organic compounds

4,6-Dinitro-N,N'-di-n-octylbenzene-1,3-diamine, 4,6-dinitro-N,N'-di-n-undecylbenzene-1,3-diamine and N,N'-bis(2,4-dinitrophenyl)octane-1,8-diamine

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4,6-Dinitro-N,N'-di-n-octylbenzene-1,3-diamine, $C_{22}H_{38}N_4O_4$, (I), 4,6-dinitro-N,N'-di-n-undecylbenzene-1,3-diamine, $C_{28}H_{50}N_4O_4$, (II), and N,N'-bis(2,4-dinitrophenyl)octane-1,8-diamine, $C_{20}H_{24}N_6O_8$, (III), are the first synthetic *meta*-dinitroarenes functionalized with long-chain aliphatic amine groups to be structurally characterized. The intra- and intermolecular interactions in these model compounds provide information that can be used to help understand the physical properties of corresponding polymers with similar functionalities. Compounds (I) and (II) possess near-mirror symmetry, with the octyl and undecyl chains adopting fully extended *anti* conformations in the same direction with respect to the ring. Compound (III) rests on a center of inversion that occupies the mid-point of the central C—C bond of the octyl chain. The middle six C atoms of the chain form an *anti* arrangement, while the remaining two C atoms take hard turns almost perpendicular to the rest of the chain. All three molecules display intramolecular N—H···O hydrogen bonds between the amine and nitro groups, with the same NH group forming a bifurcated intermolecular hydrogen bond to the nitro O atom of an adjacent molecule. In each case, these interactions link the molecules into one-dimensional molecular chains. In (I) and (II), these chains pack so that the pendant alkyl groups are interleaved parallel to one another, maximizing non-bonded C—H contacts. In (III), the alkyl groups are more isolated within the molecular chains and the primary non-bonded contacts between the chains appear to involve the nitro groups not involved in the hydrogen bonding.

Comment

We have recently reported the preparation and characteristics of polyamines containing two aromatic nitro groups in the polymer repeat units (Teng *et al.*, 2006). These polymers were prepared by the reactions of various aliphatic diamines with 1,5-difluoro-2,4-dinitrobenzene (DFDNB) in dimethyl-acetamide (DMAC) and diphenyl sulfone (DPS) at elevated temperatures. Anhydrous potassium carbonate was used as the acid scavenger and the resulting by-product, *viz.* water, was removed by toluene *via* azeotropic distillation. The aforementioned reaction conditions, in particular the need for higher reaction temperatures to achieve high molecular weight polymers, were ascertained from the preparation of various model compounds. For example, the higher degree of solubility of 4,6-dinitro-N,N'-di-n-octylbenzene-1,3-diamine, (I), in DMAC, in contrast with N,N'-bis(2,4-dinitro-phenyl)octane-1,8-diamine, (III), which precipitates out of refluxing DMAC, led us to use DPS (a higher boiling point dipolar aprotic solvent) as co-solvent during polymer syntheses. The prepared polymers were soluble only in strong mineral acids with bulky counter-ions, including nitric, sulfuric and perchloric acids at room temperature. This exceptional solvent resistance can be attributed to both inter- and intra-chain hydrogen bonding and possible hydrophobic inter-actions. In addition, the chain flexibility associated with longer aliphatic chains (hexyl and higher) allows for semihelical chains, which further facilitates a higher order of chain packing. This was evidenced from the complex wide-angle X-ray data for these polymers. Notwithstanding these strong interactions, it is possible to obtain fingernail-creasable films by compression-molding these polymers above their melting points. This paper is part of our continuing study of the structures of the monomer units for these polymers (Walczak *et al.*, 2008). Compounds (I), (II) (4,6-dinitro-N,N'-di-n-undecylbenzene-1,3-diamine) and (III) constitute a new family of dinitroarenes functionalized with long-chain alkyl amines. These model compounds and their intermolecular interactions offer insight into the physical properties of polymers prepared from diamines and the corresponding difluoro compound.

Molecules of (I) come close to having an internal mirror plane but in fact reside on general positions (Fig. 1). The H atoms on the N atoms of the *n*-octylamine groups participate in strong intramolecular hydrogen bonds with the O atoms of the adjacent nitro group (Table 1). This pattern has been
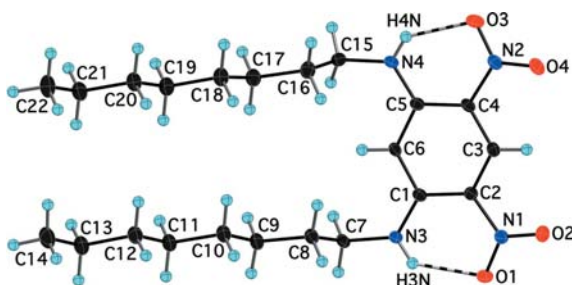
Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Intramolecular hydrogen bonds are shown as dashed bonds.

Figure 3
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Intramolecular hydrogen bonds are shown as dashed lines.
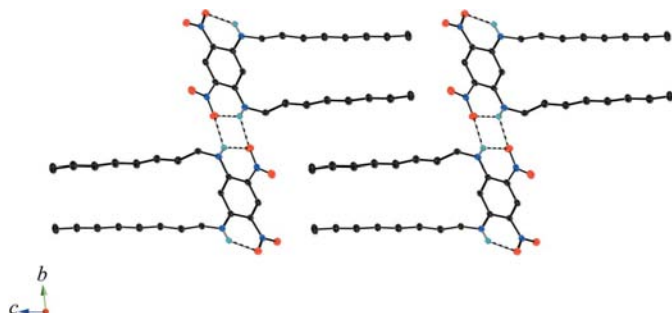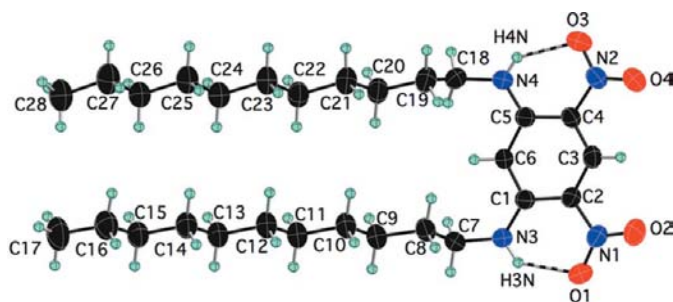

Figure 2
Portions of two adjacent molecular chains of (I) that run approximately parallel to (120), viewed along the *a* axis. Intra- and intermolecular N—H···O hydrogen bonds are shown as dashed bonds.

Figure 4
Portions of two adjacent molecular chains of (II) that run approximately parallel to (120), viewed along the *a* axis. Intra- and intermolecular N—H···O hydrogen bonds are shown as dashed lines.

observed previously in molecules with primary amine groups on both sides of a nitro group (Ammon *et al.*, 1982). A search of the Cambridge Structural Database (Version 5.29 plus updates in January 2008 and August 2008; Allen, 2002) reveals three structures of 1,5-bis(amino)-substituted 2,4-dinitrobenzene derivatives with 3-amino-1-pentanoic acid (Williams *et al.*, 1993), hydroxyethylamine (Lee *et al.*, 2006) and 3-(2,2,5,5-tetramethylpyrrolidinyl *N*-oxide)amine (Hilti *et al.*, 1976) groups, respectively, that display the same intramolecular N—H···O hydrogen bonding. In these other cases, the amine functional groups contain strong hydrogen-bonding donors and/or acceptors which create very different intermolecular interactions. Compound (I) is the first example we are aware of in which the amine functional groups are long alkyl chains with no additional substitution.

The octyl groups in (I) adopt an *anti* conformation throughout the chain. However, unlike what was observed in 1,3-bis(*n*-octylamino)-2-nitrobenzene (Walczak *et al.*, 2008), the chains are not coplanar with the ring. Rather, the axis of the parallel chains in (I) is roughly 38° out of the plane containing the ring, nitro groups and amine N atoms. This difference is most likely associated with the formation of intramolecular N—H···O interactions in (I) that are not observed in 1,3-bis(*n*-octylamino)-2-nitrobenzene. These H atoms are further involved in bifurcated intermolecular interactions (Table 1) that link the molecules of (I) into chains that run in the [2$\bar{1}$0] direction and stack parallel to (120) (Fig. 2). This type of bifurcated N—H···O interaction invol-

ving nitro O atoms from different molecules has been observed before (Panunto *et al.*, 1987), but it appears to be more commonly associated with the formation of isolated dimers (akin to the behavior of carboxylic acid groups) rather than chains. The linking of amine- and nitro-substituted organic molecules into chains is more commonly accomplished by bifurcated hydrogen bonds in which the N—H group of one molecule interacts with two O atoms from the same nitro group of an adjacent molecule (Panunto *et al.*, 1987). In the crystal structure of (I) described here, the chains are formed such that the octyl groups of adjacent molecules point to opposite sides of the chain. As a result, when the chains pack in the *c* direction, the octyl groups interleave, thus forming hydrophobic domains dominated by C—H interactions. In addition, the arene rings are stacked on top of each other along the *a* axis at distances of *ca* 3.8–3.9 Å apart. This is also different from what was found for 1,3-bis(*n*-octylamino)-2-nitrobenzene (Walczak *et al.*, 2008).

Molecules of (II) adopt essentially the same molecular structure as those of (I), with the alkyl chains simply extended by three methylene groups (Fig. 3). Intramolecular N—H···O amine–nitro hydrogen bonds occur on both sides of the ring (Table 2), the undecyl chains are in the *anti* conformation for the length of the chain and the parallel chains are canted by *ca* 36° with respect to the plane of the arene ring. The packing in the *ab* plane is virtually identical to that in (I), as indicated by the similarity of the cell dimensions, with the same intermolecular hydrogen-bonding pattern and interleaving of the

Figure 5
The molecular structure of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Intramolecular hydrog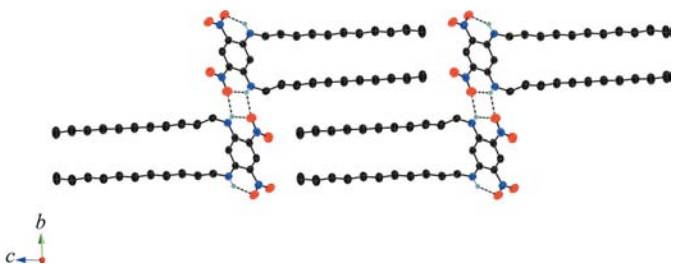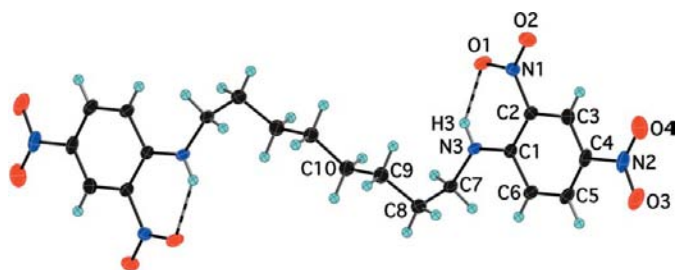en bonds are shown as dashed lines. The asymmetric unit consists of one half-molecule, and unlabeled atoms are related to labeled atoms by the symmetry operator $(1 - x, 1 - y, -z)$.
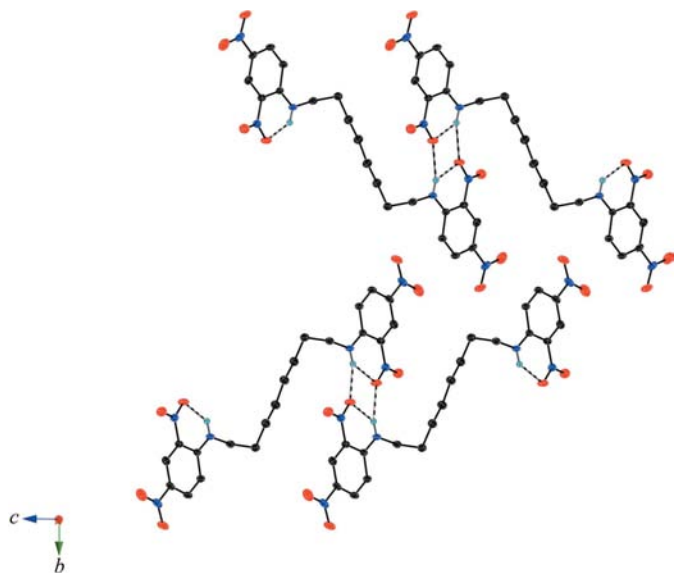

Figure 6
Portions of two adjacent molecular chains of (III) running along the c direction, viewed along the a axis. Intra- and intermolecular N—H···O hydrogen bonds are shown as dashed lines.

alkyl chains (Fig. 4). As a result of the additional methylene units, the c axis of (II) is about 4 Å longer than that of (I).

Molecules of (III) possess internal inversion symmetry about the center of the C10—C10^i bond [symmetry code: (i) $1 - x, 1 - y, -z$] (Fig. 5). The amine H atom participates in an intramolecular hydrogen bond with the nearest nitro O atom (Table 3). The majority of the octyl chain forms an extended *anti* conformation (torsion angles all within 4° of 180°). However, the last C atom at each end is *gauche* to the rest of the chain (C10—C9—C8—C7 torsion angle *ca* 71°). As a result, although the planes of the arene rings are parallel, they are not coplanar. The octyl chain forms a modified S-shaped connector between the rings. This conformation gives support to the proposition that polymer chains made from this monomer could have semihelical arrangements.

Similarly to the case in (I) and (II), the molecules of (III) are linked by four-center hydrogen bonds involving two amine H atoms and two nitro O atoms, the same groups being involved in the intramolecular N—H···O interactions.

Because each molecule can form two such bifurcated interactions, the net result is a motif of chains running along the c direction (Fig. 6). These chains then stack along the b direction, with the nitro groups that are not involved in the hydrogen bonds in close proximity to one another. Contrary to (I) and (II), the packing in (III) does not cleanly maximize contacts between either the alkyl chains or the arene rings. We believe that this is the first *N,N'*-(2,4-dinitrophenyl)alkanediamine to be structurally characterized.

Experimental

For the preparation of (I), octylamine (1.29 g, 0.01 mol), 1,5-difluoro-2,4-dinitrobenzene (DFDNB) (1.02 g, 0.005 mol), anhydrous potassium carbonate (2.20 g, excess), dimethylacetamide (DMAC) (20 ml) and toluene (15 ml) were placed in a four-necked 100 ml round-bottomed flask fitted with a thermometer, a nitrogen inlet, an overhead stirrer and a Dean–Stark trap fitted with a condenser. The reaction vessel was heated by an external oil bath to an initial temperature of 333 K and the reaction was allowed to continue at this temperature, with stirring, for 30 min. The temperature of the reaction mixture was gradually raised to 423 K over a period of 2 h. Water, the by-product of the reaction mixture, was removed by azeotropic distillation with toluene. After complete removal of water, the reaction mixture was cooled to room temperature, diluted with tetrahydrofuran (25 ml), filtered, and the filtrate poured into a rapidly stirred water–acetic acid mixture (1:1 v/v). The crude yellow precipitate was isolated by filtration and washed with a saturated sodium bicarbonate solution to remove residual acetic acid. The product was air-dried under suction overnight, dissolved in dichloromethane and washed twice with water, and the organic layer was dried over anhydrous magnesium sulfate. It was then filtered and the volume of the solution was reduced using a rotary evaporator. Compound (I) was then allowed to crystallize from the concentrated solution [yield 80%, m.p. 355 K (differential scanning calorimetry)]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.17 (d, 1H), 8.28 (t, 2H), 5.60 (s, 1H), 3.25 (m, 4H), 1.75 (m, 4H), 1.36 (m, 20H), 1.05 (t, 6H); ^{13}C NMR (CDCl$_3$): δ 148.78, 129.75, 124.18, 90.22, 43.59, 32.00, 29.47, 29.39, 28.67, 27.33, 22.87, 14.32; IR (KBr, $v > 1400$ cm^{-1}): 3379, 2921, 2847, 1616, 1581, 1542, 1411; MS (m/z) (% base peak): 422 (18), 387 (100), 323 (75), 305 (36).

Compound (II) was prepared by a similar procedure [yield 78%, m.p. 365 K (differential scanning calorimetry)]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.24 (d, 1H), 8.33 (t, 2H), 5.64 (s, 1H), 3.27 (m, 4H), 1.77 (m, 4H), 1.38 (m, 32H), 0.88 (t, 6H); ^{13}C NMR (CDCl$_3$): δ 148.51, 129.50. 123.91, 90.50, 43.31, 31.86, 29.56, 29.53, 29.46, 29.29, 29.24, 28.39, 27.05, 22.64, 14.07; IR (KBr, $v > 1400$ cm^{-1}): 3379, 2916, 2848, 1618, 1581, 1411, 1254; MS (m/z) (% base peak): 506 (11), 471 (100), 389 (24), 365 (29).

Compound (III) was prepared from octane-1,8-diamine and two equivalents of 2,4-dinitrofluorobenzene using a similar reaction procedure. However, the resulting compound was sparingly soluble in DMAC at its reflux temperature. The reaction mixture was cooled to room temperature and then filtered. The residue was purified using a Soxhlet apparatus. Acetone, water and acetone, in that order, were used to remove residual salts and DMAC. The crude product was dried and recrystallized from refluxing trichloromethane to obtain suitable crystals for X-ray analysis [yield 75%, m.p. 415 K (differential scanning calorimetry)]. ^{1}H NMR (400 MHz, D$_2$SO$_4$): δ 8.6 (m, 1H), 8.1 (m, 1H), 5.6 (s, 1H), 7.4 (m, 1H), 3.0 (t, 2H), 1.2 (m, 2H), 0.9 (m, 4H); ^{13}C NMR (D$_2$SO$_4$): δ 147.08, 139.45, 132.60, 131.02,

127.20, 122.30, 54.90, 26.67, 24.61, 23.98; IR (KBr, $\nu > 1400$ cm^{-1}): 3363, 1621, 1585, 1522, 1420; MS (m/z) (% base peak): 476 (2), 264 (12), 196 (100), 180 (55).

Compound (I)

Crystal data

$C_{22}H_{38}N_4O_4$	$\gamma = 86.421\ (1)°$
$M_r = 422.56$	$V = 1138.49\ (8)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 4.6679\ (2)$ Å	Mo $K\alpha$ radiation
$b = 15.5897\ (6)$ Å	$\mu = 0.09$ mm^{-1}
$c = 15.7690\ (6)$ Å	$T = 120\ (2)$ K
$\alpha = 83.760\ (1)°$	$0.38 \times 0.12 \times 0.05$ mm
$\beta = 89.356\ (1)°$	

Data collection

Bruker SMART 6000 CCD area-detector diffractometer	20817 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	5647 independent reflections
	4846 reflections with $I > 2\sigma(I)$
$T_{min} = 0.866$, $T_{max} = 0.996$	$R_{int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	423 parameters
$wR(F^2) = 0.116$	All H-atom parameters refined
$S = 1.06$	$\Delta\rho_{max} = 0.38$ e Å^{-3}
5647 reflections	$\Delta\rho_{min} = -0.23$ e Å^{-3}

Compound (II)

Crystal data

$C_{28}H_{50}N_4O_4$	$\gamma = 87.069\ (2)°$
$M_r = 506.72$	$V = 1459.44\ (5)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 4.7349\ (1)$ Å	Mo $K\alpha$ radiation
$b = 15.6273\ (3)$ Å	$\mu = 0.08$ mm^{-1}
$c = 19.7771\ (3)$ Å	$T = 293\ (2)$ K
$\alpha = 87.282\ (2)°$	$0.41 \times 0.06 \times 0.01$ mm
$\beta = 88.549\ (2)°$	

Data collection

Rigaku RAPID diffractometer	22872 measured reflections
Absorption correction: empirical (using intensity measurements) (*D*TREK*; Pflugrath, 1999)	5726 independent reflections
	4432 reflections with $I > 2\sigma(I)$
$T_{min} = 0.822$, $T_{max} = 1.000$ (expected range = 0.821–0.999)	$R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$	525 parameters
$wR(F^2) = 0.176$	All H-atom parameters refined
$S = 1.11$	$\Delta\rho_{max} = 0.17$ e Å^{-3}
5726 reflections	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Compound (III)

Crystal data

$C_{20}H_{24}N_6O_8$	$V = 1069.75\ (5)$ Å^3
$M_r = 476.45$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 4.6740\ (1)$ Å	$\mu = 0.12$ mm^{-1}
$b = 25.7389\ (8)$ Å	$T = 105\ (2)$ K
$c = 8.9254\ (3)$ Å	$0.30 \times 0.20 \times 0.12$ mm
$\beta = 94.949\ (1)°$	

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3N$\cdots$O1	0.843 (16)	2.008 (16)	2.6535 (13)	132.7 (14)
N3—H3N$\cdots$O1^i	0.843 (16)	2.354 (16)	3.0166 (12)	135.8 (14)
N4—H4N$\cdots$O3	0.799 (17)	2.027 (17)	2.6412 (14)	133.5 (15)
N4—H4N$\cdots$O3^{ii}	0.799 (17)	2.312 (17)	2.9647 (13)	139.3 (15)

Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x - 1, -y + 1, -z$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3N$\cdots$O1	0.89 (2)	1.95 (2)	2.6456 (19)	134 (2)
N3—H3N$\cdots$O1^i	0.89 (2)	2.42 (2)	3.0927 (19)	132.5 (18)
N4—H4N$\cdots$O3	0.80 (2)	2.01 (2)	2.646 (2)	135.9 (19)
N4—H4N$\cdots$O3^{ii}	0.80 (2)	2.39 (2)	3.048 (2)	140.3 (18)

Symmetry codes: (i) $-x + 3, -y + 1, -z$; (ii) $-x + 1, -y + 2, -z$.

Table 3
Hydrogen-bond geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$\cdots$O1	0.85 (2)	2.00 (2)	2.6382 (18)	131.9 (18)
N3—H3$\cdots$O1^i	0.85 (2)	2.28 (2)	3.0202 (18)	146.3 (18)

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

Data collection

Bruker SMART 6000 CCD area-detector diffractometer	8443 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick,1996)	2096 independent reflections
	1973 reflections with $I > 2\sigma(I)$
$T_{min} = 0.759$, $T_{max} = 0.986$	$R_{int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	202 parameters
$wR(F^2) = 0.109$	All H-atom parameters refined
$S = 1.11$	$\Delta\rho_{max} = 0.34$ e Å^{-3}
2096 reflections	$\Delta\rho_{min} = -0.24$ e Å^{-3}

All H atoms were located from difference Fourier syntheses and refined isotropically [for all compounds, arene C—H = 0.89 (2)–0.94 (2) Å and alkyl C—H = 0.94 (4)–1.04 (2) Å].

Data collection: *SMART* (Bruker, 2003) for (I) and (III); *Crystal Clear* (Rigaku, 2002) for (II). Cell refinement: *SAINT-Plus* (Bruker, 2003) for (I) and (III); *D*TREK* (Pflugrath, 1999) for (II). Data reduction: *SAINT-Plus* for (I) and (III); *D*TREK* for (II). For all three compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalMaker* (Palmer, 2008); software used to prepare material for publication: *SHELXL97*.

organic compounds

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