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tert-Butyloxycarbonyl-L-cysteinyl-L-cysteine Disulfide Methyl Ester

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Abstract. $C_{12}H_{20}N_2O_5S_2$, orthorhombic, $P2_12_12_1$, $a = 17.404$ (1), $b = 10.565$ (2), $c = 9.137$ (5) Å, $D_m = 1.328$ (by flotation in CCl_4–*n*-hexane), $D_x = 1.330$ g cm^{-3} for $Z = 4$. The title compound is a cyclo cystine compound. The structure was solved by direct methods and refined by the block-diagonal least-squares technique to a final R of 0·078 ($R_w = 0.065$). The peptide group has a *cis* conformation. The torsion angle about the S–S bond is 95·7° and those about the two S–C bonds are −76·8 and −48·6°.

Introduction. Colorless, transparent, needle-shaped single crystals elongated along **c** were obtained by slow evaporation from a mixture of ethyl acetate and chloroform. A crystal with dimensions 0·2 × 0·3 × 0·5 mm was used for the X-ray analysis. The unit-cell dimensions were obtained by least-squares refinement of the settings of 13 reflections measured on a diffractometer. Intensity data were measured on an automatic Rigaku four-circle diffractometer, equipped with a rotating anode, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) and a monitor-counting technique. The θ–2θ scan mode with a scan rate of 16° min^{-1} in 2θ was employed. The θ scan range was calculated as $(1.2 + 0.35 \tan\theta)°$. Intensity data of 2314 independent reflections were collected with $(\sin\theta)/\lambda \leq 0.66$ Å^{-1}; of these, 200 were measured with $|F_o| = 0.0$. No absorption correction was applied [μ(Mo $K\alpha$) = 3·32 cm^{-1}]. The structure was solved by direct methods, using the symbolic addition method for noncentrosymmetric crystals (Karle & Karle, 1966) and the weighted tangent-formula technique (Germain, Main & Woolfson, 1971). All nonhydrogen atoms were located from the E map based on the phases of 281 reflections with $|E| \geq 1.2$. The parameters were refined by block-diagonal least-squares calculations with *HBLS*-5 (Ashida, 1973), first using isotropic temperature factors and then anisotropic. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. A difference map revealed the positions of all but two of the H atoms. The contributions of the H atoms to the structure factors were included in further refinement, but their parameters were not refined; their thermal parameters were assumed to be isotropic ($B = 3.8$ Å^2). The final R is 0·078 for 2114 non-zero reflections and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ was 0·065 for all reflections. The weighting scheme finally adopted was $w = 0.2$ for $|F_o| = 0.0$ and $w = [\sigma^2(F_o) + 0.001|F_o|^2]^{-1/2}$ for $|F_o| > 0.0$. The atomic coordinates are given in Table 1.†

Discussion. Structures of various cystine compounds have been determined by X-ray or neutron diffraction methods to study the conformation of the disulfide bridge. The title compound is a cyclo cystine compound, which contains an eight-membered disulfide ring. Thus it is of interest to compare the conformation of this compound with those of other cystine compounds and/or proteins.

Bond lengths and angles in the molecule are listed in Table 2; they lie within the normal range found in other cystine compounds. In the crystal structure, as shown in Fig. 1, each molecule is linked by intermolecular hydrogen bonds [O(2)···H–N(1) 2·894 (5) Å] to

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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 32824 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final atomic parameters*

(*a*) Fractional atomic coordinates of the nonhydrogen atoms ($\times 10^4$) with their standard deviations in parentheses

	x	*y*	*z*
S(1)	427 (1)	5047 (1)	2108 (2)
S(2)	1208 (1)	4151 (1)	824 (1)
O(1)	1971 (2)	3964 (3)	5540 (3)
O(2)	3775 (2)	2984 (3)	1874 (3)
O(3)	3776 (2)	1475 (3)	3646 (3)
O(4)	2337 (3)	8164 (3)	4246 (4)
O(5)	1949 (2)	8472 (3)	1977 (4)
N(1)	1783 (2)	5742 (3)	4278 (4)
N(2)	2870 (2)	2889 (3)	3638 (4)
C(1)	1766 (3)	3213 (4)	2109 (5)
C(2)	2366 (2)	3865 (4)	3049 (4)
C(3)	2015 (5)	4532 (4)	4389 (4)
C(4)	1706 (2)	6471 (4)	2933 (4)
C(5)	869 (3)	6570 (5)	2444 (5)
C(6)	3504 (2)	2495 (4)	2956 (5)
C(7)	4503 (3)	855 (5)	3192 (6)
C(8)	4465 (4)	435 (6)	1632 (7)
C(9)	4519 (3)	−264 (5)	4208 (7)
C(10)	5147 (3)	1758 (7)	3541 (10)
C(11)	2033 (3)	7785 (4)	3156 (5)
C(12)	2203 (5)	9776 (5)	2055 (8)

(*b*) Fractional atomic coordinates ($\times 10^3$) of the hydrogen atoms. H(9) and H(20) [bonded to C(10) and C(12) respectively] were not found from a difference Fourier map.

	Bonded to	*x*	*y*	*z*
H(1)	C(8)	400	6	161
H(2)	C(8)	483	−14	139
H(3)	C(8)	450	125	111
H(4)	C(9)	450	−11	519
H(5)	C(9)	502	−67	407
H(6)	C(9)	413	−83	407
H(7)	C(10)	555	133	339
H(8)	C(10)	517	236	278
H(10)	N(2)	268	254	457
H(11)	C(2)	267	439	251
H(12)	C(1)	206	261	142
H(13)	C(1)	144	276	268
H(14)	C(5)	80	703	151
H(15)	C(5)	55	693	332
H(16)	C(4)	201	612	213
H(17)	N(1)	164	610	512
H(18)	C(12)	213	1000	296
H(19)	C(12)	195	1028	148

Table 2. *Bond lengths* (Å) *and angles* (°) *with their estimated standard deviations in parentheses*

S(1)–S(2)	2·029 (2)	S(1)–C(5)	1·810 (5)
S(2)–C(1)	1·818 (5)	C(1)–C(2)	1·518 (6)
C(2)–C(3)	1·540 (6)	C(3)–O(1)	1·213 (5)
C(3)–N(1)	1·345 (5)	N(1)–C(4)	1·460 (5)
C(4)–C(5)	1·526 (6)	C(2)–N(2)	1·456 (5)
N(2)–C(6)	1·335 (6)	C(6)–O(2)	1·211 (5)
C(6)–O(3)	1·335 (5)	O(3)–C(7)	1·485 (6)
C(7)–C(8)	1·494 (8)	C(7)–C(9)	1·503 (8)
C(7)–C(10)	1·506 (10)	C(4)–C(11)	1·510 (6)
C(11)–O(4)	1·197 (7)	C(11)–O(5)	1·307 (6)
O(5)–C(12)	1·450 (9)		
S(1)–S(2)–C(1)	103·8 (2)	S(2)–S(1)–C(5)	103·2 (2)
S(2)–C(1)–C(2)	119·1 (3)	C(1)–C(2)–C(3)	112·6 (3)
C(1)–C(2)–N(2)	107·6 (3)	C(2)–C(3)–N(1)	119·7 (3)
C(2)–C(3)–O(1)	119·2 (4)	N(1)–C(3)–O(1)	121·1 (4)
C(3)–N(1)–O(4)	126·6 (3)	N(1)–C(4)–C(5)	111·6 (4)
C(4)–C(5)–S(1)	113·4 (3)	C(3)–C(2)–N(2)	105·6 (3)
C(2)–N(2)–C(6)	123·1 (4)	N(2)–C(6)–O(2)	124·7 (4)
N(2)–C(6)–O(3)	109·0 (4)	O(2)–C(6)–O(3)	126·4 (4)
C(6)–O(3)–C(7)	121·8 (4)	O(3)–C(7)–C(8)	111·1 (4)
O(3)–C(7)–C(9)	101·0 (4)	O(3)–C(7)–C(10)	107·1 (5)
C(8)–C(7)–C(9)	110·9 (5)	C(8)–C(7)–C(10)	115·1 (5)
C(9)–C(7)–C(10)	110·7 (5)	N(1)–C(4)–C(11)	109·8 (3)
C(5)–C(4)–C(11)	109·9 (4)	C(4)–C(11)–O(4)	125·8 (5)
C(4)–C(11)–O(5)	110·8 (4)	O(4)–C(11)–O(5)	123·4 (5)
C(11)–O(5)–C(12)	116·9 (5)		

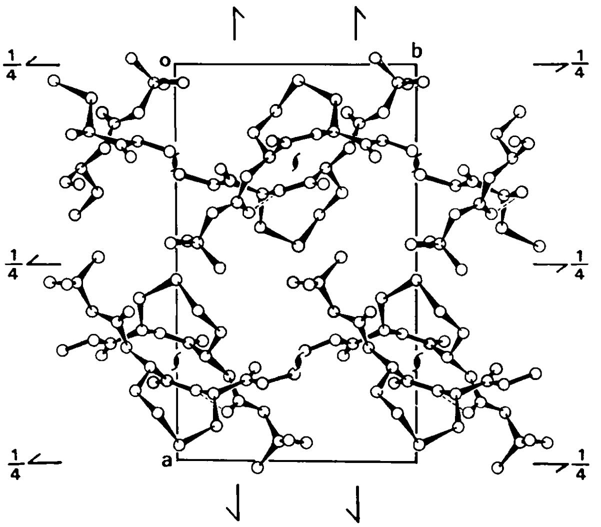

Fig. 1. Projection of the crystal structure along **c**. Hydrogen bonds are represented by broken lines.

adjacent molecules related by a 2_1 screw axis parallel to the crystallographic *c* axis.

Fig. 2 shows the molecular structure and the atom designations used in this paper. Torsion angles for the ring in the molecule are given in Table 3. [C(4),C(11),O(4),O(5)], [C(3),O(1),N(1),C(2)] and [N(2),C(6),O(2),O(3)] are all approximately planar with largest deviations of 0·004, 0·009 and 0·005 Å, respectively, from their best planes. The peptide group O(1)–C(3)–N(1)–H(17) adopts a twisted *cis* conformation with a torsion angle ω [C(2)–C(3)–N(1)–C(4)] of 10·8°. [O(2)–C(6)–N(2)–H(10)] has a *trans* conformation with an O(3)–C(6)–N(2)–C(2) torsion angle of −170·7°. It is known that the atom in the γ position of the side chain in an amino acid lies close to one of the three positions which correspond to χ^1 torsion angles of 60, 180 and −60°, and that the *gauche* position ($\chi^1 = 60°$) is favored by a large atom such as sulfur (Ramachandran & Lakshminarayanan, 1966; Lakshminarayanan, Sasisekharan & Ramachandran, 1967). In the present compound, the $S^\gamma(1)$

occupies the position with $\chi^1 = -59{\cdot}2°$, while $S^{\gamma}(2)$ occupies the position with $\chi^1 = -163{\cdot}7°$.

The χ^2 torsion angles about the S—C bonds and χ^3 about the S—S bond are important values for describing the conformation of the disulfide bridge. Cystine compounds whose structures have been determined so far have been classified into two types according to their χ^2 and χ^3 values (Gupta, Sequeira & Chidambaram, 1974). It has been observed that the χ^2 and χ^3 values are both close to −90° in type 1 and both close to 90° in type 2. As shown in Table 4, the type 1 conformation has been found in such compounds as L-cystine.2HBr (Peterson, Steinrauf & Jensen, 1960), L-cystine dimethyl ester dihydrochloride monohydrate (Vijayalakshmi & Srinivasan, 1975), and L-cystine dihydrobromide dihydrate (Rosenfield & Parthasarathy, 1975). The type 2 conformation has been found in such compounds as hexagonal L-cystine (Oughton & Harrison, 1959) and tetragonal L-cystine (Chaney & Steinrauf, 1974). In the title compound, the χ^2 torsion angles are −76·8° for S(1)—S(2)—C(1)—C(2) and −48·6° for S(2)—S(1)—C(5)—C(4), and the torsion angle χ^3 is 95·7°. Thus the present cyclo cystine compound cannot be characterized as either of the above two types.

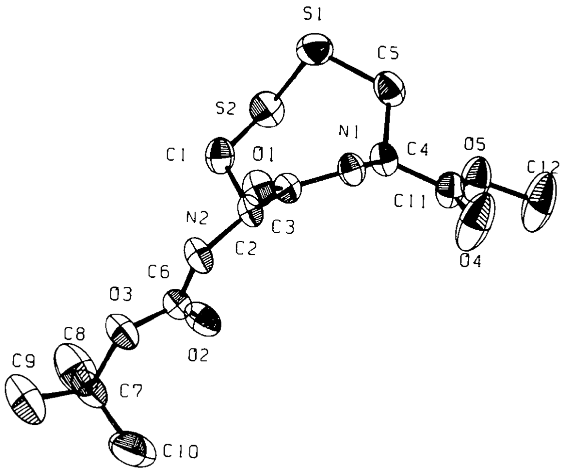

Fig. 2. A perspective view of the molecule and the atom designations, drawn by *ORTEP* (Johnson, 1965). The thermal ellipsoids are drawn at the 50% probability level.

Table 3. *Torsion angles (°) about various bonds in the title compound*

C(1)—S(2)—S(1)—C(5)	95·7
C(2)—C(1)—S(2)—S(1)	−76·8
S(2)—S(1)—C(5)—C(4)	−48·6
S(1)—C(5)—C(4)—N(1)	−59·2
S(1)—C(5)—C(4)—C(11)	178·8
C(4)—N(1)—C(3)—C(2)	10·8
N(2)—C(2)—C(1)—S(2)	−163·7
C(3)—C(2)—C(1)—S(2)	80·3
C(5)—C(4)—N(1)—C(3)	101·7
C(11)—C(4)—N(1)—C(3)	−136·2
C(1)—C(2)—N(2)—C(6)	89·9
C(2)—N(2)—C(6)—O(2)	8·2
C(2)—N(2)—C(6)—O(3)	−170·7

Table 4. *Torsion angles (°) about the* C—S (χ^2) *and* S—S (χ^3) *bonds*

(*a*) Cystine compounds

	χ^2	χ^3	χ^2
Type 1 compounds			
L-Cystine dihydrobromide	−88·9	−81·3	−88·9
L-Cystine dimethyl ester dihydrobromide monohydrate	−77·4	−84·4	−79·2
L-Cystine dihydrobromide dihydrate	−70·0	−79·8	−82·4
Type 2 compounds			
Hexagonal L-cystine	81·6	73·7	81·6
Tetragonal L-cystine	66·9	69·3	75·1
Cyclic compound			
Title compound	−76·8	95·7	−48·6

(*b*) Proteins*

	χ^2	χ^3	χ^2	
Lysozyme				
Cys 6	−52	−95	−41	Cys 127
Cys 30	−80	−101	−96	Cys 115
Cys 64	−53	93	88	Cys 80
Cys 76	42	81	139	Cys 94
Papain				
Cys 22	66	−85	−56	Cys 63
Cys 56	−91	99	5	Cys 95
Cys 153	176	−123	−20	Cys 200

* The torsion angles in the proteins were calculated using the atomic coordinates obtained from Brookhaven National Laboratory Protein Data Bank.

Various types of conformation of the disulfide bridge have been found in proteins. In lysozyme and papain, as shown in Table 4, the $|\chi^3|$ values are close to 90° as in type 1 and type 2, but some pairs of the χ^2 values in the cystinyl residues are quite different from those in both these types.

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3-Isopropyl-6,6-dimethyl-5-(1-naphthylamino)-1,2,4-trioxane

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Abstract. $C_{18}H_{23}NO_3$, monoclinic, $P2_1/c$, a = 10·061 (2), b = 9·117 (2), c = 18·027 (2) Å, β = 91·49 (2)°, $Z = 4$, $D_m = 1·19$, $D_x = 1·202$ g cm^{-3}. The torsion angle of the peroxide bond is only −68·4 (2)° and its length is 1·469 (2) Å. The exposed O—O bond may be easily cleaved by alkali in solution, which is a trigger for chemiluminescence of this compound.

Introduction. The title compound is a chemiluminescent substance which emits light in basic DMSO solution (Akutagawa, Aoyama, Omote & Yamamoto, 1976; Yamamoto, Aoyama, Omote, Akutagawa, Takenaka & Sasada, 1977). Crystals were obtained from an *n*-hexane solution. Density was measured by flotation. A crystal, 0·4 × 0·5 × 0·6 mm in size, was

Table 1. *Fractional atomic coordinates*

Standard deviations are in parentheses.

	x (×10^5)	y (×10^5)	z (×10^5)		x (×10^4)	y (×10^4)	z (×10^4)
N	34967 (18)	38148 (21)	34049 (11)	H(N)	3490 (19)	3542 (24)	2940 (11)
O(1)	53934 (16)	72129 (17)	32647 (10)	H(13)	4806 (17)	2955 (20)	4611 (10)
O(2)	66816 (15)	64858 (17)	31812 (9)	H(14)	4266 (19)	1141 (22)	5464 (11)
C(3)	67366 (23)	53930 (25)	37413 (13)	H(15)	2387 (20)	−367 (23)	5219 (11)
O(4)	57795 (14)	43191 (16)	35588 (8)	H(17)	504 (20)	−1065 (24)	4431 (12)
C(5)	44538 (23)	49090 (26)	35844 (13)	H(18)	−971 (21)	−629 (27)	3371 (13)
C(6)	43211 (24)	62132 (25)	30558 (14)	H(19)	−471 (21)	1496 (27)	2612 (13)
C(7)	81116 (24)	47362 (27)	37617 (14)	H(20)	1408 (18)	2841 (21)	2814 (10)
C(8)	91417 (27)	58719 (32)	40028 (18)	H(3)	6457 (17)	5861 (20)	4237 (10)
C(9)	81449 (26)	34396 (31)	42893 (17)	H(5)	4294 (17)	5247 (20)	4096 (10)
C(10)	43888 (26)	58080 (29)	22420 (15)	H(7)	8295 (17)	4384 (20)	3256 (10)
C(11)	31056 (27)	71239 (32)	32335 (18)	H(81)	9124 (22)	6727 (26)	3669 (13)
C(12)	32269 (22)	26837 (25)	39135 (13)	H(82)	10026 (24)	5432 (28)	4016 (14)
C(13)	39930 (23)	24142 (26)	45382 (13)	H(83)	8898 (23)	6272 (27)	4493 (13)
C(14)	36649 (25)	12926 (28)	50303 (14)	H(91)	7564 (23)	2646 (26)	4117 (13)
C(15)	26011 (26)	4168 (28)	48891 (15)	H(92)	7892 (22)	3845 (26)	4810 (13)
C(16)	17827 (23)	6484 (27)	42506 (14)	H(93)	9041 (23)	3031 (26)	4336 (13)
C(17)	6538 (26)	−2329 (29)	40908 (15)	H(101)	3599 (21)	5238 (25)	2115 (12)
C(18)	−1449 (26)	142 (33)	34908 (17)	H(102)	5235 (24)	5258 (28)	2138 (13)
C(19)	1271 (25)	11655 (34)	30177 (15)	H(103)	4343 (21)	6754 (26)	1937 (12)
C(20)	12050 (24)	20477 (30)	31462 (14)	H(111)	2351 (24)	6515 (27)	3212 (14)
C(21)	20745 (22)	18040 (26)	37614 (13)	H(112)	3046 (25)	7942 (29)	2909 (15)
				H(113)	3123 (24)	7469 (27)	3783 (14)