compounds (1)–(3)

A selection of bond distances and angles is given in Table 2, together with bond orders (*in italic*) and π -delocalization parameters, λ and Del%, of the heterodienic group. Hydrogen-bond formation is associated with large ¹H NMR chemical shifts in the ranges 11.56–11.87 p.p.m. for (1)–(3) and 14.82–15.03 p.p.m. for (4) and (5) (to be compared with the 7–9 p.p.m. observed for weak hydrogen bonds) and with red-shifted ν_{NH} stretching frequencies from 3175 to 3288 cm⁻¹ for (1)–(3) and from 2862 to 2880 cm⁻¹ for (4) and (5) (to be compared with 3400 cm⁻¹ for the free N—H bond).

Table 3 reports the hydrogen-bond parameters. *ORTEPIII* (Burnett & Johnson, 1996) views are shown in Figs. 1–5. The structural data retrieved from CSD files are given in Supplementary Tables S1–S6.

Compounds (1), (2) and (3) are *N*-alkyl-1,3-diaryl- β -enaminones derived from 1,3-diaryl- β -diketone enols. They exhibit intramolecular N—H $\cdots$ O hydrogen bonds with N $\cdots$ O distances of 2.693 (1), 2.694 (2) and 2.650 (2) Å, which are in agreement with the average value of 2.67 (2) Å (Table 4) calculated from a sample of 46 simple β -enaminones (Table S1) retrieved from the CSD and carrying alkyl or aryl substituents in positions 1 and 3.

In (1), where the 1,3-substituents are both phenyl groups, the enaminone fragment undergoes an extended delocalization ($\lambda = 0.39$). In spite of this large delocalization the N—H $\cdots$ O bond remains moderately strong with respect to the shortest N $\cdots$ O distances of up to 2.53 Å found in some β -enaminones carrying peculiar substituents (Gilli *et al.*, 2000). The internal angles at atoms C1, C2 and C3 are significantly greater than 120° (on average 123°), indicating that the attractive force of the intramolecular N—H $\cdots$ O hydrogen bond is counterbalanced by repulsive interactions inside the β -enaminonic cycle (Table 2).

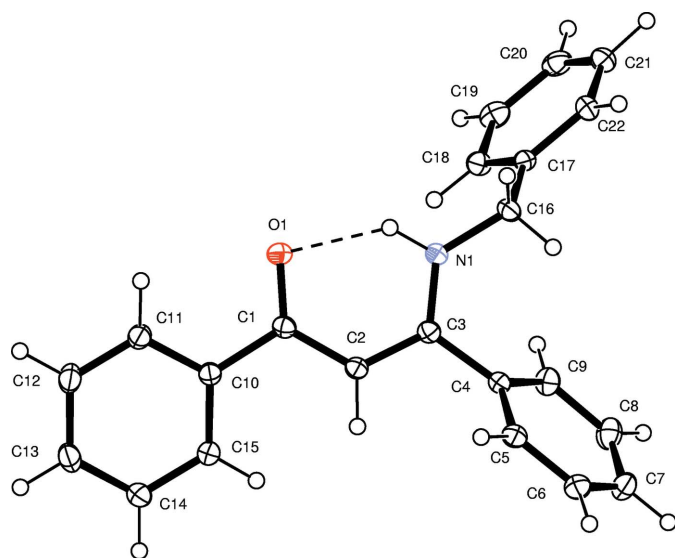


Figure 1
ORTEP (Burnett & Johnson, 1996) view of (1), showing displacement ellipsoids at the 40% probability level.

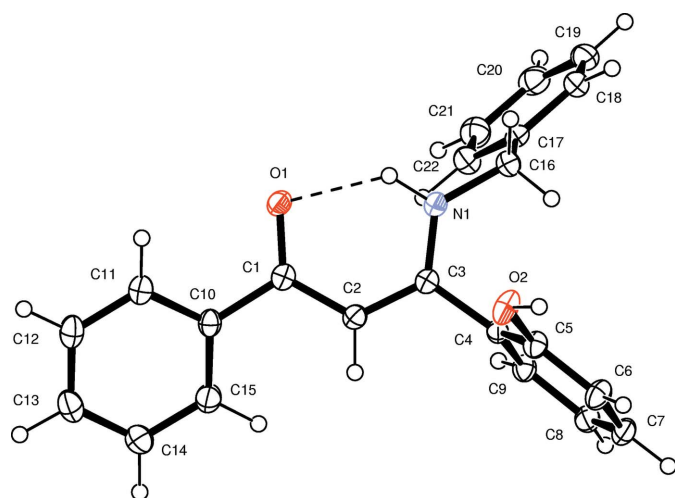


Figure 2
ORTEP view of (2), showing displacement ellipsoids at the 40% probability level.

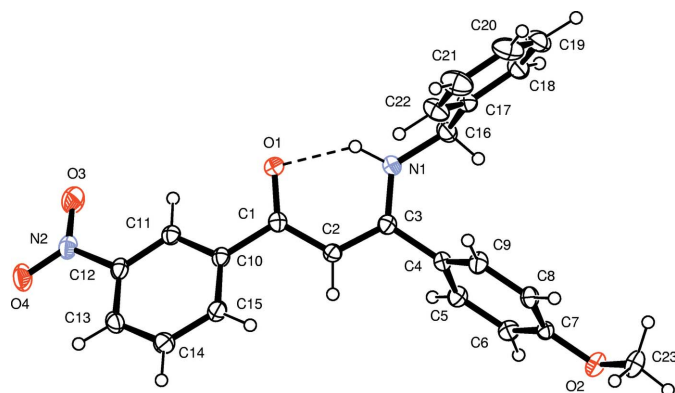


Figure 3
ORTEP view of (3), showing displacement ellipsoids at the 40% probability level.

In (2), the O2H hydroxy group, on the C4–C9 phenyl ring, is disordered, with the two opposed *ortho* positions in the ratio 80:20. Both are in a suitable orientation to form intermolecular O2–H···O1 hydrogen bonds with the same C1=O1 carbonyl group. These bonds seem responsible for a further polarization of the C1=O1 bond, which exhibits a remarkable lengthening [to 1.272 (1) Å] with respect to the same bonds in (1) and (3) [1.254 (1) and 1.256 (2) Å, respectively]. As a consequence, the delocalization within the heterodienic group also slightly increases, up to $\lambda = 0.43$, while the interatomic interactions within the heterodienic ring

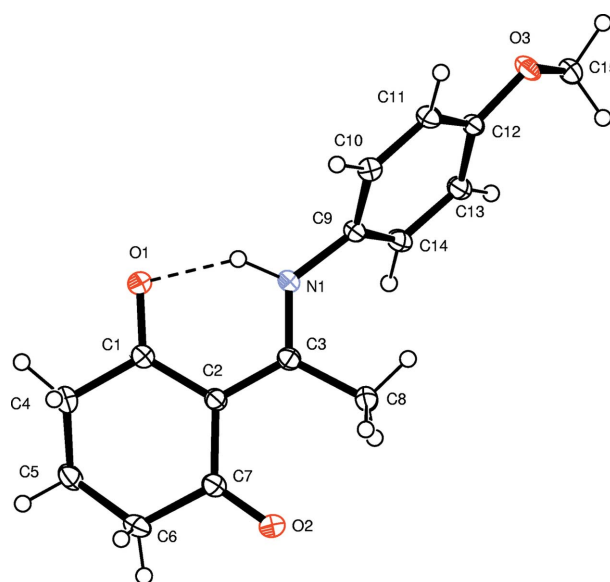


Figure 4
ORTEP view of (4), showing displacement ellipsoids at the 40% probability level.

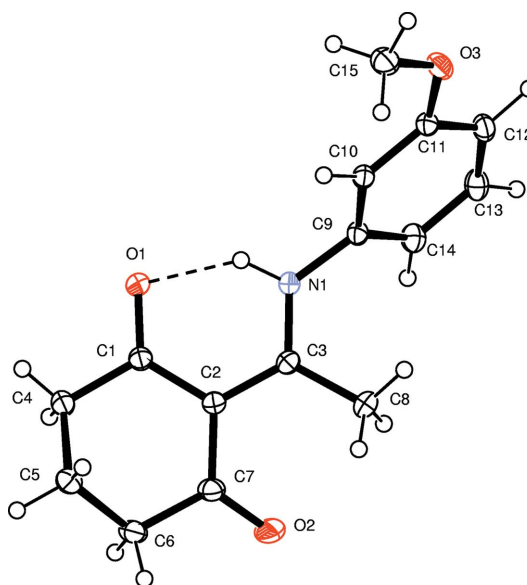


Figure 5
ORTEP view of (5), showing displacement ellipsoids at the 40% probability level.

remain unchanged, the internal angles at atoms C1, C2 and C3 and the N $\cdots$ O hydrogen-bond distance being comparable to the values for compound (1).

In (3) the substituents at the 1- and 3-positions are *m*-nitrophenyl and *p*-methoxyphenyl groups, respectively. In spite of a comparable delocalization of the heterodienic system ($\lambda = 0.41$), this structure shows a small narrowing of the internal angles at atoms C1, C2 and C3 associated with a significant shortening of the intramolecular N—H $\cdots$ O hydrogen bond. This shortening may be ascribed to an increased π -polarizability of the two phenyl rings carrying the *m*-NO₂ and *p*-OCH₃ substituents, which increases the flux of π -electrons inside the RAHB ring. In this respect, it is interesting to note that the corresponding (*i.e.* equally substituted) β -diketone enol displays one of the shortest observed O $\cdots$ O distances of 2.434 (1) Å (Bertolasi *et al.*, 1991; Gilli *et al.*, 2004).

3.2. Compounds (4) and (5)

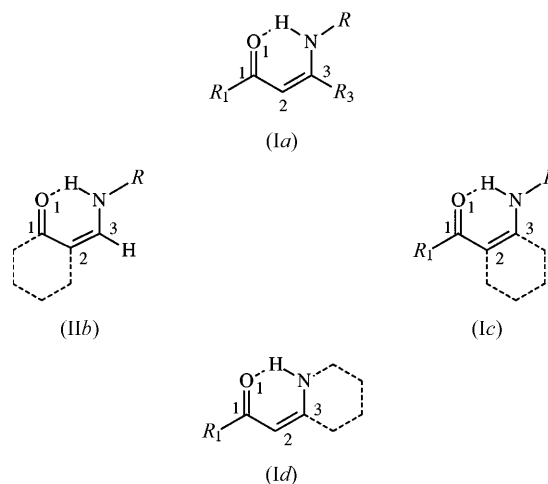
Compounds (4) and (5) show intramolecular N—H $\cdots$ O hydrogen-bond distances of 2.544 (2) and 2.554 (2) Å, which are much shorter than those observed in (1)–(3) [on average 2.66 (2) Å]. The shortening has been attributed to the electronic effect produced by the second β -diketone groups (Gilli *et al.*, 2000). In addition, in the present structures, this second β -enaminonic group, HN1—C3=C2—C7=O2, is seen to affect the RAHBs through a further delocalization of the C2—C7=O2 group, which displays a small shortening of the C2—C7 (Csp^2 — Csp^2) bond (1.46 Å) and a lengthening of the C7=O2 double bond (1.23 Å; Table 1). However, other factors of simple steric nature seem to be important, in particular (i) the inclusion of the C1—C2 bond in a cyclohexanedione ring and (ii) the short intramolecular contact between atom O2 and the methyl group in position 3 (Scheme 2). These structural features are consistent with the observed narrowing of the enaminone internal angles C1—C2—C3 and N1—C3—C2, the anomalous lengthening of the C1—C2 and C2—C3 bonds, and, as a consequence, the increased approach of the NH group to atom O1. The slightly different N $\cdots$ O distances in (3) and (4) can be ascribed to the different electronic effects produced by the methoxy groups in the *para* and *meta* positions on the phenyl ring linked to the N1 atom, in agreement with what was previously observed in the analogous series of diketohydrazones (Bertolasi *et al.*, 1993).

3.3. Comparison with CSD-retrieved structures

The relative importance of the factors responsible for the N—H $\cdots$ O hydrogen-bond shortening can be appreciated by a systematic survey of the CSD files of structures containing the β -enaminone fragment. According to previous indications (Gilli *et al.*, 2000), these compounds have been divided into two classes: (I) (simple β -enaminones) (Scheme 3) and (II) (β , β' -diketoenamines) (Scheme 4).

3.3.1. Structures of class (I). The structures of class (I) have been further divided in the four subclasses (Ia)–(Id) of

Scheme 3, where the enaminonic system is differently fused, at the C1—C2, C2—C3 or C3—N bonds, with a six-membered aliphatic cycle. Structures where the enamine group is fused with an aromatic ring, such as salicylideneanilines, have been excluded for the reasons given in §1; those where at least two bonds of the heterodienic system are included in six-membered aliphatic cycles have also been excluded. Average geometric and delocalization parameters for each class are given in Table 4.



Scheme 3

Simple β -enaminones (Ia) display bond distances within the heterodienic system corresponding to an almost complete π -delocalization, in agreement with what was found for (1)–(3), and a widening of the three internal angles that sum to an average value of 369°. The average N $\cdots$ O hydrogen-bond distance of 2.67 (2) Å is not much shorter than the same intramolecular distance in non-resonant systems [2.72 (2) Å; Gilli *et al.*, 2000; Chisolm *et al.*, 2000], indicating that the repulsions inside the β -enaminonic systems efficiently counteract the electronic attractive interactions due to RAHB effects.

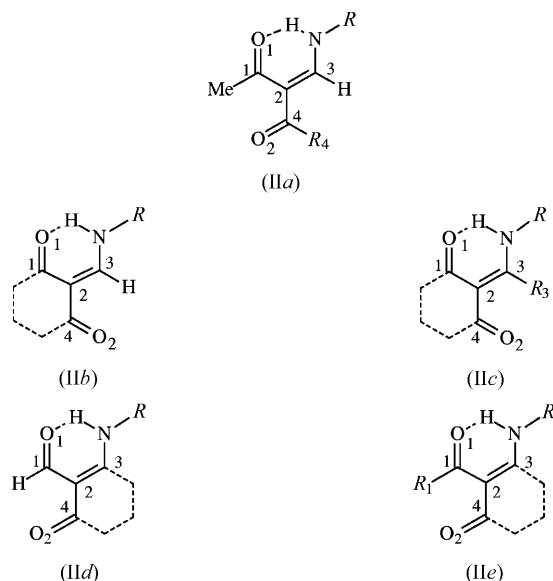
Compounds of subclasses (Ib), (Ic) and (Id) are indicative of the effects induced by fusion of the C1—C2, C2=C3 or C3—N bonds with the aliphatic six-membered cycle. In spite of the fact that few compounds have been retrieved for subclass (Ib), some general conclusions can be drawn. In (Ia) the N $\cdots$ O distance cannot be shortened by a narrowing of the C1—C2=C3 angle as long as the C2=C3—N angle can undergo an analogous enlargement, so the sum of the internal angles remains unchanged, as does the N $\cdots$ O distance (Table 4). Conversely, in subclasses (Ic) and (Id) the fusion of the enaminonic C2=C3 or C3—N bonds with an aliphatic six-membered ring gives rise to an equalization of the C1—C2=C3 and C2=C3—N internal angles to about 121°. As a consequence, the sum of the internal angles decreases to 366° while the N $\cdots$ O distances is shortened to 2.59–2.61 Å. Note that the π -delocalization indices remain fairly constant in all compounds of class (I), indicating that the electronic RAHB

Table 4Average structural data (Å and °) of β -enaminones of the classes reported in Schemes 3 and 4 retrieved from CSD files.Bond numbers are reported in *italics*. λ and Del% are delocalization parameters (see text); $\Sigma\alpha$ is the sum of the internal angles at the β -enaminone group.

Subclass	<i>n</i>	$\langle \text{O} \cdots \text{N} \rangle$	$\langle \text{O1}=\text{C1} \rangle$	$\langle \text{C1}-\text{C2} \rangle$	$\langle \text{C2}=\text{C3} \rangle$	$\langle \text{C3}-\text{N} \rangle$	$\langle \text{O1}=\text{C1}-\text{C2} \rangle$	$\langle \text{C1}-\text{C2}=\text{C3} \rangle$	$\langle \text{C2}=\text{C3}-\text{N} \rangle$	$\Sigma\alpha$	$\langle \lambda \rangle$	$\langle \text{Del}\% \rangle$
(Ia)	46	2.67 (2)	1.25 (1) <i>1.65</i>	1.41 (1) <i>1.41</i>	1.38 (1) <i>1.61</i>	1.34 (1) <i>1.41</i>	123 (1)	124.4 (9)	121.1 (9)	369	0.39	78
(Ib)	2	2.650	1.256 <i>1.61</i>	1.418 <i>1.37</i>	1.362 <i>1.74</i>	1.354 <i>1.32</i>	122.4	121.6	125.5	369	0.34	68
(Ic)	5	2.59 (2)	1.25 (1) <i>1.65</i>	1.432 (5) <i>1.29</i>	1.385 (7) <i>1.58</i>	1.345 (3) <i>1.38</i>	123.7 (3)	120.5 (3)	121.8 (6)	366	0.36	72
(Id)	17	2.61 (2)	1.26 (1) <i>1.59</i>	1.42 (1) <i>1.35</i>	1.39 (1) <i>1.54</i>	1.35 (1) <i>1.35</i>	122.7 (6)	122.5 (7)	121.0 (8)	366	0.39	78
(IIa)	17	2.61 (3)	1.240 (5) <i>1.71</i>	1.450 (9) <i>1.19</i>	1.390 (9) <i>1.54</i>	1.32 (1) <i>1.56</i>	120.5 (5)	119.8 (4)	126 (1)	366	0.38	76
(IIb)	3	2.63 (2)	1.24 (2) <i>1.71</i>	1.43 (2) <i>1.30</i>	1.40 (1) <i>1.48</i>	1.33 (3) <i>1.49</i>	122 (2)	122.1 (6)	123 (2)	367	0.40	80
(IIc)	14	2.55 (1)	1.257 (5) <i>1.61</i>	1.442 (6) <i>1.23</i>	1.428 (9) <i>1.31</i>	1.315 (6) <i>1.60</i>	123.6 (4)	120.6 (3)	118.1 (7)	362	0.48	96
(IId)	1	2.644	1.244 <i>1.69</i>	1.426 <i>1.32</i>	1.409 <i>1.42</i>	1.350 <i>1.35</i>	125.9	122.6	118.4	367	0.39	78
(IIe)	2	2.584	1.240 <i>1.71</i>	1.450 <i>1.19</i>	1.412 <i>1.40</i>	1.328 <i>1.50</i>	121.7	120.2	122.0	364	0.40	80

effects are essentially constant. The reason for the $\text{N} \cdots \text{O}$ shortening must be steric in nature and there is, in fact, evidence that the $\text{N} \cdots \text{O}$ distance is strictly related to the sum of the values of the internal β -enaminone angles.

3.3.2. Structures of class II. The structures of class II have been divided in the five subclasses (IIa)–(IIe), as displayed in Scheme 4. All these compounds are β, β' -diketoenamines, that is β -enaminones substituted by a further β' -keto group.

**Scheme 4**

The structures of subclass (IIa) exhibit an average $\text{N} \cdots \text{O}$ distance of 2.61 (3) Å, which is significantly shorter than that observed in simple β -enaminones (Ia). This shortening has been imputed (Gilli *et al.*, 2000) to the electronic effects

associated with the supplementary π -delocalization within the second $\text{HN}-\text{C3}=\text{C2}-\text{C4}=\text{O2}$ β' -enaminonic group, complemented by the steric effects generated by the intramolecular short repulsive interactions between atom O2 and the Me substituent in position 1, which are made possible by the planarity of the β, β' -diketoenamine group. This can explain why the internal angles at atoms C1 and C2 undergo a significant narrowing, while the angle at atom C3, which carries a simple H atom, can become wider, so keeping the sum of the internal angles around 366°. These data are in agreement with those reported for β, β' -diketohydrazone by Bertolasi *et al.* (1993, 1994, 1999) and Gawinecki *et al.* (2001).

Subclasses (IIb) and (IIc) include compounds where the C1–C2 bond is embedded in an aliphatic six-membered ring, as in compounds (4) and (5) of this paper. The structures of subclass (IIb) do not exhibit significant intramolecular short repulsive interactions because the substituent at C3 is an H atom and, accordingly, the structures display an average $\text{N} \cdots \text{O}$ distance of 2.63 (2) Å, which is significantly shorter than in simple β -enaminones (Ia), but slightly longer than in β, β' -diketoenamines (IIa). Therefore, the presence of a cycle, such as cyclohexanedione, that includes atoms C1 and C2 is not sufficient to shorten $\text{N} \cdots \text{O}$ distances below 2.63 Å. To obtain a greater $\text{N} \cdots \text{O}$ shortening, the β -enaminone group must be involved in stronger intramolecular steric effects, a requirement satisfied by the structures of subclass (IIc) because of the presence of an alkyl or aryl R3 group in position 3. Owing to the $\text{O2} \cdots \text{R3}$ steric repulsion the $\text{N} \cdots \text{O}$ distance is shortened, on average, to 2.55 (1) Å, while the sum of the internal angles is decreased to 362°, which is the smallest average value reported in Table 4. This very short hydrogen bond is associated with an almost complete delocalization ($\lambda = 0.48$, Del% = 96) of the heterodienic unit.

A similar effect can be predicted for subclasses (IId) and (IIe) where the $\text{C2}=\text{C3}$ double bond is included in an aliphatic six-membered ring. In spite of the fact that very few

structures were retrieved from the CSD, there is no doubt that the trend observed here is analogous to that found for subclasses (IIb) and (IIc). The only structure of subclass (IId), which displays an H atom as substituent in position 1, exhibits the longer N...O distance of 2.64 Å and a sum of internal angles of 367°, while the structures of subclass (IIe), because of the strong intramolecular steric hindrance between O2 and R1, exhibit a shorter N...O distance of 2.58 Å, with a concomitant narrowing of the enamionic internal angles, whose sum is 364°.

4. Conclusions

All the reported structural data of intramolecularly hydrogen-bonded β -enaminones suggest that the N...O bond length is determined by two main factors: the π -conjugation of the resonant fragment and the intramolecular steric interactions involving the substituents at the heterodienic system. Simple β -enaminones (Ia) display extended π -conjugation of the heterodienic group, but the RAHB effect alone does not produce a significant shortening of N...O hydrogen-bond distances below 2.67 Å because of the different proton affinities of the N and O atoms and because of the absence of strong intramolecular steric compression. Moderate shortenings down to 2.61 Å are, however, produced in subclasses (Ib)–(Id) by the introduction of aliphatic six-membered rings fused with the enamionic moiety, which contribute to stiffening the overall structure.

Significant N...O shortenings down to 2.55 Å can be achieved only in compounds (II) having, at the same time, the β -enaminone system included in a six-membered aliphatic ring, a further β' -keto group substituted in position 2 and substituents able to produce strong intramolecular repulsive interactions.

It seems interesting that the π -delocalization index (Table 4) remains essentially fixed to the value of 78% of simple β -enaminones (Ia), irrespective of the shortening of the N...O distance, the only exception being the strongest hydrogen bonds in (IIc) (N...O of 2.55 Å), for which this index suddenly rises to 96%. This can be interpreted on the grounds of the observation that resonance-assisted hydrogen bonding simply attests the existence of an intercorrelation between N...O shortening and increased π -delocalization (Gilli *et al.*, 2005), but tells nothing about the original cause of the shortening (*i.e.* the π -delocalization itself or the steric compression on the hydrogen-bonded ring). The present data are consistent with the idea that the π -delocalization is certainly the driving force of N...O contraction up to 2.67 Å [the value observed for simple β -enaminones (Ia)]. Below this limit the steering factors become steric and are controlled by the relative encumbrances of the different substituents. Only when this compression reaches a maximum [and the N...O distance a minimum of 2.55 Å in (IIc)] can the RAHB mechanism induce a further delocalization of the resonant fragment, delocalization which, however, is not the driving force but the driven factor of the process.

We thank MIUR (Rome) for COFIN 2004 financial support as part of our project 'Smart Hydrogen Bonds in Nature and Functional Materials'.

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