Nitrocellulose: birefringence and molecular conformation

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Conformational data on nitrocellulose have been used to predict the variation in birefringence with degree of substitution. Of the three possible positions of the 6-nitric ester group, only the *gt* and *tg* structure are consistent with the observed birefringence variations.

Keywords Nitrocellulose; cellulose nitrate; birefringence; polarizability; nitric ester; molecular conformation

INTRODUCTION

In general, crystalline fibres give poorly defined X-ray patterns, and it is not possible from only these data to calculate the position of all atoms within the unit cell. Recourse must be made to other independent structural information and to the techniques of conformational analysis.

Birefringence measurements can sometimes yield useful information. It is not a powerful technique owing to uncertainties concerning individual atomic refractivities and to the lack of specificity relating to any individual chemical group. However, it is particularly applicable to the case of the nitrocelluloses. The birefringence changes in going from a degree of substitution of, say, 2.3 to that of 2.6 are very large, and, if it is assumed that there is no change in conformation other than the replacement of hydroxyl by nitrate ester groups, then the average inclination of these nitrate ester groups to the optic axis may be calculated.

In a recent conformational study of cellulose trinitrate, Meader *et al.*[1] were unable to distinguish between three possible orientations of the primary nitrate group. It is the purpose of the present note to show that only two of these orientations are consistent with the observed birefringences.

METHOD

In 1924 Bragg[2] showed that the birefringences of calcite and aragonite could be satisfactorily calculated using classical formulae for dipole–dipole interaction. The method is particularly useful when dealing with groups of highly polarizable atoms linked in linear or planar conformations. In ionic crystals the CO_3^{2-} and the NO_3^- ions are examples of the latter, and the method has been applied[3] to the linear azide ion, N_3^-.

The polarizability of an atom in the presence of polarizable neighbours is given by:

$$\alpha' = \alpha/(1 - \Sigma\beta\alpha'') \qquad (1)$$

where α is the polarizability of the same atom for random arrangement by neighbours, α'' the polarizability of the influencing neighbour, and β is given by:

$$\beta = (3x^2 - r^2)/r^5. \qquad (2)$$

where r is the distance between the dipoles and x the component of this distance in the direction of the electric vector. Thus, to obtain the polarizability of, for instance, a particular oxygen atom in the presence of polarizable neighbours, a value of β is calculated for each neighbouring atom from equation (2). Equation (1) then gives α', the modified oxygen polarizability. The refractive index n corresponding to the particular direction of the electric vector is then obtained from the Lorentz–Lorenz equation

$$(n^2 - 1)/(n^2 + 2) = (D/M)\Sigma a_i R_i \qquad (3)$$

a_i being the number of atoms or ions of refractivity R_i, which is itself given by:

$$R_i = 4\pi N\alpha'/3 \qquad (4)$$

N being Avogadro's number, D the crystal density and M the molecular weight.

The values of α'' used in equation (1) are those for random arrangement of neighbours. Successive approximations are then made by using the calculated values of α' for α'' in (1) and thus obtaining a new value for α'.

The steps in the calculation were as follows:

(1) Calculation of refractivity of the nitric ester group from the refractive indices of (mainly) liquid nitric esters, using equation (3).

(2) Assignment of this total refractivity to the individual atoms of the group.

(3) Calculation of the modified refractivities, in the x, y and z directions, of each of the nine oxygen atoms of the three nitrate groups, using equations (1), (2) and (4). The coordinates of the oxygen atom were taken from Meader *et al.*[1] Two calculations were made. In the first only the influence of other oxygen atoms within the same nitrate group were considered; in the second the mutual influence

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Table 1 Refractive index density data for NG, DEGDN and NC

	Molecular wt. (*m*)	Refractive index (*n*)	Density (*D*)	R_m (cm^3)
NG	227.1	1.4732	1.596	39.9
DEGDN	196	1.4517	1.385	38.16
NC	297	1.51	1.69	53.83

Table 2 β values for all oxygen—oxygen interactions considered for the nitric ester group in the (2) position

		x	*y*	*z*
O (2)	O (2A)	0.0618	0.0298	−0.0707
	O (2B)	−0.0706	0.0797	−0.0033
	O (3)	−0.0431	−0.0282	0.0753
	O (3A)	−0.0117	0.0052	0.0066
	O (3B)	0.0065	−0.0313	0.0245
O (2A)	O (2)	0.0618	0.0278	−0.0707
	O (2B)	−0.0353	−0.0897	0.1100
	O (3)	−0.0081	−0.0016	0.0097
	O (3A)	−0.0015	0.0017	−0.0001
	O (3B)	0.0041	−0.0040	0
O (2B)	O (2)	−0.0706	0.0797	−0.0033
	O (2A)	−0.0353	−0.0897	0.1100
	O (3)	−0.0316	0.0429	−0.0111
	O (3A)	−0.0049	0.0109	−0.0059
	O (3B)	−0.0003	−0.0013	−0.0098

of the oxygens of the two secondary nitrate groups were also taken into account.

(4) Recent ^{13}C n.m.r. studies[4] have measured the difference in the number of nitrate groups in the 2, 3 and 6 positions between an overall degree of substitution 2.37 and 2.62. Using these data the expected birefringence change over this range has been calculated, using equation (3). Refractivities perpendicular to the fibre axis (the *z* direction) were taken as the average of those calculated at Step 3 for the *x* and *y* direction. It should be emphasized that neither absolute refractive indices nor absolute birefringences are involved. For this to be done directional refractivities of all atoms of the molecule would need to be considered. In using equation (3), all atomic refractivities except those of the nitrate oxygens were taken as those of the unperturbed state.

CALCULATIONS

Step 1

The total refractivity of the nitric ester group was calculated from the refractive indices and the densities of nitroglycerine (glycerol trinitrate), diethyleneglycol dinitrate and nitrocellulose itself. These values are given in *Table 1*.

The values of R_m, the molecular refractivity, is calculated by equation (3). These molecular refractivities may be split into their component atomic refractivities:

$$R_{\mathrm{NG}} = 3R_{\mathrm{C}} + 5R_{\mathrm{H}} + 3R_{\mathrm{NO_3}} \quad \text{etc.}$$

If a value of 1.6 is assigned to each ether oxygen in DEGDN and NC, then three equations are obtained in terms of R_{C}, R_{H} and $R_{\mathrm{NO_3}}$. The solution of these gives $R_{\mathrm{C}} = 2.42$, $R_{\mathrm{H}} = 1.09$ and $R_{\mathrm{NO_3}} = 9.05$. The figures for R_{C} and R_{H} are in good agreement with standard literature values ($R_{\mathrm{C}} = 2.50$, $R_{\mathrm{H}} = 1.03$)[5], and this gives a degree of confidence to the calculated value for $R_{\mathrm{NO_3}}$.

Step 2

The allocation of the total refractivity of the nitrate group into atomic refractivities is a somewhat subjective exercise. Bragg[2], in his pioneer work on calcite, divided the refractivity of the carbonate group equally between the three oxygen atoms, leaving zero for the central carbon. But the three oxygens of the nitric ester group are not equivalent. The group refractivity of the nitrate ion in inorganic compounds is lower than that of the carbonate ion (10.4 against 11.1). For calcite Bragg arbitrarily reduced R_{O} from 3.7 to 3.3, but there appeared to be no case for making a similar reduction for the nitric ester group. The refractivity of the –C–O–N– oxygen presumably falls somewhere between that of ether and hydroxyl oxygens (1.6 and 1.5) and that of the end oxygens (which were considered to have a maximum of 3.3).

The final values taken were 2.45 for the oxygen atoms in the C–O–N positions and 3.3 for the terminal oxygens. It should be emphasized that although changing refractivities makes a considerable difference in the calculated refractive indices, the birefringence is more sensitive to position than to refractivity and, so long as the adopted values are of the correct order, the conclusions concerning structure arrived at below are still valid.

Step 3

Table 2 shows the values of β for the three coordinate directions for all the oxygen–oxygen interactions affecting the refractivity of the nitric ester group in the (2) position.

A similar table was drawn up for the three oxygens of the nitric ester group in the (3) position and for the primary nitric ester group (6 position) for the *gg*, *gt* and *tg* structures. These values were then used to calculate the refractivity in 3 directions of each individual oxygen atom. These results are listed in *Table 3*. As many as five successive approximations using the newly calculated values of α' in place of the isotropic values α'' were necessary before convergence to the second decimal place occurred.

Table 4 gives the total refractivities of the nitric ester groups in (a) the average *x*/*y* direction, and (b) the *z* direction.

It is only the (3), (6*gt*) and (6*tg*) nitric ester groups which give the observed negative birefringence to nitrocellulose. *Figure 1* illustrates how the plane of the primary nitrate group is approximately at right angles to the fibre axis in the *tg* and *gt* positions, but not in the *gg* position.

Table 3 Calculated values of atomic refractivity

		x	*y*	*z*
O (2)		2.33	2.66	2.43
O (2A)		3.34	3.01	3.69
O (2B)		2.85	3.43	3.80
O (3)		3.13	2.52	2.17
O (3A)		3.04	4.65	2.81
O (3B)		3.89	3.73	2.87
O (6)	*gg* structure	2.10	2.72	2.91
O (6A)		3.11	3.02	3.99
O (6B)		3.19	3.67	3.09
O (6)	*gt* structure	3.54	2.23	2.07
O (6A)		3.40	4.62	2.82
O (6B)		3.43	4.52	2.86
O (6)	*tg* structure	3.38	2.23	2.11
O (6A)		3.34	4.74	2.82
O (6B)		3.34	4.67	2.85

Step 4

Before using the refractivities listed in *Table 4* to calculate the effect of the degree of substitution on birefringence it is necessary to know precisely which positions the nitric ester groups are occupying. This has recently been carried out[4] by ^{13}C n.m.r. A number of different degrees of substitution were examined, but only the two values of 2.37 and 2.62 will be considered, since it is over this range that the experimental birefringence is most accurately known. *Table 5* gives the degree of substitution at the individual 2, 3 and 6 positions for the two overall values.

To calculate a 'relative' refractive index from equation (3) the values taken for R_C, R_H, $R_{O(ether)}$ and R_{OH} were those calculated in Step 1. Since these are only average values and will be augmented or reduced according to the position of neighbouring groups, neither the calculated refractive indices nor the corresponding birefringences are in any way absolute. But if it is assumed that any anisotropy in the refractivity of these atoms will be unchanged over a limited range of degrees of substitution, any changes in birefringence over this range will be absolute and due only to the increased concentration of nitric ester groups. The variation of D with M is also not known, and the ratio D/M was assessed to be constant at 0.00569. Thus to calculate the refractive index for a DOS of 2.37:

$$\frac{n^2-1}{n^2+1}=0.00569(6R_C+7R_H+2R_O+0.63R_{OH}+0.77R_{NO_3(2)}+0.66R_{NO_3(3)}+0.94R_{NO_3(6)}$$

The calculated refractive indices, parallel and perpendicular to the fibre axis, are summarized in *Table 6*. Only the final column, $\Delta(n_{\parallel}-n_{\perp})$ has absolute significance and can be compared with experiment.

Table 4 The refractivities of the nitric ester groups

	x/*y*	*z*
NO_3 (2)	8.81	9.92
NO_3 (3)	10.48	7.85
NO_3 (6) *gg*	8.91	9.99
NO_3 (6) *gt*	10.87	7.75
NO_3 (6) *tg*	10.85	7.78

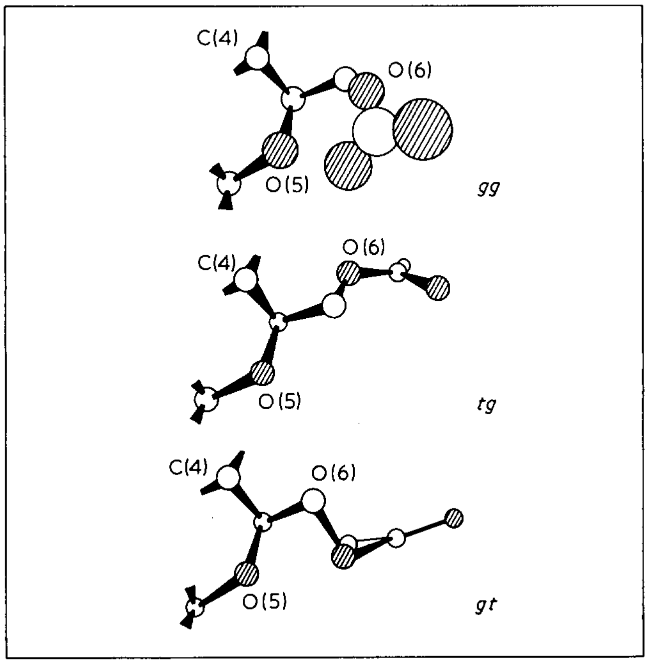

Figure 1 Approximate positions of the primary nitrate group with O(6) in the *gg*, *tg* and *gt* positions respectively. In the *tg* structure O(6) is *trans* to O(5) and *gauche* to C(4)

Table 5 Degree of substitution at various positions

DOS (overall)	DOS (2)	DOS (3)	DOS (6)
2.37	0.77	0.66	0.94
2.62	0.87	0.75	1.00

COMPARISON WITH EXPERIMENT

Birefringences of nitrocellulose fibres over the substitution range considered in this paper have been measured[6]. Whilst it is a simple matter to measure optical path difference, the conversion of these values into birefringences is only approximate owing to the uncertainty of the fibre thickness in the direction of the light path. Nitrocellulose fibres tend to be in the form of ribbons, and the lateral thickness of the observed image may bear little relationship to its depth. A method of calculation was suggested in the paper cited above, but it involved taking averages over a large number of fibres and could only be approximate.

We have now developed a method which, although tedious, does allow birefringence measurements to be made on single fibres. It was found that the temperature coefficient of path difference, averaged over many fibres within a sample, was, to a first approximation, independent of the average degree of substitution of the sample. If this is so, and the average thickness of the various fibre samples is constant, then the temperature coefficient of path difference observed in individual fibres will be proportional to their thickness. If it is also assumed that the mean depth of a fibre sample is the same as the mean observable breadth, then an absolute relationship between temperature coefficient and depth of fibre in the direction of the light path can be obtained. Then, since the path difference is known, an absolute birefringence can be calculated.

Using this technique, a number of nitrocellulose samples of various nitrogen contents have been examined.

Table 6 Calculated refractive indices and birefringences

	DOS = 2.37			DOS = 2.62			
	$n_{\parallel}$	$n_{\perp}$	$n_{\parallel}-n_{\perp}$	$n_{\parallel}$	$n_{\perp}$	$n_{\parallel}-n_{\perp}$	$\Delta(n_{\parallel}-n_{\perp})$
gg	1.4724	1.4708	0.0016	1.4900	1.4890	0.0010	−0.0006
gt	1.4490	1.4916	−0.0426	1.4648	1.5114	−0.0466	−0.0040
tg	1.4493	1.4914	−0.0420	1.4651	1.5112	−0.0460	−0.0040

Table 7 Experimental values of birefringence

%N	DOS	$n_{\parallel}-n_{\perp}$
12.10	2.289	0.0013
12.45	2.399	−0.0011
13.10	2.616	−0.0046
13.44	2.735	−0.0063

In all cases the standard deviation in the measured birefringences of individual fibres within a batch was about half of that observed by the method suggested in ref 6. The values obtained are recorded in *Table 7*.

From these figures a sample with a DOS of 2.37 would have a birefringence of −0.0006 and one of DOS = 2.62 a birefringence of −0.0047. The change in birefringence between these substitution levels is −0.0041, in good agreement with the calculated values for the *gt* and *tg* structures, but quite different from that of the *gg* structure.

DISCUSSION

These calculations have shown that useful structural information may be obtained from birefringence measurements on organic fibres. But at the same time they reveal the limitation of the technique. Nitrocellulose is a particularly suitable fibre for study. It contains a highly anisotropic group which can be added in a controlled manner without the loss of the overall morphology of the fibre. But even in this case, great simplifications must be made. The following are a few of the most obvious.

(1) No account has been taken of the interaction with oxygen atoms outside the immediate anhydroglucose ring—either in the same chain (there can be close approach of the nitric ester group in 3 position with that in the 6 position in the next anhydroglucose unit) or in neighbouring chains. Available structural information is inadequate for any estimation of such interactions to be made. The present calculations show that interactions between oxygen atoms other than those in the same nitric ester group can be important. If interaction between the nitric ester groups in the 2 and 3 positions is neglected (all β values in *Table 2* except those between 2, 2A and 2B taken as zero) the calculated values of $(n_{\parallel}-n_{\perp})$ *for the gg*, *gt*, and *tg* structures become −0.0016, −0.0049 and −0.0049 respectively, considerably greater than those listed in *Table 6*.

(2) No account is taken of any anisotropy of the hydroxyl group which the nitric ester group replaces.

(3) No account is taken of the possible polarizability of the nitrogen atoms, or that the centres of the induced dipoles may not coincide with the atomic nuclei[3]. In view of the success of the method in calculating the refractive indices of calcite and aragonite, these effects are unlikely to be important.

CONCLUSIONS

Birefringence measurements, despite a number of limitations, can give useful information on the structure of nitrocellulose. The observed variation in birefringence with degree of substitution is consistent with conformational studies in which the primary nitric ester group is in either the *gt* or *tg* position. It is not consistent with a nitric ester group in the *gg* position.

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