Conformation and packing analysis of polysaccharides and derivatives: 6. Detailed refinement of tri-*O*-ethylamylose–solvent complexes TEA1—C1 and TEA1—DCM1

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(Received 24 May 1978)

The crystal structures of two tri-*O*-ethylamylose polymorphs, with chloroform (TEA1-C1) and with dichloromethane (TEA1-DCM1) inside the crystal lattice, have been investigated. Both polymorphs are very similar: they crystallize in an orthorhombic unit cell, space group $P2_12_12_1$. The chain conformations are 4_3 helices with a 4.005 Å rise per residue. The X-ray diffraction diagrams can be indexed with a = 16.76 ± 0.02 Å, b = 14.28 ± 0.03 Å, c = 16.02 ± 0.03 Å (fibre repeat) for TEA-C1 and a = 16.52 ± 0.02 Å, b = 13.95 ± 0.02 Å, c = 16.02 ± 0.02 Å (fibre repeat) for TEA1-DCM1. Two chains pass through the unit cell, and four solvent molecules are located in the interstitial spaces of the unit cell with close Cl . . . O interatomic contact distances.

INTRODUCTION

Several polymorphs of tri-*O*-ethylamylose have been discovered recently, and the conformation and crystal packing of a few of them published[1–3]. The original polymorph, TEA1, from which all the others can be derived, was obtained by casting a film from dioxane solution, stretched and annealed at 235°C[1]. Placing such a TEA1 fibre over or in a 5:1 (v/v) non-solvent–solvent mixture of ethanol and nitromethane (or chloroform or dichloromethane) resulted in polymorphs with solvent built into the crystal lattices. These polymorphs were denoted TEA1-N (tri-*O*-ethylamylose with nitromethane), TEA1-C2 (with chloroform), and TEA1-DCM2 (with dichloromethane) and their structures determined and found to be very similar[3]. The polymer chains form left-handed four-fold (4_3) helices and the solvent molecules were distributed in a statistical manner in the grooves of the helices. Removing the solvent from these polymer–solvent complexes by placing the fibres in vacuum, another polymorph, TEA3, was found[2]. This polymorph resembles TEA1 in conformation and packing, forming a 4_3 helix in an orthorhombic unit cell.

In addition further polymorphs of TEA1 complexed with chloroform and dichloromethane have been discovered. In a continuing investigation into the processes of solvation and transformations occurring in tri-*O*-ethylamylose polymer crystals, we report complexes of tri-*O*-ethylamylose with chloroform, TEA1-C1, and dichloromethane, TEA1-DCM1.

EXPERIMENTAL

Tri-*O*-ethylamylose fibres of the TEA1 polymorph were prepared as previously described[1]. These TEA1 fibres were then placed in sealed beryllium glass capillaries over a 20:1 (v/v) mixture of ethanol (non-solvent) to either chloroform or dichloromethane (solvent) and converted to TEA1-C1 and TEA1-DCM1 complexes, respectively. Attempts to produce a complex containing nitromethane in a similar fashion were not successful. X-ray diffractograms of TEA1-C1 and TEA1-DCM1 polymorphs are shown in *Figure 1*.

The *d*-spacings were measured from diffractograms recorded with CuKα radiation on flat films. The intensity data were taken on multiple film packs in an evacuated cylindrical camera and recorded along each layer line with a Joyce–Loebl recording densitometer. Areas of individual peaks were measured by planimetry and used as a measure of uncorrected relative intensity. Intensities thus obtained were corrected for Lorentz[4] and polarization factors, arcing of reflections, unequal film-to-sample distances of diffracted rays and were then converted to relative structure amplitudes. In those instances where observed intensities were actually a composite of contributions from two or more unique diffraction planes, the value of the calculated structure amplitude was taken as

$$|F_c| = (\Sigma m_i F_{ci}^2)^{1/2}$$

with m_i the multiplicity and the summation being over all planes contributing to the composite. The structure amplitudes of unobserved reflections were assigned one half of the minimum observable intensity in the corresponding region of diffraction angle.

The unit cells, as refined by least squares methods, were both orthorhombic with similar dimensions: a = 16.76 ± 0.02 Å, b = 14.28 ± 0.02 Å, c = 16.02 ± 0.03 Å (fibre repeat) for TEA1–C1 and a = 16.52 ± 0.02 Å, b = 13.95 ±

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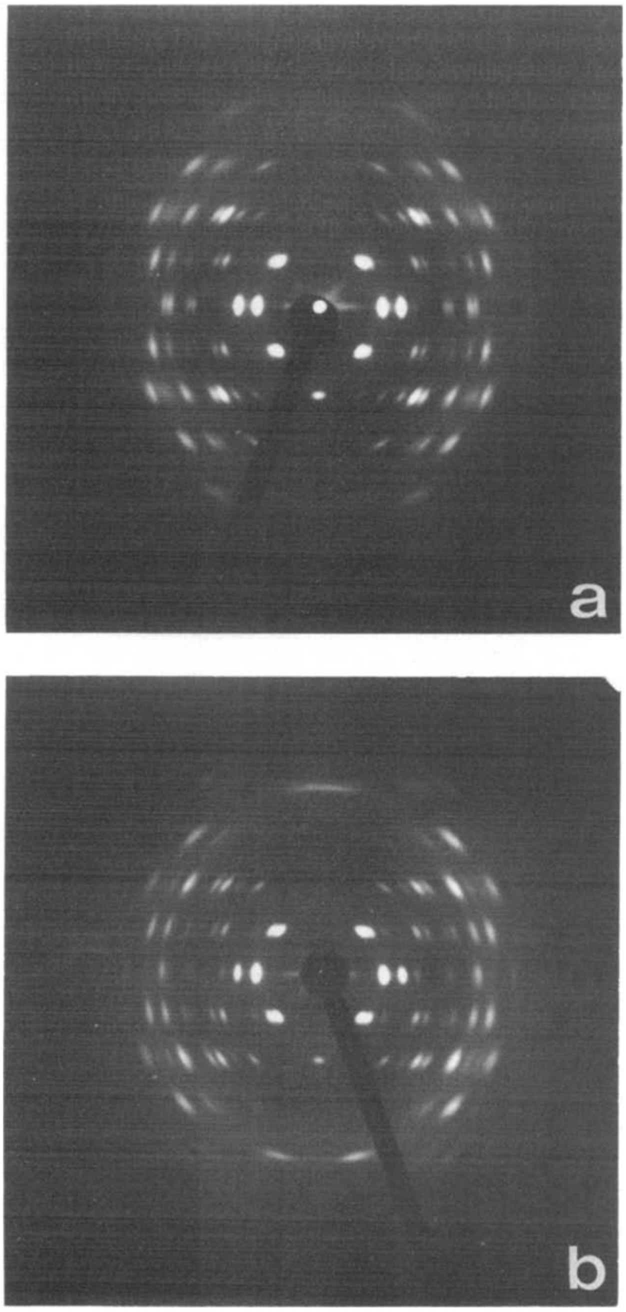

Figure 1 X-ray fibre diffraction diagrams: (a) TEA1-C1 and (b) TEA1-DCM1 taken using a cylindrical camera of 5.73 cm radius

0.02 Å, $c = 16.02 \pm 0.02$ Å (fibre repeat) for TEA1-DCM1. Second and fourth order meridional reflections were observed for both polymorphs. Systematic absences of reflections indicated $P2_12_12_1$ as the space group.

RESULTS AND DISCUSSION

Stereochemical Model Analysis.

The method of generating models of helical structure has been described in previous papers[5–7]. A flexible ring conformation was introduced which allowed variation, when desired, in bond lengths, bond and torsion angles within given limits, using as the refinement criterion the optimization of the function:

$$Y = \sum_{i=1}^{N} STD_{oi}^{-2}(A_i - A_{oi})^2 + W^{-2} \sum_{\substack{i=1\\ j=1}}^{n} w_{ij}(d_{ij} - d_{oij})^2$$

The first term in this expression represents the bonded and the second term the non-bonded interactions with A_i any calculated bond length, bond angle or torsion angle of the molecule; A_{oi} average or standard value of A_i; STD_{oi} weight or standard deviation for the average value A_{oi}; N number of optimization parameters selected; d_{oij} non-bonded equilibrium distance between atoms i and j; d_{ij} non-bonded distance between atoms i and j (only repulsive interactions are used, that is, the second term in the above equation is set to zero if $d_{ij} > d_{oij}$); w_{ij} the weight factor for the atom pair i, j; W overall weight factor of non-bonded interactions; n number of non-bonded contacts considered. The actual constants and limits used for the calculation are summarized in refs 6 and 8.

The strategy used was to establish first a suitable chain conformation to be refined later for optimal packing. As a trial model for the α-(1 → 4)-linked glucan any α-D-glucose residue in the C1 chair conformation may serve, as the latter is thus far the only conformation found in amylose and its derivatives. Pendant atoms and branches are added to the monomer residue to complete the chain description. The model is then refined by minimizing the function Y. Models with high values in Y and with many short contacts below the established limits[10] are disregarded.

A four-fold helical conformation was assumed for TEA1-C1 and TEA1-DCM1 due to the similarities in fibre repeat

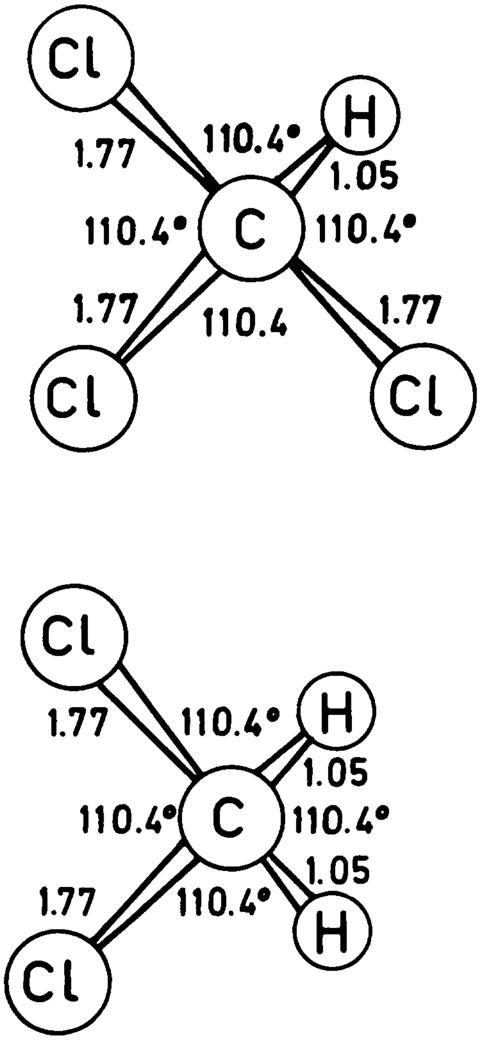

Figure 2 Stereochemical data of chloroform and dichloromethane[9]. All bond lengths are given in angstroms

Table 1 Cartesian coordinates of one residue[a] for tri-*O*-ethylamylose–solvent complexes TEA1-C1 and TEA1-DCM1 (virtual bond length 4.45 Å)

	TEA1-C1			TEA1-DCM1		
Atom	X	Y	Z	X	Y	Z
O-4	4.661	−1.288	1.810	4.644	−1.271	1.610
C-1	1.919	−1.005	4.928	1.895	−1.081	4.728
C-2	2.332	−2.411	4.522	2.355	−2.472	4.322
C-3	3.588	−2.391	3.660	3.609	−2.410	3.460
C-4	3.399	−1.450	2.472	3.388	−1.476	2.272
C-5	2.943	−0.072	2.955	2.886	−0.114	2.755
C-6	2.624	0.890	1.827	2.535	0.836	1.627
O-2	2.578	−3.160	5.708	2.625	−3.212	5.508
O-3	3.872	−3.703	3.166	3.937	−3.711	2.966
O-4$_2$	2.902	−0.471	5.815	2.859	−0.514	5.615
O-5	1.762	−0.191	3.775	1.710	−0.273	3.575
O-6	3.711	1.771	1.514	3.639	1.653	1.214
C-2′	1.588	−4.132	5.999	1.669	−4.218	5.799
C-2″	1.051	−4.089	7.414	1.060	−4.134	7.182
C-3′	4.644	−4.495	4.060	4.736	−4.477	3.860
C-3″	4.591	−5.941	3.643	4.838	−5.898	3.371
C-6′	3.762	2.207	0.167	3.283	2.845	0.535
C-6″	3.426	3.688	−0.024	4.147	4.054	0.902
H-1	1.012	−1.045	5.455	0.989	−1.152	5.255
H-2	1.549	−2.866	3.991	1.588	−2.954	3.791
H-3	4.404	−2.068	4.237	4.414	−2.060	4.037
H-4	2.679	−1.848	1.820	2.682	−1.898	1.620
H-5	3.712	0.376	3.512	3.640	0.360	3.312
H-6A	1.776	1.455	2.077	1.736	1.450	1.922
H-6B	2.355	0.347	0.969	2.178	0.288	0.805
H-2′1	1.968	−5.090	5.798	2.104	−5.164	5.664
H-2′2	0.793	−4.038	5.319	0.906	−4.196	5.078
H-3′1	4.264	−4.396	5.034	4.302	−4.465	4.816
H-3′2	5.640	−4.164	4.050	5.696	−4.057	3.919
H-6′1	3.112	1.623	−0.415	2.274	3.066	0.721
H-6′2	4.714	2.009	−0.230	3.327	2.684	−0.502
H-2″1	1.088	−5.051	7.832	1.175	−5.056	7.672
H-2″2	0.057	−3.750	7.401	0.038	−3.905	7.102
H-2″3	1.634	−3.433	7.990	1.543	−3.382	7.733
H-3″1	5.115	−6.528	4.339	5.255	−6.500	4.123
H-3″2	5.026	−6.049	2.694	5.447	−5.932	2.156
H-3″3	3.590	−6.257	3.602	3.881	−6.254	3.128
H-6″1	2.883	3.811	−0.914	4.242	4.682	0.065
H-6″2	4.315	4.245	−0.076	5.098	3.727	1.204
H-6″3	2.851	4.025	0.788	3.694	4.584	1.687
Guest Molecule Coordinates						
C	3.899	−9.241	4.065	2.468	−9.353	4.880
CL1	2.141	−9.461	4.068	0.708	−9.536	4.923
CL2	4.551	−9.464	5.695	3.314	−9.090	6.412
CL3	4.639	−10.414	2.966			

[a] The residue has been shifted 1/4 in *a* as required for space group $P2_12_12_1$. As compared to the standard position of O-4 as (O,-y_0,O), the residue has been rotated 20.1° and translated 1.81 Å along the *z* axis for TEA1-C1 and 22.0° and 1.61 Å for TEA1-DCM1. Hydrogen atoms of the guest molecules were not located.

to the polymorph TEA1. However, the conformation was adjusted to the 16.02 Å fibre repeat found in both solvent complexes compared with 15.48 Å in TEA1. Ring bond lengths, bond angles and torsion angles were varied. The bond lengths and bond angles of the substituent ethyl groups were kept constant, however, and only the torsion angles were optimized. The best conformation remained a left-handed 4_3 helix. This conformation was used in subsequent packing analysis.

In a second refinement step, the allowed conformation with the substituents in all possible rotational positions were packed within the unit cell, in agreement with space group $P2_12_12_1$. This symmetry limited the possible chain arrangements considerably by imposing antiparallel packing of chains and two-fold screw axes in all three directions of the unit cell. The best packing of the chains was sought by first rotating and translating a fixed chain backbone with rotational refinement of the substituents. Due to similar base plane areas of the previously investigated tri-*O*-ethylamylose-solvent complexes[3], it was assumed that sections of two polymer chains pass through the unit cell. Very little further change was observed in the chain backbone when the conformation was subsequently simultaneously refined with packing. The packing analysis without guest molecules indicated a range of helix rotation of approximately 10° without real short contacts between adjacent helices. The position of O-6 was found in the vicinity of *tg**.

In a third step the position of the solvent molecules, chloroform and dichloromethane were approximately located in the unit cell with difference Fourier maps. Observed structure amplitudes were compared against structure amplitudes calculated for the unit cell containing the two polymer

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* *tg* means *trans* to O–5 and *gauche* to C–4, *gg* and *gt* correspondent.

Table 2 Bond lengths, bond angles, and torsion angles for one residue of TEA1-C1 and TEA1-DCM1[a]

TEA1-C1		
Bond lengths (Å)		
O-4—C-4	1.435 (9)	
C-4—C-3	1.527 (4)	
C-4—C-5	1.529 (4)	
C-1—C-2	1.520 (−3)	
C-1—O-4$_2$	1.427 (12)	
C-3—C-2	1.523 (2)	
C-5—O-5	1.442 (6)	
C-2—O-2	1.424 (1)	
C-3—O-3	1.430 (1)	
C-5—C-6	1.517 (3)	
C-6—O-6	1.434 (7)	
C-1—O-5	1.420 (6)	
Bond angles (deg.)		
O-4—C-4—C-3	108.6	(3.1)[b]
O-4—C-4—C-5	107.9	(−0.7)
C-3—C-4—C-5	110.3	(0.0)
C-4—C-3—C-2	110.3	(−0.2)
C-3—C-2—C-1	111.3	(0.8)
C-4—C-5—O-5	110.4	(0.4)
C-5—O-5—C-1	114.7	(0.7)
C-2—C-1—O-5	110.0	(0.8)
C-2—C-1—O-4$_2$	109.0	(0.6)
O-5—C-1—O-4$_2$	111.5	(−0.1)
C-3—C-2—O-2	109.6	(−1.2)
C-1—C-2—O-2	108.1	(−1.2)
C-4—C-3—O-3	108.8	(−0.9)
C-2—C-3—O-3	110.3	(0.7)
C-4—C-5—C-6	113.5	(0.8)
O-5—C-5—C-6	107.6	(0.7)
C-5—C-6—O-6	113.1	(1.3)
C-1—O-4$_2$—C-4$_2$	122.6	
Torsion angles (deg.)		
O-5—C-1—C-2—C-3	55.1	(−0.9)
C-1—C-2—C-3—C-4	−53.4	(−0.2)
C-2—C-3—C-4—C-5	52.8	(−0.2)
C-3—C-4—C-5—O-5	−54.3	(1.1)
C-4—C-5—O-5—C-1	59.0	(−2.1)
C-5—O-5—C-1—C-2	−58.9	(3.3)
O-4—C-4—C-5—O-5	−172.8	
O-4—C-4—C-3—C-2	170.8	
O-4$_2$—C-1—C-2—C-3	−67.4	
O-4$_2$—C-1—O-5—C-5	62.2	
O-5—C-5—C-6—O-6	140.5	
C-4$_2$—O-4$_2$—C-1—H-1	−55.5	
C-1—O-4$_2$—C-4$_2$—H-4$_2$	−42.0	
Ethyl group pendant atoms[c]		
Bond lengths (Å)		
O-2—C-2′	1.418	
C-2′—C-2″	1.514	
O-3—C-3′	1.422	
C-3′—C-3″	1.506	
O-6—C-6′	1.417	
C-6′—C-6″	1.531	
Bond angles (deg.)		
C-2—O-2—C-2′	114.3	
O-2—C-2′—C-2″	114.8	
C-3—O-3—C-3′	113.7	
O-3—C-3′—C-3″	110.0	
C-6—O-6—C-6′	115.1	
O-6—C-6′—C-6″	114.1	
Torsion angles (deg.)		
C-3—C-2—O-2—C-2′	107.6	
C-2—O-2—C-2′—C-2″	−129.8	
O-2—C-2′—C-2″—H-2″1	−129.7	
C-2—C-3—O-3—C-3′	152.6	
C-3—O-3—C-3′—C-3″	165.2	
O-3—C-3′—C-3″—H-3″1	−176.7	
C-5—C-6—O-6—C-6′	151.0	
C-6—O-6—C-6′—C-6″	110.0	
O-6—C-6′—C-6″—H-6″1	−143.0	
O-5—C-5—C-6—O-6	140.5	
TEA1-DCM1[d]		
Ethyl group pendant atoms[c]		
Torsion angles (deg.)		
C-2—O-2—C-2′—C-2″	−125.7	
O-2—C-2′—C-2″—H-2″1	−126.1	
C-3—O-3—C-3′—C-3″	170.5	
O-3—C-3′- C-3″- H-3″1	−168.5	
C-5—C-6—O-6—C-6′	−158.6	
C-6—O-6—C-6′ C-6″	141.0	
O-6—C-6′—C-6″- H-6″1	147.5	
O-5—C-5- C-6 O-6	147.0	

[a] Deviation from Arnott and Scott[8] average values are shown in brackets [b] Deviations from average value for α-D-glucans; see ref 5. [c] All hydrogen parameters not listed are fixed at bond distances of 1.05 Å and at tetrahedral bond angles. [d] All values not listed for TEA1-DCM1 are identical to those of TEA1-C1.

helices in best packing position. For both complexes, the resulting difference Fourier maps indicated four small molecules per unit cell located in the interstitial spaces. Packing calculations comparable those of ref 6 including the guest molecules confirmed these sites as sterically possible locations for the guest molecules.

Detailed packing analysis was then performed with the small molecules attached as pendant atoms to the polymer chain at variable van der Waal's distances. Helix rotations, helix translations, ethyl group rotations, as well as the distance of the small molecules from the polymer chains and their orientations were varied simultaneously until the most advantageous stereochemical packing arrangement was obtained. The conformation of the small molecules (i.e. their bond lengths and bond angles) were held constant. The stereochemical data of chloroform and dichloromethane are illustrated in *Figure 2*.

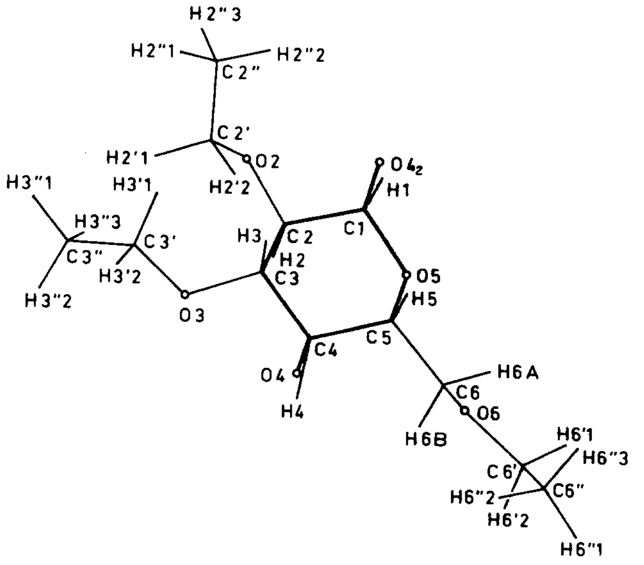

Figure 3 Representation of one residue of tri-*O*-ethylamylose showing atom labelling

Table 3 Observed and calculated structure amplitudes for TEA1-C1 and TEA1-DCM1

TEA1-C1		
hkl	$\|F_o\|$	$\|F_c\|$
110	65	88
200	65	82
020, 210	28	7
120[a]	13	2
220	45	47
310	48	20
130	62	41
320	55	23
400[a]	17	27
230[a]	17	29
410[a]	17	4
040, 420, 330	35	59
140[a]	21	24
510, 240	39	39
101	36	12
011	23	8
111	23	64
201	23	24
211, 021	46	52
121	38	35
301	36	55
221, 311	49	42
321, 031, 131	62	57
231, 411, 401	83	70
431[a], 331[a]	21	30
141, 041	40	64
501, 241, 511	32	53
341, 431, 521	42	45
102, 012	18	11
112	27	71
202	40	35
212, 022	69	41
122	57	68
302[a]	14	26
222, 312	68	69
032, 132, 322	67	125
232, 402, 412	89	65
103	11	6
113, 013	34	44
203[a]	11	1
213, 023	35	22
123	53	34
223, 303, 313	81	69
033, 133	55	50
104, 014	20	7
114	23	40
204	28	20
024, 214, 124	76	67
224, 304	37	57
314	24	22
034. 134	41	28
404, 324	42	23

TEA-DCM1		
110	89	86
200	61	42
210, 020	29	18
120[a]	11	12
220	38	23
310	31	11
130	44	28
400	27	25
320	68	32
230	28	25
410[a]	18	17
420, 330	57	54
040[a]	20	0
140[a]	21	11

TEA1-DCM1 (cont)		
hkl	$\|F_o\|$	$\|F_c\|$
510, 240	39	43
430[a]	23	5
520[a]	24	16
340[a]	25	5
610, 530, 600, 150	42	49
101	45	36
011	36	36
111	20	51
201[a]	8	41
211, 021	48	45
121	42	40
301, 221, 311	60	82
321, 031, 131	92	57
401, 411, 231	97	75
041, 421, 331	48	47
141, 501	42	23
511, 241	34	30
521, 341, 431	42	38
012, 102	11	16
112	34	43
202	26	11
212, 022	58	47
122	49	71
222, 302, 312	91	79
132, 032	60	92
322	54	56
232, 412, 402	87	75
332, 422	32	40
502, 042, 142	35	34
512, 242	37	32
103, 013	17	57
113	21	100
203[a]	9	12
023, 213	27	17
123	47	39
223, 313, 303	86	86
323, 033, 133	39	32
114, 014, 104	68	46
204, 214, 024	29	29
124, 304, 224, 314	53	63
134, 034	27	39
324, 404	27	26
234[a]	22	26
414[a]	22	7
424, 504, 334, 044, 144	35	57
244[a]	25	5
514[a]	24	6
434[a]	27	13
524[a]	25	17
244[a]	24	20
604, 614, 444, 534 054, 154	41	71
115, 105	14	35
205[a]	9	5
215, 125, 025	29	28
305[a]	15	17
315, 225	30	39
035[a]	18	26
135[a]	19	5
325, 405, 235, 415	40	30
335, 425, 145, 045	47	55
245, 515, 435, 505	51	48
026, 126, 216	22	33
226, 306, 036, 136, 316	27	39
236, 326, 416, 406	46	62

[a] Unobserved structure amplitudes

Table 4 Shortest atom – atom contacts (in Angstrom)

TEA1-C1

Intermol. Contact Distance[a]

C-3''$_2$	...	C-6''^{d}	3.50
C-2''$_2$	...	C-6''$^{c}_{2}$	3.35
H-2''2$_2$	...	C-6''$^{c}_{2}$	2.51
C-2''$_2$	...	H-6''3$^{c}_{2}$	2.68
H-6''3$_2$	...	H-2''2$^{c}_{2}$	1.78
H-6''1$_2$	...	H-2''2$^{c}_{2}$	2.42
H-6''3	...	H-3''1$^{d}_{2}$	2.51
H-6''1	...	H-3''1$^{d}_{2}$	2.53
CL-2	...	H-6A$^{f}_{2}$	2.67
CL-3	...	H-6''3^{f}	2 82
CL-3	...	H-6B$^{f}_{2}$	2.86
CL-2	...	H-2'1$^{e}_{2}$	2.98
CL-1	...	H-3''2$^{d}_{2}$	3.14
CL-3	...	C-6''^{f}	3.23
CL-2	...	C-6$^{f}_{2}$	3.30
CL-3	...	C-6'^{f}	3.37
C	...	C-3''^{f}	3.57
CL-3	...	O-6^{f}	2 71
CL-2	...	O-5$^{f}_{2}$	3.22

Intramolecular Contact Distance for TEA1-C1

O-2	...	O-4$^{b}_{2}$	2.71
C-5	...	O-4$^{b}_{2}$	2.89
C-3	...	O-4$^{b}_{2}$	2.97
C-1	...	O-3$_2$	2.97
O-5	...	C-4$^{b}_{2}$	3.04
O-2	...	H-3'1	2.20
H-1	...	O-3$_2$	2.25
O-5	...	H-6A^{b}	2.37

Intramolecular Contact Distance for TEA1-C1 (cont.)

H-5	...	O-6^{b}	2.44
O-2	...	H-2''3^{b}	2.48
C-1	...	C-3$^{3}_{2}$	3.18
C-2	...	H-2'2^{b}	2.38
C-6	...	H-6'1^{b}	2.41
H-3	...	C-3'^{b}	2.44
H-6B	...	C-6'^{b}	2.47
H-2	...	H-2'2	1.93
H-6B	...	H-6'1	2.03

TEA1-DCM1

Intermol. Contact Distance[a]

C-3''$_2$	...	C-6''^{d}	3;26
C-2''$_2$	...	C-6'$^{c}_{2}$	3;33
H-6'1$_2$	...	C-2''$^{c}_{2}$	2.31
C-6'$_2$	...	H-2''2$^{c}_{2}$	2.56
H-6'1$_2$	...	H-2''2$^{c}_{2}$	1.66
H-6'1$_2$	...	H-2''1$^{c}_{2}$	2.20
H-6''1	...	H-3''1$^{d}_{2}$	2.21
H-6'1	...	H-2''2^{d}	2.32
CL-1	...	H-2^{d}	2 43
CL-1	...	H-2'2^{d}	3.04
CL-2	...	H-1$^{f}_{2}$	3 34
CL-1	...	C-2^{d}	3.30
CL-1	...	C-1^{d}	3.41
CL-2	...	C-1$^{f}_{2}$	3.51
CL-2	...	O-5$^{f}_{2}$	2.76
CL-1	...	O-5^{d}	3.36

* Due to different torsion angles of pendant atoms, the distances for TEA1–DCM1 may vary up to 0.05 Å

[a] All distances not due to 1.. . . 4 contacts are greater than the minimum contact distances as set forth in ref. 10, except one hydrogen–hydrogen contact involving methyl H-2''2

[b] 1 . . . 4 contacts; [c] Related by symmetry operator: 1/2 + x, 1/2 – y, $\bar{z}$; [d] $\bar{x}$, 1/2 + y, 1/2 – z; [e] 1/2 + x, –1/2 – y, 1 – z;

[f] Contact between guest molecule and corner chain.

X-ray intensity analysis.

The final stereochemically allowed packing model was used as the starting model for X-ray refinement. Refinement was performed against the X-ray disagreement index R defined as

$$R = \Sigma \, ||F_o| - |F_c|| / \Sigma |F_o|$$

where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively. The refinement parameters were reduced in this procedure to chain rotation and translation, rotation of the residue around the virtual bond O–4 . . . O–4$_2$ and rotation of pendant ethyl groups. The refinement resulted in only small changes in each of the packing models. The resulting R values were for TEA1-C1 $R = 0.35$ with only the observed reflections and $R = 0.36$ with the unobserved reflections included; for TEA1-DCM1 $R = 0.30$ with only the observed reflections and $R = 0.35$ with the unobserved reflections included. An isotropic temperature factor of $B = 5.0$ [temperature factor = $\exp(-B\sin^2\theta)$] was used in the calculations.

The final coordinates for one residue of each complex and the coordinates of the small molecules are reported in *Table 1*. The representation of one residue of tri-*O*-ethylamylose with atom labelling is shown in *Figure 3*. The initial position of the standard residue is defined with O-4 at the position $(O, -y_o, O)$. Rotation of the vector from the origin to O–4 about the z-axis of the coordinate system and translation of this vector along the z-axis produce the helix rotations and translations. The rotation is 20.1° and the translation 1.81 Å for TEA1-C1 and 22.0° and 1.61 Å for TEA1-DCM1. Bond lengths, bond angles, and torsion angles for both structures are reported in *Table 2*. The differences to the average or standard values[8] are shown in brackets. The ring bond lengths, bond angles, and torsion angles were obtained on optimizing the function Y by a simultaneously performed conformation and packing analysis. The small differences to the standard values demonstrate that only little changes are needed to fit the residue well to a 4_3 helix with a fibre repeat of 16.02 Å. The glycosidic bond angle C–1–O–4$_2$–C–4$_2$ is 122.6° in both complexes. The calculated and observed structure amplitudes are shown in *Table 3*. The shortest inter- and intramolecular contacts are listed in *Table 4*.

CONCLUSIONS

Using knowledge of the crystal structures of TEA1-C1 and TEA1-DCM1, we are now able to report the transitions occurring with the transformations TEA1-C1–TEA1-C2 and TEA1-DCM1–TEA1-DCM2. The conversions occur in the preceeding direction with increasing amount of solvent in the solvent–non-solvent mixture over which the complexes are produced. The space group remains $P2_12_12_1$, but the number of complexing molecules increases from 4 to 8 per unit cell. The unit cell changes from orthorhombic with second and fourth order meridional reflections to pseudo-tetragonal

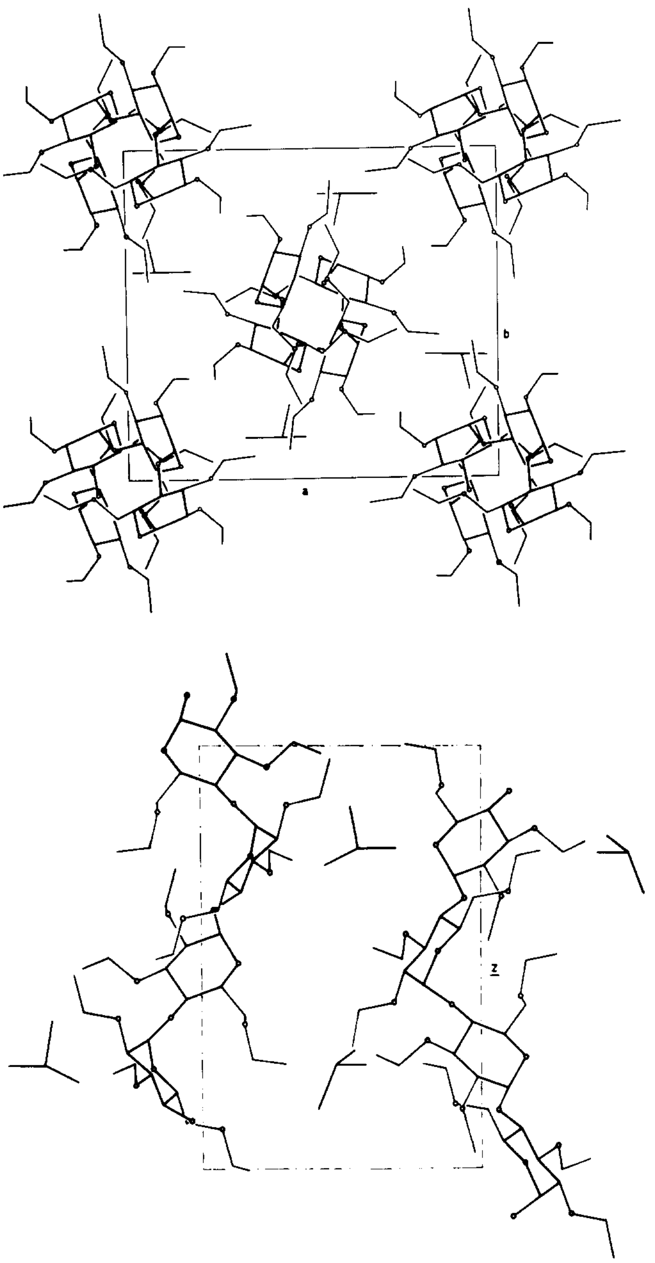

Figure 4 View of TEA1-C1: (a) *a–b* plane; (b) $\bar{1}10$ plane

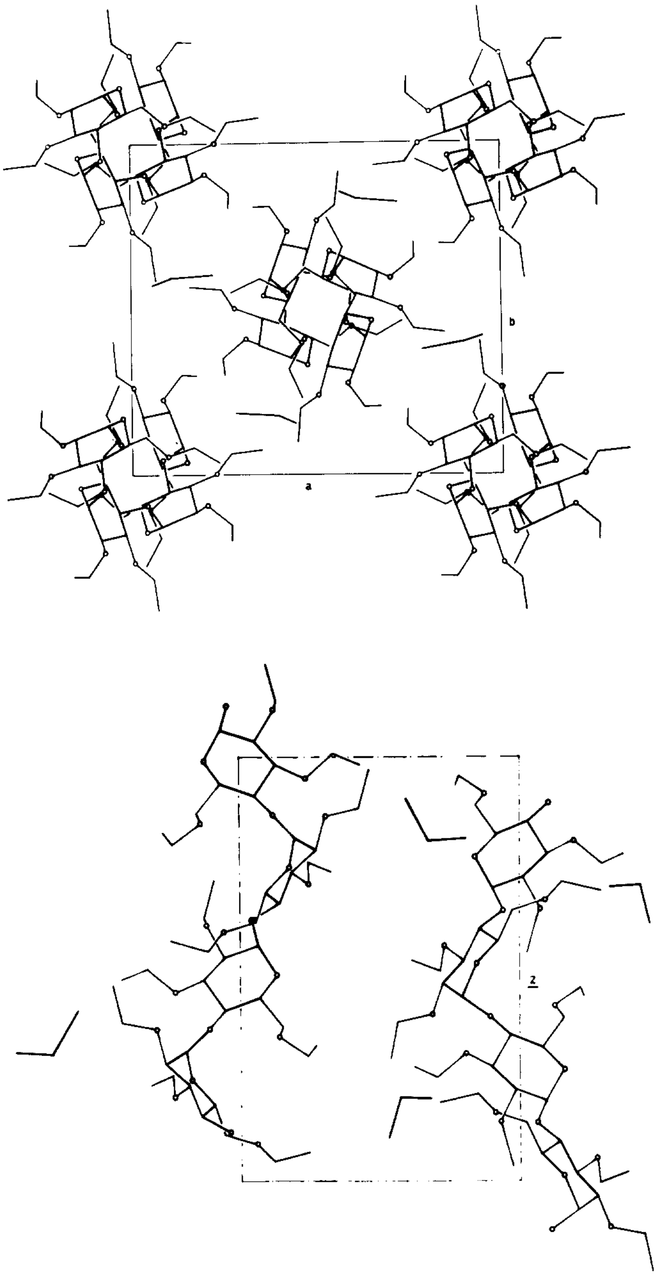

Figure 5 View of TEA1-DCM1: (a) *a–b* plane; (b) $\bar{1}10$ plane

with a fourth order meridional reflection only. The fibre repeat decreases from 16.02 Å to 15.48 Å. The unit cell base plane area is 239 Å^2 for TEA1-C1, 230 Å^2 for TEA1-DCM1 and decreases to 216 Å^2 for TEA1-C2 and TEA1-DCM2; the corresponding unit cell volumes are 3834 Å^3, 3692 Å^3, and 3345 Å^3, respectively. The distances between corner and centre chains are 11.01 Å for TEA-C1, 10.81 Å for TEA1-DCM1, and 10.40 Å for both TEA1-C2 and TEA1-DCM2. The d_{110} spacings are 10.87 Å, 10.66 Å, and 10.40 Å for TEA1-C1, TEA1-DCM1, and both TEA1-C2 and TEA1-DCM2 complexes, respectively.

In TEA1-C2 and TEA1-DCM2 the small molecules are placed in the grooves of the helices with their dipole moments statistically oriented, while in TEA1-C1 and TEA1-DCM1 the small molecules are found well oriented in the interstitial spaces. In TEA1-C1 a close contact distance of 2.71 Å occurs between a chlorine atom of chloroform and O-6 of the tri-O-ethylamylose chain. A second Cl . . . O contact of 3.22 Å between the same chloroform molecule and O-5 of the same tri-*O*-ethylamylose chain exists. In TEA1-DCM1 a close contact distance of 2.76 Å is found between one chlorine atom and O-5 of the corner chain. However, the second close Cl . . . O contact of 3.36 Å occurs between the same dichloromethane molecule and O-5 of the centre chain. These contacts are illustrated in *Figures 4* and *5*.

ACKNOWLEDGEMENT

This work was supported by a grant from Deutsche Forschungsgemeinschaft. The authors thank Mr G. Bührer for preparing the samples. The computations were carried out at the Computing Centre of the University of Freiburg.

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