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Key indicators

Single-crystal X-ray study
T = 160 K
Mean σ(C–C) = 0.004 Å
R factor = 0.036
wR factor = 0.096
Data-to-parameter ratio = 6.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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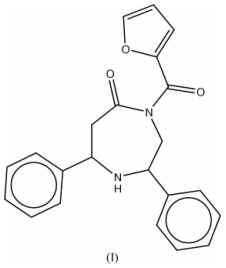
In the title compound, $C_{22}H_{20}N_2O_3$, the phenyl substituents adopt equatorial orientations. The seven-membered heterocyclic ring adopts a distorted chair conformation. In the solid state, the symmetry-related molecules are linked by intermolecular C—H···O hydrogen bonds to form a supramolecular aggregation.

Comment

A wide range of diazepines have been identified as potential drugs for various diseases (Hamor & Martin, 1984). Most of them contain phenyl rings fused to the diazepine ring at the 2,3 and/or 6,7 positions. The fusion of the aromatic phenyl rings makes the boat form of the diazepines more stable. We are interested in the stereochemical effect of substituting, rather than fusing, the phenyl rings at the 2 and 7 positions of the diazepine ring.



(I)

Fig. 1 shows a perspective view of the title molecule, (I), with the atom numbering. The bond lengths and angles in (I) are comparable with those reported for related structures (Priya *et al.*, 1992; Ravikumar *et al.*, 1994). The sum of the three angles C7—N1—C2, C7—N1—H1 and C2—N1—H1 is 331° and the displacement of N1 from the plane defined by the atoms C7, N1, C2 and H1 is 0.295 (10) Å, showing essentially pyramidal geometry at N1. The seven-membered ring in nitrosodiazepinone (Priya *et al.*, 1992) has been reported to adopt the boat conformation, while the title compound adopts a distorted chair conformation. The puckering parameters (Cremer & Pople, 1975) are Q = 0.805 (3) Å, q_2 = 0.418 (3) Å, q_3 = 0.687 (3) Å, φ_2 = 165.9 (4)° and φ_3 = 353.3 (2)° for the atom sequence N1—C2—C3—N4—C5—C6—C7. In (I), the phenyl substituents are in equatorial positions. The phenyl rings are inclined at an angle of 87.71 (9)° to each other. The dihedral angle between the mean planes of the five-membered and diazepine rings is 54.26 (8)°.

Surprisingly, it is observed that the N—H group does not form a hydrogen bond in the title compound. The structure of (I) is stabilized by a network of weak intermolecular C—

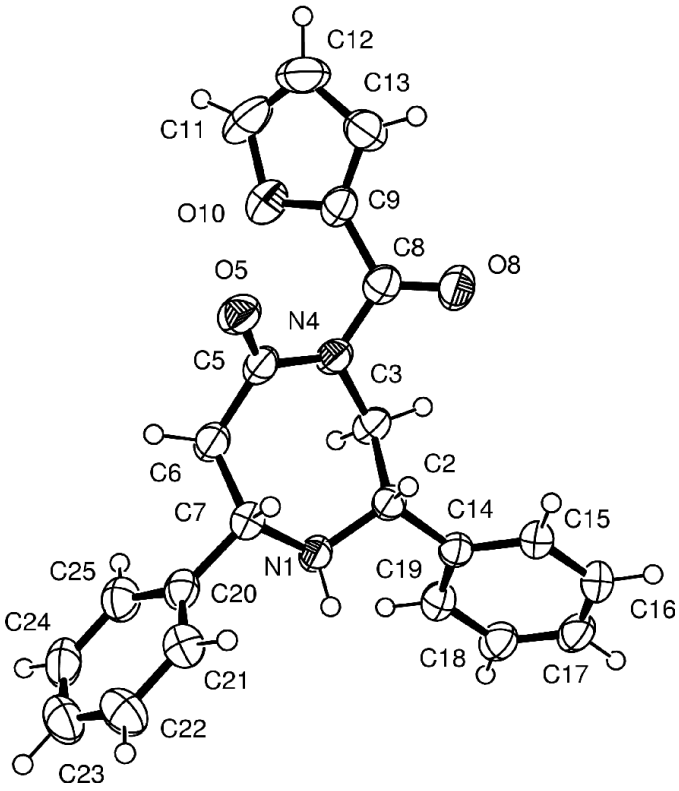


Figure 1
View of the asymmetric unit of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary radii.

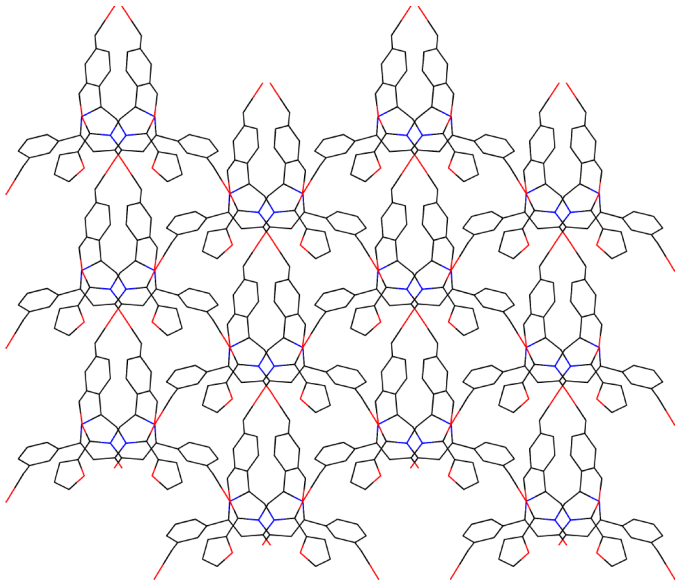


Figure 2
Part of the crystal structure, showing the supramolecular aggregation through weak C—H···O intermolecular interactions.

H···O interactions (Table 2). Carbonyl atom O8 and its symmetry-related equivalent are involved in two different intermolecular C—H···O interactions, one each coming from atoms C19 and C24 in different neighbouring molecules. These two form a continuous chain and have graph set motifs of $C(8)$ and $C(10)$ running parallel to the c and b axes, respectively. The carbonyl atom O5 is involved in a C—H···O intermolecular interaction with atom C17, forming a graph-set motif of $C(10)$ (Bernstein *et al.*, 1995) parallel to the c axis. All these interactions are responsible for the formation of a supramolecular aggregation (Fig. 2).

Four types of intermolecular C—H···π interactions are detected in the structure of (I) (Table 2). Atoms C15 (*via* H15) and C22 (*via* H22) act as donors for weak intermolecular C—H···π interactions. Both interactions are with the centroid, *Cg*2, of the phenyl ring substituted at C2 of the diazepine moiety in the molecules at $(\frac{1}{2}+x, \frac{1}{2}-y, z)$ and $(2-x, -y, \frac{1}{2}+z)$, respectively. Atoms C17 (*via* H17) and C11 (*via* H11) act as donors for weak intermolecular C—H···π interactions. The former interaction is with the centroid, *Cg*1, of the five membered ring in the molecule at $(x-\frac{1}{2}, \frac{1}{2}-y, z-1)$, while the latter is with the centroid, *Cg*3, of the phenyl ring substituted at C7 of the diazepine ring in the molecule at $(\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z)$ (Table 2).

Experimental

Dry hexahydro-*r*-2,*c*-7-diphenyldiazepine (1.34 g, 5.0 mmol) was dissolved in anhydrous benzene (75 ml), triethylamine (0.7 ml, 5.0 mmol) was added and the mixture was stirred. The reaction temperature was maintained at 273–283 K by placing the reaction flask in an ice-bath. To this, a solution of 2-furoyl chloride (0.66 ml, 5.0 mmol) in anhydrous benzene (15 ml) was added slowly for a period of 1 h with vigorous stirring. The mixture was heated over a water bath for 1 h and poured into cold water. The organic layer was separated and washed with dilute sodium bicarbonate solution. Then it was washed several times with water, dried over anhydrous sodium sulfate and passed through a short column of silica. The colourless solid obtained on concentration under reduced pressure was crystallized from ethanol (yield: 1.21 g, 65%; m.p. 401–404 K).

Crystal data

$C_{22}H_{20}N_2O_3$
M_r = 360.40
Orthorhombic, $Pna2_1$
a = 8.9941 (2) Å
b = 19.8913 (4) Å
c = 10.3244 (2) Å
V = 1847.08 (7) Å^3
Z = 4
D_x = 1.296 Mg m^{-3}
Mo Kα radiation
Cell parameters from 1904 reflections
θ = 2.0–25.0°
μ = 0.09 mm^{-1}
T = 160 (2) K
Prism, colourless
0.30 × 0.18 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: none
24574 measured reflections
1730 independent reflections
1538 reflections with $I > 2\sigma(I)$
R_{int} = 0.065
θ_{max} = 25.0°
$h = -10 \rightarrow 10$
$k = -23 \rightarrow 23$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.096
S = 1.06
1728 reflections
249 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.2477P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.034 (5)

Table 1
Selected geometric parameters (Å, °).

O5—C5	1.218 (3)	N4—C3	1.475 (3)
N1—C2	1.463 (3)	C2—C3	1.536 (4)
N1—C7	1.474 (3)	C5—C6	1.504 (4)
N4—C5	1.393 (4)	C6—C7	1.536 (4)
C2—N1—C7	115.6 (2)	C7—N1—H1	106.9 (19)
C2—N1—H1	108.5 (19)		
C7—N1—C2—C3	−69.8 (3)	N4—C5—C6—C7	76.6 (3)
C5—N4—C3—C2	−54.4 (3)	C2—N1—C7—C6	66.7 (3)
N1—C2—C3—N4	82.7 (3)	C5—C6—C7—N1	−83.0 (3)
C3—N4—C5—C6	−16.3 (4)		

Table 2
C—H···O and C—H···π interactions (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C17—H17···O5^{i}	0.95	2.50	3.322 (4)	144
C19—H19···O8^{ii}	0.95	2.59	3.342 (4)	136
C24—H24···O8^{iii}	0.95	2.39	3.278 (4)	155
C11—H11···*Cg*3^{iv}	0.95	2.69	3.538 (4)	149
C15—H15···*Cg*2^{v}	0.95	3.02	3.925 (4)	160
C17—H17···*Cg*1^{i}	0.95	3.24	4.008 (4)	140
C22—H22···*Cg*2^{vi}	0.95	2.72	3.540 (3)	145

Symmetry codes: (i) $x-\frac{1}{2},\frac{1}{2}-y,z-1$; (ii) $x-\frac{1}{2},\frac{1}{2}-y,z$; (iii) $\frac{3}{2}-x,y-\frac{1}{2},\frac{1}{2}+z$; (iv) $\frac{3}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z$; (v) $\frac{1}{2}+x,\frac{1}{2}-y,z$; (vi) $2-x,-y,\frac{1}{2}+z$. *Cg*1, *Cg*2 and *Cg*3 are the centroids of rings O11–C11, C14–C19 and C20–C25, respectively.

The position of the amine H atom was determined from a difference Fourier map and refined freely along with its isotropic displacement parameter. All remaining H atoms were placed in geometrically idealized positions (C—H = 0.95–1.00 Å) and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. Due to the absence of any significant anomalous scatterers in the compound, attempts to confirm the absolute polarity by refinement of the Flack (1983) parameter in the presence of 1382 sets of Friedel pairs led to an inconclusive value (Flack & Bernardinelli, 2000) of 0.4 (13) for this parameter. Therefore, the absolute direction of the polar axis was assigned arbitrarily and the Friedel pairs were merged before the final refinement. Reflections 011 and 020 were partially obscured by the beam stop and were omitted.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Version 1.07; Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2003).

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References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Flack, H. D. & Bernardinelli, G. (2000). *J. Appl. Cryst.* **33**, 1143–1148.
Hamor, H. A. & Martin, I. L. (1984). *X-ray Crystallography and Drug Action*, edited by A. S. Horn and C. J. De Ranter, pp. 275–301. Oxford: Clarendon Press.
Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
Priya, V., Shamala, N., Viswamitra, M. A., Senthilkumar, U. P. & Jeyaraman, R. (1992). *Acta Cryst.* C**48**, 1048–1051.
Ravikumar, K., Rajan, S. S., Parthasarathi, V., Thiruvalluvar, A., Jeyaraman, R. & Senthilkumar, U. P. (1994). *Acta Cryst.* C**50**, 827–829.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.