(1957). Therefore, it is assumed that molecular deformations under pressure do not influence the experimental results.

The scaling of the translation and libration tensors by an average Grüneisen parameter cannot describe the changes of the thermal motion completely. If the average Grüneisen parameter is introduced as an additional adjustment parameter, the value of χ^2 drops from 54 to 15 [equation (1)] with $\bar{\gamma} = 6.63$. Therefore, it is supposed that the residual discrepancies between refinement and experimental data are caused mainly by insufficient correction of the thermal motion.

With a parameterized $\bar{\gamma}$ the angle between the long axis of the reference molecule and the vertical shows a decrease of about $0.1 (1)°$ at 0.5 GPa. The resulting coordinates of the C and H atoms deviate at most by $0.012 (16)$ and $0.017 (23)$ Å, respectively, from the values cited in Table 1. However, the striking reorientation of the molecule with pressure as shown in Fig. 4 is not influenced significantly due to these deviations.

The packing analyses give values of θ and ψ which agree with measurements up to 0.7 and $1.5°$ respectively, whereas φ deviates about $4°$. All parameter sets yield almost the same molecular orientation. The variations of φ and ψ with pressure are within the experimental errors, whereas the decrease of θ is slightly too small. We interpret the results of the model calculations as follows.

The main part of the intermolecular interactions is described correctly by all parameter sets used. In order to achieve complete agreement with the measured structure without any constraint on the lattice constants, the temperature must be included which gives rise to the thermal expansion of the lattice. In addition to the '6-exp' potential, representing essentially the van der Waals terms of the molecular interactions, further

contributions – for example, electrostatic multipole forces (Neto, Righini, Califano & Walmsley, 1978) – are to be considered.

References

ALMENNINGEN, A., BASTIANSEN, O. & DYVIK, F. (1961). Acta Cryst. 14, 1056–1065.
CRUICKSHANK, D. W. J. (1956). Acta Cryst. 9, 754–756.
CRUICKSHANK, D. W. J. (1957). Acta Cryst. 10, 504–508.
DOWS, D. A., HSU, L., MITRA, S. S., BRAFMAN, O., HAYEK, M., DANIELS, W. B. & CRAWFORD, R. K. (1973). Chem. Phys. Lett. 22, 595–599.
EL HAMAMSY, M., ELNAHWY, S., DAMASK, A. C., TAUB, H. & DANIELS, W. B. (1977). J. Chem. Phys. 67, 5501–5504.
GOLDSTEIN, H. (1963). Klassische Mechanik. Frankfurt am Main: Akademische Verlagsgesellschaft.
KITAIGORODSKY, A. (1966). J. Chim. Phys. Phys. Chim. Biol. 63, 9–16.
MCWEENY, R. (1951). Acta Cryst. 4, 513–519.
MIRSKAYA, K. V., KOZLOVA, I. E. & BEREZNITSKAYA, V. F. (1974). Phys. Status Solidi B, 62, 291–294.
NETO, N., RIGHINI, R., CALIFANO, S. & WALMSLEY, S. H. (1978). Chem. Phys. 29, 167–179.
NICOL, M., VERNON, M. & WOO, J. T. (1975). J. Chem. Phys. 63, 1992–1999.
PAWLEY, G. S. (1967). Phys. Status Solidi, 20, 347–360.
PAWLEY, G. S. & MIKA, K. (1974). Phys. Status Solidi B, 66, 679–686.
PAWLEY, G. S. & YEATS, E. A. (1969). Acta Cryst. B25, 2009–2013.
SCHMELZER, U. (1981). Thesis, Univ. of Bayreuth.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.
TADDEI, G., RIGHINI, R. & MANZELLI, P. (1977). Acta Cryst. A33, 626–628.
WHITMER, J. C., CYVIN, S. J. & CYVIN, B. N. (1978). Z. Naturforsch. Teil A, 33, 45–54.
WILLIAMS, D. E. (1967). J. Chem. Phys. 47, 4680–4684.
WILSON, A. J. C. (1965). Röntgenstrahl-Pulverdiffraktometrie: mathematische Theorie. Eindhoven: Centrex.

Structures of the Triclinic and Monoclinic Modifications of (2-Oxo-1-pyrrolidinyl)acetamide

BY G. ADMIRAAL, J. C. EIKELENBOOM AND AAFJE VOS

Department of Chemical Physics, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Abstract

$C_6H_{10}N_2O_2$ crystallizes in a triclinic (T) and a monoclinic (M) modification. T has space group $P\bar{1}$ with $a = 6.403 (3)$, $b = 6.618 (4)$, $c = 8.556 (6)$ Å, $\alpha = 79.85 (3)$, $\beta = 102.39 (3)$, $\gamma = 91.09 (3)°$, $Z = 2$. M has space group $P2_1/n$ with $a = 6.525 (2)$, $b = 6.440 (2)$, $c = 16.463 (5)$ Å, $\beta = 92.19 (3)°$, $Z = 4$. Least-squares refinement gave $R(T) = 5.8\%$ for 2499 and $R(M) = 6.4\%$ for 2435 independent reflections

measured at room temperature on a diffractometer with Zr-filtered Mo radiation ($\mu = 0\cdot114$ mm^{-1}). The planes of the non-H atoms of the pyrrolidone and acetamide groups are almost perpendicular to each other. In both structures the molecules form dimers *via* N—H$\cdots$O bonds between acetamide groups around an inversion centre. Successive dimers are linked together by further N—H$\cdots$O bonds to form chains. The chains are packed by van der Waals interactions. The two structures differ in the packing along **c**. For T successive dimers along **c** are translationally equivalent. In M the n glide planes transform the packing around (x,x,z) for $-\frac{1}{4} < z < \frac{1}{4}$ into a packing around $(x,\bar{x},z)$ for $\frac{1}{4} < z < \frac{3}{4}$, so that these two types of packing, which in T are in different planes, are observed on top of each other in M.

Introduction

(2-Oxo-1-pyrrolidinyl)acetamide is a drug which plays a part in learning processes. It enhances acquisition in rats, goldfish and man (Nickolson & Wolthuis, 1976, and references therein).

We have studied the crystal structure of (2-oxo-1-pyrrolidinyl)acetamide to obtain a better insight into the intermolecular interactions, especially the hydrogen bonding. Different types of hydrogen bonding exist in the two crystal modifications of unsubstituted acetamide. The stable form, rhombohedral acetamide, contains a three-dimensional network in which (.H—N—H$\cdots$O.)$_3$ rings can be recognized (Denne & Small, 1975). The metastable orthorhombic form has one-dimensional columns in which pairs of hydrogen-bonded acetamide molecules are linked together by hydrogen bonding to form chains (Hamilton, 1965). (2-Oxo-1-pyrrolidinyl)acetamide also crystallizes in two modifications, triclinic (T) and monoclinic (M). Both crystal structures have been determined, but no thermodynamic research on the relative stability of the two forms has been carried out.

Experimental

The compound was kindly provided by UCB, Netherlands. Crystals were grown by cooling a saturated solution in 2-propanol from 353 K to room temperature at a slow rate of 10 K per day. In one batch triclinic (T) and monoclinic (M) crystals were observed. The experimental work was carried out with a crystal $0\cdot6 \times 0\cdot5 \times 0\cdot5$ mm for T and $0\cdot6 \times 0\cdot6 \times 0\cdot6$ mm for M. The space groups were determined by inspection of Weissenberg photographs combined with a statistical analysis of the reflection intensities, which in both cases strongly indicated the space group to be centrosymmetric. Diffraction angles 2θ and reflection intensities $I(hkl)$ were measured on an automatic Nonius CAD-3 diffractometer with Zr-filtered Mo

radiation ($\lambda = 0\cdot71069$ Å). The cell dimensions were calculated from the 2θ values of 144 optimized reflections for T and 83 optimized reflections for M. Intensities were collected with the θ–2θ technique with scan angle $(0\cdot84 + 0\cdot69$ tg $\theta)°$ and counter width $1\cdot90°$. For T the measurement was restricted to the independent reflections up to $\theta = 35°$. For M the reflections hkl and $h\bar{k}l$ were measured up to $\theta = 35°$. Corrections were made for the variations observed for the three reference reflections ($\pm3\%$ for T and $\pm2\%$ for M) and for Lorentz and polarization effects. No correction for absorption was applied. The set for T contains 3012 independent reflections including 420 reflections with I(net) < 0. For M corrected intensities $I(hkl)$ and $I(h\bar{k}l)$ were averaged. The resulting set contains 3048 reflections including 417 reflections with I(average) < 0.

Structure determination

The structures were determined by direct methods with the program *MULTAN* (Germain, Main & Woolfson, 1971), and refined by least squares. All calculations were carried out on a Cyber 7416 with the programs of the XRAY system (1976). Isotropic temperature factors were considered for H and anisotropic temperature factors for the non-H atoms. Positions of H, which were all clearly indicated by $[F_o - F_c(\text{non-H})]$ maps, were constrained at C—H = $1\cdot08$ and N—H = $1\cdot001$ Å after C(N)—H directions had been determined from least-squares refinements in which r(H) was varied. The scattering factors for C, N and O were taken from Cromer & Mann (1968) and that for H from Stewart, Davidson & Simpson (1965). Reflections with I(net) < 0 and $|F_o| < 2\sigma(\text{count}; |F_o|)$ were not taken into account. For T the weighting scheme is $w = [\sigma^2(\text{count}; |F_o|) + 0\cdot0025|F_o|^2]^{-1}$ and for M, $w = [\sigma^2(\text{count}; |F_o|) + 0\cdot0015|F_o|^2]^{-1}$. For T a correction for extinction was made which amounts to

Table 1. *Fractional coordinates* ($\times 10^4$) *and* U_{eq} *values* (Å^2, $\times10^4$) *for the non-H atoms in the triclinic modification*

$U_{eq} = \frac{1}{3}\sum_i U_{ii}$, with U_{ii} taken from the diagonalized U tensor. For numbering see Fig. 1. Here and elsewhere in this paper standard deviations are given in parentheses in units of the last decimal places.

	x	y	z	U_{eq}
C(1)	−724 (2)	1318 (2)	−3314 (1)	303 (3)
C(2)	−1694 (3)	−625 (2)	−2569 (2)	403 (4)
C(3)	100 (3)	−2230 (3)	−2104 (2)	493 (5)
C(4)	2147 (3)	−1034 (3)	−2182 (2)	395 (4)
C(5)	2858 (2)	2611 (2)	−3445 (1)	310 (3)
C(6)	3822 (2)	3491 (2)	−1915 (1)	296 (3)
N(1)	1395 (2)	982 (2)	−3126 (1)	296 (2)
N(2)	5712 (2)	4376 (2)	−1911 (1)	393 (3)
O(1)	−1693 (2)	2934 (2)	−3994 (1)	448 (3)
O(2)	2842 (2)	3418 (2)	−816 (1)	439 (3)

2·5% in $|F|$ for the strongest reflection 002. For M no such correction was necessary. In this case five strong low-order reflections with too small intensities (presumably due to the large crystal dimensions with respect to the X-ray beam) were removed from the list. Final values for the refinement indices $R = [\sum |F_o| -$

$F_c|/\sum |F_o|]$ are 5·8% for 2499 independent reflections of T and 6·4% for 2435 independent reflections of M. The goodness-of-fit $G = [(\sum w|F_o - F_c|^2)/(N_o - N_v)]^{1/2}$ is 1·63 for T and 1·71 for M. Final parameters of the non-H atoms are listed in Table 1 for T and in Table 2 for M.*

Table 2. *Fractional coordinates* ($\times 10^4$) *and* U_{eq} *values* ($\mathring{A}^2$, $\times 10^4$) *for the non-H atoms in the monoclinic modification* (*see legend to Table* 1)

The numbering is given in Fig 2.

	x	y	z	U_{eq}
C(1)	80 (2)	656 (2)	−1665 (1)	295 (3)
C(2)	−1119 (2)	−1110 (2)	−1310 (1)	412 (4)
C(3)	469 (2)	−2684 (2)	−1005 (1)	476 (5)
C(4)	2560 (2)	−1620 (2)	−1076 (1)	379 (3)
C(5)	3679 (2)	1754 (2)	−1715 (1)	302 (3)
C(6)	4304 (2)	3005 (2)	−958 (1)	281 (3)
N(1)	2102 (1)	250 (2)	−1552 (1)	281 (3)
N(2)	6142 (2)	3921 (2)	−971 (1)	370 (3)
O(1)	−635 (1)	2218 (2)	−2010 (1)	425 (3)
O(2)	3122 (2)	3187 (2)	−395 (1)	423 (3)

Description of the structure

Schematic drawings of the molecules with bond lengths and angles and numbering scheme are given in Figs. 1 and 2. The molecules in the triclinic (T) and monoclinic (M) modifications are strongly similar. In each molecule two approximately planar parts can be distinguished for the non-H atoms: the plane C(1)C(2) C(3)C(4)C(5)N(1)O(1) for the pyrrolidone group and the plane C(5)C(6)N(2)O(2) for the acetamide group. Figs. 1 and 2 show the deviations of the atoms from the respective planes. The angles between the two planes

* Lists of structure factors, anisotropic thermal parameters for the non-H atoms and parameters for H have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36912 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
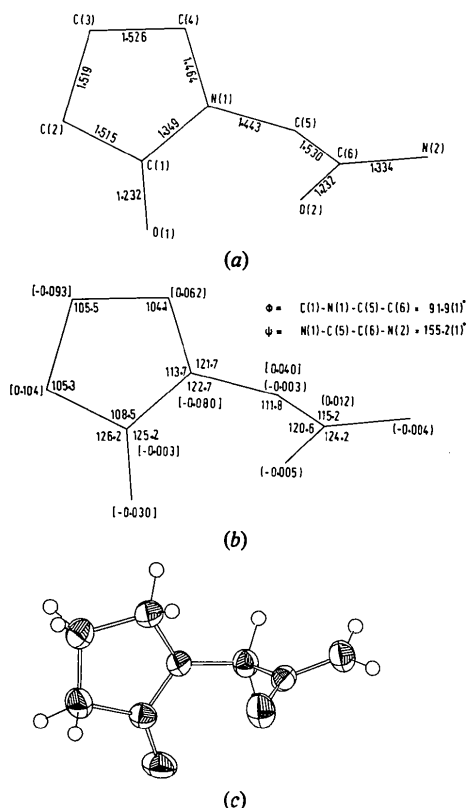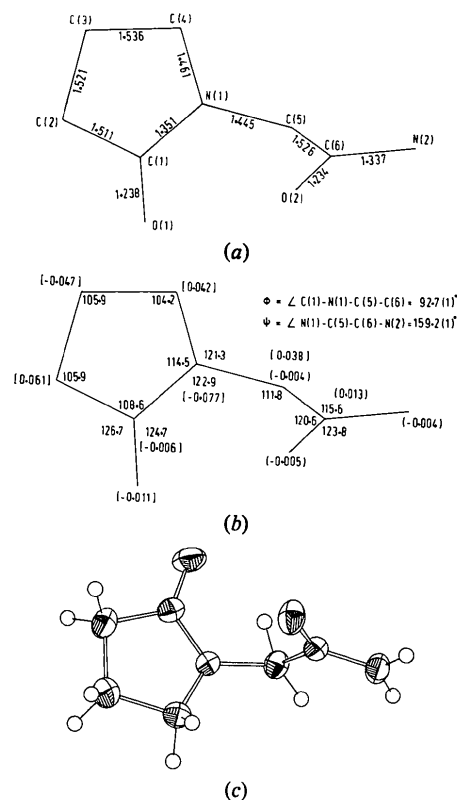

(a)

(b)

(c)

Fig. 1. Triclinic phase. Schematic drawing of the molecule with (a) numbering scheme and bond lengths (Å), and (b) valence angles (°) and distances to best least-squares plane C(1)C(2)C(3) C(4)C(5)N(1)O(1) in square brackets and to C(5)C(6)N(2)O(2) in parentheses (Å). E.s.d.'s are 0·002–0·004 Å in the distances and 0·2° for the angles. (c) Molecule with 50% probability plots for thermal ellipsoids.

(a)

(b)

(c)

Fig. 2. Monoclinic phase. Schematic drawing of the molecule. See legend to Fig. 1. E.s.d.'s are 0·002 Å in the distances and 0·1–0·2° in the angles. (c) Molecule with thermal ellipsoids at the 50% probability level.
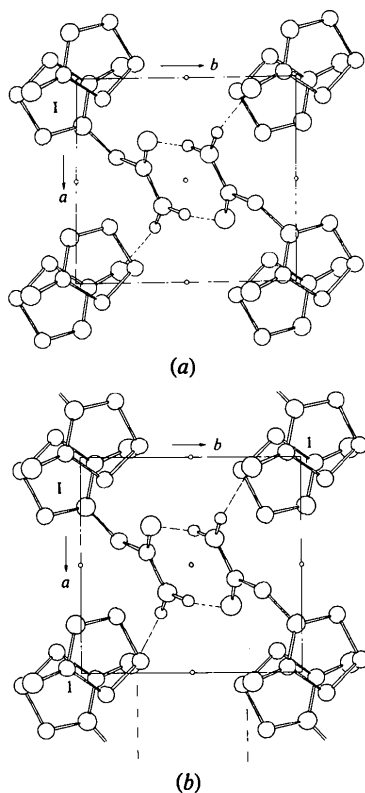
(a)

(b)

Fig. 3. (a) Triclinic phase. Projection on the *ab* plane along the normal to this plane. (b) Monoclinic phase. Projection on the *ab* plane along the normal to this plane of structure at $-\frac{1}{4} < z < \frac{1}{4}$. Molecule (I) corresponds to the coordinates of Table 1 for *T* or to the coordinates of Table 2 for *M*. Hydrogen bonds are shown by dashed lines.
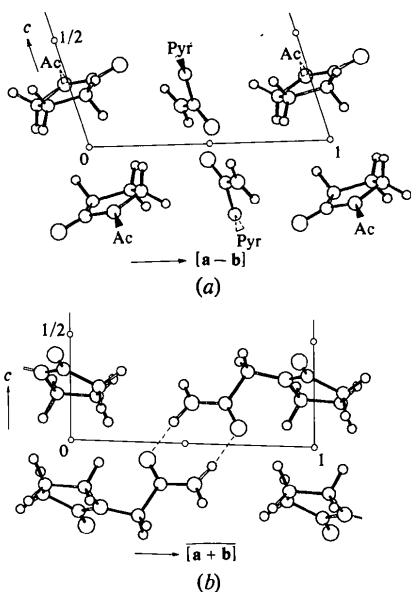

(a)

(b)

Fig. 4. Triclinic phase. (a) Projection along $[1\bar{1}0]$ of the structure between the planes $(x + \frac{1}{2}, \bar{x}, z)$ and $(x - \frac{1}{2}, \bar{x}, z)$. (b) Projection along $[1\bar{1}0]$ of the structure between the planes $(x, x - \frac{1}{2}, z)$ and $(x, x + \frac{1}{2}, z)$.

are approximately 90°, exact values being 89·8 (2)° for *T* and 88·3 (2)° for *M*. Details of the molecular geometry will be discussed below.

For *T* the projection on the *ab* plane is given in Fig. 3(a). Fig. 4(b) shows the projection along $[1\bar{1}0]$ of the packing around the plane (x,x,z) and Fig. 4(a) the projection along $[1\bar{1}0]$ of the packing around $(x,\bar{x},z)$. In the structure the molecules form dimers by two $N-H \cdots O$ hydrogen bonds around the inversion centre $(\frac{1}{2},\frac{1}{2},0)$. Successive dimers are linked together in chains along **a** by hydrogen bonds $N(2)-H \cdots O$ $(1; x + 1, y,$

Table 3. *Hydrogen bonding*

$(\frac{1}{2},\frac{1}{2},0)-P$ = distance of $(\frac{1}{2},\frac{1}{2},0)$ from plane $C(5)C(6)N(2)O(2)$; λ = $[N(1)C(4)C(3)C(2)C(1)O(1)] \wedge C(1)O(1)N(2; x - 1, y, z)$. Lengths in Å, angles in °. Standard deviations in distances or angles in which H is involved are estimated from refinements in which H was varied.

(a) Bond $N(2)-H(N2-2) \cdots O(2; 1 - x, 1 - y, -z)$

	T	*M*
$N \cdots O$	2·942 (2)	2·945 (2)
$N \cdots O-C$	121·82 (10)	123·08 (8)
$(\frac{1}{2},\frac{1}{2},0)-P$	0·20 (1)	0·21 (1)
$H \cdots O$	1·95 (2)	1·96 (2)
$N-H \cdots O$	169 (2)	170 (2)
$H \cdots O-C$	126 (1)	126 (1)

(b) Bond $N(2)-H(N2-1) \cdots O(1; 1 + x, y, z)$

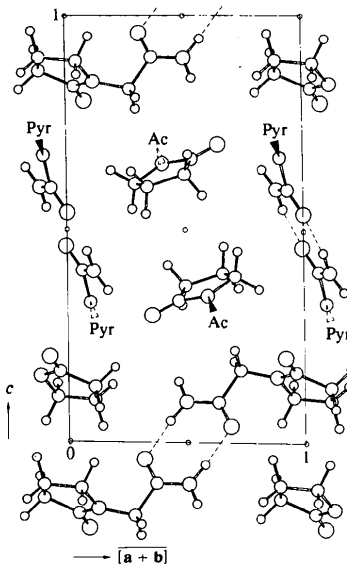|	*T*	*M*
$N \cdots O$	2·963 (2)	2·971 (2)
$N \cdots O-C$	111·34 (10)	107·31 (8)
λ	55·3 (1)	49·8 (1)
$H \cdots O$	2·00 (2)	2·03 (2)
$N-H \cdots O$	160 (2)	155 (2)
$H \cdots O-C$	118 (1)	115 (1)

Fig. 5. Monoclinic phase. Projection along $[1\bar{1}0]$ of the structure between the planes $(x, x - \frac{1}{2}, z)$ and $(x, x + \frac{1}{2}, z)$.

z). Along **b** and **c** the packing is by van der Waals interactions. None of the intermolecular distances between non-H atoms is significantly smaller than the relevant sum of the van der Waals radii + 0·2 Å [r(C) = 1·7, r(N) = 1·5, r(O) = 1·4 Å; Pauling, 1960]. Details of the hydrogen bonds are listed in Table 3.

Fig. 3(*b*), which illustrates the projection on the *ab* plane of the monoclinic structure at $-\frac{1}{4} < z < \frac{1}{4}$, is strongly similar to the projection on *ab* of the triclinic structure in Fig. 3(*a*). The packing of the layers along **c** is different, however, for the two phases. In *T* successive layers along **c** are translationally equivalent. In *M* successive layers along **c** are generated by the *n* glide plane. This glide operation transforms the packing around (*x,x,z*) for $-\frac{1}{4} < z < \frac{1}{4}$ into a packing around (*x,x̄,z*) for $\frac{1}{4} < z < \frac{3}{4}$. In the projection along [1 10] the two packings are thus observed on top of each other (Fig. 5). None of the intermolecular distances between non-H atoms is smaller than the relevant sum of the van der Waals radii + 0·2 Å. Details of the hydrogen bonds are listed in Table 3.

Discussion

Hydrogen bonding

Dimer formation *via* a ring system of six non-H atoms is quite common. It is favourable for angles N—H···O ≃ 180° (Luck, 1976). In the present case there are deviations of 11 (2)° from this idealized value (Table 3). Compounds with analogous dimer formation are the orthorhombic phase of acetamide (Hamilton, 1965), diethylpropionamide (DEPM) and dipropyl-propionamide (DPPM) (Cohen-Addad & D'Assenza, 1975). In Table 4 the geometries of amide CNO groups in different amides are compared. Participation in hydrogen bonding makes C—N shorter and C=O larger. This indicates that hydrogen bonding increases the resonance in the N—C=O fragment, in agreement with Ottersen's (1975) theoretical calculations.

The angles N—H···O of the hydrogen bonds linking the dimers into chains along **a** deviate by 20–25 (2)° from the value of 180° (Table 3*b*). The large value of

the dihedral angle λ shows that N(2) does not approach O(1) in the plane of its *sp*² lone-pair hybrids. Linkage of dimers into chains also occurs in amides C(R_1R_2H)—C(O)NH₂ which do not contain an O atom in the substituent R_1 or R_2. Examples are orthorhombic acetamide, DEPM and DPPM. In these cases each amide O atom acts as an acceptor for two H atoms. Amides of type C(R_1R_2H)—C(O)N(H)R_3 no longer form dimers, but still contain chains. Examples are *N*-methylacetamide (Katz & Post, 1960) and *N*-propyldipropylacetamide (Cohen-Addad & Grand, 1974).

The pyrrolidone groups

In both molecules the (H₂)C—C(H₂) bonds in the five-membered ring are almost eclipsed (Figs. 1 and 2). The average length for (H₂)C—C(H₂) is smaller than in cyclopentane [1·539 (3) Å; Almenningen, Bastiansen & Skancke, 1961], but equal to the average (H₂)C—C(H₂) value in 1-vinyl-2-pyrrolidinethione [1·520 (5) Å; Kálmán, Argay & Cser, 1976] and in ε-aminocaproic acid [1·519 (3) Å; Bodor, Bednowitz & Post, 1967]. In *T* where the ring is less planar than in *M*, the bond C(3)—C(4) is slightly shorter than in *M*. The trend that C(3)—C(4) is larger than C(3)—C(2) observed in both molecules also occurs in (2*S*,4*R*)-4-[(1*S*)-amino(carboxy)methyl]-5-oxo-2-pyrrolidine-carboxylic acid [1·531 (5) and 1·546 (5) Å; Dupont, Dideberg & Welter, 1975].

Apart from the difference in C(3)—C(4) the lengths of corresponding bonds in *T* and *M* are equal within experimental error. N(1)—C(4) has the same value as in 1-vinyl-2-pyrrolidinethione. The elongation with respect to N(1)—C(5) may be due to the strain in the five-membered ring. The relatively small value for C(1)—N(1) may be ascribed to conjugation of the lone-pair electrons of N(1) with the C=O group. C—O is somewhat larger than C=O in non-conjugated systems. For example the r_g value for C=O in acetone is 1·213 Å (gas electron diffraction; Iijima, 1972). The values of N—C and C=O lie close to those observed in peptides [average values: C—N = 1·325 (5), C=O =

Table 4. *Geometry of* CNO *groups in acetamides* (*Ac*) *and lengths and number of hydrogen bonds*

rh = rhombohedral, No. = number of hydrogen bonds to O of CNO. Lengths in Å, angles in °.

	Ac (gas)	T	M	DPPM	DEPM	Ac (rh)
C—O	1·220 (3)	1·231 (2)	1·234 (2)	1·242 (3)	1·235 (3)	1·243 (4)
C—N	1·380 (4)	1·334 (2)	1·337 (2)	1·319 (4)	1·321 (4)	1·336 (4)
O—C—N	122·0 (6)	124·1 (1)	123·8 (1)	122·0 (3)	121·6 (3)	122·3 (2)
N(H)···O	—	2·943 (3)	2·945 (2)	2·99	2·95	2·913 (3)
No.	0	1	1	2	2	2
Reference	(1)	(2)	(2)	(3)	(3)	(4)

References: (1) Kitano & Kuchitsu (1973); (2) Present paper; (3) Cohen-Addad & D'Assenza (1975); (4) Denne & Small (1975). for values at 108 K, *cf.* Ottersen (1975).

1·23 (1) Å; Momany, McGuire, Burgess & Scheraga, 1975].

The angles in the pyrrolidone ring obey the rule that repulsion between bonds increases with the bond orders. The N–C–C valence angle at C(5) is slightly larger than the tetrahedral value as is commonly observed for –C(H$_2$)– groups. In ε-aminocaproic acid C–C–N = 110·9 (4)°.

We thank Mr A. B. Verweij for growing the crystals and Mr R. Kloosterman for making the drawings. The computations were carried out at the computing centre of the University of Groningen.

References

ALMENNINGEN, A., BASTIANSEN, O. & SKANCKE, P. N. (1961). *Acta Chem. Scand.* **15**, 711–712.

BODOR, G., BEDNOWITZ, A. L. & POST, B. (1967). *Acta Cryst.* **23**, 482–490.

COHEN-ADDAD, C. & D'ASSENZA, G. (1975). *Acta Cryst.* **B31**, 835–841.

COHEN-ADDAD, C. & GRAND, A. (1974). *Acta Cryst.* **B30**, 1342–1346.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

DENNE, W. A. & SMALL, R. W. H. (1975). *Acta Cryst.* **B27**, 1094–1098.

DUPONT, L., DIDEBERG, O. & WELTER, A. (1975). *Acta Cryst.* **B31**, 1018–1022.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 866–870.

IIJIMA, T. (1972). *Bull. Chem. Soc. Jpn*, **45**, 3526–3530.

KÁLMÁN, A., ARGAY, GY. & CSER, F. (1976). *Acta Cryst.* **B32**, 2672–2674.

KATZ, J. L. & POST, B. (1960). *Acta Cryst.* **13**, 624–628.

KITANO, M. & KUCHITSU, K. (1973). *Bull. Chem. Soc. Jpn*, **46**, 3048–3051.

LUCK, W. A. P. (1976). *The Hydrogen Bond*, Vol. II, pp. 527–562. Amsterdam: North-Holland.

MOMANY, F. A., McGUIRE, R. F., BURGESS, A. W. & SCHERAGA, H. A. (1975). *J. Phys. Chem.* **79**, 2361–2381.

NICKOLSON, V. J. & WOLTHUIS, O. T. (1976). *Brain Res.* **113**, 616–619.

OTTERSEN, T. (1975). *Acta Chem. Scand. Ser. A*, **29**, 939–944.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell Univ. Press.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

XRAY system (1976). Dutch version of the XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Struktur von Naphtho[2,3-c][1,2,5]thiadiazol-4,9-dion und der homologen Se-Verbindung Naphtho[2,3-c][1,2,5]selenadiazol-4,9-dion

VON ALFRED GIEREN UND VIKTOR LAMM

Max-Planck-Institut für Biochemie, Abteilung Strukturforschung I, 8033 Martinsried bei München, Bundesrepublik Deutschland

Abstract

C$_{10}$H$_4$N$_2$O$_2$S (1) crystallizes in the monoclinic space group $P2_1/c$ with $a = 16·072$ (5), $b = 8·295$ (3), $c = 13·740$ (12) Å, $\beta = 107·38$ (5)°, $Z = 8$; there are also two other modifications. C$_{10}$H$_4$N$_2$O$_2$Se (2) crystallizes in the monoclinic space group $P2_1$ with $a = 3·885$ (1), $b = 7·319$ (3), $c = 15·156$ (4) Å, $\beta = 92·14$ (2)°, $Z = 2$. The structure of (1) has been determined by direct methods and that of (2) by Patterson and successive Fourier syntheses. The refinement converged for (1) to $R(w) = 0·041$ with 1868 independent reflections collected by an automatic diffractometer and for (2) to $R(w) = 0·042$ for 811 reflections. Both molecules show a significant π interaction of the chalcogen diimide moiety with the π system of the condensed 1,4-naphthoquinone system. The S–N distances are 1·619 (2) Å and the Se–N distances 1·800 (6) Å on average. The π-bond order of the S–N bonds is somewhat increased in comparison with the Se–N bonds, and in correlation the π interaction of the chalcogen diimide fragment in (1) with the substituting 1,4-naphthoquinone system is diminished. The π-bond orders of the chalcogen–nitrogen bonds are also correlated with the length of short S···O and Se···O contact distances [S···O 3·095 (4), 3·146 (4) Å; Se···O 2·945 (6) Å] occurring in the crystal structure.