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β-Turn structure of a tripeptide *N*-(*tert*-butoxycarbonyl)-Phe-D-Pro-Gly methyl ester monohydrate

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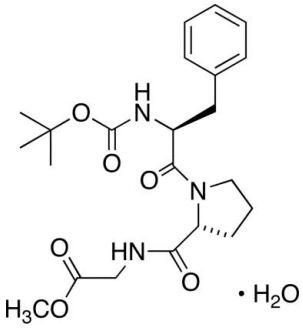
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.006 Å; R factor = 0.060; wR factor = 0.177; data-to-parameter ratio = 10.4.

The title peptide, *N*-(*tert*-butoxycarbonyl)phenylalanyl-D-prolylglycine methyl ester monohydrate, $C_{22}H_{31}N_3O_6\cdot H_2O$, was designed to form a β-turn structure. The crystal structure exhibits a type-II β-turn structure which is stabilized through the intermolecular hydrogen bond between the Gly–NH group and the *tert*-butyloxycarbonyl O atom. The water molecule further interacts with the carbonyl O atoms of the peptide, stabilizing the β-turn structure. The circular dichroism spectra suggest the existence of a stable conformation.

Related literature

For related literature, see: Cremer & Pople (1975); Espinosa & Gellman (2000); Reiersen & Rees (2000); Schwyzer & Ludescher (1968); Tamaki *et al.* (1985); Venkatraman *et al.* (2001).



Experimental

Crystal data

$C_{22}H_{31}N_3O_6\cdot H_2O$
M_r = 451.51
Orthorhombic, $P2_12_12_1$
a = 9.0814 (8) Å
b = 11.6889 (10) Å
c = 22.685 (2) Å
V = 2408.1 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 296 (2) K
0.40 × 0.20 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.912, T_{max} = 0.982
28185 measured reflections
3002 independent reflections
2771 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.177
S = 1.11
3002 reflections
289 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N40—H40···O14	0.86	2.27	3.097 (4)	162
O1—H1···O41	0.87	2.21	3.080 (7)	174
O1—H2···O14	0.84	2.01	2.843 (6)	171
N20—H20···O28^{i}	0.86	2.01	2.864 (3)	174

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+2$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2053).

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supplementary materials

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β-Turn structure of a tripeptide *N*-(*tert*-butoxycarbonyl)-Phe-D-Pro-Gly methyl ester monohydrate

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Comment

The certain motifs have been studied to engineer peptide mimics with well defined conformation and novel functions (Venkatraman *et al.*, 2001). The structural studies of these motifs will provide the important fundamental information for peptide design. A protected tripeptide *Boc-Phe-D-Pro-Gly*-O*Me*, that *Boc* = *N-t*-butyloxycarbonyl moiety, was designed to form β-turn from motifs of *Gramicidin S* (Schwyzer & Ludescher, 1968) and analogues (Tamaki *et al.*, 1985) considering a *D-Pro-Gly* segment of β-hairpin peptide (Espinosa & Gellman, 2000).

The molecular structure of the title compound (**I**) is shown in Fig.1. A l l peptide bonds are planar with a *trans* conformation. The distances of the atoms from the best planes of peptide bond are lower than 0.062Å for the C14—N20, C28—N30 and C34—N40 bond planes. The *Pro* residue shows a ring puckering with amplitude of Q2 = 0.408 (5)Å and phase of φ2 = 261.2 (5)° (Cremer & Pople, 1975). The torsion angles, (C14—N20—C20—C28, N20—C20—C28—N30) and (C28—N30—C30—C34, N30—C30—C34—N40), are (−54.6 (4)°, 129.8 (3)°) and (86.9 (4)°, −14.0 (5)°), respectively, and classified as type II β-turn. A N–H···O=C intramolecular hydrogen bond is formed between *Gly*–NH and *Boc*=O: N40···O14 = 3.097 (4)Å stabilizing of the β-turn structure. In this crystal, the hydrated water molecule further stabilizes the folded structure by forming O–H···O=C interactions with the carbonyl oxygen atoms (O1···O14 and O1···O41). A N–H···O=C interaction is established between the *Gly* residue (N20) and *Pro* residue (O28) translated by (1/2 + *x*, 3/2 − *y*, 2 − *z*). This motif propagates along the *a* axis (Fig. 2).

The CD spectra of **I** are measured in acetonitrile solutions changing the trifluoroethanol (*TFE*) concentration. *TFE* provides a specific environment conducive to hydrophobic interactions between peptide side chains (Reiersen & Rees, 2000), and is often used to induce structural changes of polypeptides. The isosbestic point around 220 nm indicates the conformational equilibrium, but several concentrations of *TFE* had little effect on the spectra (Fig.3), indicating that the solution conformations of **I** are stable with respect to *TFE* titration. These results indicate that this tripeptide motif forms a stable β-turn structure and could be a candidate to induce β-turn into poplypeptides.

Experimental

The title compound was synthesized by a conventional liquid-phase method, and purified by silica-gel column chromatography and re-crystallization, respectively. Crystals were grown from ethylacetate and methanol (3:1) solutions by vapor diffusion method. CD spectra were measured by JASCO J-820 dichrograph at approximate 0.05 mmol dm^{-3} peptide concentrations. Spectra were scanned at 5 $nm{\cdot}min^{-1}$ speed with 0.1 nm interval-uptake to a computer. Data were averaged at each 1 nm and plotted.

Refinement

H atoms were treated as riding atoms with distances C–H = 0.96–0.98Å and N–H = 0.86 Å; U_{iso}(H) = 1.2U_{eq}(C), U_{iso}(H) = 1.5U_{eq}(C_{methyl}) and U_{iso}(H) = 1.2U_{eq}(N). H atoms of the water molecule were found in a difference Fourier map considering hydrogen-bond networks and refined with U_{iso}(H) = 1.5U_{eq}(O). In the absence of any significant anomalous scattering, 2290 Friedel pairs were merged prior to the final refinements, and the absolute structure was set by reference to the known chirality of the amino acid employed.

Figures

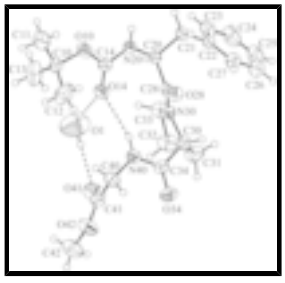


Fig. 1. Views of **I** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as spheres of arbitrary radius. Dotted lines represent hydrogen bonds.

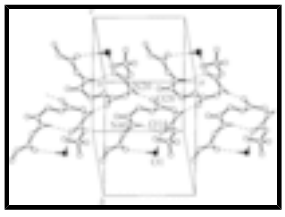


Fig. 2. Packing diagram of **I**. Side chains of amino acids are omitted for clarity. H atoms related to hydrogen bonds are included in drawing. Dotted lines represent hydrogen bonds. Open and closed circles represent non-hydrogen atoms and water molecules - O1.

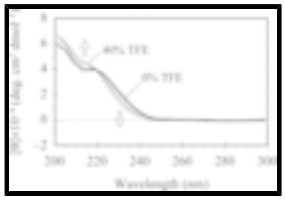


Fig. 3. CD spectra of **I**. Trifluoroethanol was added to acetonitrile solutions to concentrations of 0, 10, 20, 30 and 40%.

Boc-Phe-D-Pro-Gly-OMe monohydrate

Crystal data

$C_{22}H_{31}N_3O_6{\cdot}H_2O$	F_{000} = 968
M_r = 451.51	D_x = 1.245 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 7049 reflections
a = 9.0814 (8) Å	θ = 2.4–22.1°
b = 11.6889 (10) Å	μ = 0.09 mm^{-1}
c = 22.685 (2) Å	T = 296 (2) K
V = 2408.1 (4) Å^3	Needle, colourless
Z = 4	0.40 × 0.20 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	3002 independent reflections
Radiation source: MacScience M18XCE (rotating anode)	2771 reflections with $I > 2\sigma(I)$
Monochromator: Confocal multilayer optics	$R_{int} = 0.031$
Detector resolution: 8.366 pixels mm^{-1}	$\theta_{max} = 27.1°$
$T = 296(2)$ K	$\theta_{min} = 1.8°$
ω–scan	$h = -11 \rightarrow 11$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$k = -14 \rightarrow 14$
$T_{min} = 0.912$, $T_{max} = 0.982$	$l = -28 \rightarrow 29$
28185 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: Difmap
Least-squares matrix: Full	Hydrogen site location: Geom
$R[F^2 > 2\sigma(F^2)] = 0.060$	H-atom parameters constrained
$wR(F^2) = 0.177$	$w = 1/[\sigma^2(F_o^2) + (0.1079P)^2 + 0.5338P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.001$
3002 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
289 parameters	$\Delta\rho_{min} = -0.27$ e Å^{-3}
Primary atom site location: Direct	Extinction correction: None

Special details

Geometry. Cremer & Pople Puckering Parameters ——————————— Q(2) = 0.4080 (47) Å, Phi(2) = 261.2 (5)°

The equation of the plane is of the form: P * *x* + Q * *y* + *R* * *z* - S = 0 where P, Q, *R*, S are constants and *x*, *y*, *z* are fractional co-ordinates.

P = 6.063 (7), Q = 5.023 (11), *R* = −13.79 (2), S = −3.43 (3) Atom Distance *x y z X* Y *Z* O10 0.033 (3) 0.9104 1.0015 1.0110 8.2677 11.7064 22.9345 O14 − 0.023 (3) 0.7517 0.9726 0.9348 6.8265 11.3686 21.2050 N20 − 0.007 (3) 0.9224 0.8418 0.9611 8.3767 9.8397 21.8016 C14 − 0.003 (3) 0.8530 0.9413 0.9665 7.7464 11.0028 21.9251 C20 0.032 (3) 0.8853 0.7638 0.9135 8.0398 8.9280 20.7223 H20 − 0.03253 0.9899 0.8235 0.9859 8.9897 9.6258 22.3651

P = −2.027 (10), Q =11.121 (5), *R* = 4.81 (3), S = 11.14 (3) Atom Distance *x y z X* Y *Z* O28 0.008 (2) 0.6619 0.7070 0.9607 6.0110 8.2641 21.7944 N30 max 0.062 (2) 0.6433 0.7499 0.8650 5.8421 8.7655 19.6218 C20 − 0.041 (2) 0.8853 0.7638 0.9135 8.0398 8.9280 20.7223 C28 0.023 (2) 0.7192 0.7387 0.9147 6.5313 8.6346 20.7497 C30 − 0.051 (4) 0.4893 0.7135 0.8609 4.4435 8.3400 19.5297

P = −1.364 (12), Q = −5.598 (12), *R* = 19.621 (12), S = 12.24 (2) Atom Distance *x y z X* Y *Z* O34 0.009 (3) 0.2493 0.7954 0.8686 2.2640 9.2973 19.7040 N40 0.002 (3) 0.4315 0.8956 0.9095 3.9186 10.4686 20.6322 C30 − 0.011 (3) 0.4893 0.7135 0.8609 4.4435 8.3400 19.5297 C34 0.002 (3) 0.3787 0.8057 0.8802 3.4391 9.4177 19.9664 C40 − 0.012 (3) 0.3298 0.9842 0.9270 2.9950 11.5042 21.0288 H40 0.01105 0.5237 0.9006 0.9178 4.7559 10.5270 20.8203

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
C10	0.8478 (4)	1.1109 (3)	1.02972 (16)	0.0502 (8)
O10	0.9104 (4)	1.0015 (2)	1.01100 (14)	0.0718 (9)
C11	0.9449 (6)	1.1437 (4)	1.0808 (3)	0.0986 (19)
H11A	1.0446	1.1518	1.0673	0.148*
H11B	0.9404	1.0853	1.1105	0.148*
H11C	0.9117	1.2150	1.0971	0.148*
C12	0.6942 (6)	1.0963 (5)	1.0481 (3)	0.0984 (18)
H12A	0.6356	1.0749	1.0146	0.148*
H12B	0.6580	1.1669	1.0641	0.148*
H12C	0.6884	1.0375	1.0775	0.148*
C13	0.8604 (8)	1.1983 (4)	0.9807 (3)	0.0990 (19)
H13A	0.9619	1.2070	0.9698	0.149*
H13B	0.8224	1.2704	0.9941	0.149*
H13C	0.8048	1.1728	0.9472	0.149*
C14	0.8530 (4)	0.9413 (3)	0.96650 (14)	0.0468 (7)
O14	0.7517 (3)	0.9726 (2)	0.93476 (12)	0.0571 (7)
N20	0.9224 (3)	0.8418 (2)	0.96106 (12)	0.0442 (6)
H20	0.9899	0.8235	0.9859	0.053*
C20	0.8853 (3)	0.7638 (2)	0.91348 (12)	0.0358 (6)
H20A	0.9126	0.7976	0.8755	0.043*
C21	0.9679 (3)	0.6509 (3)	0.92253 (13)	0.0432 (7)
H21A	1.0725	0.6667	0.9258	0.052*
H21B	0.9360	0.6165	0.9593	0.052*
C22	0.9433 (4)	0.5669 (3)	0.87295 (14)	0.0444 (7)
C23	1.0342 (5)	0.5667 (3)	0.82448 (15)	0.0584 (9)
H23	1.1119	0.6184	0.8223	0.070*
C24	1.0108 (6)	0.4904 (4)	0.77903 (18)	0.0772 (13)
H24	1.0737	0.4909	0.7467	0.093*
C25	0.8975 (7)	0.4143 (4)	0.7808 (2)	0.0861 (16)
H25	0.8818	0.3640	0.7496	0.103*
C26	0.8071 (6)	0.4129 (4)	0.8288 (2)	0.0812 (14)
H26	0.7302	0.3604	0.8306	0.097*
C27	0.8288 (5)	0.4889 (3)	0.87470 (19)	0.0617 (9)
H27	0.7659	0.4876	0.9070	0.074*
C28	0.7192 (3)	0.7387 (2)	0.91469 (12)	0.0356 (6)
O28	0.6619 (2)	0.7070 (2)	0.96074 (9)	0.0492 (5)
N30	0.6433 (3)	0.7499 (2)	0.86497 (10)	0.0401 (5)
C30	0.4893 (4)	0.7135 (3)	0.86091 (15)	0.0480 (7)
H30	0.4743	0.6437	0.8841	0.058*
C31	0.4722 (5)	0.6873 (4)	0.79539 (19)	0.0746 (13)
H31A	0.5092	0.6117	0.7858	0.090*
H31B	0.3702	0.6931	0.7830	0.090*
C32	0.5646 (5)	0.7791 (5)	0.76797 (16)	0.0762 (13)
H32A	0.5131	0.8518	0.7680	0.091*
H32B	0.5904	0.7595	0.7277	0.091*

C33	0.7009 (4)	0.7845 (4)	0.80662 (14)	0.0576 (9)
H33A	0.7761	0.7320	0.7929	0.069*
H33B	0.7413	0.8613	0.8078	0.069*
C34	0.3787 (3)	0.8057 (3)	0.88016 (15)	0.0468 (7)
O34	0.2493 (3)	0.7954 (3)	0.86859 (15)	0.0707 (8)
N40	0.4315 (3)	0.8956 (2)	0.90951 (13)	0.0482 (6)
H40	0.5237	0.9006	0.9178	0.058*
C40	0.3298 (4)	0.9842 (3)	0.92699 (15)	0.0550 (8)
H40A	0.3772	1.0344	0.9553	0.066*
H40B	0.2450	0.9497	0.9460	0.066*
C41	0.2794 (4)	1.0531 (3)	0.87493 (16)	0.0509 (8)
O41	0.3458 (4)	1.0663 (3)	0.83062 (14)	0.0852 (10)
O42	0.1512 (4)	1.1022 (3)	0.88564 (11)	0.0715 (8)
C42	0.0908 (6)	1.1746 (5)	0.8400 (2)	0.0863 (15)
H42A	−0.0019	1.2051	0.8529	0.129*
H42B	0.0764	1.1304	0.8048	0.129*
H42C	0.1578	1.2362	0.8321	0.129*
O1	0.6824 (7)	1.0983 (6)	0.8311 (2)	0.164 (3)
H1	0.5875	1.0888	0.8283	0.246*
H2	0.7008	1.0675	0.8637	0.246*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C10	0.0463 (17)	0.0414 (15)	0.0630 (19)	−0.0005 (14)	0.0013 (16)	−0.0147 (14)
O10	0.0724 (17)	0.0570 (15)	0.0861 (18)	0.0250 (14)	−0.0374 (16)	−0.0325 (14)
C11	0.102 (4)	0.076 (3)	0.118 (4)	0.021 (3)	−0.040 (4)	−0.056 (3)
C12	0.071 (3)	0.107 (4)	0.118 (4)	−0.025 (3)	0.031 (3)	−0.045 (3)
C13	0.142 (5)	0.054 (2)	0.102 (4)	−0.025 (3)	0.013 (4)	0.002 (2)
C14	0.0425 (16)	0.0442 (15)	0.0538 (17)	0.0041 (13)	−0.0115 (14)	−0.0057 (14)
O14	0.0592 (14)	0.0439 (12)	0.0682 (15)	0.0113 (11)	−0.0210 (12)	−0.0070 (11)
N20	0.0409 (13)	0.0408 (12)	0.0508 (14)	0.0078 (11)	−0.0126 (11)	−0.0085 (11)
C20	0.0359 (13)	0.0376 (13)	0.0338 (13)	0.0024 (11)	0.0017 (11)	−0.0030 (11)
C21	0.0406 (15)	0.0422 (15)	0.0469 (16)	0.0069 (13)	−0.0018 (13)	−0.0044 (13)
C22	0.0482 (16)	0.0366 (14)	0.0485 (16)	0.0106 (13)	−0.0047 (14)	−0.0050 (13)
C23	0.066 (2)	0.0539 (19)	0.0554 (19)	0.0128 (18)	0.0079 (17)	−0.0022 (16)
C24	0.098 (3)	0.074 (3)	0.059 (2)	0.030 (3)	0.004 (2)	−0.013 (2)
C25	0.123 (4)	0.065 (3)	0.070 (3)	0.027 (3)	−0.024 (3)	−0.029 (2)
C26	0.080 (3)	0.059 (2)	0.104 (4)	−0.002 (2)	−0.020 (3)	−0.023 (2)
C27	0.061 (2)	0.0507 (19)	0.074 (2)	0.0009 (18)	0.000 (2)	−0.0106 (17)
C28	0.0368 (14)	0.0333 (13)	0.0368 (13)	0.0023 (11)	0.0047 (11)	−0.0060 (11)
O28	0.0439 (11)	0.0626 (13)	0.0410 (11)	0.0012 (11)	0.0082 (10)	0.0063 (10)
N30	0.0385 (12)	0.0438 (13)	0.0381 (12)	0.0012 (11)	−0.0003 (10)	−0.0048 (10)
C30	0.0407 (15)	0.0455 (16)	0.0579 (18)	−0.0008 (14)	−0.0050 (14)	−0.0133 (14)
C31	0.065 (2)	0.092 (3)	0.068 (2)	0.004 (2)	−0.018 (2)	−0.040 (2)
C32	0.077 (3)	0.114 (4)	0.0384 (17)	0.023 (3)	−0.0121 (18)	−0.012 (2)
C33	0.059 (2)	0.078 (2)	0.0359 (15)	0.008 (2)	0.0032 (14)	0.0001 (15)
C34	0.0370 (15)	0.0526 (17)	0.0507 (17)	−0.0009 (14)	−0.0010 (13)	−0.0005 (14)

O34	0.0381 (12)	0.0759 (17)	0.098 (2)	−0.0033 (13)	−0.0020 (13)	−0.0149 (16)
N40	0.0412 (14)	0.0477 (14)	0.0556 (15)	0.0058 (12)	−0.0032 (12)	−0.0073 (12)
C40	0.056 (2)	0.0549 (18)	0.0539 (19)	0.0105 (17)	0.0059 (16)	−0.0049 (15)
C41	0.0487 (18)	0.0490 (17)	0.0550 (19)	0.0046 (15)	−0.0004 (15)	−0.0061 (14)
O41	0.077 (2)	0.103 (2)	0.0761 (19)	0.019 (2)	0.0196 (18)	0.0275 (18)
O42	0.0710 (17)	0.0838 (19)	0.0597 (14)	0.0340 (16)	0.0007 (14)	−0.0016 (14)
C42	0.093 (3)	0.097 (4)	0.069 (3)	0.037 (3)	−0.018 (3)	−0.003 (2)
O1	0.137 (5)	0.208 (6)	0.145 (4)	−0.028 (5)	−0.035 (4)	0.081 (5)

Geometric parameters (Å, °)

C10—O10	1.462 (4)	C26—H26	0.9300
C10—C12	1.466 (6)	C27—H27	0.9300
C10—C11	1.505 (6)	C28—O28	1.224 (3)
C10—C13	1.514 (6)	C28—N30	1.328 (4)
O10—C14	1.336 (4)	N30—C30	1.465 (4)
C11—H11A	0.9600	N30—C33	1.480 (4)
C11—H11B	0.9600	C30—C31	1.526 (5)
C11—H11C	0.9600	C30—C34	1.537 (5)
C12—H12A	0.9600	C30—H30	0.9800
C12—H12B	0.9600	C31—C32	1.498 (7)
C12—H12C	0.9600	C31—H31A	0.9700
C13—H13A	0.9600	C31—H31B	0.9700
C13—H13B	0.9600	C32—C33	1.518 (5)
C13—H13C	0.9600	C32—H32A	0.9700
C14—O14	1.224 (4)	C32—H32B	0.9700
C14—N20	1.329 (4)	C33—H33A	0.9700
N20—C20	1.453 (3)	C33—H33B	0.9700
N20—H20	0.8600	C34—O34	1.210 (4)
C20—C21	1.531 (4)	C34—N40	1.333 (4)
C20—C28	1.537 (4)	N40—C40	1.444 (4)
C20—H20A	0.9800	N40—H40	0.8600
C21—C22	1.510 (4)	C40—C41	1.501 (5)
C21—H21A	0.9700	C40—H40A	0.9700
C21—H21B	0.9700	C40—H40B	0.9700
C22—C23	1.375 (5)	C41—O41	1.182 (5)
C22—C27	1.384 (5)	C41—O42	1.320 (5)
C23—C24	1.380 (6)	O42—C42	1.445 (5)
C23—H23	0.9300	C42—H42A	0.9600
C24—C25	1.361 (8)	C42—H42B	0.9600
C24—H24	0.9300	C42—H42C	0.9600
C25—C26	1.364 (8)	O1—H1	0.872
C25—H25	0.9300	O1—H2	0.838
C26—C27	1.383 (6)		
O10—C10—C12	110.5 (4)	C27—C26—H26	119.7
O10—C10—C11	102.6 (3)	C26—C27—C22	120.6 (4)
C12—C10—C11	111.6 (4)	C26—C27—H27	119.7
O10—C10—C13	110.3 (3)	C22—C27—H27	119.7
C12—C10—C13	111.0 (5)	O28—C28—N30	122.3 (3)

C11—C10—C13	110.5 (4)	O28—C28—C20	119.3 (3)
C14—O10—C10	121.9 (3)	N30—C28—C20	118.4 (2)
C10—C11—H11A	109.5	C28—N30—C30	121.3 (3)
C10—C11—H11B	109.5	C28—N30—C33	127.1 (3)
H11A—C11—H11B	109.5	C30—N30—C33	111.1 (3)
C10—C11—H11C	109.5	N30—C30—C31	102.5 (3)
H11A—C11—H11C	109.5	N30—C30—C34	113.7 (3)
H11B—C11—H11C	109.5	C31—C30—C34	110.6 (3)
C10—C12—H12A	109.5	N30—C30—H30	109.9
C10—C12—H12B	109.5	C31—C30—H30	109.9
H12A—C12—H12B	109.5	C34—C30—H30	109.9
C10—C12—H12C	109.5	C32—C31—C30	101.8 (3)
H12A—C12—H12C	109.5	C32—C31—H31A	111.4
H12B—C12—H12C	109.5	C30—C31—H31A	111.4
C10—C13—H13A	109.5	C32—C31—H31B	111.4
C10—C13—H13B	109.5	C30—C31—H31B	111.4
H13A—C13—H13B	109.5	H31A—C31—H31B	109.3
C10—C13—H13C	109.5	C31—C32—C33	104.3 (3)
H13A—C13—H13C	109.5	C31—C32—H32A	110.9
H13B—C13—H13C	109.5	C33—C32—H32A	110.9
O14—C14—N20	124.3 (3)	C31—C32—H32B	110.9
O14—C14—O10	125.5 (3)	C33—C32—H32B	110.9
N20—C14—O10	110.2 (3)	H32A—C32—H32B	108.9
C14—N20—C20	120.6 (2)	N30—C33—C32	102.6 (3)
C14—N20—H20	119.7	N30—C33—H33A	111.3
C20—N20—H20	119.7	C32—C33—H33A	111.3
N20—C20—C21	109.1 (2)	N30—C33—H33B	111.3
N20—C20—C28	109.5 (2)	C32—C33—H33B	111.3
C21—C20—C28	108.3 (2)	H33A—C33—H33B	109.2
N20—C20—H20A	110.0	O34—C34—N40	122.4 (3)
C21—C20—H20A	110.0	O34—C34—C30	120.2 (3)
C28—C20—H20A	110.0	N40—C34—C30	117.4 (3)
C22—C21—C20	112.8 (2)	C34—N40—C40	118.2 (3)
C22—C21—H21A	109.0	C34—N40—H40	120.9
C20—C21—H21A	109.0	C40—N40—H40	120.9
C22—C21—H21B	109.0	N40—C40—C41	111.3 (3)
C20—C21—H21B	109.0	N40—C40—H40A	109.4
H21A—C21—H21B	107.8	C41—C40—H40A	109.4
C23—C22—C27	118.2 (3)	N40—C40—H40B	109.4
C23—C22—C21	120.5 (3)	C41—C40—H40B	109.4
C27—C22—C21	121.2 (3)	H40A—C40—H40B	108.0
C22—C23—C24	120.4 (4)	O41—C41—O42	123.4 (4)
C22—C23—H23	119.8	O41—C41—C40	125.7 (3)
C24—C23—H23	119.8	O42—C41—C40	110.9 (3)
C25—C24—C23	121.1 (4)	C41—O42—C42	117.2 (3)
C25—C24—H24	119.4	O42—C42—H42A	109.5
C23—C24—H24	119.4	O42—C42—H42B	109.5
C24—C25—C26	119.1 (4)	H42A—C42—H42B	109.5
C24—C25—H25	120.5	O42—C42—H42C	109.5

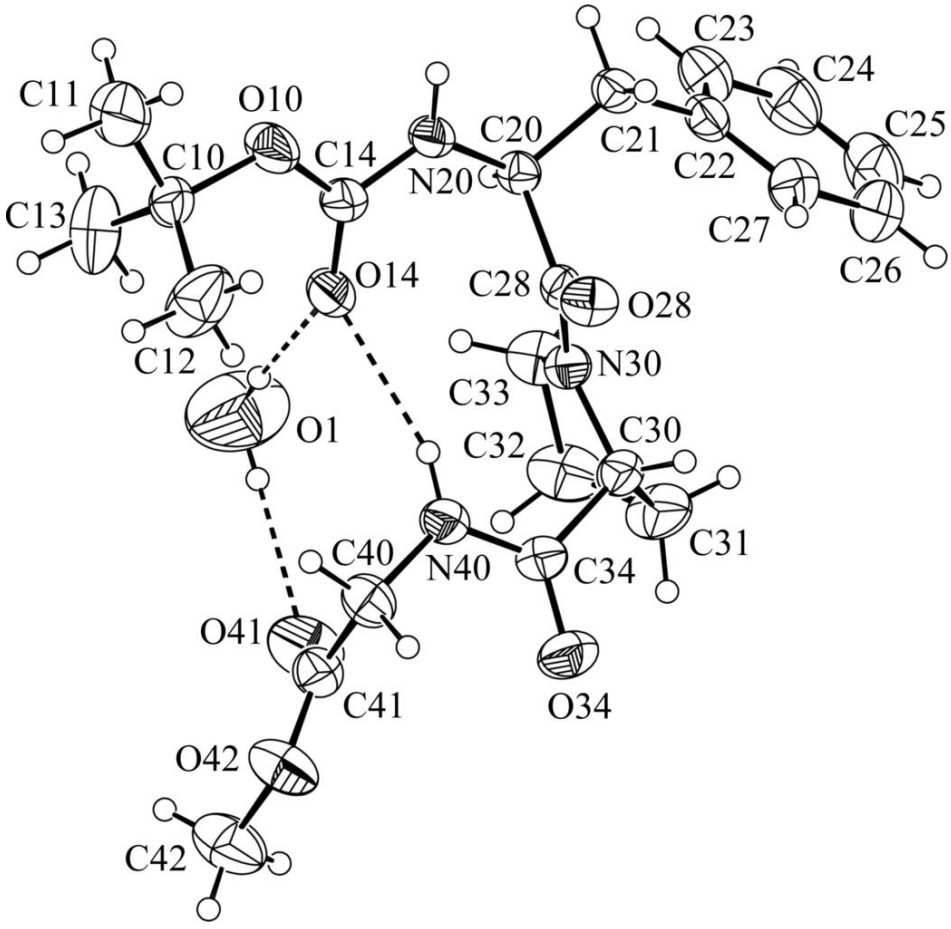
C26—C25—H25	120.5	H42A—C42—H42C	109.5
C25—C26—C27	120.5 (5)	H42B—C42—H42C	109.5
C25—C26—H26	119.7	H1—O1—H2	101.9
C12—C10—O10—C14	59.6 (5)	O28—C28—N30—C30	−6.4 (4)
C11—C10—O10—C14	178.7 (4)	C20—C28—N30—C30	172.1 (3)
C13—C10—O10—C14	−63.6 (5)	O28—C28—N30—C33	−178.4 (3)
C10—O10—C14—O14	5.0 (6)	C20—C28—N30—C33	0.1 (5)
C10—O10—C14—N20	−175.4 (3)	C28—N30—C30—C31	−153.7 (3)
O14—C14—N20—C20	3.1 (5)	C33—N30—C30—C31	19.4 (4)
O10—C14—N20—C20	−176.5 (3)	C28—N30—C30—C34	86.9 (4)
C14—N20—C20—C21	−173.0 (3)	C33—N30—C30—C34	−100.0 (3)
C14—N20—C20—C28	−54.6 (4)	N30—C30—C31—C32	−37.2 (4)
N20—C20—C21—C22	−176.4 (3)	C34—C30—C31—C32	84.4 (4)
C28—C20—C21—C22	64.4 (3)	C30—C31—C32—C33	42.0 (4)
C20—C21—C22—C23	89.4 (4)	C28—N30—C33—C32	178.8 (3)
C20—C21—C22—C27	−90.1 (4)	C30—N30—C33—C32	6.2 (4)
C27—C22—C23—C24	0.0 (5)	C31—C32—C33—N30	−30.0 (4)
C21—C22—C23—C24	−179.5 (3)	N30—C30—C34—O34	165.9 (4)
C22—C23—C24—C25	0.5 (6)	C31—C30—C34—O34	51.2 (5)
C23—C24—C25—C26	−0.9 (7)	N30—C30—C34—N40	−14.0 (5)
C24—C25—C26—C27	1.0 (7)	C31—C30—C34—N40	−128.7 (4)
C25—C26—C27—C22	−0.6 (7)	O34—C34—N40—C40	−1.1 (6)
C23—C22—C27—C26	0.1 (6)	C30—C34—N40—C40	178.8 (3)
C21—C22—C27—C26	179.6 (4)	C34—N40—C40—C41	−72.1 (4)
N20—C20—C28—O28	−51.7 (4)	N40—C40—C41—O41	−26.2 (6)
C21—C20—C28—O28	67.2 (3)	N40—C40—C41—O42	156.3 (3)
N20—C20—C28—N30	129.8 (3)	O41—C41—O42—C42	0.5 (6)
C21—C20—C28—N30	−111.3 (3)	C40—C41—O42—C42	178.0 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N40—H40···O14	0.86	2.27	3.097 (4)	162
O1—H1···O41	0.87	2.21	3.080 (7)	174
O1—H2···O14	0.84	2.01	2.843 (6)	171
N20—H20···O28^{i}	0.86	2.01	2.864 (3)	174

Symmetry codes: (i) *x*+1/2, −*y*+3/2, −*z*+2.

Fig. 1


C11
O10
C10
C14
N20
C20
C21
C23
C24
C25
C22
C27
C26
C13
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C28
O28
C12
N30
C33
O1
C32
C30
C31
C40
N40
C34
O41
C41
O34
O42
C42

Fig. 2

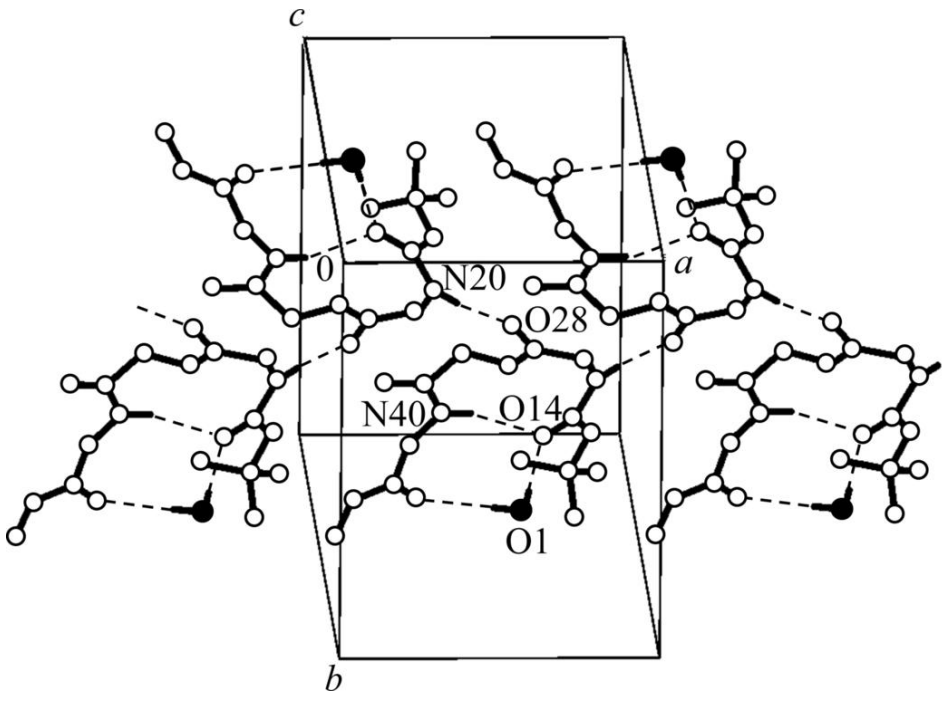
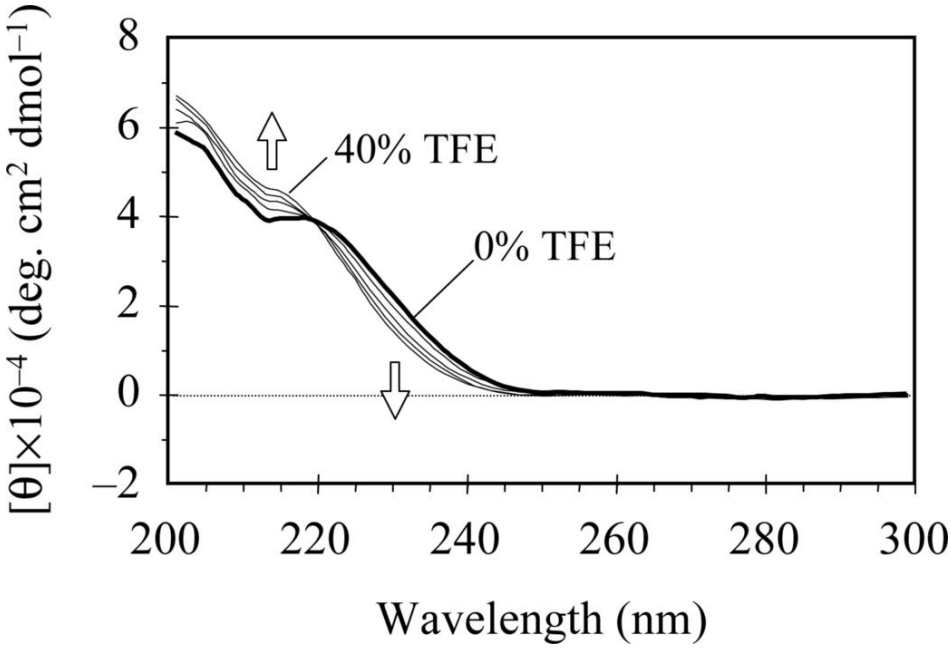


Fig. 3


8
6
4
2
0
–2
200
220
240
260
280
300
40% TFE
0% TFE
[θ]×10–4 (deg. cm2 dmol–1)
Wavelength (nm)