

The Structure and Orientational Disorder in Solid *n*-Butane by Neutron Powder Diffraction

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Abstract

The structure of deuterated *n*-butane (C_4H_{10}), $M_r = 68$, has been determined in its three crystalline forms by neutron powder diffraction with $\lambda = 2.980 \text{ \AA}$. All three have two molecules in the unit cell and space group $P2_1/c$. The stable phase III at 5 K has unit cell $a = 4.110(1)$, $b = 7.621(2)$, $c = 8.097(2) \text{ \AA}$, $\beta = 118.603(6)^\circ$, $V = 222.7(2) \text{ \AA}^3$ ($R = 4.3\%$) and at 90 K $4.1463(6)$, $7.629(1)$, $8.169(1) \text{ \AA}$, $118.656(4)^\circ$, $226.7(1) \text{ \AA}^3$ ($R = 3.6\%$). The corresponding values for the metastable form II at 65 K and the disordered phase I at 120 K are $5.708(1)$, $5.174(1)$, $7.870(2) \text{ \AA}$, $105.98(1)^\circ$, $223.5(2) \text{ \AA}^3$ ($R = 4.2\%$) and $5.693(1)$, $5.508(1)$, $8.361(2) \text{ \AA}$, $115.294(5)^\circ$, $237.0(2) \text{ \AA}^3$ ($R = 3.0\%$). Constrained profile refinement with *EDINP* is used throughout and yields bond angles in phase III at 5 K of $CCC = 111.0(7)$, $HCH = 106.5(8)$ and $107.5(6)^\circ$. All molecules are in the *trans* state. The C-H bond length (uncorrected) is $1.087(7) \text{ \AA}$. The packing in form III is such that the long axes of symmetry-related molecules are approximately parallel whereas in both forms II and I they are at nearly 90° to each other. In phase I the molecules are disordered by rotation about an axis which passes within 4° of the line joining the outermost carbon atoms. Different forms of the probability distribution around this axis are compared. The main features are a single broad peak with full-width half-height of 38° and a non-zero occupancy at all angles.

Introduction

n-Butane exists in three distinct crystalline forms. There is a first-order phase transition at 108 K with a large latent heat (Aston & Messerly, 1940). Below the transition there are two possible structures which may co-exist (II and III will be used to denote the metastable and stable ones respectively). Phase I which exists at temperatures above the transition is disordered.

Orientational disorder in molecular crystals is a subject of current interest. Long-chain hydrocarbons such as $C_{33}H_{68}$ (Ewen & Strobl, 1980) show 180° reorientational jumps around their long axis, often coupled with a translation, which are associated with a phase transition. Smaller molecules with a high symmetry, e.g. CBr_4 or SF_6 (Dolling, Powell & Sears,

1979) on the other hand show a high degree of disorder and have no particular rotation axis. *n*-Butane (C_4H_{10}) is intermediate between these extremes as it has a low symmetry but is only four units long. It is of particular interest to compare the structure with 1,2-dichloroethane which has the same molecular symmetry and shape as *n*-butane. It exists in a low-temperature ordered phase and a high-temperature form in which the molecules become disordered about the Cl-Cl axis (Milberg & Lipscomb, 1951). However, the specific heat does not have an anomaly at a 'transition temperature' but merely a finite rounded maximum (Pitzer, 1940). Thus, in contrast to butane, it does not have a phase transition.

The disordered phase of butane has been previously studied by NMR. Hoch (1976) found a considerable decrease in the proton second moment in phase I as compared with III. This was fitted by a model in which the molecules make 180° reorientations. However, other models were not tested and might have fitted the data equally well.

The first-order nature of the transition is likely to make it difficult to obtain a single crystal of the low-temperature phases, as a crystal of phase I would probably become polycrystalline during the transition to phase III. Powder diffraction was therefore used to solve all three phases. Neutrons were used in preference to X-rays in order to give as much information as possible on the positions of the hydrogen atoms.

Experimental

The experimental sample of deuterated *n*-butane was obtained from Cambrian Gases and was specified as 98% isotopic purity. It was liquefied in a refrigerator and solidified by pouring the liquid into a mortar in a bath of liquid nitrogen in a dry atmosphere. It was ground to a fine powder and put into a vanadium canister. During this process it was contaminated by nitrogen, whose presence was clearly seen in the data. Temperature was controlled in a helium cryostat and was stable to 0.1 K but because the sensor was not in contact with the sample itself the absolute value could have been up to 3 K higher.

According to Cangeloni & Schettino (1975) the metastable low-temperature phase (II) may be pro-

duced by rapid cooling to 77 K from the plastic phase (I). A further transition to the stable phase (III) occurs if the sample is maintained between 85 and 90 K. To obtain a pure specimen of phase III our sample was left at 90 K for 48 h, which was certainly excessive. It was later heated to 120 K and quenched in liquid nitrogen to produce phase II.

The neutron powder diffraction was done using the D1A powder diffractometer at the Institut Laue-Langevin at Grenoble (Hewat & Bailey, 1976). Data were collected at 5 and 90 K in phase III, 65 K in phase II and 120 K in phase I. The suspected contamination with nitrogen was taken into account when choosing temperatures at which measurements were to be made since the extra nitrogen Debye-Scherrer peaks make analysis more difficult. The temperature is especially important for phase II as annealing to phase III takes place above 85 K but the nitrogen is crystalline below 63.9 K. Because of the possibility of annealing in phase II and of crystallite growth in phase I the data were monitored for any change with time. In both the 120 and the 65 K runs the output from counter 10 was compared with that from counter 1 and in both cases there was no change during the four hours which elapsed between the two counters scanning the same points. The sample was rotated by hand and further short runs taken at 120 K to test for preferred orientation effects. None were found. All the scans had a range of $2\theta = 6$ to 160° in steps of 0.05° using a wavelength of $2.980(2) \text{ \AA}$.

The presence of nitrogen was confirmed by comparing the 5 and 90 K scans of phase III. Extra peaks were present in the 5 K data at positions corresponding to those expected for the cubic α phase of nitrogen. In all the other scans there was a broad and featureless distribution of fairly low intensity scattering from about 40 to $70^\circ 2\theta$ from the liquid or dense gas.

All the scans were indexed using the Kohlbeck & Hoerl (1978) program. It is a tribute to the recent advances in indexing techniques that we had very little difficulty in this, while having no previous knowledge of the structures. The systematic absences showed that all three phases are monoclinic with space group $P2_1/c$.

Refinement

The data were analysed by the Rietveld profile fitting method using the program *EDINP* (Pawley, 1980). In order to assess the quality of the fit to the data, all the scans were first fitted by the program *ALLHKL* (Pawley, 1981). This is a modification of *EDINP* which refines the intensity of each peak as a separate variable as well as the unit cell, peak shape and background. The *R* factor thus obtained differs from that of *EDINP* only because it is not limited by the model structure and is thus the value which the best

possible fit of structural parameters would give with *EDINP*. The quality of fit was assessed by means of the *R* factor, defined as

$$R(\%) = 100 \sum |I^{\text{obs}} - I^{\text{calc}}| / \sum I^{\text{obs}}$$

The dimensions of the butane molecule in the gas phase have been determined by electron diffraction (Kuchitsu, 1961; Bonham & Bartell, 1959). One possible course of action would be to use this molecular geometry in a constrained refinement. However, since the forces experienced by a molecule are very different in the solid from the gas phase we chose to make certain of the molecular structural parameters variables of the refinement. In order to make maximum use of the low information content of the powder diffraction the technique of constrained refinement was used as implemented in the *EDINP* program. The constrained parameters for the molecule were the Euler angles for overall rotation, three bond angles, the methyl-group dihedral angle and the C-H bond length (see Fig. 1). The Euler angles are as defined by Goldstein (1959) with respect to a reference frame in which the inner two carbons lie on the *x* axis and the outermost two are at approximately $\pm(1.2, 1.4, 0)$ in units of \AA . It was found necessary to fix the C-C bond length at the known value of 1.539 \AA because of the high correlation between this and the other parameters. It is a reasonable assumption that bond lengths are less sensitive to the crystal environment and temperature than bond angles. The model molecule was set up in the centrosymmetric *trans* conformation as shown by Raman and infrared spectroscopy (Cangeloni & Schettino, 1975). Isotropic temperature factors expressed in the customary *B* units were used throughout, but to take account of the librational and internal modes the carbon and deuterium atoms had separately refined parameters. The peak-shape function used was the three-Gaussian form of Howard (1982) in which an

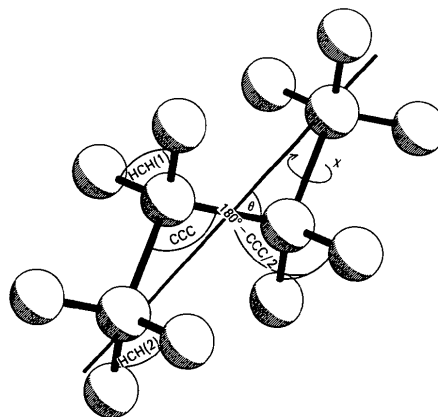


Fig. 1. *n*-Butane molecule with definitions of refined parameters. Also shown is the definition of the disorder axis for phase I.

Table 1. Peak-shape parameters from all refinements

	5 K (III)	90 K (III)	65 K (II)	120 K (I)
Overall scale	0.201 (6)	0.185 (4)	0.195 (4)	0.0072 (1)
Flat background	128 (2)	150 (1)	151 (2)	150.2 (7)
Scan zero angle (°)	-0.07 (3)	-0.07 (2)	-0.05 (3)	-0.07 (2)
<i>u</i>	0.32 (5)	0.22 (2)	0.29 (3)	0.20 (3)
<i>v</i>	-0.51 (8)	-0.51 (4)	-0.56 (6)	-0.49 (6)
<i>w</i>	0.43 (4)	0.42 (2)	0.46 (3)	0.42 (3)
Asymmetry, <i>P</i>	0.20 (6)	0.19 (4)	0.13 (7)	0.18 (4)

'asymmetry' parameter *P* is added to the usual three in order to account for the curvature of the Debye-Scherrer cones. Although the measured scan steps were 0.05° in 2θ the data sets were reduced to a step of 0.1° for the refinements without any apparent loss of definition.

Pawley (1980) has discussed the problem of standard errors in least-squares refinement. The usual error contains the factor $1/N^{1/2}$ which assumes that adjacent points in the scan are statistically independent. (*N* is the total number of points in the scan.) This is clearly not the case and consequently the errors quoted for structural parameters are calculated by replacing *N* by *N/n* where *n* is the average number of points in the full width at half height of a peak. The final refined values of the peak-shape parameters are listed in Table 1.

Scattering from the contaminant nitrogen was observed in all the data. In the 5 K scan extra Debye-Scherrer peaks were present with substantial intensity; the 111 at 54.4° reached over 1800 counts. Fortunately there was no significant overlap with the butane peaks and the contaminant peaks were given zero weight in the refinement. The extra scattering from the liquid in the higher-temperature scans was manifest as a very broad low-intensity rise in the background. In the case of phase I the background also included a contribution of diffuse scattering increasing with angle as is usual for disordered systems. A background function was evaluated by linear interpolation between the values at points distant from the butane peaks and subtracted from the data before fitting.*

Phase III

Refinement was started from an initial structure guessed from packing considerations. The space group and density indicated that the unit cell contained two molecules and it was assumed that the molecule's shortest dimension lay almost parallel to the rather small unit-cell length, *a*. This greatly

* The numbered intensity of each measured point on the profiles has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42808 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. The refined structural parameters in phase III

		5 K	90 K
Unit cell	<i>a</i> (Å)	4.110 (1)	4.1463 (6)
	<i>b</i> (Å)	7.621 (2)	7.629 (1)
	<i>c</i> (Å)	8.097 (2)	8.169 (1)
	β (°)	118.603 (6)	118.656 (4)
	Volume (Å ³)	222.7 (2)	226.7 (1)
Temperature factor	(C)	0.4 (6)	1.6 (4)
	(H)	1.1 (3)	1.7 (3)
Euler angles	φ (°)	-127.2 (5)	-126.7 (4)
	θ (°)	67.3 (3)	67.1 (3)
	ψ (°)	84.6 (2)	84.4 (2)
	CCC (°)	111.0 (7)	110.6 (5)
Bond angles	HCH(1) (°)	106.5 (8)	107.1 (6)
	HCH(2) (°)	107.5 (6)	107.2 (4)
	χ (°)	-1.7 (8)	-2.5 (5)
Dihedral angle			
C-H bond length (Å)		1.087 (7)	1.072 (6)
<i>R</i> factor (%) (EDINP/ALLHKL)		4.3/3.8	3.6/2.9

reduced the number of possible starting structures and convergence was easily obtained.

The final values of the refined parameters for the 5 and 90 K data are presented in Table 2. The parameters refined were the overall scale, peak shape and flat background, unit cell, temperature factors for C and D atoms and the molecular structure parameters. The value of *R* obtained from the 5 K fit was 4.3% compared with a best possible value from ALLHKL of 3.8%. For the 90 K data the values were 3.6% and 2.9% respectively. The 5K structure is presented in Fig. 2 and the atomic coordinates in Table 3.

Phase II

The starting structure used for the metastable phase refinement was that of 1,2-dichloroethane which was suggested by the similarity in unit cells and molecular structure. Initially all of the structural parameters were allowed to vary during refinement. The *R* factor decreased to 7.7% compared with 5.4% given by ALLHKL. This scan had the same number of points

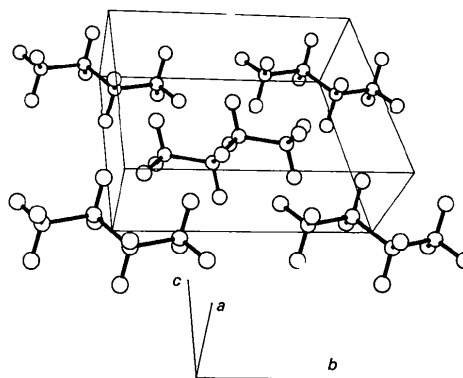


Fig. 2. Structure of phase III at 5 K.

Table 3. *Orthogonal atomic coordinates in all phases*

The other seven atoms are generated by inversion and the second molecule by the crystal symmetry. Units are Å.

(a) Phase III at 5 K

	x	y	z
C	0.1919	0.4856	-0.5652
C	-0.1112	1.9416	-0.1692
H	1.2484	0.3799	-0.7987
H	-0.3520	0.2296	-1.4710
H	0.1851	2.6351	-0.9522
H	-1.1724	2.0897	0.0142
H	0.4196	2.2247	0.7362

(b) Phase III at 90 K

	x	y	z
C	0.1943	0.4811	-0.5682
C	-0.1150	1.9366	-0.1751
H	1.2382	0.3793	-0.7881
H	-0.3427	0.2247	-1.4595
H	0.1884	2.6249	-0.9385
H	-1.1631	2.0870	-0.0103
H	0.3918	2.2185	0.7261

(c) Phase II at 65 K

	x	y	z
C	0.6147	-0.1091	0.4498
C	1.3748	1.2098	0.6760
H	0.3028	-0.5228	1.4054
H	1.2768	-0.8426	-0.0031
H	2.2276	1.0677	1.3350
H	1.7491	1.6169	-0.2598
H	0.7349	1.9635	1.1276

(d) Phase I at 120 K, $\zeta = 0$ orientation

	x	y	z
C	0.5448	0.3312	-0.4308
C	1.3854	1.3144	0.4029
H	1.1890	-0.4317	-0.8605
H	0.0864	0.8547	-1.2659
H	2.1474	1.7697	-0.2245
H	0.7445	2.0929	0.8088
H	1.8661	0.7844	1.2212

as the 90 K data, consequently the final value of R should not be very different. Closer inspection revealed that the discrepancy was due to about ten peaks which were anomalously broad, and whose shape could not be fitted by the usual peak-shape function. These were the $11\bar{1}$, $11\bar{2}$, $11\bar{3}$, $11\bar{4}$, $22\bar{0}$, $22\bar{1}$, $22\bar{2}$, $22\bar{3}$, 012 , 210 reflections and possibly also the 310 . The amount of broadening varied from around 20% wider than nearby peaks at $2\theta = 60^\circ$ to 100% at 130° . A striking example of this is shown in Fig. 3 where the peak-shape function fits the 202 reflection well but the $22\bar{1}$ very poorly. A further fit was done with zero weight assigned to these peaks, except for the $11\bar{1}$, 210 , $22\bar{0}$ and 310 which were not sufficiently broad to cause a serious error. Twenty one peaks remained, which proved sufficient to determine the structure. With this reduced set the molecule-shape parameters were not allowed to vary but were fixed at the values given by the 5 K refinement, apart from the methyl-group dihedral angle χ which was thought likely to be structure dependent. Despite this constraint the R factor decreased to 4.2% (*cf.* 3.6%

Table 4. *The refined structural parameters in phases II and I*

		65 K (II)	120 K (I)
Unit cell	a (Å)	5.708 (1)	5.693 (1)
	b (Å)	5.174 (1)	5.508 (1)
	c (Å)	7.870 (2)	8.361 (2)
	β (°)	105.98 (1)	115.294 (5)
Volume (Å ³)	223.5 (2)	237.0 (2)	
Temperature factor		1.8 (2)	4.4 (3)
Euler angles	φ (°)	83.4 (5)	-144.8 (2)
	θ (°)	36.0 (4)	76.5 (5)
	ψ (°)	-71.8 (6)	139.4 (2)
Bond angle	HCH(2) (°)	not refined	109.2 (2)
Dihedral angle	χ (°)	-1.7 (8)	not refined
Axis angle	θ (°)	n/a	51.3 (5)
R factor (%) (<i>EDINP/ALLHKL</i>)		4.2/3.6	3.0/2.7

ALLHKL) which is as good a fit as obtained from the 5 and 90 K scans. The final values of the unit cell and molecular orientation parameters are given in Table 4 and the structure in Fig. 4.

On comparing the calculated and observed scans, it was apparent that the anomalous peaks were not only broadened but were also smaller in such a way that the integrated scattering intensity agreed closely with the calculated value (see Fig. 3). This broadening is characteristic of anisotropic thermal diffuse scattering and it is tempting to speculate that it may be an effect of some process of reordering to the stable phase III, but unfortunately crystallographic structural studies can never be conclusive about dynamical phenomena.

Phase I

The scattering function may be written as the sum of two terms, a coherent (Bragg) term and a diffuse term. In a disordered crystal the second term is often large

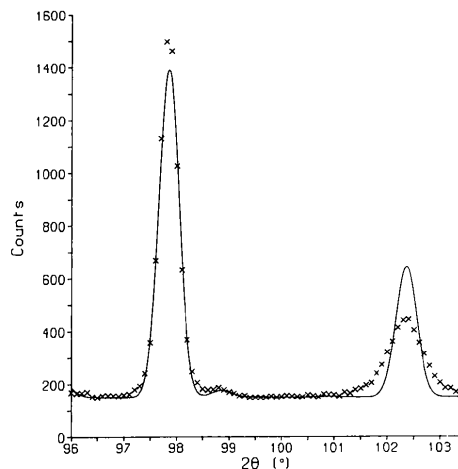


Fig. 3. A section of the phase II data comparing the broadened $22\bar{1}$ peak with the 202 . The crosses are the measured intensities and the continuous line is calculated from the final fit of Table 4.

and only varies slowly with scattering angle. Diffuse scattering was observed as part of the background in phase I of butane and is shown in Fig. 7(d). This background was subtracted from the observed data before fitting and in what follows only Bragg scattering is considered.

The solution of the plastic phase structure involved a number of new features and required a less straightforward method than sufficed for the others. Whereas in the ordered phases the orientational probability distribution of the molecules is a δ function this is certainly not true in phase I. There are two extreme possibilities in the nature of the disorder. The first is that the distribution is a sum of δ functions, that is the molecules jump between two or more discrete orientations. The other is that a continuous function of the three quantities specifying the rotation is required. The NMR study of *n*-butane (Hoch, 1976) assumed the first possibility which gave good agreement with experiment and therefore the first refinements tried used this model. It proved easy to modify the *EDINP* program in order to permit a 'multi-site' model in which several molecules were superimposed. The orientation and occupancy at each site could be refined. All the molecules were constrained to have the same centre-of-mass position, an assumption which disallowed combined rotation/translation jumps, and is justified *a posteriori* by the results obtained using the model.

At this point it is worth considering the limitations of the information in the scan. There are 28 resolved peaks, but the disorder leads to a very large effective temperature factor and hence to the absence of peaks of significant magnitude with 2θ greater than 120° . Thus the Fourier component of shortest wavelength present is around 1.6 \AA so disordered-atom positions closer than some fraction of this, say $1.6/4 = 0.4 \text{ \AA}$,

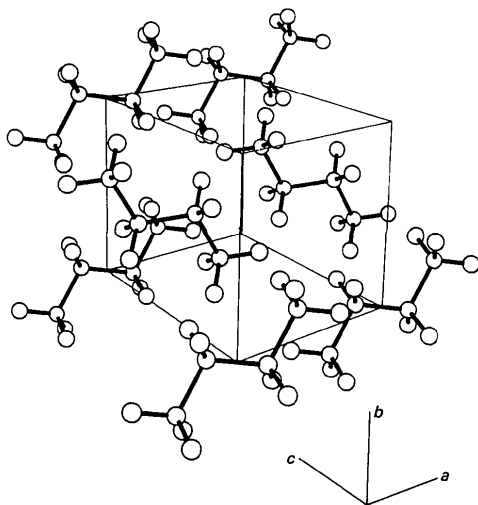


Fig. 4. Structure of phase II at 65 K.

cannot be resolved. A model which has many occupied atomic sites closer than this cannot be distinguished from a continuous distribution.

Because the data contained only 28 peaks, it was necessary to limit the number of parameters refined. Since the lower-phase results are in agreement as to the molecular shape the values of the corresponding parameters were, with one exception mentioned later, taken from the 5 K results. Each independent molecular site required four parameters in the refinement; three Euler angles for orientation plus a probability of occupancy. It will be shown that up to five partial molecules were needed to fit the data which required 20 parameters to be refined simultaneously. This number is clearly greater than the data can support and leads to the second major assumption of the model: that all the molecules are assumed to be related by a rotation about a single axis. This was suggested by the elongated shape of the molecule and by analogy with 1,2-dichloroethane. Refinements were done with two and three independent molecules, and the results were consistent with single-axis rotation. The final *R* factors were similar to the 'single-axis' results. All the following results used a model of one-dimensional rotation in which the axis for each molecule was further assumed to lie in the plane of its four carbon atoms. Each molecule therefore required only two additional parameters, giving 13 for five partial molecules. As before the assumptions are justified by the quality of the final fit.

Trial orientations of the partial molecules for these refinements were obtained from those of phase II by a rotation of the molecule through ζ about the line joining the end carbon atoms. A range of ζ values was tried but only those which gave the best fits are reported. The final values of ζ and the occupancy probabilities are listed in Table 5 along with the final *R* factors. The quality of fit increased with the number of molecules and the 'smearing' due to the temperature factor decreased as the disorder was taken into account by the multiple orientations. It is apparent that just one orientation was consistently present with an occupancy of about 0.5 in all cases. None of the occupancies approached zero and the molecules stayed distinct, a clear indication that the one-, two-, three- and four-orientation models were all inadequate. However, the *R* factor of the five-molecule fit at 3.1% was very close to the best-fit value of 2.7%. These results appear to indicate that a discrete model with less than five orientations is not a good representation.

The discrete model is bound to be unsatisfactory in a system undergoing librational motion of large enough amplitude since the locus of atomic positions cannot be described by an ellipsoid. This also imposes a limit on the amount of detail that can be determined due to the absence of high-angle peaks in the scan. In this case the refinements will not produce well

Table 5. Results of 'multi site' model fit of plastic phase data

	Number of molecules				
	1	2	3	4	5
R factor (%)	7.4	5.4	4.5	3.4	3.1
B	11.6 (10)	7.9 (4)	7.0 (4)	5.1 (4)	4.4 (3)
Euler angles of molecule 0					
φ (°)	-146.4 (6)	-141.2 (7)	-144.6 (5)	-144.8 (2)	-145.3 (2)
θ (°)	72 (1)	64 (1)	74 (1)	79 (1)	70 (2)
ψ (°)	141.1 (5)	145.7 (7)	139.9 (5)	138.7 (3)	141.3 (5)
Axis angle, θ (°)	—	53.9 (14)	55.6 (10)	51.3 (5)	51.3 (4)
Molecular rotation angles ζ (°)					
1	—	47 (2)	-65 (2)	-147 (3)	-145 (3)
2	—	—	54 (1)	-43 (2)	-50 (3)
3	—	—	—	75 (2)	40 (4)
4	—	—	—	—	98 (4)
Occupancies					
0	1	0.57 (3)	0.57 (2)	0.50 (2)	0.49 (2)
1	—	0.43	0.20 (2)	0.13 (1)	0.13 (8)
2	—	—	0.23	0.21 (1)	0.12 (1)
3	—	—	—	0.16	0.15 (2)
4	—	—	—	—	0.11

defined orientations, and the temperature factor will be inversely related to the number of molecules. It is apparent from these considerations that a continuous probability distribution is more realistic as well as physically revealing.

Such a distribution can be represented as a function of a single angle with a small number of adjustable parameters. The continuous function was replaced by one evaluated at 32 angles in the range 0 to 2π . In practice this meant refining the occupancies of 32 molecules related by a rotation axis in the plane of the molecule. The overall orientation was again specified by one set of Euler angles.

Refinements were done using two different functional forms,

$$(a) \quad P(\zeta) = \left(1 + \sum_{l=1}^n a_l \cos l\zeta \right) / 2\pi$$

and

$$(b) \quad P(\zeta) = [1 + a \exp(-\zeta^2/\sigma^2)] / N, \\ N = 2\pi + a\sigma(2\pi)^{1/2}.$$

The first is a general form which can represent any (even) function and the purpose of (b) was as a test on the significance of the results obtained using (a). The highest term in the sum, n , determines the level of detail in the fitted function and should be chosen to correspond to the limit of detail in the diffraction data. The component of smallest wavelength present is about 1.6 \AA which corresponds to an arc of $2\pi/5$ for the outermost atoms. Thus a_5 should be the highest coefficient determined by the data.

Refinements were done with values of n ranging from 1 to 6. The coefficients obtained are listed in Table 6 with the form $P(\zeta)$ plotted for certain n in Fig. 5(a). There is clear convergence as the R factor drops to a minimum of 2.98% compared with a statistical best from ALLHKL of 2.7%. The effect of the limited resolution is manifest in the e.s.d.'s associated with the coefficients, which increase from 9%

Table 6. Coefficients of $\cos l\zeta$ in plastic phase refinement

n	R factor (%)	a_1	a_2	a_3	a_4	a_5	a_6
1	5.75	0.240 (15)					
2	4.66	0.232 (9)	0.127 (12)				
3	3.75	0.180 (7)	0.141 (9)	0.131 (11)			
4	3.05	0.175 (5)	0.143 (7)	0.121 (8)	0.095 (9)		
5	2.99	0.175 (5)	0.145 (7)	0.123 (8)	0.098 (9)	0.079 (39)	
6	2.98	0.175 (5)	0.146 (7)	0.124 (8)	0.096 (9)	0.081 (39)	0.035 (34)

for $l=4$ through 48% for $l=5$ to 97% for $l=6$. An attempt to include $l=7$ resulted in a large coefficient, 0.9 (8), which gave a form for $P(\zeta)$ with negative values, which is clearly unphysical.

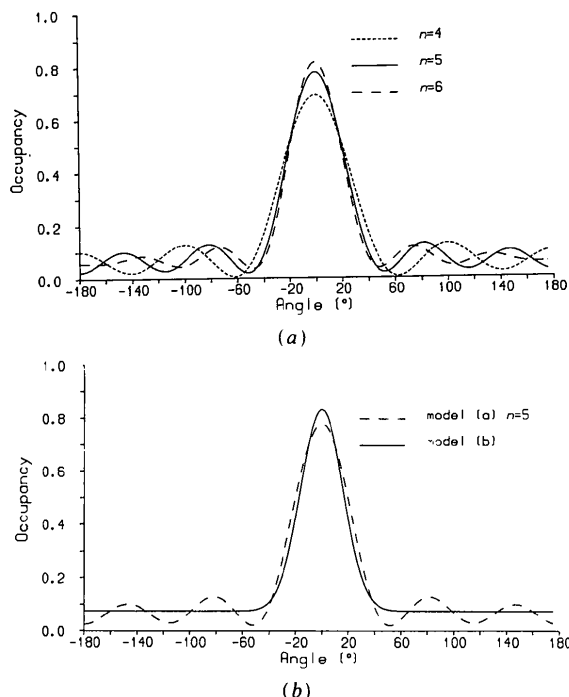


Fig. 5. Orientational probability distribution, $P(\zeta)$. (a) Model a with $n=4$, $n=5$, $n=6$. (b) Model a with $n=5$ and model (b).

These results are consistent with the multi-site model which inspired them. The Euler angles of the $\zeta = 0$ molecule (Table 4) are close to those of molecule 0 in Table 5 and the peak in the distribution function at $\zeta = 0$ corresponds to the site with the greatest occupancy.

In order to try to fit the main features of the distribution with fewer parameters, the functional form (b) was tried. The *R* factor decreased to 3.00%, which is not significantly different from that given by the $n = 5$ fit of (a). The essential features of $P(\zeta)$ were very similar, a broad central peak with significant occupancy at large angles (see Fig. 4b). The final values of the parameters *a* and σ were 10.3(3) and 16.0(6)° respectively.

The final values of the parameters obtained with form (a) using $n = 5$ are listed in Table 4. None of the $n = 4, 5, 6$, or form (b) fits gave significantly different results. Fig. 6 shows the structure with all the molecules at the $\zeta = 0$ orientation. It should be noted that in order to obtain a good fit it was found necessary that the HCH angle of the methyl groups was allowed to vary during all these refinements. The final value is 1.7° greater than given by the 5K fit.

The observed and difference (observed minus calculated) scans and the subtracted background function are plotted in Fig. 7.

It will be observed that the statistical errors in the unit-cell parameters are around five times smaller than the uncertainty in the neutron wavelength. Therefore there will be a small systematic error (<0.001) in all the lengths from the latter.

Discussion

Refinement of phase III yields the molecular dimensions in addition to the crystal structure. The

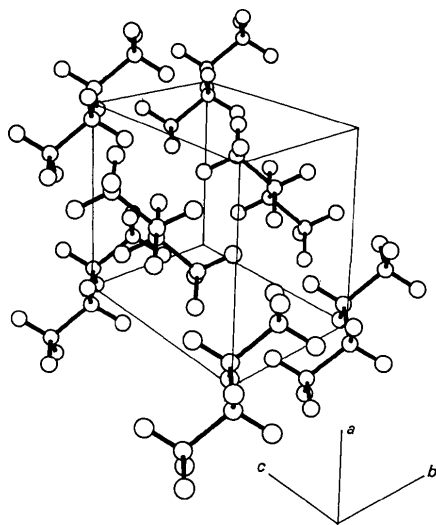


Fig. 6. Structure of phase I at 120 K. All molecules shown are in the $\zeta = 0$ orientation.

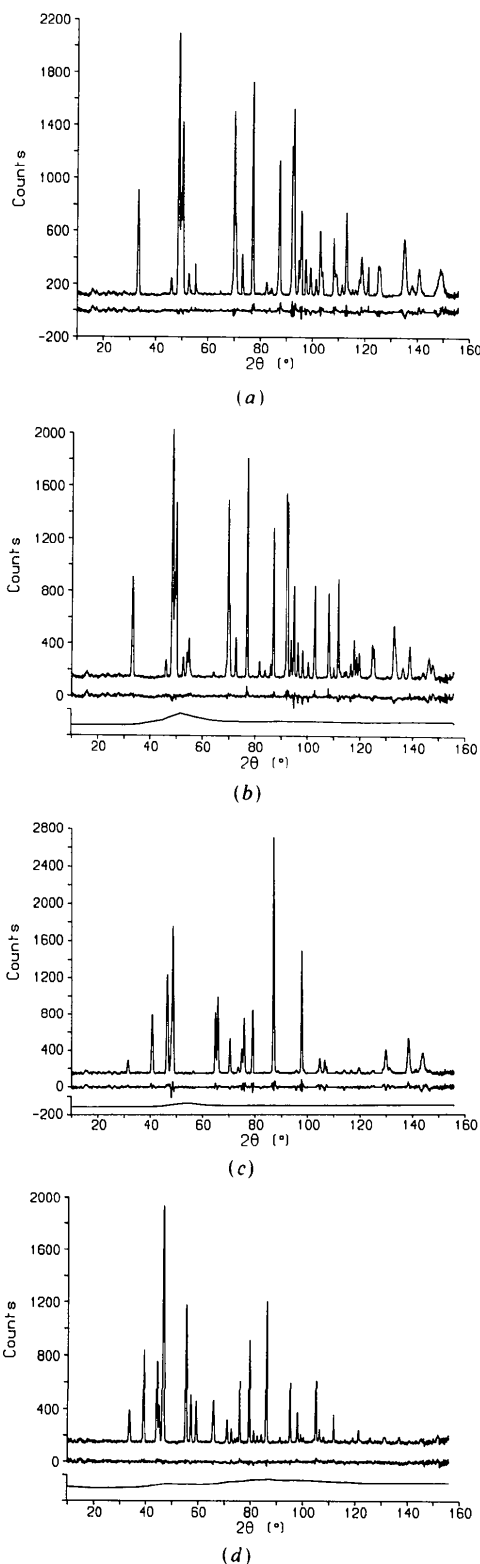


Fig. 7. Observed and difference intensities. (a) Phase III, 5 K. (b) Phase III, 90 K. (c) Phase II, 65 K. (d) Phase I, 120 K, model *a* using $n = 5$. The extra curve in (b), (c) and (d) is the background which was subtracted from the observed data. Nitrogen peaks in (a) and the broadened peaks which were not fitted in (c) are not shown.

apparent C–H bond length is smaller by 1.5% at 90 than at 5 K. This shortening is caused by the ‘swing-arm’ effect of rigid-body molecular librations, whereby the arc which is the locus of the deuterium position has a centroid closer to the carbon than the true bond length. The magnitude of this effect is probably sufficient to account for the discrepancy between this result, 1.087 (7) Å, and the values obtained by electron diffraction (Kuchitsu, 1961; Bonham & Bartell, 1959) of 1.100 (3) and 1.108 (5) Å. Since the thermal motion is much less at 5 than at 90 K, the low-temperature values of the molecular dimensions are correspondingly more reliable. It is notable that the angle CCC, 111.0 (7)°, differs slightly from that obtained in the gas phase, 112.15 (15)°, and that χ , the methyl-group dihedral angle, is non-zero in both low-temperature phases. These phenomena can be accounted for by the van der Waals forces experienced by a molecule in the crystalline environment.

Forms II and I have a very similar unit cell and molecular packing. In both cases the longest dimension of the molecule, the line passing through the outermost carbon atoms, is at almost 90° to that of the symmetry-related molecule. This is in contrast to phase III where they are nearly parallel. It is also the same axis about which the molecules disorder in phase I to within 4°. Furthermore, the orientation in phase II is very close to that of a molecule orientated at $\zeta = -105^\circ$ in phase I. It is clear, therefore, that the transition II \rightarrow I is associated with a disordering about this axis. No such simple relationship is apparent between phases III and I and therefore the transition must be reconstructive in character. This is consistent with the observation of Aston & Messerly (1940) that the transition took eight hours to complete after the addition of energy at the transition temperature.

The results of the refinements of the phase I data must be interpreted with care, giving due weight to information provided by the different models fitted. It may be concluded that:

(1) A continuous orientational probability distribution with a general form fits the data as well as the statistics allow. Both calculation and the results of refinement show that $\cos 5\zeta$ is the highest component determined by the data. To establish that the disorder is between discrete sites the number of partial molecules would have to be less than the resolution limit of the data. Since the quality of fit continues to improve beyond this limit such a form is not justified for butane.

(2) The detailed form of the distribution $P(\zeta)$ is not well established since there is a negligible difference in the final R factors obtained using significantly different models.

In these models a number of assumptions are made, namely:

(1) that all the molecules have the *trans* conformation. This is established by Raman and IR spectroscopic work which shows the existence of a centrosymmetric structure;

(2) that combined rotation/translation jumps do not occur (*cf.* C₃₃H₆₈). Such jumps are unlikely because of the close packing of molecules in this phase;

(3) that the molecules rotate about one axis which lies in the plane of the four C atoms. Refinement of a discrete model with three independent orientations tends to confirm this;

(4) that $P(\zeta)$ is an even function. This is simply an expedient to reduce the number of refined parameters so as not to exceed the information content of the data.

The refinement is shown to be very sensitive to the deuterium-atom mean positions, since the R factor becomes very much worse given a small change in any bond length or angle, especially the methyl-group HCH angle. The apparent increase of this angle in phase I cannot be accounted for merely by the ‘swing-arm’ effect, which would tend to make the angle appear smaller. It is probably associated with the complex atomic motion produced by the disorder which is not adequately described by the assumption of isotropic thermal vibration. The sensitivity to atom positions would appear to confirm assumptions (1)–(3).

On the other hand, the almost equally good fits given by model (a) with $n = 4, 5, 6$ and model (b) show an insensitivity to the detailed form of $P(\zeta)$. It is unlikely, therefore, that assumption (4) is adequately tested. In view of the large error associated with a_6 , model (a) with $n = 5$ is clearly the best form of $P(\zeta)$ that the data support. However, it is not possible to assert conclusively that it is correct in detail. All these distributions have certain features in common: the height and width of the central peak and the average occupancy at high angles. These may therefore be accepted with more confidence.

These results show that in phase I the molecules are disordered predominantly around a single axis, which is as found by Hoch (1976). However, they are clearly at variance with Hoch’s proposed model of 180° reorientations. As NMR measures only one quantity, the proton second moment, it cannot provide sufficient information to distinguish between several models, including that presented here which could equally well account for Hoch’s data.

The nature of the disorder in *n*-butane is clearly different from that of the longer *n*-paraffins. The latter usually have orthorhombic or hexagonal structures (Ungar, 1983) with the rotation axis along a crystal symmetry direction. In contrast the axis in *n*-butane does not have a unique direction in space but only with respect to the molecule. Indeed, the axes of any molecule and its symmetry-related neighbour are at

nearly 90° to each other. Substances like SF₆ and CBr₄ have plastic phases in which the molecules re-orient between equivalent directions. The butane molecule has no such symmetry equivalents, neither does the disorder introduce a higher mean structural symmetry.

It is interesting however to note the similarities between the structures of *n*-butane and 1,2-dichloroethane since the molecules of both are of a similar shape. The unit cell, space group and packing of butane in phase II are very close to those of dichloroethane in its only low-temperature state, and the orientationally disordered phases are similarly alike (Reed & Lipscomb, 1953; Milberg & Lipscomb, 1951). Butane, however, has an additional stable phase III. It is the transition from phase III to phase I which causes butane to have a discontinuity in its specific heat and hence a true phase transition, whereas dichloroethane does not.

We end by reminding the reader of the unexplained broadening of some peaks in phase II. Although several hypotheses can be propounded, the possibility of analysing for a peak-shape broadening function has been lost by the instrumental broadening. However, when very high resolution becomes available through back scattering from a spallation or synchrotron source, a new field of science may be opened up, exploiting the detail that we are beginning to see in this work.

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The Correlation Between Hydrogen-Bond Lengths and Proton Chemical Shifts in Crystals

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Abstract

A critical evaluation of the neutron diffraction crystal structure data used in correlating proton chemical-shift tensors with hydrogen-bond distances indicates that there is a linear relationship between the H...O bond length and the trace of the anisotropic chemical shift that extends from the short bonds observed with hydrogen-bonded anions to the long bonds from the water molecules in hydrated salts and carboxylic acids.

Introduction

Recent advances in solid-state NMR spectroscopy (Mehring, 1983; Fyfe, 1983) have prompted a dialogue between the crystallographers and the NMR spectroscopists. Some interesting correlations have been made between the results of crystal structure analyses and the traces of the ¹³C anisotropic chemical-shift tensors obtained by the CP/MAS (cross-polarization magic-angle spinning) method for powdered specimens (Jeffrey, Wood, Pfeffer & Hicks,