A General Monte Carlo Approach to Structure Solution from Powder-Diffraction Data: Application to Poly(ethylene oxide)$_3$LiN(SO$_2$CF$_3$)$_2$

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Abstract

A new approach based on the Monte Carlo method of solving molecular crystal structures from full-pattern profile analysis of powder diffraction data is described. The new approach represents a significant advance on previous Monte Carlo methods in that it permits the solution of flexible (i.e. with variable bond lengths, bond and torsion angles) molecules. It does this by not only allowing random rotations and translations of individual atoms and rigid-body fragments comprising an asymmetric unit, but by permitting changes of internal configuration of stereochemically constrained moieties. The last option was crucial in the case of the structure solution of poly(ethylene oxide)$_3$LiN(SO$_2$CF$_3$)$_2$, containing 25 non-H atoms in the asymmetric unit. Using a specifically designed computer code the atomic positions of the flexible poly(ethylene oxide) [(CH$_2$-CH$_2$- O)$_n$] chain and imide N(SO$_2$CF$_3$)$_2$- group are described in terms of bond lengths, angles and torsion angles, offering a means of introducing chemical constraints which, in turn, significantly reduce the number of parameters to be varied in a random fashion. Furthermore, tests for reasonable inter-fragment distances avoid the unnecessary calculation of chemically unreasonable structures. A detailed account of the random-search procedure combined with simulated annealing is given.

1. Introduction

The arrival of the Rietveld method of profile refinement (Rietveld, 1969) marked a revival of interest in powder-diffraction techniques. However, the obvious advantages of the full-pattern-profile analysis did not initiate development of new structure-solution techniques based on the same type of data treatment. In contrast, most efforts in the field of ab initio structure determination from powders concentrated on adaption of single-crystal methods such as direct methods (Cascarano, Favia & Giacobazzo, 1992) or maximum entropy (David, 1990; Gilmore, Henderson & Bricogne, 1991) which requires values of integrated intensities of diffraction peaks. Despite the availability of advanced pattern-decomposition techniques (e.g. Le Bail, Duroy & Fourquet, 1988) and examples of successful application of both methods to powder data (e.g. Cernik et al., 1991; Tremayne et al., 1992), structure solution has remained largely the domain of single-crystal techniques because of the intrinsic incompleteness of a one-dimensional powder data set aggravated by the overlap of non-equivalent reflections.

It is obvious that a plausible method of solving structures using full-powder-pattern analysis could have been obtained by a straightforward conversion of the Rietveld method from structure refinement into a structure solution technique. Mathematically it requires a substitution of least-squares algorithms, used at present and capable of finding the nearest (and hopefully the deepest) minimum of the figure-of-merit function, by a method which can find the global minimum in a multi-parameter non-linear space. Apart from an exhaustive grid search requiring currently unavailable computing capacities, Monte Carlo (MC) seems to be the only method capable of tackling the problem. In essence, the method uses an MC procedure to generate trial atomic position in the unit cell which are tested by the level of agreement with the observed diffraction profile. The potential of the MC method combined with simulated annealing for this particular purpose was first shown by Newsam, Deem & Freeman (1992), who solved the previously known crystal structure of benzene by random translations and rotations of a rigid C$_6$ ring using a simulated powder-diffraction pattern as a matching target. More recently, Harris, Tremayne, Lightfoot & Bruce (1994) used the MC method for the determination of the previously unknown crystal structure of p-BrC$_6$H$_4$CH$_2$CO$_2$H. A two-stage approach was adopted in which the Br atom alone was introduced into the unit cell and positions generated by a MC routine. For each, the powder pattern was calculated and compared with the observed. The lowest $R_{wp}$ yielded the Br position. In the second stage the benzene ring and C atom para to the Br atom were treated as a rigid body and the optimum position located again by MC. While successful, this version of the method did not include an automated simulated annealing scheme and, as a result, requires subsequent analysis of minima obtained at the end of the scan and is inconvenient to apply when more parameters...
are in question. Another limitation of the previous MC procedure was that distances between atoms belonging to neighbouring asymmetric units were not tested for reasonableness, resulting not only in unjustified computational expense but also giving rise to false minima. The recent successful application of the MC method has also been reported by Ramprasad, Pez, Toby, Markley & Pearlstein (1995) for the structure solution of \( \text{Li}_3[\text{Co(CN)}_5] \)-2DMF. In this case the solution was found by random translations and rotations of three rigid bodies: two DMF molecules and one Co(CN)\(_5\) unit.

This paper presents a more powerful MC method capable of solving the structure of flexible molecules. It is demonstrated by determining a complex molecular crystal structure, specifically a crystalline polymer complex poly(ethylene oxide)\(_3\):\( \text{LiN(SO}_2\text{CF}_3)\)_2, comprising stereochemically constrained fragments, from X-ray powder diffraction data. An exhaustive geometrical description of the fragments allows essential reduction of the number of variable parameters whilst preserving flexibility of the non-rigid units, which is necessary and sufficient for the structure solution. A randomized minimization procedure is combined with a simulated annealing algorithm and tests for reasonableness of interatomic distances.

\[ \begin{align*}
   \textbf{R} \cdot \begin{bmatrix}
   x_i^C \\
   y_i^C \\
   z_i^C
   \end{bmatrix} &= \begin{bmatrix}
   x_{i\text{or}}^C \\
   y_{i\text{or}}^C \\
   z_{i\text{or}}^C
   \end{bmatrix}, \quad \textbf{R} = \textbf{R}^{-1},
\end{align*} \]

where \( x_{i\text{or}}^C \) stands for the \( x \) coordinate, expressed in the general Cartesian frame, of the atom at the origin of the local frame i.e. \( C7 \) and \( C1 \) for PEO and imide, respectively; \( x_i^C \) is the coordinate of the \( i \)th atom in the local frame and \( x_i^C \) is that in the general Cartesian frame. Components of the \( \textbf{R} \) matrix are given by equation (21) (see Appendix B). Such a transformation requires six

2. The method

2.1. Calculation of crystallographic coordinates via stereochemical descriptors

There are several critical aspects of the method. The first is the reduction of the number of atomic parameters which must be randomly generated by the MC process. The content of the asymmetric unit was partitioned into three separate fragments, namely, the imide group \( \text{N(SO}_2\text{CF}_3)_2^- \), the poly(ethylene oxide) (PEO) chain composed of three ethylene oxides and a Li atom. The coordinates of non-H atoms forming the PEO chain (Fig. 1a) can be calculated in a local Cartesian frame in terms of the values of consecutive bond lengths, bond and torsion angles as suggested in Appendix A. By assuming that all bond lengths for a given bond type are equal (e.g. all C–O bond lengths \( l_{\text{C–O}} \) are the same) and that all bond angles of a given type are also equal (e.g. all C–C–O angles \( \varphi_{\text{C–C–O}} \) are the same), then this reduces the total number of parameters needed to compute the coordinates in the above frame from 27 to 10. Typical values for the parameters were taken from previous studies (e.g. Takahashi & Tadokoro, 1973). The general arrangement of atoms comprising the imide group (Fig. 1b) and typical values of the internal bond lengths and angles were taken from the previously reported structure of \( \text{LiN(SO}_2\text{CF}_3)_2 \) (Nowinski, Lightfoot & Bruce, 1994). As in the case of the PEO chain, the total number of parameters describing the coordinates of atoms in the local Cartesian frame was reduced from 45 to 14 by invoking the approximation that all like lengths \( l_{\text{S–C}}, l_{\text{S–O}}, l_{\text{S–N}}, l_{\text{C–F}} \), angles \( \varphi_{\text{C–S–O}}, \varphi_{\text{S–C–F}}, \varphi_{\text{O–S–O}}, \varphi_{\text{F–C–F}}, \varphi_{\text{N–S–O}} \) and torsion angles \( \gamma_{\text{N–S–C–F}} \) are equal.

The atomic coordinates thus determined for the two moieties, each in its local Cartesian frame, are transformed to a general Cartesian frame chosen as follows. The \( X^C \) axis of the general Cartesian frame coincides with the \( X \) axis of the crystallographic frame, \( Y^C \) is set perpendicular to \( X^C \) and in the plane defined by \( X \) and \( Y \), and \( Z^C \) completes the right-handed orthogonal set. The transformations for each \( i \)th atom in the local frame of each moiety to the general Cartesian frame are performed using the following matrix equation

\[ \begin{bmatrix}
   x_i^C \\
   y_i^C \\
   z_i^C
   \end{bmatrix} = \textbf{R} \cdot \begin{bmatrix}
   x_{i\text{or}}^C \\
   y_{i\text{or}}^C \\
   z_{i\text{or}}^C
   \end{bmatrix}, \quad \textbf{R} = \textbf{R}^{-1}, \]

Fig. 1. Constituent molecular fragments in their local Cartesian frames: (a) PEO chain, (b) imide group.
additional parameters specifying position \((x_{Cr}^C, y_{Cr}^C, z_{Cr}^C)\) and the spatial orientation in terms of Euler angles \((\Theta, \Phi, \Psi)\) of each fragment. The final transformation of atomic coordinates from the general Cartesian to the crystallographic frame is made using the square matrix given in International Tables for X-ray Crystallography (1959), components of which are determined by the lattice constants.

2.2. Generation of trial configuration

Each new value \(p_i^{\text{new}}\) of the \(i\)th variable parameter (e.g. a bond length) is calculated as follows

\[
p_i^{\text{new}} = p_i^{\text{old}} + r_i \cdot \Delta p_i,
\]

where \(p_i^{\text{old}}\) is a previously accepted value, \(\Delta p_i\) is a predefined maximum stepwidth, and \(r_i\) is a random number in the range from 0 to 1 whose sign is chosen in accordance with a randomly picked bit \([0(-)\text{ or } 1(+)]\). The new value is accepted if it lies within the range \([p_i^{\text{min}}, p_i^{\text{max}}]\) specified beforehand, otherwise \(p_i^{\text{new}} = p_i^{\text{old}}\).

Once a new set of variable parameters \(\{p_i^{\text{new}}\}\) is obtained, a new set of atomic coordinates is calculated following the coordinate transformation given in the preceding section.

The resulting new configuration is tested for reasonableness of interatomic distances. Such a test includes checking the distances between atoms belonging to different \(SO_2CF_3\) moieties in the imide group and between atoms comprising each pair of the three fragments partitioned above. If any of the distances becomes less than 80\% of the sum of the corresponding van der Waals radii (or ionic radii in the case of the Li–O distance) the trial configuration is rejected and a new one has to be chosen. An additional check verifies the distance between C and O atoms (C8 and O5' in Fig. 1a) that belong to two successive parts of the PEO chain bridging the junction of consecutive asymmetric units, since from the outset the chain is known to be continuous in such compounds.

Coordinates of the atoms comprising the accepted configuration of the asymmetric unit are now used to calculate the powder-diffraction profile to be compared with the experimental pattern (with background subtracted). Miller indices, multiplicities, atomic form factors and Lorentz-polarization factors for all peaks in the angular range under consideration are computed in advance and at this stage used as tabulated values. Lattice parameters are fixed at the refined values obtained from indexing, halfwidths obtained from the observed profile and peak-shape parameters appropriate for the diffractometer in use are set at fixed values. The scale factor is recalculated for each trial structure using the linear least-squares method. Calculation of the reduced Pearson-distribution \(\chi^2_{\text{new}}\) criterion value indicating the quality of profile fit marks the end of what is called hereafter an MC move.

2.3. Minimization procedure

Minimization of \(\chi^2\) is based on the standard Metropolis importance sampling algorithm (Metropolis, Rosenbluth, Rosenbluth, Teller & Teller, 1953) with values of \(\chi^2_{\text{new}}\) and \(\chi^2_{\text{old}}\) acting as energy analogues for new and for the previously accepted trial moves, respectively. A new move is accepted if either \(\chi^2_{\text{new}} < \chi^2_{\text{old}}\) or if \(\exp[-(\chi^2_{\text{new}} - \chi^2_{\text{old}})/\Delta\chi^2_{\text{cur}}] > r\), where \(r\) is a random number in the range from 0 to 1 and \(\Delta\chi^2_{\text{cur}}\) is a current marginal value of \(\chi^2\) variation serving as a temperature analogue in a Boltzmann distribution. Once the move is accepted then \(\{p_i^{\text{old}}\} = \{p_i^{\text{new}}\}\) and \(\chi^2_{\text{old}} = \chi^2_{\text{new}}\) and the process iterates until the total number of moves exceeds the preset value of \(N_{\text{tot}}\) or until the number of accepted moves becomes bigger than \(f_1 \cdot N_{\text{tot}}\), with the \(f_1\) values also chosen in advance. As soon as this happens the value of \(\Delta\chi^2_{\text{cur}}\) is reset to \(\Delta\chi^2_{\text{cur}} - f_2 \cdot \Delta\chi^2_{\text{cur}}\) with a predetermined value of \(f_2\) and the whole procedure continues. Minimization terminates when there are no successful moves at a current value of \(\Delta\chi^2_{\text{cur}}\).

2.4. Computing software and hardware

The code implementing the above procedure was written in C++ using the Microsoft Visual C++ Development System and Tools (version 2.0). Peak intensities and pattern-profile calculation were carried out using code adapted from the CPSR software package (Andreev, Lundström & Sorokin, 1995). Routines RAN3 and IRBITI from Press, Teukolsky, Vetterling & Flannery (1992) were used as random-number and random-bit generators, respectively. The program was run on a dual Pentium 100 MHz PC under Windows NT (version 3.5).

3. Results

Details on the sample preparation, indexing and space-group determination are given elsewhere (Andreev, Lightfoot & Bruce, 1996). The space group was identified as \(P2_1/c\) with all the atoms in the general positions. The diffraction pattern of PEO3:LiN(SO2CF3)2 was collected in steps of 0.02° in 2θ over the range 5–60°, in transmission mode on a STOE STADI/P powder diffractometer, using Cu Kα radiation and a small-angle position-sensitive detector. The sample was mounted in a 0.5 mm glass capillary.

A similarity between the lattice parameters of the sample under investigation (\(a = 12.034, b = 8.660, c = 19.139\ \text{Å}, \beta = 128.5°\)) and another compound with the same polymer:salt ratio, namely, PEO3:LiSO3CF3 \([a = 10.064, b = 8.613, c = 16.77\ \text{Å}, \beta = 121.0°\] (Lightfoot, Mehta & Bruce, 1993), suggested that the conformation of the PEO chain in PEO3:LiN(SO2CF3)2 may be similar to that found in the PEO3:LiSO3CF3 complex.
It should be noted that despite this, all attempts to refine the structure of PEO$_3$:LiN(SO$_2$CF$_3$)$_2$ on the basis of the known structure of PEO$_3$:LiSO$_3$CF$_3$, adjusted to the new dimensions of the unit cell, failed, as did attempts to solve the structure by approaches based on direct methods using SHELXS86 (Sheldrick, 1985) and SIR88 (Burla et al., 1989) packages and difference-Fourier synthesis. This motivated our development of the new MC approach.

The first MC run was made using as a starting point the position and internal configuration of the PEO chain from the PEO$_3$:LiSO$_3$CF$_3$ modified for the different unit cell. The initial position of the imide group (Fig. 2a) was adapted from an earlier attempt to solve the structure by the difference-Fourier synthesis, although as it appeared later the actual starting configuration was not important since it changed completely during the course of the MC run. The required values of Euler angles controlling the spatial orientation of the imide were determined following the procedure given in Appendix B. 24 parameters (including coordinates of the Li atom) were varied in a random fashion with $N_{\text{tot}} = 5000$ and $f_1 = f_2 = 0.1$. The initial value of $\Delta \chi^2_{\text{cut}}$ was set to 5, thus allowing fairly large variations in $\chi^2$ and permitting a significant number of uphill steps at this early stage of minimization. In a 47 h run, 183 347 random moves were made with 15 388 being accepted. The rest of the steps were rejected either on the basis of the chemical tests for distances of closest approach or by the Metropolis algorithm. The effect of the MC procedure combined with the use of simulated annealing is clearly seen in Fig. 3. Unlike the least-squares method, it allows uphill steps of $\chi^2$ and these are larger and more frequent at higher ‘temperatures’. Gradual and automatic decrease of the $\Delta \chi^2_{\text{cut}}$ value during the run reduces the acceptance of uphill fluctuations in favour of downhill ones, thus enhancing the opportunity for the whole set of variable parameters to become ‘frozen’ at the values which more likely correspond to the global minimum of the figure-of-merit function than those provided by least squares. The location and configuration of the imide group giving the best fit to the experimental pattern ($\chi^2 = 22.2^*$ at $\Delta \chi^2_{\text{cut}} = 0.02$) is shown in Fig. 2(a) with numerical values of the final set of parameters listed in Table 1.

The structure obtained was further refined using the GSAS program package (Larson & Von Dreele, 1987). For the purpose of refinement, H atoms were added in idealized tetrahedral positions with respect to C atoms comprising the PEO chain, while the Li atom was initially placed in a position within the chain similar to that previously found in PEO$_3$:LiCF$_3$SO$_3$. The refinement was performed using soft constraints on the bond lengths and angles which were introduced by constraining interatomic distances. Contrary to the MC structural model, the applied constraints allow all the

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During MC runs the weight values involved in the calculation of $\chi^2$ were obtained assuming that the observed intensities obey Poisson statistics and neglecting the background subtraction. Such a procedure led to an increase of the absolute value of $\chi^2$ while not adversely affecting the results obtained at this stage.
Table 1. Ranges, maximum stepwidths and values of stereochemical parameters

<table>
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<tr>
<th>Imide group</th>
<th>Parameter</th>
<th>Range</th>
<th>Maximum step</th>
<th>Initial value</th>
<th>Final value</th>
<th>Refinement*</th>
<th>Initial value</th>
<th>Final value</th>
<th>Refinement*</th>
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<td>0.625</td>
<td>0.626</td>
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<td>0.148</td>
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</table>

* Recalculated from the refined values of atomic coordinates. † In the general Cartesian frame.
distances to vary within certain limits independently of each other, thus permitting local relaxation of the structure to lower molecular symmetry. Isotropic displacement factors were subdivided into three groups and varied separately for all non-H atoms comprising the PEO chain and for all atoms in the imide moiety, while those for Li and H were fixed at $B = 7.0$ (value chosen in the basis of previous experience). Background intensities were introduced manually. A total of 123 parameters were refined with the constraint matrix having 145 terms. The refinement has altered the internal structure of the imide group (Fig. 2b) which is hardly surprising given the more rigorous constraints on the bond lengths and angles applied during the MC run. The change in the conformation of the PEO chain is less pronounced (Fig. 4a) and its initial placement in the unit cell appears to be justified. The values of the stereochemical parameters calculated from the refined values of atomic coordinates are given in Table 1. Although the values of agreement indices ($\chi^2 = 1.54$, $R_{pp} = 8.64\%$) of the final fit are reasonably good, the match of the observed and calculated patterns leaves something to be desired (Fig. 5). \* The main conclusion to be drawn from the unsatisfactory fit obtained from the refinement is that sufficient flexibility of the structure had not been included during the MC run.

The MC procedure was revisited and the second MC run was made during which the position and conformation of the PEO were varied in addition to the set of parameters involved in the first run. The starting configuration was based on the refinement results, with the only difference that all like bond lengths and angles in the imide group were averaged (see Table 1 and Fig. 6a). However, the use of a starting configuration based on the refined structure had no bearing on the random structures generated by MC as can be seen by the fact that they differed markedly from this initial configuration. Initial values of Eulerian angles for both fragments were determined as before. This time, 36 parameters were varied in a random fashion with an additional check for reasonable interatomic distances between parts of the PEO chain belonging to adjacent asymmetric units (determined by the $1/2 - x, 1/2 + y, -z$ symmetry operator). Annealing scheme values were chosen to be $N_{\text{tot}} = 7000$, $f_1 = f_2 = 0.1$. The initial value of $\Delta\chi_\text{crit}^2$ was set to 0.5, preventing large variations of the parameter values when making an uphill step. In a 7.3 h run, 104140 random moves were made with only 861 being accepted (Fig. 7). Approximately 90% of the rejected steps were discarded on the grounds of breaking the continuity of the PEO chain. The system was frozen at

---

* The numbered intensity of each point on the profile has been deposited with the IUCr (Reference: TH0003). Copies may be obtained through the Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester, CH1 2HU, England.
\[ \Delta \chi^2 = 0.10 \] giving the best \( \chi^2 = 17.6 \) at accepted move no. 708 which provided the structural model for a new refinement. Apart from giving a slightly different chain conformation (Fig. 4b), the second MC run has revealed an additional twist of the SO\(_2\)CF\(_3\) fragments of the imide group around the S2–N bond (see Fig. 6a), which had not been revealed during the first MC run with the chain fixed. Subsequent refinement performed in exactly the same manner as before converged with the values of the agreement indices being \( \chi^2 = 0.57 \), \( R_{wp} = 5.59\% \). Despite the statistically meaningless value of the \( \chi^2 \) criterion, owing to a lack of counting statistics and the relatively poor signal-to-noise ratio of the raw experimental data set, a drastic improvement of the quality of fit (compare the inserts in Figs. 5 and 8†) counts in favour of the latest structural model. In retrospect, it is evident that the chain position, orientation and conformation should have been permitted to vary in the first MC run. Had this been the case, a structural model suitable for final refinement could have been obtained at this stage. The final values of the stereochemical descriptors and atomic coordinates are listed in Tables 1 and 2, respectively, while the discussions concerning the chemical and structural aspects of PEO\(_3\):LiN(SO\(_2\)CF\(_3\))\(_2\) may be found in Andreev, Lightfoot & Bruce (1996).

4. Concluding remarks

The successful solution of the crystal structure of PEO\(_3\):LiN(SO\(_2\)CF\(_3\))\(_2\) containing 25 non-H atoms in the asymmetric unit resulted from the use of a new MC technique for solving structures based on the full-profile analysis of powder diffraction data. Along with the previously used rotation and translation of rigid bodies, flexibility of the internal configuration of the component molecular fragments is a crucial factor in the success of the new approach. The exhaustive procedure for the expression of crystallographic coordinates of the constituent atoms via stereochemical descriptors presented

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* When calculated according to not-generally-accepted definitions, proposed by Hill & Fisher (1990) as 'a sound basis for comparing the degree of fit of peak profile and crystal structure model refinements in the general case', which are independent of the signal-to-noise ratio due to the exclusion of background, the values of the agreement indices are \( \chi^2 = 4.52 \), \( R_{wp} = 15.74\% \). The value of the most recommended criterion \( R_p \) is equal to 17.77%.
† See deposition footnote.
here not only offers the necessary flexibility but also allows significant reduction of the number of parameters to be varied in a random fashion by equating chemically similar distances and angles within each fragment. The introduction of tests for reasonableness of the intera-

Table 2. Refined atomic parameters for poly(ethylene oxide)$_3$:LiN(CF$_3$SO$_2$)$_2$

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.808 (1)</td>
<td>0.140 (2)</td>
<td>0.2344 (8)</td>
</tr>
<tr>
<td>C1</td>
<td>0.614 (2)</td>
<td>0.142 (2)</td>
<td>0.127 (1)</td>
</tr>
<tr>
<td>F1</td>
<td>0.619 (3)</td>
<td>0.130 (3)</td>
<td>0.057 (1)</td>
</tr>
<tr>
<td>F2</td>
<td>0.554 (2)</td>
<td>0.013 (2)</td>
<td>0.130 (2)</td>
</tr>
<tr>
<td>F3</td>
<td>0.558 (2)</td>
<td>0.279 (2)</td>
<td>0.124 (1)</td>
</tr>
<tr>
<td>N1</td>
<td>0.799 (3)</td>
<td>0.187 (2)</td>
<td>0.310 (1)</td>
</tr>
<tr>
<td>O1</td>
<td>0.853 (3)</td>
<td>-0.015 (2)</td>
<td>0.242 (2)</td>
</tr>
<tr>
<td>O2</td>
<td>0.873 (3)</td>
<td>0.269 (2)</td>
<td>0.224 (2)</td>
</tr>
<tr>
<td>S2</td>
<td>0.764 (1)</td>
<td>0.089 (1)</td>
<td>0.3617 (8)</td>
</tr>
<tr>
<td>C2</td>
<td>0.592 (2)</td>
<td>0.181 (2)</td>
<td>0.324 (1)</td>
</tr>
<tr>
<td>O3</td>
<td>0.862 (2)</td>
<td>0.116 (3)</td>
<td>0.456 (1)</td>
</tr>
<tr>
<td>O4</td>
<td>0.734 (2)</td>
<td>-0.071 (2)</td>
<td>0.336 (1)</td>
</tr>
<tr>
<td>F4</td>
<td>0.556 (2)</td>
<td>0.102 (3)</td>
<td>0.369 (2)</td>
</tr>
<tr>
<td>F5</td>
<td>0.496 (2)</td>
<td>0.149 (3)</td>
<td>0.236 (1)</td>
</tr>
<tr>
<td>F6</td>
<td>0.622 (2)</td>
<td>0.332 (2)</td>
<td>0.343 (2)</td>
</tr>
<tr>
<td>O5</td>
<td>0.017 (3)</td>
<td>-0.491 (3)</td>
<td>0.381 (2)</td>
</tr>
<tr>
<td>C3</td>
<td>-0.059 (3)</td>
<td>-0.349 (3)</td>
<td>0.358 (2)</td>
</tr>
<tr>
<td>C4</td>
<td>-0.194 (3)</td>
<td>-0.367 (4)</td>
<td>0.260 (2)</td>
</tr>
<tr>
<td>O6</td>
<td>-0.171 (3)</td>
<td>-0.328 (3)</td>
<td>0.199 (2)</td>
</tr>
<tr>
<td>C5</td>
<td>-0.256 (3)</td>
<td>-0.418 (3)</td>
<td>0.120 (2)</td>
</tr>
<tr>
<td>C6</td>
<td>-0.245 (3)</td>
<td>-0.366 (3)</td>
<td>0.048 (2)</td>
</tr>
<tr>
<td>O7</td>
<td>-0.208 (3)</td>
<td>-0.207 (3)</td>
<td>0.059 (2)</td>
</tr>
<tr>
<td>C7</td>
<td>-0.180 (3)</td>
<td>-0.156 (3)</td>
<td>0.002 (2)</td>
</tr>
<tr>
<td>C8</td>
<td>-0.136 (3)</td>
<td>0.015 (3)</td>
<td>0.027 (2)</td>
</tr>
<tr>
<td>Li1</td>
<td>-0.054 (6)</td>
<td>-0.144 (5)</td>
<td>0.195 (3)</td>
</tr>
<tr>
<td>H1</td>
<td>-0.083 (5)</td>
<td>-0.335 (6)</td>
<td>0.396 (3)</td>
</tr>
<tr>
<td>H2</td>
<td>-0.001 (4)</td>
<td>-0.268 (3)</td>
<td>0.364 (3)</td>
</tr>
<tr>
<td>H3</td>
<td>-0.266 (4)</td>
<td>-0.302 (9)</td>
<td>0.251 (3)</td>
</tr>
<tr>
<td>H4</td>
<td>-0.224 (6)</td>
<td>-0.472 (6)</td>
<td>0.251 (3)</td>
</tr>
<tr>
<td>H5</td>
<td>-0.224 (8)</td>
<td>-0.523 (3)</td>
<td>0.136 (3)</td>
</tr>
<tr>
<td>H6</td>
<td>-0.351 (3)</td>
<td>-0.412 (8)</td>
<td>0.098 (3)</td>
</tr>
<tr>
<td>H7</td>
<td>-0.334 (6)</td>
<td>-0.380 (6)</td>
<td>-0.009 (2)</td>
</tr>
<tr>
<td>H8</td>
<td>-0.175 (7)</td>
<td>-0.425 (4)</td>
<td>0.051 (5)</td>
</tr>
<tr>
<td>H9</td>
<td>-0.105 (6)</td>
<td>-0.212 (5)</td>
<td>0.011 (4)</td>
</tr>
<tr>
<td>H10</td>
<td>-0.262 (6)</td>
<td>-0.162 (6)</td>
<td>-0.058 (2)</td>
</tr>
<tr>
<td>H11</td>
<td>-0.110 (6)</td>
<td>0.057 (6)</td>
<td>-0.006 (3)</td>
</tr>
<tr>
<td>H12</td>
<td>-0.209 (4)</td>
<td>0.071 (4)</td>
<td>0.020 (4)</td>
</tr>
</tbody>
</table>

Fig. 6. Starting (grey circles, thin lines) and final (black circles, thick lines) configurations of the imide group during the MC run II (a) and subsequent refinement (b) (general Cartesian frame).

Fig. 7. Variation of the $\chi^2$ value during the MC run II.

Fig. 8. Observed (crosses), calculated (solid line) after the refinement following MC run II and difference X-ray diffraction profiles of PEO$_3$:LiN(CF$_3$SO$_2$)$_2$. The insert shows a portion of the observed and calculated profiles on a magnified scale.
tomic distances between the fragments and within the flexible imide group had a beneficial effect on the minimization procedure helping to avoid false minima. The annealing scheme used during minimization in the course of the present study provided the solution of the relatively complex structure at relatively modest computational expense. Although designed specifically to manipulate a chain and an imide group, the underlying ideas of the geometrical formulation can be used as a basis for making a customized description of any other molecular fragment. Thus, more recently the approach described was successfully used for the structure determination of β-oxynaphthoic acid (Andreev, 1996) and PEO:NaSO$_3$CF$_3$ complex (Andreev, MacGlashan & Bruce, 1996). Some work towards extending the method for the solution of framework structures is already underway. Although at present each new structure-determination task requires certain programming efforts, it is not impossible to create a versatile user-friendly code by designing an interactive intelligent graphical interface capable of handling various types of constituent fragments in the structure to be solved.

The financial support of this work by the EPSRC and the Leverhulme Trust is gratefully acknowledged. The authors are also indebted to Dr Mark C. Wićcik from the University of Uppsala for his help in elaboration of the mathematical procedure given in Appendix B.

**Appendix A**

**Stereochemical description of the moieties in local Cartesian frames**

**A1. Poly(ethylene oxide) chain consisting of $N$ non-H atoms**

The origin of the frame is fixed on the $(N - 1)$th (C7 in this case) atom; the $X$ axis lies along the bond between the $(N - 1)$th and $(N - 2)$th (O7) atoms; the $Y$ axis is perpendicular to the $X$ axis and lies within an obtuse angle $\phi_{N-2,N-1,N}$; and the $Z$ axis completes a right-handed orthogonal set (see Fig. 1a).

Coordinates of the atoms closest to the origin are as follows:

$$
\begin{bmatrix}
  x'_N \\
  y'_N \\
  z'_N
\end{bmatrix} = \begin{bmatrix}
  -l_{N-1,N} \sin(\phi_{N-2,N-1,N} - \pi/2) \\
  l_{N-1,N} \cos(\phi_{N-2,N-1,N} - \pi/2) \\
  0
\end{bmatrix},
$$

$$
\begin{bmatrix}
  x'_{N-1} \\
  y'_{N-1} \\
  z'_{N-1}
\end{bmatrix} = \begin{bmatrix}
  0 \\
  y'_{N-2} \\
  z'_{N-2}
\end{bmatrix} = \begin{bmatrix}
  l_{N-2,N-1} \\
  0 \\
  0
\end{bmatrix},
$$

where $l_{i,j}$ and $\phi_{i,j,k}$ are bond lengths and angles formed by the $i$th, $j$th and $k$th atoms.

Coordinates of each $m$th ($m = 1, N - 3$) atom $x'_m, y'_m, z'_m$ are computed using the approach put forward by Arnott & Wonacott (1966)

$$
\begin{bmatrix}
  x'_m \\
  y'_m \\
  z'_m
\end{bmatrix} = \sum_{i=m}^{N-3} \left( \prod_{j=N-3-i}^{N-2} [A^j] \right) \begin{bmatrix}
  l_{i+1} \\
  0 \\
  0
\end{bmatrix} + \begin{bmatrix}
  l_{N-2,N-1} \\
  0 \\
  0
\end{bmatrix}.
$$

Elements of the rotational matrices $[A^j]$ are defined by

$$
[A^j] = \begin{bmatrix}
  -\cos \varphi^j & -\sin \varphi^j & 0 \\
  \sin \varphi^j \cos \tau^j & -\cos \varphi^j \cos \tau^j & \sin \tau^j \\
  -\sin \varphi^j \sin \tau^j & \cos \varphi^j \sin \tau^j & \cos \tau^j
\end{bmatrix},
$$

where $\tau_{j+1,j+2,j+3}$ denotes the torsion angle formed by the atoms whose numbers are listed in the subscript.

**A2. Imide**

The origin of the frame is fixed on the C1 atom; the $X$ axis lies along the bond between the C1 and S1 atoms; the $Y$ axis is perpendicular to the $X$ axis and lies within an obtuse angle $\varphi_{F1-C1-S1}$; and the $Z$ axis completes a right-handed orthogonal set (see Fig. 1b).

Similar to the chain case coordinates of the atoms closes to the origin are the following:

$$
\begin{bmatrix}
  x'_{F1} \\
  y'_{F1} \\
  z'_{F1}
\end{bmatrix} = \begin{bmatrix}
  -l_{C1-F1} \sin(\varphi_{F1-C1-S1} - \pi/2) \\
  l_{C1-F1} \cos(\varphi_{F1-C1-S1} - \pi/2) \\
  0
\end{bmatrix},
$$

$$
\begin{bmatrix}
  x'_{C1} \\
  y'_{C1} \\
  z'_{C1}
\end{bmatrix} = \begin{bmatrix}
  0 \\
  y'_{S1} \\
  z'_{S1}
\end{bmatrix} = \begin{bmatrix}
  l_{C1-S1} \\
  0 \\
  0
\end{bmatrix}.
$$
Coordinates of the F2 and F3 atoms are determined via rotation from their imaginary positions in the S1–C1–F1 plane around the S1–C1 bond making use of the $[\rho]$ rotational matrix (International Tables for X-ray Crystallography, 1959):

\[
\begin{bmatrix}
X'_{F2} \\
Y'_{F2} \\
Z'_{F2}
\end{bmatrix} = 
\begin{bmatrix}
-l_{C1-F2} \sin (\phi_{S1-C1-F2} - \pi/2) & l_{C1-F2} \cos (\phi_{S1-C1-F2} - \pi/2) \\
\end{bmatrix} \cdot \begin{bmatrix}
\rho_{F2}
\end{bmatrix},
\]

(8)

\[
\begin{bmatrix}
X'_{F3} \\
Y'_{F3} \\
Z'_{F3}
\end{bmatrix} = 
\begin{bmatrix}
-l_{C1-F3} \sin (\phi_{S1-C1-F3} - \pi/2) & l_{C1-F3} \cos (\phi_{S1-C1-F3} - \pi/2) \\
\end{bmatrix} \cdot \begin{bmatrix}
\rho_{F3}
\end{bmatrix},
\]

(9)

\[
\begin{bmatrix}
\rho_{F2(F3)}
\end{bmatrix} = 
\begin{bmatrix}
\cos \alpha_{F2(F3)} + l^2_{1}(1 - \cos \alpha_{F2(F3)}) \\
l_{1}l_{2}(1 - \cos \alpha_{F2(F3)}) - l_{3} \sin \alpha_{F2(F3)} \\
l_{2}l_{3}(1 - \cos \alpha_{F2(F3)}) - l_{1} \sin \alpha_{F2(F3)}
\end{bmatrix}.
\]

(10)

where $l_1$, $l_2$, $l_3$ are the Cartesian direction cosines of the rotation axis (S1–C1 bond in this case). The value of the rotation angle $\alpha_{F2}$ ($\alpha_{F3}$ is calculated in a similar fashion) is given by

\[
\alpha_{F2} = 2 \arcsin \left\{ r/[2l_{C1-F2} \sin (\pi - \phi_{S1-C1-F2})] \right\},
\]

where $r$ is the distance between the actual and imaginary positions of the F2 atom which in turn is calculated as follows:

If $l_{C1-F2} \sin \phi_{S1-C1-F2} \geq l_{C1-F1} \sin \phi_{S1-C1-F1}$ then

\[
r = \left( r_1^2 - r_2^2 - r_3^2 - r_4^2 - r_5^2 / r_4 \right)^{1/2},
\]

(12a)

else

\[
r = \left[ (r_1 r_2^2 / r_4 - r_3 r_4) / (2 + r_1 / r_4) \right]^{1/2},
\]

(12b)

where

\[
\begin{align*}
l_1 &= 2l_{C1-F2} \sin \phi_{S1-C1-F2}, \\
\end{align*}
\]

(13)

\[
\begin{align*}
l_2 &= (l_{C1-F2}^2 - r_3^2)^{1/2}, \\
\end{align*}
\]

(14)

\[
\begin{align*}
l_3 &= r_1 - r_4, \\
\end{align*}
\]

(15)

\[
\begin{align*}
l_4 &= [2l_{C1-F2} + l_{C1-F1}^2 - 2l_{C1-F1} l_{C1-F2} \\
& \times \cos (\phi_{S1-C1-F1} - \phi_{S1-C1-F2}) - r_3^2]^{1/2}, \\
\end{align*}
\]

(16)

\[
\begin{align*}
l_5 &= l_{C1-F1} \cos \phi_{S1-C1-F1} - l_{C1-F2} \cos \phi_{S1-C1-F2}. \\
\end{align*}
\]

(17)

In the case of $\phi_{S1-C1-F1} = \phi_{S1-C1-F2} = \phi_{S-C-F}$ and $l_{C1-F1} = l_{C1-F2}$ (11) becomes simply

\[
\alpha_{F2} = 2 \arcsin \left\{ \sin (\phi_{F1-C1-F2}/2) / \sin \phi_{S-C-F} \right\}.
\]

(18)

The value of the rotation angle is positive if rotation is clockwise when viewed along the rotation axis towards the rotation centre.

Coordinates of the N, S2, C2 and F4 atoms are calculated using (5). In this case the sequence C1–S1–N–S2–C2–F4 is treated as a chain with atoms being numbered in a descending order.

Coordinates of the O1, O2, O3, O4, F5 and F6 atoms are computed in much the same way as those of the F2 and F3 atoms, namely via rotation from the corresponding imaginary positions in the C1–S1–N plane around the C1–S1 bond (O1 and O2 atoms), in the S2–C2–F4 plane around the S2–C2 bond (F5 and F6), and in the N–S2–C2 plane around the S2–C2 bond (O3 and O4). For the latter two pairs of atoms the fact that the rotation axis does not intercept the frame origin should also be taken into account. Thus, the coordinates of the F5 atom are given by

\[
\begin{align*}
[X'_{F5} Y'_{F5} Z'_{F5}] = & \left[ X_{F5} + X_{S2} - X_{S2} + Y_{S2} - Y_{F5} + Y_{C2} - Y_{S2} \\
& + X'_{F5} - Z_{F5} - Z_{S2} \right] \cdot \begin{bmatrix} \rho_{F5} \end{bmatrix} \\
& + \left[ X_{S2} Y_{S2} Z_{S2} \right],
\end{align*}
\]

(19)

where $X_{F5}, Y_{F5}, Z_{F5}$ denote the coordinates of the imaginary position of the F5 atom in the S2–C2–F4 plane. The latter values are calculated much like the $X'_{F4}, Y'_{F4}, Z'_{F4}$ coordinates with the difference that $l_{C2-F4}$ and $\phi_{S2-C2-F4}$ are replaced by $l_{C2-F5}$ and $\phi_{S2-C2-F5}$ correspondingly when using (5). In a similar manner the coordinates of the imaginary position of the O3 atom in the N–S2–C2 plane are calculated similarly to $X_{C2}, Y_{C2}, Z_{C2}$ with $l_{S2-C2}$ being substituted by $l_{S2-O3}$, and $\phi_{N-S2-C2}$ by $(\phi_{N-S2-C2} - \phi_{N-S2-O3})$.

Appendix B

Determination of the Eulerian angles

The problem is reduced to the solution of the following matrix equation which performs a transformation of coordinates of each $i$th atom from the general to a local Cartesian frame for the values of the Eulerian angles $\phi, \theta, \psi^*$:

\[
\begin{bmatrix} x_i' \\
y_i' \\
z_i'
\end{bmatrix} = [R_i] \cdot \begin{bmatrix} x_i \\
y_i \\
z_i
\end{bmatrix},
\]

(20)
Given a set of coordinates of three unit vectors (denoted with the superscript \( V \)) defined in both frames, (20) can be converted to

\[
[R_y] = \begin{bmatrix}
\cos \Psi \cos \Phi - \cos \Theta \sin \Psi & \cos \Psi \sin \Phi + \cos \Theta \cos \Phi \sin \Psi & \sin \Theta \sin \Psi \\
-\sin \Psi \cos \Phi - \cos \Theta \sin \Psi & -\sin \Psi \sin \Phi + \cos \Theta \cos \Phi \sin \Psi & \cos \Psi \sin \Theta \\
\sin \Theta \sin \Phi & -\sin \Theta \cos \Phi & \cos \Theta 
\end{bmatrix}. \tag{21}
\]

It is convenient to choose two unit vectors directed outwards from the atom placed in the centre of the local frame along two bonds to the nearest neighbouring atoms with the third one being their vector product.

After solving (22) for the \( R_y \) values [routine GAUSSJ given by Press et al. (1992) is an appropriate algorithm for this purpose], values of the Eulerian angles can be readily calculated as follows:

\[
\Theta = \arccos (R_{33}), \quad \Phi = \arcsin [R_{31}/(1 - R_{33}^2)^{1/2}], \quad \Psi = \arcsin [R_{13}/(1 - R_{33}^2)^{1/2}]. \tag{23}
\]

Since (23) give values only in certain angular regions, the true angles can be obtained by taking into account simultaneously the signs of both \( \sin \) and \( \cos \) functions of \( \Theta, \Phi \) and \( \Psi \) and specific features of the compiler used while making the computer code. Thus, after determining the signs of

\[
\cos \Phi = -R_{32}/(1 - R_{33}^2)^{1/2}, \quad \cos \Psi = R_{23}/(1 - R_{33}^2)^{1/2},
\]

the values of \( \Phi \) and \( \Psi \) (denoted below as \( \Omega \)) can be modified implying the following rules:

\[
\Omega = \pi - \Omega \text{ if } \sin \Omega > 0 \text{ and } \cos \Omega < 0 \text{ or }
\]
\[
\Omega = 2\pi + \Omega \text{ if } \sin \Omega < 0 \text{ and } \cos \Omega < 0;
\]

\[
\Omega = 2\pi + \Omega \text{ if } \sin \Omega < 0 \text{ and } \cos \Omega > 0.
\]

**References**


* Following the \( x \)-convention (Goldstein, 1980).


