and V_{g_2}, where g_1 and g_2 are non-parallel, implies that the origin (or the origin translated by a lattice vector) is restricted to lie in a line normal to the set of planes defined by g_1 and g_2, and knowledge of the phases of three Fourier coefficients corresponding to non-parallel vectors completely determines the position of the origin (or the origin translated by a lattice vector).

Analogous arguments apply in the case where the lattice is translated by some vector Δr. It can therefore be concluded that when phases are assigned to describe a structure, three of them corresponding to non-parallel vectors can be chosen arbitrarily reflecting the freedom in choice of origin. When this has been done, all the other phases are uniquely determined to be members of a, by definition, consistent set of phases for the structure.

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Order–Disorder Phase Transition in Dichlorodurene

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The structure of dichlorodurene in the ordered phase was determined from neutron diffraction data at 70 K with the help of intra- and intermolecular potential calculations already published [Messager & Sanquer (1974). *Mol. Cryst. Liq. Cryst.* **26**, 373–380]. The space group is the same as at room temperature, $P2_1/a$, but the cell parameters are integer multiples of those at room temperature, and there are three molecules in the asymmetric unit, instead of half a molecule. The phase transition is of order–disorder type and the first-order nature of this transition is established by the observation of a weak hysteresis.

Introduction

The crystal structure of dichlorodurene, $[C_6(CH_3)_4Cl_2]$ or DCD, was previously determined at room temper-

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ature and we recall briefly some important results (Messager & Blot, 1971): DCD crystallizes in space group $P2_1/a$ with two molecules on centres of symmetry in the unit cell of parameters $a = 17.05$ (5), $b = 3.96$ (2), $c = 8.26$ (3) Å, $\beta = 117.5$ (1)°.

Very large thermal-motion parameters and X-ray diffraction observations on equivalent substituents of

the benzene ring led to a model with a statistical distribution of the two methyl groups and the Cl atom in DCD because of a dynamical orientational disorder in the structure (Eveno & Meinned, 1966).

Potential-energy calculations

To explain the dynamic properties of DCD we had performed some calculations using interaction potential functions between non-bonded atoms, of the type

$$V = -AR^{-6} + B \exp(-CR).R^{-D}$$

where A, B, C, D are semi-empirical constants which can be found in the literature and R is the interatomic distance (Messager & Sanquer, 1974).

For potential-energy calculations it is very important to choose a good geometric model, and although bond lengths are well known in the benzene ring, it is impossible to obtain information about the methyl H atoms from X-ray analysis because of the disorder in the structure. It is often argued that potential constants which are refined to reproduce crystal properties cannot be used to predict internal properties: for example, the molecular configuration; because within the molecules, distances between atoms are shorter than those which occur in the crystal. Nevertheless, we have shown that the best agreement between calculated and experimental properties of benzene crystals is obtained by using functions first derived by Bartell to predict the internal configurations of molecules (Sanquer & Messager, 1973). Such intramolecular potential-energy calculations were successfully applied to determining the molecular geometry and the orientation of the methyl groups in the case of durene (Sanquer & Messager, 1975).

Physical arguments and the use of these intramolecular potential functions led to the molecular model of DCD (Fig. 1) similar to the durene molecule. Calculations carried out with this model, the molecule considered as rigid, give satisfactory results for the

sublimation heat (relative to those of similar compounds), and the equilibrium structure is found very close to the position given by X-ray diffraction.

From X-ray analysis at room temperature we know that the molecule of DCD occupies three equivalent sites; with the possibility of jumps from one site to the other occurring. If we suppose that Cl atoms and methyl groups have the same overcrowding, the molecular model can be compared to a hindered single-axis rotor, the rotation axis being a pseudo sixfold axis perpendicular to the plane of the benzene ring.

Different reorientation processes and the corresponding barrier heights were calculated with help of interatomic potential functions (Messager & Sanquer, 1974). We found then that the most stable structure which corresponds to a minimum of the potential energy is obtained by superposition of the molecules of DCD along the very short packing axis **b**, each of them being turned through $\pi/3$ or $2\pi/3$ relative to the preceding one. Thus, we must have at least three non-equivalent molecules in the asymmetric unit. If there is a change of phase at low temperature, the b axis must be tripled.

Single-crystal rotation photographs, obtained by X-ray diffraction at 120 K, were taken of a crystal mounted along **b** and this hypothesis was verified: $b' = 3b$. At the same time we find that c is doubled. Long exposures are necessary because reflexions which correspond to the superlattice are very weak. This change of phase had not been found during our first investigations, although specific-heat measurements showed a singularity of λ type (Laguarrigue, 1973). Cell dimensions are: a, $3b$, $2c$, β, taking no account of the variations with temperature.

In order to verify our molecular model and the structure expected from the crystal-packing forces we have undertaken a study by neutron diffraction at a low temperature, 70 K.

Experimental

The hydrogenated single crystal used for neutron diffraction was grown from the melt by the Bridgman technique. Elongated along the [110] axis, it had dimensions $5.5 \times 4 \times 2.5$ mm. The experiment was performed on the D10 four-circle neutron diffractometer located on a thermal neutron guide (H24) at the Institut Laue–Langevin. A Cu [111] monochromator was used at an incident wavelength $\lambda = 1.445$ Å. Collimation was provided by the guide and Soller slits between sample and monochromator. The sample was mounted in a He cryostat and the temperature was controlled to within 0.1 K. A detailed description of the cryostat and the general equipment has already been given (Jost, Rees & Yelon, 1975; Claudet, Tippe & Yelon, 1976). Crystals of DCD are very plastic and
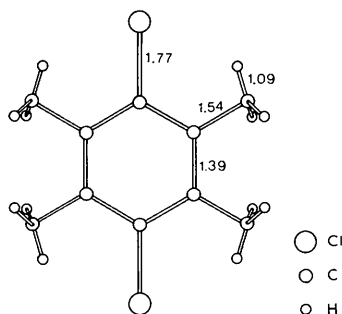

Fig. 1. Molecular model for DCD (with bond lengths in Å).

must be treated with caution. Cell parameters were obtained at 70 K by a least-squares analysis of the settings of some reflexions. Crystal data are: $a = 16.83$ (5), $b = 11.56$ (4), $c = 16.12$ (6) Å, $\beta = 117.02$ (30)°, space group $= P2_1/a, Z = 12$.

The space group was deduced from systematic absences and found to be the same as at room temperature $P2_1/a$. This is a rare but not unprecedented occurrence, as mentioned by Pawley & Dietrich (1975) with the very similar case of octafluoronaphthalene where they did not observe superlattice reflexions. We believe these were difficult to observe with powder diffraction because they are very weak, as in DCD. Here, the symmetry of the crystal is lowered since the cell parameters are multiplied.

The intensities of about 1300 reflexions were collected up to $\theta = 45°$ with the ω-scan mode. During data collection, the intensities of two standard reflexions were measured after every 25 reflexions with no significant variation in intensity observed. The data were reduced to F^2 and $\sigma(F^2)$ by a procedure similar to that previously described by Lehmann & Larsen (1974). The large mosaic of the crystal and the parasitic
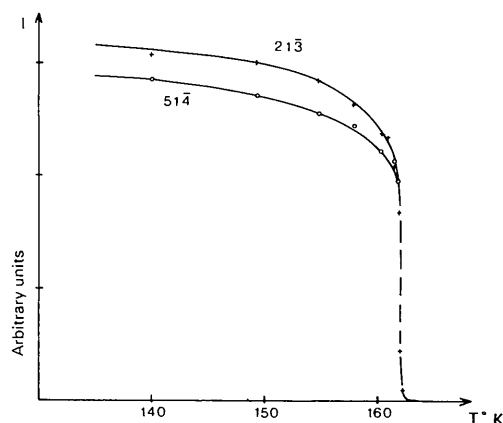

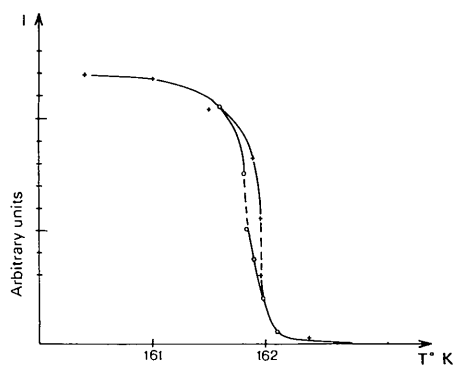Fig. 2. Temperature dependence of the intensity of the reflexions $21\bar{3}$ and $51\bar{4}$.

Fig. 3. Temperature dependence of the intensity of the reflexion $21\bar{3}$ close to the transition.

diffraction of the cryostat presented a problem in the measurement of Bragg intensities. Therefore, any reflexion whose peak did not fall in the centre of the scan was rejected, as were all peaks showing considerable asymmetry. Reflexions with $I < 3\sigma(I)$ were also eliminated. 584 reflexions were accepted, 168 of which were superlattice reflexions. No correction for absorption was applied.

The coherent scattering amplitudes used were taken from International Tables for X-ray Crystallography (1974): $b_C = 0.663$, $b_{Cl} = 0.958$ and $b_H = -0.372 \times 10^{-12}$ cm.

The change of phase

Several superlattice reflexions ($21\bar{0}$, $12\bar{5}$, $51\bar{4}$ and mainly $21\bar{3}$) and two lattice reflexions ($20\bar{6}$ and 200) were selected for the measurement of the temperature dependence of their intensity. The intensity of the lattice reflexions remains constant over the temperature range of interest, so the change in Debye–Waller factor is negligible. The temperature dependence of the intensity of the reflexion $21\bar{3}$ is shown as an example in Figs. 2 and 3.

The transition temperature was determined as $T_c = 160.9$ (0.2) K. The absolute temperature was not known accurately, however, because of the possible presence of temperature gradients and also uncertainties in the absolute calibration of the sensor. The intensity decreases with increasing temperature very slowly. A discontinuity and hysteresis effects were detected when cooling and heating slowly through the transition temperature. Furthermore, it is necessary to wait a long time before thermal equilibrium is reached close to the transition temperature. So, the first-order nature of the transition is established unambiguously. However, the presence of a λ-type anomaly in the specific heat and the small hysteresis ($\Delta T < 0.1$ K) suggest that second-order behaviour might be seen under other experimental conditions, such as increasing pressure.

Refinement of the structure

Since there are three molecules in the asymmetric unit of the lower phase there are now 72 independent atoms (taking into account the H atoms) while in the high-temperature phase there were only six. Unfortunately, the information has not been multiplied to the same extent. We have only 168 observed superlattice reflexions and it is necessary to minimize the number of parameters. Since superlattice reflexions are very weak (Table 1) it is reasonable to assume that the molecular planes remain parallel along the packing axis b and that molecules are separated by translations of the unit-cell parameters of the upper phase. The centre of symmetry

of each molecule is also maintained. We thereby reduce the number of C atoms in the benzene ring to three. In addition, we have two C atoms of the methyl groups and one Cl to treat in each molecule. These we consider as three average substituents X whose scattering amplitudes is now $b_X = (2b_C + b_{Cl})/3$. H atoms are placed according to the potential-energy calculations. So we now have 24 independent atoms: 3 C atoms of the ring, 3 substituent atoms and 18 H atoms with $b_{H\,eff} = 6/18\ b_H$ for the refinement.

From an R value of 0·22 ($R = \Sigma |F_o - F_c|/\Sigma F_o$) obtained directly with our model, a full-matrix least-squares refinement reached $R = 0·086$ and $R_w = 0·077$ ($R_w = \Sigma w|F_o - F_c|/\Sigma wF_o$) for lattice reflexions, with anisotropic temperature factors for heavy atoms and isotropic terms for H.* A perspective view of the three molecules in the asymmetric unit is given in Fig. 4.

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* Lists of structure factors and atomic parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33152 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars. Chester CH1 1NZ, England.

Table 1. *Comparison of the observed and calculated structure factors for the strongest lattice and superlattice reflexions in dichlorodurene*

Superlattice reflexions			Lattice reflexions		
$h\,k\,l$	F_o	F_c	$h\,k\,l$	F_o	F_c
2 1 $\bar{3}$	5·74	5·52	14,0,$\bar{6}$	29·68	29·99
5 1 $\bar{4}$	5·48	5·08	12,0,$\bar{4}$	27·13	26·60
$\bar{1}$ 1 $\bar{2}$	5·44	6·65	4 0 $\bar{8}$	26·86	27·51
4 1 $\bar{1}$	4·44	4·89	14,0,$\bar{4}$	24·72	24·04
3 2 $\underline{0}$	4·33	3·32	6,6,$\overline{10}$	24·42	23·23
4 2 $\bar{4}$	3·81	1·97	6 0 8	23·73	23·12
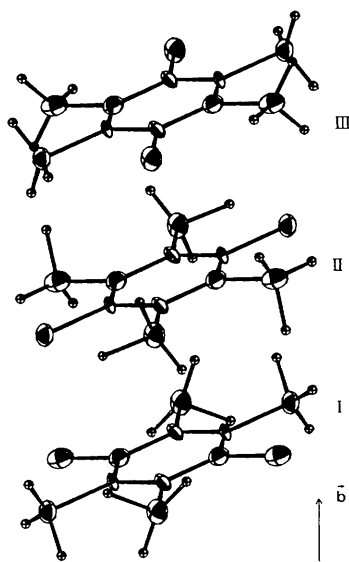
The mean value of the bond lengths in the benzene ring is 1·39 Å with an estimated standard deviation of 0·02 Å; C$-X$ 1·61; $X-$H 1·10 Å (5) and the angles in the methyl groups are those usually observed. We indeed have some dispersion, but this can be explained by the quality of the crystal and instability of the refinement.

It should be remarked that the values of $|F_o - F_c|$ calculated for lattice reflexions at the end of this refinement are of the same order as the F_o's of superlattice reflexions, although the value of R is relatively low for such a compound. Therefore, we have used superlattice reflexions only to find the packing of the molecules in the unit cell. If molecules are labelled as in Fig. 4 the sequences (I,II,III), (II,III,I) and (III,I,II) are different in the crystal. The best value of the R factor, calculated with superlattice reflexions without refinement is obtained with the (II,III,I) molecular packing shown in Fig. 5. The symmetry centres of molecules are situated respectively at $(0,0,\frac{1}{4})$, $(0,\frac{1}{3},\frac{1}{4})$ and $(0,\frac{2}{3},\frac{1}{4})$. The R_{sup} so calculated is relatively high ($R_w = 0·33$) but can be explained by the preceding considerations.

To minimize the number of parameters we have made some assumptions about the molecular model, and to verify these hypotheses we have proceeded with a constrained refinement. Starting from the model of Fig. 1 and assuming the molecular packing found above, we now have as parameters the Euler angles defining the orientation of the three molecules in the asymmetric unit and the rotation of the methyl groups around the C$-$C bond; in all, 21 parameters. Thermal parameters are isotropic and fixed to the mean value calculated in the preceding refinement: $B_C = 1·55$

Fig. 4. Perspective view of the three molecules in the asymmetric unit.
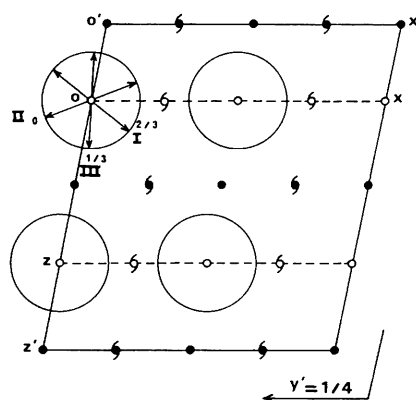

Fig. 5. Molecular packing and space group symmetry $P2_1/a$ in dichlorodurene. The projection xoz represents the unit cell of the upper phase while $x'o'z'$ is that of the lower phase, obtained by suppressing the symmetry elements on the dotted lines and the glide plane at $y = b/4$. Parameters are $a' = a$, $b' = 3b$, $c' = 2c$. Circles represent the molecular packing and arrows show the orientation of the Cl$-$Cl axis of the molecules II, III, I, whose symmetry centres are situated respectively at $y' = 0$, $\frac{1}{3}$ and $\frac{2}{3}$.

Table 2. *Orientation matrices of the three molecules in the asymmetric unit*

The angle between the b axis and the normal to the plane of the molecules is about $24°$.

Molecule I	−0.26858	−0.91735	0.29382
	−0.87875	0.35828	0.31533
	−0.39454	−0.17351	−0.90235
Molecule II	−0.26221	−0.91922	0.29373
	−0.06618	0.32079	0.94484
	−0.96274	0.22831	−0.14495
Molecule III	−0.28228	−0.92699	0.24701
	0.78528	−0.07538	0.61454
	−0.55105	0.36744	0.74922

(0.16), $B_{Cl} = B_{C(methyl)} = 2.00$ (0.16), $B_H = 3.23$ (1.00) $Å^2$. We reach an R_w factor of 0.12 with the lattice reflexions. Table 2 gives the cosines of the orientation of the three molecules. We note very little variation: $3°$ maximum between the normals to the planes of molecule III and molecule I with an estimated standard deviation of $1°$. For methyl groups, the precision obtained is not very good and deviations are not statistically reliable. Nevertheless these deviations could be explained by the presence of a crystal field which is assumed to be zero in intramolecular potential calculations.

Conclusion

Although the structure determination is not accurate, the results obtained here are very coherent. It is difficult to get good crystals which would give some improvement but intra- and intermolecular potential calcu-

lations were each successfully applied. They complement the missing diffraction data.

The phase transition in dichlorodurene is of order–disorder type similar to magnetic phase transitions: a pseudospin can be attributed to each molecule to specify the three possible orientations. This transition corresponds to the condensation of a point, taking place at wave vector $(0, \frac{1}{3}, \frac{1}{2})$ within the high-temperature Brillouin zone. This has never been observed to our knowledge for a structural phase transition in molecular crystals.

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