

Interplay of hydrogen bonding and other molecular interactions in determining the crystal packing of a series of *anti*- β -ketoarylhydrazones

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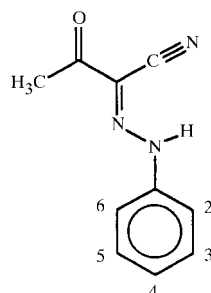
Abstract

The crystal structures of six *anti*- β -ketoarylhydrazones are reported: (a1) (*E*)-2-(4-cyanophenylhydrazono)-3-oxobutanenitrile; (a2) (*E*)-2-(4-methylphenylhydrazono)-3-oxobutanenitrile; (a3) (*E*)-2-(4-acetylphenylhydrazono)-3-oxobutanenitrile; (a4) (*E*)-2-(2-methoxyphenylhydrazono)-3-oxobutanenitrile; (a5) (*E*)-2-(2-acetylphenylhydrazono)-3-oxobutanenitrile; (a6) (*E*)-2-(2-nitrophenylhydrazono)-3-oxobutanenitrile. All compounds contain the π -conjugated heterodienic group $\text{HN}=\text{N}=\text{C}=\text{C}=\text{O}$ and could form, at least in principle, chains of intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds assisted by resonance (RAHB-inter). Compounds (a1) and (a2) form this kind of hydrogen bond though with rather long $\text{N}\cdots\text{O}$ distances of 2.948 (3) and 2.980 (2) Å, and compound (a6) undergoes the same interaction but even more weakened [$\text{N}\cdots\text{O}$ 3.150 (1) Å] by the intramolecular bifurcation of the hydrogen bond donated by the $\text{N}-\text{H}$ group. The intrinsic weakness of the intermolecular RAHB makes possible the setting up of alternative packing arrangements that are controlled by an antiparallel dipole–dipole (DD) interaction between two $\text{C}=\text{O}$ groups of the β -ketohydrazone moiety [compounds (a4) and (a5)]. The critical factors that cause the switching between the different packings turn out to be the presence of hydrogen bonding accepting substituents on the phenyl and, most frequently, the intramolecular $\text{N}-\text{H}\cdots\text{O}$ bond with the O atom of the phenyl *o*-substituent. The crystal packing is widely determined by RAHB-inter (three cases) or DD (two cases) interactions. Only compound (a3) displays a different packing arrangement, where the DD interaction is complemented by a non-resonant hydrogen bond between a *p*-acetyl phenyl substituent and the hydrazone $\text{N}-\text{H}$ group [$\text{N}\cdots\text{O}$ 2.907 (2) Å]. Crystal densities range from 1.24 to 1.44 Mg m^{-3} and are shown to increase with the number of intermolecular hydrogen bonds and other non-van der Waals interactions.

1. Introduction

Because of our continuing interest in the structural studies of heterodienic systems forming $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds assisted by resonance (Bertolasi *et al.*, 1993, 1995, 1998; Bertolasi, Nanni *et al.*, 1994; Bertolasi,

Gilli *et al.*, 1994), the crystal structures of a series of six *anti*- β -ketoarylhydrazones (I) are reported. All these



- (a1): 4-CN
- (a2): 4-CH₃
- (a3): 4-COCH₃
- (a4): 2-OCH₃
- (a5): 2-COCH₃
- (a6): 2-NO₂

(I)

compounds contain the heterodienic system $\text{H}(\text{Ar})\text{N}=\text{N}=\text{C}(\text{CN})-\text{C}=\text{O}$ [see (I)], with the $\text{N}(\text{Ar})\text{H}$ and ketonic groups in *anti* positions with respect to the $\text{C}=\text{N}$ double bond, and are imputed to form intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds assisted by resonance (RAHB; Gilli *et al.*, 1994, 1996) in analogy with $\cdots\text{HN}=\text{C}=\text{C}=\text{O}\cdots$ β -enaminones, where it has already been shown (Bertolasi *et al.*, 1995, 1998) that the intermolecular $\text{N}-\text{H}\cdots\text{O}$ bond can be strengthened by RAHB only in the presence of substituents at the heterodienic moiety having specific electronic properties. These findings were interpreted in terms of two main facts: (i) the $\text{N}-\text{H}\cdots\text{O} \leftrightarrow \text{N}\cdots\text{H}-\text{O}$ resonance is only a potential factor of $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bond strengthening because of the large proton affinity (PA) difference between the hydrogen-bond donor and acceptor atoms; (ii) the RAHB is, however, made stronger by the concomitant presence of chemical substituents able to reduce such a PA gap. The present paper is intended to extend to the analogous $\cdots\text{HN}=\text{N}=\text{C}=\text{O}\cdots$ *anti*- β -ketohydrazones the previous analysis carried out on the β -enaminone system by assessing the strength of the hydrogen bonds formed and their relevance in determining the crystal packing of these compounds.

2. Experimental

Compounds have been obtained from coupling of arene diazonium ions with 3-aminocrotonitrile. Their detailed

Table 1. *Experimental details*

	(a1)	(a2)	(a3)	(a4)
Crystal data				
Chemical formula	C ₁₁ H ₈ N ₄ O	C ₁₁ H ₁₁ N ₃ O	C ₁₂ H ₁₁ N ₃ O ₂	C ₁₁ H ₁₁ N ₃ O ₂
Chemical formula weight	212.21	201.23	229.24	217.23
Cell setting	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pnma</i>
<i>a</i> (Å)	7.196 (3)	7.052 (2)	8.638 (3)	15.236 (2)
<i>b</i> (Å)	14.125 (2)	13.211 (2)	10.841 (2)	6.618 (1)
<i>c</i> (Å)	10.862 (2)	11.996 (2)	12.208 (2)	11.379 (1)
α (°)	90	90	90	90
β (°)	97.34 (3)	104.96 (2)	94.69 (2)	90
γ (°)	90	90	90	90
<i>V</i> (Å ³)	1095.0 (5)	1079.7 (4)	1139.4 (5)	1147.4 (3)
<i>Z</i>	4	4	4	4
<i>D_x</i> (Mg m ⁻³)	1.287	1.238	1.336	1.258
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25	25
θ range (°)	7–12	7–13	8–12	9–14
μ (mm ⁻¹)	0.089	0.083	0.094	0.090
Temperature (K)	293 (2)	293 (2)	293 (2)	293 (2)
Crystal form	Needle	Prism	Prism	Prism
Crystal size (mm)	0.43 × 0.12 × 0.10	0.52 × 0.21 × 0.20	0.28 × 0.19 × 0.14	0.52 × 0.33 × 0.26
Crystal colour	Pale yellow	Yellow	Yellow	Yellow
Data collection				
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans
No. of measured reflections	2556	2804	2921	1488
No. of independent reflections	2366	2595	2741	1488
No. of observed reflections	1102	1814	1735	881
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
<i>R</i> _{int}	0.030	0.020	0.012	0.0000
θ_{\max} (°)	26.96	27.96	27.97	27.95
Range of <i>h, k, l</i>	0 → <i>h</i> → 9 0 → <i>k</i> → 18 -13 → <i>l</i> → 13	0 → <i>h</i> → 9 0 → <i>k</i> → 17 -15 → <i>l</i> → 15	0 → <i>h</i> → 11 0 → <i>k</i> → 14 -16 → <i>l</i> → 16	0 → <i>h</i> → 20 0 → <i>k</i> → 8 0 → <i>l</i> → 14
No. of standard reflections	3	3	3	3
Frequency of standard reflections	Every 120 min	Every 120 min	Every 120 min	Every 120 min
Refinement				
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
$R[F^2 > 2\sigma(F^2)]$	0.0626	0.0451	0.0532	0.0501
$wR(F^2)$	0.1690	0.1400	0.1548	0.1458
<i>S</i>	0.945	1.057	1.046	1.025
No. of reflections used in refinement	2366	2595	2741	1488
No. of parameters used	178	180	198	126
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0852P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0786P)^2 + 0.0758P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0888P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0846P)^2 + 0.0080P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.029	0.004	0.013	0.033
$\Delta\rho_{\max}$ (e Å ⁻³)	0.179	0.175	0.256	0.146
$\Delta\rho_{\min}$ (e Å ⁻³)	-0.188	-0.171	-0.197	-0.276
Extinction method	<i>SHELXL97</i> (Sheldrick, 1997)	None	None	None
Extinction coefficient	0.002 (3)	0	0	0
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C)	<i>International Tables for Crystallography</i> (1992, Vol. C)	<i>International Tables for Crystallography</i> (1992, Vol. C)	<i>International Tables for Crystallography</i> (1992, Vol. C)

Table 1 (*cont.*)

	(a1)	(a2)	(a3)	(a4)
Computer programs				
Data collection	CAD-4 (Enraf-Nonius, 1984)	CAD-4 (Enraf-Nonius, 1984)	CAD-4 (Enraf-Nonius, 1984)	CAD-4 (Enraf-Nonius, 1984)
Cell refinement	CAD-4 (Enraf-Nonius, 1984)	CAD-4 (Enraf-Nonius, 1984)	CAD-4 (Enraf-Nonius, 1984)	CAD-4 (Enraf-Nonius, 1984)
Data reduction	MolEN (Fair, 1990)	MolEN (Fair, 1990)	MolEN (Fair, 1990)	MolEN (Fair, 1990)
Structure solution	SIR92 (Altomare <i>et al.</i> , 1994)	SIR92 (Altomare <i>et al.</i> , 1994)	SIR92 (Altomare <i>et al.</i> , 1994)	SIR92 (Altomare <i>et al.</i> , 1994)
Structure refinement	SHELXL97 (Sheldrick, 1997)	SHELXL97 (Sheldrick, 1997)	SHELXL97 (Sheldrick, 1997)	SHELXL97 (Sheldrick, 1997)
Preparation of material for publication	PARST (Nardelli, 1983, 1995), SHELXL97 (Sheldrick, 1997)	PARST (Nardelli, 1983, 1995), SHELXL97 (Sheldrick, 1997)	PARST (Nardelli, 1983, 1995), SHELXL97 (Sheldrick, 1997)	PARST (Nardelli, 1983, 1995), SHELXL97 (Sheldrick, 1997)
		(a5)		(a6)
Crystal data				
Chemical formula		C ₁₂ H ₁₁ N ₃ O ₂		C ₁₀ H ₈ N ₄ O ₃
Chemical formula weight		229.24		232.2
Cell setting		Triclinic		Monoclinic
Space group		$P\bar{1}$		$P2_1/n$
<i>a</i> (Å)		6.878 (2)		7.184 (1)
<i>b</i> (Å)		8.241 (1)		19.491 (2)
<i>c</i> (Å)		11.395 (1)		8.084 (1)
α (°)		105.21 (1)		90
β (°)		96.62 (2)		109.27 (1)
γ (°)		102.92 (2)		90
<i>V</i> (Å ³)		597.0 (2)		1068.5 (2)
<i>Z</i>		2		4
<i>D_r</i> (Mg m ⁻³)		1.275		1.443
Radiation type		Mo <i>K</i> α		Mo <i>K</i> α
Wavelength (Å)		0.71073		0.71073
No. of reflections for cell parameters		25		25
θ range (°)		8–13		9–13
μ (mm ⁻¹)		0.090		0.111
Temperature (K)		293 (2)		293 (2)
Crystal form		Prism		Prism
Crystal size (mm)		0.62 \times 0.26 \times 0.12		0.60 \times 0.26 \times 0.21
Crystal colour		Yellow		Orange
Data collection				
Diffractometer		Enraf-Nonius CAD-4		Enraf-Nonius CAD-4
Data collection method		$\omega/2\theta$ scans		$\omega/2\theta$ scans
No. of measured reflections		3007		2750
No. of independent reflections		2860		2580
No. of observed reflections		1963		1996
Criterion for observed reflections		$I > 2\sigma(I)$		$I > 2\sigma(I)$
R_{int}		0.012		0.025
θ_{max} (°)		27.97		27.96
Range of <i>h</i> , <i>k</i> , <i>l</i>		0 \rightarrow <i>h</i> \rightarrow 9 -10 \rightarrow <i>k</i> \rightarrow 10 -15 \rightarrow <i>l</i> \rightarrow 14		0 \rightarrow <i>h</i> \rightarrow 9 0 \rightarrow <i>k</i> \rightarrow 25 -10 \rightarrow <i>l</i> \rightarrow 10
No. of standard reflections		3		3
Frequency of standard reflections		Every 120 min		Every 120 min
Refinement				
Refinement on		F^2		F^2
$R[F^2 > 2\sigma(F^2)]$		0.0487		0.0401
$wR(F^2)$		0.1495		0.1173
<i>S</i>		1.065		1.085
No. of reflections used in refinement		2860		2580
No. of parameters used		198		186
H-atom treatment		All H-atom parameters refined		All H-atom parameters refined
Weighting scheme		$w = 1/[\sigma^2(F_o^2) + (0.0876P)^2 + 0.0213P]$, where $P = (F_o^2 + 2F_c^2)/3$		$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 0.1463P]$, where $P = (F_o^2 + 2F_c^2)/3$

Table 1 (cont.)

	(a5)	(a6)
$(\Delta/\sigma)_{\max}$	0.005	0.002
$\Delta\rho_{\max}$ ($e \text{ \AA}^{-3}$)	0.157	0.229
$\Delta\rho_{\min}$ ($e \text{ \AA}^{-3}$)	-0.195	-0.196
Extinction method	None	None
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C)	<i>International Tables for Crystallography</i> (1992, Vol. C)
Computer programs		
Data collection	CAD-4 (Enraf-Nonius, 1984)	CAD-4 (Enraf-Nonius, 1984)
Cell refinement	CAD-4 (Enraf-Nonius, 1984)	CAD-4 (Enraf-Nonius, 1984)
Data reduction	<i>MolEN</i> (Fair, 1990)	<i>MolEN</i> (Fair, 1990)
Structure solution	<i>SIR92</i> (Altomare <i>et al.</i> , 1994)	<i>SIR92</i> (Altomare <i>et al.</i> , 1994)
Structure refinement	<i>SHELXL97</i> (Sheldrick, 1997)	<i>SHELXL97</i> (Sheldrick, 1997)
Preparation of material for publication	<i>PARST</i> (Nardelli, 1983, 1995), <i>SHELXL97</i> (Sheldrick, 1997)	<i>PARST</i> (Nardelli, 1983, 1995), <i>SHELXL97</i> (Sheldrick, 1997)

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$U_{\text{eq}} = (1/3)\sum_i \Sigma_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$					Table 2 (cont.)				
	x	y	z	U_{eq}	x	y	z	U_{eq}	
(a1)					N1	-0.07426 (18)	0.36408 (14)	0.60706 (13)	0.0407 (4)
O1	0.0782 (3)	-0.24978 (15)	0.34765 (19)	0.0696 (7)	N2	-0.05251 (16)	0.29449 (13)	0.52129 (12)	0.0386 (4)
N1	-0.1995 (3)	-0.10435 (16)	-0.0056 (2)	0.0475 (6)	N3	0.1989 (2)	0.14192 (19)	0.71043 (17)	0.0700 (6)
N2	-0.1416 (3)	-0.10652 (14)	0.11385 (18)	0.0441 (6)	C1	0.0631 (2)	0.12560 (17)	0.43237 (15)	0.0436 (4)
N3	-0.0347 (5)	-0.3376 (2)	0.0472 (3)	0.1024 (12)	C2	0.0419 (2)	0.20171 (16)	0.52987 (14)	0.0399 (4)
N4	-0.5340 (4)	0.2995 (2)	-0.2765 (3)	0.0941 (11)	C3	-0.0324 (4)	0.1540 (3)	0.3294 (2)	0.0621 (6)
C1	-0.0035 (4)	-0.1809 (2)	0.3003 (3)	0.0533 (7)	C4	0.1307 (2)	0.16739 (18)	0.63113 (16)	0.0465 (5)
C2	-0.0725 (4)	-0.18337 (18)	0.1674 (2)	0.0458 (7)	C5	-0.17546 (19)	0.46556 (15)	0.59488 (14)	0.0358 (4)
C3	-0.0398 (7)	-0.0954 (3)	0.3737 (4)	0.0759 (11)	C6	-0.2475 (2)	0.49876 (17)	0.49332 (14)	0.0402 (4)
C4	-0.0517 (4)	-0.2703 (2)	0.1023 (3)	0.0620 (9)	C7	-0.3452 (2)	0.59993 (17)	0.48727 (14)	0.0402 (4)
C5	-0.2681 (3)	-0.02011 (17)	-0.0613 (2)	0.0397 (6)	C8	-0.37382 (19)	0.66866 (15)	0.57949 (13)	0.0358 (4)
C6	-0.3343 (4)	-0.0211 (2)	-0.1863 (3)	0.0540 (8)	C9	-0.2998 (2)	0.63279 (18)	0.67998 (15)	0.0464 (5)
C7	-0.4039 (4)	0.0608 (2)	-0.2437 (3)	0.0571 (8)	C10	-0.2017 (2)	0.53268 (18)	0.68853 (15)	0.0479 (5)
C8	-0.4068 (4)	0.14297 (19)	-0.1751 (3)	0.0514 (7)	C11	-0.4779 (2)	0.77824 (16)	0.57467 (14)	0.0394 (4)
C9	-0.3401 (4)	0.1431 (2)	-0.0501 (3)	0.0520 (7)	C12	-0.5520 (3)	0.8214 (2)	0.46668 (18)	0.0533 (5)
C10	-0.2693 (4)	0.06204 (18)	0.0077 (3)	0.0457 (7)	(a4)				
C11	-0.4784 (4)	0.2298 (2)	-0.2325 (3)	0.0679 (9)	O1	0.02844 (17)	1/4	0.52530 (14)	0.1259 (9)
					O2	0.10460 (9)	1/4	-0.07118 (13)	0.0741 (5)
					N1	0.01796 (10)	1/4	0.12454 (12)	0.0520 (4)
(a2)					N2	-0.02023 (11)	1/4	0.22601 (12)	0.0562 (4)
O1	0.55541 (18)	0.24559 (8)	0.33934 (9)	0.0639 (3)	N3	0.19437 (18)	1/4	0.3077 (3)	0.1285 (11)
N1	0.26532 (16)	0.09213 (8)	-0.00410 (9)	0.0410 (3)	C1	-0.0167 (2)	1/4	0.43685 (17)	0.0918 (9)
N2	0.34472 (15)	0.08998 (8)	0.10647 (9)	0.0401 (3)	C2	0.02668 (15)	1/4	0.32217 (16)	0.0679 (6)
N3	0.4054 (3)	0.34512 (12)	0.06338 (14)	0.0890 (6)	C3	-0.1145 (3)	1/4	0.4402 (3)	0.1226 (13)
C1	0.4932 (2)	0.16810 (10)	0.28849 (12)	0.0467 (3)	C4	0.1208 (2)	1/4	0.3184 (2)	0.0844 (7)
C2	0.40903 (19)	0.17286 (10)	0.16307 (11)	0.0427 (3)	C5	-0.03075 (11)	1/4	0.02026 (14)	0.0467 (4)
C3	0.4951 (3)	0.06939 (15)	0.34793 (16)	0.0644 (5)	C6	0.01596 (12)	1/4	-0.08446 (15)	0.0524 (5)
C4	0.4058 (2)	0.26981 (12)	0.10833 (13)	0.0550 (4)	C7	-0.02834 (17)	1/4	-0.19033 (16)	0.0684 (6)
C5	0.20080 (17)	0.00155 (9)	-0.06422 (10)	0.0380 (3)	C8	-0.11815 (18)	1/4	-0.1906 (2)	0.0828 (7)
C6	0.1240 (2)	0.00591 (11)	-0.18243 (12)	0.0458 (3)	C9	-0.16428 (15)	1/4	-0.0879 (2)	0.0846 (7)
C7	0.0637 (2)	-0.08170 (12)	-0.24403 (13)	0.0508 (4)	C10	-0.12069 (13)	1/4	0.01847 (19)	0.0637 (6)
C8	0.0768 (2)	-0.17477 (11)	-0.18892 (14)	0.0492 (4)	C11	0.1568 (2)	1/4	-0.1752 (3)	0.1109 (11)
C9	0.1516 (2)	-0.17712 (11)	-0.07061 (14)	0.0522 (4)	(a5)				
C10	0.2144 (2)	-0.09033 (10)	-0.00734 (12)	0.0460 (3)	O1	0.2577 (3)	-0.0215 (2)	0.53703 (11)	0.0987 (5)
C11	0.0101 (3)	-0.27041 (15)	-0.2564 (2)	0.0730 (5)	O2	0.23578 (17)	-0.29952 (13)	-0.04881 (10)	0.0580 (3)
(a3)					N1	0.24747 (16)	-0.02907 (14)	0.13378 (10)	0.0421 (3)
O1	0.15747 (17)	0.04192 (14)	0.43980 (12)	0.0601 (4)	N2	0.25454 (17)	0.05167 (15)	0.25018 (10)	0.0465 (3)
O2	-0.50189 (17)	0.83438 (13)	0.65804 (11)	0.0556 (4)	N3	0.2365 (3)	-0.3601 (2)	0.27239 (17)	0.0935 (6)

Table 2 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C1	0.2617 (3)	0.0588 (3)	0.46217 (15)	0.0695 (5)
C2	0.2517 (2)	-0.0332 (2)	0.33163 (13)	0.0521 (3)
C3	0.2763 (6)	0.2483 (4)	0.4977 (2)	0.1011 (8)
C4	0.2417 (3)	-0.2159 (2)	0.30019 (14)	0.0613 (4)
C5	0.25261 (17)	0.06358 (16)	0.04689 (11)	0.0388 (3)
C6	0.25152 (17)	-0.02450 (16)	-0.07770 (11)	0.0405 (3)
C7	0.2615 (2)	0.0742 (2)	-0.16154 (14)	0.0514 (4)
C8	0.2683 (2)	0.2480 (2)	-0.12429 (16)	0.0605 (4)
C9	0.2645 (2)	0.3294 (2)	-0.00314 (16)	0.0577 (4)
C10	0.2573 (2)	0.23906 (18)	0.08260 (15)	0.0487 (3)
C11	0.2386 (2)	-0.21298 (18)	-0.12026 (12)	0.0457 (3)
C12	0.2270 (4)	-0.3009 (3)	-0.25512 (17)	0.0714 (5)
(a6)				
O1	-0.01208 (19)	0.29010 (5)	-0.29443 (15)	0.0624 (3)
O3	0.2797 (2)	-0.02195 (6)	0.48349 (14)	0.0682 (4)
O2	0.2401 (2)	0.07871 (6)	0.37349 (14)	0.0736 (4)
N1	0.17042 (16)	0.09605 (5)	0.03822 (14)	0.0363 (2)
N2	0.12301 (15)	0.12882 (5)	-0.11270 (13)	0.0353 (2)
N3	0.0215 (3)	0.25581 (7)	0.1420 (2)	0.0710 (4)
N4	0.26505 (18)	0.01702 (6)	0.36236 (14)	0.0451 (3)
C1	0.0209 (2)	0.22906 (7)	-0.29076 (18)	0.0439 (3)
C2	0.06635 (19)	0.19232 (6)	-0.12169 (16)	0.0376 (3)
C3	0.0150 (4)	0.18849 (10)	-0.4473 (2)	0.0637 (5)
C4	0.0427 (2)	0.22907 (7)	0.02465 (19)	0.0449 (3)
C5	0.23043 (17)	0.02783 (6)	0.04526 (15)	0.0320 (2)
C6	0.28031 (18)	-0.01077 (6)	0.20023 (15)	0.0347 (3)
C7	0.3447 (2)	-0.07831 (7)	0.20570 (18)	0.0405 (3)
C8	0.3568 (2)	-0.10876 (7)	0.05646 (19)	0.0445 (3)
C9	0.3024 (2)	-0.07186 (7)	-0.09862 (18)	0.0423 (3)
C10	0.24042 (19)	-0.00492 (6)	-0.10542 (16)	0.0365 (3)

syntheses have been reported elsewhere (Brown *et al.*, 1995; Jollimore *et al.*, 1996). Compounds (a1), (a2) and (a5) were recrystallized from a mixture of ethyl acetate and acetonitrile; (a3) and (a6) from ethyl acetate; (a4) from ethanol. Crystal data, data collection and refinement details are given in Table 1.† All X-ray diffraction data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation with the $\omega/2\theta$ scan technique. Lattice constants were determined by least-squares fitting of the setting angles of 25 reflections. Intensities of three standard reflections were measured every 2 h and did not show significant variations for any of the six compounds investigated. All intensities were corrected for Lorentz and polarization effects. Scattering factors were taken from Cromer & Waber (1974). The structures were solved by direct methods using the SIR92 (Altomare *et al.*, 1994) system of programs, and all other calculations were accomplished using SHELXL97 (Sheldrick, 1997) and PARST (Nardelli, 1983, 1995). All structures were refined by full-matrix least-squares methods with anisotropic non-H atoms and isotropic H atoms.

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0097). Services for accessing these data are described at the back of the journal.

Table 3. Selected bond lengths (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

	O1—C1	C1—C2	C2—N2	N1—N2	N1—C5
(a1)	1.216 (4)	1.466 (4)	1.300 (3)	1.311 (3)	1.396 (3)
(a2)	1.214 (2)	1.469 (2)	1.306 (2)	1.300 (1)	1.411 (2)
(a3)	1.218 (2)	1.472 (2)	1.294 (2)	1.316 (2)	1.406 (2)
(a4)	1.219 (3)	1.463 (3)	1.307 (2)	1.293 (2)	1.400 (2)
(a5)	1.208 (3)	1.468 (2)	1.300 (2)	1.308 (2)	1.399 (2)
(a6)	1.212 (2)	1.481 (2)	1.297 (2)	1.318 (2)	1.393 (2)
	O1—C1—C2	C1—C2—N2	C2—N2—N1	N2—N1—C5	
(a1)	118.8 (3)	118.9 (2)	121.1 (2)	119.9 (2)	
(a2)	118.4 (1)	119.4 (1)	120.8 (1)	120.0 (1)	
(a3)	119.0 (2)	119.3 (2)	120.7 (2)	119.5 (1)	
(a4)	118.8 (2)	120.0 (2)	120.1 (2)	121.2 (1)	
(a5)	119.3 (2)	119.8 (1)	120.2 (1)	119.8 (1)	
(a6)	118.6 (1)	118.8 (1)	119.6 (1)	118.8 (1)	

Table 4. Hydrogen bonding parameters (\AA , $^\circ$) with *e.s.d.*'s in parentheses

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
(a1)				
N1—H1...O1 ⁱ	0.81 (2)	2.30 (2)	2.948 (3)	137 (2)
(a2)				
N1—H1...O1 ⁱⁱ	0.88 (2)	2.16 (2)	2.980 (2)	154 (2)
(a3)				
N1—H1...O2 ⁱⁱⁱ	0.91 (2)	2.03 (2)	2.907 (2)	160 (2)
(a4)				
N1—H1...O2	0.85 (2)	2.29 (2)	2.589 (2)	101 (2)
(a5)				
N1—H1...O2	0.93 (2)	1.86 (2)	2.598 (1)	135 (1)
(a6)				
N1—H1...O2	0.86 (2)	1.98 (2)	2.611 (2)	129 (1)
N1—H1...O1 ^{iv}	0.86 (2)	2.76 (2)	3.150 (1)	109 (1)

Symmetry codes: (i) $x - \frac{1}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $-x - \frac{1}{2}, y - \frac{1}{2}, \frac{3}{2} - z$; (iv) $x + \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$.

Table 5. Pauling's bond orders and π -conjugation parameters within the ketohydrazone moiety

	n_1	n_2	n_3	n_4	$\eta_{1,2}$	$\eta_{3,4}$
(a1)	1.88	1.11	1.72	1.44	0.12	0.36
(a2)	1.89	1.10	1.67	1.52	0.10	0.42
(a3)	1.87	1.08	1.78	1.41	0.10	0.32
(a4)	1.86	1.12	1.66	1.57	0.13	0.46
(a5)	1.94	1.10	1.72	1.46	0.08	0.37
(a6)	1.91	1.04	1.75	1.40	0.06	0.32

3. Results

Final coordinates are given in Table 2 and a selection of bond distances and angles in Table 3. Table 4 reports the hydrogen-bond parameters, Table 5 reports the bond orders (Pauling, 1947) and π -delocalization parameters within the β -ketohydrazone moiety. Table 6 summarizes other intermolecular interactions, which have been classified as dipole-dipole (DD) or electrostatic/donor acceptor (ES/DA) interactions, and Table 7 summarizes the short C—H...O/N contacts. ORTEP (Johnson,

Table 6. Dipole...dipole (DD) and electrostatic or donor acceptor (ES/DA) interactions (Å)

Compound	Interaction	Distance	Type
(a1)	O1...C11 ⁱ	3.295 (4)	ES/DA
(a3)	O1...C1 ⁱⁱ	3.138 (2)	DD
(a4)	O1...C1 ⁱⁱ	3.342 (1)	DD
(a5)	O1...C1 ⁱⁱⁱ	3.387 (3)	DD
(a6)	O1...C4 ^{iv}	3.069 (2)	ES/DA
	O3...N4 ⁱⁱⁱ	3.092 (2)	DD

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y, 1 - z$; (iii) $1 - x, -y, 1 - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

Table 7. Short C—H...O/N contacts (Å, °; Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984; Desiraju, 1996; Steiner, 1996) with e.s.d.'s in parentheses

D—H...A	D—H	H...A	D...A	D—H...A
(a1)				
C6—H6...O1 ⁱ	0.96 (2)	2.73 (2)	3.326 (4)	121 (2)
C9—H9...O1 ⁱⁱ	0.82 (3)	2.74 (3)	3.320 (5)	129 (2)
C10—H10...N4 ⁱⁱⁱ	0.97 (3)	2.68 (3)	3.342 (4)	125 (2)
C7—H7...N3 ^{iv}	0.92 (3)	2.80 (3)	3.571 (5)	142 (2)
(a2)				
C6—H6...O1 ^v	0.95 (2)	2.60 (2)	3.338 (2)	135 (1)
C6—H6...N3 ^v	0.95 (2)	2.85 (2)	3.622 (2)	139 (1)
(a3)				
C10—H10...O2 ^{vi}	0.98 (2)	2.47 (2)	3.269 (2)	138 (2)
C3—H31...N3 ^v	0.91 (3)	2.85 (3)	3.441 (4)	123 (2)
(a4)				
C7—H7...O1 ^{vii}	0.92 (3)	2.48 (3)	3.349 (3)	158 (3)
C10—H10...N3 ^{viii}	0.90 (2)	2.65 (2)	3.443 (4)	147 (2)
(a5)				
C7—H7...O1 ^{ix}	0.94 (2)	2.41 (2)	3.312 (2)	159 (2)
C9—H9...O2 ^x	0.88 (2)	2.50 (3)	3.278 (2)	148 (2)
C10—H10...N3 ^x	0.93 (2)	2.81 (2)	3.485 (2)	130 (1)
(a6)				
C3—H33...O2 ^{ix}	0.92 (3)	2.61 (3)	3.292 (3)	132 (2)
C10—H10...O3 ^{ix}	0.93 (2)	2.84 (2)	3.443 (2)	124 (1)
C9—H9...O1 ^{xi}	0.93 (2)	2.72 (2)	3.334 (2)	124 (1)
C8—H8...O1 ^{xi}	0.96 (2)	2.73 (2)	3.345 (2)	122 (1)
C7—H7...N3 ^{xii}	0.94 (2)	2.86 (2)	3.480 (2)	125 (1)
C8—H8...N3 ^{xii}	0.96 (2)	2.87 (2)	3.503 (2)	124 (1)

Symmetry codes: (i) $x - \frac{1}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x - \frac{1}{2}, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $-x - \frac{1}{2}, \frac{1}{2} + y, -z - \frac{1}{2}$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (vi) $-x - \frac{1}{2}, y - \frac{1}{2}, \frac{3}{2} - z$; (vii) $x, \frac{1}{2} - y, z - 1$; (viii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$; (ix) $x, y, z - 1$; (x) $x, y + 1, z$; (xi) $\frac{1}{2} - x, y - \frac{1}{2}, -z - \frac{1}{2}$; (xii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

1976) views of the molecules, projected on the mean hydrazone plane, are shown in Figs. 1–6 together with their most relevant intra- and intermolecular interactions.

In all compounds the β -keto-hydrazone fragment displays a zigzag planar conformation with the N(Ar)H in an *anti* configuration with respect to the C=O group, and has the correct geometry for forming, at least in principle, chains of intermolecular N—H...O bonds assisted by resonance. These hydrogen bonds, however, are observed only in the crystals of compounds (a1) and (a2), where the planar molecules are linked in hydrogen-

bonded zigzag chains of 2₁ symmetry to form isostructural crystal packings (Figs. 1b and 2b). Their N...O distances of 2.948 (3) and 2.980 (2) Å, respectively, are only slightly shorter than the mean value of 3.08 (14) Å

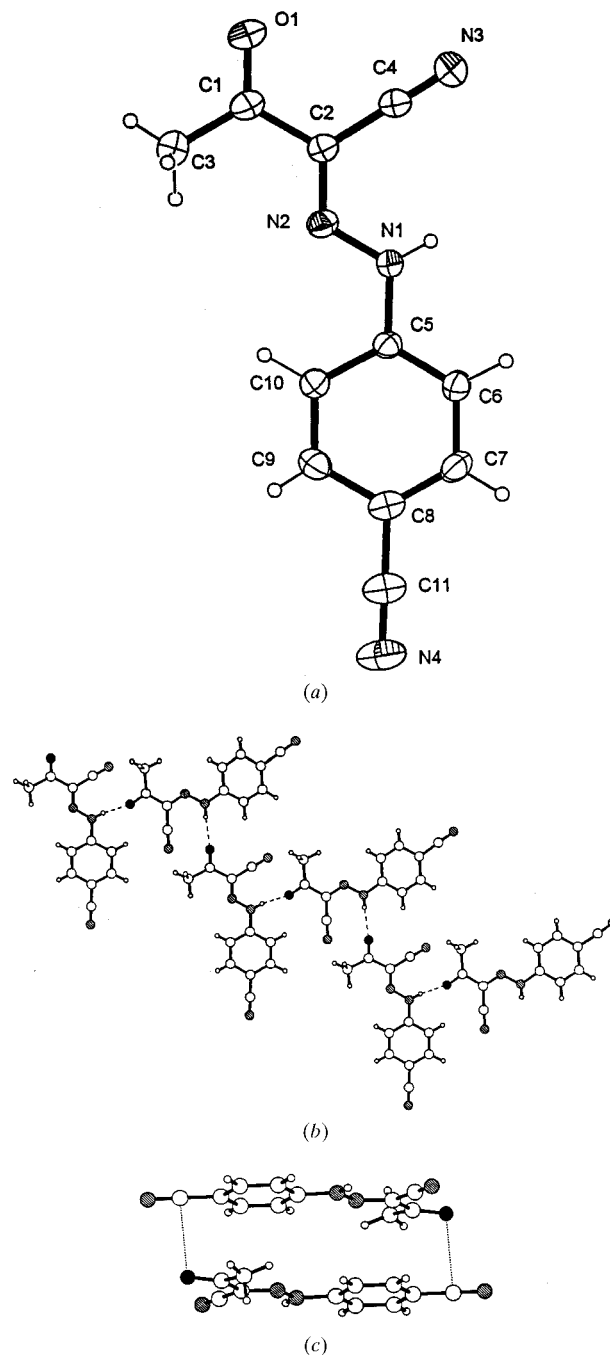


Fig. 1. (a) ORTEP (Johnson, 1976) view and atom numbering for compound (a1). Thermal ellipsoids are drawn at the 30% probability level. (b) The hydrogen-bonding arrangement. (c) Electrostatic/donor acceptor (ES/DA) interaction between O1 of the C1=O1 carbonyl and C11 of the C11≡N4 cyano group.

determined from 27 non-resonant $C(sp^3)_2N-H \cdots O=C$ hydrogen-bonded systems (Bertolasi *et al.*, 1998) and do not show any shortening with respect to the mean distance of 2.89 (11) Å calculated for a sample of 1357 intermolecular neutral $N-H \cdots O$ hydrogen bonds (Taylor *et al.*, 1984). These distances can be compared with those observed in β -enaminones forming intermolecular RAHB (Bertolasi *et al.*, 1995, 1998) which are 2.86 (5) Å (average on 24 structures) for simple enaminones (that is, enaminones not carrying hydrogen-bond-strengthening substituents) and 2.73 (4) Å (average of 18 structures) for those carrying such substituents. The comparison indicates that the $N-H \cdots O$ bonds formed by compounds (a1) and (a2) are to be considered rather weak, in spite of the possible

contribution of resonance, and this can be ascribed to the fact that the 2-CN substitution is inefficient in reducing the PA difference between the hydrogen-bond donor and acceptor atoms, in agreement with the weak π -delocalization of the $C-C=O$ moiety in the $\cdots HN-N=C-C=O \cdots$ fragment (Table 5), which is incompatible with the delocalization expected for strong RAHBs. The π -delocalizations were evaluated in terms of Pauling bond order n (Pauling, 1947) in the two separate $O=C-C$ and $C=N-NH$ subfragments as:

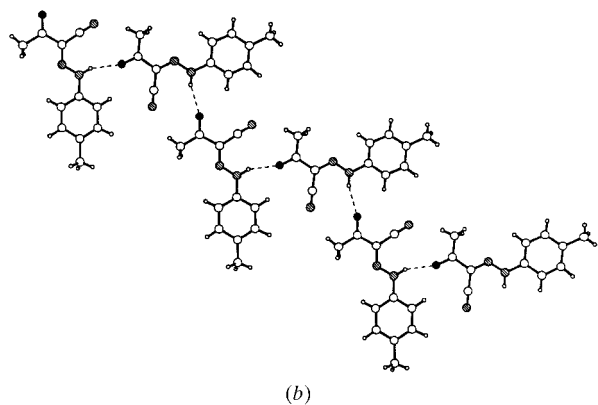
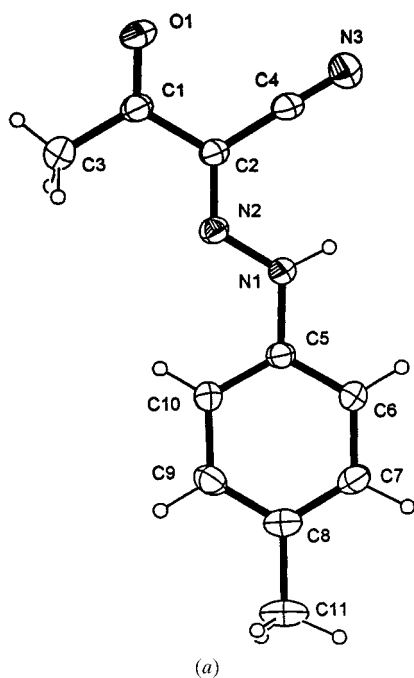


Fig. 2. (a) ORTEP view and atom numbering for compound (a2). Thermal ellipsoids are drawn at the 30% probability level. (b) The hydrogen-bonding arrangement.

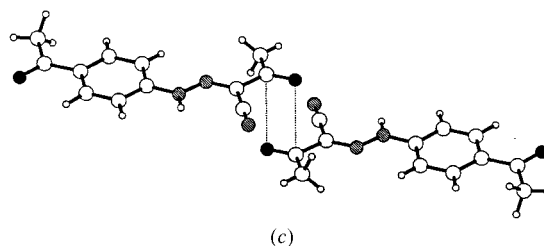
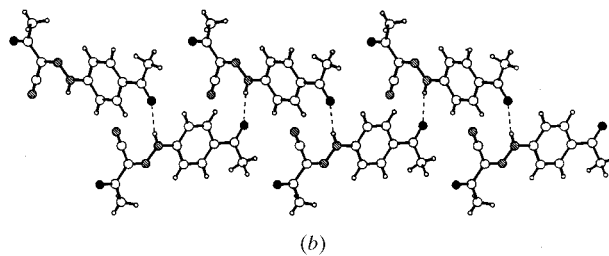
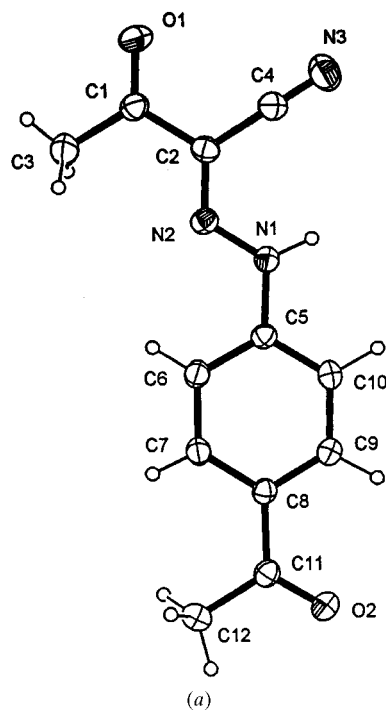


Fig. 3. (a) ORTEP view and atom numbering for compound (a3). Thermal ellipsoids are drawn at the 30% probability level. (b) The hydrogen-bonding arrangement. (c) Dipole-dipole interaction between two $C1=O1$ carbonyls.

$\eta_{1,2} = 1/2[(2 - n_1) + (n_2 - 1)]$ and $\eta_{3,4} = 1/2[(2 - n_3) + (n_4 - 1)]$, where $\eta_{1,2}$ and $\eta_{3,4}$ are, by definition, equal to 0 and 1 for the non-delocalized systems, $\text{HN}=\text{N}=\text{C}=\text{C}=\text{O}$ and $\text{HN}^+=\text{N}=\text{C}=\text{C}=\text{O}^-$, respectively, and 1/2 for the fully π -delocalized system. Values reported in Table 5 show that the large $\eta_{3,4}$ values (0.32–0.46) are not paralleled by those of $\eta_{1,2}$, which are rather small (0.06–0.13) and not such to suggest any RAHB delocalization.

In both crystals the two RAHB chains are centrosymmetrically stacked along the *a* axis in a close-packed van der Waals packing; this arrangement, in compound (a1), helps establish a weak ES/DA interaction between the negatively charged oxygen of the $\text{C1}=\text{O1}$ and the electrophilic carbon of the $\text{C11}\equiv\text{N4}$ group (Table 6, Fig. 1c) with an $\text{O1}\cdots\text{C11}$ distance of 3.295 (4) Å. This further interaction, together with a larger number of $\text{C}-\text{H}\cdots\text{O}/\text{N}$ contacts (Table 7), can account for the slightly greater density of 1.287 Mg m^{-3} in (a1) than that of 1.238 Mg m^{-3} in (a2).

Because of the *p*-acetyl group on the phenyl, the packing of compound (a3) is dominated by non-resonant intermolecular hydrogen-bonded chains linking $\text{N1}-\text{H}$ of the hydrazone moiety to the carbonyl group

of this *p*-acetyl substituent [$\text{N1}\cdots\text{O2}$ 2.907 (2) Å] forming the helical arrangement around a 2_1 axis shown in Fig. 3(b). These chains are connected two-by-two (Fig. 3c) by dipole–dipole (DD) interactions between two $\text{C1}=\text{O1}$ carbonyls (Gavezzotti, 1990; Allen *et al.*, 1998; Allan *et al.*, 1999) not involved in any hydrogen-bond formation. This antiparallel carbonyl \cdots carbonyl interaction is characterized by a $\text{C1}\cdots\text{O1}$ distance of 3.138 (2) Å (Fig. 3c). The higher density of this crystal (1.336 Mg m^{-3}) indicates that the sum of the non-resonant $\text{N1}-\text{H}\cdots\text{O2}$ chain and DD interaction provides a more efficient packing than the simple RAHB chain found in (a1) and (a2).

Compound (a4) displays an *o*-methoxy group on the phenyl ring whose O atom is implied in a weak intramolecular hydrogen bond with the $\text{N}-\text{H}$ group [$\text{N1}\cdots\text{O2}$ 2.589 (2) Å, $\text{N1}-\text{H}\cdots\text{O2}$ 101 (2)°]. This bond, together with the relative positions of methoxy and cyano groups (which are on the same side of the NH group and do not favour a good NH and $\text{C1}=\text{O1}$ approaching), hinders the formation of the intermolecular RAHB observed in compounds (a1) and (a2). The crystal packing remains controlled, besides van der Waals stacking interactions, only by antiparallel

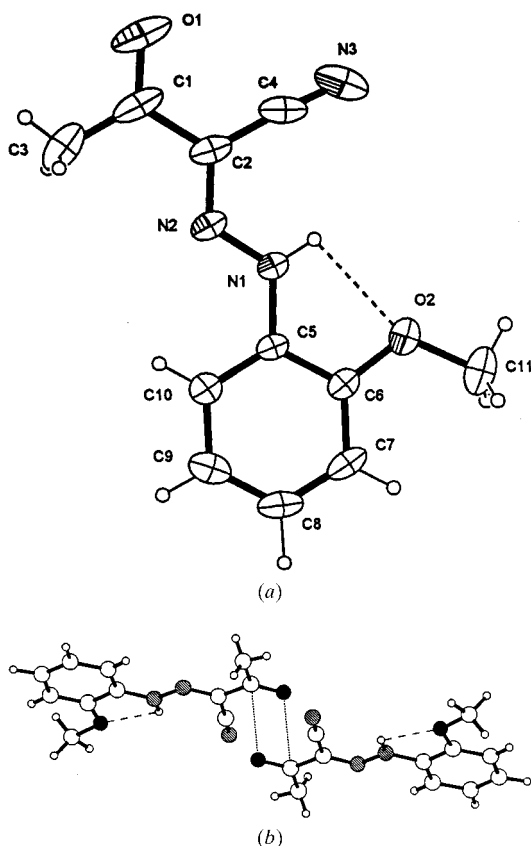


Fig. 4. (a) ORTEP view and atom numbering for compound (a4). Thermal ellipsoids are drawn at the 30% probability level. (b) Dipole–dipole interaction between two $\text{C1}=\text{O1}$ carbonyls.

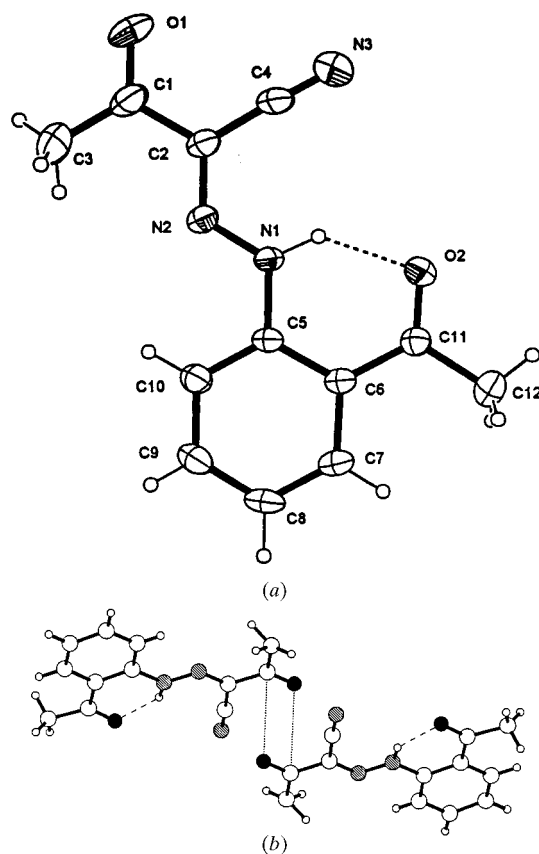


Fig. 5. (a) ORTEP view and atom numbering for compound (a5). Thermal ellipsoids are drawn at the 30% probability level. (b) Dipole–dipole interaction between two $\text{C1}=\text{O1}$ carbonyls.

carbonyl–carbonyl DD interactions having $C1 \cdots O1$ distances of 3.342 (1) Å (Fig. 4*b*). Accordingly, the density is lowered to its present value of 1.258 Mg m^{-3} .

Compound (a5) is strictly similar: the formation of the intermolecular RAHB is prevented by the intramolecular hydrogen bond $N1-H \cdots O2$ [$N1 \cdots O2$ 2.598 (1) Å, $N1-H \cdots O2$ 135 (1)°; Fig. 5(*a*)] so that the only specific interaction left is the antiparallel DD

interaction (Fig. 5*b*) between $C1=O1$ carbonyls [$C1 \cdots O1$ 3.387 (3) Å]. Its density of 1.275 Mg m^{-3} is strictly comparable with that of the similar compound (a4).

Compound (a6) has a greater density (1.443 Mg m^{-3}) and a more complex packing which includes four different interactions. The intramolecular $N1-H \cdots O2$ hydrogen bond [$N1 \cdots O2$ 2.611 (2) Å; $N1-H \cdots O2$ 129 (1)°; Fig. 6(*a*)] and the hindering effect of the cyano group do not avoid the formation of the intermolecular RAHB chain $N1-H \cdots O1$ (Fig. 6*b*), but the chain so formed is heavily distorted and its intermolecular hydrogen bond weakened [$N \cdots O$ 3.150 (1) Å]. The packing is, however, tightened by two other weak interactions, the first of plausible ES/DA nature [$C1 \cdots O4$ 3.069 (2) Å between the negative $O1$ of the

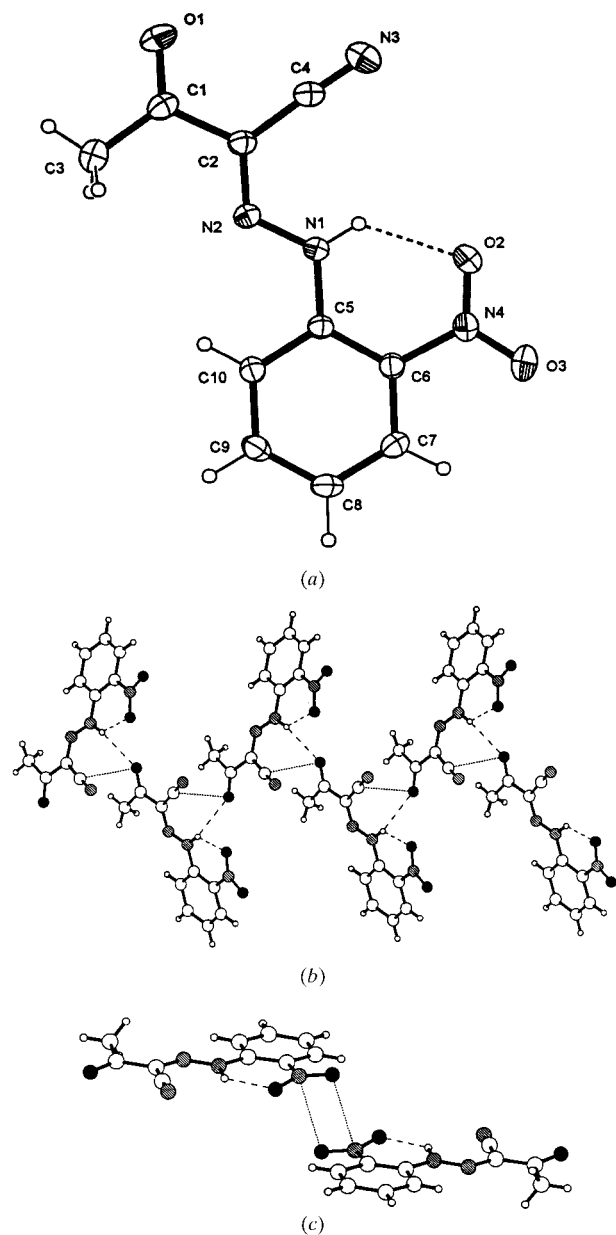


Fig. 6. (a) ORTEP view and atom numbering for compound (a6). Thermal ellipsoids are drawn at the 30% probability level. (b) The hydrogen-bonding arrangement showing also the electrostatic/donor acceptor (ES/DA) interaction between $O1$ of the $C1=O1$ carbonyl and $C4$ of the $C4 \equiv N3$ cyano group. (c) Dipole–dipole interaction between two $N4-O3$ moieties of the nitro group.

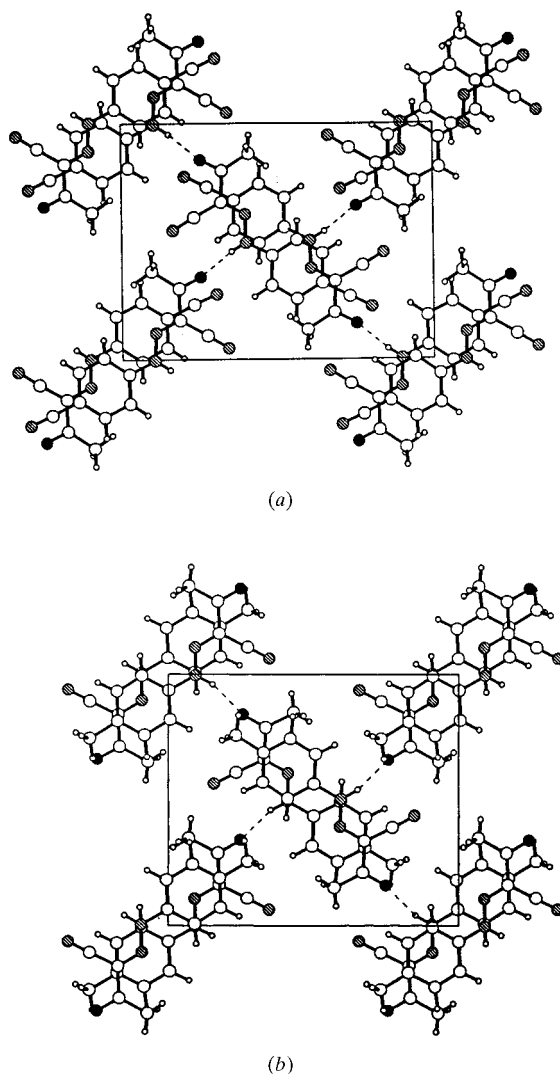


Fig. 7. (a) Molecular packing of compound (a1) in the unit cell projected along the a axis. (b) Molecular packing of compound (a2) in the unit cell projected along the a axis.

Table 8. Summary of molecular interactions, other than van der Waals interactions, in the six crystal packings studied (distances in Å; calculated crystal densities D_c in Mg m^{-3})

Compound	HB intra	RAHB inter	HB inter	DD	ES/DA	C—H...O/C—H...N (number)	D_c
(a1)	—	2.948 (3)	—	—	3.295 (4)	2 + 2	1.287
(a2)	—	2.980 (2)	—	—	—	1 + 1	1.238
(a3)	—	—	2.907 (2)	3.138 (2)†	—	1 + 1	1.336
(a4)	2.589 (2)	—	—	3.342 (1)†	—	1 + 1	1.258
(a5)	2.598 (1)	—	—	3.387 (3)†	—	2 + 1	1.275
(a6)	2.611 (2)	3.150 (1)	—	3.092 (2)‡	3.069 (2)	4 + 2	1.443

† C...O. ‡ N...O.

C1=O1 carbonyl and the positively charged C4 of the cyano group; Fig. 6(b)] and the second classifiable as a DD interaction between two N4—O3 groups of adjacent molecules [N4...O3 3.092 (2) Å; Fig. 6(c)].

4. Discussion

The packing of the six compounds considered appears to be controlled, besides the normal attractive and repulsive van der Waals forces, by a number of specific interactions which are summarized in Table 8. By itself,

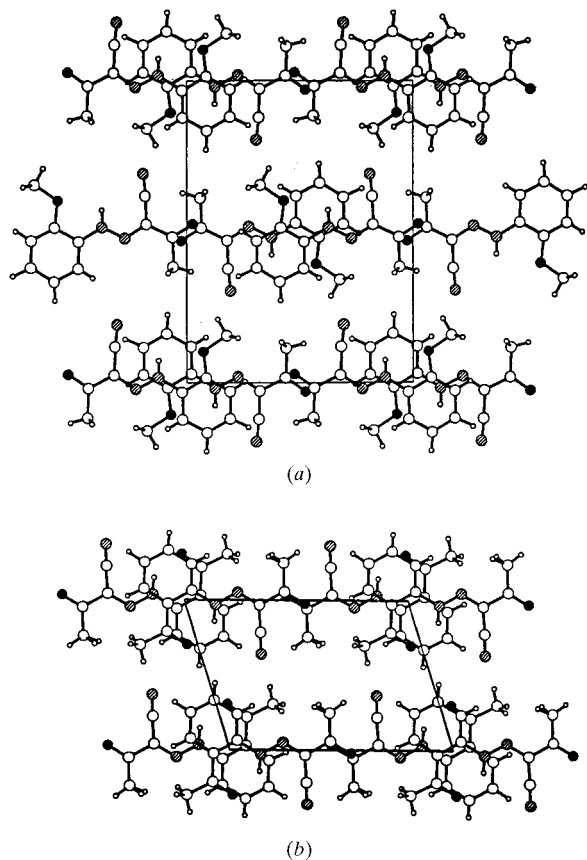
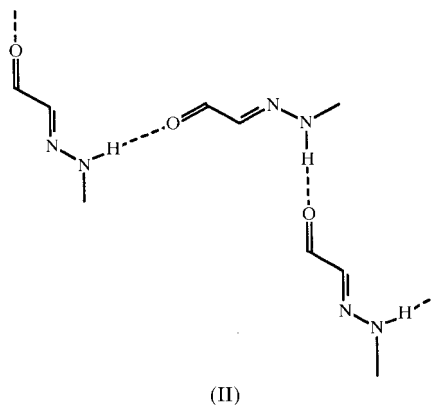
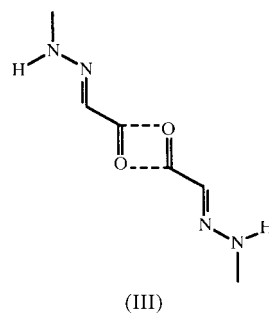


Fig. 8. (a) Molecular packing of compound (a4) in the unit cell projected along the b axis. (b) Molecular packing of compound (a5) in the unit cell projected along the a axis.

the β -keto-hydrazone fragment appears to be able to form only two types of interaction: (i) an intermolecular N1—H...O1 RAHB linking the fragments in an infinite



chain [RAHB-inter; see (II)]; and (ii) a dipole-dipole interaction between C1=O1 groups linking two molecules in antiparallel dimers [DD; see (III)]. The two



interactions give rise to two distinct ways of packing: (i) two intercrossing systems of almost planar zigzag hydrogen-bonded chains in the case of RAHB-inter [see the two isostructural packings of (a1) and (a2) in Figs. 7(a) and 7(b)]; and (ii) parallel antidromic chains where the molecules are alternatively linked by antiparallel DD and van der Waals stacking interactions [see the two almost identical chains in different space groups for compounds (a4) and (a5) of Figs. 8(a) and 8(b)].

At least within the present set, the two interactions are mutually exclusive and appear to give comparable contributions to the intermolecular attraction, as shown

by the similar densities of (a1)/(a2) ($\langle D_c \rangle = 1.26 \text{ Mg m}^{-3}$) and (a4)/(a5) ($\langle D_c \rangle = 1.27 \text{ Mg m}^{-3}$), whose packings are dominated by RAHB-inter and DD interactions, respectively. This competition (Allen *et al.*, 1998) is made possible by the intrinsic weakness of the N—H...O RAHB (Bertolasi *et al.*, 1998), as discussed above, and has never been observed in the case of the stronger intermolecular O—H...O RAHBs (Gilli *et al.*, 1993; Bertolasi *et al.*, 1996). Moreover, each compound studied is endowed with different phenyl substituents, and these mostly determine the packing mode. The main factor is the N1—H...O1 intramolecular bond made possible by oxygenated substituents at the *o*-phenyl position (HB-intra). Its effect is that of weakening the bifurcated RAHB-inter as in (a6) or to delete it as in (a4) and (a5), switching the packing from RAHB-inter to DD interactions. Compound (a3) is the only example where an accidental substituent (an acetyl in the *p*-phenyl position) gives rise to a different packing arrangement based on a non-resonant hydrogen bond (but supported by the usual DD interaction).

Other possible interactions (ES/DA and C—H...X interactions; Table 8) are clearly unable to change the packing mode. They can contribute, however, to packing efficiencies as shown by the crystal density which is, on average, 1.264 for just one interaction [(a1), (a2), (a4) and (a5)], 1.336 for two (a3) and 1.443 Mg m^{-3} for three main interactions and a greater number of C—H...X bonds (a6).

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