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A comparative study of intermolecular interactions in the crystal structures of phenyl/phenyl end-capped oligoanilines

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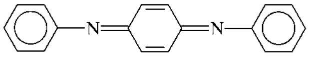
Three crystal structures have been analysed from the point of view of intermolecular interactions: *N*,*N*′-diphenyl-1,4-benzoquinone diimine, $C_{18}H_{14}N_2$, (I), its reduced form *N*,*N*′-diphenyl-1,4-phenylenediamine, $C_{18}H_{16}N_2$, (II), and *N*,*N*′-diphenyl-1,4-phenylenediammonium bis(*p*-toluenesulfonate), $C_{18}H_{18}N_2^{2+}\cdot 2C_7H_7O_3S^-$, (III), which contains fully protonated (II) with *p*-toluenesulfonic acid. The local molecular C_i symmetry is preserved in all three structures and the packing seems to be dominated by the mutual arrangement of the simple polyaniline oligomers in the different protonation states. In (I), the most significant molecular interactions are stacking forces, forming columns of molecules along [001]. Close packing of the columns results in *C*-centring of the structure. In (II), only van der Waals interactions can be observed. In the structure of (III), the *p*-toluenesulfonate ions serve as acceptors in relatively strong N—H···O hydrogen bonds. The *N*,*N*′-diphenyl-1,4-phenylenediammonium cation intercalates between two anions related by a centre of symmetry.

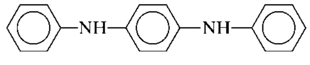
Comment

Polyaniline oligomers containing alternating benzoid and quinoid rings, with amine and/or imine groups in between, are very interesting subjects for research. Detailed analysis of their crystal structures can help in the understanding of the spectroscopic behaviour of the compounds and explain a possible mechanism for their electrical conductivity (Hadek, 1968; Hadek *et al.*, 1969).

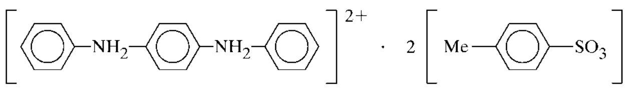
The mutual interaction of polyaniline oligomers in the crystalline state seems to be significant for the prediction of their properties. Investigations of intermolecular interactions in the crystal structures of polyaniline oligomers are important because single crystals of polyaniline itself, suitable for X-ray diffraction, are extremely difficult to obtain, and usually only powder data from thin films are available [*e.g.* polyaniline 10-camphorsulfonate, either from an *m*-cresol solution (Łużny *et al.*, 1997) or from 1,1,1,3,3,3-hexafluoro-2-propanol (Gawlicka, 1997)]. Here, we report the crystal structures of the title compounds, (I), (II) and (III), which are examples of simple phenyl/phenyl end-capped polyaniline oligomers.



(I)



(II)



(III)

The molecular geometry of (I) was found to be similar to that previously described by Baughman *et al.* (1988), and its structural, optical and electrochemical properties have been published separately by Shacklette *et al.* (1988). The structure of orthorhombic (II) appeared to be essentially the same as described earlier in an isotropic approximation by Povet'eva *et al.* (1976). We were not able to obtain the triclinic polymorph of (II) reported by Boyer *et al.* (2000), the spectroscopic properties of which were recently described by Quillard *et al.* (2001). The structure of (III) has not been published previously.

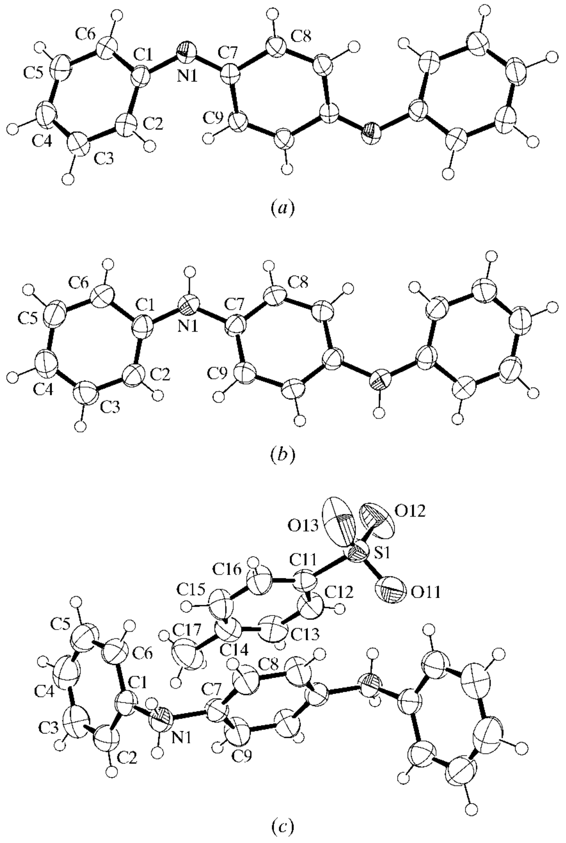


Figure 1
(*a*) A view of the molecule of (I), (*b*) a view of the molecule of (II) and (*c*) a view of the two ions in the salt of (III), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Obviously, there is a significant difference in the geometry of the molecules depending on the protonation states (Figs. 1*a*, *b*, *c*). In (I), the imine N atoms have a planar configuration. The amine N atoms of (II) have a pyramidal configuration and those of (III) show a tetrahedral configuration. The most indicative descriptor of the N-atom configuration is the value of the C1—N1—C7 angle. The essential geometric details of the molecules, which allow the recognition of the protonation states of the oligomers, are given in Tables 1–3.

The lone electron pair of the imine N atom of (I) makes the N—C single and double bonds shorter. Its influence on the terminal benzene ring is counteracted by the opposing effect of the quinoid system, as can be seen from the value of the C2—C1—C6 angle in Table 1.

The geometry of the molecule of (II) is influenced by an interaction between the lone electron pair of the N atom and the π-electron systems of both neighbouring benzene rings, which causes a shortening of the N—C bonds and a diminution of the appropriate endocyclic C—C—C angles to 118.2 (2) and 117.7 (2)°.

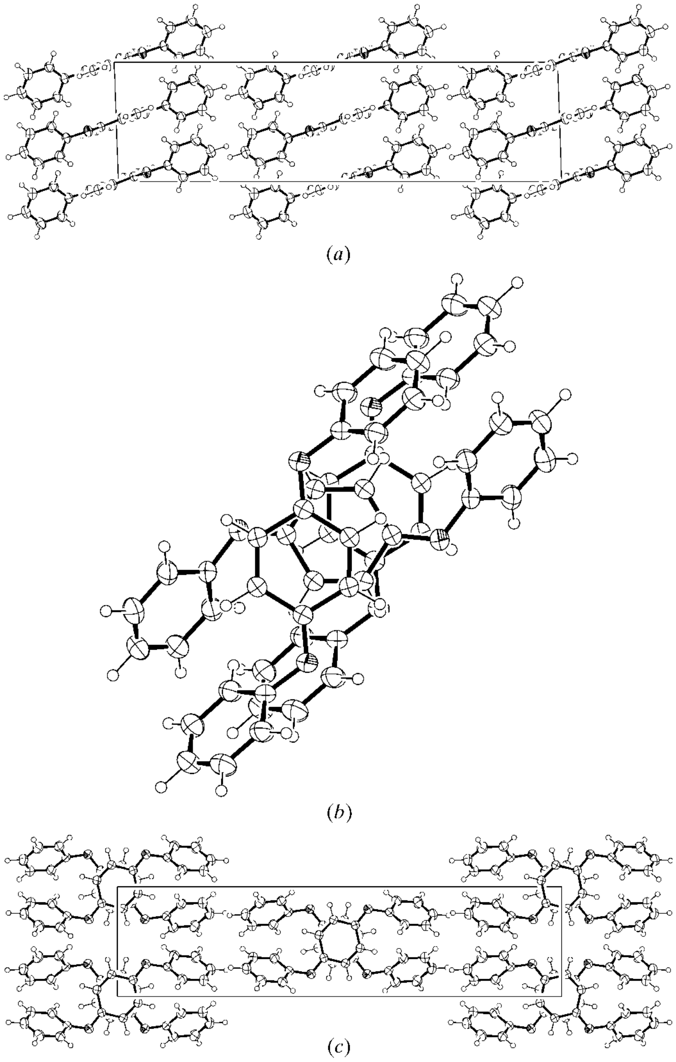


Figure 2
(*a*) The packing in the crystal structure of (I) projected onto (010). (*b*) The stacking of the molecules viewed along a direction close to [001]. (*c*) A view of the crystal structure along [001], showing the close packing of the stacks.

The –NH_2^+– group of (III) has a withdrawing effect on the benzene rings, enlarging the endocyclic C—C—C angles to 122.0 (3) and 121.6 (2)°. The geometry of the *p*-toluene-sufonate anion is typical, apart from the relatively long S1—O11 bond, which is caused by atom O11 acting as the acceptor in an N—H···O-type hydrogen-bond interaction.

The conformations of the molecules of (I), (II) and (III), described by the C1—N1—C7—C9 and C7—N1—C1—C2 torsion angles, depend on both the molecular configurations and the packing in the crystal structures.

The packing in the crystal structure of (I) is shown in Fig. 2(*a*) as a projection on to the (010) plane. A stacking of the molecules along [001] can be considered, resulting in a distance of 3.505 (2) Å between parallel quinoid rings, with a centroid offset of 1.219 (3) Å. The mutual arrangement of the rings in the stack is presented in Fig. 2(*b*). Between such columns, the close packing of which is shown in Fig. 2(*c*), there are only van der Waals interactions.

The packing of the molecules of (II), in the orthorhombic polymorph studied here, is shown in Fig. 3(*a*). The H1 atoms of the NH groups point in opposite directions, from the diamine moiety towards the π-electron systems of adjacent molecules. The distance of atom H1 from the centroid of the C7/C8–C9

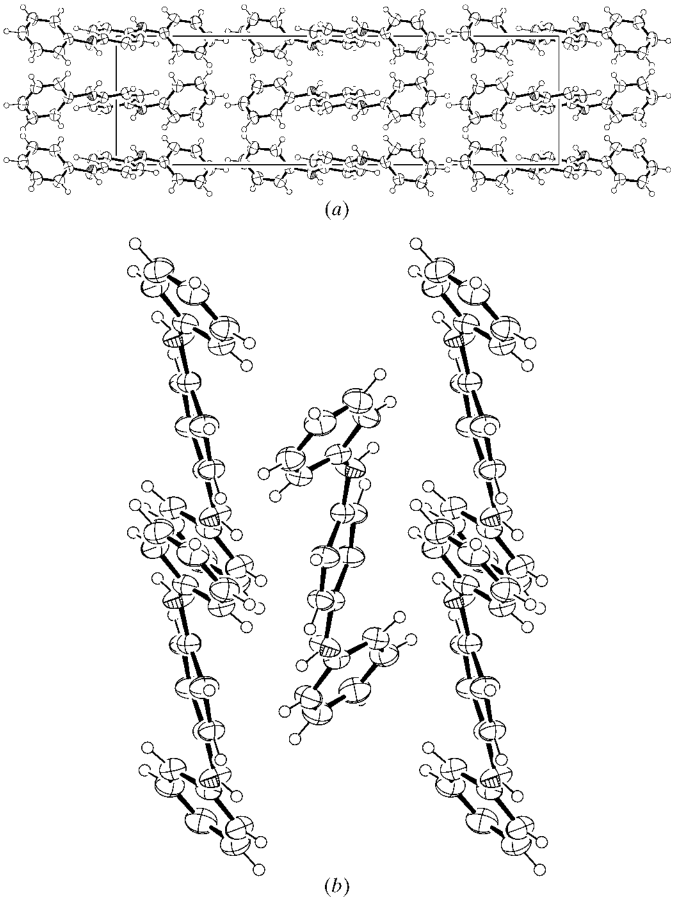
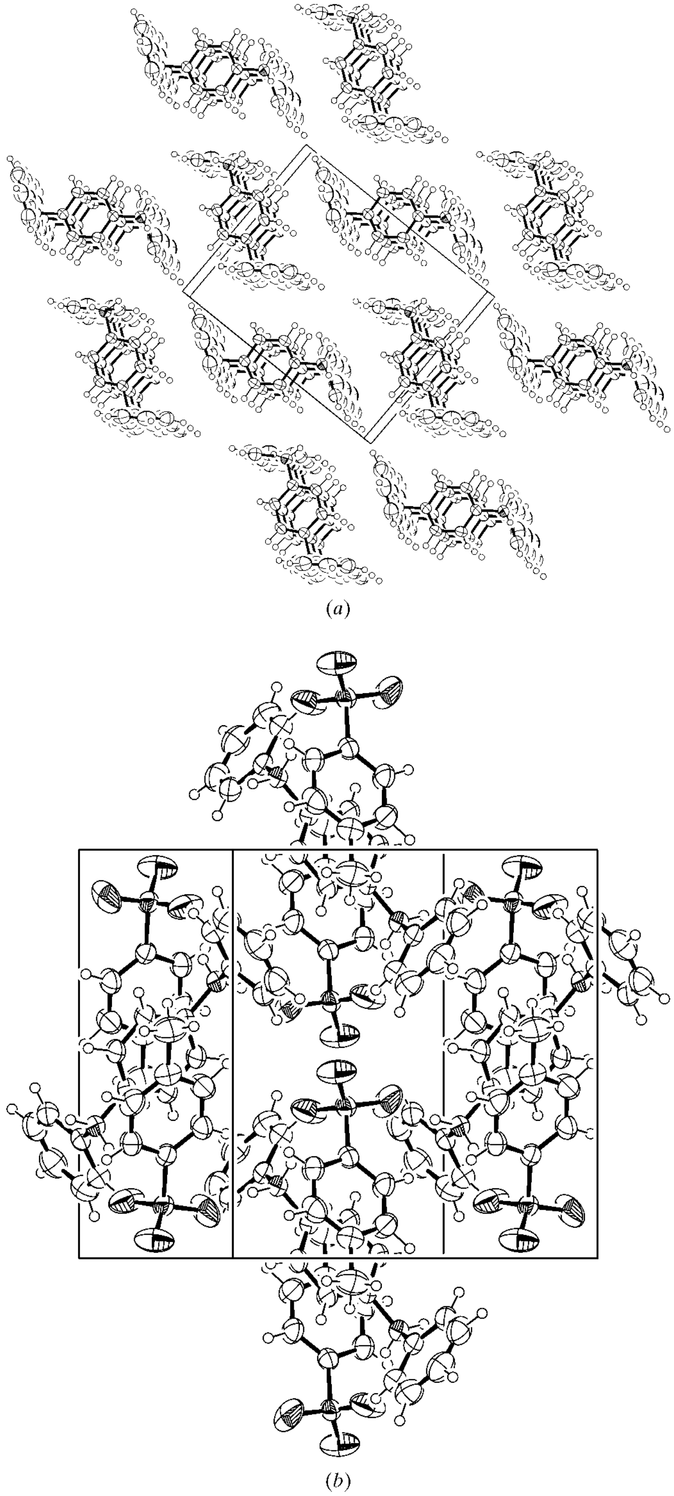


Figure 3
(*a*) The packing in the crystal structure of (II), viewed along [001]. (*b*) The arrangement of the molecules along [100]. The thickness of the projected layer is between $\frac{a}{4}$ and $\frac{3a}{4}$.

ring at $(-x, y+\frac{1}{2}, \frac{1}{2}-z)$ is 2.97 (2) Å, whereas its distance from the best plane of the ring is 2.93 (3) Å. Fig. 3(*b*) shows the mutual arrangement of the molecules along [100].

In the structure of (III), close-packed layers built up of oligomer cations can be distinguished (Fig. 4*a*), with the shortest distance of 2.90 (4) Å being between atom H8 and the best plane of the C1/C2–C6 ring of the adjacent molecule at $(\frac{5}{2}-x, y-\frac{1}{2}, 1-z)$. Each amine layer is linked to *p*-toluenesulfonate anions through π–π interactions, in such a way that the benzoid ring of the cation intercalates between the benzene rings of two *p*-toluenesulfonate anions (Fig. 4*b*). Additionally, relatively strong intermolecular N—H···O hydrogen bonds are formed (Table 4).


(*a*)

(*b*)

Figure 4
(*a*) The mutual arrangement of oligomer-cation layers observed in the structure of (III). (*b*) The intercalation of the benzoid ring of the cation in between the rings of two *p*-toluenesulfonate anions, related by a centre of symmetry, seen in an (001) projection.

In conclusion, the packing in the crystal structures of (I), (II) and (III) seems to be dominated by a mutual arrangement of the molecules of the polyaniline oligomers. In (I), the most significant intermolecular interactions are stacking forces between parallel quinoid rings. The columns of molecules parallel to [001] are close packed, resulting in a *C*-centred three-dimensional structure. In (II), the reduced form of (I), only the molecular shape and van der Waals interactions determine the packing. In the structure of (III), the salt of fully protonated (II), in addition to the hydrophobic interactions in the oligomer layers, the *p*-toluenesulfonate ions act as acceptors in relatively strong N—H···O hydrogen bonds.

Experimental

N,*N*′-Diphenyl-1,4-phenylenediamine (ex Aldrich), (II), used without further purification, was recrystallized from benzene by slow evaporation at room temperature. A mixture of (II) and 4-toluenesulfonic acid, in a 1:2 stoichiometric ratio, was finely ground and then dissolved in acetonitrile. Crystals of the salt, (III), were obtained by slow evaporation at room temperature. *N*,*N*′-Diphenyl-1,4-benzoquinone diimine, (I), was prepared by oxidation of (II) in toluene with 1.2 equivalents of dibenzoyl peroxide, as suggested by MacDiarmid *et al.* (1999). Crystals of (I) were grown from a saturated toluene solution.

Compound (I)

Crystal data

$C_{18}H_{14}N_2$
$M_r = 258.31$
Monoclinic, $C2/c$
$a = 27.4797\ (2)$ Å
$b = 6.7734\ (2)$ Å
$c = 7.4212\ (5)$ Å
$\beta = 92.026\ (1)^\circ$
$V = 1380.5\ (1)$ Å^3
$Z = 4$

$D_x = 1.243$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3078 reflections
$\theta = 1.0$–32.6°
$\mu = 0.07$ mm^{-1}
$T = 293\ (2)$ K
Needle, orange
0.25 × 0.07 × 0.05 mm

Table 1
Selected geometric parameters (Å, °) for (I).

N1—C1	1.413 (2)	C4—C5	1.380 (2)
N1—C7	1.297 (2)	C5—C6	1.386 (2)
C1—C2	1.395 (2)	C7—C8	1.462 (2)
C1—C6	1.392 (2)	C7—C9	1.462 (2)
C2—C3	1.389 (2)	C8—C9$^{\mathrm{i}}$	1.337 (2)
C3—C4	1.381 (2)		
C7—N1—C1	121.7 (1)	C9—C7—N1	126.5 (1)
C2—C1—C6	119.3 (1)	C8—C7—N1	116.7 (1)
C2—C1—N1	123.3 (1)	C9$^{\mathrm{i}}$—C8—C7	122.2 (1)
C6—C1—N1	117.2 (1)	C8$^{\mathrm{i}}$—C9—C7	121.0 (1)
C9—C7—C8	116.8 (1)		
C7—N1—C1—C2	55.8 (2)	C1—N1—C7—C9	4.1 (2)

Symmetry code: (i) $-x, -y, -z$.

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill Ewald sphere
7175 measured reflections
2457 independent reflections
1868 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\rm max} = 32.4°$
$h = 0 \rightarrow 41$
$k = -10 \rightarrow 8$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.170$
$S = 1.11$
2457 reflections
119 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 0.6075P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}

Compound (II)

Crystal data

$C_{18}H_{16}N_2$
$M_r = 260.33$
Orthorhombic, *Pbca*
$a = 25.678$ (4) Å
$b = 7.4815$ (13) Å
$c = 6.9588$ (12) Å
$V = 1336.9$ (4) Å^3
$Z = 4$
$D_x = 1.293$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 38 reflections
$\theta = 1.6$–$11.1°$
$\mu = 0.08$ mm^{-1}
$T = 295$ (2) K
Plate, colourless
0.40 × 0.28 × 0.08 mm

Data collection

Kuma KM-4 four-circle diffractometer
$\theta/2\theta$ scans
6410 measured reflections
1269 independent reflections
931 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\rm max} = 25.7°$
$h = -31 \rightarrow 31$
$k = -9 \rightarrow 9$
$l = -4 \rightarrow 8$
3 standard reflections every 50 reflections intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.133$
$S = 1.14$
1269 reflections
123 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 0.8676P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

N1—C1	1.402 (3)	C4—C5	1.377 (4)
N1—C7	1.410 (3)	C5—C6	1.370 (4)
C1—C2	1.381 (3)	C7—C8	1.384 (3)
C1—C6	1.393 (3)	C7—C9	1.382 (3)
C2—C3	1.389 (4)	C8—C9^{i}	1.386 (3)
C3—C4	1.370 (4)		
C1—N1—C7	129.7 (2)	C6—C5—C4	120.5 (3)
C2—C1—C6	118.2 (2)	C5—C6—C1	121.2 (3)
C2—C1—N1	124.8 (2)	C9—C7—C8	117.7 (2)
C6—C1—N1	116.9 (2)	C9—C7—N1	125.4 (2)
C1—C2—C3	119.7 (2)	C8—C7—N1	117.0 (2)
C4—C3—C2	121.6 (3)	C7—C8—C9^{i}	121.9 (2)
C3—C4—C5	118.6 (3)	C7—C9—C8^{i}	120.4 (2)
C7—N1—C1—C2	−28.5 (4)	C1—N1—C7—C9	−6.6 (4)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Compound (III)

Crystal data

$C_{18}H_{18}N_2^{2+}\cdot 2C_7H_7O_3S^-$
$M_r = 604.72$
Monoclinic, $P2_1/a$
$a = 10.9886$ (4) Å
$b = 12.3322$ (4) Å
$c = 11.9612$ (5) Å
$\beta = 112.8293$ (2)°
$V = 1493.93$ (10) Å^3
$Z = 2$
$D_x = 1.344$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 443 reflections
$\theta = 0.7$–$27.5°$
$\mu = 0.23$ mm^{-1}
$T = 293$ (2) K
Plate, green
0.39 × 0.37 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill Ewald sphere
11 246 measured reflections
3325 independent reflections
2635 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.090$
$\theta_{\rm max} = 27.4°$
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.196$
$S = 0.97$
3325 reflections
254 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.1076P)^2 + 1.0838P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.53$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.50$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (III).

N1—C1	1.473 (4)	S1—O13	1.421 (3)
N1—C7	1.482 (3)	S1—O12	1.426 (3)
C1—C2	1.381 (4)	S1—O11	1.443 (3)
C1—C6	1.392 (4)	S1—C11	1.774 (3)
C2—C3	1.387 (5)	C11—C16	1.376 (4)
C3—C4	1.381 (6)	C11—C12	1.392 (4)
C4—C5	1.377 (6)	C12—C13	1.384 (5)
C5—C6	1.382 (5)	C13—C14	1.388 (5)
C7—C8	1.372 (4)	C14—C15	1.380 (5)
C7—C9	1.384 (3)	C14—C17	1.515 (5)
C8—C9^{i}	1.383 (4)	C15—C16	1.384 (4)
C9—C8^{i}	1.383 (4)		
C1—N1—C7	114.9 (2)	C8^{i}—C9—C7	119.1 (2)
C2—C1—C6	122.0 (3)	O13—S1—O12	112.6 (3)
C2—C1—N1	119.7 (2)	O13—S1—O11	114.4 (3)
C6—C1—N1	118.3 (3)	O12—S1—O11	109.2 (2)
C9—C7—C8	121.6 (2)	O13—S1—C11	106.5 (1)
C9—C7—N1	119.4 (2)	O12—S1—C11	108.1 (1)
C8—C7—N1	119.0 (2)	O11—S1—C11	105.5 (1)
C7—C8—C9^{i}	119.3 (2)		
C7—N1—C1—C2	102.6 (3)	C1—N1—C7—C9	−59.1 (3)

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

Table 4
Hydrogen-bonding geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H11$\cdots$O13^{i}	0.95 (4)	1.75 (4)	2.695 (4)	171 (3)
N1—H10$\cdots$O11^{ii}	0.86 (4)	1.84 (4)	2.691 (3)	169 (3)

Symmetry codes: (i) $\frac{5}{2} - x, \frac{1}{2} + y, 1 - z$; (ii) $2 - x, 1 - y, 1 - z$.

In all three title structures, the H atoms were located from a difference Fourier map and were included in the refinement without constraints and with isotropic displacement factors. The ranges and average values of the refined C—H distances were as follows: 0.96–1.02 and 0.99 (2) Å for (I), 0.89–0.99 and 0.95 (4) Å for (II), and 0.89–1.06 and 0.97 (5) Å for (III). N—H distances were 0.91 (3) Å in (II), and 0.86 (4) and 0.95 (4) Å in (III).

For compounds (I) and (III), data collection: *COLLECT* (Nonius, 1997); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*. For compound (II), data collection: *KM*-4 *Software* (Kuma, 1995); cell refinement: *KM*-4 *Software*; data reduction: *DATAPROC* (Gałdecki *et al.*, 1995). For all three compounds, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1999); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1567). Services for accessing these data are described at the back of the journal.

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