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1-Benzyl-4-(4-nitrophenyl)-2,3-dihydro-1*H*-1,5-benzodiazepine: a three-dimensional framework structure generated by two C—H···O hydrogen bonds and one C—H···π(arene) hydrogen bond

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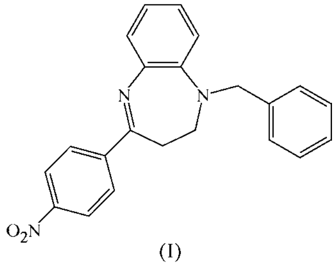
In the title compound, $C_{22}H_{19}N_3O_2$, the seven-membered ring adopts a boat conformation. The molecules are linked by a combination of two C—H···O hydrogen bonds and one C—H···π(arene) hydrogen bond into a complex three-dimensional framework structure; each individual hydrogen bond generates a one-dimensional substructure, and pairwise combinations of two hydrogen bonds generate a further set of three one-dimensional substructures.

Comment

Benzodiazepines are an important class of psychotherapeutic compounds. We describe here the molecular and supramolecular structures of a benzodiazepine resulting from the cyclocondensation of a substituted 1,2-diaminobenzene with the Mannich adduct precursor of a vinyl ketone.



(I)

The seven-membered ring in the title compound, (I), adopts a boat conformation, with an approximate local mirror plane through atom C3 and the mid-point of the C5*A*—C9*A* bond (Table 1 and Fig. 1); it is of interest that atoms N1 and N5 are not coplanar with the adjacent aryl ring, as shown both by the N5—C5*A*—C9*A*—N1 torsion angle (Table 1) and by the deviations of the two N atoms, *viz*. 0.242 (5) Å for N1 and −0.092 (2) Å for N5, from the plane of the aryl ring. Although the configuration of atom N1 is pyramidal, neither this atom nor atom N5 acts as an acceptor of hydrogen bonds. The remaining bond lengths and angles present no unusual values.

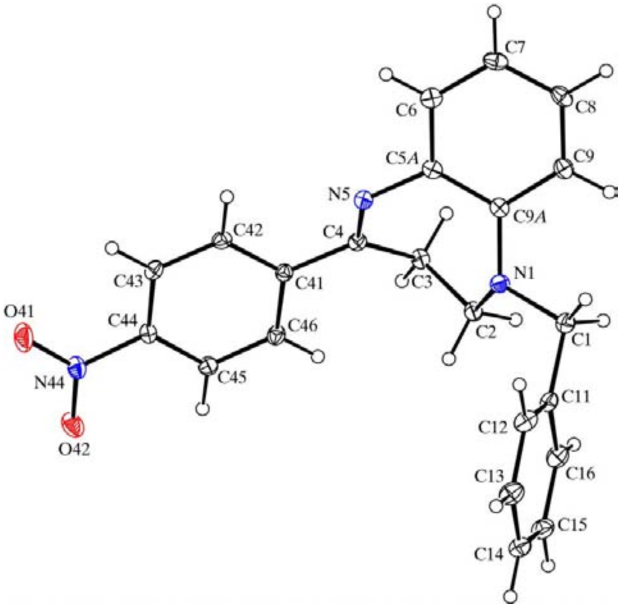


Figure 1
A molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

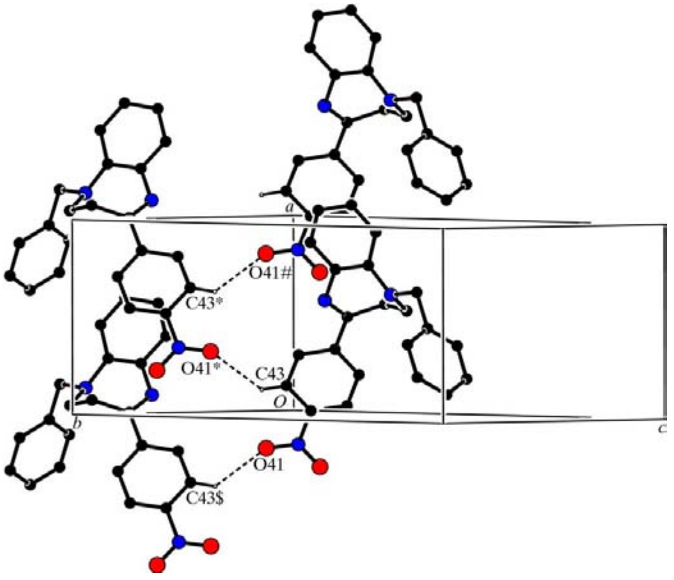


Figure 2
Part of the crystal structure of (I), showing the formation of a *C*(5) chain along [100]. For clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*), a hash (#) or a dollar sign ($) are at the symmetry positions $(\frac{1}{2}+x, \frac{1}{2}-y, -z)$, $(1+x, y, z)$ and $(-\frac{1}{2}+x, \frac{1}{2}-y, -z)$, respectively.

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The molecules of (I) are linked into a three-dimensional framework of some complexity by a combination of two C—H$\cdots$O hydrogen bonds and one C—H$\cdots\pi$(arene) hydrogen bond (Table 2). It is convenient to consider firstly the substructures generated by each of these three hydrogen bonds acting individually, and then the substructures generated by each of the three pairwise combinations of the hydrogen bonds.

In the shorter of the two C—H$\cdots$O hydrogen bonds, aryl atom C43 in the molecule at (x, y, z) acts as a hydrogen-bond donor to nitro atom O41 in the molecule at $(\frac{1}{2} + x, \frac{1}{2} - y, -z)$, so producing a $C(5)$ chain running parallel to the [100] direction and generated by the 2_1 screw axis along $(x, \frac{1}{4}, 0)$ (Fig. 2). In the second C—H$\cdots$O hydrogen bond, aryl atom C14 in the molecule at (x, y, z) acts as a hydrogen-bond donor to nitro atom O42 in the molecule at $(-\frac{1}{2} - x, -y, \frac{1}{2} + z)$, so producing a $C(16)$ chain running parallel to the [001] direction and generated by the 2_1 screw axis along $(-\frac{1}{4}, 0, z)$ (Fig. 3). The third hydrogen bond is of the C—H$\cdots\pi$(arene) type, and aryl atom C46 in the molecule at (x, y, z) acts as a donor to the C5*A*/C6–C9/C9*A* aryl ring in the molecule at $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, so forming a chain running parallel to the [010] direction and generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{1}{4})$ (Fig. 4). Hence, each of the three individual hydrogen bonds generates a chain, and these chains run in mutually orthogonal directions.

In addition, each pairwise combination of hydrogen bonds generates a further chain motif, in a direction orthogonal to the chain directions generated by each of the two components acting individually. Thus, for example, atom C43 in the molecule at $(-\frac{1}{2} - x, -y, \frac{1}{2} + z)$ acts as a donor to atom O41 at $(-1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, while atom C14 at $(-1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ acts as a donor to atom O42 at $(-\frac{1}{2} + x, -\frac{1}{2} - y, -z)$; atom C43 at $(-\frac{1}{2} + x, -\frac{1}{2} - y, -z)$ in turn acts as a donor to atom O41 at $(x, -1 + y, z)$, so completing a $C_2^2(21)$ chain running parallel to the [010] direction (Fig. 5). By contrast, the two individual hydrogen bonds generate homogeneous $C(5)$ and $C(16)$ chains along [100] and [001], respectively (Figs. 2 and 3). In a similar way, the two hydrogen bonds involving C14 and C46 as donors (Figs. 3 and 4) combine to form a chain

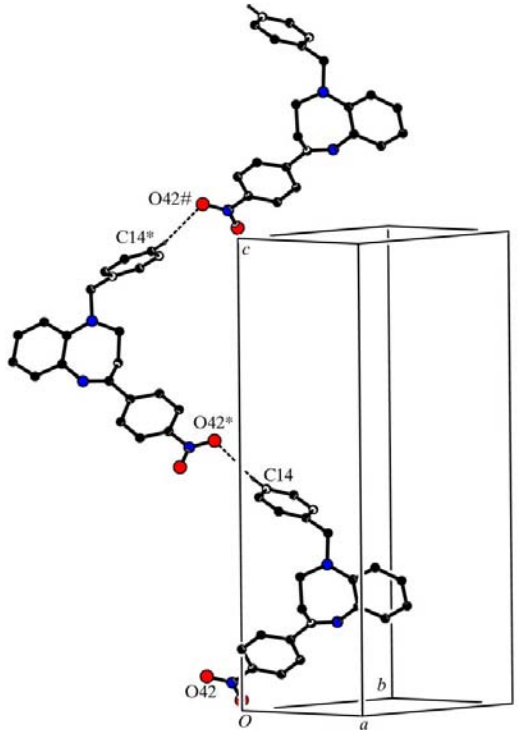

Figure 3
Part of the crystal structure of (I), showing the formation of a $C(16)$ chain along [001]. For clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-\frac{1}{2} - x, -y, \frac{1}{2} + z)$ and $(x, y, 1 + z)$, respectively.

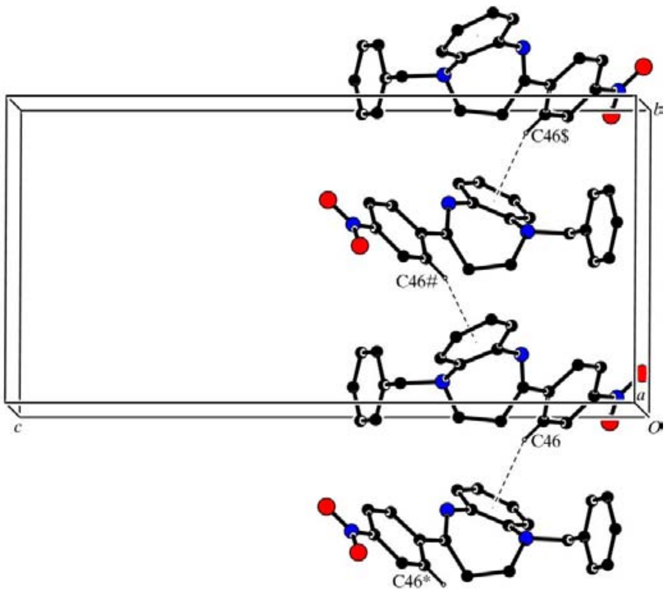

Figure 4
Part of the crystal structure of (I), showing the formation of a chain along [010] generated by the C—H$\cdots\pi$(arene) hydrogen bond. For clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*), a hash (#) or a dollar sign ($) are at the symmetry positions $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$ and $(x, 1 + y, z)$, respectively.

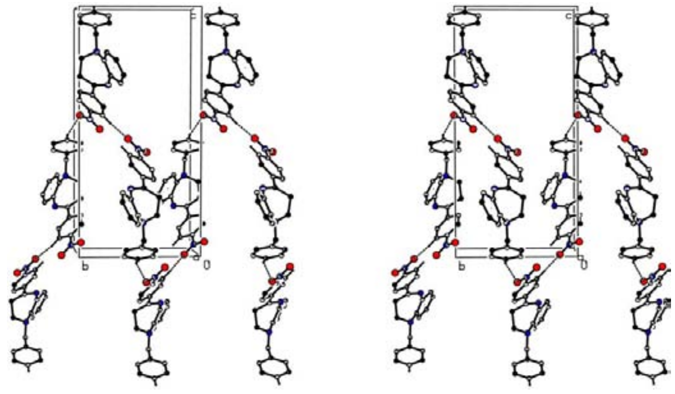

Figure 5
A stereoview of part of the crystal structure of (I), showing the formation of a $C_2^2(21)$ chain along [010] generated by the combination of the two C—H$\cdots$O hydrogen bonds. For clarity, H atoms not involved in the motif shown have been omitted.

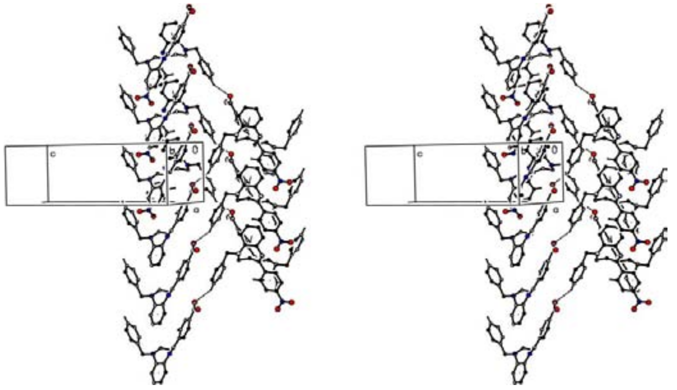

Figure 6
A stereoview of part of the crystal structure of (I), showing the formation of a triple helix along [100] generated by the combination of one C—H···O hydrogen bond and one C—H···π(arene) hydrogen bond. For clarity, H atoms not involved in the motif shown have been omitted.

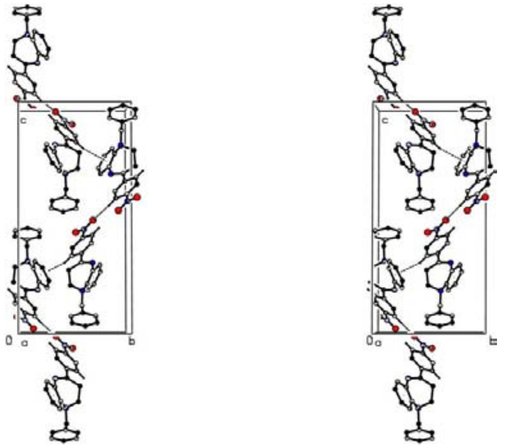

Figure 7
A stereoview of part of the crystal structure of (I), showing the formation of a chain along [001] generated by the combination of one C—H···O hydrogen bond and one C—H···π(arene) hydrogen bond. For clarity, H atoms not involved in the motif shown have been omitted.

along [100], whose repeat unit spans three unit cells and hence which generates a triple-helical substructure (Fig. 6); the bonds involving atoms C43 and C46 as donors (Figs. 2 and 4) combine to form a chain along [001] (Fig. 7). The combination of all three hydrogen bonds, and all of the resulting one-dimensional substructures, then generates a single but rather elaborate three-dimensional framework.

Experimental

A solution in ethanol (50 ml) of *N*-benzyl-*o*-phenylenediamine (0.5 mmol), 2-(dimethylamino)ethyl 4-nitrophenyl ketone hydrochloride (0.5 mmol) and glacial acetic acid (1 ml) was heated under reflux for 12 h. The solvent was then removed under reduced pressure and the resulting solid residue was purified by column chromatography on silica using hexane/ethyl acetate (4:1 *v*/*v*) as eluant (yield 53%, m.p. 392 K). MS (70 eV) *m*/*z* (%): 357 (63, M^+), 266 (35, $[M - \mathrm{PhCH_2}]^+$), 119 (56), 91 (100, $[\mathrm{C_7H_7}]^+$). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in ethanol.

Crystal data

$\mathrm{C_{22}H_{19}N_3O_2}$
$M_r = 357.40$
Orthorhombic, $P2_12_12_1$
$a = 7.3810$ (2) Å
$b = 10.8016$ (3) Å
$c = 22.1319$ (5) Å
$V = 1764.50$ (8) Å^3
$Z = 4$
$D_x = 1.345$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 2314 reflections
$\theta = 2.9$–$27.5°$
$\mu = 0.09$ mm^{-1}
$T = 120$ (2) K
Block, red
0.38 × 0.36 × 0.34 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.963$, $T_{\max} = 0.971$
12 216 measured reflections
2314 independent reflections
2127 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -28 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.107$
$S = 1.16$
2314 reflections
245 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.1595P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.097 (7)

Table 1
Selected torsion angles (°).

N1—C2—C3—C4	−55.9 (2)	N5—C5*A*—C9*A*—N1	−9.1 (3)
C2—C3—C4—N5	73.7 (2)	C5*A*—C9*A*—N1—C2	66.3 (2)
C3—C4—N5—C5*A*	−0.8 (2)	C9*A*—N1—C2—C3	−24.8 (2)
C4—N5—C5*A*—C9*A*	−41.8 (2)	C43—C44—N44—O41	2.6 (3)

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

Cg is the centroid of the C5*A*/C6–C9/C9*A* benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···O42$^{\rm i}$	0.95	2.55	3.378 (3)	146
C43—H43···O41$^{\rm ii}$	0.95	2.42	3.153 (3)	134
C46—H46···*Cg*$^{\rm iii}$	0.95	2.74	3.578 (2)	147

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

The space group $P2_12_12_1$ was uniquely assigned from the systematic absences. All H atoms were located from difference maps in fully ordered sites; these atoms were then treated as riding, with C—H distances of 0.95 (aromatic) or 0.99 Å (CH$_2$), and with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C). In the absence of significant anomalous scattering, the Flack (1983) parameter was indeterminate (Flack & Bernardinelli, 2000). Accordingly, the Friedel equivalent reflections were merged prior to the final refinements.

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: SK1842). Services for accessing these data are described at the back of the journal.

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