be compared with the values in the two thioethylene derivatives which range between 102·5 (1) and 103·6 (1)°.

The molecular packing is illustrated in Fig. 2. The molecules are aligned with their long axes along **c**. There are no unusually short intermolecular contacts (see Table 4). The two closest involve the oxo oxygen, O(2), which lies 3·23 Å from C(12) and 3·33 Å from C(19) of an adjacent molecule related by the inversion centre at [½00].

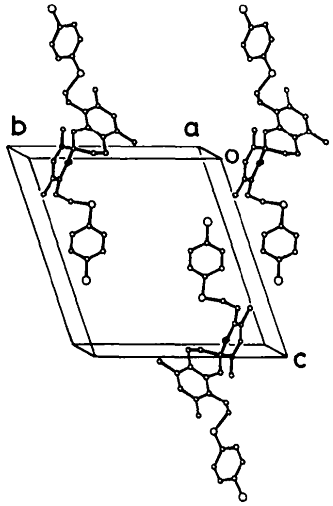

Fig. 2. The crystal packing.

Table 4. *Intramolecular approaches less than* 3·70 Å

E.s.d.'s are 0·01 Å. Transformations of the coordinates x, y, z are denoted by superscripts: (i) $1-x, 1-y, 1-z$; (ii) $-x, -y, -1-z$; (iii) $1-x, -y, -z$; (iv) $1+x, y, z$; (v) $x, y, 1+z$; (vi) $1+x, y, 1+z$; (vii) $1-x, y, -1-z$.

S(1)···S(1^{i})	3·51	C(5)···C(18^{iv})	3·55
Cl(2)···C(19^{ii})	3·59	C(12)···C(14^{iii})	3·51
O(1)···O(4^{iii})	3·65	C(13)···C(14^{iii})	3·57
O(2)···C(11^{iii})	3·42	C(21)···C(32^{v})	3·50
O(2)···C(11^{iv})	3·69	C(22)···C(32^{v})	3·66
O(2)···C(12^{iii})	3·23	C(23)···C(30^{vi})	3·64
O(2)···C(19^{iii})	3·33	C(23)···C(31^{vi})	3·50
O(3)···C(19^{iii})	3·56	C(26)···C(32^{v})	3·68
O(4)···C(10^{iii})	3·51	C(29)···C(29^{vii})	3·67
C(4)···C(18^{iv})	3·58		

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Conformation and Structure of *cyclo*(-*N*-Benzylglycyl-L-prolyl-L-prolyl-)

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Abstract. $C_{19}H_{23}N_3O_3$, $M_r = 341{\cdot}40$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 5{\cdot}688\ (2)$, $b = 11{\cdot}782\ (3)$, $c = 25{\cdot}727\ (9)$ Å, $V = 1724{\cdot}0\ (9)$ Å^3, $D_c = 1{\cdot}315$ Mg m^{-3}; single-crystal diffractometer data up to $\sin\theta/\lambda = 0{\cdot}48$ Å^{-1}; $R_w(F) = 0{\cdot}027$ for 909 independent reflections. The molecule has a crown conformation. One of the three *cis* peptide bonds deviates significantly from planarity.

Introduction. The title compound was synthesized by Krämer (1976). Single crystals were obtained by recrystallization from chloroform. A specimen with

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dimensions 0·2 × 0·2 × 0·3 mm was selected for the experiments and sealed in a glass capillary. Precession and Weissenberg photographs showed an orthorhombic lattice with space group $P2_12_12_1$. Data were collected in three octants of reciprocal space up to $\sin\theta/\lambda = 0{\cdot}48$ Å^{-1}, on a Syntex $P2_1$ diffractometer with Nb-filtered Mo $K\alpha$ radiation. 3904 reflections were obtained, of which 996 were independent. Background corrections were made by profile analysis (Blessing, Coppens & Becker, 1974). Three standard reflections remeasured after every 60 reflections showed long-term fluctuations up to about 3%. The data were rescaled with respect to the standards. A standard deviation was assigned to each reflection according to $\sigma(I) = [\sigma^2(I)_{\text{counting}} + (0{\cdot}03I)^2]^{1/2}$. The equivalent reflections were averaged. The internal consistency index was $R = \sum |I - \langle I \rangle| / \sum I = 0{\cdot}035$. Of the 996 resulting reflections, 909 had $I > 0$ and were used in the analysis. The structure was determined by *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) and refined by least-squares methods. No H atoms could be located; their positions were calculated. They were included in the least-squares refinement but with their isotropic thermal parameters fixed to values derived from the corresponding C atoms.

Table 1. *Positional parameters and equivalent isotropic temperature parameters*

$U_{\text{eq}} = \frac{1}{3}$ trace $\mathbf{U}$.

	x	y	z	U_{eq} (Å^2)
O(1)	0·4771 (7)	−0·0487 (3)	0·2314 (1)	0·069 (3)
O(2)	0·5361 (7)	0·1425 (3)	0·0491 (1)	0·075 (3)
O(3)	0·0557 (7)	0·3249 (3)	0·1889 (1)	0·060 (3)
N(1)	0·3048 (7)	0·2054 (3)	0·2284 (2)	0·039 (3)
N(2)	0·6196 (7)	0·0384 (3)	0·1603 (2)	0·043 (3)
N(3)	0·4400 (7)	0·2771 (3)	0·1074 (1)	0·042 (3)
C(1)	0·1297 (8)	0·1682 (4)	0·2663 (2)	0·052 (3)
C(2)	0·2716 (9)	0·1155 (4)	0·3109 (2)	0·055 (4)
C(3)	0·5288 (9)	0·1387 (4)	0·2971 (2)	0·051 (4)
C(4)	0·5345 (8)	0·1534 (4)	0·2389 (2)	0·036 (3)
C(5)	0·5427 (8)	0·0386 (5)	0·2103 (2)	0·044 (4)
C(6)	0·6434 (10)	−0·0705 (5)	0·1328 (2)	0·072 (4)
C(7)	0·8319 (11)	−0·0510 (5)	0·0930 (2)	0·088 (5)
C(8)	0·9304 (9)	0·0659 (4)	0·1022 (2)	0·063 (4)
C(9)	0·7347 (9)	0·1302 (4)	0·1306 (2)	0·043 (3)
C(10)	0·5591 (10)	0·1843 (5)	0·0924 (2)	0·050 (4)
C(11)	0·4514 (9)	0·3295 (4)	0·1592 (2)	0·040 (3)
C(12)	0·2549 (12)	0·2863 (5)	0·1939 (2)	0·044 (4)
C(13)	0·2830 (8)	0·3339 (4)	0·0697 (2)	0·049 (3)
C(14)	0·3691 (7)	0·4530 (4)	0·0584 (2)	0·042 (3)
C(15)	0·2413 (12)	0·5464 (6)	0·0736 (2)	0·058 (5)
C(16)	0·3327 (16)	0·6552 (6)	0·0639 (3)	0·073 (6)
C(17)	0·5396 (16)	0·6683 (7)	0·0395 (3)	0·071 (6)
C(18)	0·6655 (14)	0·5769 (8)	0·0244 (3)	0·069 (5)
C(19)	0·5844 (10)	0·4693 (6)	0·0339 (2)	0·055 (5)
H(11)	0·042 (9)	0·233 (4)	0·279 (2)	0·065*
H(12)	0·012 (9)	0·101 (4)	0·245 (2)	0·065
H(21)	0·227 (10)	0·147 (4)	0·345 (2)	0·080
H(22)	0·244 (10)	0·029 (4)	0·306 (2)	0·080
H(31)	0·600 (9)	0·202 (4)	0·313 (2)	0·055
H(32)	0·631 (8)	0·080 (4)	0·308 (2)	0·055
H(4)	0·674 (7)	0·201 (4)	0·229 (2)	0·050
H(61)	0·700 (10)	−0·119 (5)	0·163 (2)	0·080
H(62)	0·499 (10)	−0·078 (5)	0·122 (2)	0·080
H(71)	0·966 (10)	−0·109 (4)	0·091 (2)	0·085
H(72)	0·752 (10)	−0·060 (5)	0·058 (2)	0·085
H(81)	1·073 (9)	0·059 (5)	0·128 (2)	0·080
H(82)	0·957 (9)	0·107 (4)	0·069 (2)	0·080
H(9)	0·791 (9)	0·183 (4)	0·153 (2)	0·045
H(111)	0·611 (8)	0·312 (4)	0·175 (2)	0·055
H(112)	0·427 (9)	0·408 (4)	0·155 (2)	0·055
H(131)	0·293 (8)	0·290 (4)	0·035 (2)	0·070
H(132)	0·122 (9)	0·344 (4)	0·086 (2)	0·070
H(15)	0·103 (9)	0·525 (5)	0·088 (2)	0·075
H(16)	0·235 (9)	0·711 (5)	0·072 (2)	0·075
H(17)	0·603 (9)	0·748 (5)	0·030 (2)	0·080
H(18)	0·828 (9)	0·589 (4)	0·005 (2)	0·070
H(19)	0·692 (9)	0·402 (4)	0·023 (2)	0·070

* H-atom thermal parameters not refined.

The structure refined to $R(F) = 0{\cdot}056$, $R_w(F) = 0{\cdot}027$ and $S = [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO}-\mathrm{NV})]^{1/2} = 1{\cdot}60$. A final difference synthesis was featureless. Scattering factors for C, N and O were from *International Tables for X-ray Crystallography* (1974), those for H from Stewart, Davidson & Simpson (1965). The calculations were performed with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on the Univac 1108 computer of the University of Frankfurt.

Positional parameters are reported in Table 1.* Bond lengths and angles are given in Figs. 1 and 2, and a stereoscopic view of the molecular conformation is in Fig. 3.

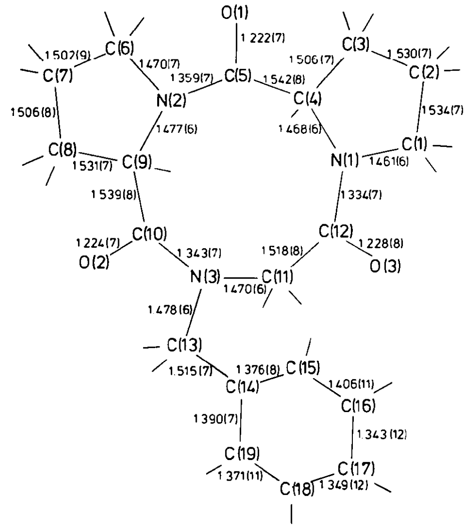

Fig. 1. Bond distances (Å) for *cyclo*[-*N*-BzlGly-(L-Pro)$_2$-]. E.s.d.'s are in parentheses.

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* Lists of structure factors and temperature parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36448 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

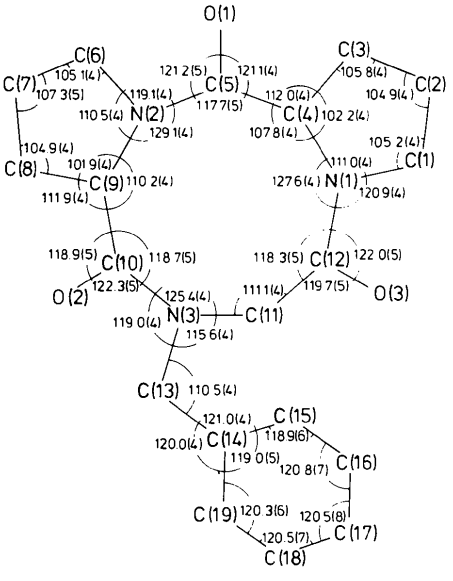

Fig. 2. Bond angles (°) for *cyclo*[-*N*-BzlGly-(L-Pro)$_2$-]. E.s.d.'s are in parentheses.

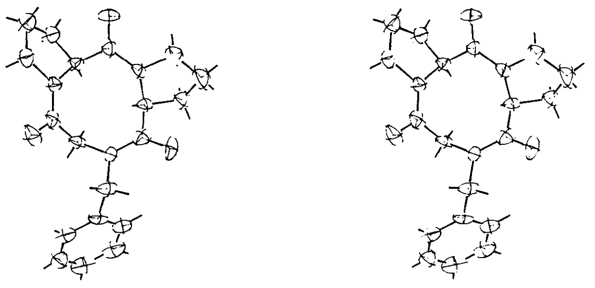

Fig. 3. A stereoscopic view of the molecule. The thermal ellipsoids are the 50% probability surfaces.

Discussion. The structure determination of the title compound is part of our study of the relationship between the conformation of cyclic tripeptides in solution and the crystalline state. It has been shown by Kessler, Kondor, Krack & Krämer (1978) that in solution *cyclo*[-*N*-BzlGly-(L-Pro)$_2$-] exhibits an equilibrium between a boat and a crown conformation. The boat conformation is the dominant form in chloroform, while in more polar solvents the amount of crown increases.

The present structure analysis in the crystalline state reveals only the crown conformation.

All three peptide bonds have the *cis* configuration, which is a requirement for cyclic tripeptides.

Bond distances and angles (Figs. 1 and 2) for the three peptide groups are very similar and agree well with values observed in the other cyclic tripeptides (Druyan, Coulter, Walter, Kartha & Ambady, 1976; Kartha & Ambady, 1975; Bats & Fuess, 1980). The main difference between the prolyl and the *N*-benzylglycyl residues is the angle C^{α}—N—C^{δ} which is smaller in the strained proline ring than in the more flexible glycine group.

The main dihedral angles in the tripeptide ring are summarized in Table 2. Again the results for the three peptide units are very similar and in agreement with those for the other cyclic tripeptides with a crown conformation: *cyclo*[-(L-Pro)$_3$-] (Druyan, Coulter, Walter, Kartha & Ambady, 1976), *cyclo*[-L-Hyp-(L-Pro)$_2$-] (Kartha & Ambady, 1975) and *cyclo*[-(*N*-BzlGly)$_2$-L-Pro-] (Bats & Fuess, 1980).

Consequently, there is no clear difference in the conformation of the backbone in cyclic tripeptides constituted from the inflexible prolyl or the more flexible glycyl group.

The planarity of the peptide group is given by the dihedral angle ω, which is 0° for a planar *cis* peptide bond. Only the C(5)—N(2) peptide bond shows a small but significant non-zero value. The planarity of the amide N atoms can be described by the deviation of the N atom from the plane through its three neighbours: 0·05 (1), 0·09 (1) and 0·00 (1) Å for N(1), N(2) and N(3) respectively. Consequently, the N atoms of the proline groups have a small amount of pyramidal character, while the N atom of the glycine group is perfectly planar.

The C—C bond lengths in the benzene ring appear unusually short (average value 1·37 Å), due to the larger thermal motion of this group. The packing of the structure shows two short intermolecular contact distances between H and O atoms (Table 3). No other contacts are shorter than the sum of the van der Waals radii of the atoms involved.

The authors thank Professor Dr Kessler, Institut für Organische Chemie, Frankfurt, for providing the single crystals.

Table 2. *Selected dihedral angles* (°) *in the peptide ring* (*e.s.d.* = 0·7°)

φ: C′—N—C_α—C′		ψ: N—C_α—C′—N′	
C(12)–N(1)–C(4)–C(5)	−100	N(1)–C(4)–C(5)–N(2)	88
C(5)–N(2)–C(9)–C(10)	−104	N(2)–C(9)–C(10)–N(3)	94
C(10)–N(3)–C(11)–C(12)	−94	N(3)–C(11)–C(12)–N(1)	100
ω: C_α'—C′—N—C_α		θ'': C_δ—N—C_α—C′	
C(11)–C(12)–N(1)–C(4)	2	C(1)–N(1)–C(4)–C(5)	88
C(4)–C(5)–N(2)–C(9)	11	C(6)–N(2)–C(9)–C(10)	90
C(9)–C(10)–N(3)–C(11)	−4	C(13)–N(3)–C(11)–C(12)	86

Table 3. *Short intermolecular contacts*

	C—H (Å)	H···O (Å)	C···O (Å)	C—H—O (°)
C(9)–H(9)···O(3)*	0·90 (5)	2·44 (5)	3·294 (6)	159 (4)
C(11)–H(111)···O(3)*	1·01 (5)	2·56 (5)	3·521 (6)	159 (4)

* Symmetry code: 1 + *x*, *y*, *z*.

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Structure of (3,4-Dihydroxyphenethyl)trimethylammonium Bromide (Coryneine Bromide)*

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Abstract. $C_{11}H_{18}NO_2^+.Br^-$, $M_r = 276\cdot2$, monoclinic, $P2_1/c$, $a = 9\cdot730\,(1)$, $b = 10\cdot141\,(3)$, $c = 12\cdot989\,(2)$ Å, $\beta = 101\cdot55\,(5)°$, $Z = 4$, $D_c = 1\cdot461$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0\cdot71069$ Å) $= 3\cdot17$ mm^{-1}. Final $R = 0\cdot041$ for 1638 observed counter amplitudes. The ethylammonium side chain is in the extended conformation, C—C—C—N$^+$ torsion angle 179·8 (6)°. The plane of these atoms is inclined at 76 (1)° to the plane of the phenyl ring.

Introduction. Coryneine, the trimethylammonium derivative of dopamine, has high nicotine-like ganglion-stimulant activity and is also a potent neuromuscular blocking agent (Barlow, Bowman, Ison & McQueen, 1974). It is of interest, therefore, to compare its dimensions and conformation with those of the closely related epinine (Giesecke, 1976), dopamine (Giesecke, 1980) and other sympathomimetic phenethylamines (Carlström, Bergin & Falkenberg, 1973).

Single crystals were obtained from aqueous solution. After preliminary examination by photographic methods, a crystal 0·4 × 0·3 × 0·05 mm was mounted on an Enraf–Nonius CAD-4 diffractometer. Cell dimensions were obtained by least squares from the setting angles of 25 reflections measured with graphite-monochromated Mo $K\alpha$ radiation. 2206 reflections (2° < 2θ < 50°) were scanned in the ω–2θ mode, of which 1638 [$I > 2\cdot5\sigma(I)$] were considered observed and used in the analysis. Two standard reflections, remeasured every hour, showed no significant variation with time. The intensities were not corrected for absorption.

The structure was solved by Patterson and Fourier methods and refined by least-squares methods with anisotropic temperature factors for all non-H atoms. H

Table 1. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3)

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	x	y	z	U_{eq}
C(1)	4151 (4)	4292 (4)	1380 (3)	36 (2)
C(2)	5421 (4)	3628 (4)	1629 (3)	33 (2)
C(3)	6237 (4)	3696 (4)	2645 (3)	26 (2)
C(4)	5744 (4)	4396 (4)	3411 (3)	35 (2)
C(5)	4497 (4)	5056 (4)	3168 (3)	43 (2)
C(6)	3693 (5)	5011 (4)	2161 (3)	42 (2)
C(7)	3309 (5)	4267 (4)	258 (3)	46 (2)
C(8)	2558 (4)	2967 (4)	26 (3)	35 (2)
C(9)	1060 (4)	1506 (4)	−1210 (4)	42 (2)
C(10)	2536 (5)	3084 (5)	−1892 (3)	49 (3)
C(11)	498 (4)	3842 (4)	−1239 (3)	42 (2)
N	1688 (4)	2860 (3)	−1079 (3)	32 (2)
O(1)	7525 (3)	3118 (3)	2924 (2)	56 (2)
O(2)	6517 (3)	4488 (4)	4412 (2)	43 (2)
Br	8914 (1)	2329 (1)	966 (1)	44 (2)

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* Contribution from the Crystallography Unit, Universities of Aston and Birmingham.

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