

Acta Cryst. (1975). B31, 911 **γ -Phase *p*-Dichlorobenzene at 100 K**

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Abstract. C₆H₄Cl₂, monoclinic γ -phase, $P2_1/c$, $a=8.624$ (2), $b=6.021$ (2), $c=7.414$ (2) Å, $\beta=127.51$ (1)°, $Z=2$, $R=0.044$ for 797 reflections. Crystals of γ -DCB were grown from ethanol solution at 250 K and analyzed at 100 K. The benzene ring bond lengths are in good agreement (1.391 ± 0.004 Å) and the chlorine atoms are displaced 0.045 Å from the benzene plane.

Introduction. Hexagonal plates suitable for X-ray analysis were obtained from a saturated ethanol solution at -25°C . Evaporation of the solvent was aided by passing a gentle stream of nitrogen over the solvent. To prevent the $\gamma \rightarrow \alpha$ phase transition, the filtering and crystal mounting procedures were performed in a large freezer maintained at -20°C . A specimen $0.3 \times 0.3 \times 0.1$ mm was selected and placed in a quartz capillary which had been previously attached to an Air Products cryo-tip goniometer. After the capillary was sealed and covered with a beryllium vacuum shroud, the cryostat was activated and the goniometer removed from the freezer. Cell dimensions and a total of 890 ($797 > 3\sigma F$) intensity data were determined at 100 ± 5 K on a Picker FACS-I diffractometer using Mo radiation and a graphite monochromator ($\lambda=0.71069$ Å). The data set included all reflections to $2\theta=55^\circ$ plus a portion of the 55 – 60° shell and was collected by a 1.4° 2θ scan at 1°min^{-1} with two 10 s backgrounds. The data were corrected for Lorentz and polarization effects; absorption corrections were not made. Systematic absences in the intensity data revealed space group $P2_1/c$. Assuming the same density as the room temperature α phase, the unit-cell volume of 305 Å³ corresponded to $Z=2$, requiring the molecule to occupy a $\bar{1}$ site. The chlorine position was obtained by the heavy-atom method and an electron density map phased with the chlorine model revealed the three carbon atoms of the asymmetric unit. The C and Cl parameters were refined by the full-matrix least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$ where $w=1/\sigma(F_o)^2$. The data which had been observed at

less than $3\sigma(I_o)$ were included in the calculation in only those instances where $I_c > 3\sigma(I_o)$. Convergence was obtained with isotropic temperature factors at $R=0.09$ and with anisotropic terms at $R=0.056$. The hydrogen atoms were clearly evident in a difference map and were well behaved during final refinement, which employed isotropic H and anisotropic C and Cl temperature factors. The final $R[\sum |F_o| - |F_c| / \sum |F_o|]$ and weighted $R[\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]$; $w=1/\sigma^2(F_o)$ were 0.047 and 0.044. Fractional coordinates and temperature factors of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)]$ are given in Table 1.*

Scattering factors for C and Cl were generated from the analytical expressions of Cromer & Mann (1968); the factors for H were those of Stewart, Davidson & Simpson (1965). All major crystallographic calculations were done on the Yale University IBM 370/158 using the X-RAY System (1972).

Discussion. *p*-Dichlorobenzene (DCB) crystallizes in three different phases, and therefore provides a versatile system for studying weak intermolecular interactions in organic molecular crystals. At present, the assumptions of a given theoretical model for evaluating intermolecular interactions are being checked by calculating spectroscopic 'fine structure' for a number of crystals of different *molecules*. An alternative approach is to study several different *crystalline forms* of the same molecule, thus separating the inter- from the intramolecular properties. There is a considerable spectroscopic literature on crystalline DCB, including a recent study in this laboratory of the γ and α phase triplet electronic spectra at 2 K (Gash, Hellmann & Colson, 1973). Our X-ray crystallographic study of the γ -phase was undertaken to complete the crystal-structure information

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30800 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional coordinates, thermal parameters (Å²) and e.s.d.'s (in parentheses) for γ -phase *p*-dichlorobenzene at 100 K

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> or <i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cl	0.3579 (1)	-0.3197 (1)	0.2324 (1)	0.0211 (4)	0.0238 (4)	0.0243 (4)	0.0052 (3)	0.0106 (3)	0.0004 (3)
C(1)	0.1581 (4)	-0.1390 (5)	0.1007 (5)	0.019 (1)	0.018 (1)	0.019 (1)	0.001 (1)	0.012 (1)	0.002 (1)
C(2)	0.0827 (4)	0.0701 (5)	0.1939 (5)	0.018 (1)	0.020 (1)	0.018 (1)	-0.003 (1)	0.010 (1)	-0.002 (1)
C(3)	-0.0216 (4)	-0.2111 (5)	-0.0919 (5)	0.022 (1)	0.017 (1)	0.018 (1)	-0.002 (1)	0.012 (1)	-0.001 (1)
H(2)	0.312 (5)	0.117 (6)	0.334 (6)	0.019 (9)					
H(3)	-0.038 (7)	-0.366 (8)	-0.193 (8)	0.05 (1)					

on DCB and to provide a basis for further spectroscopic and theoretical work in this laboratory.

Under normal conditions, DCB crystallizes from the melt at 55°C in the triclinic ($P\bar{1}$) β -phase with $Z=1$ (Housty & Clastre, 1957) and transforms to the common monoclinic α -phase ($P2_1/a$, $Z=2$) at 30.8°C (Frasson, Garbuglio & Bezzi, 1959). Below 0°C or at high pressure (Reynolds, Kjemis & White, 1972; Balashov & Ikhemov, 1968) DCB crystallizes in a second monoclinic $Z=2$ modification, the γ -phase reported here. A previous neutron powder diffraction study (Reynolds, Kjemis & White, 1972) reported the γ -phase at 100 K to have monoclinic cell dimensions $a=14.25$, $b=6.06$, $c=7.35$ Å, $\beta=101.5^\circ$ and $Z=4$. These parameters were based on very limited data (10 reflections) and are erroneous, although they roughly correspond to a $B2_1/c$ setting of the $Z=2$, $P2_1/c$ cell reported here.

The γ -phase was first reported by Dean & Lindstrand (1956) as a transient low-temperature phase, and later observed (Kushida, Benedek & Bloembergen, 1956) as a stable high-pressure (1600 bar) modification of DCB. Gehlfenstein & Szwarc (1971) investigated the phase diagram of DCB by low-frequency Raman spectroscopy, and reported a sluggish but reversible $\alpha \rightleftharpoons \gamma$ phase transition at about -5°C and atmospheric pressure. Using well formed α -crystals grown by sublimation we attempted to monitor the $\alpha \rightarrow \gamma$ transition using variable-temperature X-ray diffraction (Colson & Wheeler, 1974). We repeatedly failed to observe any such transformation even after cooling for several weeks at varying rates. It is likely that the $\alpha \rightarrow \gamma$ transition resembles the well studied $\beta \rightarrow \alpha$ transition in that the mechanism depends on defects in the crystal lattice. Kitaigorodskii, Mnykh & Asadov (1963) have shown that high purity and crystal quality are associated with supercooling effects for the $\beta \rightarrow \alpha$ transition.

Although the $\alpha \rightarrow \gamma$ transition was not seen by us, the reverse $\gamma \rightarrow \alpha$ transition was very distinct above about 10°C and resulted in a polycrystalline α phase which may in time anneal to a single crystal. We observed this process both visually under a polarizing microscope and indirectly by the loss of X-ray diffraction upon warming the crystal following data collection.

Bond lengths and angles for γ -DCB are given in Fig. 1 and reveal a nominal benzene ring containing equal C-C bond lengths within the standard deviations of 0.005 Å with an average C-C length of 1.391 Å. The interior angle at the position of chlorine substitution is enlarged by 2° while the other interior angles are about 1° less than the normal 120° angle. Two least-squares planes were calculated: an eight-atom plane containing the benzene carbons plus the two chlorines, and a

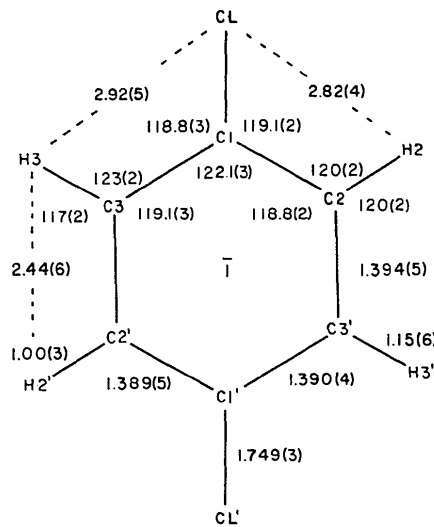


Fig. 1. Bond lengths (Å) and angles ($^\circ$) for γ -DCB at 100 K. Estimated standard deviations are in parentheses.

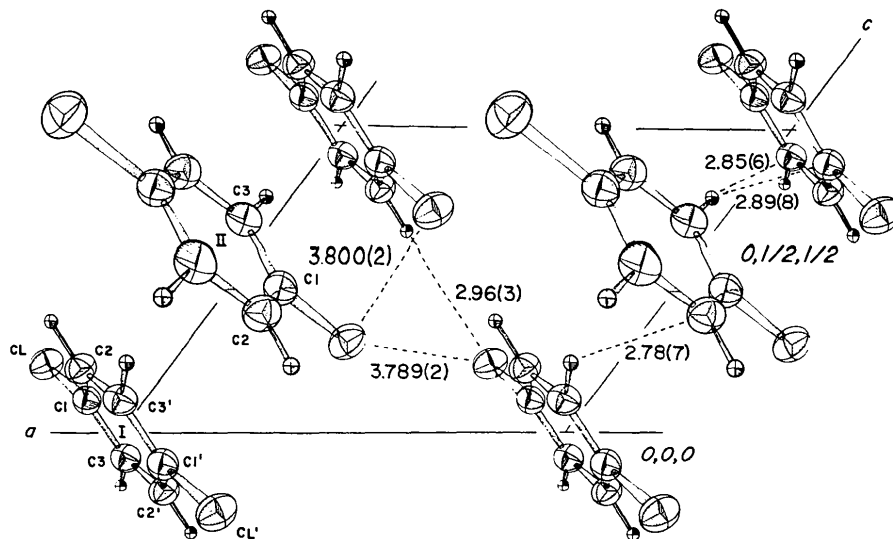


Fig. 2. An ORTEP-II (Johnson, 1971) packing diagram normal to the ac plane showing 75% probability ellipsoids.

six-atom plane containing only the benzene carbons. The results given in Table 2 show deviations from the eight-atom plane averaging 0.011 Å, while the deviations from the six-atom plane are only 0.002 Å. Clearly the benzene is planar within the standard deviations and the chlorine atoms are displaced significantly (0.045 Å) above and below the benzene plane.

Table 2. *Least-squares planes and deviations* (Å)

Atoms related by a center of symmetry are primed.

$$\text{Plane 1: } -6.2925x - 2.2189y + 6.6815z = -4.2557$$

$$\text{Plane 2: } -6.2285x - 2.2607y + 6.6765z = -4.2446$$

	Plane 1 (6 atoms)	Plane 2 (8 atoms)
Cl	0.045	0.010*
C(1)	0.002*	-0.013*
C(2)	-0.002*	-0.010*
C(3)	-0.002*	-0.010*
C(3')	0.002*	0.010*
C(2')	0.002*	0.010*
C(1')	-0.002*	0.013*
Cl'	-0.045	-0.010*

* Atoms used in calculating the least-squares plane.

The molecular packing of γ -DCB, shown in Fig. 2, consists of molecule I centered at 0,0,0 and molecule II at $0, \frac{1}{2}, \frac{1}{2}$. There are two unique Cl...Cl interactions within the approximate range of van der Waals forces. These observed Cl...Cl distances of 3.79 and 3.80 Å would be decreased by 0.06 and 0.09 Å respectively if the chlorine atoms were constrained to lie precisely in the least-squares benzene planes. Thus, the slight out-of-plane Cl displacement discussed above probably arises out of combined Cl...Cl repulsions in the crystal lattice. The remaining closest approaches consist of a near van der Waals ($1.80 + 1.20 = 3.0$ Å; Pauling, 1960) separation (2.96 Å) of Cl (X, Y, Z) and H(2') ($1 - X, -Y, 1 - Z$); and three C-H contacts of about 2.8 Å involving H(2) of one molecule and carbons C(1), C(2), C(3) of the corresponding nearest neighbor.

Note added in proof: - During the proofing of this paper an independent investigation of γ -DCB by Figuiere, Gehlfenstein & Szwarc (1974) has appeared. Our work considerably extends their preliminary find-

ings; they only recorded a restricted portion of the reciprocal lattice, did not measure the cell angle β , and were unable to refine the atoms independently.

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