

Structure of *cyclo*(-L-Pro-L-Val-L-Pro-L-Val-) Dimethyl Sulfoxide Solvate, C₂₀H₃₂N₄O₄·C₂H₆OS

BY IKUHIKO UEDA

College of General Education, Kyushu University, Ropponmatsu, Chuo-ku, Fukuoka 810, Japan

AND TOSHIHISA UEDA, ISAO SADA, TETSUO KATO,* MASAHIRO MIKURIYA, SIGEO KIDA AND NOBUO IZUMIYA
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan

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Abstract. $M_r = 470.64$, trigonal, $P3_1$, $Z = 3$, $a = 9.584$ (4), $c = 23.692$ (8) Å, $V = 1884.7$ Å³, $D_m = 1.30$, $D_x = 1.24$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.177$ mm⁻¹, $F(000) = 762$, $T = 298$ K, $R = 0.071$ for 1866 observed reflexions. The *cyclo*(-L-Pro-L-Val-)₂ molecule has a *cis-trans-cis-trans* backbone-ring conformation with C_2 symmetry which allows a (CH₃)₂SO molecule of solvent to be connected by forked O···HN hydrogen bonds to the valyl moieties.

Introduction. L-Prolyl-L-valine anhydride was isolated from cultivated broths of several microorganisms and reported to show retardative or promotive effects on the growth of plant seedlings (Koaze, 1958*a,b*; Chen, 1960). The dimer (*A*) of L-prolyl-L-valine anhydride was synthesized to study possible activity. The results of a tentative bioassay showed a similar retardative activity of (*A*) on the root growth of rice seedlings. The details of the synthesis will be reported elsewhere.

Signals of ¹³C NMR spectra of (*A*) in CDCl₃ were unambiguously assigned. The difference in the chemical shifts between the β and γ C atoms in proline ($\Delta\delta_{\beta\gamma} = 9.9$ p.p.m.) shows the Val-Pro bond to be in the *cis* conformation. The X-ray diffraction study of the title complex was carried out to elucidate precisely the conformation.

Experimental. Single crystals only obtained from dimethyl sulfoxide (Me₂SO) solution; D_m by flotation in KI solution; colorless trigonal prism, 0.5 mm on edge, sealed in a thin glass capillary with solution to prevent efflorescence; X-ray diffraction data collected on a Rigaku AFC-5 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation, 25 reflexions used for measuring lattice parameters; three standard reflexions (211, 111 and 121) measured every 100 reflexions, intensity variations 3%; $2\theta \leq 50^\circ$, 3107 reflexions measured, h 0–11, k 11–11, l 0–28; intensity corrected for Lorentz and polarization effects, but not for absorption; 1866 independent reflexions with

$|F_o| \geq 1.53\sigma(F_o)$; direct methods (*MULTAN*, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); all coordinates, anisotropic thermal parameters for non-H and isotropic ones for fragments of disordered methyl moieties of Me₂SO and H atoms refined by the block-diagonal least-squares procedure to minimize $\sum w(|F_o| - |F_c|)^2$, $w = 1.0$; final $R = 0.071$, $wR = 0.068$, $S = 1.23$; $(\Delta/\sigma)_{\max} = 0.4$ for non-H; final residual electron density < 0.26 e Å⁻³; scattering and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974) and, for H, from Stewart, Davidson & Simpson (1965); no correction for secondary extinction; test for absolute configuration not successful, present configuration adopted because raw materials of chemical syntheses were L-proline and L-valine; crystallographic calculations performed on a FACOM M-200 computer in the Computer Center of Kyushu University using a local version of the UNICSIII program system (Sakurai & Kobayashi, 1979).

Discussion. The atomic coordinates and thermal parameters are given in Table 1.† Fig. 1 shows a stereoview of the molecular conformation along **b** (*ORTEP*, Johnson, 1965), together with the atom-numbering scheme. The bond lengths and angles are in Table 2. The molecule of (*A*) has C_2 symmetry, as shown in Fig. 1 and Table 2. The twelve-membered ring has a distorted boat conformation.

At the top of the peptide ring, the O atom of Me₂SO is connected to the ring by the strong forked hydrogen bonds O···H(N2) and O···H(N4) [distances respectively 2.08 (10) and 2.06 (6) Å]. The S atom is statistically distributed at positions S(1) and S(2) with equal occupancies. They respectively make contact with H(N2) and H(N4) by van der Waals interactions.

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and selected torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38845 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* To whom correspondence should be addressed.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal factors (Å²) and population parameters (p.p.)

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B _{eq} /B _{iso}	p.p.
S(1)	0.4029 (6)	0.2039 (5)	0.0578 (2)	5.1 (2)	0.50
S(2)	0.2635 (7)	0.1347 (6)	0.0234 (2)	5.2 (2)	0.50
O	0.3338 (10)	0.0229 (7)	0.0414 (4)	6.2 (3)	1.0
O(1)	0.5086 (9)	-0.3747 (8)	0.0798 (3)	6.1 (3)	1.0
O(2)	0.2328 (8)	-0.1029 (8)	0.1786 (3)	6.1 (3)	1.0
O(3)	0.1567 (9)	-0.5501 (7)	0.0017 (3)	5.9 (3)	1.0
O(4)	0.4337 (8)	-0.0017 (9)	-0.0963 (3)	6.3 (3)	1.0
N(1)	0.5357 (8)	-0.0961 (9)	-0.0314 (3)	4.2 (3)	1.0
N(2)	0.4707 (7)	-0.1606 (7)	0.0843 (3)	3.3 (2)	1.0
N(3)	0.1326 (8)	-0.2990 (8)	0.1127 (3)	4.1 (2)	1.0
N(4)	0.1973 (7)	-0.2967 (7)	-0.0024 (3)	3.4 (2)	1.0
C(1)	0.6942 (12)	0.0505 (14)	-0.0376 (4)	6.3 (4)	1.0
C(2)	0.8059 (12)	0.0046 (17)	-0.0070 (5)	7.9 (5)	1.0
C(3)	0.7283 (13)	-0.1721 (16)	-0.0142 (4)	6.9 (5)	1.0
C(4)	0.5484 (11)	-0.2280 (12)	-0.0056 (4)	4.6 (3)	1.0
C(5)	0.5063 (10)	-0.2617 (11)	0.0573 (4)	4.4 (3)	1.0
C(6)	0.4157 (10)	-0.1856 (9)	0.1422 (3)	4.0 (3)	1.0
C(7)	0.5459 (11)	-0.0607 (11)	0.1817 (4)	5.4 (3)	1.0
C(8)	0.5960 (13)	0.1118 (11)	0.1652 (5)	6.6 (4)	1.0
C(9)	0.6892 (14)	-0.0875 (15)	0.1856 (5)	7.6 (5)	1.0
C(10)	0.2538 (10)	-0.1902 (10)	0.1465 (3)	4.2 (3)	1.0
C(11)	-0.0285 (12)	-0.3112 (14)	0.1183 (5)	6.5 (4)	1.0
C(12)	-0.1413 (12)	-0.4726 (16)	0.0892 (5)	7.7 (5)	1.0
C(13)	-0.0606 (12)	-0.5692 (12)	0.0957 (4)	6.8 (4)	1.0
C(14)	0.1179 (10)	-0.4436 (9)	0.0871 (4)	4.4 (3)	1.0
C(15)	0.1582 (10)	-0.4343 (10)	0.0249 (4)	4.2 (3)	1.0
C(16)	0.2509 (10)	-0.2675 (10)	0.0610 (3)	4.0 (3)	1.0
C(17)	0.1216 (11)	-0.2716 (12)	-0.1006 (4)	5.1 (4)	1.0
C(18)	0.0701 (13)	-0.1518 (15)	-0.0839 (5)	6.7 (5)	1.0
C(19)	-0.0214 (14)	-0.4388 (17)	-0.1032 (5)	8.0 (6)	1.0
C(20)	0.4126 (10)	-0.1107 (11)	-0.0654 (3)	4.4 (3)	1.0
Me(S1)	0.445 (4)	0.316 (4)	-0.002 (1)	5.0 (6)†	0.30
Me(S2)	0.238 (2)	0.215 (2)	0.089 (1)	5.1 (4)†	0.50
Me(S3)	0.456 (3)	0.308 (3)	0.013 (1)	5.4 (5)†	0.40
Me(S4)	0.357 (3)	0.271 (3)	-0.017 (1)	5.3 (6)†	0.34
Me(S5)	0.455 (4)	0.264 (4)	-0.027 (1)	5.6 (7)†	0.28
Me(S6)	0.310 (4)	0.261 (4)	0.091 (1)	5.4 (6)†	0.31
Me(S7)	0.197 (3)	0.181 (3)	0.068 (1)	5.4 (6)†	0.35
Me(S8)	0.179 (4)	0.142 (4)	0.101 (2)	5.5 (7)†	0.27
Me(S9)	0.466 (5)	0.353 (5)	-0.020 (2)	5.6 (8)†	0.25

† B_{iso} values.

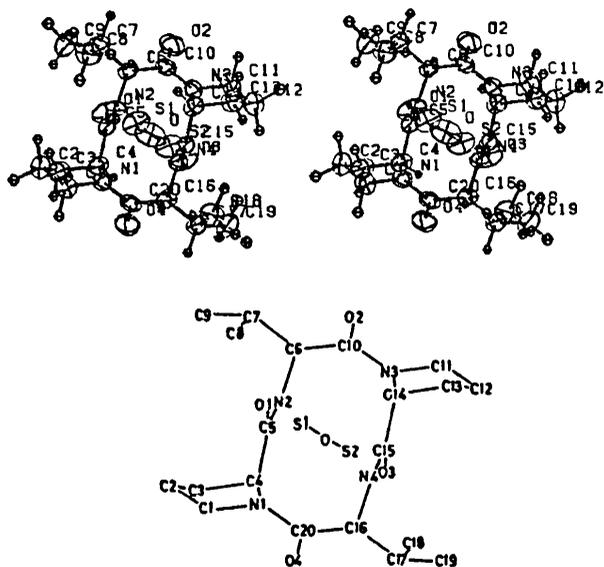


Fig. 1. A stereoview of the molecular conformation, and the numbering scheme.

The dimethyl moiety of Me₂SO is statistically distributed at positions Me(S1)—Me(S9) to fill vacant spaces of the crystal.

The results obtained show several characteristic features of the conformation of (A). (1) Dihedral angles of the two prolyl-valine sequences are similar. Since the sequence repeats twice, it is reasonable that the molecule of (A) has C₂ symmetry. (2) Most bond angles and lengths agree with those proposed by Corey & Pauling (1953). Although the two *trans* peptide bonds are nearly planar, the two *cis* bonds deviate from planarity by 20°. This is unusual because cyclo-tetrapeptides containing *cis-trans-cis-trans* conformations usually have nearly planar *cis* bonds although *trans* bonds are somewhat distorted (Ovchinnikov & Ivanov, 1982). The reason for the deviation of the *cis* bonds may be interactions with the hydrogen-bonded Me₂SO molecule. (3) The torsion angles C(5)—N(2)—C(6)—C(10) [−124.2 (9)°] and C(15)—N(4)—C(16)—C(20) [−125.7 (9)°] of the valine parts are usual and comparable with the value of −128.5° estimated from NMR spectra by the method suggested by Bystrov, Ivanov, Portonova, Balashova & Ovchinnikov (1973). On the other hand, C(20)—N(1)—C(4)—C(5) [−102.2 (11)°] and C(10)—N(3)—C(14)—C(15) [−102.7 (10)°] of the prolyl parts differ markedly from the usually observed values (−60 to −80°) (Ovchinnikov & Ivanov, 1982).

Table 2. Selected intramolecular distances (Å) and bond angles (°)

S(1)—O	1.57 (1)	S(2)—O	1.58 (1)
O(1)—C(5)	1.22 (1)	O(3)—C(15)	1.23 (1)
O(2)—C(10)	1.22 (1)	O(4)—C(20)	1.21 (1)
N(2)—C(5)	1.34 (1)	N(4)—C(15)	1.34 (1)
N(2)—C(6)	1.45 (1)	N(4)—C(16)	1.46 (1)
N(1)—C(1)	1.47 (1)	N(3)—C(11)	1.49 (2)
N(1)—C(4)	1.46 (2)	N(3)—C(14)	1.45 (1)
N(1)—C(20)	1.38 (1)	N(3)—C(10)	1.37 (1)
C(1)—C(2)	1.53 (2)	C(11)—C(12)	1.54 (2)
C(2)—C(3)	1.48 (2)	C(12)—C(13)	1.48 (2)
C(3)—C(4)	1.54 (2)	C(13)—C(14)	1.54 (1)
C(4)—C(5)	1.54 (1)	C(14)—C(15)	1.51 (1)
C(6)—C(7)	1.54 (1)	C(16)—C(17)	1.54 (1)
C(6)—C(10)	1.53 (1)	C(16)—C(20)	1.53 (1)
C(7)—C(8)	1.52 (1)	C(17)—C(18)	1.51 (2)
C(7)—C(9)	1.52 (2)	C(17)—C(19)	1.50 (1)
C(1)—N(1)—C(4)	112.0 (9)	C(11)—N(3)—C(14)	111.0 (7)
C(1)—N(1)—C(20)	117.5 (8)	C(10)—N(3)—C(11)	117.3 (9)
C(4)—N(1)—C(20)	126.4 (7)	C(10)—N(3)—C(14)	127.8 (9)
C(5)—N(2)—C(6)	122.5 (8)	C(15)—N(4)—C(16)	123.1 (8)
N(1)—C(1)—C(2)	102.4 (9)	N(3)—C(11)—C(12)	102.6 (11)
C(1)—C(2)—C(3)	104.5 (9)	C(11)—C(12)—C(13)	105.0 (9)
C(2)—C(3)—C(4)	102.5 (12)	C(12)—C(13)—C(14)	102.8 (8)
N(1)—C(4)—C(3)	101.9 (8)	N(3)—C(14)—C(13)	103.4 (8)
N(1)—C(4)—C(5)	117.4 (10)	N(3)—C(14)—C(15)	116.7 (7)
C(3)—C(4)—C(5)	109.4 (8)	C(13)—C(14)—C(15)	109.1 (7)
O(1)—C(5)—N(2)	124.0 (9)	O(3)—C(15)—N(4)	122.8 (9)
O(1)—C(5)—C(4)	119.5 (10)	O(3)—C(15)—C(14)	119.6 (8)
N(2)—C(5)—C(4)	116.5 (10)	N(4)—C(15)—C(14)	117.7 (9)
N(2)—C(6)—C(7)	111.2 (6)	N(4)—C(16)—C(17)	111.9 (8)
N(2)—C(6)—C(10)	110.3 (7)	N(4)—C(16)—C(20)	109.9 (6)
C(7)—C(6)—C(10)	113.4 (8)	C(17)—C(16)—C(20)	113.0 (8)
C(6)—C(7)—C(8)	112.4 (9)	C(16)—C(17)—C(18)	112.7 (8)
C(6)—C(7)—C(9)	110.8 (9)	C(16)—C(17)—C(19)	110.2 (10)
C(8)—C(7)—C(9)	112.2 (8)	C(18)—C(17)—C(19)	110.6 (10)
O(2)—C(10)—N(3)	121.3 (10)	O(4)—C(20)—N(1)	120.2 (7)
O(2)—C(10)—C(6)	122.2 (7)	O(4)—C(20)—C(16)	122.7 (8)
N(3)—C(10)—C(6)	116.4 (8)	N(1)—C(20)—C(16)	117.1 (8)

These unusual features seem to result from the strong intermolecular hydrogen bonding with Me₂SO. The presence of this enhanced hydrogen-bonding donor may explain the plant-growth activity of this molecule.

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Structure of the 1:1 Complex of 1,4-Dithiintetracarboxylic *N,N'*-Dimethyldiimide and Acridine, [C₁₀H₆N₂O₄S₂][C₁₃H₉N]

BY YASUCHIKA YAMAGUCHI

Faculty of Pharmaceutical Sciences, Kyushu University, Maidashi, Higashi-ku, Fukuoka 812, Japan

AND IKUHIKO UEDA*

College of General Education, Kyushu University, Ropponmatsu, Chuo-ku, Fukuoka 810, Japan

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Abstract. $M_r = 461.52$, monoclinic, space group Pn , $a = 13.701$ (11), $b = 10.244$ (4), $c = 7.208$ (2) Å, $\beta = 92.20$ (5)°, $V = 1010.9$ (9) Å³, $Z = 2$, $D_m = 1.515$, $D_x = 1.511$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.2998$ mm⁻¹, $F(000) = 482$, $T = 298$ K, final $R = 0.039$ for 1544 observed reflections. The title complex contains 1,4-dithiintetracarboxylic *N,N'*-dimethyldiimide and acridine which have planar structures. These almost parallel molecules are alternately stacked along the c axis.

Introduction. 1,4-Dithiins have the boat structure, e.g. 1,4-dithiin (Howell, Curtis & Lipscomb, 1954) and thianthrene (Rowe & Post, 1956, 1958; Lynton & Cox, 1956). Recently, it has been reported that 1,4-dithiintetracarboxylic *N,N'*-dimethyldiimide (*A*) reacts with various anthracenes *via* charge-transfer (CT) complexes to give Diels–Alder adducts and that, in contrast, the reaction of *A* with acridine (*B*) gives a stable 1:1 complex which does not give rise to any adducts (Hayakawa, Mibu, Osawa & Kanematsu, 1982). This complex in chloroform shows no new ultraviolet absorption bands indicative of the formation of a CT complex. To explain these facts, the X-ray structure of the title complex was determined.

Experimental. Green pillars grown from chloroform, density measured by flotation in KI solution, crystal data collected from single crystal of approximately 0.2 × 0.15 × 0.3 mm on an automated Syntex P1 diffractometer, using graphite-monochromatized Mo $K\alpha$, cell parameters determined by least squares from the setting angles of 15 reflections, 1802 reflections measured using θ – 2θ variable scans (4.8–24.0° min⁻¹ for 2θ) up to $2\theta = 55^\circ$, range of hkl : $-16 \leq h \leq 16$, $-12 \leq k \leq 0$, $0 \leq l \leq 8$, three standard reflections (150, 241, 140) measured every 100 reflections (intensity variation 10%), data corrected for geometrical factors and for monitored intensities but not for absorption, 1544 independent reflections [$I > 3.0\sigma(I)$] considered observed and used for the analysis; heavy-atom method; the 100 peaks were selected from a Patterson synthesis and the S atoms located with the *RMINH* 80 program (Kawano, 1983); all non-H atoms determined by a Fourier synthesis, all H atoms determined by a difference Fourier synthesis, all coordinates, anisotropic thermal parameters for the non-H atoms and isotropic ones for H atoms refined by the block-diagonal least-squares procedure, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1.0$, final $R = 0.039$, $wR = 0.058$, $S = 1.09$, final $\Delta\rho$ excursions < 0.3 e Å⁻³; atomic scattering factors involving the anomalous-dispersion terms for non-H atoms from *International*

* Author to whom correspondence should be addressed.