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Single crystals of the γ-phase of p-dichlorobenzene have been grown from a saturated solution in diethyl ether at 250 K. Using precession x-ray diffraction data recorded at 260 K, the molecular packing has been found and group-refined.

The unit cell is monoclinic, space group $P2_1/a$, a = 13.96, b = 6.06, c = 7.14 A, β = 149.44°. A discussion of previous results and a comparison of the α and γ-phases are given.

HISTORICAL

The γ-phase of p-dichlorobenzene was first observed by means of NQR spectroscopy by Dean and Lindstrand[1] as a transient low temperature phase and then studied by others with the same technique.[2-10] It was then proved to be a high pressure modification.[2,9,10] It also seems to have been observed during thermal conductivity experiments.[11] After Buyle-Bodin's work,[3] Woesnner and Gutowsky[4] then Moross and Story[6] inferred that the γ-phase was the atmospheric pressure low temperature stable modification of p-dichlorobenzene. This assumption was proved when two of us,[12] using low frequency Raman spectroscopy, showed that the equilibrium between the α and the γ phase was revers-

ible. Afterwards, results obtained by Raman and far infrared spectroscopies led us to assume that there were two molecules per unit cell in the γ-phase crystalline structure.[13] But Reynolds, Kjems and White[14] proposed a crystalline structure, derived from powder neutron diffraction, which was monoclinic with four molecules per unit cell. Starting from this assumption, Gash, Hellmann and Colson[15] recently analysed the T_1 absorption and emission spectra of this solid phase; most of their observations are consistent with a four molecules per unit cell structure but the absence of exciton splitting is then quite surprising.

Furthermore, the γ-phase specific volume determined by Reynolds et al[14] did not seem to agree with the α-phase specific volume as determined by x-ray measurements,[16,17] because it gave a negative volume change at the γ→α transition.†

At this point, it was considered worthwhile to carry out some x-ray measurements on a γ-phase single crystal, since no such data were available, in contrast with the α[17] and β phases.[19]

γ-PHASE SINGLE CRYSTAL GROWTH

Kantimati[7,8] was able to obtain γ-single crystals by direct transformation of β-single crystals around 200 K at atmospheric pressure. Although this fact is rather surprising when one looks at the phase diagram of p-dichlorobenzene,[18] there seems to be no doubt that she did get them.

As the γ-phase is the low temperature stable modification, we tried and grew γ-single crystals from saturated solutions in diethyl ether or ethyl alcohol between 240 and 268 K, which was successfull. Furthermore, in one case, while we studied the low frequency Raman spectrum of a α-single crystal, the emergence of the γ-phase characteristic spectrum was observed; the sample thus obtained was monocrystalline because the relative line intensities were sensitive to its orientation with respect to the incident laser beam.

X-RAY MEASUREMENTS: EXPERIMENTAL

Γ-crystals were grown from a saturated solution in diethyl ether at 250 K. The glass flask containing these crystals was immersed in a dewar filled with cold methanol and transferred from the cooling bath to a cold room. A single crystal

† It is to be noticed that Reynolds *et al's* results are self coherent because the specific volume they determined for the α-phase was not greater than that they determined for the γ-phase (Reynolds, P.A., private communication).

(approximative size: 0.5 x 0.5 x 0.2 mm^3) was selected and stuck to a glass capillary attached to a goniometer head; then, using the dewar again, the goniometer head was transferred to a low temperature precession camera.[20] During the whole process, the crystal was thus kept at about 250 K.

Diffraction data were recorded at 260 K; cell parameters were determined from several precession photographs. Due to the very unfavourable orientation of the crystal, the β cell angle was derived from a least squares refinement of reciprocal vectors lengths and not from a direct inspection of the photographs. Extinctions were consistent with space group $P2_1/a$. Crystal data are:

γ-paradichlorobenzene, formula $C_6H_4Cl_2$, M.W = 147 g, monoclinic cell, space group $P2_1/a$; at 260 K, a = 13.96 (4), b = 6.06 (2), c = 7.14 (2) Å, β= 149.44(30)°, V = 307 $Å^3$, d_{calc} = 1.59 $g.cm^{-3}$ for z = 2 molecules per unit cell.†

Molecular symmetry: point group mmm; in crystal: $\bar{1}$.

It soon appeared that the crystal either was slowly sublimating or was dissolved by the adhesive and only a portion of the reciprocal lattice was recorded, in fact 0kl to 3kl layers. The relative intensities of the integrated reflexions were measured by means of a scaled optical densitometer. Lorentz and polarization corrections were applied in the usual way and crude values for the level scale factors and an overall thermal parameter were computed by statistical methods.

STRUCTURE DETERMINATION

P-dichlorobenzene is a quite simple molecule with an accurately known shape. As the space group of the γ-phase is $P2_1/a$ with only two molecules per unit cell, the centre of the benzene ring may be placed on the origin. Thus, if the molecule is assumed to be a rigid group (Figure 1), only three angular parameters θ_1, θ_2, θ_3[21] describing the molecular orientation with respect to the cell axis need to be determined to find the packing.

A technique which involves a Monte-Carlo calculation was used;[21] packing configurations are randomly generated and then group-refined, using a set of a few low-angle heavy reflexions; the configurations with a low reliability index are selected for additional refinement cycles with an increasing amount of data. Using only 0kl reflexions, the programme readily selected a solution with a reliability index of 14 % which gave also a satisfactory agreement between observed and calculated structure factors for the whole data, and plausible intermolecular distances.

† The a axis is selected so that the relations between the α and γ phases are easily described (fig. 3). Taking usual crystallographic conventions, the unit cell is: space group $P2_1/a$, a = 7.45, b = 6.06, c = 8.61 A, β = 127.83°.

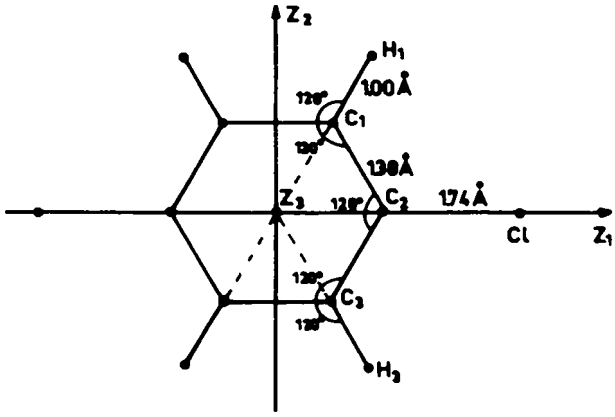

FIGURE 1 The flat molecular model used for structure analysis and group-refinement, with the orthogonal system bound to it.

REFINEMENT

The structure was first refined through three full matrix least-squares cycles; the atomic coordinates and isotropic thermal parameters of nonhydrogen atoms were varied, bringing the reliability index to 6.8 %. The molecule was found somewhat distorted, with a C-Cl bond length shortened to 1.70 Å and high standard-deviations. This arises from the fact that only a restricted set of data is available, and a constrained refinement gives in such a situation more reliable results. The initial solution was then refined by a group-refinement programme[22], using the molecular model shown in Figure 1. The quantity minimized was $W(|F_o| - |F_c|)^2$ where $W = 1/(a + |F_o| + c\,|F_o|^2)$, according to the weighting scheme proposed by Cruickshank,[23] with $a = 2 * |F_{min}|$ and $c = 2/|F_{max}|$. The three angular parameters of the group, the isotropic temperature factors of carbon and chlorine atoms and the level scale factors where varied for three cycles, which smoothly decreased the reliability index to 7.4 % (weighted residual: 9.8 %); the shifts in the last cycle were less than 1/25 of the estimated standard-deviations. Observed and calculated structure factors are given in Table 1, the final structural parameters in Table 2. The estimated standard-deviations are computed from the variance-covariance matrix of the variable parameters.

TABLE 1

Experimental and calculated structure factors (×10); and asterisk denotes a reflexion too weak to be measured.

0,K,0		3 66 -66		1,K,2		2,K,2	
2 405	-385	1,K,-3		1 92	-99	0 128	145
4 89	-79			2 106	106	1 50	62
6 97	101	1 48	45	3 96	109	2 106	-107
		2 164	16	4 76	-79		
0,K,1		3 162	-151	5 91	-105	3,K,-5	
		4 79	68				
0 694	699	5 68	70	1,K,3		2 74	70
1 95	-100					3 113	129
2 264	-266	1,K,-2		2 54	44		
3 90	83			3 164	22	3,K,-4	
4 57	-59	1 58	49	4 92	-90		
5 110	108	2 178	-190	5 48	-43	1 63	-59
6 84	90	3 197	-190			2 192	182
7 48	-39	4 150	161	2,K,-4		3 115	113
		5 81	79			4 83	-79
0,K,2		6 121	-125	0 124	-119		
						3,K,-3	
1 209	-216	1,K,-1		2,K,-3			
2 69	-63					1 54	-49
3 46	35	1 169	154	0 351	-358	2 246	262
4 55	-46	2 356	-370	1 108	-97	3 88	-57
5 110	111	3 89	-81	2 160	137	4 137	-123
6 58	50	4 197	189	3 156	120		
7 78	-52	5 164	6			3,K,-2	
		6 126	-136	2,K,-2			
0,K,3						4 159	-159
		1,K,0		2 154	140	5 184	174
0 132	-129						
1 181	-183	1 169	184	2,K,-1		3,K,-1	
2 63	60	2 186	-182				
		3 109	101	2 108	95	4 76	-79
0,K,4		4 136	145	3 122	-122	5 171	180
		5 105	-107	4 170	4		
0 77	-89	6 55	-50	5 146	-147	3,K,0	
1 95	-96						
2 73	78	1,K,1		2,K,0		3 181	-210
						4 86	81
1,K,-5		1 53	-53	3 180	-94	5 80	77
		2 115	96	5 117	-102		
2 86	78	3 187	170			3,K,1	
		4 164	27	2,K,1			
1,K,-4		5 125	-144			4 128	140
				0 222	252	5 174	-17
1 54	50			1 339	368		
2 109	101						

TABLE 2

Angular group parameters, fractional atomic coordinates and isotropic thermal parameters from the last cycle of group-refinement; esd are in parenthesis.

$\theta_1 = -34.54°(0.43)$		$\theta_2 = -9.51°(0.35)$		$\theta_3 = -141.68°(0.12)$
Atom	x/a	y/b	z/c	B(Å^2)
Cl	−0.1267	0.3162	0.1079	3.29(0.15)
C1	−0.0685	0.2074	−0.1574	2.31(0.28)
C2	−0.0560	0.1399	0.0477	1.73(0.30)
C3	0.0125	−0.0675	0.2051	2.68(0.34)
H1	−0.1181	0.3576	−0.2714	3.00 assumed
H3	0.0215	−0.1164	0.3537	3.00

The equation of the molecular plane referred to the cell axis is:

$$5.940\ u + 2.250\ v + 0.379\ w = 0$$

where u, v, w are fractional coordinates.

MOLECULAR PACKING

A stereoscopic drawing[24] of the crystal structure is shown in Figure 2. Selected intermolecular distances are listed in Table 3. The shortest approaches are near usual contact distances from the sum of van der Waals atomic radii.

Relations between α and β-packings have already been found.[19] A similar inspection was done for α and γ phases; both structures are monoclinic $P2_1/a$; Figures 3a and 3b show their projections along the unique axis b. It appears that the γ-phase may be approximately derived by translating one layer parallel to (001) in the α-phase over two (translation vector: $\vec{a}/2$). The equilibrium between those two phases is reversible and the relative volume change at the transition fairly small:[18] a single crystal-single crystal reversible transformation might well be obtained and it would be worthwhile to look for relations between the orientations of the two lattices.

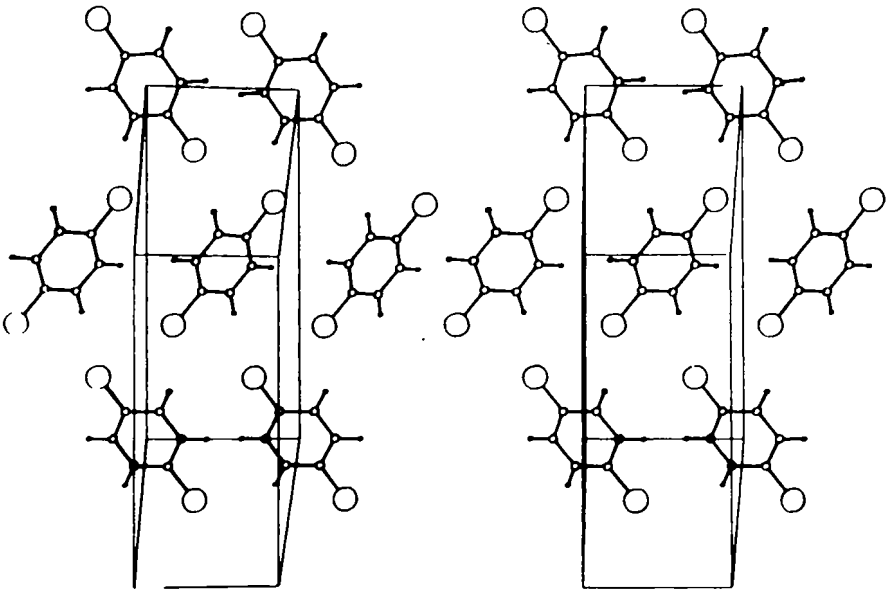

FIGURE 2 Stereoscopic drawing of the molecular packing in γ-p-dichlorobenzene. View is essentially down the perpendicular to a and b axis.

TABLE 3
Shortest intermolecular distances

First atom	Generated atom	distance (A)
Cl	C1(3)	3.78
	C1(1)	3.77
	C3(3)	3.71
	C3(6)	3.65
	H1(1)	3.17
	H3(2)	2.95
	H3(3)	3.18
Cl	C1(1)	3.72
	C1(5)	3.76
	C2(6)	3.59
	C3(6)	3.72
	H1(1)	3.06
	H1(4)	3.09
C2	H1(5)	3.13
C3	H1(5)	3.00
H1	H1(1)	2.62

Symmetry code:

(1) $-x$	$-y+1$	$-z$	(4) $-x-1/2$	$y-1/2$	$-z-1$
(2) $-x$	y	$-z+1$	(5) $x+1/2$	$-y+1/2$	$z+1$
(3) $-x-1/2$	$y+1/2$	$-z$	(6) $x-1/2$	$-y+1/2$	$z-1$

DISCUSSION

The unit cell volume which has been determined for the γ-phase is 307 $Å^3$ at 260 K. Previous X-ray determinations give for the α-phase 299 $Å^3$ at 133 K and 314 $Å^3$ at 293 K.[16,17] Assuming that the thermal expansion for the α-phase is linear as a function of temperature between 133 K and 293 K, we get ~311 $Å^3$ at 260 K and a relative change of volume at the $\gamma \rightarrow \alpha$ transition of ~ 1.3 %. This value is in good agreement, within the limits of uncertainties, with the relative volume change determined in our previous paper,[18] i.e. 1.5 to 2 %, while Reynolds *et al's* results indicate a negative variation.

The fact there are two molecules per unit cell proves that all the low frequency optical modes have been observed by Raman[12] and infrared[13] spectroscopies, so that the assignment of these modes would be easy, provided that the relations between crystal habit and cell axis are found; a reinvestigation of the T_1 absorption spectrum[15] would also be of interest.

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