Molecular conformational studies of cellulose nitrate

D. A. Winkler

Weapons Systems Research Laboratory, Defence Science and Technology Organisation, Department of Defence, GPO Box 2151, Adelaide, SA 5001, Australia
(Received 4 September 1985)

Molecular conformations of cellulose nitrate (NC) models have been studied by potential energy calculations. Three low energy conformations were found for rotation of the primary nitrate group. Two relatively broad low energy minima were found on the Φ, Ψ map, the lowest energy of which implies a backbone configuration for NC of a 5_2 helix, consistent with published X-ray data.

INTRODUCTION

Cellulose nitrate, or nitrocellulose (NC), is a ubiquitous, energetic binder in many gun and rocket propellants[1]. Little is known about the molecular conformations which it may adopt and the influence the degree of nitration and hydrogen bonding have on these conformations.

The low energy conformations of the glycosidic linkages in NC, in particular, play a crucial role in determining which backbone configurations the polymer chain can adopt. Molecular conformation of polymers, including NC, is also considered responsible for the transitions which occur in many physical properties at specific temperatures[2]. Such transitions, which have been studied by dynamic mechanical analysis (d.m.a.), d.s.c. and similar techniques[3], can markedly influence polymer mechanical properties such as fracture toughness[4]. This is of particular interest in propellant science as it suggests a way in which the low temperature mechanical properties of gun propellants can be improved.

Conformational analyses have been undertaken in this work on several models of NC based on β-D-glucopyranoside and β-cellobiose containing various numbers of nitrate substituents. Conformations were calculated by a classical potential energy method and compared with the proton n.m.r. spectra of Carignan and Malinowski[5].

EXPERIMENTAL

The conformational calculations were performed on an IBM 370/3033 computer using program CONES[6]. This program performs classical potential energy calculations using an empirical force field. It considers the non-bonded (Van der Waals) interactions between atoms, and electrostatic effects. The parametrization used in CONES was developed by Giglio[7] and has been used to study a number of related systems[8]. The results are consistent with those obtained from molecular orbital calculations[9], but CONES tends to overestimate the energy barriers between conformers as it does not allow the geometry to relax as the torsion angles are rotated.

Molecular geometries were based on crystal or microwave structures of polysaccharides[10,11] and related compounds[12,13] and bondlengths and angles from standard compilations[14]. The glucopyranose rings were assumed to be in the $^4C_1$ chair conformation[15] and the bond angle at the glycosidic bridge in cellobiose was taken as $116.5°$[10]. Typical models are illustrated in *Figures 1* and *2* together with their conformational degrees of freedom.

RESULTS AND DISCUSSION

Conformations of the side-groups: β-D-glucopyranoside models

In the parent unsubstituted species the hydroxyl groups are essentially free to rotate, with small potential barriers. Substitution by a nitrate ester at the 6-position introduces considerable steric hindrance and only the three staggered conformers around C_5-C_6 are possible (see *Figure 3*). Barriers to rotation around this bond are approximately 25 kJ mol^{-1}, although calculations which allow the geometry to relax during torsion angle rotation
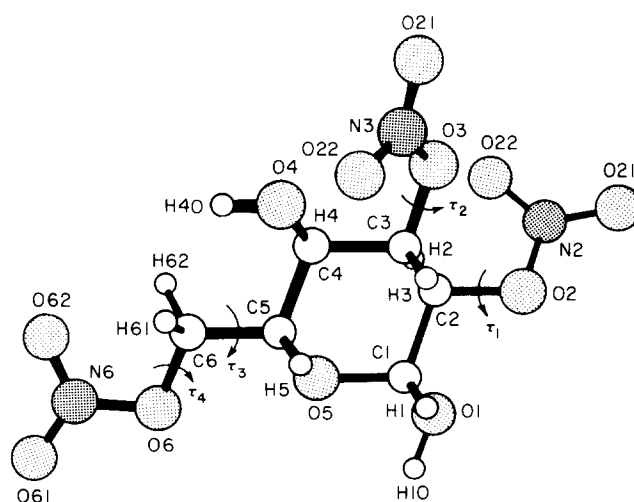

Figure 1 β-D-Glucopyranoside model showing atom numbering and torsion angles
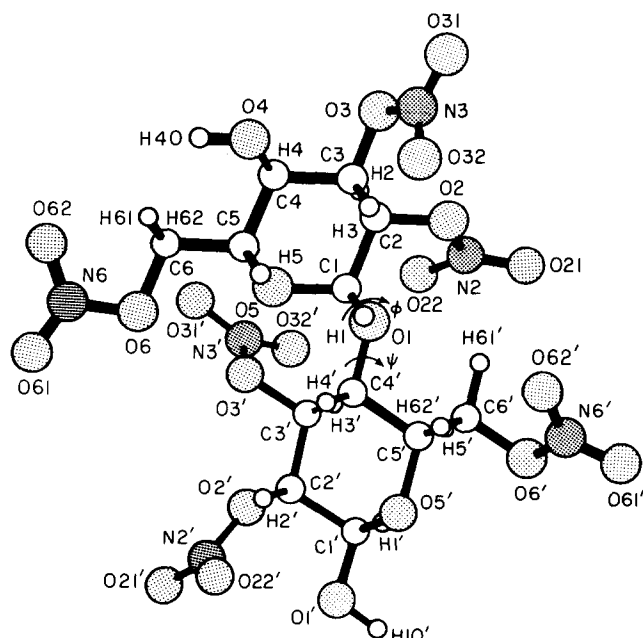
Figure 2 Cellobiose model showing atom numbering and torsion angles

would yield lower values. The nitrate esters at the 2- and 3-positions interact with each other sterically but do not affect the torsion angles which the primary nitrate ester group at the 6-position can adopt. The nitrate groups at the 2- and 3-positions can each adopt two low energy conformations, with torsion angles of 90° and 150° for the 2-nitrate group and 210° and 270° for the 3-nitrate group. Each of these conformations constrains the O–N bond to lie approximately *cis* to the appropriate axial ring proton. Lewis[16] used birefringence measurements to deduce the conformation of the 6-nitrate groups. He found that only the *trans–gauche* (*tg*)* and *gauche–trans* (*gt*) conformations were consistent with the birefringence data. As discussed, conformational analysis undertaken in this work indicates that all three conformers *gg*, *tg* and *gt* are of low energy. The *gg* conformer had the lowest energy with *tg* lying approximately 4 kJ mol^{-1} and *gt* approximately 3 kJ mol^{-1} higher in energy.

The proton n.m.r. spectra of β-D-glucopyranoside tetranitrate and β-cellobiose octanitrate have been recorded by Carignan and Malinowski[5]. The vicinal couplings between protons on C_5 and C_6 were not analysed for conformational information in their paper. As the couplings were reasonably well resolved, and refined values for the coupling constants were available from a computer fit (LAOCN 3) to the experimental spectra, these data were used to deduce the likely conformation or conformations of the C_5–C_6 bond. Pachler[17] and Abraham and Pachler[18] have investigated the relationship between vicinal coupling constants and torsion angles and have derived appropriate parameters for the Karplus relationship. Using these parameters it was not possible to account for the observed vicinal coupling constants of $J_{5,6} = 3.0$ Hz and $J_{5,6'} = 6.2$ Hz in terms of a single conformation.

An equilibrium between the three staggered conformers, which represent the three energy minima for rotation about C_5–C_6, undoubtedly exists. Analysis of the vicinal coupling data in terms of an equilibrium between

* Defined as O_6 *trans* to O_5 and *gauche* to C_4.

the conformers *gg*, *gt* and *tg* yielded populations in these states of 0.71, 0.20 and 0.09 respectively. These data imply that the *gt* conformer is approximately 3.2 kJ mol^{-1} and *tg* is 5.2 kJ mol^{-1} higher in energy than the global minimum *gg*. This order of energies is different from that deduced from the conformational analysis reported here, although the differences in energy are similar. The most plausible reason for this discrepancy is the influence of the additional nitrate group on C_4 in β-cellobiose octanitrate, which would interact significantly with the primary nitrate group on C_6. This interaction would alter the relative populations in the *gg*, *gt* and *tg* conformers relative to those in β-cellobiose hexanitrate, used in the conformational analysis.

Conformation of the nitrocellulose backbone: cellobiose models

Conformational analyses of unnitrated cellobiose have been published previously[19]. The preferred values for the torsion angles in the glycosidic linkage, Φ and Ψ, calculated in this work were in good agreement with the published data.

Calculation of complete conformational energy surfaces for the cellobiose models represents a formidable task due to the large number of torsional variables contained in the models. Considerable simplification was afforded by using the observation of Dixon and Wilson[12] that the nitrate groups tend to adopt a planar configuration, possibly due to resonance-induced double bond character in the bond between the nitrate ester oxygen and the nitro-group. These authors calculated a barrier to rotation around this bond of approximately 40 kJ mol^{-1} in methyl nitrate, consistent with similar values in methyl nitrite[20] and nitric acid[21]. Consequently, in this work, the nitrate groups were assumed to be planar.

The observation was also made that, in any reasonable conformation, the values of the torsion angles of the groups at the 2', 3 and 6 positions were primarily those determined for β-D-glucopyranoside models. This observation implies that it is the functional groups at positions adjacent to the glycosidic bridge (i.e. at the 2, 3'
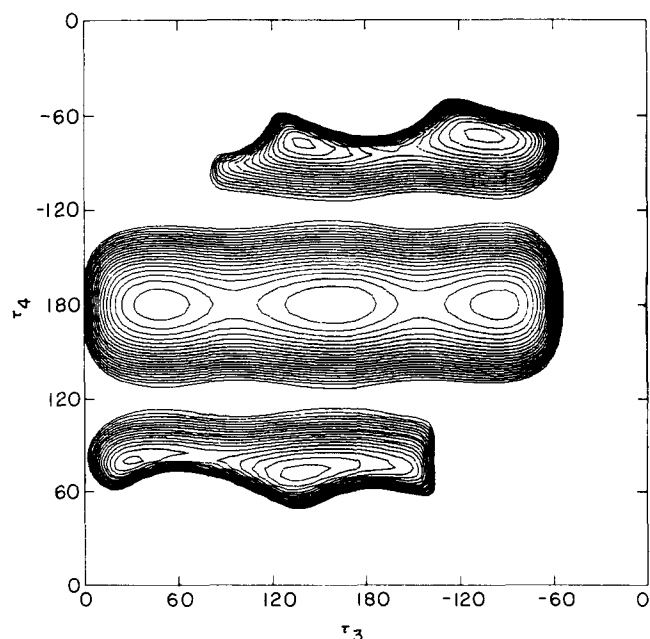

Figure 3 τ_3 *versus* τ_4 potential energy surface for β-D-glucopyranoside trinitrate (the contour interval is 10 kJ mol^{-1})

and 6' positions) that are primarily responsible for perturbing that conformational energy surface generated by the glycosidic torsion angles Φ and Ψ. This observation enabled the number of torsional variables which needed to be considered to be reduced to five (see *Figure 2*). A grid search with a stepsize of 30° was undertaken over this five-dimensional space. The minimum energy torsion angles for the nitrate groups were thus identified and used to define the conformational energy surface for rotation about the glycosidic 'bridge' torsion angles Φ and Ψ (see *Figure 4*). A summary of the lowest energy conformations of cellobiose hexanitrate is given in *Table 1*.

The glycosidic linkage torsion angles have two low energy regions. The global minimum with Φ = 170° and Ψ = 120° results in a geometry which has the two glucopyranose rings fairly coplanar and the molecule extended. Meader *et al.*[11] used a simple molecular mechanics calculation to derive the most probable chain configurations for cellulose trinitrate from X-ray data. The geometry of the lowest energy conformation derived from the current work corresponds closely to the 5_2 helical configuration proposed by Meader *et al.* (a right-handed helix with two complete turns of the backbone in the layer line repeat of 2.54 nm). The other low energy conformation with Φ = 140° and Ψ = 300° produces a more twisted geometry with the rings relatively perpendicular to each other, which would imply a more tightly wound backbone helix in this case.

Effect of degree of nitration on backbone conformations

Partial substitution of nitrate groups produced only small perturbations in the shape of the potential energy surface for rotation of the glycosidic torsion angles, Φ and Ψ. Calculations were performed with one, two and three nitrate groups on each ring. The species with only one nitrate group on each ring had this substituent exclusively in the 6- position, this position being most readily esterified[22]. The calculations involving two nitrate groups on each ring were run for all possible substitution patterns[23]. As may be intuitively expected, absence of a nitrate group at the 2- or 3'- position had the greatest

Figure 4 Φ *versus* Ψ potential energy surface for cellobiose hexanitrate (the contour interval is 10 kJ mol⁻¹)

Table 1 Low energy conformers of cellobiose hexanitrate

τ₁ (Φ)	τ₂ (Ψ)	τ₃	τ₄	τ₅	E (kJ mol⁻¹)
170±20	120±20	60	90	210	3.3
170±20		180			4.6
175±15		270			4.6
170±30		60		270	5.9
170±30		180			6.7
175±15		285			5.4
170±30		60	150	210	0.4
170±30		180			1.7
180±20		285			0.0
170±30		60		270	0.4
170±30		180			3.3
170±20	270				1.7
140±10	300±10	60	90	270	21
140±10		180			17
160±10	320±10	285			38
140±10	300±10	60	150	270	21
140±10		180			17
160±20	320±10	270			38

Definition of torsion angles

$$\tau_1 = C_4 \cdot O_1 C_1 C_2$$
$$\tau_2 = C_3 \cdot C_4 \cdot O_1 C_1$$
$$\tau_3 = O_6 \cdot C_6 \cdot C_5 \cdot C_4 \cdot$$
$$\tau_4 = N_2 O_2 C_2 C_1$$
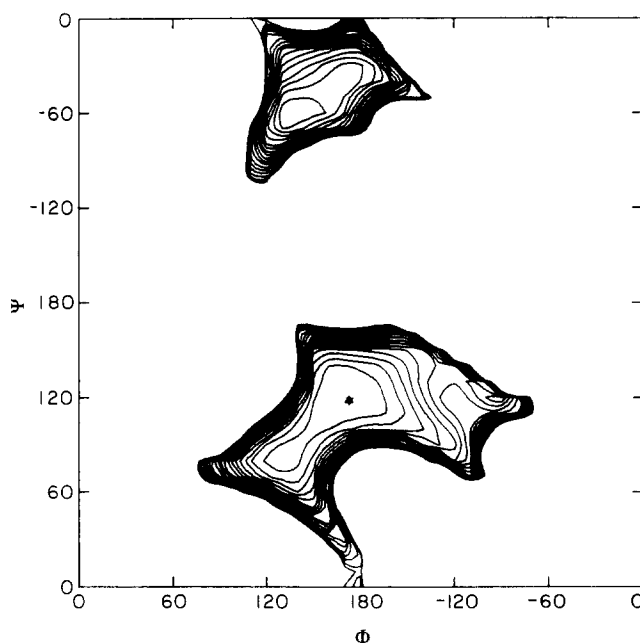$$\tau_5 = N_3 \cdot O_3 \cdot C_3 \cdot C_2 \cdot$$

Figure 5 Φ *versus* Ψ potential energy surface for cellobiose tetranitrate esterified at the 2, 3', 6, 6' positions (the contour interval is 10 kJ mol⁻¹)

influence on the glycosidic bond conformational energy surface, as these positions are adjacent to the neighbouring ring in the cellobiose model.

When either or both of these positions were not substituted, the change in the glycosidic bond energy surface was such as to open up a relatively high energy path (approximately 150 kJ mol⁻¹) between the two low energy conformers (see *Figure 5*), although this value is likely to have been over-estimated by CONES. Reduction in the number of nitrate groups on the model molecules also resulted in a reduction in strain energy and the less substituted molecules had slightly more flexibility, as determined by the angular extent of the energy minima on the conformational energy surfaces.
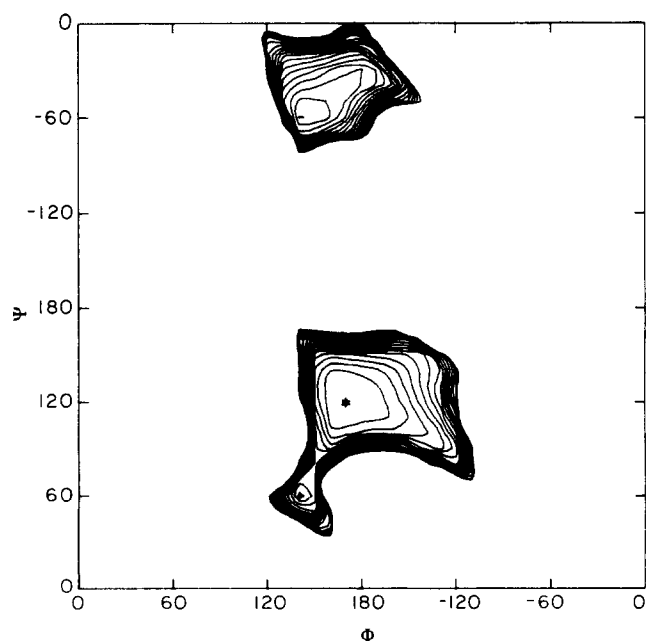
The influence of hydrogen bond formation

The backbone conformation which corresponds to the global energy minimum is one in which there is a very favourable alignment of the lone pairs on the oxygen atom (O_5) in one ring with the 3- hydroxyl on the other. The oxygen–oxygen internuclear distances are approximately 2.7 Å, which would favour the formation of a hydrogen bond. Such a bond would more strongly lock the nitrocellulose backbone into this conformation.

The other minimum with $\Phi = 140°$ and $\Psi = 300°$ has an energy approximately 20 kJ mol^{-1} higher than the global minimum. This conformation produces very favourable alignment of the oxygen atom (O_5) in one ring with the 6-hydroxyl moiety on the other, or the 3'-hydroxyl with the 2-hydroxyl or the nitrate ester oxygen $O_{2'}$. The oxygen–oxygen internuclear distances are similar to the previous case and a hydrogen bond would form here, whenever the appropriate groups were present. Fully nitrated NC would be unable to form a hydrogen bond between the ring oxygen and the 3-hydroxyl (this hydroxyl now being replaced by a nitrate ester) and the stability of this conformer would be reduced owing to the absence of this hydrogen bond energy.

CONCLUSION

The conformational information obtained from the potential energy calculations on models of NC is consistent with that obtained from published n.m.r., birefringence and X-ray data. The primary nitrate group on β-D-glucopyranoside models can adopt only the three staggered conformations around C_5–C_6. The glycosidic bridge of the β-cellobiose models can adopt either of the two possible conformations, one of which is consistent with the helical chain structure deduced from X-ray crystallographic data. The other conformer implies a more highly twisted helical backbone configuration for NC. Hydrogen bonding plays a significant role in stabilizing these low energy conformers for partially nitrated NC. Additional work is planned in this area with the aim of identifying the molecular origin of the relaxation processes observed in d.m.t.a. and related techniques, as has been reported recently[24] for comb branch polymers.

REFERENCES

1 Miles, F. D., 'Cellulose Nitrate', Oliver and Boyd, London, 1955
2 Heijboer, J. *Ann. N.Y. Acad. Sci.* 1976, **279**, 104
3 Townend, D. J. and Warren, R. C. *Polymer* 1985, **26**, 79
4 Warren, R. C. *J. Mater. Sci.*, in press
5 Carignan, Y. P. and Malinowski, E. R. *Carbohyd. Res.* 1977, **58**, 281
6 Winkler, D. A., Richardson, D., Quint, G. and Andrews, P. R. *Comput. Chem.* in preparation
7 Giglio, E. *Nature (London)* 1969, **222**, 339
8 D'Algani, M., Giglio, E. and Pavel, N. V. *Polymer* 1976, **17**, 257
9 Andrews, P. R., Brownlee, R. T. C., Mackay, M. F., Poulton, D. B., Sadek, M. and Winkler, D. A. *Aust. J. Chem.* 1983, **36**, 2219
10 Arnott, S. and Scott, W. E. *J. Chem. Soc. (Perkin Trans. II)* 1972, 324
11 Meader, D., Atkins, E. D. T. and Happey, F. *Polymer* 1978, **19**, 1371
12 Dixon, W. V. and Wilson, E. B. *J. Chem. Phys.* 1961, **35**, 191
13 Jacobson, R. A., Wunderlich, J. A. and Lipscomb, W. N. *Acta Cryst.* 1961, **14**, 598
14 Sutton, L. E. (Ed.), 'Tables of Interatomic Distances', Special Publication Nos. 11 and 18, The Chemical Society, Burlington House, London, 1958 and 1965
15 Reeves, R. E. *J. Am. Chem. Soc.* 1950, **72**, 1499
16 Lewis, T. J. *Polymer* 1982, **23**, 710
17 Pachler, K. G. R. *Spectrochim. Acta* 1964, **20**, 581
18 Abraham, R. J. and Pachler, K. G. R. *Mol. Phys.* 1963, **7**, 165
19 Melberg, S. and Rasmussen, K. *Carbohyd. Res.* 1979, **71**, 25
20 Gray, P. and Reeves, L. W. *J. Chem. Phys.* 1960, **32**, 1878
21 Palm, A. and Kilpatrick, M. *J. Chem. Phys.* 1955, **23**, 1562
22 Clark, D. T., Stephenson, P. J. and Heatley, F. *Polymer* 1981, **22**, 1112
23 Clark, D. T. and Stephenson, P. J. *Polymer* 1982, **23**, 1295
24 Cowie, J. M. G. and Ferguson, R. *Polymer* 1984, **25** (*Commun.*), 66