

**(Z)-4-(2,6-Dichlorophenyldiazenyl)-
6-[[1,3-dihydroxy-2-(hydroxy-
methyl)propan-2-ylamino]methylene]-
2-methoxycyclohexa-2,4-dienone and
the 3-methoxyphenyldiazenyl and
4-methoxyphenyldiazenyl analogues**Arzu Özek,^{a*} Çiğdem Albayrak,^b Mustafa Odabaşoğlu^b
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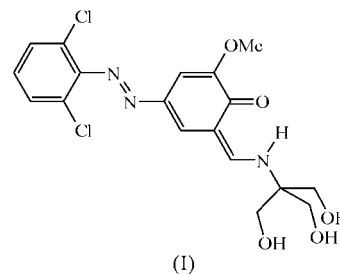
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The title compounds, (Z)-4-(2,6-dichlorophenyldiazenyl)-6-[[1,3-dihydroxy-2-(hydroxymethyl)propan-2-ylamino]methylene]-2-methoxycyclohexa-2,4-dienone, C₁₈H₁₉Cl₂N₃O₅, (I), (Z)-6-[[1,3-dihydroxy-2-(hydroxymethyl)propan-2-ylamino]methylene]-2-methoxy-4-(3-methoxyphenyldiazenyl)cyclohexa-2,4-dienone, C₁₉H₂₃N₃O₆, (II), and (Z)-6-[[1,3-dihydroxy-2-(hydroxymethyl)propan-2-ylamino]methylene]-2-methoxy-4-(4-methoxyphenyldiazenyl)cyclohexa-2,4-dienone, C₁₉H₂₃N₃O₆, (III), all adopt the keto–amine tautomeric form, and the hydroxy H atoms are located on the N atom in all three compounds. Strong intramolecular N—H···O hydrogen bonds arise as a result of the shifts achieved by the hydroxy H atoms of the Schiff bases to the N atoms. Positional disorder was observed in molecules (II) and (III). In all three compounds, C—H···π and π–π interactions affect the packing of the molecules. The compounds exhibit *trans* geometry with respect to the azo N=N double bond, and the molecules are linked by O—H···O hydrogen bonds to form three-dimensional networks.

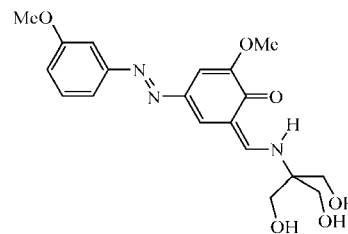
Comment

Azo compounds are the most widely used class of dyes owing to their versatile application in various fields, such as the dyeing of textiles and fibres, the colouring of different materials, and high-technology areas, such as electro-optical devices and ink-jet printers (Peters & Freeman, 1991). Most Schiff bases have antibacterial, anticancer, anti-inflammatory and antitoxic properties (Williams, 1972). Two characteristic properties of Schiff bases are photochromism and thermochromism (Cohen *et al.*, 1964; Moustakali-Mavridis *et al.*, 1978). These properties are caused by proton transfer from the hydroxy O atom to the imine N atom (Hadjoudis *et al.*, 1987;

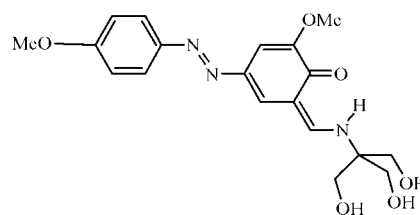
Xu *et al.*, 1994). As part of a general study of the crystal chemistry of dyes, and to provide templates for molecular-modelling studies, the crystal structures of the title compounds, (I), (II) and (III), have been determined. The molecular structures of (I), (II) and (III), with the atom-labelling schemes, are shown in Figs. 1, 2 and 3, respectively, and selected bond lengths and angles are given in Tables 1, 3 and 5, respectively.



(I)



(II)



(III)

In all three molecules, the keto–amine tautomer is favoured over the phenol–imine form, as indicated by the C10–O3, C13–N3, C11–C13 and C10–C11 bond lengths (Figs. 1–3, and Tables 1, 3 and 5). Furthermore, these data show that there are significant elongations of the C13–N3 bonds and contractions of the C10–O3 bonds. A similar effect was observed for 4-[(3-chlorophenyldiazenyl)-2-[[tris(hydroxymethyl)methyl]aminomethylene]cyclohexa-3,5-dienone [C10–O3 = 1.286 (2) Å, C13–N3 = 1.298 (3) Å, C11–C13 = 1.411 (3) Å and C10–C11 = 1.436 (3) Å; Odabaşoğlu *et al.*, 2003]. The H atom in (I)–(III) is located on atom N1, thus confirming a preference for the keto–amine tautomer in the solid state. The N1–C1 and N2–C7 bond lengths are approximately the same in (I)–(III), and these lengths indicate single-bond character, whereas the N=N bond lengths are indicative of significant double-bond character. The high s.u. values and high displacement parameters of some atoms in the molecules of both (II) and (III) are probably caused by positional and orientational disorder. In (II), atom C18 is disordered over two positions, with occupancy factors of 0.64 (7) and 0.36 (7). In (III), atom O1 shows positional disorder with occupancy factors of 0.409 (7) and 0.591 (7). At

the same time, the benzene rings also show orientational disorder with the same occupancy factors (Fig. 3).

In (I), the C—Cl bond distance is consistent with that in 5-(2-chlorophenyldiazenyl)salicylaldehyde and 4-(2-chlorophenyldiazenyl)-2-[[tris(hydroxymethyl)methyl]aminomethylene]cyclohexa-3,5-dienone (Albayrak *et al.*, 2004). The dihedral angles between the C1—C6 and C7—C12 rings are 58.91 (13), 8.89 (11) and 21.57 (3)° (the average of the two angles for the orientationally disordered benzene ring) for (I), (II) and (III), respectively.

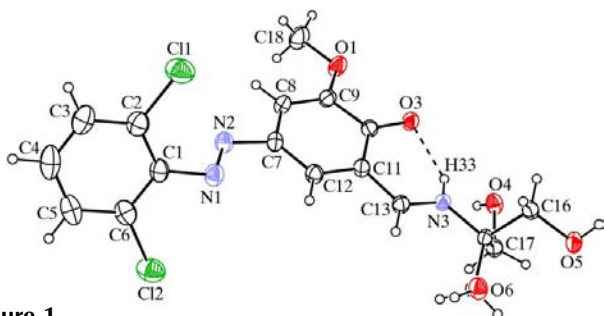


Figure 1
An ORTEP-3 (Farrugia, 1997) view of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. The dashed line indicates the intramolecular hydrogen bond.

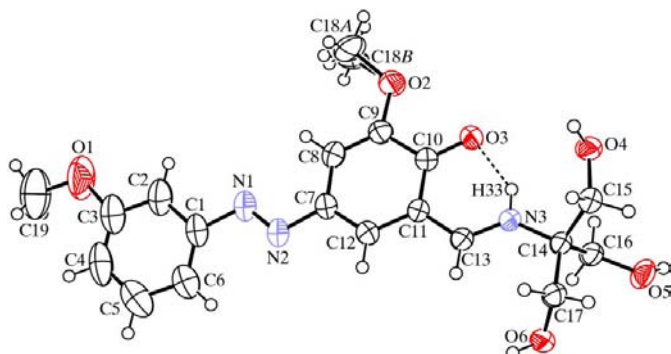


Figure 2
An ORTEP-3 (Farrugia, 1997) view of (II), showing the atom-numbering scheme and 50% probability displacement ellipsoids. The dashed line indicates the intramolecular hydrogen bond.

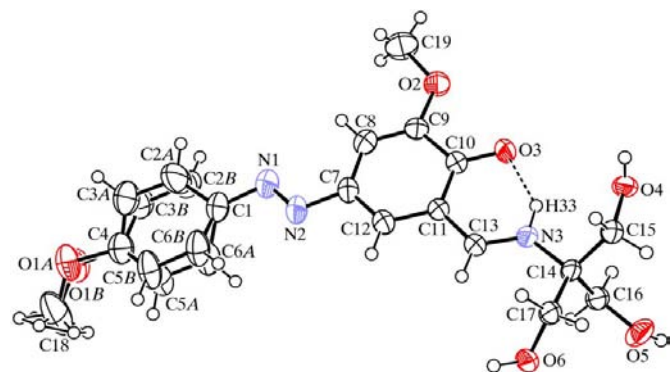


Figure 3
An ORTEP-3 (Farrugia, 1997) view of (III), showing the atom-numbering scheme and 50% probability displacement ellipsoids. The dashed line indicates the intramolecular hydrogen bond.

The intra- and intermolecular hydrogen bonds are shown in the packing diagrams of (I), (II) and (III) in Figs. 4–6, respectively. In all three structures, these O—H···O hydrogen bonds generate edge-fused $R_2^2(5)$, $R_3^2(19)$ and $R_2^2(12)$ rings. Atom H33 bonded to atom N3 forms a strong intramolecular hydrogen bond with atom O3, as observed in similar

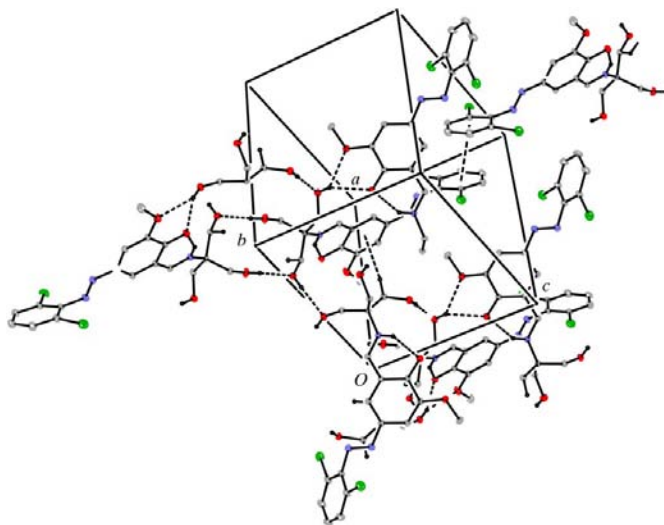


Figure 4
An ORTEP-3 (Farrugia, 1997) packing diagram of (I). Dashed lines indicate hydrogen bonds and C—H···π and π—π interactions. H atoms not involved in hydrogen bonding or C—H···π interactions have been omitted for clarity.

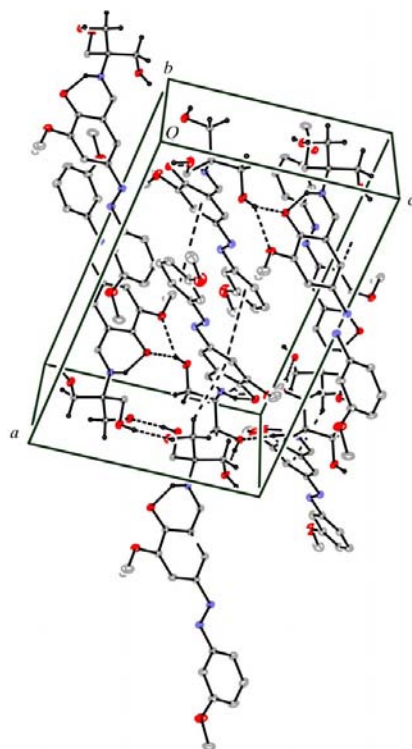


Figure 5
An ORTEP-3 (Farrugia, 1997) packing diagram of (II). Dashed lines indicate hydrogen bonds and C—H···π and π—π interactions. H atoms not involved in hydrogen bonding or C—H···π interactions have been omitted for clarity.

compounds (Odabaşoğlu *et al.*, 2003; Albayrak *et al.*, 2004). In (I)–(III), the molecules are linked by C–H··· π interactions (Tables 2, 4 and 6, and Figs. 4–6). In addition to these interactions, all three compounds contain π – π interactions (Table 7 and Figs. 4–6).

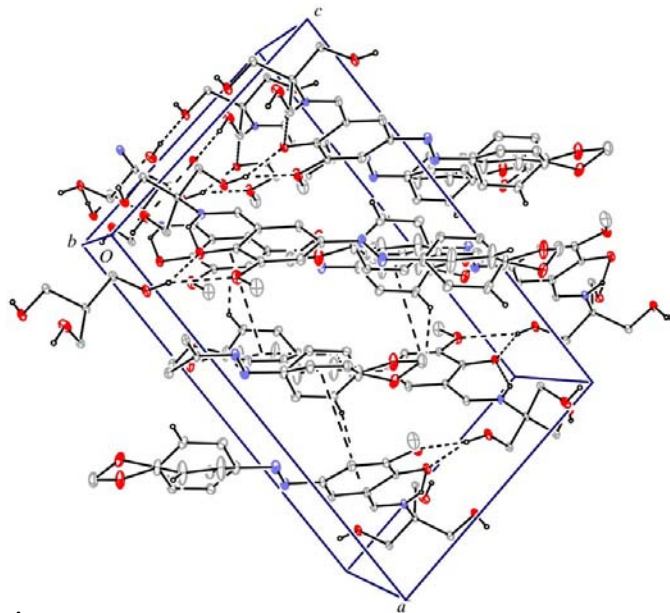


Figure 6
An ORTEP-3 (Farrugia, 1997) packing diagram of (III). Dashed lines indicate hydrogen bonds and C–H··· π and π – π interactions. H atoms not involved in hydrogen bonding or C–H··· π interactions have been omitted for clarity.

Experimental

Compounds (I), (II) and (III) were prepared as described in the literature (Odabaşoğlu *et al.*, 2003) using *o*-vanillin, 2,6-dichloroaniline for (I), 3-methoxyaniline for (II), 4-methoxyaniline for (III) and tris(hydroxymethyl)aminomethane as starting materials. The products were crystallized from ethanol, and well shaped crystals were obtained by slow evaporation of ethanol solutions [yield 74% and m.p. 480–482 K for (I); yield 76% and m.p. 462–463 K for (II); yield 78% and m.p. 489–490 K for (III)].

Compound (I)

Crystal data

$C_{18}H_{19}Cl_2N_3O_5$	$D_x = 1.474 \text{ Mg m}^{-3}$
$M_r = 428.26$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 12750 reflections
$a = 16.8445 (15) \text{ \AA}$	$\theta = 1.9\text{--}28.4^\circ$
$b = 10.7259 (5) \text{ \AA}$	$\mu = 0.37 \text{ mm}^{-1}$
$c = 11.1126 (9) \text{ \AA}$	$T = 296 \text{ K}$
$\beta = 106.037 (7)^\circ$	Stick, red
$V = 1929.6 (2) \text{ \AA}^3$	$0.78 \times 0.33 \times 0.05 \text{ mm}$
$Z = 4$	

Data collection

Stoe IPDS-II diffractometer	2715 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.056$
Absorption correction: integration (<i>X-RED32</i> ; Stoe & Cie, 2002)	$\theta_{\text{max}} = 26.0^\circ$
$T_{\text{min}} = 0.871$, $T_{\text{max}} = 0.977$	$h = -20 \rightarrow 20$
10068 measured reflections	$k = -11 \rightarrow 13$
3782 independent reflections	$l = -13 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.132$
 $S = 1.01$
 3782 reflections
 269 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2 + 0.1273P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

C1–N1	1.443 (3)	C10–O3	1.279 (3)
C2–C11	1.727 (3)	C10–C11	1.434 (3)
C6–Cl2	1.732 (3)	C11–C12	1.406 (3)
C7–C12	1.372 (3)	C11–C13	1.425 (3)
C7–C8	1.409 (3)	C13–N3	1.284 (3)
C7–N2	1.417 (3)	C14–N3	1.464 (3)
C8–C9	1.364 (3)	C18–O1	1.417 (3)
C9–O1	1.357 (3)	N1–N2	1.243 (3)
C9–C10	1.434 (3)		
C6–C1–N1	120.0 (2)	O3–C10–C11	123.37 (19)
C2–C1–N1	122.2 (2)	N3–C13–C11	122.2 (2)
C8–C7–N2	113.35 (19)	C15–C14–C17	107.13 (18)
O1–C9–C8	126.3 (2)	C13–N3–C14	129.6 (2)
C10–C11–C13–N3	0.3 (3)	C1–N1–N2–C7	179.2 (2)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (I).

Cg1 is the centroid of the C7–C12 ring.

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N3–H33···O3	0.79 (3)	1.90 (3)	2.587 (2)	144 (3)
O4–H44···O6 ⁱ	0.74 (3)	2.04 (3)	2.777 (3)	174 (3)
O5–H55···O4 ⁱⁱ	0.80 (4)	1.94 (4)	2.740 (3)	176 (3)
O6–H66···O1 ⁱⁱⁱ	0.70 (3)	2.25 (3)	2.802 (2)	137 (3)
O6–H66···O3 ⁱⁱⁱ	0.70 (3)	2.28 (3)	2.923 (2)	153 (3)
C17–H17A···Cg1 ^{iv}	0.97 (1)	2.95 (1)	3.798 (2)	147 (1)

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

Compound (II)

Crystal data

$C_{19}H_{23}N_3O_6$	Mo $K\alpha$ radiation
$M_r = 389.40$	Cell parameters from 13037 reflections
Monoclinic, $P2_1/c$	$\theta = 1.8\text{--}28.9^\circ$
$a = 16.3722 (11) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$b = 10.4506 (5) \text{ \AA}$	$T = 296 \text{ K}$
$c = 11.3239 (7) \text{ \AA}$	Prism, red
$\beta = 99.180 (5)^\circ$	$0.42 \times 0.33 \times 0.25 \text{ mm}$
$V = 1912.7 (2) \text{ \AA}^3$	
$Z = 4$	
$D_x = 1.352 \text{ Mg m}^{-3}$	

Data collection

Stoe IPDS-II diffractometer	2778 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.040$
Absorption correction: integration (<i>X-RED32</i> ; Stoe & Cie, 2002)	$\theta_{\text{max}} = 26.0^\circ$
$T_{\text{min}} = 0.970$, $T_{\text{max}} = 0.982$	$h = -20 \rightarrow 20$
13464 measured reflections	$k = -12 \rightarrow 12$
3744 independent reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.160$
 $S = 1.06$
 3744 reflections
 280 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0982P)^2 + 0.2314P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.83 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.135$
 $S = 0.99$
 3714 reflections
 311 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.009 (2)

Table 3
 Selected geometric parameters (\AA , $^\circ$) for (II).

C1–N1	1.420 (3)	C10–O3	1.284 (2)
C3–O1	1.399 (4)	C10–C11	1.426 (3)
C7–C12	1.371 (3)	C11–C12	1.410 (3)
C7–C8	1.413 (3)	C11–C13	1.417 (3)
C7–N2	1.418 (3)	C13–N3	1.291 (2)
C8–C9	1.349 (3)	C14–N3	1.463 (2)
C9–O2	1.362 (2)	N1–N2	1.256 (2)
C9–C10	1.443 (3)		
C6–C1–N1	125.8 (2)	O3–C10–C11	123.48 (16)
C2–C1–N1	113.2 (2)	N3–C13–C11	121.94 (17)
C2–C3–O1	115.2 (3)	C17–C14–C15	107.33 (15)
C8–C7–N2	122.92 (18)	C13–N3–C14	130.15 (16)
C8–C9–O2	126.24 (18)		
C10–C11–C13–N3	−1.1 (3)	C1–N1–N2–C7	179.06 (17)

Table 4
 Hydrogen-bond geometry (\AA , $^\circ$) for (II).

Cg1 is the centroid of the C7–C12 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3–H33 \cdots O3	0.86 (2)	1.84 (2)	2.584 (2)	144 (2)
O4–H44 \cdots O6 ^v	0.824 (17)	1.921 (18)	2.744 (2)	177 (3)
O5–H55 \cdots O4 ^{vi}	0.836 (17)	1.901 (18)	2.734 (2)	174 (3)
O6–H66 \cdots O3 ^{vii}	0.815 (17)	1.999 (19)	2.7792 (19)	160 (3)
O6–H66 \cdots O2 ^{vii}	0.815 (17)	2.26 (3)	2.800 (2)	124 (2)
C15–H15B \cdots Cg1 ^{viii}	0.93 (1)	3.05	3.861 (2)	142 (1)

Symmetry codes: (v) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (vi) $-x + 2, -y + 2, -z + 2$; (vii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (viii) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$.

Compound (III)

Crystal data

$C_{19}H_{23}N_3O_6$
 $M_r = 389.40$
 Monoclinic, $P2_1/c$
 $a = 16.9333$ (9) \AA
 $b = 10.7124$ (6) \AA
 $c = 10.5476$ (6) \AA
 $\beta = 98.966$ (4) $^\circ$
 $V = 1889.92$ (18) \AA^3
 $Z = 4$
 $D_x = 1.369$ Mg m^{-3}

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
 $T_{\min} = 0.973, T_{\max} = 0.993$
 17746 measured reflections
 3714 independent reflections

Mo $K\alpha$ radiation
 Cell parameters from 17273 reflections
 $\theta = 1.9\text{--}28.8^\circ$
 $\mu = 0.10$ mm $^{-1}$
 $T = 296$ K
 Plate, red
 $0.35 \times 0.23 \times 0.09$ mm

Table 5
 Selected geometric parameters (\AA , $^\circ$) for (III).

C1–N1	1.428 (3)	C10–C11	1.435 (3)
C7–C12	1.363 (3)	C11–C13	1.408 (3)
C7–N2	1.412 (3)	C11–C12	1.416 (3)
C7–C8	1.422 (3)	C13–N3	1.295 (3)
C8–C9	1.356 (3)	C14–N3	1.469 (2)
C9–O2	1.367 (2)	C19–O2	1.417 (3)
C9–C10	1.439 (3)	N1–N2	1.253 (3)
C10–O3	1.271 (2)		
C12–C7–N2	115.33 (19)	O3–C10–C11	122.26 (18)
C12–C7–C8	119.8 (2)	N3–C13–C11	123.31 (18)
N2–C7–C8	124.8 (2)	C17–C14–C15	107.03 (18)
C8–C9–O2	125.7 (2)	C13–N3–C14	128.58 (16)
C10–C11–C13–N3	0.2 (3)	C1–N1–N2–C7	176.4 (2)

Table 6
 Hydrogen-bond geometry (\AA , $^\circ$) for (III).

Cg1 is the centroid of the C7–C12 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3–H33 \cdots O3	0.92 (3)	1.84 (3)	2.619 (2)	141 (2)
O5–H55 \cdots O4 ^{ix}	0.815 (19)	1.92 (2)	2.733 (2)	174 (4)
O4–H44 \cdots O6 ^{viii}	0.837 (18)	1.98 (2)	2.789 (2)	163 (3)
O6–H66 \cdots O3 ^x	0.850 (17)	1.924 (19)	2.7125 (18)	154 (2)
O6–H66 \cdots O2 ^x	0.850 (17)	2.45 (2)	3.081 (2)	132 (2)
C3–H3 \cdots Cg1 ^{xi}	0.93 (1)	3.32 (1)	3.463 (7)	91 (1)

Symmetry codes: (viii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (ix) $-x, -y + 2, -z$; (x) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (xi) $-x + 1, -y + 1, -z + 1$.

Table 7
 Observed π – π interaction distances (\AA) for (I), (II) and (III).

Cg1 and Cg2 are the centroids of the C1–C6 and C7–C12 rings, respectively.

Compound	$Cg\cdots Cg$	$d_{\text{centroids}}$	$d_{\text{perpendicular}}$
(I)	$Cg1\cdots Cg1^{xii}$	3.556 (2)	3.38
(II)	$Cg1\cdots Cg2^{xi}$	3.937 (1)	3.57
(III)	$Cg1\cdots Cg2^{xi}$	3.996 (3)	3.66

Symmetry codes: (xi) $-x + 1, -y + 1, -z + 1$; (xii) $-x + 1, -y + 1, -z + 2$.

H atoms attached to N and O atoms were refined freely. All remaining H atoms were refined using a riding model, with C–H distances of 0.93–0.97 \AA . In (III), the H atoms of C18 were refined at two different positions owing to disorder, with 0.5 occupancy for each component. The $U_{\text{iso}}(\text{H})$ values are $1.5U_{\text{eq}}(\text{C})$ for the methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for the remaining C-bound H atoms.

For all compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick,

1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1088). Services for accessing these data are described at the back of the journal.

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