

Tris[4-(4-nitrophenyl)-3-aza-3-butenyl]amine: π -stacked chains of hydrogen-bonded $R_2^2(26)$ dimers

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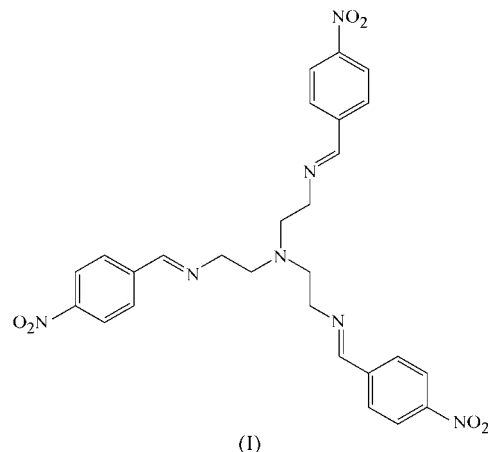
In the title compound {alternative name: *N'*-(4-nitrobenzylidene)-*N,N*-bis[2-(4-nitrobenzylideneamino)ethyl]-1,2-ethanediamine}, $C_{27}H_{27}N_7O_6$, the three independent $NCH_2CH_2N=CHC_6H_4NO_2$ fragments all exhibit different conformations, resulting from the different direction-specific intra- and intermolecular interactions experienced. The molecules are linked by a single $C-H\cdots O$ hydrogen bond into centrosymmetric $R_2^2(26)$ dimers, which are linked by π - π stacking interactions into [111] chains and, more weakly, into (011) sheets.

Comment

In a continuation of our studies on the molecular and supramolecular structures in nitrophenylimines, we now report our findings on the title compound, (I). In the molecules of (I), the three crystallographically independent $NCH_2CH_2N=CHC_6H_4NO_2$ fragments all adopt different conformations, as shown by the leading torsion angles (Table 1). In particular, the $N10-Cn9$ and $Cn8-Nn7$ bonds ($n = 1-3$) are anti-periplanar when $n = 1$, but synclinal when $n = 2$ and $n = 3$, while the $Cn9-Cn8$ and $Nn7-Nn7$ bonds are anticlinal when $n = 1$ and $n = 2$, but synperiplanar when $n = 3$. In addition, the dihedral angles between the $Cn1-Cn6$ aryl rings and the corresponding nitro groups are $15.5(2)^\circ$, $7.8(2)^\circ$ and $0.8(2)^\circ$ for $n = 1-3$, respectively.

The central atom, N10, has a pyramidal configuration (Table 1 and Fig. 1), as expected, and there is a single intramolecular $C-H\cdots N$ hydrogen bond (Table 2), with amine atom C37 as a donor and atom N10 as an acceptor in an *S*(6) motif (Bernstein *et al.*, 1995); this interaction probably has a significant influence on the conformation of the N10/C39/C38/N37/C37 fragment. In addition, the C21-C26 and C31-C36

aryl rings within the molecule make a dihedral angle of only $2.0(2)^\circ$; the interplanar spacing is *ca.* 3.64 Å and the ring-centroid separation is 3.931(2) Å, corresponding to a ring offset of *ca.* 1.48 Å. Despite the fairly large interplanar spacing, this weak intramolecular interaction may have some influence on the overall conformation.



The molecules of (I) are linked weakly into centrosymmetric dimers by a single $C-H\cdots O$ hydrogen bond (Table 2) and a single π - π stacking interaction links these dimers into a chain. Methylene atom C29 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* atom H29B, to nitro atom O32 in the molecule at $(1-x, 1-y, 1-z)$, so forming a centrosymmetric $R_2^2(26)$ ring centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 2). The C11-C16 aryl rings in the molecules at (x, y, z) and $(-x, -y, -z)$ are strictly parallel, with an interplanar spacing of $3.428(2)^\circ$; the

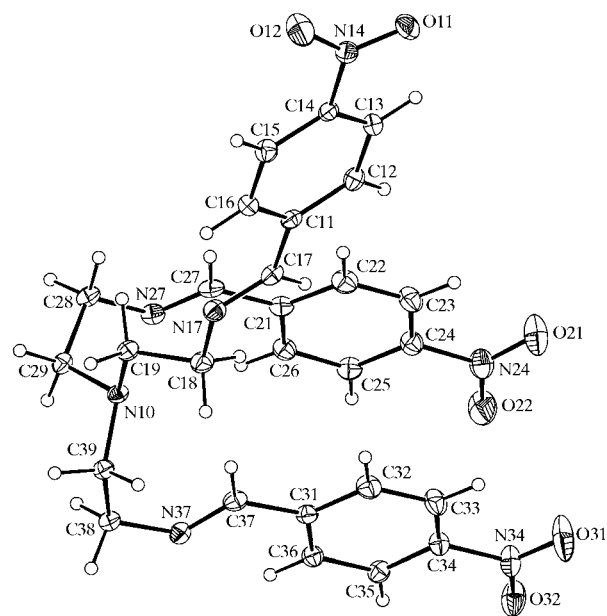
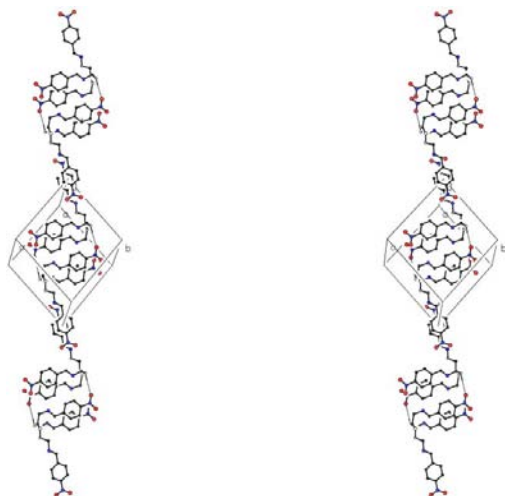


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.


Figure 2

A stereoview of part of the crystal structure of (I), showing the formation of a π -stacked [111] chain of hydrogen-bonded $R_2^2(26)$ dimers. For clarity, H atoms not involved in the motif shown have been omitted.

ring-centroid separation is 3.549 (2) Å, corresponding to a ring offset of 0.919 (2) Å. Propagation by inversion of these two interactions then generates a chain running parallel to the [111] direction (Fig. 2).

Just one chain passes through each unit cell; the only possible direction-specific interaction between adjacent chains is a second π - π stacking interaction, this time intermolecular, between the C21–C26 and C31–C36 rings in the molecules at (x, y, z) and $(1 \pm x, y, z)$. Again, the dihedral angle between the rings is only 2.0 (2)°, with an interplanar spacing now of *ca* 3.46 Å; the ring-centroid separation is 3.924 (2) Å, corresponding to a ring offset of *ca* 1.85 Å, so this interaction is possibly weaker than the intramolecular stacking interaction. The effect of this interaction is to link [111] chains into (011) sheets.

Thus, the three independent $\text{NCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{NO}_2$ fragments all participate in a different range of direction-specific non-covalent interactions. When $n = 1$, the aryl rings are involved in intermolecular π - π stacking, when $n = 3$, there is an intramolecular $\text{C}-\text{H}\cdots\text{N}$ hydrogen bond, while the two fragments with $n = 2$ and 3 participate not only in intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding but also in both intra- and intermolecular stacking interactions. Accordingly, it would not be expected that these three limbs of the molecule should adopt similar conformations.

Experimental

A solution of 4-nitrobenzaldehyde (0.9 g, 6 mmol) and tris(2-aminoethyl)amine (0.29 g, 2 mmol) in methanol (25 ml) was heated under reflux for 2 h. The solution was filtered hot, the filtrate was evaporated and the solid residue was recrystallized from ethanol to yield compound (I) (m.p. 416–418 K; darkens at 410–411 K). IR: 1642, 1602, 1517, 1346 cm^{-1} . Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in 1,2-dichloroethane.

Crystal data

$\text{C}_{27}\text{H}_{27}\text{N}_7\text{O}_6$
 $M_r = 545.56$
 Triclinic, $P\bar{1}$
 $a = 7.8020$ (2) Å
 $b = 12.5233$ (5) Å
 $c = 13.8920$ (6) Å
 $\alpha = 83.5872$ (18)°
 $\beta = 89.022$ (2)°
 $\gamma = 72.611$ (2)°
 $V = 1287.01$ (8) Å³

$Z = 2$
 $D_x = 1.408$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5891 reflections
 $\theta = 3.1$ – 27.6 °
 $\mu = 0.10$ mm⁻¹
 $T = 120$ (2) K
 Plate, orange
 $0.20 \times 0.09 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.977$, $T_{\max} = 0.996$
 26 427 measured reflections
 5891 independent reflections

3714 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.08$
 $\theta_{\max} = 27.6$ °
 $h = -10 \rightarrow 9$
 $k = -16 \rightarrow 16$
 $l = -18 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.124$
 $S = 1.04$
 5891 reflections
 362 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.0732P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.24$ e Å⁻³
 $\Delta\rho_{\min} = -0.22$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0089 (18)

Table 1

Selected geometric parameters (°).

C19–N10–C29	111.74 (11)	C39–N10–C19	111.24 (12)
C29–N10–C39	112.10 (12)		
C19–N10–C29–C28	74.96 (17)	C18–N17–C17–C11	178.49 (13)
C29–N10–C39–C38	67.46 (17)	C28–N27–C27–C21	175.43 (14)
C39–N10–C19–C18	76.85 (17)	C38–N37–C37–C31	178.49 (14)
N10–C19–C18–N17	171.04 (13)	N17–C17–C11–C12	–175.56 (15)
N10–C29–C28–N27	55.99 (18)	N27–C27–C21–C22	–174.65 (16)
N10–C39–C38–N37	66.70 (19)	N37–C37–C31–C32	–170.11 (16)
C19–C18–N17–C17	–128.34 (16)	C13–C14–N14–O11	–15.3 (2)
C29–C28–N27–C27	–108.10 (16)	C23–C24–N24–O21	–8.4 (3)
C39–C38–N37–C37	–1.3 (2)	C33–C34–N34–O31	0.4 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
C29–H29B \cdots O32 ⁱ	0.99	2.60	3.540 (2)	159
C37–H37 \cdots N10	0.95	2.53	3.138 (2)	122

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

Crystals of compound (I) are triclinic; space group $P\bar{1}$ was selected and confirmed by the successful structure analysis. All H atoms were located from difference maps and subsequently treated as riding atoms, with $\text{C}-\text{H}$ distances of 0.95 (aromatic and aliphatic CH) or 0.99 Å (CH_2) and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$.

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1801). Services for accessing these data are described at the back of the journal.

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