4443 reflections
347 parameters
H-atom parameters constrained
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 4. *Selected bond lengths (Å) for (IV)*

O1—C5	1.218 (2)	C16—C17	1.446 (3)
O2—C17	1.220 (2)	C17—C18	1.499 (3)
O3—C20	1.220 (2)	C20—C21	1.509 (2)
O4—C32	1.221 (2)	C20—C30	1.506 (2)
C5—C6	1.501 (2)	C21—C22	1.534 (2)
C5—C15	1.501 (3)	C22—C23	1.537 (2)
C6—C7	1.532 (3)	C22—C34	1.520 (3)
C7—C8	1.528 (2)	C23—C24	1.502 (2)
C7—C19	1.519 (3)	C24—C25	1.512 (2)
C8—C9	1.501 (3)	C24—C31	1.336 (2)
C9—C10	1.500 (3)	C25—C26	1.530 (2)
C9—C16	1.337 (2)	C25—C33	1.531 (2)
C10—C11	1.529 (2)	C26—C27	1.529 (2)
C10—C18	1.527 (3)	C26—C30	1.531 (2)
C11—C12	1.522 (3)	C27—C28	1.498 (3)
C11—C15	1.532 (2)	C28—C29	1.527 (3)
C12—C13	1.532 (4)	C29—C30	1.541 (2)
C13—C14	1.513 (4)	C31—C32	1.456 (2)
C14—C15	1.541 (3)	C32—C33	1.506 (3)

The refinements were carried out based on all the reflections with $|F_o| \neq 0$. The threshold, $I > 2\sigma(I)$, was used only for calculation of the R factor. The positions of all the H atoms were calculated geometrically and a riding model was used in their refinement (C—H 0.96 Å). U_{iso}(H) values were refined.

For all compounds, data collection: *AFC/MSC Diffractometer Control System* (Rigaku Corporation, 1993); cell refinement: *AFC/MSC Diffractometer Control System*; data reduction: local programs; program(s) used to solve structure: *CRYSTAN-GM* (Edwards *et al.*, 1996); program(s) used to refine structure: *CRYSTAN-GM*; molecular graphics: *CRYSTAN-GM*; software used to prepare material for publication: *CRYSTAN-GM*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1088). Services for accessing these data are described at the back of the journal.

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7-Phenyl-2,3,4,5-tetrahydro-1*H*-1,4-diazepin-5-one

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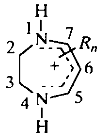
Abstract

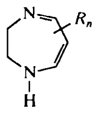
The geometry of the title diazepinone, $C_{11}H_{12}N_2O$, reflects the presence of cross-conjugated amide and vinylogous amide functions. The packing is dominated by hydrogen-bonding interactions which link the molecules into corrugated sheets.

Comment

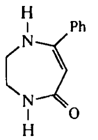
2,3-Dihydrodiazepines, (1), have been extensively characterized both in the form of salts (1*s*) and free bases (1*b*) by X-ray crystallography (Lloyd & McNab, 1993; Brisander *et al.*, 1998), and we now extend this work by reporting the first structure of a related diazepinone, (2). While the path of conjugation in (1) is endocyclic, it is exocyclic in (2), and we discuss here the structural implications of this difference. Of the three dihydrodiazepine bases, (1*b*), whose structures have been reported (Brisander *et al.*, 1998; Jordan *et al.*, 1998), those of (3) and (5) are disordered, and so the present discussion will focus on (4).



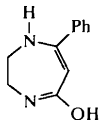
(1*s*)



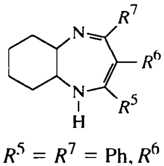
(1*b*)



(2)



(2′)



(3) $R^5 = R^7 = \text{Ph}, R^6 = \text{H}$
(4) $R^5 = R^7 = \text{H}, R^6 = \text{Ph}$
(5) $R^5 = R^7 = \text{Me}, R^6 = \text{H}$

Compound (2) exists exclusively in the solid state in the diazepinone form rather than the tautomeric diazepinol form, (2′). With the exception of the N4—C5═O51 fragment, the bond lengths of the conjugated

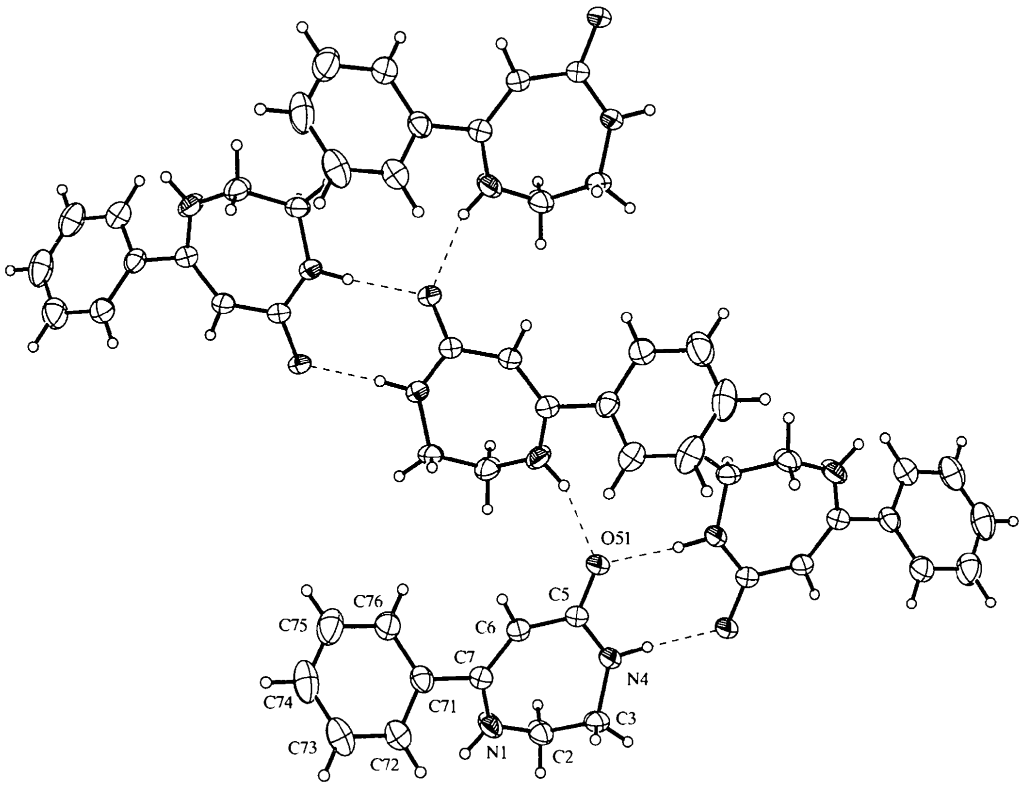


Fig. 1. The molecular structure of (2) with some neighbouring molecules and hydrogen bonding. Displacement ellipsoids are at the 30% probability level.

system in (2) are similar to those of related bonds in (4), which indicates that the overall electron-withdrawing effect of the exocyclic carbonyl in (2) is very similar to that of the endocyclic imine function in (4) [and also in (3)]. The carbonyl group in (2) is involved in two cross-conjugated systems, *viz*. the amide function N4—C5═O51 and the vinylogous amide N1—C7═C6—C5═O51. In keeping with this scheme, the C═O bond is unusually long at 1.2614 (15) Å by comparison with typical values for lactams [1.234 (11) Å; Chakrabarti & Dunitz, 1982]; because of the cross-conjugation, the N4—C5 bond [1.3408 (17) Å] is long by comparison with typical lactam values [1.332 (11) Å]. The electron-withdrawing effect of the carbonyl group has similar influences on the lengths of the amide C—N bond [N4—C5 1.3408 (17) Å] and the vinylogous amide C—N bond [N1—C7 1.3460 (17) Å]. The phenyl group shows some asymmetry in the C—C bond lengths [1.377 (3)–1.395 (2) Å], with the shortest being furthest from the site of substitution [as in (3)].

The presence of an H atom at N4 in (2) leads to a change in the position of the lone pair relative to that on the corresponding imine N4 atom in the diazepine bases (*1b*), resulting in an increase of the C3—N4—C5 angle from 120.1 (2) in (4) to 124.75 (12)° in (2). There is a corresponding decrease in the N4—C5—C6 angle [from 132.2 (2) in (4) to 122.23 (12)° in (2)] due to the exocyclic carbonyl group, which is compensated by an increase in the C5—C6—C7 angle [from 124.4 (2) in (4) to 133.18 (12)° in (2)]. The conjugated system in (2), comprising N1—C7═C6—C5(═O51)—N4, is approximately planar [maximum deviation at N1 of 0.1515 (8) Å]; C2 and C3 lie above and below this plane by 0.419 (2) and 0.511 (2) Å, respectively. The phenyl ring subtends an angle of 36.74 (5)° with this plane.

Pairs of molecules of (2) form hydrogen-bonded ring systems in a classic Etter-type $R_2^2(8)$ configuration *via* centrosymmetrically-related N4—H···O51^{i} and N4^{i}—H4^{i}···O51 interactions [N···O 2.826 (2) Å]. These then link together through O51···H1^{ii}—N1^{ii} hydrogen bonds to form corrugated sheets of molecules [N···O 2.800 (2) Å; symmetry codes: (i) $-x+\frac{1}{2}$, $-y+\frac{1}{2}$, $-z+\frac{1}{2}$; (ii) $\frac{1}{2}+x$, $-y$, z] (Fig. 1).

Experimental

Compound (2) was prepared as described by Chammache *et al.* (1993) and crystallized by slow evaporation from ethanol. δ_H (p.p.m.): 7.51 (2H, *m*), 7.39 (3H, *m*), 7.36 (1H, *br s*), 7.19 (1H, *br s*), 4.54 (1H, *s*), 3.45 (4H, *m*); δ_C (p.p.m.): 170.48 (*q*), 152.44 (*q*), 139.60 (*q*), 129.31, 128.40, 127.08, 91.49, 47.73 and 42.62 (where *q* = quaternary); *m/z* (electrospray): 189 $(M+1)^+$, 100%; m.p. 482–484 K (literature 483–485 K).

Crystal data

$C_{11}H_{12}N_2O$
$M_r = 188.23$
Monoclinic
$I2/a$
$a = 12.1685\,(19)$ Å
$b = 13.724\,(2)$ Å
$c = 13.315\,(3)$ Å
$\beta = 114.792\,(9)^\circ$
$V = 2018.7\,(6)$ Å^3
$Z = 8$
$D_x = 1.239$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 54 reflections
$\theta = 15\text{–}16^\circ$
$\mu = 0.082$ mm^{-1}
$T = 220.0\,(2)$ K
Lath
$0.66 \times 0.31 \times 0.31$ mm
Colourless

Data collection

Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)
ω–θ scans
Absorption correction: none
4252 measured reflections
1789 independent reflections

1428 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\rm max} = 25.03^\circ$
$h = -14 \rightarrow 1$
$k = -1 \rightarrow 16$
$l = -14 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.089$
$S = 1.048$
1789 reflections
136 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.6438P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.151$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.165$ e Å^{-3}
Extinction correction: *SHELX*97 (Sheldrick, 1997)
Extinction coefficient: 0.0056 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

H1 and H4 were located from a ΔF map and were refined freely. Other H atoms (also clearly visible in maps) were constrained with a riding model and with $U(\rm H) = 1.2\,U_{\rm eq}(C)$.

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SHELX*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELX*97. Molecular graphics: *SHELXTL* (Sheldrick, 1995).

We thank EPSRC for provision of a four-circle diffractometer and Kodak Ltd for a studentship to MCE.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1321). Services for accessing these data are described at the back of the journal.

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N-(6-Amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)methionine

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Abstract

The absolute configuration of the title compound, $C_{10}H_{15}N_5O_4S$, has been determined and is in agreement with that of the starting material, L-methionine. Two identical hydrogen-bonded buckled sheets run parallel to the [101] and [$\bar{1}$01] planes. Molecules lying in either of these planes are linked together by a ring structure to form these sheets, in which two chains of molecules run antiparallel to each other along the *b* axis. A further hydrogen-bonded ring structure links the [10$\bar{1}$] and [101] sheets together, resulting in an infinite three-dimensional hydrogen-bonded network.

Comment

Our interest in amino acid/nucleobase adducts is in their use as intermediates in the formation of metal complexes which have potential biological applications. The coordinating ability of the title compound, H*L*, is demonstrated by the preparation of three solid metal–ligand species, $(\mathrm{Zn}L_2\cdot 2\mathrm{H_2O})_n$, $(\mathrm{Cd}L_2\cdot 3\mathrm{H_2O})_n$ and $(\mathrm{Mn}L_2\cdot 3\mathrm{H_2O})_n$. In these, the carboxyl group acts as deprotonated (L^-), resulting in a bidentate coordination mode through the carboxylate of the amino-acid moi-