Cellulose trinitrate: molecular conformation and packing considerations

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X-ray diffraction patterns from highly oriented fibres of cellulose trinitrate indicate that the molecule crystallizes in a five-fold helical conformation with an axial advance per monomer of 0.508 nm. Computerized molecular model building studies favour a 5_2 helix, i.e. a right-handed helix with two complete turns of the backbone in the layer line repeat of 2.54 nm. Two possible unit cells, one of which has been proposed previously (Happey, F. *J. Text. Inst.* 1950, **41**, 381), are described and the packing of the chains is discussed.

INTRODUCTION

Analyses of the X-ray diffraction patterns obtained from native cellulose fibres argue for crystalline domains of chains running parallel to the fibre axis and with a common polarity[1,2]. Each chain has a two-fold helical conformation with an axial advance per D-glucose monomer of 0.52 nm. The patterns exhibit layer lines with a spacing of twice this value at 1.04 nm.

Nitrated derivatives of cellulose, typically prepared by immersing the native fibres in aqueous solutions of mixtures of nitric, acetic and phosphoric acid, provide a series of quite different X-ray diffraction patterns[3]. The maximum theoretical nitrogen content, corresponding to cellulose trinitrate, is 14.14%. In practice this is never achieved, the nitration proceeding until an equilibrium is reached, typically somewhere between the dinitrate and trinitrate derivatives.

Figure 1 illustrates a typical fibre-type X-ray diffraction pattern from highly nitrated cellulose (13.9% N) and native cellulose for comparison. The nitrated derivative exhibits layer lines of spacing 2.54 nm which is five times the expected projection of a single monomer. A meridional reflection[†] is observed on the fifth layer line (spacing 0.508 nm) which suggests some type of five-fold helix for the highly nitrated cellulose chain, with an axial advance per monomer (***h***) slightly less than the value observed for the native cellulose chain.

In this contribution we have scrutinized the X-ray diffraction results in more detail and, using computerized model-building procedures, have investigated the stereochemical feasibility of a number of models exhibiting five-fold helical symmetry. In addition we have briefly considered the packing of such helices in several unit cells especially with reference to previous suggestions by Mathieu[4] and Happey[3].

EXPERIMENTAL

Sample preparation

Various types of parent celluloses were nitrated in nitric acid/acetic acid/acetic anhydride or nitric acid/phosphoric acid/phosphoric anhydride mixtures which caused the $-OH$ groups in the cellulose to be replaced by $-ONO_2$ throughout the whole fibre. By varying the constitution of the nitrating acid, samples with a nitrogen content of between 11% and 13.9% were produced.

X-ray diffraction

X-ray diffraction photographs were recorded on a flat film, fibre camera using Ni-filtered CuKα radiation and pinhole collimation. The specimen to film distance was 3.0 cm.

Molecular model building

Molecular models were generated using a linked-atom procedure. An outline of the method has been reported by Gardner *et al.*[5], while a more rigorous description has been given by Smith and Arnott[6]. Stereochemical parameters for the cellulose backbone were taken from an average set derived by Arnott and Scott[7] for the pyranose residue in the $^4C_1$ chair conformation

Very little information is available about the detailed structures of nitrate esters. Early work[8] indicated a non-planar geometry for the $-ONO_2$ group; however, more recent studies[9–11] suggest that the molecule is in fact planar. A mean set of values for the stereochemical parameters of the $-ONO_2$ group is shown in *Figure 2a*. Because insufficient evidence could be found to assign values to the C–O–N bond angles, β_1, β_2 and β_3 in *Figure 2b*, they were taken as variables in the model building procedure and a weighting scheme was employed to restrict their allowed values to the range 109.5°–120°. Apart from this, all bond lengths and bond angles were held constant, including the glycosidic bond angle which was given a value of 116.5° [7].

Torsion angles τ_1 to τ_9 and bond angles β_1 to β_3 were allowed to vary subject to constraints imposing helical symmetry, pitch and continuity on the model. Within the limits

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[†] Some weaker meridional arcs are often observed on other layer lines which do not readily relate to the expected monomer repeat distance and are thought to arise from the slight non-stoichiometry of the nitrate groups.

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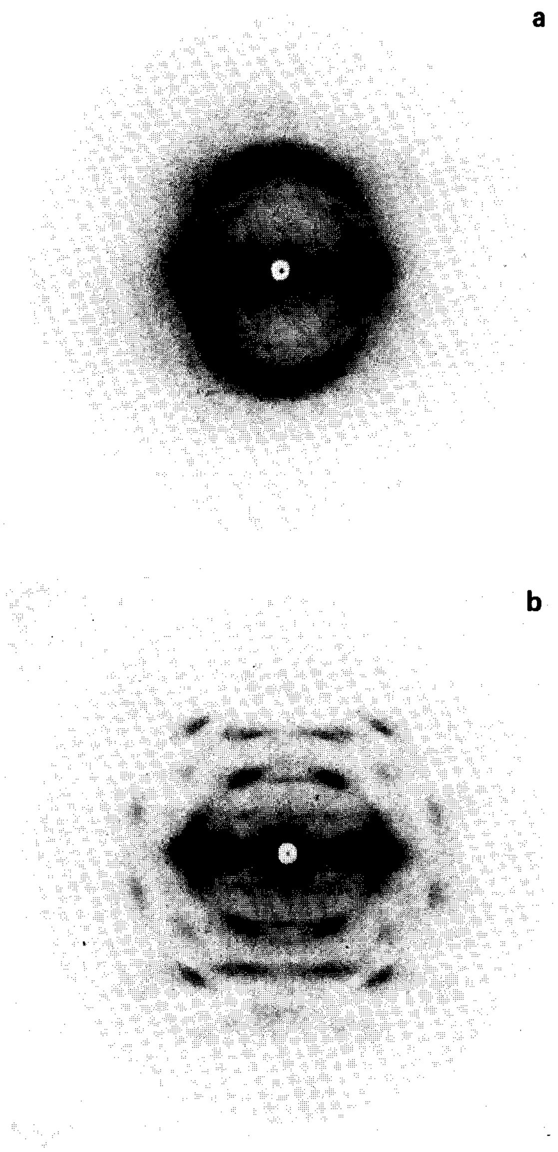

Figure 1 X-ray fibre-type diffraction patterns: (a) cellulose nitrate (13.9% nitrogen) showing a layer line spacing of 2.54 nm and exhibiting five-fold helical symmetry; (b) native cellulose showing a layer line spacing of 1.04 nm and exhibiting two-fold helical symmetry

defined by these constraints the number of close intrachain contacts between atoms was minimized.

The four possible five-fold helical symmetries 5_1, 5_2, 5_3 and 5_4 were investigated‡. In this notation the subscript refers to the number of complete turns of the helix in the axial repeat distance (2.54 nm).

RESULTS AND DISCUSSION

Conformation of a single chain

Sathyanarayana and Rao[12] have shown that the 5_1 and 5_4 conformations are impossible for a molecule with a (1 → 4)-linked β-D-glucose backbone and with a value of h = 0.508 nm. Our calculations confirm this conclusion.

Although it was possible to build 5_3 helices, these invariably gave unacceptable close contacts between some atoms in the chain backbone. Only in the 5_2 helical conformation could reasonably satisfactory models be constructed. At this level of analysis it was not possible to distinguish between models with O(6) near the *gg*, *gt* and *tg* positions § as in each case the conformation of the backbone and the side-groups on C(2) and C(3) were identical, and the side-group on C(6) did not give rise to any over-short contacts. However, each of these models incurs two short contacts as given in *Table 1*. Since these contacts are not severe, we would anticipate that they could be removed by slight variations in the glycopyranose ring geometry. The Cartesian coordinates of the asymmetric unit of the most acceptable models are listed in *Table 2* and the three side-group orientations indicated. Computer-drawn projections of the *gt* case are shown in *Figure 3*.

Unit cell considerations

The measured *d* spacings taken from the X-ray diffraction pattern shown in *Figure 1a* are listed in *Table 3*.

Mathieu[4] originally proposed a unit cell with the dimensions: a = 0.90 nm, b = 1.39 nm, c (fibre axis) = 2.56 nm, $\alpha = \beta = \gamma = 90°$. Happey[3] argued that Mathieu's cell was incorrectly calculated from the crystallographic data and pos-

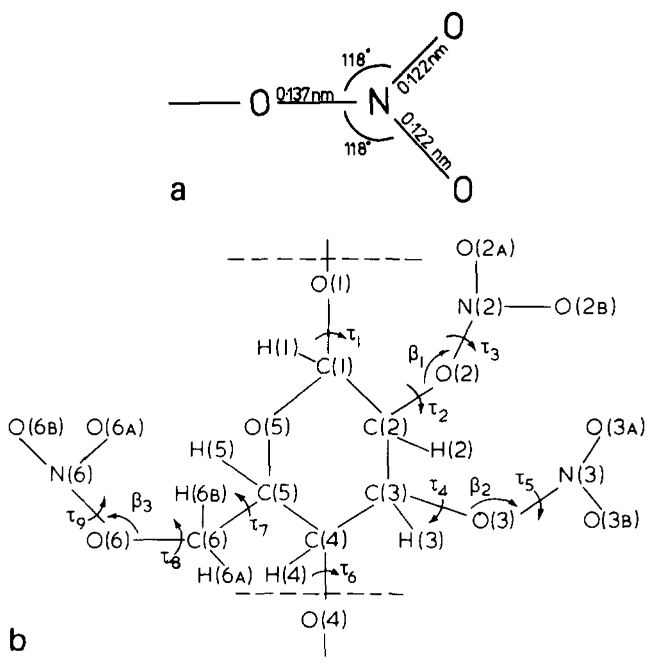

Figure 2 (a) Mean bond distances and valency angles for the O–NO_2 group[9,10,11]. (b) Schematic drawing of cellulose trinitrate monomer with appropriate atoms labelled. The nine torsional angles and variable bond angles are marked τ_1 to τ_9 and β_1 to β_3, respectively

Table 1 Close intrachain contacts for the most acceptable 5_2 helical conformations

Atoms	Separation (nm)	Contact criteria[14](nm) Extreme	Normal	Energy* (kJ/mol)
O(3)–H'(1)	0.214	0.220	0.240	5.8
N(3)–C(2)	0.270	0.280	0.290	2.1

The prime refers to the next residue in the chain. * The energy was calculated using a standard Lennard-Jones potential function with parameters given by Scott and Scheraga[13]

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‡ The 5_3 and 5_4 helices are left-handed versions of 5_2 and 5_1 respectively.

§ Pure *gg* is τ_7 = 60°, *gt* is τ_7 = 180° and *tg* is τ_7 = −60°

Table 2 Cartesian coordinates of the asymmetric repeating unit for the most acceptable 5_2 helical conformations
Unit common to all models

Atom	*X*(nm)	*Y*(nm)	*Z*(nm)
O(1)	0.1064	0.0000	0.0000
C(1)	0.0352	−0.0145	0.1184
C(2)	0.1317	−0.0590	0.2274
C(3)	0.0618	−0.0625	0.3624
C(4)	−0.0056	0.0711	0.3906
C(5)	−0.0947	0.1109	0.2734
O(5)	−0.0182	0.1138	0.1519
H(1)	−0.0469	−0.0873	0.1100
O(2)	0.1843	−0.1870	0.1944
H(2)	0.2167	0.0108	0.2319
O(3)	0.1570	−0.0911	0.4651
H(3)	−0.0138	−0.1424	0.3625
O(4)	−0.0861	0.0625	0.5080
H(4)	0.0712	0.1484	0.4062
C(6)	−0.1556	0.2484	0.2903
H(5)	−0.1768	0.0383	0.2634
N(2)	0.1042	−0.2962	0.2163
O(2A)	0.0206	−0.3238	0.1319
O(2B)	0.1209	−0.3597	0.3191
N(3)	0.2839	−0.0415	0.4495
O(3A)	0.3014	0.0778	0.4682
O(3B)	0.3723	−0.1193	0.4178

O(6) nearly *gg*

Atom	*X*(nm)	*Y*(nm)	*Z*(nm)
H(6A)	−0.2168	0.2505	0.3817
H(6B)	−0.2189	0.2715	0.2034
O(6)	−0.0548	0.3507	0.3011
N(6)	−0.0700	0.4452	0.2030
O(6A)	−0.0107	0.4285	0.0977
O(6B)	−0.1421	0.5408	0.2263

O(6) nearly *gt*

Atom	*X*(nm)	*Y*(nm)	*Z*(nm)
H(6A)	−0.0755	0.3231	0.3003
H(6B)	−0.2185	0.2499	0.3806
O(6)	−0.2375	0.2849	0.1776
N(6)	−0.3707	0.2776	0.2091
O(6A)	−0.4254	0.1688	0.2021
O(6B)	−0.4274	0.3804	0.2425

O(6) nearly *tg*

Atom	*X*(nm)	*Y*(nm)	*Z*(nm)
H(6A)	−0.2110	0.2755	0.1992
H(6B)	−0.0758	0.3221	0.3079
O(6)	−0.2468	0.2532	0.4017
N(6)	−0.3769	0.2578	0.3586
O(6A)	−0.4308	0.3670	0.3510
O(6B)	−0.4316	0.1525	0.3303

The helix axis corresponds to the *Z*-axis of the Cartesian coordinate system used

tulated a modified cell, assuming the same indexing. This corrected cell has the *b*-axis contracted to 1.225 nm with the *a*-axis and angles remaining unaltered. The *c*-axis takes the slightly smaller value of 2.54 nm. The calculated *d*-spacings from this modified cell are also given in *Table 3*. While rescrutinising the measured *d* spacings it was noticed that if Mathieu's indexing was not assumed an alternative unit cell is possible with dimensions: *a* = 0.90 nm, *b* = 1.46 nm, *c*(fibre axis) = 2.54 nm. The calculated *d* spacings for this cell are also given in *Table 3*. The paucity of observed reflections in the X-ray diffraction pattern make it difficult to define a unique cell on this information alone.

Packing considerations

Hexagonal close packing is the most symmetrical and commonly observed arrangement of polymeric molecules having approximately circular cross-section; each molecule is equidistant from its six nearest neighbours. Clearly the five-fold nature of the cellulose trinitrate molecule perturbs this packing arrangement somewhat, giving rise to additional Bragg reflections and larger unit cells. The lattice with *a* = 0.90 nm, *b* = 1.46 nm has the advantage that the angle between the diagonals is close to 60° (63.3°). If we place molecules at the corners and centre of such a cell then the chains pack approximately on a hexagonal lattice. This arrangement, which we feel is representative of the essential features of the juxtapositioning of the molecules, is illustrated in *Figure 4*.

It must be emphasised that the proposed models were built in isolation. It is not surprising, therefore, that some over-short interchain contacts arise when the chains are placed on the lattice sites as in *Figure 4*. Owing to the difficulties in defining a unique unit cell, we can draw no firm

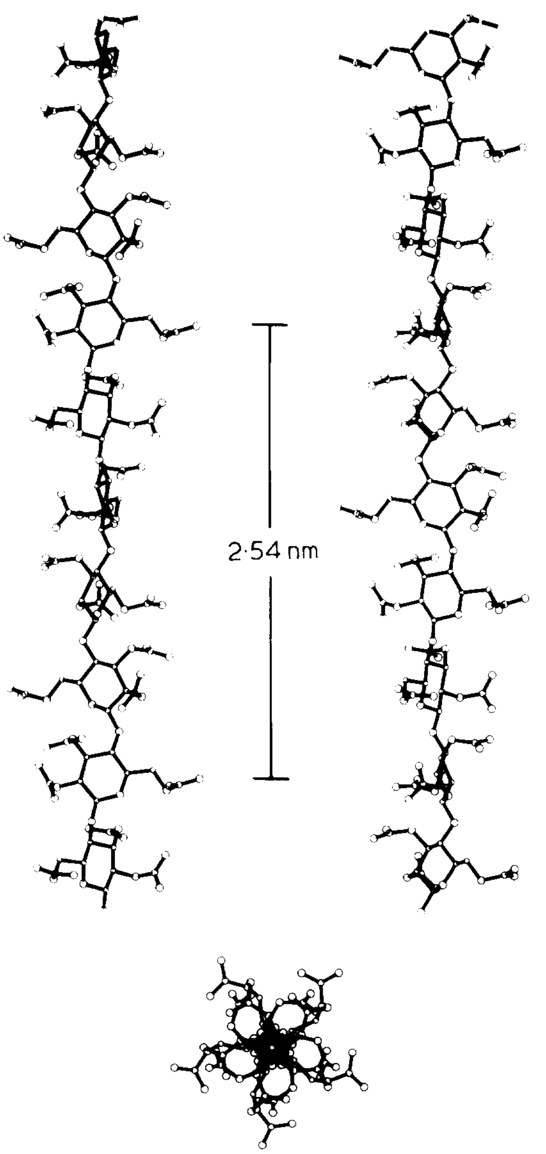

Figure 3 Projections of the proposed 5_2 helix for cellulose trinitrate with O(6) *gt*

Table 3 Comparison of observed *d* spacings with those calculated for two proposed unit cells

		a = 0.90 nm, *b* = 1.224 nm and *c* (fibre axis) = 2.54 nm		*a* = 0.90 nm, *b* = 1.46 nm and *c* (fibre axis) = 2.54 nm	
Measured *d* spacing (nm)		Index	*d*-spacing	Index	*d*-spacing
Equator					
	0.724	110	0.725	020	0.730
	0.367	130	0.371	040	0.365
1st Layer line					
	0.442	201	0.443	201	0.443
2nd Layer line					
	0.763–1.09	012	0.882	012	0.958
3rd Layer line					
	0.854	003	0.847	003	0.847
	0.541	113	0.551	023	0.553
	0.334	223	0.333	043	0.335
4th Layer line					
	0.638	004	0.635	004	0.635
	0.481	114	0.478	024	0.479
	0.367	204	0.367	204	0.367
5th Layer line					
	0.508	005	0.508	005	0.508
	0.485	015	0.469	015	0.480
6th Layer line					
	0.428	006	0.423	006	0.423
	0.371	116	0.366	116	0.371

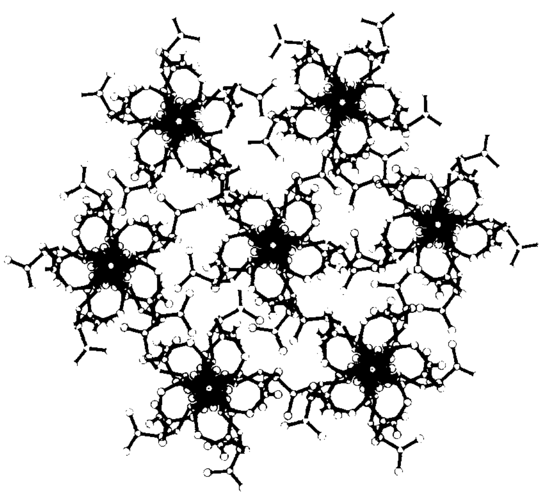

Figure 4 Projection of tentative lattice for cellulose trinitrate with O(6) *gt*. The projections down the chain axis are oriented randomly on a face centred lattice with *a* = 0.90 nm and *b* = 1.46 nm. This is approximately a hexagonal array. Some chains appear with opposite polarity

conclusions as to the most likely polarity of the chains but a crude analysis indicates that the proposed models have most room when they are antiparallel. For this reason some of the chains in *Figure 4* are shown inverted.

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