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π-Stacked hydrogen-bonded sheets in *N*,*N*′-bis(4-nitrobenzylidene)ethane-1,2-diamine and π-stacked hydrogen-bonded chains in *N*,*N*′-bis(4-nitrobenzylidene)propane-1,3-diamine

Joao A. S. Bomfim,[a] James L. Wardell,[a] John N. Low,[b] Janet M. S. Skakle[b] and Christopher Glidewell[c]*

[a]Instituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil, [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [c]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

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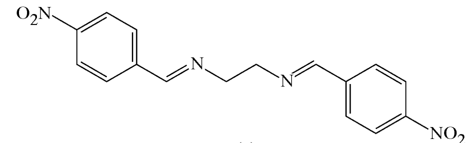
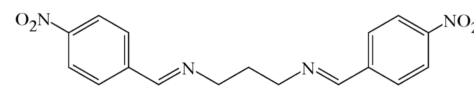
Molecules of *N*,*N*′-bis(4-nitrobenzylidene)ethane-1,2-diamine, $C_{16}H_{14}N_4O_4$, (I), lie across centres of inversion in space group $P2_1/n$ and are linked into $(10\bar{1})$ sheets by a single C—H⋯O hydrogen bond [H⋯O = 2.40 Å, C⋯O = 3.2166 (13) Å and C—H⋯O = 146°]; these sheets are linked into a three-dimensional array by a single aromatic π–π stacking interaction. Molecules of *N*,*N*′-bis(4-nitrobenzylidene)propane-1,3-diamine, $C_{17}H_{16}N_4O_4$, (II), lie across twofold rotation axes in space group $C2/c$ and are linked into chains of spiro-fused rings by a single C—H⋯O hydrogen bond [H⋯O = 2.54 Å, C⋯O = 3.267 (2) Å and C—H⋯O = 130°]; these chains are linked into sheets by a single aromatic π–π stacking interaction.

Comment

As part of a study of the supramolecular structures of compounds containing nitro groups, the structures of the title compounds were determined. The structure of *N*,*N*′-bis(4-nitrobenzylidene)ethane-1,2-diamine, (I), has been reported very recently (Sun *et al.*, 2004) and it is clear that the determination reported here refers to the same phase as that in the previous report. A larger data set is employed here (2717 reflections as opposed to 1635), leading to slightly higher precision. Although Sun *et al.* (2004) drew attention to the presence in the structure of a C—H⋯O hydrogen bond and to the occurrence of an aromatic π–π stacking interaction, the structural consequences of these interactions were not analysed or discussed in detail. In particular, the dimensionality of the resulting supramolecular structure was not specified. Accordingly, we feel it is justifiable to discuss this structure in detail along with that of its homologue *N*,*N*′-bis(4-nitrobenzylidene)propane-1,3-diamine, (II).



(I)



(II)

Molecules of (I) (Fig. 1) lie across centres of inversion in space group $P2_1/n$, and the reference molecule was selected to lie across $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The key torsion angles (Table 1) show that the N11—C11 bond almost eclipses the C12—H12*A* bond; the C11—N11—C12—H12*A* angle is only 2.3°. The two halves of the molecule are otherwise each nearly planar. The bond lengths and interbond angles agree closely with those found by Sun *et al.* (2004) and show no unusual values.

The molecules of (I) are linked into sheets by a single, fairly short, C—H⋯O hydrogen bond (Table 2). Atoms C6 at (x, y, z) and ($1 - x$, $1 - y$ $1 - z$), which lie in the molecule centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, act as hydrogen-bond donors, respectively, to atoms O41 at $(-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z)$ and $(\frac{3}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z)$, which themselves lie in the molecules centred at (0, 1, 0) and (1, 0, 1). In a similar way, atoms O41 at (x, y, z) and ($1 - x$, $1 - y$, $1 - z$) accept hydrogen bonds from atoms C6 at $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$ and $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, respectively, which lie in the

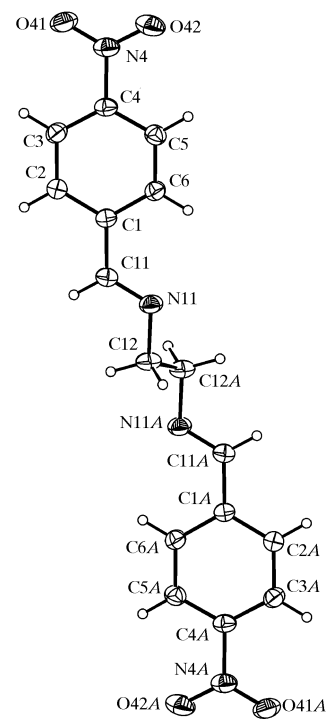


Figure 1
The molecule of (I), showing the atom-labelling scheme. Atoms labelled with the suffix '*A*' are at the symmetry position ($1 - x$, $1 - y$, $1 - z$), and displacement ellipsoids are drawn at the 30% probability level.

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molecules centred at (1, 1, 1) and (0, 0, 0), respectively. In this manner, each molecule is linked to four others, forming a $(10\overline{1})$ sheet (Fig. 2) in the form of a (4,4)-net (Batten & Robson, 1998), built from a single type of $R_4^4(42)$ ring (Bernstein *et al.*, 1995).

A single π–π stacking interaction links adjacent sheets. The aryl rings at (x, y, z) and $(1 - x, 1 - y, 2 - z)$ are components of the molecules centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$, respectively. These rings are strictly parallel, with an interplanar separation of 3.419 (2) Å; the ring-centroid separation is 3.696 (2) Å, corresponding to a near-ideal ring-centroid offset of 1.404 (2) Å. Propagation of this stacking interaction by translation and inversion links the molecules into a molecular ladder running parallel to the [001] direction (Fig. 3), and this ladder suffices to link each $(10\overline{1})$ sheet to the two adjacent sheets, hence forming a continuous three-dimensional array.

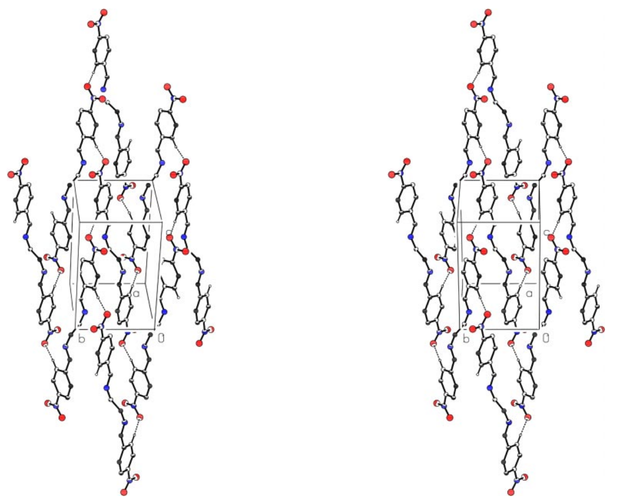

Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a $(10\overline{1})$ sheet. For clarity, H atoms not involved in hydrogen bonding have been omitted.

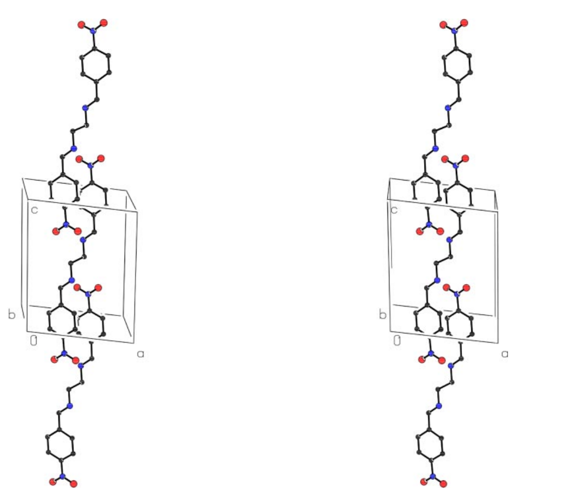

Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a π-stacked molecular ladder along [001]. For clarity, all of the H atoms have been omitted.

Molecules of (II) (Fig. 4) lie across twofold rotation axes in space group *C*2/*c*, and the reference molecule was selected to lie across the axis along $(\frac{1}{2}, y, \frac{1}{4})$. The central spacer unit has a conformation exhibiting almost perfect staggering about the C—C bonds (Table 3) and, as in (I), the outer portions of the molecule are nearly planar.

Molecules of (II) are linked into chains of spiro-fused rings by a single C—H···O hydrogen bond (Table 4). Atom C13 at $(\frac{1}{2}, y, \frac{1}{4})$ acts as a hydrogen-bond donor to nitro atoms O41 at $(x, 1 - y, -\frac{1}{2} + z)$ and $(1 - x, 1 - y, 1 - z)$, which themselves are components of the molecules across the twofold rotation axes $(\frac{1}{2}, -y, -\frac{1}{4})$ and $(\frac{1}{2}, -y, \frac{3}{4})$, respectively. Propagation by rotation of this single hydrogen bond then generates a chain of spiro-fused centrosymmetric $R_2^2(22)$ rings running parallel to the [001] direction, in which atom C13 is the spiro atom (Fig. 5).

Two chains of this type, related to one another by the C-centring operation, pass through each unit cell, and the chains are linked into sheets by a single aromatic π–π stacking

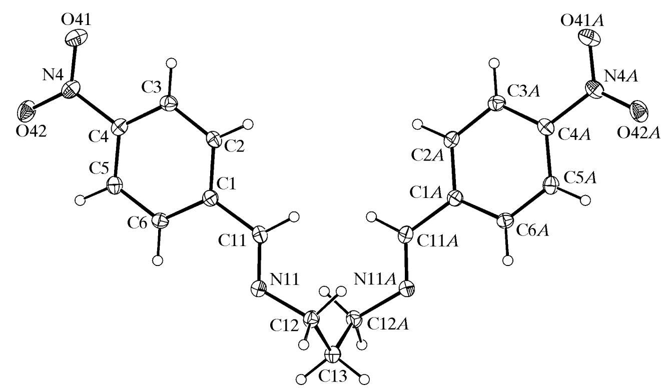

Figure 4
The molecule of (II), showing the atom-labelling scheme. Atoms labelled with the suffix '*A*' are at the symmetry position $(1 - x, y, \frac{1}{2} - z)$, and displacement ellipsoids are drawn at the 30% probability level.

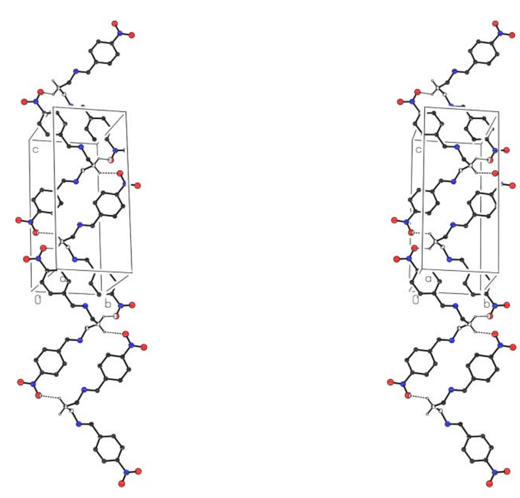

Figure 5
A stereoview of part of the crystal structure of (II), showing the formation of a [001] chain of spiro-fused $R_2^2(22)$ rings. For clarity, H atoms not involved in hydrogen bonding have been omitted.

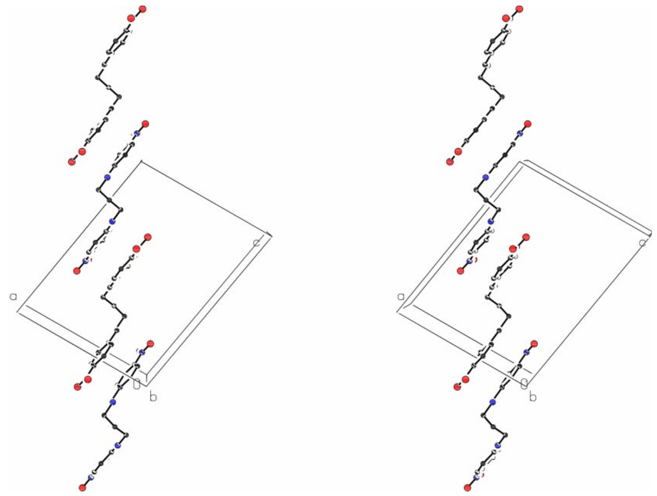

Figure 6
A stereoview of part of the crystal structure of (II), showing the formation of a [101] π-stacked chain, which links the hydrogen-bonded chains into (010) sheets. For clarity, all of the H atoms have been omitted.

interaction. The aryl rings at (x, y, z) and $(\frac{3}{2} - x, \frac{3}{2} - y, 1 - z)$, which lie in molecules across the axes $(\frac{1}{2}, y, \frac{1}{4})$ and $(1, -y, \frac{3}{4})$, respectively, are strictly parallel, with an interplanar separation of 3.366 (2) Å; the ring-centroid separation is 3.664 (2) Å, corresponding to a near-ideal centroid offset of 1.447 (2) Å. Propagation of this interaction by inversion and rotation then generates a π-stacked [101] chain (Fig. 6). Since each molecule in this chain is also a component of a hydrogen-bonded chain along [001], the overall supramolecular structure takes the form of a (010) sheet.

Experimental

The title compounds were prepared by the reactions of 4-nitrobenzaldehyde with the appropriate α,ω-diaminoalkane (2:1 molar ratio) in refluxing methanol; crystals suitable for single-crystal X-ray diffraction were grown from solutions in ethanol. For (I), m.p. 470–474 K; IR: 1640 (C$\equiv$N), 1520 and 1340 cm^{-1} (NO_2); for (II), m.p. 466–467 K (melts with decomposition to black liquid): IR: 1644 (C$\equiv$N), 1518 and 1341 cm^{-1} (NO_2).

Compound (I)

Crystal data

$C_{16}H_{14}N_4O_4$
M_r = 326.31
Monoclinic, $P2_1/n$
a = 9.1606 (5) Å
b = 7.2295 (4) Å
c = 11.5201 (6) Å
β = 97.515 (1)°
V = 756.38 (7) Å^3
Z = 2
D_x = 1.433 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2717 reflections
θ = 2.7–32.6°
μ = 0.11 mm^{-1}
T = 291 (2) K
Block, colourless
0.47 × 0.37 × 0.25 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.946, T_{max} = 0.974
7869 measured reflections
2717 independent reflections
2008 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 32.6°
$h = -13 \rightarrow 13$
$k = -10 \rightarrow 10$
$l = -13 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.158
S = 1.05
2717 reflections
109 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.095P)^2 + 0.0285P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected torsion angles (°) for (I).

C12^i—C12—N11—C11	118.31 (13)	N11—C11—C1—C2	177.91 (9)
C12—N11—C11—C1	−176.58 (8)	C3—C4—N4—O41	−5.86 (15)

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

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O41^{ii}	0.93	2.40	3.2166 (13)	146

Symmetry code: (ii) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$.

Compound (II)

Crystal data

$C_{17}H_{16}N_4O_4$
M_r = 340.34
Monoclinic, $C2/c$
a = 12.9412 (6) Å
b = 7.3062 (3) Å
c = 16.9061 (8) Å
β = 99.559 (2)°
V = 1576.29 (12) Å^3
Z = 4
D_x = 1.434 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1827 reflections
θ = 3.2–27.6°
μ = 0.11 mm^{-1}
T = 120 (2) K
Needle, orange
0.20 × 0.09 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.984, T_{max} = 0.996
8695 measured reflections
1827 independent reflections
1306 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 27.6°
$h = -16 \rightarrow 16$
$k = -9 \rightarrow 9$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.158
S = 1.06
1827 reflections
114 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0884P)^2 + 0.3187P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 3
Selected torsion angles (°) for (II).

C12^{iii}—C13—C12—N11	67.65 (11)	N11—C11—C1—C2	174.52 (17)
C13—C12—N11—C11	−121.50 (17)	C3—C4—N4—O41	2.4 (2)
C12—N11—C11—C1	179.33 (14)		

Symmetry code: (iii) $1 - x, y, \frac{1}{2} - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13A···O42^{iv}	0.99	2.54	3.267 (2)	130

Symmetry code: (iv) $x, 1 - y, z - \frac{1}{2}$.

For compound (I), the space group $P2_1/n$ was uniquely assigned from the systematic absences. For compound (II), the systematic absences permitted Cc and $C2/c$ 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 in (I) of 0.97 (CH_2) or 0.93 Å (all other H atoms) and in (II) of 0.99 (CH_2) or 0.95 Å (all other H atoms), and with U_{iso}(H) values of $1.2U_{eq}$(C).

For compound (I), data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*. For compound (II), data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*. For both compounds, program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

X-ray data for (I) were collected at the University of Aberdeen; the authors thank the University of Aberdeen for funding the purchase of the diffractometer. X-ray data for (II) were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1795). Services for accessing these data are described at the back of the journal.

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