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Refinement of the Orientational Distribution Function in Plastic *n*-Butane Guided by Computer Simulations

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Abstract

Neutron powder diffraction data for the plastic crystalline phase of *n*-butane are refined with a model suggested from molecular dynamics (MD) computer simulation work. A small decrease in the *R* factor is achieved, corresponding to a reduction of the discrepancy between fit and experiment of about 30%. This supports the MD result that the orientational distribution function (ODF) describing the disorder is an asymmetric sum of four angular Gaussian distributions, one of which is dominant. The orientational disorder is uniaxial about the axis between the end C atoms of a molecule. Refinement of the four-Gaussian function is stable, and results in a distribution closely related to that obtained from the MD work. It is suggested that the ODF is temperature dependent, and that this dependence could be found by a further series of high-quality experiments.

Introduction

Although *n*-butane ($CH_3CH_2CH_2CH_3$) is a very simple well known molecule, its crystal structures were not successfully studied until recently. Our analysis of neutron powder diffraction data obtained with perdeuterobutane yielded the structures of three phases (Refson & Pawley, 1986; paper I). The phase below the melt, phase I, is a plastic crystal phase showing orientational disorder about a unique axis, and it is this phase which is now the subject of further analysis. The other phases which occur on cooling are a metastable phase II followed by a stable truly crystalline structure, phase III, which persists to very low temperatures.

A considerable body of information from model calculations has been built up since the work of paper I concerning the possible nature of the disorder in the plastic phase. The aim of the present work is to examine whether there is any experimental evidence to confirm the results from the model, and whether there is enough information in the experimental results to justify further structure refinements guided by the model.

Our work on *n*-butane started with computer simulations of the condensed phases using molecular dynamics (MD). The MD model consisted of 2048 molecules in a volume with periodic boundary conditions, each molecule interacting with its neighbours through atom-atom potentials between all its C and D atoms. Three torsional internal degrees of freedom were included, though it was found later that the two methyl-group torsions had no effect on the cooperative dynamics and could have been omitted. Simulations were performed before any of the true structures were determined in the hope that the structures found by MD would be as in nature and thus of great help in the crystallographic determination (Refson & Pawley, 1987*a*; paper II).

The model predicted three phases as found in nature, but with incorrect structures. Consequently the determination of the natural structures and their refinements, paper I, was done without the aid of MD simulations. The structures so found have since been used as the start for further simulations which have proved the model to be good (Refson & Pawley, 1987*b*; paper III). The results from the simulation

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are now to be used in an attempt to improve the fit of the data of paper I.

The first refinements

All the three phases of *n*-butane form in the space group $P2_1/c$ with $Z = 2$. In the plastic phase there is orientational disorder about a unique axis, the axis joining the two extreme C atoms. We therefore describe the disorder in terms of an orientational distribution function (ODF) which is a function, $P(\zeta)$, of ζ, the rotational angle for the molecule about the unique axis from a zero as defined in paper I.

The first ODF attempted was simply the placement of a small number of molecules at individual ζ values which were refinable along with occupancy parameters. With no guidance as to where to place the molecules we could not obtain a satisfactory fit, but it was clear that about 50% of all molecules occupied one main peak of the ODF.

Subsequent ODF fits were done with $P(\zeta)$ defined at 32 equally spaced angles. This spacing was found to be fine enough for the representation of any continuous function for $P(\zeta)$. Two functions were used for the fit, one being a constant plus a single Gaussian peak, the other being a sum of cosine functions. The best fit with a five-peak cosine sum is shown in Fig. 3(*c*), which is described in context later. All these functions for $P(\zeta)$ were symmetrical in ζ about the central peak, a simplifying assumption made solely out of expediency.

The present work goes beyond the assumption of a symmetric $P(\zeta)$, and is prompted by the MD simulations subsequent to the result of paper I.

The MD simulation result

The model used for the simulation has been briefly described above; full details are available in paper III. The result of particular interest is the simulation ODF. The orientational disorder can be appreciated from a plane of the MD cell. Each molecule is represented by a diagram such as Fig. 1, where the methyl groups are the large filled circles and the irregular tetrahedra have vertices at the end two C atoms and the corresponding methylene H atoms. Fig. 2 shows the molecular arrangement in a MD (010) plane, and although the disorder is most apparent it is easy to see that there is an ordering of the unique axes of the molecules parallel to the unique axis of the molecule in Fig. 1. All the molecules in this plane are related by lattice translational symmetry, whereas molecules in the neighbouring planes are related to those shown here by the monoclinic screw axis and have their unique molecular axes roughly at right angles, but appear parallel in projection.

The ODF is found to develop as a function of time during the MD phase transition from phase II, and Fig. 3(*a*) shows the ODF when stability is reached. The simulation is at 125 K and zero pressure. It is quite clear that at this temperature the simulated ODF has four peaks, a central peak with about 50% occupancy, and three other peaks which are not symmetrical about the main peak. A close fit to this ODF can be found as a sum of four Gaussians, all with the same width. The best fit is shown in Fig. 3(*b*), giving $P(\zeta)$ as a function of nine variables, the four ζ values, the four occupancies and the Gaussian width.

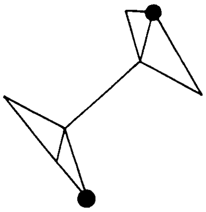

Fig. 1. Diagrammatic representation of an *n*-butane molecule. The methyl groups are the large filled circles and the irregular tetrahedra have vertices at the end two C atoms and the corresponding methylene H atoms.

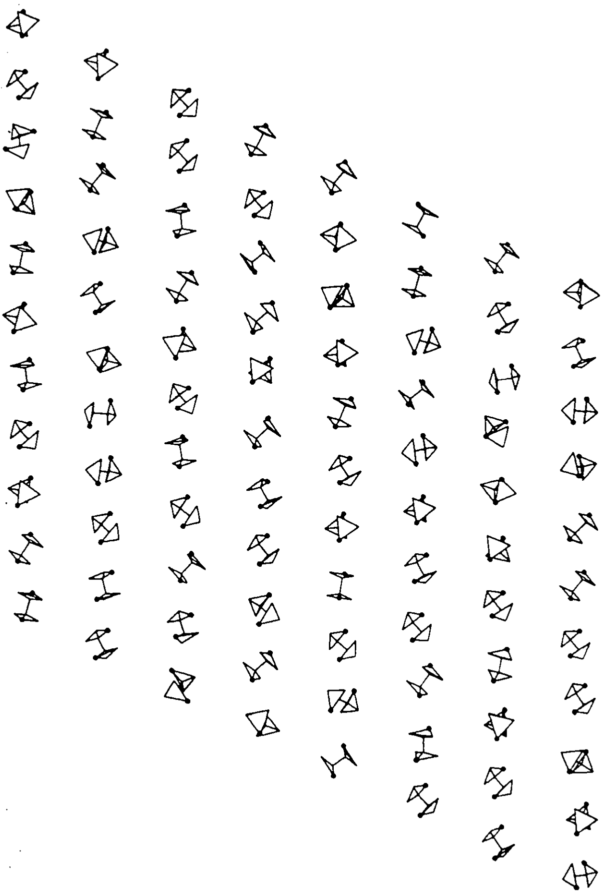

Fig. 2. The molecular arrrangement in a single (010) MD plane. All the molecules in this plane have a common direction for the unique axis. Molecules in the neighbouring planes are related to those shown here by the monoclinic screw axis and have their unique axes roughly at right angles (though parallel in projection).

The new refinement

The new refinement concerns only the neutron powder diffraction data taken at 120 K. The *EDINP* program (Pawley, 1980) as used in paper I was further modified to include the nine parameters (ζ_i, p_i and σ of Table 1) governing the ODF of Fig. 3(*b*). We argue that the MD simulation suggests where the peaks of $P(\zeta)$ are most likely to be, but the nine parameters should be refined because there is most likely to be a temperature variation in the ODF and the correspondence between experiment and simulation may not therefore be sufficiently close.

The model ODF required a rotation of about 4° in ζ for its maximum value to correspond with the maximum of the five-peak cosine sum $P(\zeta)$. This then gave the starting values for the new refinement.

The nine parameters were added to the refinement, and their combined effect is such that the overall scale factor and the axis rotation angle of paper I are both redundant. Inclusion of these latter two parameters would lead to a singular least-squares matrix. All the other parameters for the fit were taken from the five-peak cosine sum result. The deviation between the model ODF and the best-fit five-peak function is shown in Fig. 3(*c*), and it is clear that the differences are small. Nevertheless we believe from our argument in paper I that there is still some information contained in the scan that has not yet been fitted. The five-peak function fits with an *R* factor of 3·0% whereas the fit of individual peak intensity parameters using *ALLHKL* (Pawley, 1981) yields a minimum attainable *R* factor of 2·7%.

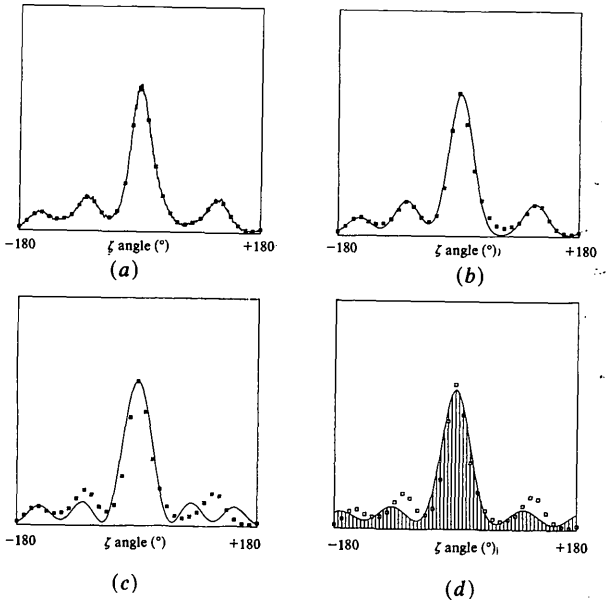

Fig. 3. (*a*) The simulation ODF. The filled squares are averages over 11·25°. The central maximum is placed at the $\zeta = 0$ value found for the maximum in paper I; this necessitated a ζ rotation of about 4°. The area under the curves for this figure and those of parts (*b*)–(*d*) are identically normalized. ζ varies from −180 to +180° in all these figures. (*b*) The best four-Gaussian fit to (*a*). This is the starting ODF for the refinement. (*c*) The best five-peak cosine-sum fit from paper I, compared with the ODF from the MD simulation. (*d*) The final refined ODF showing the change from the MD ODF.

The course of the five refinement cycles required to achieve a best fit is given in Table 1. The full details are given to indicate the stability of the result. A comparison of the final fitted ODF with the model ODF is shown in Fig. 3(*d*). The asymmetry is retained in the fitted ODF, and this has slightly wider Gaussian functions. The three subsidiary peaks have moved in the refinement and now account for about 30% of the molecules. The main peak has remained centrally placed as expected at the position of the maximum of the five-peak cosine ODF.

The number of refined parameters, at 24, is four more than used in the five-peak cosine-sum fit. Thus there are 13 structural parameters (the last 14 of Table 1 less one for an overall scale parameter) to be determined by a diffraction scan with 28 resolved peaks. It is not possible to make a reliable statistical test but it is thought significant that the model ODF has led to a fit even closer to the ultimate 2·7% than the best symmetrical $P(\zeta)$ model.

The values of ζ in Table 1 along with the crystallographic information in paper I should be sufficient to allow the reader to generate the disordered structure. As a precaution we present in Table 2 the orthogonal atomic coordinates for the C atoms for four molecules, representative of the four peaks in Fig. 3(*d*). The D positions follow from these using the constraint conditions. The errors quoted in Table 1 are as given directly from the least-squares fit, and may be overestimates by about a factor of four.

Concluding remarks

The new refinement has reduced the discrepancy between fit and experiment by about 30%, although this is not reflected in a large change in the *R* factor. This assessment makes use of the 'best possible fit' as found using *ALLHKL* (Pawley, 1981) and could be the basis of a more formal method of estimating statistical significance in powder diffraction refinements. In asserting that the result is a significant improvement we argue that the stability of the refinement, as shown in Table 1, is strongly supportive.

This work is possibly the first example where MD simulations have produced a model which is then used as the basis for structure refinement. The simulation predicted an asymmetric orientational distribution function with four most-probable orientations about the unique molecular axis. The refinements support this model, but show a slightly wider Gaussian distribution at each orientation, and a greater concentration in the major peak. A temperature variation of the ODF is certainly to be expected, most probably giving a further widening of the

Table 1. *The course of the five refinement cycles, showing all the parameters refined*

The error is as given by the standard least-squares procedure, as in paper I. The probabilities p_i correspond to the orientational peaks at ζ_i.

Parameter		Before cycle					
		1	2	3	4	5	Error
Flat background		150·00	150·37	150·28	150·27	150·27	0·21
Scan zero shift (°)		−0·067	−0·072	−0·072	−0·072	−0·072	0·006
Peak-shape parameters	u	0·198	0·201	0·195	0·196	0·196	0·009
	v	−0·490	−0·492	−0·484	−0·485	−0·486	0·016
	w	0·418	0·418	0·414	0·415	0·415	0·008
Skewness		0·179	0·189	0·188	0·188	0·189	0·012
Unit-cell edges (Å)	a	5·6928	5·6931	5·6931	5·6931	5·6931	0·0003
	b	5·5080	5·5082	5·5082	5·5082	5·5082	0·0003
	c	8·3616	8·3616	8·3617	8·3617	8·3617	0·0005
Cell angle (°)	β	115·291	115·296	115·296	115·296	115·296	0·0015
Overall B (Å^2)		4·40	4·30	4·35	4·36	4·36	0·07
Euler angles (°)	ψ	−144·867	−144·867	−144·821	−144·832	−144·826	0·8
	θ	76·501	75·688	76·507	76·564	76·564	11·5
	φ	139·412	139·624	139·355	139·343	139·343	3·4
CH_3 tetrahedral (°)		109·177	109·183	109·143	109·148	109·148	0·076
ζ_1 (°)		2·3	0·8	0·2	0·2	0·2	11·9
ζ_2 (°)		114·0	110·2	99·8	100·3	100·4	12·1
ζ_3 (°)		−148·5	−165·2	−173·4	−171·9	−171·8	12·1
ζ_4 (°)		−77·8	−88·3	−98·2	−95·2	−95·0	12·0
p_1		0·767	0·712	0·746	0·748	0·749	0·007
p_2		0·178	0·092	0·103	0·105	0·105	0·003
p_3		0·097	0·077	0·089	0·090	0·090	0·003
p_4		0·192	0·087	0·119	0·119	0·119	0·004
Gaussian σ		1·62	1·99	1·92	1·91	1·91	0·02
R(%)		3·8	4·1	3·0	2·9	2·9	

Gaussian function and change of occupancy of the minor orientations on heating. As a result of this work we intend to study the MD model ODF as a function of temperature.

The success of the refinement suggests that it would be worth measuring the powder diffraction scan at a number of temperatures within the plastic crystal range from 108 to 135 K, in order to determine the variation of the ODF. Plastic crystal structures have been much neglected by crystallographers, but our result suggests that detailed progress is possible with the high-quality powder diffraction measurements that can now be made.

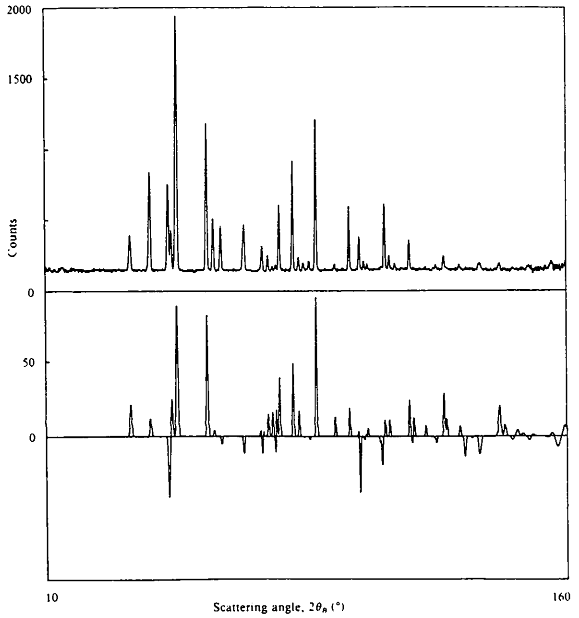

Fig. 4. The upper part is the observed scan from $2\theta = 10$ to 160°. The lower part is the difference between two calculated scans differing only by the nine ODF parameters, scaled by a factor of ten with respect to the observed scan; the scan for the final refined ODF is subtracted from that for the MD ODF.

Table 2. *Orthogonal positions for the C atoms of molecules near the peak positions of Fig.* 3(*d*)

The definition of ζ is given in paper I.

ζ (°)	x	y	z
0·00	0·5475	0·3291	−0·4290
	1·3842	1·3148	0·4059
101·25	−0·0795	0·7591	0·0982
	1·2542	1·4039	0·5152
−168·75	0·1957	0·2376	0·7053
	1·3113	1·2958	0·6410
−90·00	0·7103	−0·1153	0·2726
	1·4179	1·2227	0·5513

To maximize the value of experiments it is worth knowing what part of the scan profile is the most important. This is shown in Fig. 4 where the difference between the calculated scan using the MD ODF and that found as the result of refinement is presented. Only the nine ODF parameters differ in the two calculated scans, and the intensity difference has been scaled by a factor of ten for comparison with the measured scan, the upper part of Fig. 4. It is clearly necessary to include the full range of the original measurements in any future work.

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SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

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Calculation of structure factors from molecular models with anisotropic atoms.

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Abstract

The mathematical basis and test results are presented for an efficient method of calculation of structure factors from large molecular models with anisotropic atoms.

The development of area detectors and synchrotron sources for X-rays has led to a significant improvement in both the quality and resolution of observed data from crystalline macromolecules. The existence of data to a resolution of 1·5 Å may ultimately permit the refinement of some protein structures using anisotropic thermal parameters, provided these parameters are subject to restraints in the least-squares refinement (Hendrickson & Konnert, 1980). Essential to any refinement routine is an efficient method for the generation of structure factors. Ten Eyck (1977) presented an efficient approach to the calculation of structure factors for isotropic atoms, which requires the generation of a model electron density map followed by Fourier inversion of the map. We present here the mathematics and trial results of an approach analogous to Ten Eyck's but using anisotropic atoms. We find that Ten Eyck's two-step process produces structure factors of high accuracy to a resolution of at least 1·0 Å.

Ten Eyck, based on earlier work of Vand, Eiland & Pepinsky (1957), gave a suitable analytical approximation to the form factor

$$f(s)=C_1\exp[-\tfrac{1}{4}D_1s^2]+C_2\exp[-\tfrac{1}{4}D_2s^2]+C_3. \quad (1)$$

Numerical values for C_1, D_1, C_2, D_2 and C_3 derive from a least-squares fit of (1) to values of $f(s)$ calculated from first principles. The quantity s is the length of the reciprocal-lattice vector associated with the indices h, k, l:

$$s^2=h^2a^{*2}+k^2b^{*2}+l^2c^{*2}2hka^*b^*\cos\gamma^*$$
$$+2hla^*c^*\cos\beta^*+2klb^*c^*\cos\alpha^*.$$

We define the anisotropic temperature factor as $\exp[-\frac{1}{4}\sum_{i=1}^3\sum_{j=1}^3 B^{ij}s_is_j]$, where the B^{ij} are the standard doubly contravariant components of an anisotropic thermal tensor and the s_i are the components of the reciprocal-lattice vector $\mathbf{s}$. Explictly, $s_1=ha^*$, $s_2=kb^*$ and $s_3=lc^*$. Multiplication of (1) by the anisotropic temperature factor gives

$$\begin{aligned}
f(s)\exp&\left(-\tfrac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B^{ij}s_is_j\right)\\
&=C_1\exp\left[-\tfrac{1}{4}\left(D_1s^2+\sum_{i=1}^{3}\sum_{j=1}^{3}B^{ij}s_is_j\right)\right]\\
&\quad+C_2\exp\left[-\tfrac{1}{4}\left(D_2s^2+\sum_{i=1}^{3}\sum_{j=1}^{3}B^{ij}s_is_j\right)\right]\\
&\quad+C_3\exp\left(-\tfrac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B^{ij}s_is_j\right). \qquad (2)
\end{aligned}$$

Ten Eyck demonstrated the reduction of error in calculating structure factors by inflating the isotropic thermal parameters of all atoms by a constant value. The appropriate form for the inflation factor is $\exp[-\frac{1}{4}Bs^2]$, where B is an arbitrary constant. Multiplication of (2) by the inflation factor gives

$$\begin{aligned}
f(s)\exp&\left(-\tfrac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B^{ij}s_is_j\right)\exp(-\tfrac{1}{4}Bs^2)\\
&=C_1\exp\left[-\tfrac{1}{4}\left(D_1s^2+Bs^2+\sum_{i=1}^{3}\sum_{j=1}^{3}B^{ij}s_is_j\right)\right]\\
&\quad+C_2\exp\left[-\tfrac{1}{4}\left(D_2s^2+Bs^2+\sum_{i=1}^{3}\sum_{j=1}^{3}B^{ij}s_is_j\right)\right]\\
&\quad+C_3\exp\left[-\tfrac{1}{4}\left(Bs^2+\sum_{i=1}^{3}\sum_{j=1}^{3}B^{ij}s_is_j\right)\right]. \qquad (3)
\end{aligned}$$

Using the definitions above for s_i and s^2 in the exponent of the first term of the right-hand side of (3), we have, after collecting common terms,

$$\begin{aligned}
D_1s^2&+Bs^2+\sum_{i=1}^{3}\sum_{j=1}^{3}B^{ij}s_is_j\\
&=(B^{11}+B+D_1)a^{*2}h^2\\
&\quad+(B^{22}+B+D_1)b^{*2}k^2+(B^{33}+B+D_1)c^{*2}l^2\\
&\quad+2[B^{12}+(B+D_1)\cos\gamma^*]a^*b^*hk\\
&\quad+2[B^{13}+(B+D_1)\cos\beta^*]a^*c^*hl\\
&\quad+2[B^{23}+(B+D_1)\cos\alpha^*]b^*c^*kl.
\end{aligned}$$

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