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Crystal Structures of Cyclohexane I and II

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Cyclohexane C_6H_{12} (m.p. 279·8 °K) undergoes an isothermal transition at 186 °K. The so-called phase I is stable between 279·8 and 186 °K, phase II below 186 °K. Starting from a single crystal I grown by a zone melting technique at 187 °K, suitable single crystals II were obtained through a careful control of the phase transformation and annealing at 185 °K for two days. X-ray diffraction data have been collected at 195 and 115 °K by the low-temperature precession technique. At 115 °K, crystal data are: monoclinic cell, $a = 11·23$ (2), $b = 6·44$ (2), $c = 8·20$ (2) Å, $\beta = 108·83$ (17)°, $Z = 4$; space group *Cc* or *C*2/*c* (the analysis confirmed the centrosymmetric group). The crystal and molecular structures were refined to an *R* index of 0·061; the 'chair'-shaped molecule departs slightly but significantly from D_{3d} symmetry. The rigid-body model is a good approximation for the thermal motion. At 195 °K, crystal data for the plastic phase I are: cubic cell, $a = 8·61$ (2) Å, $Z = 4$, space group *Fm*3*m*. Using the molecular shape previously found, two types of orientational disorder have been investigated: isotropic reorientations of the molecules about their centre of gravity (Pauling–Fowler model) and step reorientations between 24 equivalent positions (Frenkel model). In this case, the packing was found by a Monte-Carlo method coupled with a rigid-group least-squares refinement. The Frenkel model gives a better agreement with experiment. A tentative interpretation of the transformation is given. The same general procedure can probably be applied to other plastic crystals.

Introduction

Cyclohexane is a six-membered ring of fundamental importance which has been extensively investigated. Although several contributions have been published on the crystal structures of the polymorphic forms of this compound, they appear to be incomplete and somewhat contradictory. The interpretation of many experimental results suffered from this lack of reliable crystallographic data and a new investigation, using single-crystal X-ray diffraction techniques, was undertaken.

Two stable and one metastable phase of cyclohexane are known; a few important results on each form will be briefly reviewed, with a special interest in those which were useful for the present work.

Phase I

This phase is stable between 279·82 and 186·1 °K (Aston, Szasz & Fink, 1943); the transition at 186·1 °K is isothermal, with an entropy variation of 8·655 e.u., in contrast with the low entropy of fusion (2·286 e.u.) (Ruehrwein & Huffmann, 1943). All thermodynamic properties are characteristic of a plastic crystal (Timmermans, 1938); this conclusion is supported by other experimental results. From n.m.r. measurements it was concluded that, in phase I, the molecules have a considerable freedom of reorientation, such that the intramolecular contribution to the second moment becomes negligibly small (Andrew & Eades, 1953); above 220 °K, the intermolecular contribution vanishes which suggests that the molecules may diffuse through the lattice.

Infrared and Raman spectroscopy indicate a centrosymmetric molecular site (Carpenter & Halford, 1947; Zhizhin & Sterin, 1965; Ito, 1965; Obremski, Brown & Lippincott, 1968; Brown, Obremski & Lippincott, 1970). X-ray results were first obtained from powder patterns (Hassel & Kringstad, 1930; Hassel & Sommerfeldt, 1938) which were interpreted on the basis of a primitive cubic cell; more recently, single-crystal photographs gave a face-centred cubic cell (Oda, 1948; Renaud & Fourme, 1966*a*). Moreover, Oda explained the diffuse scattering by a free rotation of the molecules about their centre of gravity.

Phase II

This phase is stable below 186 °K. The second moment of the measured n.m.r. spectrum for temperatures at which the lattice is rigid, namely below 150 °K, is consistent with a molecular structure having D_{3d} symmetry and tetrahedral bond angles; on warming from 155 to 180 °K, the second moment decreases to a value which indicates the reorientation of the molecules about their triad axis; just below 186 °K, the reorientation frequency is of the order 1 MHz (Andrew & Eades, 1953).

Infrared and Raman spectroscopy are at least in agreement in suggesting a centrosymmetric molecular site (Zhizhin & Sterin, 1965; Ito, 1965; Sechkarev & Brutan, 1965; Le Roy, 1965; Obremski *et al.*, 1968; Brown *et al.*, 1970); the only exception is the work by Dows (1965). X-ray results have been obtained from powder patterns (Lonsdale & Smith, 1939; Krishna Murti, 1958; Leibler & Przedmojski, 1962; Renaud & Fourme, 1966*a*). We have published preliminary results from single-crystal data (Kahn, Fourme, André & Renaud, 1970).

Phase III

Various studies have shown the importance of the thermal treatments on cyclohexane samples (Grajcar & Leach, 1963; Szwarc, 1962; Bullot, Déroulède & Kieffer, 1966; Dworkin & Guillamin, 1966; Leach, Lopez-Delgado & Grajcar, 1966). Powder patterns gave evidence for a distinct phase which is obtained by quenching a sample (either liquid or phase I) at 77°K; a pure phase is obtained only from a very small or finely divided sample: careless cooling generally results in a mixture of phases II and III. Annealing of phase III at temperatures between 120 and 186°K irreversibly gives phase II (Renaud & Fourme, 1966*a*). Further attempts will be made to interpret the powder photographs, since single-crystal work is not possible for such a metastable phase.

Crystal and molecular structure of cyclohexane II

Experimental

Eastman Kodak spectroscopic quality grade cyclohexane was used without further purification. Single crystals were grown in sealed Lindemann glass capillaries (diameter: 0·2 mm) directly on the goniometer head of a precession camera. The attached cooling system gave a nearly laminar flow of cold nitrogen which prevented any frosting of the sample (Renaud & Fourme, 1967); the goniometer head was kept nearly at room temperature by means of a small built-in furnace. The temperature of the gas was continuously monitored and the overall long-range fluctuations were estimated to be at most ± 0·5°K. The calibration curve $T=f(\mathrm{mV})$ of the copper-constantan thermocouple was corrected by checking the melting point of selected pure organic compounds sealed in capillaries. Linear variations of the temperature (from 1 to 100°K.hr^{-1}) could be obtained by means of a mechanical device connected to the recorder.

A single crystal of I is easily grown near the melting point by a zone melting technique (Renaud & Fourme, 1966*b*). When such a crystal is slowly cooled at 186°K, the transition is always delayed and, when induced, cannot be controlled; a coarse powder is thus obtained. After a number of unsuccessful attempts, a single crystal of I was grown *just above the transition point*; for this stressed sample, the transformation I → II is not appreciably delayed and control becomes possible. After annealing for twenty to thirty hours at 185°K, according to a technique described by Rudman (1966), a sample consisting of a few single crystals is usually obtained. The presence of several crystals with different orientations is not too serious a drawback if narrow slits are used to record precession photographs.

Crystal data are: formula C_6H_{12}, M.W. 84·16; monoclinic cell, space group $C2/c$ or Cc; at 115°K, $a=11{\cdot}23\ (3)$, $b=6{\cdot}44\ (2)$, $c=8{\cdot}20\ (2)$ Å, $\beta=108{\cdot}83\ (17)°$, $V=561\ (5)$ Å^3; $D_x=0{\cdot}996\ (9)$ g.cm^{-3} for $Z=4$; $D_m=1{\cdot}028\ (17)$ g.cm^{-3} (after Green & Scheie, 1967); $F(000)=192$; X-radiation: Mo radiation, Zr-filtered ($\lambda=0{\cdot}7107$ Å). The analysis confirmed the centrosymmetric group $C2/c$.

Two sets of intensity data were collected at 175 and 115°K. These temperatures were chosen because, at 175°K, molecular reorientations are detected by n.m.r. whilst the lattice is rigid below 150°K (Andrew & Eades, 1953).

At 175°K, an $h\bar{h}l$ layer was recorded and the intensities of 85 independent reflexions were measured with a flying-spot densitometer (Joyce–Loebl). At 115°K, hkl layers ($k=0\rightarrow 3$) were recorded using the multiple-film technique with mechanical integration; 252 reflexions were measured with a carefully scaled Nonius densitometer. Lorentz–polarization corrections were applied in the usual way; the absorption effects were neglected ($\mu R=0{\cdot}006$). Scale factors and an overall temperature factor were roughly determined by statistical methods for each set.

Structure determination and refinement

There are only minor differences between the two sets of data recorded at 175 and 115°K. The cell parameters are only slightly shortened at the lowest temperature and the extinction rules are the same. Thermodynamics does not detect any transition below 186°K (Aston *et al.*, 1943; Ruehrwein & Huffmann, 1943). N.m.r. results have been interpreted on the basis of reorientational motion of the chair-shaped molecules about their ternary axis (Andrew & Eades, 1953). It was likely, at this point, that each molecule could occupy three orientations corresponding to its own symmetry. If atoms are not 'labelled', all orientations are equivalent and the onset of orientational disorder does not require a phase transition; in contrast to the thermodynamical or X-ray diffraction point of view, the quantized state of the nuclear spins provides a natural 'labelling' for the atoms and this explains why n.m.r. can reveal orientional jumps between orientations which are thermodynamically indistinguishable (Darmon & Brot, 1967).

As was previously noticed, most spectroscopic data on cyclohexane II indicated a centrosymmetric molecular site; moreover, tests on E values gave a strong indication for a centric distribution. The space group $C2/c$ and a D_{3d} molecular model were then assumed. The determination of the molecular packing was reduced to assigning a correct location to the molecular centre (either at 0,0,0 or at $\frac{1}{4},\frac{1}{4},0$) and to determining the orientation of the model in the cell. The structure was readily solved by a program (*PYTHIE*) which associates a random generation of molecular parameters to a rigid-group refinement, with an increasing set of low-angle reflexions. Each generation is called a trial and the procedure is controlled by the evolution of a weighted residual wR [$wR=\{\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2\}^{1/2}$ where $w=(1/d_{hkl})^{1/2}$] (André, Fourme & Renaud, 1972). Convergence was only observed when the centre was fixed at $\frac{1}{4},\frac{1}{4},0$ and about one out of five trials yielded the correct solution ($wR=0{\cdot}18$). After two cycles of least-squares refinement of one scale factor, an overall temperature factor and three molecular parameters, the conventional R index decreased to 0·13 and the coordinates of the carbon atoms were used for a further three-dimensional refinement with the data collected at 115°K.

The structure was refined by a least-square program (*ORION*) in which atoms can be constrained in groups (André, Fourme & Renaud, 1971). The quantity minimized was $W(|F_o|-|F_c|)^2$ where $W=1/(a+|F_o|+c|F_o|^2)^2$ with $a=2|F_{\text{min}}|$ and $c=2/|F_{\text{max}}|$ (Cruickshank, 1961) and the scattering factors from *International Tables for X-ray Crystallography* (1962). A group refinement of the carbon skeleton, an overall temperature parameter and scale factors gave an R value of 0·15; an anisotropic refinement decreased R to 0·10. After a difference synthesis and a peak search, the six peaks with heights greater than 0·25 e.Å^{-3} were identified as hydrogen atoms; the coordinates of these atoms were corrected to give tetrahedral bond angles and C–H bond lengths of 1·00 Å, and were held fixed for two anisotropic cycles (R=0·061, WR= 0·0989). The final coordinates and thermal parameters of the carbon atoms are listed in Table 1, hydrogen parameters in Table 2 and observed and calculated structure factors in Table 3. The standard deviations for the y coordinates and β_{22} parameters are fairly large owing to the limited range of the k index ($k \le 3$).

Molecular structure

A stereoscopic plot of the molecule is shown in Fig. 1.

The bond lengths and bond angles (atoms are labelled as in Fig. 1) are:

C(1)–C(2)	1·528 (6) Å	C(6)–C(1)–C(2)	110·40 (62)°
C(2)–C(3)	1·521 (12)	C(1)–C(2)–C(3)	111·29 (40)
C(3)–C(4)	1·510 (11)	C(2)–C(3)–C(4)	112·34 (40).

The X-ray mean values are 1·523 Å and 111·34° and the mean C–C length corrected for molecular librations is 1·526 Å. The electron diffraction values (Davis & Hassel, 1963) are 1·528 (5) Å and 111·55 (15)°. The equation of the 'best' plane referred to the cell axis is

$$2{\cdot}610u+1{\cdot}390v-8{\cdot}208w=1$$

where u, v, w are fractional coordinates.

The distances of the atoms to this plane are

C(1)	0·288 Å
C(2)	−0·228
C(3)	0·230.

Table 1. *Coordinates of carbon atoms in phase* II *and anisotropic temperature factors* (× 10^5)

$$B=\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right].$$

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0·2061 (3)	0·4677 (12)	−0·0057 (4)	380 (28)	733 (403)	888 (39)	121 (84)	242 (32)	105 (106)
C(2)	0·3434 (3)	0·4088 (13)	0·0852 (4)	322 (29)	1400 (398)	907 (40)	−31 (84)	176 (33)	−13 (102)
C(3)	0·3797 (3)	0·2149 (13)	0·0064 (4)	288 (26)	1240 (425)	861 (37)	76 (79)	186 (29)	176 (99)

Table 2. *Coordinates of hydrogen atoms in phase* II (*a*) *difference-synthesis*, (*b*) *assumed*

	x/a		y/b		z/c	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
H(*a*1)	0·1975	0·1963	0·4835	0·5042	−0·1160	−0·1271
H(*e*1)	0·1876	0·1831	0·6112	0·5879	0·0653	0·0488
H(*a*2)	0·3526	0·3550	0·3834	0·3813	0·2158	0·2083
H(*e*2)	0·4056	0·3985	0·5000	0·5254	0·0780	0·0803
H(*a*3)	0·3787	0·3755	0·2504	0·2462	−0·1253	−0·1144
H(*e*3)	0·4649	0·4682	0·2017	0·1776	0·0749	0·0690

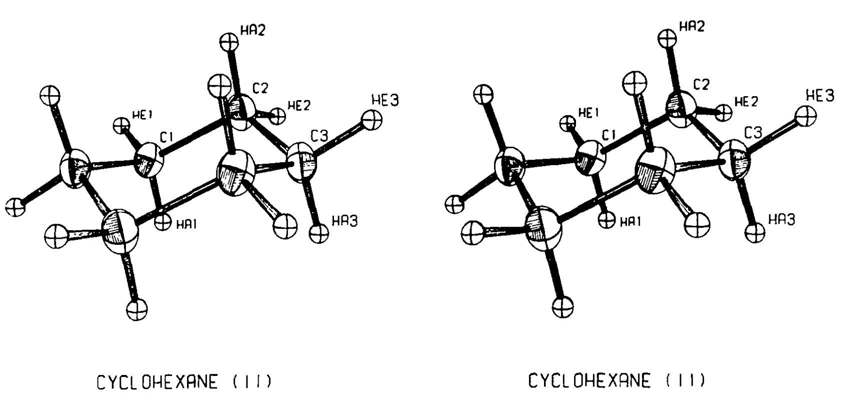

Fig. 1. Stereoscopic drawing of the cyclohexane molecule at 115°K; thermal ellipsoids are scaled to include 50% probability.

The angle between the *c* axis and the normal to this plane is 13·3°.

In the space group $C2/c$, the ternary symmetry is not required and an attempt was made to determine whether the unconstrained molecule gave a better fit with experimental data than a constrained D_{3d} model. An anisotropic refinement with the latter model gave a weighted R index of 0·1033. The significance test of Hamilton (1965) was then applied.

There are 221 degrees of freedom and the dimension of the hypothesis is 6; wR constr./wR unconstr. = 1·044; $\mathscr{R}_{6,221,0.005} = 1{\cdot}043$. Thus there is a slight distortion from ternary symmetry at the 0·005 probability level.

Table 3. *Observed and calculated structure factors* (× 10) *for cyclohexane* II

	0,0,L	
2	939	963
4	248	252
6	87	94
8	107	111
10	120	120
	2,0,L	
-10	50	-43
-8	23	-20
-6	116	-102
-4	339	-323
-2	691	-700
0	549	-515
2	41	35
4	65	66
8	76	-68
10	48	-48
	4,0,L	
-10	63	-64
-8	47	-54
-6	37	24
-4	42	63
-2	50	-50
0	458	-428
2	306	-301
4	80	-87
	6,0,L	
-8	66	-63
-6	87	-96
-4	51	-45
-2	90	106
0	199	184
4	91	-91
6	78	-79
	8,0,L	
-10	80	83
-8	120	121
-4	31	-30
-2	99	-63
0	50	53
2	128	128
4	85	92
	10,0,L	
-8	57	55
-6	134	145
-4	169	176
-2	113	114
0	36	30
2	52	42
6	106	113
	12,0,L	
-8	169	-182
-6	199	-206
-4	146	-153
-2	87	-89
0	98	-95
2	143	-138
4	129	-141
	14,0,L	
-4	37	-29
0	42	35
	1,1,L	
-11	54	-57
-10	42	40
-9	51	-54
-7	55	-54
-6	101	-91
-5	141	-127
-4	232	-233
-3	267	-292
-2	307	-289
2	82	90
3	81	-76
7	31	-32
8	107	-108
9	55	-52
10	47	-48
11	53	-35
	3,1,L	
-9	55	-54
-8	106	101
-7	44	-50
-6	201	199
-4	183	200
-3	43	-27
-2	64	75
-1	177	-185
0	23	26
1	334	-322
2	202	198
3	176	-193
4	192	204
5	97	-102
6	155	161
7	33	-35
8	73	72
	5,1,L	
-11	58	56
-10	72	-69
-9	61	63
-8	123	-125
-7	39	36
-6	84	-97
-1	183	199
3	84	81
4	166	-168
6	69	-67
	7,1,L	
-10	86	87
-9	68	66
-8	100	74
-7	102	103
-5	82	86
-3	56	48
-2	128	120
-1	35	36
0	234	232
1	107	102
2	160	166
3	120	125
4	67	64
5	100	99
7	41	45
	9,1,L	
-10	62	-58
-9	66	-69
-8	24	-23
-7	51	-47
-4	83	-88
-2	177	-181
-1	66	-51
0	156	-161
1	105	-92
2	57	-58
3	64	-55
	11,1,L	
-9	57	-53
-7	104	-103
-6	46	41
-5	116	-120
-4	107	101
-3	92	-94
-2	96	93
1	64	-60
2	50	-48
3	87	-83
5	82	-84
	13,1,L	
-9	70	70
-7	74	77
-6	30	-24
-5	52	48
-2	58	55
0	103	98
1	49	44
2	71	70
3	34	49
	15,1,L	
-7	50	47
-5	80	76
-4	62	-65
-3	70	71
-2	94	-98
-1	35	39
0	74	-71
	17,1,L	
-7	54	-45
-6	49	47
-5	39	-35
-2	52	48
	0,2,L	
9	68	-65
7	64	-63
6	42	-39
4	24	-32
3	102	114
	2,2,L	
-7	100	93
-6	42	-46
-5	197	188
-4	175	-170
3	71	69
4	54	-62
5	138	138
6	85	-82
7	127	126
8	82	-80
9	53	52
10	50	-57
	4,2,L	
-10	56	63
-8	112	114
-7	131	-118
-6	193	195
-5	89	-81
-4	289	281
-3	52	49
2	127	126
3	131	-127
4	122	122
5	110	-113
6	118	116
7	34	-31
8	80	78
	6,2,L	
-9	43	52
-8	52	-48
-6	51	-52
-5	71	-75
-3	131	-128
-2	85	79
-1	39	-32
0	102	96
1	114	104
2	37	43
3	77	77
7	53	-48
8	39	34
	8,2,L	
-9	46	-30
-8	68	-68
-7	28	26
-6	116	-119
-5	25	34
-4	160	-177
-2	197	-212
-1	146	-147
0	191	-182
1	126	-123
2	125	-115
4	92	-83
5	41	29
6	83	-80
8	62	-68
	10,2,L	
-8	40	51
-6	83	86
-5	59	61
-4	81	90
-3	144	140
-2	49	57
-1	121	133
0	28	21
1	36	35
6	31	30
	12,2,L	
-5	62	-54
-3	49	-43
-2	34	32
-1	28	32
1	86	78
3	66	52
	14,2,L	
-8	62	60
-6	49	50
-4	48	40
-3	67	-65
-2	57	49
-1	92	-100
0	59	68
1	59	-68
2	64	71
	16,2,L	
-8	56	-57
-6	54	-49
-5	42	31
-4	60	-55
-3	59	57
-2	77	-70
0	65	-69
	3,3,L	
-5	184	181
	5,3,L	
-5	196	-219
-7	141	-152
	7,3,L	
-3	166	-201
-2	161	177
-1	239	-252
	9,3,L	
-3	173	194

Thermal vibration analysis

The thermal motion of the molecule was analysed in terms of the rigid-body motion. A singularity occurs in the least-squares normal-equations matrix when the atoms lie on a quadratic curve (Schomaker & Trueblood, 1968). Although cyclohexane is non-planar, the departure of carbon atoms from the mean plane is small and some terms in the tensors are badly determined. A statistical technique of regression on principal components was thus preferred to the usual matrix inversion (André, Fourme & Zechmeister, 1972); a disadvantage of this technique is that reliable estimates of the standard deviations for the variables are difficult to obtain. Translation and libration tensors are given in Table 4, and observed and computed U_{ij} in Table 5; a comparison of the observed and calculated ellipsoids was made according to size, shape and orientation using the criteria of Burns, Ferrier & McMullan (1967). The molecule behaves as a rigid-body.

Table 4. *Translation and libration tensors referred to centre-of-mass system*

$$\mathbf{T} = \begin{bmatrix} 2{\cdot}01 & -0{\cdot}24 & 0{\cdot}23 \\ & 1{\cdot}45 & -0{\cdot}03 \\ & & 1{\cdot}92 \end{bmatrix} \text{Å}^2\,.\,10^2$$

r.m.s. amplitude of translation: 0·12, 0·15, 0·13 Å.

$$\mathbf{L} = \begin{bmatrix} 10{\cdot}0 & 3{\cdot}5 & 0{\cdot}0 \\ & 10{\cdot}7 & 4{\cdot}4 \\ & & 12{\cdot}9 \end{bmatrix} (^\circ)^2$$

r.m.s. amplitude of libration: 2·33, 4·13, 3·33 (°).

Molecular packing

A stereoscopic drawing of the crystal structure is shown in Fig. 2. Shortest intermolecular distances are listed in Table 6. The shortest approaches between C···C, C···H and H···H atoms are respectively 3·68, 3·15 and 2·54 Å, whilst contact distances are

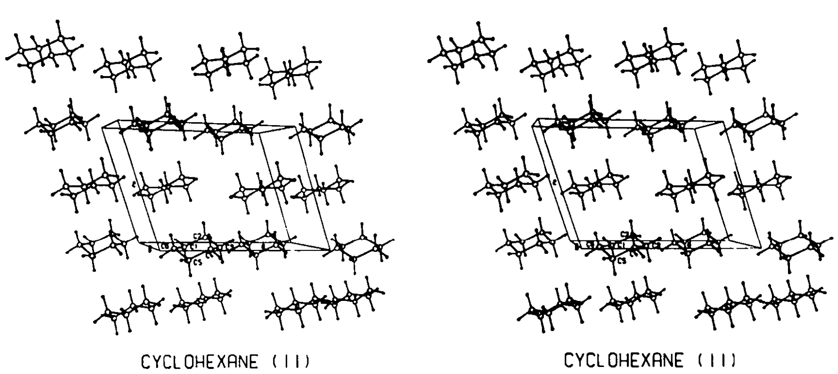

Fig. 2. Stereoscopic illustration of the contents of the unit cell II at 115°K.

Table 5. *Observed and calculated* U_{ij} *referred to centre-of-mass system* (Å^2 × 10^4)

	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.
C(1)	162	211	217	224	249	249	−44	−51	37	40	−24	−30
C(2)	294	248	183	190	281	281	3	21	−4	−1	−11	−8
C(3)	274	270	165	151	245	245	−32	−42	36	30	−16	−13

Standard deviation: 21

approximately 3·4, 2·9 and 2·4 Å. The packing is fairly loose, which is compatible with the onset of reorientational motions above 150°K.

Table 6. *Shortest intermolecular distances in cyclohexane* II (Å)

I:	x	y	z
II:	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
III:	x	$1-y$	$\frac{1}{2}+z$
IV:	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z

I II		I II$_{-a-c}$
H(*a*2)···H(*e*6)	2·552	H(*a*5)···H(*e*3)
H(*e*3)···H(*a*5)		H(*e*6)···H(*a*2)
H(*e*3)···H(*e*6)	2·717	H(*e*6)···H(*e*3)
C(2)····H(*a*5)	3·258	C(5)····H(*a*2)
H(*a*2)···C(5)		H(*a*5)···C(2)
C(2)····H(*e*6)	3·265	C(5)····H(*e*3)
H(*e*3)···C(5)		H(*e*6)···C(2)
C(3)····H(*a*5)	3·308	C(6)····H(*a*2)
H(*a*2)···C(6)		H(*a*5)···C(3)
C(3)····H(*e*6)	3·309	C(6)····H(*e*3)
H(*e*3)···C(6)		H(*e*6)···C(3)
C(2) ···C(5)	3·681	C(5) ···C(2)

I IV		I IV$_{-a-b}$
H(*e*2)···H(*a*6)	2·847	H(*e*5)···H(*a*3)
H(*a*3)···H(*e*5)		H(*a*6)···H(*e*2)
C(3)····H(*e*5)	3·241	C(6)····H(*e*2)
H(*e*2)···C(6)		H(*e*5)···C(3)

I IV$_{-a}$		I IV$_{-b}$
H(*e*1)···H(*e*3)	2·538	H(*e*4)···H(*e*6)
H(*e*6)···H(*e*4)		H(*e*3)···H(*e*1)
H(*e*6)···H(*e*3)	2·778	H(*e*3)···H(*e*6)
C(6)····H(*e*3)	3·227	C(3)····H(*e*6)
H(*e*6)···C(3)		H(*e*3)···C(6)
C(1)····H(*e*3)	3·341	C(4)····H(*e*6)
H(*e*6)···C(4)		H(*e*3)···C(1)

I I$_{-b}$		I I$_{+b}$
H(*e*4)···H(*e*2)	2·751	H(*e*1)···H(*e*5)
H(*e*5)···H(*e*1)		H(*e*2)···H(*e*4)
H(*e*4)···H(*e*1)	2·898	H(*e*1)···H(*e*4)
C(4)····H(*e*1)	3·211	C(1)····H(*e*4)
H(*e*4)···C(1)		H(*e*1)···C(4)
C(4)····C(1)	3·767	C(1)····C(4)

Crystal structure of cyclohexane I

Experimental

The experimental method has been described for cyclohexane II. A single crystal I was grown at 273°K; the sample is ice-like and isotropic; a glass fibre was introduced in the capillary to prevent plastic flow. The sample was slowly cooled to 195°K, so as to reduce as much as possible thermal motion and molecular diffusion through the lattice.

At 195°K, the cell is face-centred cubic; $a=8·61$ (2). (Cu radiation, Ni-filtered, $\lambda=1·5405$ Å); $Z=4$.

The non-extinction rules are:

hkl: $h+k$, $k+l$, $(l+h)=2n$
hhl: $(l+h=2n)$ }
$0kl$: $(k, l=2n)$ }

which are valid for space groups $F23$, $Fm3$, $F432$, $F\bar{4}3m$ and $Fm3m$. Groups belonging to the Laue group $m3$ were discarded because reflexions hkl and $\bar{k}hl$ were found to have the same intensity,* in agreement with the conclusions of Oda (1948).

The crystal was oriented with [100] and [011] parallel to the dial and precession axis respectively, so that all measurable reflexions could be recorded on two layers only. 58 integrated reflexions, reducing to 11 independent reflexions were measured with the optical densitometer, corrected for Lorentz and polarization effects and put on a common arbitrary scale through symmetry-related reflexions measured on both layers.

The absorption effects were neglected ($\mu R=0·053$ for Cu $K\alpha$ radiation). The very rapid fall-off in intensity with increasing angle was observed as usual for plastic crystals. In addition, photographs showed a halo ring and strong diffuse spots around reflexions

Table 6 (*cont.*)

I III	I III$_{-b}$	I III$_{-c}$	I III$_{-b-c}$	
H(*a*6)···H(*a*1)	H(*a*4)···H(*a*3)	H(*a*1)···H(*a*6)	H(*a*3)···H(*a*4)	2·536
H(*e*1)···H(*a*1)	H(*a*4)···H(*e*4)	H(*a*1)···H(*e*1)	H(*e*4)···H(*a*4)	2·627
H(*a*2)···H(*a*1)	H(*a*4)···H(*a*5)	H(*a*1)···H(*a*2)	H(*a*5)···H(*a*4)	2·659
H(*a*2)···H(*a*3)	H(*a*6)···H(*a*5)	H(*a*3)···H(*a*2)	H(*a*5)···H(*a*6)	2·765
H(*e*1)···H(*a*5)	H(*a*2)···H(*e*4)	H(*a*5)···H(*e*1)	H(*e*4)···H(*a*2)	2·841
C(1)····H(*a*1)	H(*a*4)···C(4)	H(*a*1)···C(1)	C(4)····H(*a*4)	3·147
C(6)····H(*a*1)	H(*a*4)···C(3)	H(*a*1)···C(6)	C(3)····H(*a*4)	3·239
C(2)····H(*a*3)	H(*a*6)···C(5)	H(*a*3)···C(2)	C(5)····H(*a*6)	3·246
C(2)····H(*a*1)	H(*a*4)···C(5)	H(*a*1)···C(2)	C(5)····H(*a*4)	3·335

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* Only one reflexion (420 and related) had three distinct Miller indices; reflexions 420, $\bar{4}20$, 402, $\bar{4}02$, $04\bar{2}$ and $0\bar{2}4$ were recorded on the same photograph and their intensities were found to be equal within the experimental errors.

111 and 200. These features have already been observed and discussed by Oda (1948) and Renaud & Fourme (1966*a*).

Structure determination

Two models for the disorder were examined: an isotropic rotational motion (Pauling, 1930), then a more elaborate model in which the molecules occupy only a discrete number of orientations (Frenkel, 1935). In both cases, the molecules reorient about their centre of mass, which must be fixed at a special position of multiplicity 4 (*i.e.* 0,0,0 for $F432$, 0,0,0 or $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ for $F\bar{4}3m$, 0,0,0 for $Fm3m$). All spectroscopic data on this phase indicating a centrosymmetric molecular site, this condition is fulfilled only for 0,0,0 in $Fm3m$.

(*a*) *Isotropic model*

Assuming that the vibrations of the whole molecule are independent of its orientation, the structure factor for a reflexion with indices h,k,l is the product of two terms: the first term is the scattering power of a rigid molecule rotating about a fixed centre, all orientations being equally probable (James, 1962).

$$F_o=\sum f_i \frac{\sin \varphi_i}{\varphi_i}$$

where f_i is the scattering factor of atom i at 0°K and $\varphi_i=4\pi r_i \sin \theta/\lambda$ with r_i=distance of atom i to the centre of rotation; the second term is a Debye–Waller factor: $\exp(-B \sin^2 \theta/\lambda^2)$.

A program was written to compute the structure factors and refine the temperature factor and the scale factor, which are the adjustable parameters for such a model. The best value for B was 13·5 Å^2; $WR=0{\cdot}099$. Observed and calculated structure factors are given in Table 7.

(*b*) *Frenkel model*

If n_1 and n_2 are the number of discernible orientations in phases I and II, the variation of entropy is $\Delta S \simeq R \log(n_1/n_2)$; since $n_2=1$, $\Delta S \simeq R \log n_1$. The experimental variation of entropy at 186°K is 8·655 e.u. In fact, a part of the entropy variation should be attributed to the lowering of vibrational levels at the transition: this contribution is approximately 2–2·5 e.u. (Brot, 1971, 1972), hence n_1 should not be less than ~24 ($R \log 24=6{\cdot}315$ e.u.). It was then assumed that the molecules were in general positions of space group $Fm3m$ and the orientation that best fitted the observed structure factors was searched with the program *PYTHIE*. The molecular model was constrained to D_{3d} symmetry, including hydrogen atoms (C–C = 1·523 Å, ∠C–C–C = 111·34°). The thermal parameter B was fixed at 8 Å^2; the scale factor K was adjusted for each trial structure so that $\sum KF_o=\sum F_c$. The best solution was group-refined with five variable parameters (B, K and three orientation parameters). As there were 5 parameters and only 11 reflexions, a few unobserved reflexions were included with intensities equal to $I_{\min}/3$ so as to give a smoother convergence. At the end of the refinement, $WR=0{\cdot}048$ for observed reflexions and $B=14{\cdot}8$ (1·3) Å^2. The atomic coordinates

Table 7. *Observed and calculated structure factors* (× 10) *for phase* I

Reflexions with an asterisk are unobserved and have been included for group-refinement; $2\theta<90°$.

	(*a*) Frenkel model		(*b*) Pauling model	
hkl	F_o	F_c	F_o	F_c
111	573	588	581	605
200	416	395	422	385
220	16	−14	17	−14
311	78	−72	79	−83
222	131	−120	132	−88
400	55	−46	56	−79
331	47	−62	47	−60
420	32	−36	32	−53
422	36	−40	36	−31
333	34	−41	35	−18
511	9	−5	9	−18
440*	6	5	7	−4
531*	7	4	7	1
442*	7	−6	7	2
600*	6	9	7	2
620*	6	10	7	5
533*	6	−2	6	6
622*	6	4	7	6
444*	6	−1	7	6
551*	6	8	7	6
711*	5	4	5	6
640*	5	9	5	5
642*	6	3	7	4
553*	6	1	7	3
731*	6	3	7	3

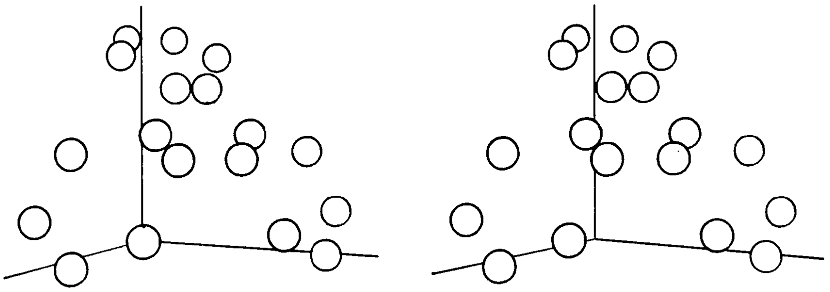

Fig. 3. Cyclohexane I; carbon atoms of the disordered molecule centred at 0,0,0 (only one eighth of the sphere has been drawn for clarity).

are listed in Table 8, observed and calculated structure factors in Table 7.

Table 8. *Atomic coordinates for cyclohexane* I

Uncertainties have been computed from e.s.d.'s of molecular parameters: $\Delta\theta_1=8\cdot1$, $\Delta\theta_2=3\cdot0$, $\Delta\theta_3=7\cdot9°$.

	x/a	y/a	z/a
C(1)	0·085 (32)	0·074 (20)	−0·128 (9)
C(2)	−0·083 (24)	0·024 (12)	−0·147 (12)
C(3)	−0·169 (2)	0·025 (32)	0·008 (23)
H(*a*1)	0·088 (47)	0·185 (18)	−0·094 (9)
H(*e*1)	0·140 (45)	0·064 (34)	−0·230 (16)
H(*a*2)	−0·086 (12)	−0·083 (11)	−0·191 (10)
H(*e*2)	−0·136 (46)	0·097 (21)	−0·220 (22)
H(*a*3)	−0·175 (16)	0·134 (36)	0·047 (28)
H(*e*3)	−0·276 (53)	−0·018 (51)	−0·008 (36)

Discussion

Although both hypotheses gave fairly good agreement with observed values, the Frenkel model gives better results. The ratio $\mathscr{R}$ of the weighted residuals is 2·084. It is difficult to decide whether the addition of parameters results in a *significant* improvement. The tests on $\mathscr{R}$ (Hamilton, 1965) should be regarded with care because small systematic errors would lead to gross errors in the hypothesis tests; moreover, the models are quite different and difficult to compare in terms of more or less constrained structures. A crude application of these tests shows that the more elaborate model is better at the 0·025 level (number of degrees of freedom: 6, dimension of the hypothesis: 3).

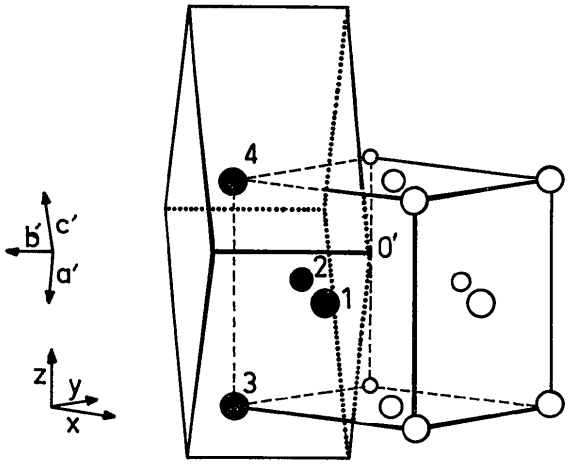

Fig. 4. One of twelve possible ways to transform a single crystal I into a crystal II.

		Cubic system I			Monoclinic system I'		
Origin of system I'	0'	$\frac{3}{4}$	0	$\frac{3}{4}$	0	0	0
Cell translations of system I'	*a'*	$\bar{\frac{1}{2}}$	$\frac{1}{2}$	$\bar{1}$	0	0	0
	b'	$\bar{\frac{1}{2}}$	$\bar{\frac{1}{2}}$	0	0	1	0
	c'	$\bar{\frac{1}{2}}$	$\frac{1}{2}$	0	0	0	0
Coordinates of molecular centres	1	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	0
	2	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{2}$
	3	0	0	0	$\frac{3}{4}$	$\frac{3}{4}$	0
	4	0	0	1	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{1}{2}$

Similar conclusions are obtained when the molecule is constrained with the triad axis along a special direction ([100] or [111]). In addition $R \log n_1$ is too small, since the number of discernible orientations is drastically reduced.

The r.m.s. amplitude of molecular vibrations is very large. It is likely that the barriers hindering reorientation are low; Andrew & Eades (1953) suggested that they are several times lower than the height of the barrier below 186°K (11 kcal.mole^{-1}).

One stereoscopic pair has been drawn to illustrate this disorder; the distribution of carbon atoms, although on the same sphere, is clearly not isotropic.

The distance between the centres of mass of two neighbouring molecules is 6·09 Å. Only orientations with no steric overlap are possible. Unfortunately, the description of local packing and molecular correlations is not possible by X-ray diffraction methods alone, which give only an averaged structure. A re-examination of the diffuse scattering would probably be fruitful.

Relations between structures I and II

Let us consider a monoclinic cell I' constructed on the basis of the cubic cell I in the following way.

a' parallel to $[\bar{1}1\bar{2}]$	$a'=$ 10·55 Å
b' parallel to $[\bar{1}\bar{1}0]$	$b'=$ 6·09
c' parallel to $[\bar{1}12]$	$c'=$ 10·55
	$\beta'=109\cdot47°$

In what follows, *a*, *b*, *c*, *β* denote the parameters of cell II.

A comparison of I' and II gives rise to the following remarks: the relative variations of *a* and *b* with respect to *a'* and *b'* are nearly identical (+6·5% and +5·8%), so that in cell II the arrangement of molecular centres in sections parallel to (100) at $z=0$ or $z=\frac{1}{2}$ keeps approximately the ternary symmetry observed in the planes (111) of cell I; *c* is drastically shortened with respect to *c'* (−22·2%); *β* and *β'* are nearly equal.

A tentative interpretation of the transformation I → II is then possible. At the transition, reorientations are restricted so that the triad molecular axis becomes approximately parallel to *c'*. In the planes of highest density [(111) and related planes] the distances between neighbouring centres increase while a displacement of these planes along *c'* occurs.

In the cubic lattice, there are four families of such planes [namely (111), $(\bar{1}\bar{1}1)$, $(1\bar{1}\bar{1})$ and $(11\bar{1})$] and, for each family, the displacement can take place along three directions {for (111), those directions are [211], [121] and [112]}. Thus, *there are* 12 *possible orientations for the transformed sample* (Fig. 4).

As the transformation generally starts in several points of a single crystal I, it is not surprising that many crystals II with various orientations are obtained. The large variation of the specific volume at the transition is an additional reason for the shattering of the sample.

Conclusion

The general features of the method which has been outlined are probably applicable to other plastic crystals. Suitable crystals of the lowest-temperature phases can be grown through an isothermal transition; cyclohexane was the most difficult experimental problem that we have experienced, but generally the procedure is straightforward as in furan II (Fourme, 1972) or dioxan II (Clec'h, 1972). Diffraction data for plastic phases are very poor and high accuracy is necessary, which would require counter techniques. The Monte Carlo method coupled with group refinement is suitable for checking quickly and easily various hypotheses for the disorder, provided a molecular model is available.

All calculations have been performed with a local version of the X-ray 69 System* including the program for the rigid-body analysis of thermal motion by Burns, Ferrier & McMullan (1968), modified for regression analysis. In addition, the Monte Carlo and refinement programs (namely *PYTHIE* and *ORION*) were used. Stereoscopic plots were drawn with *ORTEP* (Johnson, 1965).

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