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# The Structure of 7-Methyl-1,4-dithia-7-azaspiro[4.4]nonane-6,8-dione

By W. Dobrowolska and M. Bukowska-Strzyżewska

*Institute of General Chemistry, Technical University, 36 Żwirki, 90-924 Łódź, Poland*

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## Abstract

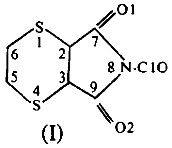
7-Methyl-1,4-dithia-7-azaspiro[4.4]nonane-6,8-dione, $C_7H_9NO_2S_2$, crystallizes in the monoclinic system, with $a = 9{\cdot}42\ (2)$, $b = 7{\cdot}33\ (2)$, $c = 25{\cdot}74\ (2)$ Å, $\beta = 93{\cdot}0\ (5)^\circ$, space group $P2_1/c$, $Z = 8$. The structure was solved from three-dimensional X-ray data by direct methods and refined by least squares to a final $R = 0{\cdot}085$ for 1413 reflections. Crystals of $C_7H_9NO_2S_2$ contain two different types of molecules, differing in the conformation of the five-membered 1,4-ditholane rings: the conformation is either almost an ideal envelope $[\Delta C_s(3) = 0{\cdot}5^\circ]$ or a deformed half-chair $[\Delta C_2(12) = 7{\cdot}1^\circ]$. The imide rings are not ideally planar within the error limits.

## Introduction

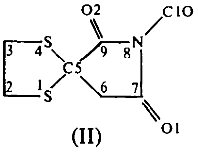
The structure of 7-methyl-1,4-dithia-7-azaspiro[4.4]-nonane-6,8-dione has been investigated as part of a study of the structures of *N*-substituted derivatives of 5,6-dihydro-1,4-dithiin-2,3-dicarboximide and 1,4-dithiane-2,3-dicarboximide, obtained at the University of Łódź (Hahn & Rybczyński, 1971, 1976).

It was assumed that the crystals investigated were the geometric isomers of *N*-methyl-*p*-dithiane-2,3-dicarboximide and that they differed in the *cis*, *trans* positions of the H atoms of C atoms joining the dithiane and imide rings.

The isomerism observed here appeared to be structural and not geometric. The numbering of the atoms and the structural formulae of both isomers are given below. (Note that the numbering shown differs from that used to name the compound.)



(I)



(II)

The present paper describes the structure of (II). This structure investigation revealed a new type of transformation (I → II), the conformations of both heterocyclic five-membered rings and their mutual configuration.

## Experimental

The title compound crystallizes from methanol in the monoclinic system. The cell dimensions were determined from Weissenberg photographs. The density of the crystal was measured by the flotation method in a mixture of benzene and $CH_3I$.

### *Crystal data*

$C_7H_9NO_2S_2$, monoclinic, $P2_1/c$, $a = 9{\cdot}42\ (2)$, $b = 7{\cdot}33\ (2)$, $c = 25{\cdot}74\ (2)$ Å, $\beta = 93{\cdot}0\ (5)^\circ$, $V = 1774{\cdot}82$ Å$^3$, $D_x = 1{\cdot}52$, $D_m = 1{\cdot}47$ Mg m$^{-3}$, $Z = 8$, $F(000) = 848$, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 4{\cdot}94$ mm$^{-1}$. Intensity data were collected by means of a multiple-film pack on a Weissenberg camera. The intensities were visually estimated with a calibrated intensity scale. No absorption correction was made.

## Determination of the structure

The structure was solved by the symbolic addition procedure using programs of the XRAY 70 system (Steward, Kundell & Baldwin, 1970) on a RIAD 22 computer.

Four S atoms were located from the *E* map. The positions of the remaining atoms were determined by successive Fourier syntheses. Refinement of the positional parameters, isotropic temperature factors and scale factors was carried out by the block-diagonal least-squares method (program *CRYLSQ* of the XRAY 70 system). *R* was reduced to 10·5%. Anisotropic refinement of temperature factors further reduced *R* to 8·5%. Form factors for neutral C, N, O and S atoms were taken from Doyle & Turner (1968) and for H atoms from *International Tables for X-ray Crystallography* (1962). The final positional parameters with their estimated standard deviations are listed in Table 1.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34685 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional* (×10$^4$) *and thermal parameters for the title compound, with e.s.d.'s in parentheses*

The positional parameters correspond to the anisotropic refinement. The isotropic temperature factors are from the last cycle of isotropic refinement with $R = 0{\cdot}105$.

| | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| S(1) | −1711 (3) | 3162 (3) | 742 (1) | 3·10 (8) |
| S(4) | 1184 (3) | 3262 (3) | 1188 (1) | 3·46 (9) |
| S(11) | 5320 (4) | −167 (3) | 1076 (1) | 4·09 (10) |
| S(14) | 3740 (3) | −3003 (3) | 516 (1) | 3·57 (9) |
| O(1) | −1759 (8) | 6043 (9) | 2453 (2) | 4·0 (2) |
| O(2) | −237 (8) | 7150 (8) | 835 (2) | 3·7 (2) |
| O(11) | 2001 (8) | −3504 (9) | 2210 (2) | 4·9 (3) |
| O(12) | 6070 (8) | −4394 (10) | 1365 (2) | 4·7 (3) |
| N(8) | −944 (8) | 6982 (9) | 1675 (2) | 2·5 (2) |
| N(18) | 4125 (9) | −4241 (10) | 1859 (3) | 3·9 (3) |
| C(2) | −445 (12) | 1912 (13) | 387 (3) | 4·0 (3) |
| C(3) | 1008 (12) | 2860 (14) | 493 (3) | 4·2 (4) |
| C(5) | −559 (10) | 4140 (10) | 1266 (3) | 2·0 (2) |
| C(6) | −1116 (11) | 3796 (11) | 1816 (3) | 2·7 (3) |
| C(7) | −1345 (10) | 5641 (11) | 2038 (3) | 2·3 (3) |
| C(9) | −546 (11) | 6251 (11) | 1212 (3) | 2·7 (3) |
| C(10) | −1017 (12) | 8987 (11) | 1772 (3) | 3·5 (3) |
| C(12) | 6213 (11) | −1095 (13) | 515 (3) | 3·6 (3) |
| C(13) | 5586 (12) | −2808 (13) | 295 (3) | 4·0 (3) |
| C(15) | 4211 (11) | −2174 (11) | 1156 (3) | 2·8 (3) |
| C(16) | 2865 (11) | −1727 (13) | 1481 (3) | 3·7 (3) |
| C(17) | 2878 (11) | −3211 (12) | 1891 (3) | 2·9 (3) |
| C(19) | 4985 (12) | −3695 (13) | 1458 (3) | 3·8 (3) |
| C(20) | 4499 (13) | −5864 (15) | 2223 (4) | 4·9 (4) |

Table 2. *Bond lengths* (Å)

| | | | |
|---|---|---|---|
| S(1)—C(2) | 1·791 (11) | S(11)—C(12) | 1·838 (10) |
| S(1)—C(5) | 1·833 (8) | S(11)—C(15) | 1·823 (10) |
| S(4)—C(3) | 1·814 (9) | S(14)—C(13) | 1·873 (12) |
| S(4)—C(5) | 1·784 (10) | S(14)—C(15) | 1·791 (8) |
| C(2)—C(3) | 1·547 (16) | C(12)—C(13) | 1·487 (14) |
| C(5)—C(6) | 1·556 (11) | C(15)—C(16) | 1·589 (14) |
| C(5)—C(9) | 1·554 (12) | C(15)—C(19) | 1·523 (13) |
| C(6)—C(7) | 1·488 (12) | C(16)—C(17) | 1·515 (12) |
| C(7)—N(8) | 1·422 (10) | C(17)—N(18) | 1·402 (13) |
| C(9)—N(8) | 1·375 (10) | C(19)—N(18) | 1·403 (13) |
| C(10)—N(8) | 1·492 (11) | C(20)—N(18) | 1·544 (13) |
| C(7)—O(1) | 1·193 (10) | C(17)—O(11) | 1·215 (12) |
| C(9)—O(2) | 1·222 (10) | C(19)—O(12) | 1·179 (14) |

Table 3. *Bond angles* (°)

| | | | |
|---|---|---|---|
| C(2)—S(1)—C(5) | 101·0 (5) | C(12)—S(11)—C(15) | 94·5 (4) |
| C(3)—S(4)—C(5) | 97·6 (5) | C(13)—S(14)—C(15) | 93·4 (5) |
| S(1)—C(2)—C(3) | 106·7 (7) | S(11)—C(12)—C(13) | 115·0 (7) |
| C(2)—C(3)—S(4) | 106·3 (7) | C(12)—C(13)—S(14) | 107·9 (7) |
| S(4)—C(5)—C(9) | 109·8 (6) | S(14)—C(15)—C(19) | 108·2 (6) |
| S(1)—C(5)—C(6) | 106·8 (4) | S(11)—C(15)—S(14) | 106·8 (4) |
| S(1)—C(5)—C(6) | 113·0 (6) | S(11)—C(15)—C(16) | 111·8 (6) |
| C(6)—C(5)—C(9) | 104·3 (6) | C(16)—C(15)—C(19) | 104·9 (7) |
| S(4)—C(5)—C(6) | 113·6 (6) | S(14)—C(15)—C(16) | 112·6 (7) |
| S(1)—C(5)—C(9) | 109·3 (5) | S(11)—C(15)—C(19) | 112·7 (7) |
| C(5)—C(6)—C(7) | 105·4 (6) | C(15)—C(16)—C(17) | 103·9 (8) |
| C(6)—C(7)—O(1) | 129·0 (8) | C(16)—C(17)—O(11) | 128·1 (9) |
| C(6)—C(7)—N(8) | 109·1 (7) | C(16)—C(17)—N(18) | 108·8 (8) |
| O(1)—C(7)—N(8) | 121·9 (7) | O(11)—C(17)—N(18) | 123·2 (8) |
| C(7)—N(8)—C(9) | 113·2 (7) | C(17)—N(18)—C(19) | 114·1 (8) |
| C(7)—N(8)—C(10) | 123·7 (7) | C(17)—N(18)—C(20) | 123·0 (8) |
| C(9)—N(8)—C(10) | 123·0 (7) | C(19)—N(18)—C(20) | 123·0 (9) |
| C(5)—C(9)—N(8) | 107·9 (6) | C(15)—C(19)—N(18) | 107·7 (9) |
| C(5)—C(9)—O(2) | 127·7 (7) | C(15)—C(19)—O(12) | 127·8 (9) |
| O(2)—C(9)—N(8) | 124·4 (8) | O(12)—C(19)—N(18) | 124·4 (9) |

## Results and discussion

### Molecular structure

In the crystals of 7-methyl-1,4-dithia-7-azaspiro[4.4]nonane-6,8-dione two structurally different molecules can be observed. The differences are seen in the conformations of the five-membered 1,4-ditholane rings. In one type of molecule the ring has the conformation of an almost ideal envelope, whereas in the other it is a slightly deformed half-chair. The imide rings in both molecules are slightly corrugated. The dithiolane and imide rings are connected through a common carbon atom [C(5)].

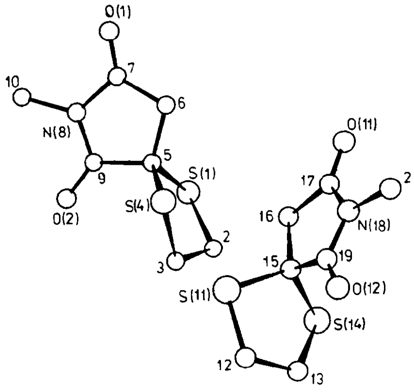


Fig. 1. A view of the two symmetrically independent molecules.

A projection of the two symmetrically independent molecules is presented in Fig. 1.

Bond lengths and angles (with standard deviations in parentheses) are listed in Tables 2 and 3.

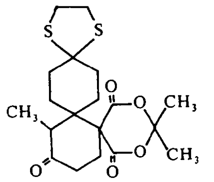
### The 1,4-*dithiacyclopentane rings*

S—C($sp^3$) bond lengths for molecule (II*a*) are 1·784 (10), 1·833 (8), 1·791 (11), 1·814 (9) Å, and for molecule (II*b*) 1·791 (8), 1·823 (10), 1·838 (10), 1·873 (12) Å. Except for the clearly elongated bond S(14)—C(13) = 1·873 (12) Å in molecule (II*a*), the values are similar to those for analogous bonds in other known structures, where they range from 1·770 (30) to 1·843 (2) Å (Montgomery, 1960; Kalff & Romers, 1965, 1966; Marsh, 1955; Carey, Smith, Maher & Bryan, 1977; McPhail, Onan & Koskimies, 1976; Bukowska-Strzyżewska & Pniewska, 1979*a*,*b*; Chao & McCullough, 1960; Kobayashi & Iitaka, 1977).

Valency angles at S atoms for molecule (II*a*) are 97·6 (5) and 101·0 (5)°, while in molecule (II*b*) they are evidently smaller: 93·4 (5) and 94·5 (4)°.

The angles between the four bonds formed by carbon atoms common to both rings range from 104·3 (6) to 113·6 (6)° for molecule (II*a*) and from 104·9 (7) to 112·6 (7)° for molecule (II*b*). They are, therefore, clearly deformed, but their mean values almost ideally correspond to tetrahedral angles.

S—S intramolecular distances are 2·904 (7) and 2·900 (6) (Å). They are clearly shorter than the S—S distance [2·940 (2) Å] found by Jones & Kennard (1977) in the dithiacyclopentane ring of 12,12,18-trimethyl-11,13-dioxa-1,4-dithiatrispiro[4.2.0.5.4.2]-icosane-10,14,17-trione (III), having the conformation of a strongly deformed envelope.



(III)

Fig. 2 presents torsion angles of the dithiacyclopentane rings in molecules (II*a*) and (II*b*), as compared with the torsion angles of the same ring in molecule (III) defined by Jones & Kennard (1977).

The rings in molecules (II*a*) and (III) have the conformation of an envelope with C(3) deviating from the plane of the four atoms. Asymmetry parameters (Duax & Norton, 1975) of the rings in relation to the plane of symmetry through C(3) and the centre of the S(1)—C(5) bond for rings (II*a*) and (III) are 0·51 and 6·58° respectively. Thus, in the structure studied, the conformation of an almost ideal envelope is present with a dihedral angle between the S(4)—C(5)—S(1)—C(2) and S(4)—C(2)—C(3) planes of 46·09°, and the deviation of C(3) from the S(4)—C(5)—S(1)—C(2) plane being 0·722 Å.

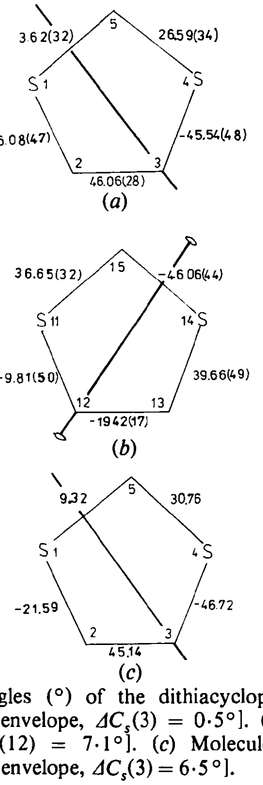


Fig. 2. Torsion angles (°) of the dithiacyclopentane rings. (*a*) Molecule (II*a*) [envelope, $\Delta C_s(3) = 0.5°$]. (*b*) Molecule (II*b*) [half-chair, $\Delta C_2(12) = 7.1°$]. (*c*) Molecule (III) (Jones & Kennard, 1977) [envelope, $\Delta C_s(3) = 6.5°$].

Table 4. *Least-squares planes of the imide rings and deviations of the atoms from the planes*

The equation of the plane in molecule (II*a*) is:

$$0.9246X - 0.0016Y + 0.3809Z = 0.5766.$$

The equation of the plane in molecule (II*b*) is:

$$0.4731X + 0.6388Y + 0.6067Z = 2.6367.$$

Distances of the atoms from the planes (Å)

| Molecule (II*a*) | | Molecule (II*b*) | |
|---|---|---|---|
| C(5) | 0·014 (9) | C(15) | −0·049 (10) |
| C(6) | −0·001 (10) | C(16) | 0·047 (10) |
| C(7) | −0·013 (10) | C(17) | −0·029 (10) |
| C(9) | −0·024 (8) | C(19) | 0·035 (11) |
| N(8) | 0·024 (10) | N(18) | −0·004 (10) |
| C(10)* | 0·041 (11) | C(20)* | −0·053 (13) |
| O(1)* | −0·019 (9) | O(11)* | −0·080 (8) |
| O(2)* | −0·078 (7) | O(12)* | 0·052 (9) |

* Not included in the calculations of the planes.

The conformation of the 1,4-dithiacyclopentane ring in molecule (II*b*) is clearly different: it has the conformation of a deformed half-chair, with the asymmetry parameter in relation to a twofold axis through C(12) and the centre of the S(14)—C(15) bond being 7·12°.

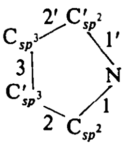
The reduction of valency angles at the S atoms below 95° and the lengthening of one C—S bond observed in molecule (II*b*) are probably due to the tendency to increase the distance between S atoms in the ring. Different conformations of 1,4-dithiacyclopentane rings in the crystals studied indicate a small energy barrier between the two conformations: half-chair and envelope.

### *Imide rings*

From the accuracy obtained in the location of the atoms, the imide rings cannot be considered ideally planar. Their calculated $\chi^2 = \sum d^2/\sigma^2$ values are 17·93 and 64·70 respectively. This corresponds to the probability $p < 0.01$ that the ideally planar ring would give such a high $\chi^2$ value.

Table 4 presents the equations of the best planes of the rings in (II*a*) and (II*b*), and the deviations of the atoms from them. O(2) deviates most strongly from the imide ring of (II*a*), whereas in (II*b*) O(11) deviates most.

Table 5. *Torsion angles* (°) *in the imide rings*



1: $C'_{sp^2}$—N—$C_{sp^2}$—$C_{sp^3}$
2: N—$C_{sp^2}$—$C_{sp^3}$—$C'_{sp^3}$
3: $C_{sp^2}$—$C_{sp^3}$—$C'_{sp^3}$—$C'_{sp^2}$

2′: $C_{sp^3}$—$C'_{sp^3}$—$C'_{sp^2}$—N
1′: $C'_{sp^3}$—$C'_{sp^2}$—N—$C_{sp^2}$

$\Delta(n)$ are asymmetry parameters in relation to the symmetry element through the centre of bond $n$.

| | Torsion angles (°) | | | | | Asymmetry parameters (°) | $\lvert\varphi_{av}\rvert$ (°) | Reference |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 2′ | 1′ | | | |
| $C_{10}H_9NO_2$ | 2·19 | 0·16 | 2·14 | 3·47 | 3·67 | $\Delta C_s(2) = 0·15$ | 2·33 | (1) |
| $C_4H_5NO_2$ | 7·50 | 1·13 | 2·77 | 1·24 | 4·26 | $\Delta C_2(3) = 2·29$ | 3·38 | (2) |
| $C_{11}H_{12}N_2O_2.H_2O$ | 5·79 | 9·76 | 9·80 | 7·08 | 0·95 | $\Delta C_s(1') = 0·91$ | 6·68 | (3) |
| $C_7H_9NO_2S_2$ (isomer I) | 4·83 | 5·60 | 4·51 | 2·08 | 1·69 | $\Delta C_2(2) = 0·35$ | 3·74 | (4) |
| $C_7H_9NO_2S_2$ (isomer II) | | | | | | | | |
| Molecule (II*a*) | 3·84 (54) | 1·33 (42) | 1·23 (47) | 3·46 (44) | 4·80 (49) | $\Delta C_2(1') = 0·27$ | 2·93 | This work |
| Molecule (II*b*) | 2·12 (57) | 6·37 (47) | 8·05 (51) | 7·13 (49) | 3·42 (53) | $\Delta C_2(3) = 1·06$ | 5·42 | |

References: (1) Argay & Kálmán (1973); (2) Mason (1961); (3) Argay, Simon & Kálmán (1974); (4) Dobrowolska & Bukowska-Strzyżewska (1980).

Table 5 compares the geometry of corrugation of the five-membered imide rings in molecules of (II*a*) and (II*b*) with their corrugation in other known structures; in addition to the values of the torsion angles are given the asymmetry parameters in relation to the predominant elements of symmetry, and the mean value of the torsion angles $\lvert\varphi_{av}\rvert$ determining the degree of corrugation of the ring. The conformation of the rings can be described as a strongly flattened half-chair or an envelope. From the six rings of this type presented in Table 5, four imide rings reveal the presence of a twofold axis through the N atom and the centre of bond 3 or through C($sp^3$) and the centre of bond 1. Two imide rings indicate the presence of a symmetry plane through a C($sp^2$) atom and the centre of bond 2 or through a C($sp^3$) atom and the centre of bond 1. From the data in Table 5 it follows that the manner of deformation of an imide ring can be very different. The geometry of the ring investigated here in two independent molecules confirms various possibilities for its corrugation.

### *Intermolecular interactions*

Fig. 3 presents the molecular packing in the unit cell. Table 6 presents the shortest intermolecular distances. Atom 1 is the one in the asymmetric part of a unit cell and atom 2 is that transformed by a given symmetry operation. As follows from Table 6, the shortened van der Waals distance [2·914 (12) Å] is observed only between C(7) and O(12) atoms from adjacent molecules. This may influence the corrugation of the imide rings and the deviations of O atoms from their best plane.

Table 6. *Shortest intermolecular distances* (Å)

| | | Symmetry operation | |
|---|---|---|---|
| S(1) | O(12) | $x-1, y+1, z$ | 3·241 (9) |
| O(12) | C(7) | $x+1, y-1, z$ | 2·914 (12) |
| N(8) | O(11) | $x, y+1, z$ | 3·053 (12) |
| S(4) | C(17) | $x, y+1, z$ | 3·493 (11) |
| S(4) | N(18) | $x, y+1, z$ | 3·675 (10) |
| N(18) | C(20) | $1-x, 0·5 \pm y, 0·5-z$ | 3·616 (14) |
| C(6) | C(10) | $x, y \pm 1, z$ | 3·529 (15) |
| S(14) | S(1) | $-x, -y, -z$ | 3·671 (4) |
| O(1) | O(12) | $x-1, y+1, z$ | 3·396 (10) |

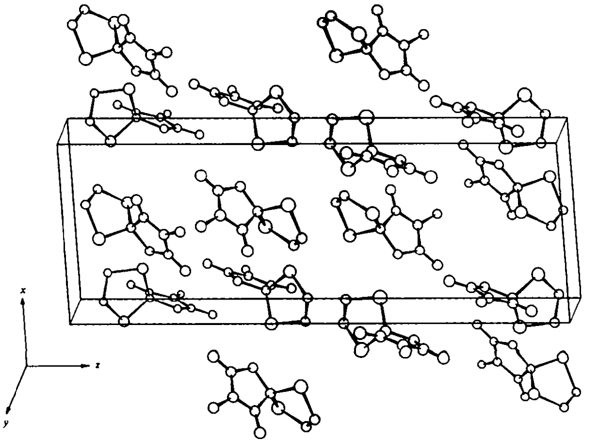


Fig. 3. The molecular packing.

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# Conformations et Interactions Moléculaires à l'Etat Solide de la Pivaloyl-D-alanyl-*N*-isopyropyl-D-prolinamide Monohydratée

PAR A. AUBRY ET J. PROTAS

*Laboratoire de Minéralogie et Cristallographie, Equipe de Recherche associée au CNRS n°* 162, *Université de Nancy* I, *Case Officielle n°* 140, 54037 *Nancy CEDEX, France*

ET G. BOUSSARD ET M. MARRAUD

*Laboratoire de Chimie Physique Macromoléculaire, Equipe de Recherche associée au CNRS n°* 23, *ENSIC,* 1 *rue Grandville,* 54000 *Nancy CEDEX, France*

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## Abstract

$C_{16}H_{29}N_3O_3.H_2O$ (grown from ethyl acetate), $M_r$ = 329, orthorhombic, $P2_12_12_1$, $a$ = 11·976 (1), $b$ = 16·978 (2), $c$ = 18·457 (3) Å, $V$ = 3753 Å$^3$, $D_{calc}$ = 1·16 Mg m$^{-3}$, $Z$ = 8. There are two independent molecules in the asymmetric unit. The final reliability index $R$ is 0·058 with 3508 reflexions. Molecular conformations show opened forms which are stabilized by hydrogen bonds.

## Introduction

On sait le rôle important que joue la proline dans le repliement des chaînes peptidiques au sein des protéines (Chou & Fasman, 1977). A partir de cette donnée, nous avons entrepris l'examen conformationnel des séquences dipeptidiques contenant le résidu proline et protégées aux deux extrémités par deux fonctions amides.

Nous avons déjà décrit les modes de repliement adoptés par les séquences L-Pro-L-Ala et L-Pro-D-Ala à l'état solide (Aubry, Protas, Boussard & Marraud, 1977) et en solution dans un solvant organique inerte (Boussard, Marraud & Néel, 1974). Dans une communication précédente, nous avons aussi caractérisé la forme repliée de la séquence D-Ala-L-Pro à l'état solide (Aubry, Protas, Boussard & Marraud, 1979) qui est aussi le conformère majoritaire en solution dans un solvant organique inerte (Boussard, Marraud & Aubry, 1979).

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