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Benz[*cd*]indol-2(1*H*)-one at 298 and 100 K

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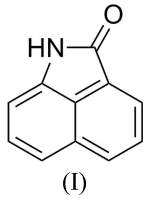
Weakly diffracting crystals of benz[*cd*]indol-2(1*H*)-one (naphtholactam), $C_{11}H_7NO$, were unsuitable for data collection by early photographic methods. However, a diffractometer data set collected at room temperature in 1989 was solved and refined. The peak scans were broad, and the results indicated disorder or a satellite crystal. Recent data collection (on another crystal from the same sample) with an area detector at 100 K revealed the same disorder, and made it possible to refine two different, more complete, disorder models. Both models assume an occasional 180° rotation of the nearly planar centrosymmetric *cis*-lactam dimer. The refinements differ, especially in the anisotropic displacement parameters for the –C(=O)—NH– portion of the molecule. Both models at 100 K give a C—N ('amide') bond distance of 1.38 Å, about 0.04 Å longer than the average distance in saturated γ-lactams in the Cambridge Structural Database. Cohesive packing interactions between molecules include opposing-dipole dimers; the packing may explain the 10:1 ratio favoring the major-occupancy molecule.

Comment

Naphtholactam, (I), may be used as a starting material in the preparation of anticancer and hypotensive agents; an improved large-scale synthesis of the title compound has been published (Marzoni & Varney, 1997). Deprotonation of (I) yields the lactamate, which has been tested as a ligand with fluorophore properties (Limmert *et al.*, 2003). The nucleoside 2-deoxyribosyltransferase from *Trypanosoma brucei* was crystallized with a molecule of (I) in the active site (Bosch *et al.*, 2006) in a study of 'fragment cocktail soaks'. The Cambridge Structural Database (CSD, Version 5.32; Allen, 2002; Macrae *et al.*, 2008) contains three-dimensional coordinates for 15 derivatives of (I), but no published crystal structure of the unsubstituted compound was found.

Before our investigation began, it was predicted that the –C(=O)—NH– ('amide') bond in (I) would be longer than that in other amides. But what is the distance in 'other amides'? The CIF dictionary contains no reference C—N bond length for amides. Clearly, the C—N and C=O bond lengths are changed by distortion of the amide unit away from planarity (Bennett *et al.*, 1990; Wang *et al.*, 1991, and references therein). In this paper, we examine evidence that, in crystal structures, these distances also depend on the intermolecular hydrogen-bonding pattern.



(I)

In the crystal structure of (I) presented here, the structural units are pairs of molecules strongly hydrogen-bonded into dimers. The dimers are shown with atom numbering in Figs. 1, 2 and 3. Tables 1, 2 and 3 give bond lengths for the five-membered ring in data set (I*a*), at 298 K, (I*b*), at 100 K, and (I*c*), with the same data set as (I*b*) but using a different disorder model.

As in 2-pyrrolidone (or 2-pyrrolidinone, 2-PD, the saturated γ-lactam), the –C(=O)—NH– conformation in (I) is required to be *cis*, and planar or nearly so (Fig. 4 and Table 4). To estimate the effect of the naphthalene rings on the lactam portion of (I), we may first examine 2-PD and its derivatives.

The length of the *cis*-amide C—N bond in cyclic lactam crystal structures was found to be nearly independent of ring size, from four- to eight-membered rings (Yang *et al.*, 1987). For five-membered rings, an average value from 41 crystal structures from the CSD [1.335 (13) Å, Table 4] was quoted. The structures surveyed included both dimeric and non-dimeric hydrogen bonding in the crystal packing, and all were considered to be planar.

However, in an *ab initio* study, the 'amide' C—N and C=O bond lengths for 2-PD were shown to differ for the single-molecule hydrogen-bonded 2-PD dimers and clusters of 2-PD with water molecules (Yekeler *et al.*, 1999). The C—N distance decreased by about 0.02 Å, and the C=O distance increased by about 0.01 Å, if 2-PD formed N—H$\cdots$O and C=O$\cdots$H hydrogen bonds with another 2-PD molecule or with water. [Out-of-plane distortions are also accompanied by a smaller change in the C=O than in the C—N bond lengths (Wang *et al.*, 1991).]

The structure of $(2\text{-PD})_3\cdot HBr_3$, which was referred to by Yekeler *et al.* (1999), shows different hydrogen-bonding patterns for the three 2-PD molecules in the asymmetric unit (Table 4). The shortest C—N (1.24 Å) and longest C=O (1.29 Å) bond lengths are attributed to a C=O$\cdots$H+$\cdots$O=C interaction (O$\cdots$O = 2.45 Å); the structure may be better described in terms of three units, *viz.* 2-PD, $(2\text{-PD})_2\cdot H^+$ and Br_3^- (Boeyens *et al.*, 1986). Ions were excluded from the searches described below.

Table 4 gives the 'amide' bond lengths (C—N and C=O) from the *ab initio* study, from appropriate structures from the CSD and from this work. Fig. 4 shows the models used to search the CSD and some example structures. These examples indicate that, even though there is little or no distortion from

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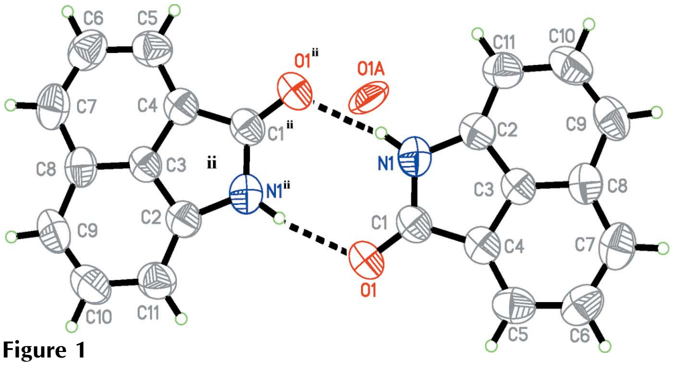

Figure 1
The structure of (I) at 298 K [data set (I*a*)]. The molecule at (*x*, *y*, *z*) is shown on the right, including the minor-occupancy atom O1*A*. Its hydrogen-bonded partner at (−*x*, −*y*, −*z* + 1) (denoted ii) is shown on the left (major-occupancy atoms only, N1^{ii}, C1^{ii} *etc.*). The occupancies for atoms O1 [0.921 (4)] and O1*A* [0.079 (4)] were refined and the occupancies for all other atoms are 1.0. Hirshfeld test for N1—C1 = 0.0090 Å^2 (Hirshfeld, 1976). The O1···N1^{ii} (O1^{ii}···N1) distance is 2.866 (3) Å. Displacement ellipsoids are drawn at the 50% probability level.

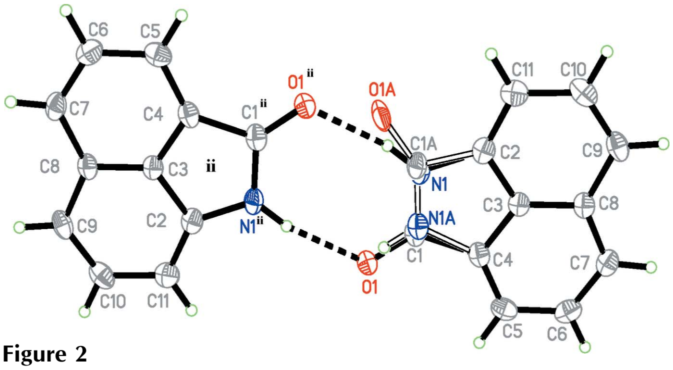

Figure 2
The structure of (I) at 100 K [data set (I*b*)]. The molecule at (*x*, *y*, *z*) is shown on the right, including the minor-occupancy atoms N1*A*, C1*A*, O1*A* and H1N*A*. Its hydrogen-bonded partner at (−*x*, −*y*, −*z* + 1) (denoted ii) is shown on the left (major-occupancy atoms only, N1^{ii}, C1^{ii} *etc.*). Hirshfeld test for N1—C2 = 0.0057 Å^2 (Hirshfeld, 1976). The O1···N1^{ii} (O1^{ii}···N1) distance is 2.845 (3) Å. Displacement ellipsoids are drawn at the 50% probability level.

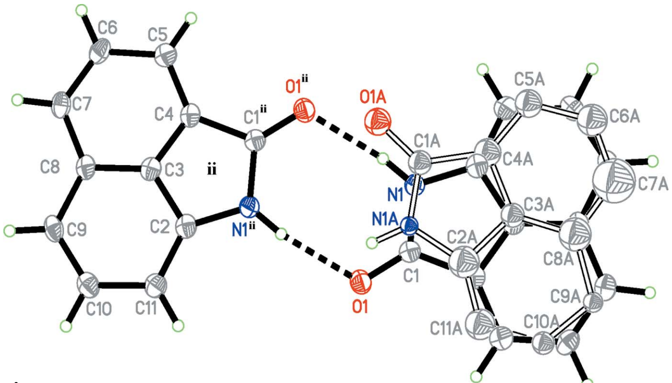

Figure 3
The structure of (I) at 100 K [data set (I*c*)]. The molecule at (*x*, *y*, *z*) is shown on the right, including the minor-occupancy molecule refined as a rigid body (atoms O1*A*–C11*A*, with isotropic U^{ij}). Its hydrogen-bonded partner at (−*x*, −*y*, −*z* + 1) (denoted ii) is shown on the left (major-occupancy atoms only). Hirshfeld test for N1—C2 = 0.0035 Å^2 (Hirshfeld, 1976). The O1···N1^{ii} (O1^{ii}···N1) distance is 2.8403 (17) Å. Note that atoms C3 and C3*A* are at nearly the same position in the two orientations. H atoms for the minor-occupancy molecule have been omitted (except for H1N*A*).

planarity, ions and cocrystals may exhibit additional hydrogen bonding that extends the resonance of the –C(═O)—NH– group. The carbonyl O atom may accept two hydrogen bonds, as demonstrated by the structure of 2-PD·H_2O (Table 4 and Fig. 4, A3). For these reasons, we have averaged the distances for centrosymmetric dimers, nondimers (including 'dimers' with no center of symmetry) and cocrystals separately.

As seen in Table 4, more recent crystal structures are, on average, in agreement with the *ab initio* cyclic dimer value of 1.338 Å (Yekeler *et al.*, 1999). For example, in a low-temperature phase of 2-PD (CSD refcode NILYAI, Fig. 4, model for Search A) the C—N bond length is 1.335 (2) Å. The average C—N and C═O bond lengths for crystal structures of 2-PD derivatives in the CSD are nearly the same for cyclic dimers and for nondimers.

Examination of the structures with unusually long and unusually short amide bonds suggests explanations for variations from the average. An example of an outlier with 'long'

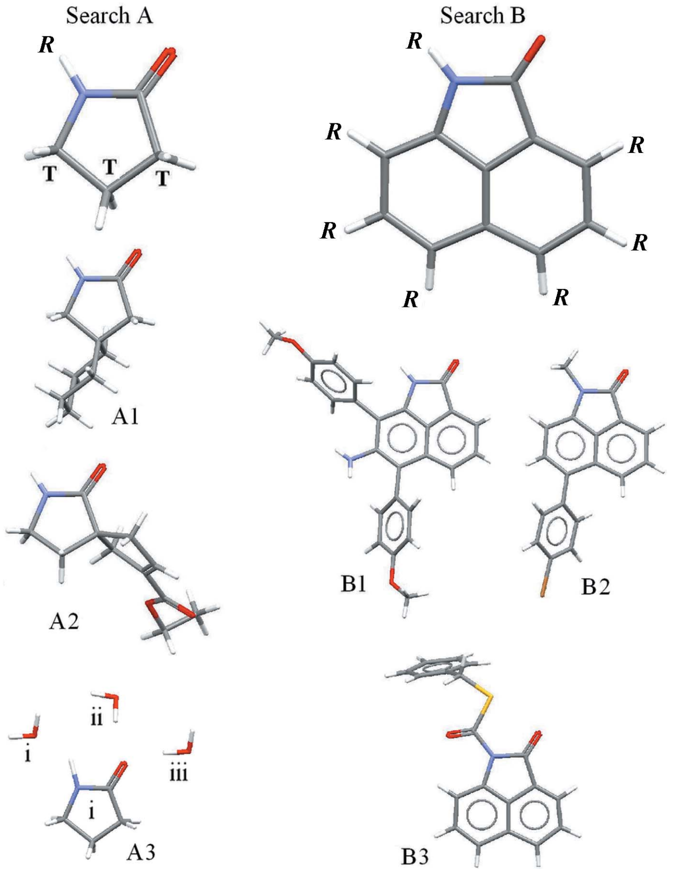

Figure 4
Capped-stick representations for the two searches in the CSD (see Table 4) (*MercuryCSD*; Macrae *et al.*, 2008). Search A: 2-PD derivatives, with C atoms designated 'T' required to be bonded to four atoms and *R* = H. Examples: A1 is 2-azaspiro[4.5]decan-3-one; A2 is (5*S**)-1-oxo-2-azaspiro[4.4]non-7-ene-7-carboxylate; A3 is 2-pyrrolidinone monohydrate. [Symmetry codes: (i) *x*, *y*, *z*; (ii) *x*, *y*, *z* − 1; (iii) *x*, −*y* + $\frac{1}{2}$, *z* − $\frac{1}{2}$.] Search B: naphtholactam derivatives, any singly-bonded substituent for *R*, no cocrystals. Examples: B1 is 7-amino-6,8-bis(4-methoxyphenyl)-benz[*cd*]indol-2(1*H*)-one; B2 is 6-(4-bromophenyl)-1-methylbenz[*cd*]-indol-2-one; B3 is *S*-benzyl 2-oxobenzo[*cd*]indole-1(2*H*)-carbothioate.

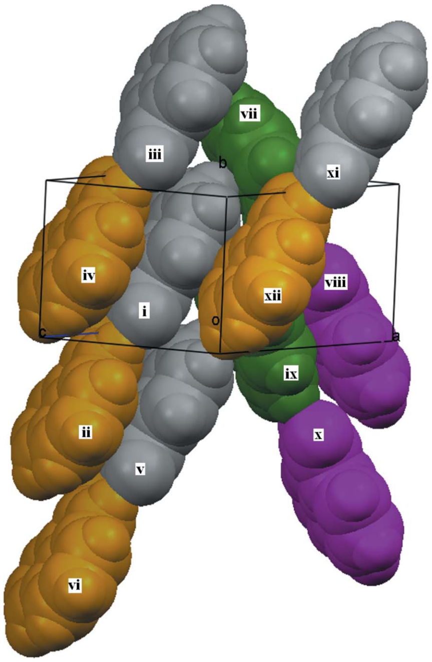

Figure 5
The crystal packing for the major-occupancy molecule of (I) at 100 K, space-filling style, colored according to symmetry operation (*Mercury-CSD*; Macrae *et al.*, 2008). The *b* axis is vertical in this view. Hydrogen-bonded pairs of molecules related by centers of symmetry form adjacent stacks. The stacks related by the *n*-glide (purple and green in the electronic version of the paper) form an angle of 56° to the (x, y, z) and $(-x, -y, -z)$ (gray and yellow) stacks. [Symmetry codes: (i) x, y, z; (ii) $-x, -y, -z+1$; (iii) $x, y+1, z$; (iv) $-x, -y+1, -z+1$; (v) $x, y-1, z$; (vi) $-x, -y-1, -z+1$; (vii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (viii) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (ix) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (x) $x+\frac{1}{2}, -y-\frac{1}{2}, z-\frac{1}{2}$; (xi) $x+1, y+1, z$; (xii) $-x+1, -y+1, -z+1$.] The center of symmetry between (i) and (ii) is at $(0, 0, \frac{1}{2})$, and that between (vii) and (viii) is at $(\frac{1}{2}, \frac{1}{2}, 0)$.

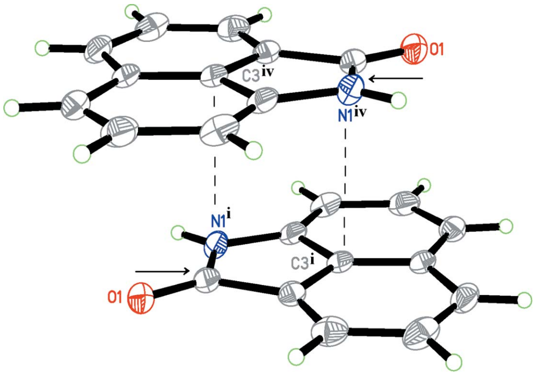

Figure 6
The 'dimer' of opposing dipoles formed by the stacking interaction between molecules at (x, y, z) [symmetry code (i)] and $(-x, -y+1, -z+1)$ [symmetry code (iv)]. The distance from N1^{i} to C3^{iv} is 3.631 (3) Å for (I*b*) and 3.630 (2) Å for (I*c*). Dipole directions are shown by arrows; the dipole charge is 1.19 (Gavezzotti, 2003). See also Fig. 5.

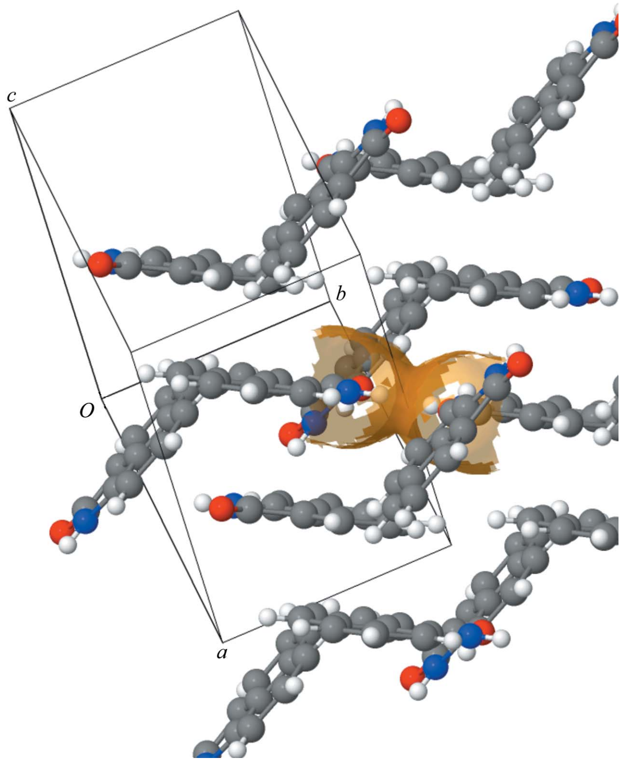

Figure 7
The packing of (I) (principal conformer), in ball-and-stick style, showing 2×2×1 unit cells. The van der Waals surfaces of the hydrogen-bonded atoms in the centrosymmetric dimer at $1,1,\frac{1}{2}$ are highlighted.

amide bonds is A2 in Fig. 4 [(5*S**)-1-oxo-2-azaspiro[4.4]non-7-ene-7-carboxylate; GASSUP; Yong *et al.*, 2005]. A centrosymmetric amide–amide dimer is formed, but the carbonyl O atom also accepts a C—H⋯O hydrogen bond and makes contact with a neighboring –C═C– C atom. The amide C—N and C═O distances are 1.355 (2) and 1.256 (2) Å, respectively, each significantly longer than the average distances in Table 4. On average, however, the sum of these two distances is nearly constant. When structures determined at 200 K and below are separated from the overall search results, the average distances for dimers and nondimers are slightly longer, as expected when thermal motion effects are reduced.

Cocrystals are averaged separately in Table 4 because they generally produce 'short' C—N (amide) bonds (and 'long' C═O bonds). For 2-PD·H_2O (DIPMUK, Table 4), the C—N bond is significantly shorter [1.319 (3) Å] and the C═O bond longer than average. Each water molecule accepts one and donates two H atoms to hydrogen bonds; see A3 in Fig. 4. (This arrangement was not included in the *ab initio* study.) Similarly, for gabapentin-lactam–benzoic acid (XOHXAU), the C—N bond is shorter than that in gabapentin-lactam (A1, AWUWOE). In the benzoic acid solvate, the –C(═O)—NH–O atom is hydrogen bonded to both solvent and another lactam in a cyclic tetramer, while the pure compound is a cyclic dimer. In a recent example, cocrystals of 2-PD with succinic acid and with fumaric acid have different chain arrangements but similarly short C—N bond lengths of 1.322 (7) and 1.321 (3) Å, respectively (Callear *et al.*, 2009). In all of these cases, additional hydrogen bonding to carbonyl O atoms appears to lengthen the C═O bond and shorten the C—N bond by approximately equal amounts.

Bond lengths also vary for primary amides (Table 4). The examples quoted were chosen from a study of molecule–molecule energies (Gavezzotti, 2010). For an illustration of the effect of intermolecular interactions in *trans* –C(═O)—

N(*R*)—H amides, we cite a recent study of the crystal structures of two symmetrical pyridine-2-carboxamide derivatives (Munro & Wilson, 2010). Chemically identical but crystallographically unique bonds differ by 0.013 Å, six times the s.u. of the distances (Table 4). The shorter C—N distance is correlated to the longer C=O distance, attributable to stronger intermolecular H$\cdots$O hydrogen bonds.

For naphtholactam, (I), the values for the C—N bond length (in the major orientation) are 1.37–1.38 Å and the corresponding C=O distances are 1.24–1.23 Å (Tables 1, 2, 3 and 4). For the ten naphtholactam derivatives (excluding cocrystals and helicenes) in the CSD, the values for C—N range from 1.38 to 1.46 Å. Again, longer C—N bonds are accompanied by shorter C=O distances. Only one of these derivatives can form the hydrogen-bonded dimeric structure found here; for QACQOA (B1, Fig. 4 and Table 4), the C—N length is 1.376 (7) Å at 228 K (Wang *et al.*, 1998), in agreement with our 100 K results. Derivatives with N—*R* have longer C—N bonds. In RAKYUY (B2), a Br atom makes contact with the carbonyl O atom. In DUXXEA (B3), the two molecules in the asymmetric unit have C—N distances of 1.42 (1) and 1.460 (8) Å; the corresponding C=O distances are 1.219 (8) and 1.209 (9) Å. The amide O atom in molecule 1 has three C—H$\cdots$O close contacts, while that in molecule 2 has only two.

Thus, the C—N bond length in (I) is ~0.04 Å longer than that in 2-PD and its derivatives. The replacement of two single C—C bonds in 2-PD (NILYAI; Goddard *et al.*, 1998) with aromatic C$\overset{\cdots}{-}$C bonds in (I) introduces other changes as well: N1—C2 is shorter (1.41 *versus* 1.46 Å), C1—C4 is shorter (1.48 *versus* 1.52 Å) and the five-membered ring is more nearly planar.

The crystal packing for (I), shown in Figs. 5, 6 and 7, is strikingly similar to that in 2-PD (NILYAI). Stacks of centrosymmetric dimers result in a packing coefficient of 0.75 (Gavezzotti, 2003). In the stacks, additional 'dimers' are formed (Fig. 6), with opposing dipoles resembling those reported for cyclobutanone and cyclopentanone (Yufit & Howard, 2011). Table 5 gives intermolecular cohesive energy values and distances (Gavezzotti, 2003). Though these are summaries of point-to-point energies, including repulsions between the N and O atoms in the centrosymmetric dimer, they are useful for comparison. It is likely that the dimer was present in the benzene solution that was used to prepare the crystals.

In (I), there are two stacks of dimers related by an *n*-glide (Fig. 5). If a dimer were rotated by ~180° before insertion in a stack, as is proposed in the disorder model, both the cohesive stacking interactions within the stacks and the cohesive interactions between adjacent stacks would be adversely affected. Thus, the packing may explain the 10:1 ratio favoring the major-occupancy molecule.

Experimental

The sample was synthesized by Professor Cyril A. Grob (Grob & Schmid, 1950).

Table 1
Selected bond lengths (Å) for data set (I*a*) at 298 K.

C1—O1	1.241 (2)	C1—C4	1.484 (3)
C1—N1	1.367 (3)	N1—C2	1.419 (3)

Table 2
Selected bond lengths (Å) for data set (I*b*) at 100 K.

O1—C1	1.230 (3)	C1*A*—N1*A*	1.339 (16)
C1—N1	1.375 (3)	C1*A*—C2	1.445 (18)
C1—C4	1.485 (3)	N1*A*—C4	1.481 (11)
N1—C2	1.412 (3)	C2—C3	1.406 (2)
O1*A*—C1*A*	1.313 (15)	C3—C4	1.400 (2)

Data set (I*a*) at 298 K

Crystal data

$C_{11}H_7NO$
M_r = 169.18
Monoclinic, $P2_1/n$
a = 9.251 (3) Å
b = 6.7748 (17) Å
c = 13.256 (4) Å
β = 93.196 (8)°
V = 829.5 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 298 K
0.35 × 0.25 × 0.10 mm

Data collection

Modified Hubers diffractometer
1462 measured reflections
1462 independent reflections
992 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.000
3 standard reflections every 97 reflections
intensity decay: 0.4%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.133
S = 1.09
1462 reflections
128 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.19 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.14 e Å^{-3}

Data set (I*b*) at 100 K

Crystal data

$C_{11}H_7NO$
M_r = 169.18
Monoclinic, $P2_1/n$
a = 9.0551 (19) Å
b = 6.7287 (14) Å
c = 13.120 (3) Å
β = 92.600 (2)°
V = 798.5 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 100 K
0.20 × 0.10 × 0.05 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{\rm min}$ = 0.982, $T_{\rm max}$ = 0.995
9032 measured reflections
1969 independent reflections
1700 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.079

Table 3
Selected bond lengths (Å) for data set (I*c*) at 100 K.

O1—C1	1.2283 (17)	O1*A*—C1*A*	1.25
C1—N1	1.383 (2)	C1*A*—N1*A*	1.33
C1—C4	1.488 (3)	C1*A*—C4*A*	1.48
N1—C2	1.405 (3)	N1*A*—C2*A*	1.39
C2—C3	1.413 (3)	C2*A*—C3*A*	1.42
C3—C4	1.393 (3)	C3*A*—C4*A*	1.41

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Table 4
C(═O)—N ('amide') distances (Å) and torsion angles (°) (Fig. 4).

2-PD, 2-PD dimers, 2-PD·H$_2$O (*ab initio* values, HF/6-31G*, s.u. values not given). Crystal structures (see Fig. 4): 2-PD; (2-PD)$_3$·HBr; 2-PD–succinic acid; 2-PD–fumaric acid; gabapentin-lactam (A1), gabapentin-lactam–benzoic acid; (5*S**)-1-oxo-2-azaspiro[4.4]non-7-ene-7-carboxylate (A2); 2-PD·H$_2$O (A3); 41 γ-lactams (average, s.u.). Search A: 59 2-PD centrosymmetric dimers (average, s.u.); 146 nondimer 2-PD derivatives (average, s.u.); 39 2-PD derivatives, cocrystals [dimers and nondimers (average, s.u.)]; 22 2-PD centrosymmetric dimers, 100–200 K (average, s.u.); 51 nondimer 2-PD derivatives, 100–200 K (average, s.u.), 13 2-PD derivatives, cocrystals, 93–93 K [dimers and nondimers (average, s.u.)]. Other examples: 12 primary amides (average, s.u.; three *trans* secondary amide groups. Search B: ten derivatives of (I) [benz[*cd*]indol-2(1*H*)-one (average, s.u.)]; three examples from the ten derivatives (see Fig. 4). This work: data sets (I*a*), (I*b*) and (I*c*). Tables S-4, S-5 and S-6 in the *Supplementary materials* give detailed refcode lists for the CSD searches.

Structure	C—N	C═O	C—N + C═O	N···O	O—C—N—H	C—C—N—C	Source
2-PD, *ab initio*	1.356	1.196	2.552	N/A	−9.39	N/A	Yekeler *et al.* (1999)
2-PD, cyclic dimer	1.338	1.209	2.557	3.00†	−6.12	N/A	Yekeler *et al.* (1999)
2-PD, dimer, one hydrogen bond	1.345	1.203	2.548	3.03†	−8.67	N/A	Yekeler *et al.* (1999)
2-PD·*x*H$_2$O (*x* = 1, 2 or 3)	1.34 (1.344–1.336)	1.21 (1.206–1.210)	2.542–2.550	N/A†, 3.01, 2.97†	−7.40, −6.36, −5.90	N/A	Yekeler *et al.* (1999)
Crystal structures							
2-PD (NILYAI)	1.335 (2)	1.237 (2)	2.572	2.92	−11	4.3	Goddard *et al.* (1998)
(2-PD)$_3$·HBr (FAJHUT)	1.33 (2) (N1—C1)	1.20 (2) (C1═O1)	2.53	2.96 (dimer)	−4	1	Boeyens *et al.* (1986)
Molecule 2 (FAJHUT)	1.24 (2) (N2—C5)	1.29 (2) (C5═O2)	2.53	2.76 (nondimer)	−2	−3	Boeyens *et al.* (1986)
Molecule 3 (FAJHUT)	1.30 (2) (N3—C9)	1.26 (2) (C9═O3)	2.56	3.01 (dimer)	2	−1	Boeyens *et al.* (1986)
2-PD–succinic acid (UHACEM)	1.322 (7)	1.247 (7)	2.569	2.94	4.0	4.0	Callear *et al.* (2009)
2-PD–fumaric acid (UHACUC)	1.321 (3)	1.254 (3)	2.575	2.92	3.0	2.0	Callear *et al.* (2009)
A1 (AWUWOE)	1.331 (2)	1.234 (3)	2.565	2.91	−3	0.3	Ananda *et al.* (2003)
A1–benzoic acid (XOHXAU)	1.319 (2)	1.249 (2)	2.568	2.97	0	2.3	Braga *et al.* (2008)
A2 (GASSUP)	1.355 (2)	1.256 (2)	2.611	2.95	0.4	5	Yong *et al.* (2005)
A3: 2-PD·H$_2$O (DIPMUK)	1.319 (3)	1.257 (3)	2.576	2.83 (H$_2$O)	0.5	0.8	Pirilä *et al.* (1999)
41 γ-lactams	1.335 (13)	1.232 (11)					CSD (Norskov-Lauritsen *et al.* 1985)
Search A (Fig. 4)							
59 2-PD dimers	1.338 (8)	1.232 (8)	2.570 (11)				CSD‡
146 2-PD nondimers	1.335 (10)	1.232 (9)	2.567 (12)				CSD‡
39 2-PD cocrystals	1.332 (11)	1.232 (14)	2.564 (12)				CSD‡
22 2-PD dimers, 100–200 K	1.341 (9)	1.235 (7)	2.576 (12)				CSD‡
51 2-PD nondimers, 100–200 K	1.337 (9)	1.235 (8)	2.571 (9)				CSD‡
13 2-PD cocrystals, 93–193 K	1.328 (8)	1.244 (10)	2.572 (6)				CSD‡
Other examples							
12 primary amides (dimers and nondimers)	1.323 (8)	1.238 (9)	2.561 (14)				Gavezzotti (2010)
Three *trans* amides: unit I	1.325 (2)	1.237 (2)	2.562	2.87 (N2···O1)	177	−178	Munro & Wilson (2010)
Unit I′	1.338 (2)	1.226 (2)	2.564	2.93 (N3···O1)	−174	177	Munro & Wilson (2010)
Unit II	1.3382 (12)	1.2289 (11)	2.567	3.09	177	−175	Munro & Wilson (2010)
Search B (Fig. 4)							
Ten naphtholactam derivatives	1.41 (3)	1.215 (11)	2.63 (2)	N/A	(O—C—N—*R*)	(C—C—N—C)	CSD§
B1 (QACQOA)	1.376 (7)	1.226 (7)	2.602	2.90	4	−1.2	Wang *et al.* (1998)
B2 (RAKYUY)	1.430 (5)	1.193 (5)	2.623	N/A (Br···O)	−3.1	−0.2	Lux *et al.* (2005)
B3, molecule 1 (DUXXEA)	1.42 (1)	1.219 (8)	2.634	N/A (no N···O)	−12	1	Sheik *et al.* (2010)
B3, molecule 2 (DUXXEA)	1.460 (8)	1.209 (9)	2.669	N/A (no N···O)	4	2	Sheik *et al.* (2010)
(I*a*) (298 K)	1.367 (3)	1.241 (3)	2.608	2.866	−0.9	−0.8	This work
(I*b*) (100 K)	1.375 (3)	1.230 (4)	2.605	2.845	−0.8	−1.3	This work
(I*c*) (100 K)	1.383 (2)	1.228 (2)	2.611	2.840	−0.9	−1.4	This work

† Calculated from N—H and H···O distances and N—H···O angle, if given; C—C—N—C not given. ‡ Search requirements for 2-pyrrolidone (2-PD): a five-membered ring with the –C(═O)—NH– group and three other C atoms (Fig. 4), each with a total of four connected atoms. Requirements also included three-dimensional crystal coordinates, only organics, no powder structures, no ions, no disorder or errors and $R \leq 0.075$. § Search requirements for (I) and derivatives: three-dimensional crystal coordinates, only organics, no powder structures, no ions, no errors. N—*R* allowed, C—*R* single bond, no solvent.

Table 5
Crystal packing.

Molecule–molecule energies calculated using *OPIX* (Gavezzotti, 2003); see Fig. 5 for symmetry codes.

Symmetry codes	Molecule–molecule distance (centers of mass) (Å)	Molecule–molecule energy (kJ mol^{-1})
(i) to (ii)	7.49	−65
(i) to (iii)	6.73	−15
(i) to (iv)	3.78	−48
(i) to (v)	6.73	−15
(i) to (vii)	5.51	−32
(i) to (ix)	5.51	−32
(i) to (xii)	7.45	−13

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.180$
$S = 1.07$
1969 reflections
135 parameters
14 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

Data set (I*c*) at 100 K

Crystal data and *Data collection*

See Data set (I*b*) at 100 K above

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.164$
$S = 1.09$
1969 reflections
138 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.45$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

At room temperature [data set (I*a*)], a peak of 0.59 e$^-$ Å^{-3} in the difference map after refinement of the 20 C, H, N and O atoms, close to atom H1N, was assumed to be a second partial O atom (O1*A*) in the model described above (Fig. 1); the occupancies for the two O atoms refined to 0.921 (4) and 0.079 (4), respectively. The C1—O1 distance in Table 1 is for the major orientation. At 100 K [data set (I*b*)] (Fig. 2), a more detailed model for refinement of the disorder was employed, using restraints SIMU, EADP, DFIX, SADI and FLAT (*SHELXL97*; Sheldrick, 2008) in the O1*A*, C1*A*, N1*A* and H1N*A* region. The occupancies refined to 0.919 (4) for atoms C1, O1, N1 and H1N, and to 0.081 (4) for atoms C1*A*, O1*A*, N1*A* and H1N*A*. The restraints were not completely successful, as shown in the selected bond lengths reported in Table 2. In addition, *checkCIF* reported a Hirshfeld test greater than five times the s.u., as was also true at room temperature. A second model for the 100 K data [data set (I*c*)] (Fig. 3) employed whole molecule disorder where the entire minor-occupancy orientation was refined with isotropic displacement parameters and restrained to have similar bond lengths and angles to those of the major-occupancy orientation (constructed using the *SHELXL97* SAME instruction); the occupancies refined to 0.912 (3) and 0.088 (3). Changes in bond lengths, angles, and R and R_w values for the major-occupancy molecule were minor (Table 3). The anisotropic displacement parameters for the major-occupancy molecule were significantly improved; see Fig. 3. All H atoms were placed in geometrically calculated positions and refined using a riding model, with C—H = 0.93 or 0.95 Å and N—H = 0.86 or 0.88 Å for the models at 298 and 100 K, respectively, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N).

Data collection: *UCLA Crystallographic Package* (Strouse, 1984) for data set (I*a*) at 298 K; *APEX2* (Bruker, 2008) for data sets (I*b*) and (I*c*) at 100 K. Cell refinement: *UCLA Crystallographic Package* for data set (I*a*) at 298 K; *SAINT* (Bruker, 2008) for data sets (I*b*) and (I*c*) at 100 K. Data reduction: *UCLA Crystallographic Package* for data set (I*a*) at 298 K; *SAINT* for data sets (I*b*) and (I*c*) at 100 K. For all data sets, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: QS3004). Services for accessing these data are described at the back of the journal.

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