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The crystal structure of γ -phase *p*-dichlorobenzene at low temperature and high pressure by high-resolution neutron powder diffraction

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Abstract

The γ -phase crystal structure of the title compound, $C_6D_4Cl_2$, space group $P2_1/c$, $a = 8.5478(2)$, $b = 5.9519(1)$, $c = 7.2859(2)$ Å, $V = 295.12(1)$ Å³, $Z = 2$, $\rho_{calc} = 1.6993(1)$ g cm⁻³ at 5 K, has been accurately refined against high-resolution neutron powder diffraction data collected at 5 and 100 K. The equation of state has been obtained at 293 and 100 K up to 5 kbar and no evidence of a previously reported high-pressure phase was found.

1. Introduction

p-dichlorobenzene (*p*-DCB) is a widely studied molecular crystal. This is due in large part to the interesting polymorphism demonstrated by this simple molecular system. Since it crystallizes in three different phases, which can be obtained over rather broad temperature and pressure ranges and which in consequence can co-exist, *p*-DCB represents a versatile system for studying weak intermolecular interactions in organic systems.

For this reason, in the literature there are wide-ranging studies of the various forms of this material, covering both spectroscopic (George and Morris 1970, Ghelfenstein and Szwarc 1971, Figuiere and Szwarc 1974, Shabanov *et al* 1977, Bezot *et al* 1971) and crystallographic (Kitaigorodskii *et al* 1963, Fourme *et al* 1974, Wheeler and Colson 1975, Estop *et al* 1977) methods. Many of these studies have focused on the phase diagram, and a consensus formed on a likely phase diagram, illustrated in figure 1.

The accepted version represented in figure 1, recognizing that co-existence, 'hysteresis' and diffuseness of the phase boundaries can cause uncertainty in the details, can be summarized briefly. The α -phase (I—monoclinic; Estop *et al* (1977)) exists at ambient pressure in a rather narrow temperature range around room temperature. The high-temperature β -phase (II—triclinic; Housty and Clastre (1957)) exists above ~ 303 K until the melting point at ~ 326 K. The γ -phase (III—monoclinic; Reynolds *et al* (1972), Balashov and Ikhmov (1968), Wheeler

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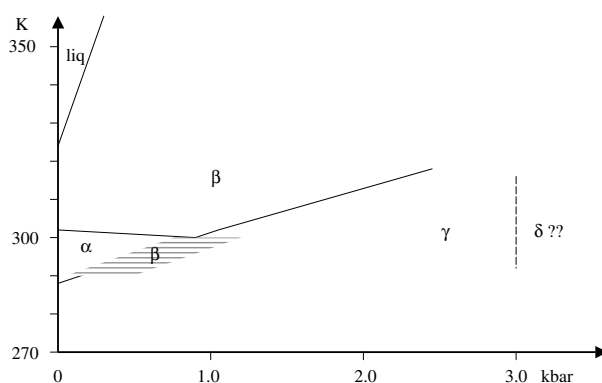


Figure 1. Key features of the phase diagram of *p*-DCB.

and Colson (1975)) exists below ~ 270 K, although the ambient pressure $\alpha \rightarrow \gamma$ transition is rather sluggish (Ghelfenstein and Szwarc 1971, Colson and Wheeler 1974), but this transition is much facilitated by high pressure (Kushida *et al* 1956). Under ambient pressure conditions, the production of single crystals of γ -phase *p*-DCB can be obtained successfully by recrystallization from solution at temperatures of around 248 K or below (Wheeler and Colson 1975).

Our interest in this material resulted from a report of the existence of a fourth phase (termed phase IV or the δ -phase) purported to exist at ambient temperature at pressures above 3 kbar (Sankaran *et al* 1986). This work, based on low-resolution x-ray powder diffraction measurements, resulted in a diffraction pattern indicative of a new orthorhombic phase, closely related to γ -phase *p*-DCB but unable to be indexed based on any of the known phases or mixtures thereof. In this previous study, only unit cell constants were reported and so the structure of the proposed δ -phase remained undetermined.

In order to clarify this situation, particularly in the light of the interesting, and complex, *p*-DCB phase diagram, we decided to reinvestigate the high-pressure behaviour in *p*-DCB in the pressure range to 5 kbar. We undertook these measurements using high-resolution neutron powder diffraction on the recently upgraded high-resolution powder diffractometer (HRPD) instrument at the ISIS Spallation neutron source. The upgrade, to the 90° scattering bank on the instrument, was of particular value to the type of experiment undertaken here. Our aims in this study were twofold:

- (i) to verify the existence of δ -*p*-DCB above 3 kbar;
- (ii) if so, to determine its structure from our high-resolution data.

2. Experimental details

Neutron powder diffraction data were recorded on a 5 g sample of perdeuterated (98%) *p*-DCB (Aldrich Chemical Co.) using the HRPD at the ISIS Facility, UK.

Data at ambient pressure were recorded for some 12 h at 5 and 100 K using a standard 11 mm diameter vanadium sample can and a He-flow 'orange' cryostat. Data at high pressure were recorded subsequently from the same sample loaded in a 'null-scattering' TiZr alloy gas-pressure cell. Measurements were made at the maximum operating pressure of 5 kbar at 293 K and at 3 kbar at 100 K for some 15 h. Shorter runs (ca 10 min) were also made in order to determine the equation of state (EOS). The pressure cell utilizes a Bridgeman seal and has a sample volume of approximately 1 cm^3 . Hydrostatic pressure is achieved by means of a He

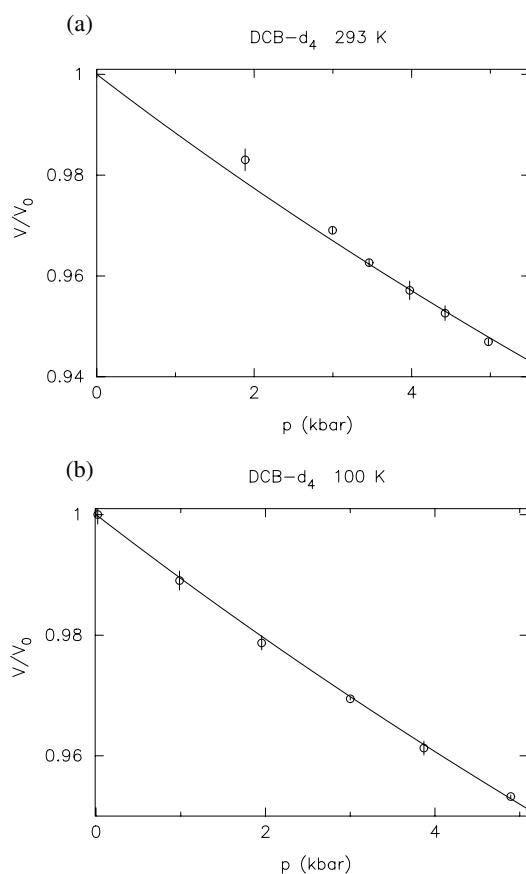


Figure 2. EOS of *p*-DCB-d₄ as determined from neutron powder diffraction at (a) 293 K and (b) 100 K.

gas intensifier system fed to the cell via capillary tubing. The gas cell apparatus is designed for use in a standard cryostat and may be operated to a precision of 25 bar.

Data sets intended for structure refinement were recorded over a time of flight range of 15–115 ms corresponding to a d -spacing range of some 0.3–2.3 and 0.4–3.2 Å in the backscattering ($2\theta = 168^\circ$) and 90° detectors, respectively. In addition, to assist in phase identification, data were also recorded between 90–190 ms extending the d -spacing range at 90° to some 5.4 Å.

3. Results and discussion

We have thus carried out EOS measurements to seek confirmation of the existence of the δ -phase, have obtained high-resolution ambient pressure, low-temperature neutron data from *p*-DCB, and we have also attempted to obtain high-resolution data at high pressure.

3.1. Equation of state measurements

We have determined the second-order Birch–Murnaghan EOS (Birch 1938, 1947) at two temperatures, 293 and 100 K, as shown in figure 2. The bulk modulus, K_0 , was determined as 83.501(7) and 92.063(5) kbar, respectively. At neither temperature do we see evidence of the reported phase change (3 kbar at 293 K) and our refinements of the lattice constant are

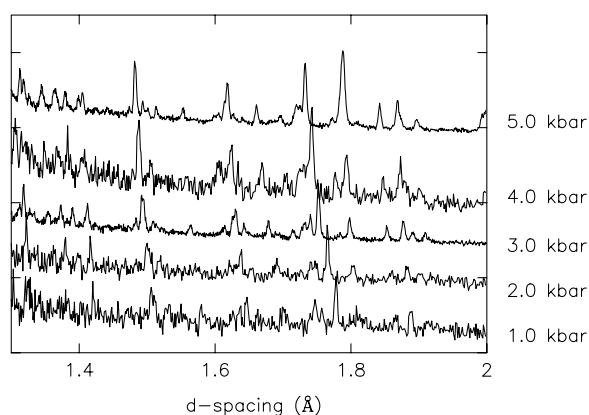


Figure 3. Diffraction patterns of *p*-DCB-d4 as a function of pressure at 293 K. No evidence is observed for a phase transition at or above 3.0 kbar.

continuous over the whole pressure range studied. This point is reinforced by the smooth evolution of the diffraction pattern in the range studied (figure 3).

Apart from some indication of enhanced preferred orientation effects as the pressure increases, we observe no substantial changes in the pattern, in disagreement with the apparently dramatic effects found in the earlier x-ray study (Sankaran *et al* 1986). High-pressure x-ray powder diffraction measurements are prone to serious preferred orientation effects and this may account for the discrepancy compared with our neutron study based on the large volume sample used here.

3.2. High-pressure structure of *p*-DCB

It is clear from section 3.2 that the structure we have observed for *p*-DCB to high pressure is essentially the γ -phase at both 293 and 100 K, in the pressure range of 0.5–5 kbar. This result appears unambiguous, but we are unfortunately unable to achieve full structural refinements on the high-pressure data. As can be seen in figure 4, which shows the best high-pressure data recorded in this study (3.0 kbar at 100 K), the γ -phase structure reproduces the observed diffraction patterns fairly well, but structure refinement is severely hampered by the effect of preferred orientation. This mitigates seriously against our obtaining a definitive determination of the high-pressure structure.

3.3. Ambient pressure structure of *p*-DCB

In contrast to the situation at high pressure, we have been able to refine the ambient pressure structure of *p*-DCB very successfully. The high-quality data at 100 and 5 K lend themselves to unconstrained Rietveld refinement (Rietveld 1969), based on a starting model of the γ -phase structure (Wheeler and Colson 1975).

Refinement was carried out on the normalized diffraction patterns, using the profile refinement method as implemented in the program TF12LS (David *et al* 1992). The refinements were carried out at each temperature, initially using isotropic thermal parameters but extending in the final cycles to encompass anisotropic thermal parameters—a measure of the very high-quality data obtained. The final refinement cycles involved 108 structural parameters, along with 19 profile parameters modelling the peak shape and background. Both refinements converged well, and resulted in excellent fits to the observed profile (figure 5).

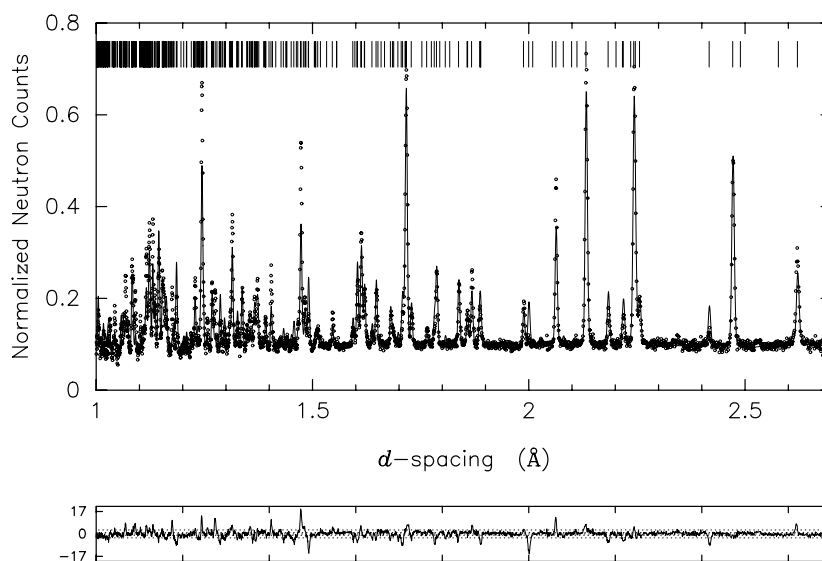


Figure 4. Observed (\circ), calculated (line) and difference/esd profiles at 90° for γ -*p*-DCB-d₄ at 100 K and 3.0 kbar. The vertical tick marks represent the calculated peak positions. The basic structure appears to be correct, but attempts at refinement are hampered by preferred orientation.

Table 1. Refined structural parameters (estimated standard deviations in parentheses) for γ -phase *p*-DCB-d₄ at 5 K. Space group: $P2_1/c$ (no 61). Lattice constants: $a = 8.537\,83(19)$ Å; $b = 5.951\,91(13)$ Å; $c = 7.285\,91(16)$ Å; $\beta = 127.235\,30(20)^\circ$; $V_c = 295.118(11)$ Å³. Asterisks denote U_{eq} values which are one third of the trace of the diagonalized matrix. $R_p = 3.95\%$, $R_{wp} = 5.02\%$, $R_E = 3.14\%$, $\chi^2 = 2.55$ for 9865 observations and 85 basic variables.

Atom	x/a	y/b	z/c	$U_{iso} * 100$
Cl	0.359 62(11)	−0.323 46(12)	0.232 68(11)	0.69(2)*
C(1)	0.158 79(15)	−0.140 63(18)	0.100 17(17)	0.63(3)*
C(2)	0.182 57(17)	0.070 95(17)	0.194 06(19)	0.75(3)*
C(3)	−0.022 10(15)	−0.213 83(19)	−0.092 49(18)	0.54(3)*
D(2)	0.324 38(16)	0.126 20(20)	0.346 11(20)	1.78(3)*
D(3)	−0.037 71(18)	−0.379 34(21)	−0.165 72(20)	1.67(3)*

Table 2. Refined structural parameters (estimated standard deviations in parentheses) for γ -phase *p*-DCB-d₄ at 100 K. Lattice constants: $a = 8.578\,27(25)$ Å; $b = 5.980\,90(18)$ Å; $c = 7.338\,38(22)$ Å; $\beta = 127.365\,70(30)^\circ$; $V_c = 299.235(15)$ Å³. Asterisks denote U_{eq} values which are one third of the trace of the diagonalized matrix. $R_p = 4.96\%$, $R_{wp} = 6.39\%$, $R_E = 5.46\%$, $\chi^2 = 1.37$ for 9866 observations and 85 basic variables.

Atom	x/a	y/b	z/c	$U_{iso} * 100$
Cl	0.358 33(18)	−0.322 40(20)	0.231 85(19)	2.26(4)*
C(1)	0.159 00(24)	−0.139 01(28)	0.101 28(27)	1.74(5)*
C(2)	0.181 62(30)	0.070 04(28)	0.192 99(32)	1.67(5)*
C(3)	−0.023 03(24)	−0.213 81(31)	−0.091 83(31)	1.67(6)*
D(2)	0.323 66(28)	0.123 18(31)	0.344 89(33)	3.26(6)*
D(3)	−0.037 42(30)	−0.377 60(36)	−0.163 44(32)	3.04(7)*

The excellent precision obtained in our neutron study is evident in the low estimated standard deviations (esds) obtained (see tables 1 and 2), and this work represents the definitive determination of the *p*-DCB structure. The resulting molecular geometry at 100 and 5 K is

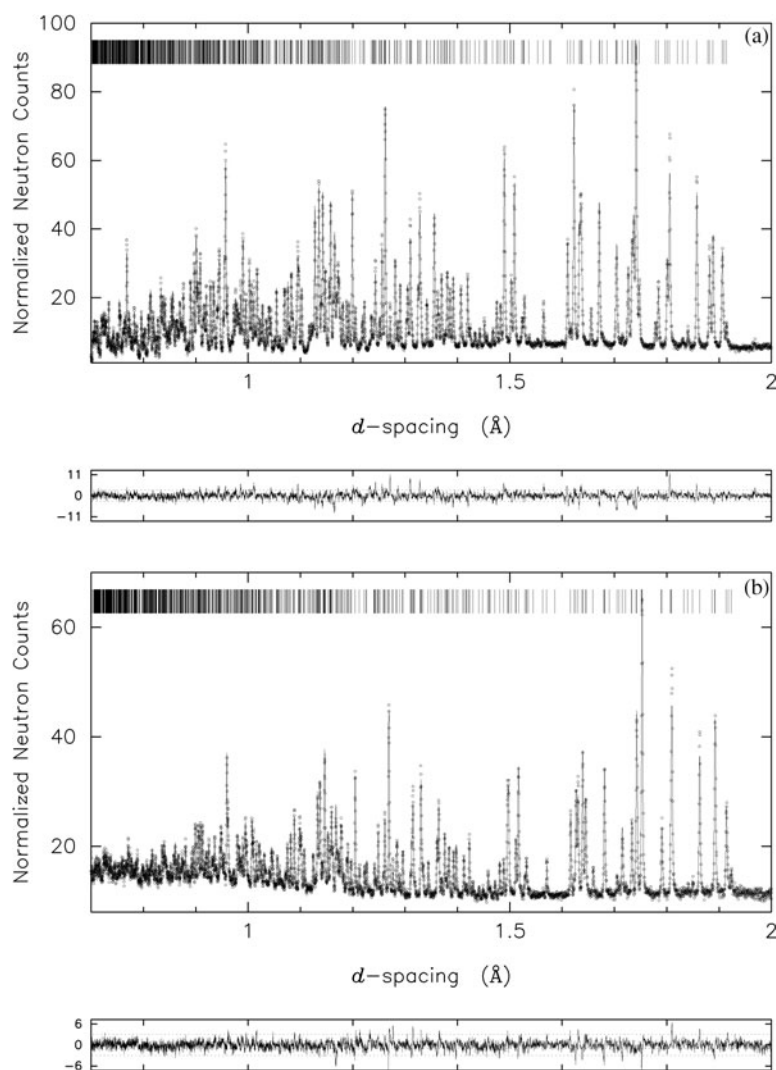


Figure 5. Observed (\circ), calculated (line) and difference/esd profiles at backscattering for γ -*p*-DCB at ambient pressure and (a) 5 K and (b) 100 K. The vertical tick marks represent the calculated peak positions.

illustrated in figure 6 and the intramolecular bond lengths and bond angles are given in table 3. The fact that we have used neutron diffraction has allowed us to add significantly to previous structural work on this system, in particular in fully defining the positional and anisotropic thermal parameters of the deuterium (hydrogen) atoms. The benzene ring is refined to be planar within two standard deviations; the average deviation is 0.001(1) and 0.004(2) Å at 5 and 100 K respectively. In contrast, the chlorine atoms are displaced significantly (0.046(1) Å at 5 K and 0.034(1) Å at 100 K) above and below the ring plane. These essential features of the crystal structure are as found in the earlier x-ray study (Wheeler and Colson 1975). The out-of-plane displacement of the chlorine atoms serves to minimize the repulsion of the two unique $\text{Cl} \cdots \text{Cl}$ interactions at distances of 3.735(2) and 3.747(2) Å. The remaining van der Waals contacts comprise $\text{Cl} \cdots \text{D}(2)$ at 2.839(1) Å and $\text{C}(2) \cdots \text{D}(3)$ at 2.867(2) Å.

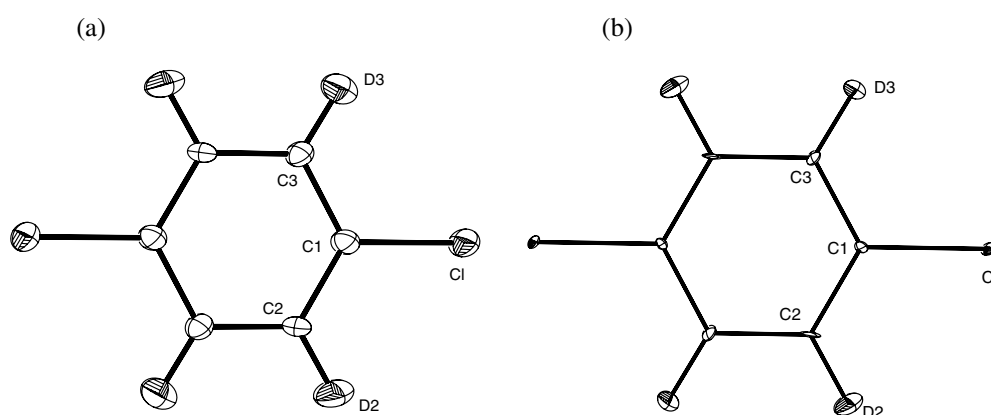


Figure 6. ORTEP (Burnett and Johnson 1996) plots of the molecular structure of *p*-DCB (γ -phase) at 100 K (left) and 5 K (right), at ambient pressure. The probability ellipsoids are plotted at the 50% level.

Table 3. Selected intramolecular distances (\AA) and angles for γ -phase *p*-DCB- d_4 (estimated standard deviations are in parentheses and atoms related by a centre of symmetry are primed).

Parameter	5 K	100 K
Cl–C(1)	1.749(2)	1.748(2)
C(1)–C(2)	1.388(2)	1.376(2)
C(1)–C(3)	1.387(2)	1.400(3)
C(2)–C(3')	1.387(2)	1.384(3)
C(2)–D(2)	1.086(2)	1.086(3)
C(3)–D(3)	1.089(2)	1.083(3)
Cl–C(1)–C(2)	119.4(1)	120.1(2)
Cl–C(1)–C(3)	119.0(1)	118.2(1)
C(2)–C(1)–C(3)	121.7(1)	121.7(2)
C(1)–C(2)–C(3')	119.4(1)	120.1(2)
C(1)–C(3)–C(2')	119.0(1)	118.3(2)
C(1)–C(2)–D(2)	121.2(1)	120.3(2)
D(2)–C(2)–C(3')	119.5(1)	119.6(2)
C(1)–C(3)–D(3)	120.7(2)	120.6(2)
D(3)–C(3)–C(2')	120.3(1)	121.1(2)

4. Conclusions

Our neutron powder diffraction study has shown that the γ -phase of *p*-DCB persists to 5 kbar at 295 K, contradicting the findings of previous x-ray work. However, it has not been possible to refine the structure at high pressure due to preferred orientation effects. It is likely that these are still more severe in the x-ray study, which may help to explain the discrepancy in the results.

At ambient pressure, the high-quality diffraction patterns obtained from the newly upgraded 90° detector banks on the HRPD instrument used in this study, have enabled full anisotropic structural refinement to be carried out. These refinements, at 100 and 5 K, represent the definitive determination of the γ -phase structure of *p*-DCB.

Acknowledgment

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Appendix

Table A.1. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^2$) for γ -phase p -DCB at 5 K. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*^2U_{11}+\dots+2hka^*b^*U_{12}+\dots]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	0.45(4)	0.40(4)	0.38(4)	0.13(3)	-0.19(3)	-0.02(3)
C(1)	0.48(5)	0.14(6)	0.60(5)	0.07(4)	-0.02(4)	-0.05(4)
C(2)	0.82(6)	0.35(6)	0.46(6)	-0.17(4)	0.06(5)	-0.34(4)
C(3)	0.39(6)	0.69(6)	0.20(5)	0.17(4)	0.00(4)	-0.03(4)
D(2)	1.07(6)	1.80(7)	1.10(6)	-0.17(5)	-0.06(5)	-0.32(5)
D(3)	1.30(6)	1.02(6)	1.48(6)	0.30(5)	0.20(5)	-0.60(5)

Table A.2. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^2$) for γ -phase p -DCB at 100 K. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*^2U_{11}+\dots+2hka^*b^*U_{12}+\dots]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	1.77(7)	1.86(7)	1.77(7)	0.28(6)	0.36(6)	-0.05(5)
C(1)	1.69(9)	1.06(9)	1.81(9)	-0.08(7)	0.72(8)	-0.07(7)
C(2)	1.56(9)	1.48(10)	1.61(10)	-0.37(7)	0.78(8)	-0.77(8)
C(3)	1.50(10)	1.60(10)	1.17(9)	0.09(8)	0.42(8)	-0.02(8)
D(2)	2.39(10)	2.96(11)	2.30(11)	-0.43(10)	0.31(10)	-0.92(9)
D(3)	3.08(12)	2.14(11)	2.83(11)	0.15(9)	1.24(9)	-0.72(9)

Table A.3. Least-squares planes and deviations (\AA). The estimated standard deviations are in parentheses, atoms related by a centre of symmetry are primed, and atoms used in calculating the least-squares planes are denoted by *. At 5 K: plane 1, $6.124(3)x+2.219(3)y-6.579z = 2.219(3)$; plane 2, $6.182(1)x+2.208(1)y-6.568(1)z = 2.208(2)$. At 100 K: plane 1, $6.180(5)x+2.203(5)y-6.636(5)z = 2.203(5)$; plane 2, $6.228(2)x+2.207(2)y-6.618(2)z = 2.207(2)$.

	5 K		100 K	
	Plane 1 (6 atoms)	Plane 2 (12 atoms)	Plane 1 (6 atoms)	Plane 2 (12 atoms)
C(1)	0.001(1)*	0.013(1)*	0.004(2)*	0.013(2)*
C(2)	-0.001(1)*	0.011(1)*	-0.004(2)*	0.008(2)*
C(3)	-0.001(1)*	-0.001(1)*	-0.004(2)*	-0.008(2)*
C(1 ⁱ)	-0.001(1)*	-0.013(1)*	-0.004(2)*	-0.013(2)*
C(2 ⁱ)	0.001(1)*	-0.011(1)*	0.004(2)*	-0.008(2)*
C(3 ⁱ)	0.001(1)*	0.001(1)*	0.004(2)*	0.008(2)*
Cl	-0.046(1)	-0.019(1)*	-0.034(1)	-0.014(1)*
D(2)	-0.011(1)	0.011(1)*	-0.017(2)	0.006(2)*
D(3)	0.018(2)	0.018(2)*	0.021(2)	0.015(2)*
Cl ⁱ	0.046(1)	0.019(1)*	0.034(1)	0.014(1)*
D(2 ⁱ)	0.011(1)	-0.011(1)*	0.017(2)	-0.006(2)*
D(3 ⁱ)	-0.018(2)	-0.018(2)*	-0.021(2)	-0.015(2)*

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