Sheets of π-stacked centrosymmetric molecules in N,N′-bis(3-nitrobenzylidene)octane-1,8-diamine

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Key indicators

In molecules of the title compound, $C_{22}H_{26}N_4O_4$, which lie across centres of inversion, the central octane fragment adopts a nearly planar all-*trans* conformation. There are no hydrogen bonds in the crystal structure but the molecules are linked into sheets by a single π–π stacking interaction.

Comment

As part of our continuing studies of the supramolecular arrangements in imines, and especially in compounds of the type $O_2NC_6H_4CH{=}N{-}(R){-}N{=}CHC_6H_4NO_2$, where R = 1,2-*cyclo*-C_6H_{10} (Glidewell, Low, Skakle & Wardell, 2005; Glidewell, Low & Wardell, 2005) or $R = (CH_2)_n$ (Bomfim *et al.*, 2005), we now report the molecular and supramolecular structure of the title compound, (I).

(I)
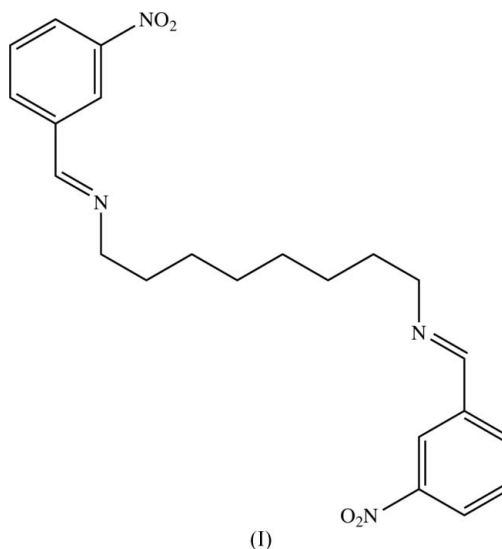
The molecules of (I) lie across centres of inversion in the space group $P2_1/c$, with the reference molecule selected as that lying across ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) (Fig. 1). The bond distances (Table 1) clearly show the presence of the double bond C11=N11, with typical skeletal bond angles at C11 and N11. The nitroaryl –CH=N–C fragment is almost planar, as is the eight-carbon fragment of the central spacer, as shown by the leading torsional angles (Table 1); however, the overall molecular conformation is very far from being planar, as shown by the torsion angles around the N11—C11 and C12—C13 bonds, where the non-H substituents are mutually anticlinal and synclinal respectively (Table 1 and Fig. 1).

The supramolecular aggregation is very simple; there are no hydrogen bonds of any kind, but a single aromatic π–π stacking interaction links the molecules into sheets. The aryl
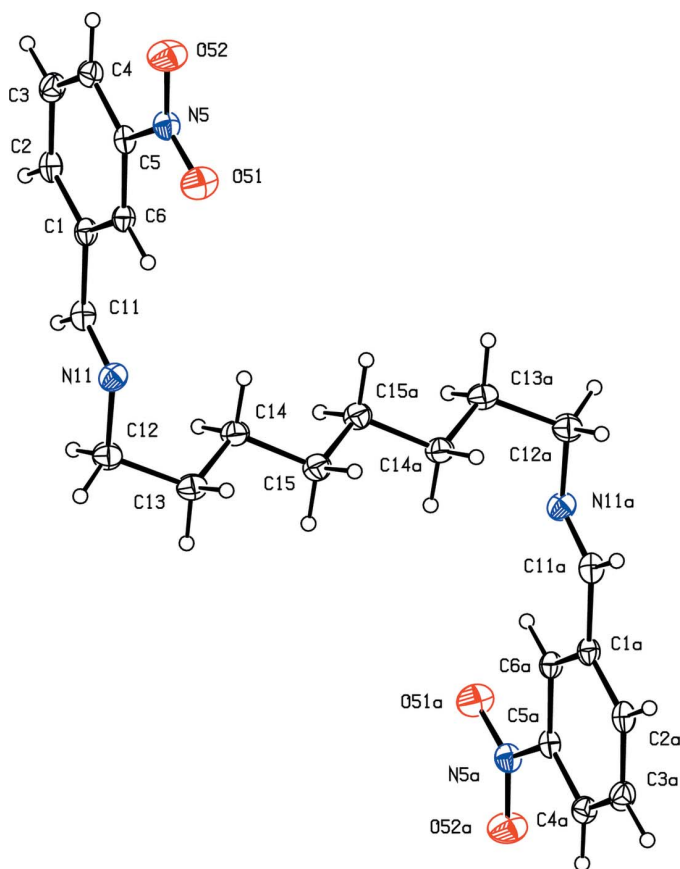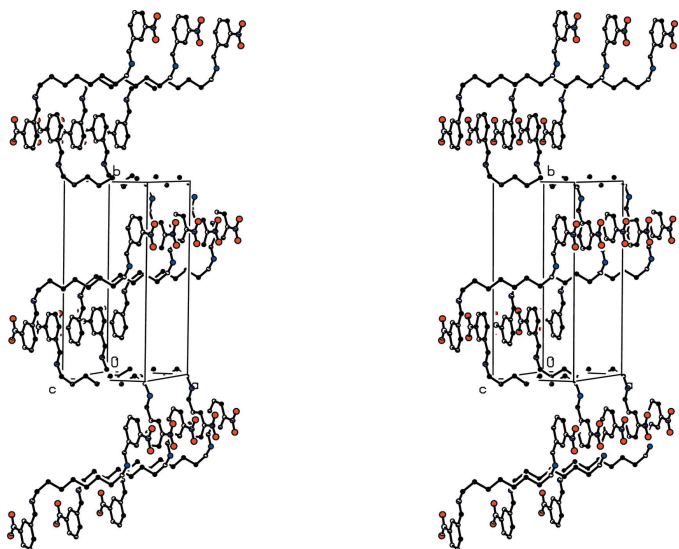
Figure 1
The molecule of compound (I), showing the atom-labelling scheme. The atoms marked 'a' are at the symmetry position $(1 - x, 1 - y, 1 - z)$ and displacement ellipsoids are drawn at the 30% probability level.

Figure 2
Stereoview of part of the crystal structure of compound (I), showing the formation of a π-stacked (100) sheet. For the sake of clarity, the H atoms have been omitted.

ring at (x, y, z), which is part of the molecule centred across $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, is almost parallel with the aryl rings at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$, which form parts of the molecules centred

across $(\frac{1}{2}, 0, 1)$ and $(\frac{1}{2}, 0, 0)$, respectively. The dihedral angle between adjacent rings is only 2.5 (2)°, with the ring-centroid separations both 3.762 (2) Å; the interplanar spacings are *ca* 3.39 Å and the ring-centroid offsets are *ca* 1.63 Å. Propagation of this single interaction by the space group symmetry then generates a (100) sheet in which each molecule is linked to four others (Fig. 2); there are, however, no direction-specific interactions between adjacent sheets.

Experimental

A solution of 3-nitrobenzaldehyde (0.4 mmol) and 1,8-diaminooctane (0.2 mmol) in methanol (20 ml) was heated under reflux for 1 h; the mixture was cooled and the solvent was removed under reduced pressure. The solid residue was recrystallized from 1,2-dichloroethane to yield crystals of compound (I) suitable for single-crystal X-ray diffraction (m.p. 359–361 K). IR (KBr): 3086, 2933–2832, 1646, 1610,1580, 1536, 1468, 1439, 1343, 1270, 1155, 1078, 1027, 971, 983, 931, 828, 805, 734, 684, 675, 629, 508 cm^{-1}.

Crystal data

$C_{22}H_{26}N_4O_4$	$D_x = 1.301$ Mg m^{-3}
$M_r = 410.47$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2407
$a = 8.1297$ (5) Å	reflections
$b = 19.2452$ (15) Å	$\theta = 3.2–27.6°$
$c = 7.4113$ (4) Å	$\mu = 0.09$ mm^{-1}
$\beta = 115.321$ (4)°	$T = 120$ (2) K
$V = 1048.15$ (12) Å^3	Plate, yellow
$Z = 2$	$0.35 \times 0.24 \times 0.06$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer	2407 independent reflections
φ and ω scans	1284 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.070$
(*SADABS*; Sheldrick, 2003)	$\theta_{max} = 27.6°$
$T_{min} = 0.978$, $T_{max} = 0.995$	$h = -10 \rightarrow 10$
11275 measured reflections	$k = -24 \rightarrow 24$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.058$	$w = 1/[\sigma^2(F_o^2) + (0.0804P)^2]$
$wR(F^2) = 0.158$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
2407 reflections	$\Delta\rho_{max} = 0.30$ e Å^{-3}
136 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C11	1.476 (3)	N11—C12	1.455 (2)
C11—N11	1.268 (2)		
C1—C11—N11	122.55 (18)	C11—N11—C12	117.28 (17)
C2—C1—C11—N11	−178.68 (19)	C12—C13—C14—C15	−175.69 (16)
C1—C11—N11—C12	−179.34 (18)	C13—C14—C15—C15^i	176.9 (2)
C11—N11—C12—C13	113.8 (2)	C4—C5—N5—O51	−177.60 (19)
N11—C12—C13—C14	−64.9 (2)		

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

All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 (aromatic) or 0.99 Å (aliphatic), and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *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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supporting information

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Crystal data

$C_{22}H_{26}N_4O_4$	$F(000) = 436$
$M_r = 410.47$	$D_x = 1.301$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2407 reflections
$a = 8.1297$ (5) Å	$\theta = 3.2$–27.6°
$b = 19.2452$ (15) Å	$\mu = 0.09$ mm^{-1}
$c = 7.4113$ (4) Å	$T = 120$ K
$\beta = 115.321$ (4)°	Plate, yellow
$V = 1048.15$ (12) Å^3	$0.35 \times 0.24 \times 0.06$ mm
$Z = 2$	

Data collection

Bruker–Nonius KappaCCD diffractometer	$T_{min} = 0.978$, $T_{max} = 0.995$
Radiation source: Bruker–Nonius FR91 rotating anode	11275 measured reflections
	2407 independent reflections
Graphite monochromator	1284 reflections with $I > 2\sigma(I)$
Detector resolution: 9.091 pixels mm^{-1}	$R_{int} = 0.070$
φ and ω scans	$\theta_{max} = 27.6°$, $\theta_{min} = 3.2°$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$h = -10 \rightarrow 10$
	$k = -24 \rightarrow 24$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.058$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.158$	
$S = 1.01$	H-atom parameters constrained
2407 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0804P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
136 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.30$ e Å^{-3}
	$\Delta\rho_{min} = -0.30$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O51	−0.4726 (2)	0.30584 (9)	0.2452 (2)	0.0497 (5)

O52	−0.4979 (2)	0.19476 (9)	0.2222 (2)	0.0554 (5)
N5	−0.4146 (2)	0.24756 (10)	0.3007 (2)	0.0337 (5)
N11	0.0789 (2)	0.41578 (9)	0.7670 (2)	0.0351 (5)
C1	0.0339 (2)	0.29242 (11)	0.7145 (3)	0.0282 (5)
C2	0.1051 (3)	0.22653 (11)	0.7750 (3)	0.0320 (5)
C3	0.0066 (3)	0.16718 (12)	0.6830 (3)	0.0364 (6)
C4	−0.1647 (3)	0.17372 (11)	0.5267 (3)	0.0333 (5)
C5	−0.2334 (2)	0.23980 (10)	0.4686 (3)	0.0272 (5)
C6	−0.1394 (2)	0.29929 (10)	0.5582 (3)	0.0277 (5)
C11	0.1398 (3)	0.35460 (11)	0.8148 (3)	0.0329 (5)
C12	0.1973 (3)	0.47278 (11)	0.8757 (3)	0.0385 (6)
C13	0.2532 (3)	0.51566 (11)	0.7389 (3)	0.0367 (6)
C14	0.3695 (3)	0.47560 (11)	0.6595 (3)	0.0348 (6)
C15	0.4381 (3)	0.51947 (11)	0.5348 (3)	0.0365 (6)
H2	0.2232	0.2217	0.8810	0.038*
H3	0.0567	0.1224	0.7275	0.044*
H4	−0.2332	0.1339	0.4612	0.040*
H6	−0.1914	0.3439	0.5146	0.033*
H11	0.2583	0.3486	0.9193	0.039*
H12A	0.3073	0.4539	0.9870	0.046*
H12B	0.1331	0.5029	0.9332	0.046*
H13A	0.1423	0.5324	0.6247	0.044*
H13B	0.3219	0.5569	0.8129	0.044*
H14A	0.2972	0.4364	0.5770	0.042*
H14B	0.4754	0.4558	0.7737	0.042*
H15A	0.3322	0.5372	0.4165	0.044*
H15B	0.5046	0.5601	0.6147	0.044*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O51	0.0358 (9)	0.0453 (11)	0.0507 (9)	0.0044 (8)	0.0019 (7)	0.0050 (8)
O52	0.0416 (9)	0.0479 (11)	0.0538 (10)	−0.0133 (8)	−0.0013 (8)	−0.0069 (8)
N5	0.0295 (9)	0.0395 (12)	0.0306 (10)	−0.0026 (9)	0.0114 (8)	−0.0007 (9)
N11	0.0303 (9)	0.0348 (12)	0.0375 (10)	−0.0032 (8)	0.0119 (8)	0.0019 (8)
C1	0.0252 (10)	0.0350 (13)	0.0259 (10)	−0.0019 (9)	0.0125 (9)	0.0017 (9)
C2	0.0261 (10)	0.0446 (14)	0.0254 (10)	0.0023 (10)	0.0109 (9)	0.0054 (10)
C3	0.0413 (12)	0.0348 (13)	0.0364 (12)	0.0087 (11)	0.0198 (11)	0.0076 (10)
C4	0.0362 (12)	0.0346 (13)	0.0319 (11)	−0.0037 (10)	0.0173 (10)	−0.0004 (9)
C5	0.0240 (10)	0.0363 (13)	0.0214 (10)	0.0001 (9)	0.0098 (9)	0.0025 (9)
C6	0.0269 (10)	0.0317 (12)	0.0272 (10)	−0.0008 (9)	0.0140 (9)	0.0020 (9)
C11	0.0255 (10)	0.0433 (14)	0.0287 (11)	−0.0028 (10)	0.0105 (9)	0.0025 (10)
C12	0.0366 (11)	0.0388 (14)	0.0379 (12)	−0.0059 (10)	0.0139 (10)	−0.0035 (10)
C13	0.0344 (11)	0.0322 (13)	0.0407 (12)	−0.0035 (9)	0.0135 (10)	−0.0029 (10)
C14	0.0374 (11)	0.0291 (12)	0.0368 (11)	−0.0028 (9)	0.0149 (10)	−0.0023 (9)
C15	0.0393 (12)	0.0323 (13)	0.0363 (12)	0.0004 (10)	0.0146 (10)	0.0007 (9)

Geometric parameters (Å, º)

C1—C2	1.386 (3)	C11—H11	0.95
C1—C6	1.396 (3)	N11—C12	1.455 (2)
C1—C11	1.476 (3)	C12—C13	1.520 (3)
C2—C3	1.394 (3)	C12—H12A	0.99
C2—H2	0.95	C12—H12B	0.99
C3—C4	1.385 (3)	C13—C14	1.520 (3)
C3—H3	0.95	C13—H13A	0.99
C4—C5	1.382 (3)	C13—H13B	0.99
C4—H4	0.95	C14—C15	1.523 (3)
C5—C6	1.379 (3)	C14—H14A	0.99
C5—N5	1.474 (2)	C14—H14B	0.99
C6—H6	0.95	C15—C15^i	1.511 (4)
N5—O51	1.218 (2)	C15—H15A	0.99
N5—O52	1.222 (2)	C15—H15B	0.99
C11—N11	1.268 (2)		
C2—C1—C6	119.24 (18)	N11—C12—C13	110.84 (17)
C2—C1—C11	120.40 (17)	N11—C12—H12A	109.5
C6—C1—C11	120.36 (18)	C13—C12—H12A	109.5
C1—C2—C3	121.21 (17)	N11—C12—H12B	109.5
C1—C2—H2	119.4	C13—C12—H12B	109.5
C3—C2—H2	119.4	H12A—C12—H12B	108.1
C4—C3—C2	119.8 (2)	C14—C13—C12	113.33 (18)
C4—C3—H3	120.1	C14—C13—H13A	108.9
C2—C3—H3	120.1	C12—C13—H13A	108.9
C5—C4—C3	118.18 (19)	C14—C13—H13B	108.9
C5—C4—H4	120.9	C12—C13—H13B	108.9
C3—C4—H4	120.9	H13A—C13—H13B	107.7
C6—C5—C4	123.19 (17)	C13—C14—C15	113.80 (18)
C6—C5—N5	118.05 (18)	C13—C14—H14A	108.8
C4—C5—N5	118.76 (17)	C15—C14—H14A	108.8
C5—C6—C1	118.40 (18)	C13—C14—H14B	108.8
C5—C6—H6	120.8	C15—C14—H14B	108.8
C1—C6—H6	120.8	H14A—C14—H14B	107.7
O51—N5—O52	123.31 (16)	C15^i—C15—C14	113.7 (2)
O51—N5—C5	118.76 (17)	C15^i—C15—H15A	108.8
O52—N5—C5	117.91 (17)	C14—C15—H15A	108.8
C1—C11—N11	122.55 (18)	C15^i—C15—H15B	108.8
N11—C11—H11	118.7	C14—C15—H15B	108.8
C1—C11—H11	118.7	H15A—C15—H15B	107.7
C11—N11—C12	117.28 (17)		
C6—C1—C2—C3	−0.2 (3)	C6—C1—C11—N11	1.0 (3)
C11—C1—C2—C3	179.51 (18)	C1—C11—N11—C12	−179.34 (18)
C1—C2—C3—C4	0.8 (3)	C11—N11—C12—C13	113.8 (2)
C2—C3—C4—C5	−0.8 (3)	N11—C12—C13—C14	−64.9 (2)

C3—C4—C5—C6	0.2 (3)	C12—C13—C14—C15	−175.69 (16)
C3—C4—C5—N5	179.22 (17)	C13—C14—C15—C15^i	176.9 (2)
C4—C5—C6—C1	0.4 (3)	C6—C5—N5—O51	1.4 (3)
N5—C5—C6—C1	−178.64 (16)	C4—C5—N5—O51	−177.60 (19)
C2—C1—C6—C5	−0.4 (3)	C6—C5—N5—O52	−179.66 (18)
C11—C1—C6—C5	179.92 (18)	C4—C5—N5—O52	1.3 (3)
C2—C1—C11—N11	−178.68 (19)		

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.