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Three isomeric *N*-(nitrophenyl)-succinimides: isolated molecules, hydrogen-bonded sheets and a hydrogen-bonded three-dimensional framework

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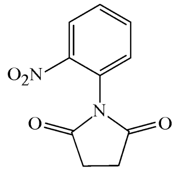
Molecules of *N*-(2-nitrophenyl)succinimide, $C_{10}H_8N_2O_4$, are linked into sheets by a combination of C—H···O and C—H···π(arene) hydrogen bonds. Molecules of *N*-(3-nitrophenyl)succinimide are linked into a three-dimensional framework by a combination of a two-centre C—H···O hydrogen bond and a three-centre C—H···$(O)_2$ hydrogen bond. Molecules of *N*-(4-nitrophenyl)succinimide which lie across twofold rotation axes in space group $C2/c$, participate in no direction-specific intermolecular interactions.

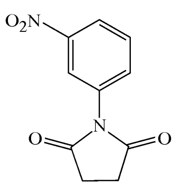
Comment

We report here the structures of three isomeric *N*-(nitrophenyl)succinimides, (I)–(III). These compounds offer, within the compass of a small molecular skeleton, a wide range of potential intermolecular interactions, including C—H···O(carbonyl/nitro) (each with aromatic and aliphatic C—H units as potential donors) and C—H···π(arene) hydrogen bonds, aromatic π–π stacking interactions, and dipolar carbonyl–carbonyl and nitro–nitro interactions.

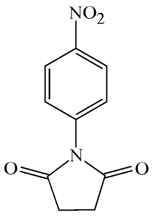
In the 2-nitro and 3-nitro isomers (I) and (II) (Figs. 1 and 2), the succinimide rings are effectively planar. However, in the 4-nitro isomer, (III), where the molecules lie across twofold rotation axes in space group $C2/c$, with the reference molecule selected as one lying across the axis along $(\frac{1}{2}, y, \frac{3}{4})$ (Fig. 3), the succinimide rings are markedly puckered. The total puckering amplitude Q_2 (Cremer & Pople, 1975) is 0.161 (3) Å, and the ring-puckering parameter φ_2 is 90.0 (9)° for the atom sequence N1—C1—C2—C2$^{\rm iii}$—C1$^{\rm iii}$ [symmetry code: (iii) $1 - x, y, \frac{3}{2} - z$], indicating a half-chair conformation for this ring. In isomers (I)–(III), the dihedral angles between the mean planes of the two rings are 57.4 (2), 46.0 (2) and 39.1 (2)°, respectively, while the dihedral angles between the aryl rings and the nitro groups are 40.0 (2), 4.9 (2) and 23.2 (2)°, respectively. In isomers (I) and (II), the molecules have point group C_1, and in isomer (III), the molecular point group is C_2; hence, in each isomer, the molecules are chiral. Thus, for isomer (II) in space group $P2_1$, each crystal contains just one enantiomer provided that inversion twinning is absent, although the bulk material is racemic. The bond distances and interbond angles in (I)–(III) show no unusual values.



(I)



(II)



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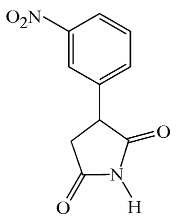
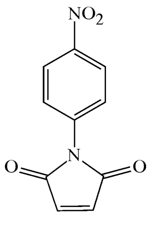


(IV)



(V)

The molecules of isomer (I) (Fig. 1) are linked into centrosymmetric dimers by a single C—H···O hydrogen bond, and these dimers are linked into sheets by a single C—H···π(arene) hydrogen bond (Table 1). Aromatic π–π stacking interactions, on the other hand, are absent. Atom C3 in the molecule at (x, y, z) acts as a hydrogen-bond donor to nitro atom O21 in the molecule at $(1 - x, 1 - y, 1 - z)$, so generating a centrosymmetric $R_2^2(16)$ (Bernstein *et al.*, 1995) dimer, centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 4). The atoms of type C2 in this dimer, at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, act as hydrogen-

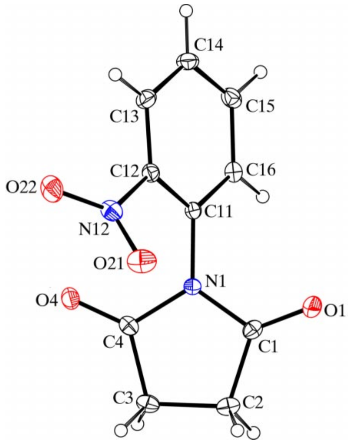


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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bond donors, respectively, to aryl rings C11–C16 in the molecules at $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$ and $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$, which themselves form parts of the dimers centred at $(\frac{1}{2}, 0, 1)$ and $(\frac{1}{2}, 1, 0)$, respectively. In a similar way, aryl rings C11–C16 in the molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ accept hydrogen bonds from atoms C2 in the molecules at $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$ and $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$, respectively, which are themselves components of the dimers centred at $(\frac{1}{2}, 1, 1)$ and $(\frac{1}{2}, 0, 0)$. In this manner, a (100) sheet is generated (Fig. 5).

There is a fairly short dipolar contact between carbonyl atoms O1 at (x, y, z) and C4 at $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$ [$\text{O1}\cdots\text{C4}^{\text{iv}}$ = 2.959 (2) Å, $\text{O1}\cdots\text{O4}^{\text{iv}}$ = 3.193 (2) Å, $\text{C1}-\text{O1}\cdots\text{C4}^{\text{iv}}$ = 148.7 (2)° and $\text{O1}\cdots\text{C4}^{\text{iv}}-\text{O4}^{\text{iv}}$ = 50.4 (2)°; symmetry code: (iv) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$], corresponding to an interaction partway between the type I and type III motifs (Allen *et al.*, 1998). However, this interaction occurs within a (100) sheet and hence does not affect the dimensionality of the supramolecular structure; there are, in fact, no direction-specific interactions between adjacent sheets.

The molecules of (II) are linked into a three-dimensional framework by a combination of one two-centre $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond and one three-centre $\text{C}-\text{H}\cdots(\text{O})_2$ hydrogen bond (Table 2), and the formation of the framework is readily analysed and described by consideration of each of these interactions in turn. In the two-centre hydrogen bond, aromatic atom C16 in the molecule at (x, y, z) acts as a donor to carbonyl atom O4 in the molecule at $(-1 + x, y, z)$, so generating by translation a *C*(6) (Bernstein *et al.*, 1995) chain running parallel to the [100] direction (Fig. 6).

In the three-centre hydrogen bond, which is planar, atom C3 in the molecule at (x, y, z) acts as a donor, *via* H3*A*, to nitro atom O31 in the molecule at $(x, y, -1 + z)$ and to carbonyl atom O1 in the molecule at $(-x, \frac{1}{2} + y, -z)$. The individual components of this three-centre system thus produce, respectively, a *C*(9) chain running parallel to the [001] direction and generated by translation, and a *C*(5) chain running parallel to the [010] direction and generated by the 2_1 screw axis along $(\frac{1}{4}, y, \frac{1}{4})$. The action of the two components of this system, acting together, forms a (100) sheet in the form of a (4,4)-net (Batten & Robson, 1998) built from a single type of $R_3^4(23)$ ring (Fig. 7). The combination of the [100] chain (Fig. 6) and the (100) sheet (Fig. 7) suffices to generate the three-dimensional framework.

In the structure of isomer (III) (Fig. 3) there are neither hydrogen bonds of any type nor aromatic π–π stacking interactions or dipolar interactions; hence, the structure of (III) consists of isolated molecules.

It is of interest to compare the supramolecular structures of isomers (I)–(III) with that of the isomeric *C*-(3-nitrophen-

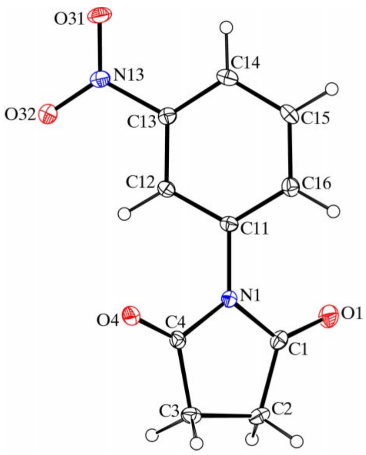

Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

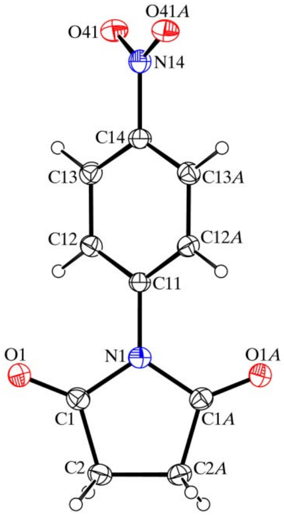

Figure 3
The molecule of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level, and atoms marked with the suffix *A* are at the symmetry position $(1 - x, y, \frac{3}{2} - z)$.

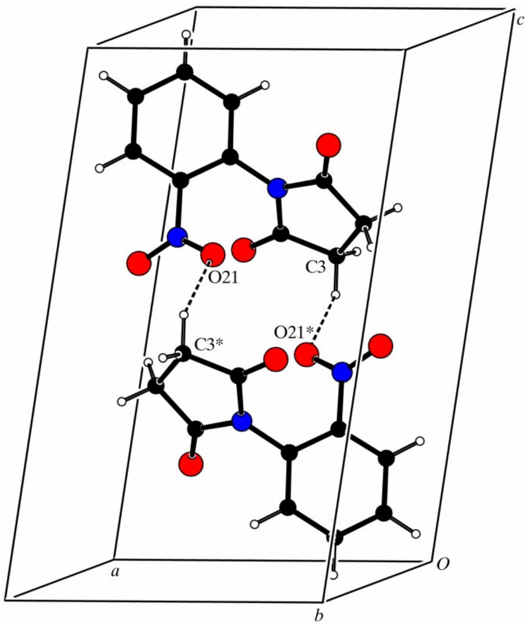

Figure 4
Part of the crystal structure of (I), showing the formation of an $R_2^2(16)$ dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

yl)succinimide, (IV) [Cambridge Structural Databse (CSD; Allen, 2002) refcode TANPUT (Kwiatkowski & Karolak-Wojciechowska, 1992)]. Compound (IV) crystallizes in the centrosymmetric space group $P2_1/c$, with $Z' = 2$, so that equal numbers of the *R* and *S* enantiomers are present in each crystal. The supramolecular structure is dominated by two N—H···O hydrogen bonds, which generate $C_2^2(8)$ chains along [010]. Although no C—H···O hydrogen bonds were mentioned in the original report, analysis of the reported atomic coordinates using *PLATON* (Spek, 2003) shows that the chains are, in fact, weakly linked into sheets by two such hydrogen bonds involving one nitro O atom and one carbonyl O atom as acceptors; however, C—H···π(arene) hydrogen bonds and aromatic π–π stacking interactions are absent from the structure of (IV). We also note that, at 293 K, *N*-(4-nitrophenyl)maleimide, (V) [CSD refcodes BEDWOX (Fruk & Graham, 2003) and BEDWOX01 (Moreno-Fuquen *et al.*, 2003)], is isostructural with (III). The structure of (V), like that of (III), contains no direction-specific intermolecular interactions, despite the different orientations of the C—H bonds in the heterocyclic ring of (V).

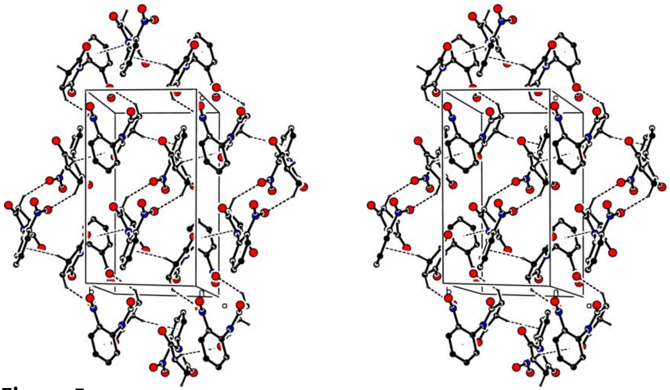

Figure 5
A stereoview of part of the crystal structure of (I), showing the formation of a (100) sheet built from C—H···O and C—H···π(arene) hydrogen bonds. For clarity, H atoms not involved in the motifs shown have been omitted

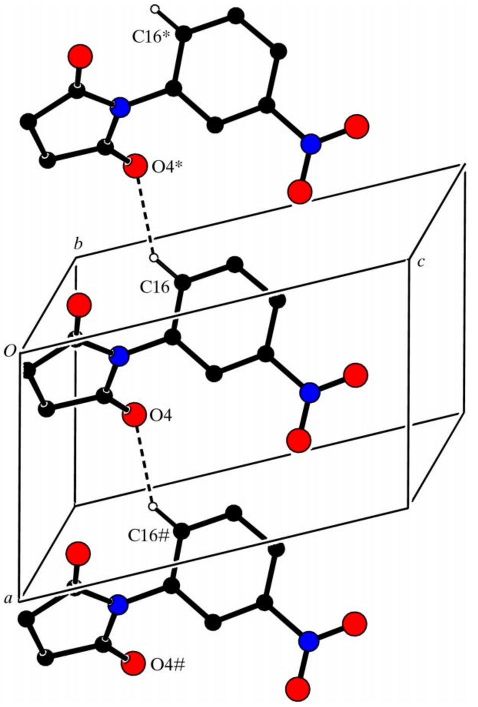

Figure 6
Part of the crystal structure of (II), showing the formation, *via* a two-centre C—H···O hydrogen bond, of a *C*(6) chain along [100]. For clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-1 + x, y, z)$ and $(1 + x, y, z)$, respectively.

The intermolecular interactions manifest in the structures of (I)–(III) are different in all three isomers. In (I), the structure is determined by one C—H···O hydrogen bond and one C—H···π(arene) hydrogen bond; both interactions involve a CH_2 donor rather than an aryl C—H bond as donor, and the C—H···O hydrogen bond has a nitro O-atom acceptor rather than the usual carbonyl O-atom acceptor; however, the carbonyl groups do participate in dipolar interactions. In isomer (II), by contrast, where only C—H···O hydrogen bonds occur, both CH_2 and aryl donors participate, and the three-centre hydrogen bond involves both nitro and carbonyl O atoms as the acceptors. Likewise in (IV), the C—H···O hydrogen bonds involve both nitro and carbonyl acceptors. In none of isomers (I)—(III) is there any aromatic π–π stacking interactions, and these interactions are possibly precluded by the overall molecular conformations. Perhaps the most surprising feature of the structures of isomers (I)–(III) is the lack of any direction-specific intermolecular interactions in isomer (III).

Thus, each of the isomers (I)–(III) exhibits a different range of intermolecular interactions, and their supramolecular structures are all of different dimensionality, *viz.* two- and three-dimensional in (I) and (II), respectively, contrasted with isolated molecules in (III). Such differences within a series of positional isomers are not yet readily predictable, either heuristically or computationally.

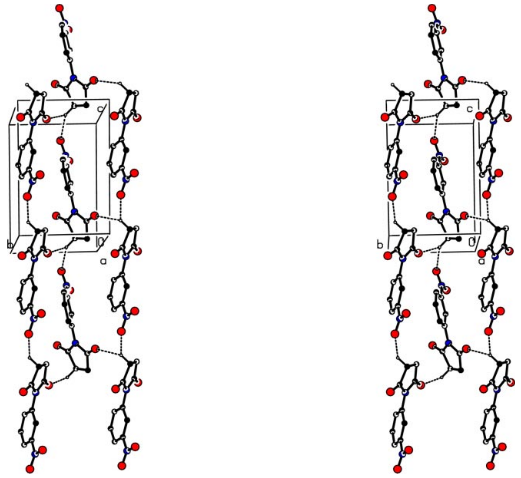

Figure 7
A stereoview of part of the crystal structure of (II), showing the formation, *via* a three-centre C—H···$(O)_2$ hydrogen bond, of a (100) sheet. For clarity, H atoms not involved in the motifs shown have been omitted.

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Experimental

For the preparation of compounds (I)–(III), finely ground mixtures containing equimolar quantities of succinic anhydride and the appropriate nitroaniline were heated in an oil bath at 473 K until effervescence ceased. The resulting solids were cooled to ambient temperature and dissolved in chloroform. Activated charcoal was added and the mixtures were then heated under reflux for 10 min; this process was followed by filtration of the hot mixtures. After removal of the solvent under reduced pressure, crystallization of the solid products from ethanol gave crystals suitable for single-crystal X-ray diffraction.

Compound (I)

Crystal data

$C_{10}H_8N_2O_4$
$M_r = 220.18$
Monoclinic, $P2_1/c$
$a = 8.3703$ (2) Å
$b = 8.2500$ (1) Å
$c = 14.1375$ (3) Å
$\beta = 101.0185$ (10)°
$V = 958.27$ (3) Å^3
$Z = 4$

$D_x = 1.526$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2192 reflections
$\theta = 3.5$–27.5°
$\mu = 0.12$ mm^{-1}
$T = 120$ (2) K
Block, yellow
0.15 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.976$, $T_{\max} = 0.988$
12 771 measured reflections
2192 independent reflections

1846 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.114$
$S = 1.10$
2192 reflections
146 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2 + 0.2225P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.081 (7)

Table 1

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

Cg is the centroid of the C11–C16 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3B···O21$^{\rm i}$	0.99	2.42	3.253 (2)	141
C2—H2B···$Cg^{\rm ii}$	0.99	2.75	3.638 (2)	149

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

Compound (II)

Crystal data

$C_{10}H_8N_2O_4$
$M_r = 220.18$
Monoclinic, $P2_1$
$a = 6.6318$ (2) Å
$b = 7.0944$ (3) Å
$c = 10.4260$ (5) Å
$\beta = 108.234$ (2)°
$V = 465.90$ (3) Å^3
$Z = 2$

$D_x = 1.570$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1152 reflections
$\theta = 3.2$–27.4°
$\mu = 0.12$ mm^{-1}
$T = 120$ (2) K
Block, colourless
0.40 × 0.35 × 0.30 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.947$, $T_{\max} = 0.964$
5403 measured reflections
1152 independent reflections

1067 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 27.4°$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 9$
$l = -12 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.078$
$S = 1.08$
1152 reflections
146 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.043P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.112 (14)

Table 2

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···O31$^{\rm v}$	0.99	2.48	3.193 (2)	129
C3—H3A···O1$^{\rm vi}$	0.99	2.47	3.158 (3)	127
C16—H16···O4$^{\rm vii}$	0.95	2.37	3.162 (2)	141

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

Compound (III)

Crystal data

$C_{10}H_8N_2O_4$
$M_r = 220.18$
Monoclinic, $C2/c$
$a = 10.3731$ (19) Å
$b = 11.590$ (2) Å
$c = 7.9761$ (18) Å
$\beta = 108.135$ (16)°
$V = 911.3$ (3) Å^3
$Z = 4$
$D_x = 1.605$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1054 reflections
$\theta = 3.3$–27.6°
$\mu = 0.13$ mm^{-1}
$T = 120$ (2) K
Lath, colourless
0.25 × 0.11 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.974$, $T_{\max} = 0.996$
9627 measured reflections
1054 independent reflections

690 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.095$
$\theta_{\max} = 27.6°$
$h = -13 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.167$
$S = 1.06$
1054 reflections
75 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0889P)^2 + 0.338P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

For isomer (I), the space group $P2_1/c$ was uniquely assigned from the systematic absences. For isomer (II), the systematic absences permitted $P2_1$ and $P2_1/m$ as possible space groups; since the unit-cell volume suggested $Z = 2$, space group $P2_1$ was selected and subsequently confirmed by the successful structure analysis. For isomer (III), the systematic absences permitted $C2/c$ and Cc as possible space groups; $C2/c$ was selected and confirmed by the successful structure analysis. All H atoms were located from difference maps and then treated as riding atoms, with C—H distances of 0.95 (aromatic) or 0.99 Å (CH_2) and U_{iso}(H) values of $1.2U_{eq}$(C). In the absence of any significant anomalous dispersion, the Flack (1983) parameter for isomer (II) was indeterminate (Flack & Bernardinelli, 2000). Hence, it was not possible to determine the absolute configuration of the molecules in the crystal selected for study (Jones, 1986); however, this configuration has no chemical significance. Accordingly, the Friedel pairs were merged prior to the final refinements. The data-to-parameter ratio for isomer (II) is thus rather low, only 7.89, although the data set is 99.8% complete to $\theta = 27.43°$.

For compounds (I) and (III), data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*. For compound (II), data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*. For all compounds, structure solution: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); structure refinement: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1817). Services for accessing these data are described at the back of the journal.

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