Comparison of equivalent bond lengths and angles among the three structures again shows good agreement, particularly within the 'Cookson-cage' framework (Cookson, Grundwell, Hill & Hudec, 1964). Two notable features in the bonding geometries of all three structures are the significant bond elongations of the C(5)—C(5*A*) and C(3)—C(3*A*) bonds (Tables 4 and 5), the former being a propellane-type bond and both reflecting the mutual repulsion between the C(4) and C(4*A*) carbonyl groups. Similar effects exist in related structures, which also exhibit similar torsional angles within the cage structure (Marchand, Suri, Earlywine, Powell & van der Helm, 1984; Mehta, Singh, Srikrishna, Cameron & Chan, 1979; Okamoto, Harano, Yasuda, Osawa & Kanematsu, 1983).

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Structures of Dipeptides Trityl-glycyl-L-phenylalanine Benzyl Ester and *tert*-Butyloxycarbonyl-L-phenylalanyl-*S*-ethyl-L-cysteine Dimethylamide

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(*Received* 16 *September* 1985; *accepted* 20 *June* 1986)

Abstract. $C_{37}H_{34}N_2O_3$ (I), $M_r = 554{\cdot}68$, monoclinic, $C2$, $a = 26{\cdot}133$ (21), $b = 10{\cdot}455$ (8), $c = 11{\cdot}809$ (10) Å, $\beta = 108{\cdot}88$ (6)°, $V = 3053$ (4) Å^3, $Z = 4$, $D_x = 1{\cdot}207$ (2) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}827$ cm^{-1}, $F(000) = 1176$, room temperature, $R = 0{\cdot}0462$ for 1259 unique observed reflections. $C_{21}H_{33}N_3O_4S$ (II), $M_r = 423{\cdot}57$, monoclinic, $P2_1$, $a = 9{\cdot}817$ (24), $b = 9{\cdot}318$ (8), $c = 13{\cdot}641$ (20) Å, $\beta = 97{\cdot}65$ (16)°, $V = 1237$ (4) Å^3, $Z = 2$, $D_x = 1{\cdot}137$ (4) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}609$ cm^{-1}, $F(000) = 456$, room temperature, $R = 0{\cdot}0531$ for 825 unique observed reflections. The values of the torsion angles observed in the peptide group are $\omega = 176{\cdot}68$ (30), $\upsilon = -2{\cdot}92$ (25)° and $\omega = 174{\cdot}96$ (32), $\upsilon = 0{\cdot}00$ (25)° for compounds (I) and (II) respectively and demonstrate the peptide bonds to be 'planar and *trans*'. The molecules are interconnected by hydrogen bonds [O(23)···H(20) = 2·427 (83) Å (I); O(22)···H(8) = 1·932 (176), O(18)···H(19) = 2·087 (95) Å (II)].

0108-2701/86/121777-04$01.50

Introduction. In a previous communication we reported the synthesis of various *N*-trityl-dipeptide benzyl esters, by the method of dicyclohexylcarbodiimide (DCC) mediated with 1-hydroxybenzotriazole (HOBt) without racemization (Matsoukas, Tsegenidis, Cordopatis & Theodoropoulos, 1984). The IR spectra of these dipeptides in $CHCl_3$ solution indicated an equilibrium mixture with the *cis* conformer strongly predominating (intense absorption band at 3400 cm^{-1}). When Gly is the C-terminal amino acid, the ^1H NMR spectra revealed that the two glycine CH_2 protons are distinctly non-equivalent, suggesting a strong anisotropic effect of the trityl group and thus a *cis* conformation of the common amide bond. (Rotations of groups or anisotropic effects in one amino acid usually affect the next amino acid when the amide bond is in a *cis* conformation.) The discrepancy of Trt-Gly-L-Phe-OBzl (Gly at the N terminus) in showing no asymmetry in spite of the presence of the trityl group and the prevailing *cis* conformation of the amide bond could be due to a rotational freedom for the two CH_2 protons which enter into the shielding zone of the trityl group. The present paper concerns the crystal structure of the dipeptide Trt-glycyl-L-phenylalanine benzyl ester (I) in order to compare the conformations observed in solution and in the solid state.

On the other hand, in a continuous effort to study the conformation of various peptide hormones, we report the crystal structure of the dipeptide Boc-L-Phe-L-Cys(Et)-N$(CH_3)_2$ (II) which is the C-terminal part of an enkephalin analogue synthesized previously in this laboratory (Theodoropoulos, Cordopatis, Barlos & Papaioannou, 1983). This analogue shows considerably lower affinity for the μ receptor in comparison to Leu^5-enkephalin.

Experimental. The synthesis of Trt-Gly-L-Phe-OBzl (I) was effected by coupling Trt-Gly and L-Phe-OBzl *p*-toluenesulfonate by the DCC/HOBt method reported previously (Matsoukas *et al.*, 1984). The dipeptide has m.p. 381–382 K after recrystallization from ether–petroleum ether (1:1 *v*/*v*), $[\alpha]_D^{25.0°C} = +10.4°$ ($CHCl_3$, 1·0 g dm^{-3}) and satisfactory elemental analysis. Crystal 0·07 × 0·15 × 0·20 mm, Syntex $P2_1$ diffractometer, 15 reflections ($2\theta < 25°$) used for measuring lattice parameters, no absorption correction applied, $2\theta = 47°$ with $\omega/2\theta$ scan, $-27 \le h \le 26$, $0 \le k \le 10$, $0 \le l \le 13$, one standard reflection measured every 50 reflections showed only random deviation from its mean intensity, 2403 unique measured reflections of which 1259 observed with $I > 2{\cdot}5\sigma(I)$, $R = 0{\cdot}0462$, $wR = 0{\cdot}040$, $\sum w(\Delta F)^2$ minimized, $w = 1{\cdot}4414/[\sigma^2(F) + 0{\cdot}00019F^2]$, max. Δ/σ (for non-H atoms) $= 0{\cdot}35$, max. and min. in final $\Delta\rho$ map 0·05 and $-0{\cdot}05$ e $Å^{-3}$. H atoms calculated expect H(20) and H(24) which were located and refined with isotropic temperature factors, anisotropic thermal parameters for all non-H atoms.

Table 1. *Positional* (×10^4) *and isotropic thermal* (×10^2) *parameters with their e.s.d.'s in parentheses*

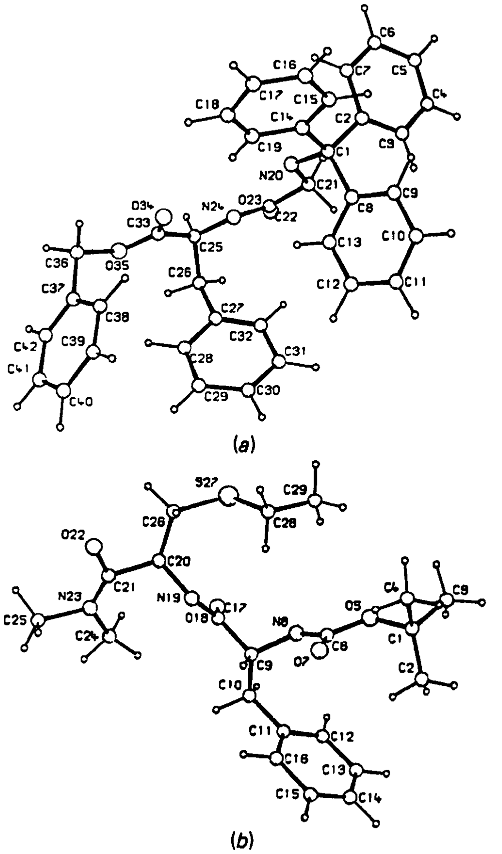
	x	*y*	*z*	B_{eq}/B_{iso}($Å^2$)
Compound (I)				
C(1)	6618 (3)	5144	1532 (7)	391
C(2)	6488 (3)	6404 (11)	2072 (8)	380
C(3)	6498 (3)	7590 (13)	1540 (7)	439
C(4)	6320 (3)	8682 (13)	1969 (8)	523
C(5)	6146 (3)	8621 (14)	2947 (10)	572
C(6)	6116 (3)	7448 (16)	3466 (8)	566
C(7)	6287 (3)	6334 (13)	3032 (8)	517
C(8)	7000 (3)	5316 (12)	777 (8)	401
C(9)	7454 (3)	6085 (13)	1201 (8)	552
C(10)	7824 (4)	6183 (14)	597 (12)	664
C(11)	7737 (4)	5560 (14)	−457 (11)	658
C(12)	7299 (4)	4763 (14)	−888 (9)	632
C(13)	6923 (3)	4643 (12)	−278 (8)	500
C(14)	6905 (3)	4188 (11)	2510 (7)	360
C(15)	7316 (3)	4599 (13)	3524 (7)	535
C(16)	7602 (4)	3720 (16)	4401 (8)	616
C(17)	7488 (4)	2467 (15)	4281 (9)	592
C(18)	7082 (4)	2029 (13)	3282 (8)	650
C(19)	6792 (3)	2886 (13)	2404 (7)	494
N(20)	6102 (2)	4547 (10)	795 (6)	380
C(21)	5739 (3)	5313 (12)	−183 (6)	397
C(22)	5306 (3)	4481 (13)	−1042 (7)	397
O(23)	4880 (2)	4886 (10)	−1689 (4)	481
N(24)	5444 (3)	3235 (12)	−1005 (6)	412
C(25)	5096 (3)	2216 (12)	−1684 (7)	418
C(26)	4985 (3)	2307 (12)	−3058 (6)	471
C(27)	5488 (4)	2271 (15)	−3410 (7)	532
C(28)	5684 (4)	1143 (16)	−3695 (8)	731
C(29)	6143 (7)	1093 (21)	−4045 (11)	1058
C(30)	6395 (6)	2191 (26)	−4127 (13)	1106
C(31)	6213 (6)	3355 (21)	−3869 (12)	1089
C(32)	5759 (5)	3352 (16)	−3521 (9)	827
C(33)	5356 (3)	973 (13)	−1144 (8)	427
O(34)	5764 (2)	906 (11)	−287 (5)	616
O(35)	5078 (2)	−16 (11)	−1724 (5)	534
C(36)	5282 (3)	−1306 (13)	−1292 (8)	517
C(37)	5645 (3)	−1826 (13)	−1954 (8)	460
C(38)	6188 (3)	−1485 (13)	−1585 (7)	534
C(39)	6521 (4)	−1972 (13)	−2172 (10)	627
C(40)	6319 (5)	−2771 (15)	−3149 (11)	764
C(41)	5777 (5)	−3097 (14)	−3521 (9)	748
C(42)	5436 (4)	−2595 (13)	−2944 (8)	605
H(20)	5918 (29)	4153 (75)	1257 (67)	573
H(24)	5781 (24)	2944 (65)	−498 (53)	302
Compound (II)				
C(1)	3567 (16)	4061 (18)	13900 (12)	671
C(2)	2777 (17)	4647 (21)	14664 (11)	936
C(3)	4634 (14)	2950 (17)	14297 (11)	863
C(4)	4303 (14)	5305 (20)	13417 (12)	920
O(5)	2687 (9)	3257 (10)	13143 (6)	541
C(6)	1632 (14)	3931 (21)	12594 (9)	409
O(7)	1442 (9)	5223 (11)	12524 (7)	595
N(8)	822 (11)	2904 (14)	12087 (7)	388
C(9)	−475 (12)	3353 (14)	11527 (7)	378
C(10)	−1715 (12)	2838 (16)	12044 (8)	557
C(11)	−1626 (13)	3466 (18)	13061 (10)	479
C(12)	−1184 (13)	2621 (19)	13886 (10)	710
C(13)	−1081 (17)	3264 (28)	14837 (12)	801
C(14)	−1432 (19)	4664 (30)	14955 (14)	843
C(15)	−1880 (19)	5517 (20)	14114 (14)	859
C(16)	−1991 (14)	4889 (18)	13186 (11)	601
C(17)	−594 (12)	2652 (17)	10503 (9)	381
O(18)	−739 (10)	1347 (11)	10388 (5)	524
N(19)	−417 (11)	3532 (13)	9769 (8)	472
C(20)	−383 (14)	3028 (13)	8742 (8)	408
C(21)	−1369 (22)	3944 (19)	8035 (10)	558
O(22)	−952 (12)	4821 (11)	7462 (7)	655
N(23)	−2715 (17)	3687 (14)	8049 (9)	601
C(24)	−3296 (14)	2735 (20)	8728 (10)	758
C(25)	−3740 (18)	4584 (17)	7384 (11)	964
C(26)	1091 (14)	3192 (16)	8435 (9)	629
S(27)	2349 (4)	2099	9187 (3)	772
C(28)	3149 (21)	3550 (24)	10057 (14)	1203
C(29)	4125 (22)	2855 (33)	10695 (15)	1735
H(8)	760 (146)	1885 (174)	12524 (100)	1090
H(19)	−423 (67)	4523 (95)	9819 (51)	1

The dipeptide Boc-L-Phe-L-Cys(Et)-N$(CH_3)_2$ (II), prepared by the same method of coupling, DCC/HOBt, without racemization, after recrystallization from ethyl acetate–petroleum ether (1:2 v/v) has m.p. 373–375 K and $[\alpha]_D^{25\cdot0\,^\circ C} = -14\cdot5^\circ$(MeOH, $1\cdot0$ g dm^{-3}) (Theodoropoulos *et al.*, 1983). Crystal $0\cdot06 \times 0\cdot12 \times 0\cdot18$ mm, Syntex $P2_1$ diffractometer, 15 reflections ($2\theta < 26^\circ$) for lattice parameters, no absorption correction, $2\theta = 47^\circ$ with $\omega/2\theta$ scan, $-9 \leq h \leq 9$, $0 \leq k \leq 10$, $0 \leq l \leq 14$, one standard reflection every 50 without deviation, 1962 unique measured reflections, 825 observed with $I > 2\cdot5\sigma(I)$, $R = 0\cdot0531$, $wR = 0\cdot0474$, $\sum w(\Delta F)^2$ minimized, $w = 1\cdot4732/[\sigma^2(F) + 0\cdot00033F^2]$, max. Δ/σ (for non-H atoms) $= 0\cdot22$, max. and min. $\Delta\rho$ $0\cdot06$ and $-0\cdot07$ e Å^{-3}. Non-H atoms refined anisotropically, H atoms calculated except H(8) and H(19) which were located and refined isotropically. Computer programs used: *MULTAN*11/84 (Main, Germain & Woolfson, 1984) (direct-methods structure solution), *SHELX*76 (Sheldrick, 1976), and *PLUTO* (Motherwell & Clegg, 1978); atomic scattering factors from *SHELX*76.

Discussion. Fractional atomic coordinates with equivalent isotropic thermal parameters for the non-H atoms are given in Table 1, important distances and bond angles in Table 2.* The numbering scheme for both compounds is shown in Fig. 1. The torsion angles of the peptide group for compound (I) [$\omega = 176\cdot68$ (30), $\upsilon = -2\cdot92$ (25)°] clearly demonstrate that the peptide bond is 'planar and *trans*', whereas the *cis* conformer is observed in solution. In this case the H atom bonded to N(24) approaches O(34) and presumably forms a hydrogen bond [2·147 (64) Å]. Moreover, the stability of the structure is achieved by hydrogen bonds between neighbouring molecules [O(23)···H(20) = 2·427 (83) Å]. The above considerations concerning the torsion angles are also valid for compound (II) [$\omega = 174\cdot96$ (32), $\upsilon = 0\cdot00$ (25)°] and confirm the presence of the *trans* conformer. In this compound two strong intermolecular hydrogen bonds [O(22)···H(8) = 1·932 (176), O(18)···H(19) = 2·087 (95) Å] and one intramolecular hydrogen bond [O(5)···H(8) = 2·345 (16) Å] exist. Also, it is well known that the urethane amide bond adopts the *cis* and *trans* conformations in crystals (Benedetti, Pedone, Toniolo, Nemethy, Pottle & Scheraga, 1980), in contrast to the strong preference of the peptide bond for the *trans* form. In the case of compound (II), a *trans* urethane bond is observed [O(5)—C(6)—N(8)—C(9) =

Table 2. *Important bond lengths* (Å), *angles* (°) *and torsion angles* (°) *with e.s.d.'s*

Compound (I)		Compound (II)	
H(20)—N(20)	0·932 (75)	C(1)—O(5)	1·462 (14)
C(1)—N(20)	1·485 (9)	O(5)—C(6)	1·349 (14)
N(20)—C(21)	1·472 (9)	C(6)—O(7)	1·221 (16)
C(21)—C(22)	1·523 (10)	C(6)—N(8)	1·372 (16)
C(22)—O(23)	1·204 (8)	N(8)—H(8)	1·127 (159)
C(22)—N(24)	1·349 (10)	N(8)—C(9)	1·456 (13)
N(24)—H(24)	0·940 (58)	C(9)—C(10)	1·560 (15)
N(24)—C(25)	1·460 (9)	C(9)—C(17)	1·532 (15)
C(25)—C(26)	1·556 (9)	C(17)—O(18)	1·232 (13)
C(25)—C(33)	1·509 (11)	C(17)—N(19)	1·323 (15)
C(33)—O(34)	1·211 (8)	N(19)—H(19)	0·926 (82)
C(33)—O(35)	1·321 (9)	N(19)—C(20)	1·482 (14)
O(35)—C(36)	1·479 (9)	C(21)—O(22)	1·238 (17)
		S(27)—C(26)	1·811 (14)
C(21)—N(20)—C(1)	117·6 (6)	C(6)—N(8)—C(9)	118·2 (11)
H(20)—N(20)—C(1)	112·6 (46)	H(8)—N(8)—C(6)	112·9 (69)
C(21)—N(20)—H(20)	112·1 (45)	C(9)—N(8)—H(8)	114·5 (74)
C(25)—N(24)—C(22)	125·1 (7)	C(17)—N(19)—C(20)	122·8 (10)
H(20)—N(24)—C(22)	121·2 (42)	H(19)—N(19)—C(17)	124·0 (49)
C(25)—N(24)—H(24)	113·6 (42)	C(20)—N(19)—H(19)	112·7 (47)
		C(26)—S(17)—C(28)	98·5 (8)
C(21)—C(22)—N(24)—C(25)	176·68 (30)	C(9)—C(17)—N(19)—C(20)	174·96 (32)
O(23)—C(22)—N(24)—C(25)	−2·92 (25)	O(18)—C(17)—N(19)—C(20)	0·00 (25)
N(20)—C(21)—C(22)—O(23)	157·54 (31)	N(8)—C(9)—C(17)—O(18)	67·86 (31)
C(22)—N(24)—C(25)—C(33)	−166·36 (32)	C(10)—C(9)—C(17)—O(18)	−52·14 (37)
C(22)—N(24)—C(25)—C(26)	67·90 (28)	C(17)—N(19)—C(20)—C(21)	129·81 (40)
		C(17)—N(19)—C(20)—C(26)	−111·47 (41)
		O(5)—C(6)—N(8)—C(9)	173·03 (39)
		O(7)—C(6)—N(8)—C(9)	−9·35 (38)
		C(1)—O(5)—C(6)—N(8)	−168·40 (36)
		C(1)—O(5)—C(6)—O(7)	14·04 (35)



(*a*)

(*b*)

Fig. 1. Perspective view of (*a*) compound (I) and (*b*) compound (II), showing atom numbering.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, a complete list of bond lengths, angles and torsion angles and equations of planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43177 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

173·03 (39)°], although it is present with the bulky Phe side chain in close proximity to the Boc group (Benedetti *et al.*, 1980). On the other hand, the value of the torsion angle N(8)—C(9)—C(17)—O(18) between the urethane moiety and the next peptide group is 67·86 (31)°, showing that the Boc derivative occurs in the crystal in a bent conformation.

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Acta Cryst. (1986). C**42**, 1780–1782

Structure of Spirosta-5,25(27)-diene-3β,11α-diol

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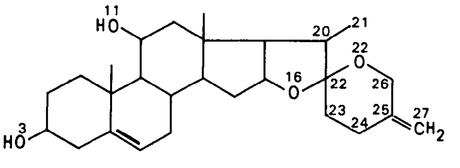
(*Received* 29 *April* 1986; *accepted* 24 *June* 1986)

Abstract. $C_{27}H_{40}O_4$, $M_r = 428{\cdot}61$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}369\,(1)$, $b = 12{\cdot}240\,(3)$, $c = 30{\cdot}547\,(5)$ Å, $V = 2381\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}195$ g cm^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}73$ cm^{-1}, $F(000) = 936$, $T = 293\,(2)$ K, $R = 0{\cdot}045$ for 1615 unique observed reflections. The compound was isolated from *Helleborus serbicus* Adam 1906 (Ranunculaceae). The rings have the following conformations: *A*, *C* and *F* chair; *B* and *E* intermediate between half chair and envelope; *D* half chair. The molecules are linked by O—H···O hydrogen bonds into chains along the *b* axis. The molecule is very similar to molecule (I) of spirosta-5,25(27)-diene-1β,3β,11α-triol monohydrate [Kálmán, Argay, Ribár, Živanov-Stakić & Vladimirov (1985). *Acta Cryst.* C**41**, 1645–1647].

Introduction. This new steroid sapogenin was isolated from the subterranean organs of the plant *Helleborus serbicus* Adam 1906 (Ranunculaceae) by column chromatography and preparative thin-layer chromatography on silica gel using mobile-phase isopropyl ether–methanol 95:5 (*v*/*v*) and chloroform–methanol 95:5. The crystals reached a melt at 496–498 K. The chemical structure (1) proposed from chemical and spectroscopic studies was substantiated by X-ray diffraction.



(1)

Experimental. Colourless crystal *ca* 0·4 × 0·6 × 0·9 mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo *K*α radiation. $0{\cdot}0327 \le \sin\theta/\lambda \le 0{\cdot}6606$ Å^{-1}, ω–2θ scan, h 0–8, k 0–16, l 0–40. Cell parameters by least-squares fit for 18 centred reflections. Systematic absences: $h = 2n + 1$ in $h00$, $k = 2n + 1$ in $0k0$, $l = 2n + 1$ in $00l$. Of 2779 unique reflections, 1615 taken as observed with $I > 2{\cdot}5\sigma(I)$. No absorption correction performed. Three standard

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