The asymmetric unit contains two crystallographically unique molecules *A* and *B* (Fig. 1). These independent molecules are alternately arranged parallel to the (10$\bar{1}$) plane and are linked by hydrogen bonds between one of the cyclic N atoms and a neighbouring amino H atom (Fig. 1 and Table 2). Both molecules exhibit almost complete C_{2v} symmetry. Recently we reported the structure of 2,5-diamino-3*H*-1,3,4-thiadiazolinium chloride monohydrate (Senda, Matsuoka & Maruha, 1986), in which the cation no longer possesses C_{2v} symmetry because an H atom is attached to one of the two endocyclic N atoms. The distances and angles in *A* and *B* are almost equal to each other (Table 2), and are in good agreement with those in unsubstituted 1,3,4-thiadiazole (Markov & Stolevik, 1970; la Cour, 1974). Four cyclic C—N bond distances suggest localized double bonding (Senda, Matsuoka & Maruha, 1986; Mathew & Palenik, 1974). The exocyclic C—N bond lengths indicate partial double-bond character. The C—S bond distances (1·746–1·753 Å) are somewhat shorter than the value of 1·77 Å for a C(sp^2)—S single bond (Mathew & Palenik, 1974). The N—N distance (mean 1·403 Å) is comparable to the normal single-bond distance (1·40 Å: Sutton, 1965). All N—H distances lie in the range 0·76–0·87 Å. The five-membered rings of the molecules are planar: the maximum deviation from the least-squares plane is 0·009 Å for C(*A*1). Exocyclic N(4) atoms also lie in these planes, but the deviations of N(3) atoms, especially of the *A* molecule, are large: 0·102 Å for the *A* and 0·021 Å for the *B* molecule.

The intermolecular contacts N(*A*1)···N($B4^{ii}$) 3·147 (2) [(ii) $1-x, -y, 1-z$], N(*B*1)···N($A3^{iii}$) 3·047 (2) [(iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$] and N(*B*3)···N($A1^{iii}$) 3·190 (2) Å are close to the sum of the van der Waals radii.

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Structure of *cyclo*(-L-Methionyl-L-prolyl-)

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Abstract. $C_{10}H_{16}N_2O_2S$, $M_r = 228{\cdot}3$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 9{\cdot}816$ (3), $b = 11{\cdot}129$ (5), $c = 10{\cdot}105$ (5) Å, $V = 1103{\cdot}9$ Å^3, $D_x = 1{\cdot}373$, D_m(by flotation) $= 1{\cdot}372$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}7107$ Å, $\mu = 2{\cdot}29$ cm^{-1}, $F(000) = 488$, room temperature, $R = 0{\cdot}056$ for 926 observed reflections. The diketopiperazine has a boat conformation with the methionyl chain in the pseudo-equatorial position. The torsional

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Table 1. *Final positional parameters and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
N(1)	0·5957 (6)	0·7554 (6)	0·6552 (5)	49 (4)
C(1)	0·5231 (6)	0·8671 (6)	0·6788 (6)	42 (5)
C(2)	0·6128 (6)	0·9532 (5)	0·7562 (6)	41 (5)
C(3)	0·3868 (6)	0·8433 (7)	0·7498 (7)	45 (5)
C(4)	0·4023 (7)	0·7722 (7)	0·8777 (7)	49 (6)
S	0·2439 (2)	0·7489 (2)	0·9648 (2)	58 (1)
C(5)	0·2214 (10)	0·8905 (7)	1·0413 (9)	63 (7)
O(1)	0·5639 (5)	1·0266 (5)	0·8350 (5)	57 (4)
N(2)	0·7443 (6)	0·9484 (5)	0·7273 (5)	42 (4)
C(6)	0·8057 (7)	0·8660 (6)	0·6339 (6)	41 (5)
C(7)	0·7290 (6)	0·7469 (7)	0·6260 (5)	44 (4)
C(8)	0·9522 (7)	0·8563 (9)	0·6819 (8)	62 (7)
C(9)	0·9791 (8)	0·9809 (9)	0·7293 (11)	70 (10)
C(10)	0·8487 (9)	1·0165 (8)	0·7998 (9)	61 (7)
O(2)	0·7877 (6)	0·6565 (5)	0·5953 (5)	70 (5)

angles and puckering parameters of the pyrrolidine ring have values between 'ideal twist' and 'envelope' conformations. The conformation of the methionyl side chain at C(1)—C(3), C(3)—C(4) and C(4)—S is *gauche–trans–gauche.*

Introduction. Crystal structure analysis of cyclic dipeptides (diketopiperazines, DKP's) shows a variety of ring conformations, from planar, as found in *cyclo*(-Gly-Gly-) (Degeilh & Marsh, 1959) and *cyclo*-(-L-Ala-D-Ala-) (Sletten, 1970), through boat with equatorial substituent for *cyclo*(-Phe-L-Pro-) (Mazza, Lucento, Pinnen & Zanotti, 1984) and *cyclo*(-L-Ala-L-Ala-) (Sletten, 1970), to boat form with axial substituents in *cyclo*[-D-Phe-L(S)-Pro-] (Van Poucke, Geise & Lenstra, 1983) and *cyclo*(-Gly-L-Tyr-) (Webb & Lin, 1971). Cyclic dipeptides are also useful as models to give information on more complex polypeptides and proteins. A large amount of data has been obtained from studies on cyclic systems containing amino acids with aromatic side chains (Mazza *et al.*, 1984). The present paper reports a study on a system with a sulfur-containing side chain.

Experimental. Colourless crystals were grown from aqueous solution of the compound (Sigma Chemical Company). The compound was thought to be L-methionyl-L-proline but the structure analysis revealed it to be the cyclic dipeptide (-L-methionyl-L-prolyl-). Crystal size: 0·03 × 0·03 × 0·05 mm. Intensity data collected with an indigenously fabricated computer-controlled four-circle diffractometer (Padmanabhan *et al.*, 1979), Zr-filtered Mo$K\alpha$ radiation, ω–2θ step scan, 1394 unique reflections recorded in range $8 < 2\theta < 55°$, 926 with $I > 2{\cdot}5\sigma(I)$ considered observed, index range h 0→12, k 0→16, l 0→10. Correction applied for Lorentz–polarization and absorption, maximum and minimum values of absorption corrections 0·994 and 0·992. Two standard reflections showed variations in intensity <2%. Unit-cell parameters obtained from least-squares fit of 2θ values of 25 reflections measured on the diffractometer. Structure was solved using heavy-atom method by *DIRDIF* program (Beurskens, Bosman, Doesburg, Gould, van den Hark & Prick, 1980). Structure was isotropically and anisotropically refined by least-squares refinement based on F values using *SHELX*76 (Sheldrick, 1976). All H atoms were found from difference Fourier maps. The H-atom coordinates (with fixed isotropic temperature factors 0·07 $Å^2$) were allowed to refine resulting in C—H bond distances between 0·712 (9) and 1·191 (8) Å. For 926 observed reflections $R = 0{\cdot}056$, $wR = 0{\cdot}084$ with $w = k/[\sigma^2(F_o) + g(F_o)^2]$ where k and g refined to 1·000 and 0·00414 respectively. Δ/σ(max.) = 0·5 for nonhydrogen atoms; $\Delta\rho$ in final difference map −0·2 to 0·3 e $Å^{-3}$. Atomic scattering factors those contained in *SHELX*76. The final positional parameters are given in Table 1.

Discussion. A view of the molecule is shown in Fig. 1; and the unit cell with four molecules in Fig. 2. The values of bond distances and angles are given in Table 2, and some important torsion angles in Table 3.*

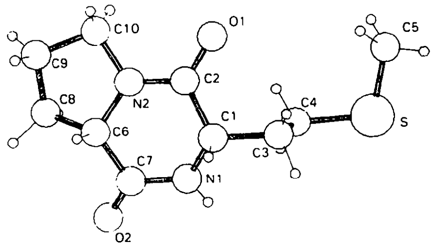

Fig. 1. General view of the molecule.

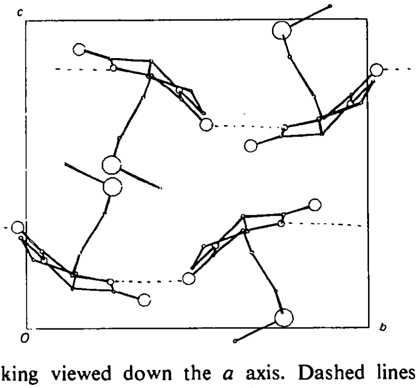

Fig. 2. Packing viewed down the a axis. Dashed lines indicate hydrogen bonds.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43396 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The DKP ring has a boat-like conformation. From the Cremer & Pople (1975) puckering coordinates (Table 3), it can be inferred that the conformation is true boat form $^{1,4}B$ (Boeyens, 1978). Table 3 shows that the two *cis* peptide bonds are twisted and that the equivalent torsion angles are unequal. The ring is folded along the line joining the two C$^{\alpha}$ atoms and the angle between the two peptide planes is 35·9 (6)° which is in the range of 37–41° found in DKP rings having a proline residue (Karle, 1981). The two N atoms N(1),N(2), and the two carbon atoms C(2),C(7) lie close to a plane with C(1) and C(6) atoms deviating by 0·44 (4) and 0·35 (4) Å respectively from this plane as shown in Table 4. The carbon atoms C(8) and C(3) are in (pseudo) equatorial positions and H(C$^{\alpha}$) atoms HC(1) and HC(6) are axial. As in *cyclo*[-D-Phe-L(γS)-Pro-] (Van Poucke *et al.*, 1983) the atom N(2) is not significantly (*ca* 0·05 Å) outside the C(2)C(6)-C(10) plane and no pyramidal configuration around the peptide N atom has been observed.

The torsional angles and the ring puckering parameters of the pyrrolidine ring have values lying between an ideal twist and an envelope form (Bucourt, 1973). The side-chain methionyl conformation at C$^{\alpha}$—B$^{\beta}$, C$^{\beta}$—C$^{\gamma}$ and C$^{\gamma}$—S bonds is *gauche–trans–gauche*. The bond lengths and bond angles of the side chain and the proline ring are normal.

The crystal packing is characterized by a hydrogen bond of 2·98 Å between N(1) of one molecule and the O(1) of the methionyl carbonyl group of the molecule generated by the screw axis along **b**.

Table 4. *Details of planes*

Plane 1	Displacement (Å)	Plane 2	Displacement (Å)
N(1)	−0·004 (2)	C(2)	0·0
C(2)	0·004 (4)	C(6)	0·0
N(2)	−0·004 (4)	C(10)	0·0
C(7)	0·004 (3)	N(2)*	−0·05 (1)
C(1)*	−0·44 (1)		
C(6)*	−0·35 (1)		

* Not included in the least-squares-plane calculations.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

N(1)–C(1)	1·453 (9)	N(2)–C(6)	1·448 (8)
C(1)–C(2)	1·518 (9)	C(6)–C(7)	1·527 (10)
C(1)--C(3)	1·541 (9)	C(7)–N(1)	1·345 (8)
C(3)–C(4)	1·524 (10)	C(7)–O(2)	1·200 (9)
C(4)–S	1·806 (7)	C(6)–C(8)	1·522 (10)
S–C(5)	1·769 (8)	C(8)–C(9)	1·491 (14)
C(2)–O(1)	1·238 (8)	C(9)–C(10)	1·518 (13)
C(2)–N(2)	1·325 (8)	N(2)–C(10)	1·469 (10)
N(1)–C(1)–C(2)	109·9 (5)	N(1)–C(7)–O(2)	125·7 (7)
C(1)–C(3)–C(4)	113·4 (5)	N(2)–C(6)–C(8)	103·3 (5)
C(3)–C(4)–S	113·7 (5)	C(6)–C(8)–C(9)	101·8 (7)
C(4)–S–C(5)	101·1 (4)	C(8)–C(9)–C(10)	104·1 (7)
C(1)–C(2)–O(1)	121·5 (6)	C(9)–C(10)–N(2)	102·7 (7)
C(1)–C(2)–N(2)	115·2 (5)	C(10)–N(2)–C(6)	111·2 (6)
O(1)–C(2)–N(2)	123·1 (6)	C(7)–N(1)–C(1)	125·0 (6)
C(2)–N(2)–C(6)	125·1 (5)	C(7)–C(6)–C(8)	114·9 (6)
N(2)–C(6)–C(7)	112·3 (5)	C(2)–C(1)–C(3)	111·8 (5)
C(6)–C(7)–O(2)	120·3 (6)	N(1)–C(1)–C(3)	110·8 (5)
C(6)–C(7)–N(1)	114·0 (6)	C(2)–N(2)–C(10)	123·3 (6)

Table 3. *Torsional angles* (°) (*e.s.d.'s are* 0·8–1·2°) *and ring puckering parameters with e.s.d.'s calculated according to Norrestam* (1981); *the sequences used are* N(1),C(1),C(2),N(2),C(6),C(7) *and* N(1),C(6),C(8),-C(9),C(10)

DKP ring			
N(2)–C(2)–C(1)–N(1)	35·4	C(6)–N(2)–C(2)–C(1)	−2·5
C(2)–C(1)–N(1)–C(7)	−38·7	C(7)–N(1)–C(1)–C(3)	−162·7
C(1)–N(1)–C(7)–C(6)	6·5	N(1)–C(7)–C(6)–C(8)	145·5
N(1)–C(7)–C(6)–N(2)	27·9	N(1)–C(7)–C(6)–HC(6)	−90·6
C(7)–C(6)–N(2)–C(2)	−30·6	N(2)–C(2)–C(1)–HC(1)	−82·4
Pyrrolidine ring			
N(2)–C(6)–C(8)–C(9)	−35·8	C(9)–C(10)–N(2)–C(6)	7·5
C(6)–C(8)–C(9)–C(10)	41·1	C(10)–N(2)–C(6)–C(8)	17·7
C(8)–C(9)–C(10)–N(2)	−30·3		
Peptide			
C(1)–N(1)–C(7)–O(2)	−173·3	C(6)–N(2)–C(2)–O(1)	−178·6
C(1)–C(2)–N(2)–C(10)	−174·2	C(10)–N(2)–C(2)–O(1)	9·7
Methionyl side chains			
C(2)–C(1)–C(3)--C(4)	−68·3	C(1)–C(3)–C(4)–S	177·7
N(1)–C(1)–C(3)–C(4)	54·7	C(3)–C(4)–S–C(5)	−78·3

$q_2 = 0·46\ (1)$ Å $\quad q_3 = -0·04\ (1)$ Å $\quad Q = 0·46\ (1)$ Å
$\varphi_2 = 181·0\ (1)°$ $\quad \theta_2 = 94·6\ (1)°$

$q_2 = 0·39\ (1)$ Å $\quad \varphi_2 = 276·8\ (1)°$

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