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A Low-Temperature Phase of 2-Pyrrolidone

Richard Goddard,[a] Oliver Heinemann,[a] Carl Krüger,[a] Ildikó Magdó,[b] Franz Mark[b] and Kurt Schaffner[b]

[a]*Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany, and* [b]*Max-Planck-Institut für Strahlenchemie, Stiftstraße 34-36, D-45470 Mülheim an der Ruhr, Germany. E-mail: goddard@mpi-muelheim.mpg.de*

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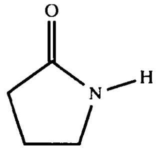
Abstract

Differential scanning calorimetry in the range 173–303 K reveals the presence of a previously unknown metastable phase of 2-pyrrolidone, C_4H_7NO, with a melting point of 286 K. Its crystal structure at 173 K is described. The molecules crystallize as centrosymmetric dimers and are linked by N—H···O hydrogen bonds with each molecule adopting an unstrained envelope conformation. Theoretical calculations confirm a slight pyramidalization of the N atom.

Comment

The report by Kondepudi *et al.* (1990) that cooling a vigorously stirred saturated aqueous solution of sodium chlorate ($NaClO_3$) results in a predominance of enantiomorphic crystals of one handedness highlights the possibility of obtaining chiral crystals in high yield from a solution of an achiral species. It appears that nucleation plays a decisive role in determining the outcome of the experiment (McBride & Carter, 1991). We have recently begun a search for organic systems that behave similarly. Our starting point was the observation that planar tetrazole can be made to crystallize as a conglomerate (Goddard *et al.*, 1997*a*). Interestingly, none of the other known isoelectronic aza derivatives of pyrrole resulting from progressive substitution of C—H by N exhibits this property (Goddard *et al.*, 1997*b*). Nevertheless, encouraged by the observation that the achiral molecule acetamide crystallizes in a non-centrosymmetric (Senti & Harker, 1940; Denne & Small, 1971; Jeffrey *et al.*, 1980) as well as a centrosymmetric space group (Hamilton, 1965), we decided to investigate the crystallization of pyrrolidone (2-pyrrolidone), (I).



(I)

While studying the thermal behaviour of (I) in the range 243–313 K by differential scanning calorimetry (DSC), we were intrigued to observe on heating that, prior to an endothermic transition at 293 K, there was an endothermic heat flow at 286 K, accounting for 13% of the energy absorbed. Cooling the sample to 173 K resulted in a reproducible retention of the endothermic transition at 286 K and disappearance of the endothermic transition at 293 K, even though the sample was heated to 303 K during each cycle (Fig. 1, top). Subsequently, we restricted the temperature range to 253–303 K and observed the gradual re-emergence of a small shoulder on the higher temperature side of the 286 K endothermic peak, but reversion to the original endothermic transition at 293 K did not occur. However, when a fresh sample was cooled to just 253 K, the endothermic transition at 285 K accounted for only 3% of the energy taken up at 297 K (Fig. 1, bottom). These observations indicate the presence of two distinct crystalline phases, with melting points of 286 and 297 K (Höhne *et al.*, 1996), and suggest that, once formed, the phase with the lower melting point is not readily converted into the higher melting-point phase. As the transition can take place in both directions (albeit slowly for the lower melting-point phase) and the thermodynamic transition temperature appears to lie below the melting point, the system is probably enantiotropic (Dunitz & Bernstein, 1995). Since a previous accurate calorimetric study gives the melting point of pure pyrrolidone crystals as 299.082 K (extrapolated to 100% purity) (Kolesov *et al.*, 1962), we decided to investigate the nature of the lower melting-point phase formed at low temperature. We describe here its crystal structure.

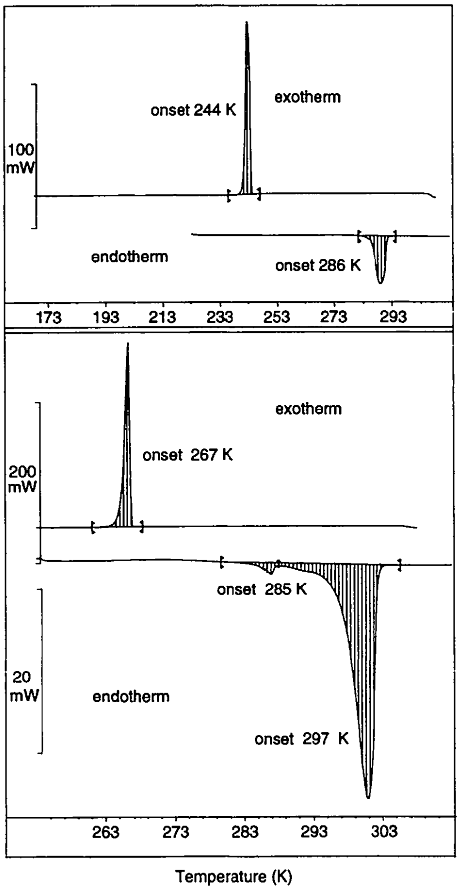


Fig. 1. DSC curves for pyrrolidone (ordinate, heat flow). Top: cooling and heating curves after the sample had been cooled to 173 K, showing a crystallization point at 244 K and a melting point at 286 K. Bottom: cooling and heating curves of a fresh sample of pyrrolidone in the range 253–303 K, showing a crystallization point at 267 K and melting points at 285 K (3%) and 297 K.

The molecular structure of (I) is shown in Fig. 2. Comparison of bond distances and angles within the ring (Table 2) with those of other lactams suggests that the ring is unstrained (Yang *et al.*, 1987). Indeed, the molecule adopts an approximate envelope geometry with the fold running from C3 to C5, and C4 at the apex. The remainder of the molecule [C3—N2—C1(O1)—C5] is approximately planar (r.m.s. deviation 0.0176 Å) and makes an angle of 23 (1)° to the C3—C4—C5 plane. This value is similar to that found in the gas phase for the related cyclopentene (23°; Laane & Lord, 1967), 1-pyrazoline (20°; Durig *et al.*, 1970) and dihydrofuran (19°; Green, 1969).

The molecules crystallize as centrosymmetric dimers, within which the molecules are held together by two N—H···O hydrogen bonds. The N2···O1^{i} [symmetry code: (i) $1-x$, $1-y$, $1-z$] distance of 2.922 (2) Å agrees well with the mean value of 2.92±0.07 Å found for N—H···O bonds in crystals of monoamides (Gavezzotti & Filippini, 1994), and in so far as can be determined, the hydrogen bond appears linear [N2—H2···O1 172 (3)°]. The small deviation from the energetically most favourable linear arrangement (Jeffrey & Saenger, 1991) indicates a relatively strong hydrogen-bonding interaction. The almost coplanar atoms C3—N2—C1(O1)—C5 and their symmetry equivalents C3^{i}—N2^{i}—C1^{i}(O1^{i})—C5^{i} do not lie exactly in a plane, but form parallel planes 0.39 (1) Å apart as a result of pyramidalization of the N atoms (see below). The packing of the molecules in the unit cell is dominated by the dimers, which stack to form columns that are themselves close-packed [packing coefficient 0.7509 (Kitaigorodsky, 1973)]. Within each column, the mean planes defined by the atoms C3, N2, C1, O1, C5, C3^{i}, N2^{i}, C1^{i}, O1^{i} and C5^{i} (r.m.s. deviation 0.07 Å) are tilted by 54° to the column axis (*a* axis) and separated by a perpendicular distance of 3.35 (2) Å.

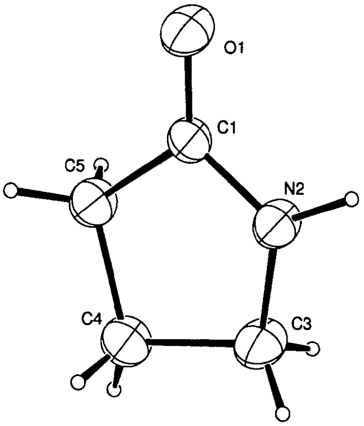


Fig. 2. View of the title molecule showing the atomic labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

The geometries of a hypothetical monomer and dimer were calculated by density functional theoretical methods using the B3LYP functional (Becke, 1993) with a 6-31G* basis set (Frisch *et al.*, 1996). Calculations for the monomer reveal the presence of a slight pyramidalization of the N atom such that the lone pair is on the same side of the ring as the apex atom C4 (deviation of N2 from the plane through C1, C3 and H2: 0.10 Å). The pyramidalization is reduced by hydrogen bonding in the dimer (deviation: 0.06 Å). A similar distortion can be inferred from the structure analysis if we consider the deviation of N2 from the plane through C1, C3 and O1^{i}, which is hydrogen bonded to N2. In the experiment, this is 0.1 Å (theory 0.08 Å). The C1—N2 distance in the crystal is 0.039 Å shorter and C1—O1 is 0.020 Å longer than the respective distances for the calculated monomer [C1—N2 1.374 and C1—O1 1.218 Å]; this mainly reflects the effect of the hydrogen bonding, since the differences are markedly reduced for the calculated dimer [0.017 (C1—N2) and −0.003 Å (C1—O1)]. The calculated N2···O1^{i} distance of 2.883 Å is, however, 0.04 Å too short. As a result, the hydrogen-bonding interaction is overemphasized and the calculated dimerization energy is probably too high ($\Delta E = -73.7$ kJ mol^{-1} at 0 K). A hydrogen-bonding energy of -31.8 kJ mol^{-1} has been experimentally determined for dimeric pyrrolidone in CCl_4 (Luck, 1991). This agrees well with the value of -28.9 kJ mol^{-1} estimated for ε-caprolactam (Aihara, 1960), which also forms centrosymmetric hydrogen-bonded dimers in the crystal (Oya & Myasnikova, 1974; Winkler & Dunitz, 1975), and corresponds to an energy of 15.9 kJ mol^{-1} per hydrogen bond, slightly larger than that measured for the pyrrolidone–*N*-methylpyrrolidone system, for which a value of 13.0 kJ mol^{-1} has been reported (Luck, 1968).

Since over 30 kJ mol^{-1} are released upon dimerization, it seems at first surprising that the phase containing the dimers is metastable, particularly in view of the fact that ε-caprolactam (seven ring atoms) (Oya & Myasnikova, 1974; Winkler & Dunitz, 1975) and β-propriolactam (four ring atoms) (Yang *et al.*, 1987) also crystallize as centrosymmetric dimers. However, in the case of acetamide it is the metastable phase that contains centrosymmetric dimers. Indeed, DSC measurements of acetamide show that the thermodynamically stable modification (space group *R*3*c*) melts at about 353 K and that on cooling from the melt, a metastable modification (space group *Pccn*) crystallizes first and this form melts at about 338 K (Höhne *et al.*, 1996). Thus, the stable phase crystallizes in a noncentrosymmetric space group. Its structure is characterized by a three-dimensional network of hydrogen bonds (Senti & Harker, 1940; Jeffrey *et al.*, 1980).

This raises the question as to the true nature of the high-temperature melting-point phase of pyrrolidone and whether it is chiral. The phase change may be caused by a simple change of symmetry of the dimer from C_i to C_2. B3LYP calculations show the C_2 structure to be 0.06 kJ mol^{-1} more stable with a barrier of only 3.2 kJ mol^{-1}. The 11 K change in melting point is, however, more likely caused by a rearrangement of the hydrogen bonds. The results of studies of the dielectric polarization of pyrrolidone in benzene as a function of temperature and concentration suggests a propensity to form dimers and tetramers (Jadzyn *et al.*, 1978), but the crystal structures of enantholactam (eight ring atoms) (Winkler & Seiler, 1979) and 4-*tert*-butyl-1-aza-2-cyclohexanone (six ring atoms) (Van der Helm & Ekstrand, 1979) contain infinite chiral chains. We are currently trying to obtain crystals.

Experimental

Commercial pyrrolidone (Aldrich) was purified by vacuum distillation at 0.5 Torr (1 Torr = 133.322 Pa) using a concentric tube column. The sample was 99.9% pure (gas chromatography). A crystal suitable for structure analysis was obtained from the cooled distillate and repeatedly dipped in liquid N_2 before mounting on the diffractometer, where it was cooled to 173 K by a cold stream of N_2 gas. Differential scanning calorimetry scans were measured on a Mettler–Toledo TA820 microcalorimeter, using the *STAR* system software (Mettler–Toledo, 1995). Details of the DSC scans: Fig. 1, top, 9.08 mg pyrrolidone, scan range 173–303 K, scan rate 5 K min^{-1}, second cycle, energy of exothermic transition -135 J g^{-1} (onset 244 K), energy of endothermic transition 167 J g^{-1} (onset 286 K); Fig. 1, bottom, 8.31 mg pyrrolidone, scan range 253–303 K, scan rate 5 K min^{-1}, second cycle, exothermic transition -140 J g^{-1} (onset 267 K), endothermic transition 4 J g^{-1} (onset 285 K), endothermic transition 150 J g^{-1} (onset 297 K).

Crystal data

C_4H_7NO
$M_r = 85.11$
Triclinic
$P\bar{1}$
$a = 4.901$ (2) Å
$b = 6.246$ (2) Å
$c = 7.748$ (3) Å
$\alpha = 85.86$ (2)°
$\beta = 73.20$ (3)°
$\gamma = 73.44$ (3)°
$V = 217.62$ (13) Å^3
$Z = 2$
$D_x = 1.299$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 16.6$–32.3°
$\mu = 0.094$ mm^{-1}
$T = 173$ K
Prism
0.35 × 0.28 × 0.28 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scan
Absorption correction: none
1346 measured reflections
1259 independent reflections
1057 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.085$
$\theta_{\rm max} = 29.92°$
$h = -6 \rightarrow 6$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 30 min
intensity decay: 10.7%

Refinement

Refinement on F^2
$R(F) = 0.066$
$wR(F^2) = 0.195$
$S = 1.273$
1259 reflections
83 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.119P)^2 + 0.0425P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.455$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.362$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
O1	0.6869 (3)	0.6959 (2)	0.3528 (2)	0.0345 (4)
N2	0.8495 (3)	0.3141 (2)	0.3611 (2)	0.0299 (4)
C1	0.8789 (3)	0.5163 (3)	0.3075 (2)	0.0255 (4)
C3	1.1197 (4)	0.1325 (3)	0.2970 (3)	0.0351 (4)
C4	1.3088 (4)	0.2387 (3)	0.1406 (2)	0.0331 (4)
C5	1.1884 (3)	0.4890 (3)	0.1815 (2)	0.0291 (4)

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.238 (2)	C3—C4	1.534 (2)
N2—C1	1.335 (2)	C4—C5	1.526 (2)
N2—C3	1.460 (2)	N1···O2^{i}	2.922 (2)
C1—C5	1.518 (2)		
C1—N2—C3	114.11 (13)	C5—C4—C3	104.30 (13)
O1—C1—N2	125.90 (14)	C1—C5—C4	104.35 (13)
O1—C1—C5	125.64 (14)	C1—N2···O1^{i}	116.0 (1)
N2—C1—C5	108.46 (13)	C1—O1···N2^{i}	117.5 (1)
N2—C3—C4	103.05 (13)		

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

All quantum-mechanical calculations were performed with the *GAUSSIAN*94 package (Frisch *et al.*, 1996). The B3LYP total energies for the monomer and dimer were −286.630098 and −573.288245 a.u., respectively. Non-H atoms were refined anisotropically and H atoms isotropically. The maximum residual electron density of 0.46 e Å^{-3} was situated midway between C1 and N2.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1995). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *DATAP* (Coppens *et al.*, 1965). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1205). Services for accessing these data are described at the back of the journal.

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Polysulfonylamines. C. Bis(4-nitrobenzenesulfonyl)amine Monohydrate†

OLIVER MOERS, PETER G. JONES* AND ARMAND BLASCHETTE

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de

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Abstract

In the title hydrate, $C_{12}H_9N_3O_8S_2.H_2O$, the disulfonylamine molecule adopts an elongated (open) conformation approximating to point group symmetry C_2. A short N—H···O*W* hydrogen bond [N···O*W* 2.716 (4) Å and N—H···O*W* 163 (3)°] connects the amine with the water molecule. In the molecular packing, formula units related *via* a translation of **b** are linked into stacks through an O*W*—H···O(S) hydrogen bond; the stacks

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† Part XCIX: Wirth *et al.* (1998).