

repositioning of the methyl groups, mainly from *G*I to *G*II.

It is very interesting that the *C* form (Akimoto & Iitaka, 1972) has the same space group (*I*2/*a*) as that of the *D* form and similarly consists of two layers, *R* and \bar{R} , with a stacking sequence $R\bar{R}R\bar{R}\dots$ along *c*, where \bar{R} is related to *R* by the translation $\frac{1}{2}(\mathbf{a} + \mathbf{b})$. The structures of layers *Q* and *R* are also very similar to each other except that all the *C*_γ atoms in layer *R* are at the positions corresponding to *trans T* to the N atom.

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SHORT COMMUNICATIONS

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The disordered crystal structure of pentachlorothiophenol. By G. WOJCIK, *Instytut Chemii Organicznej i Fizycznej, Politechnika Wrocławska, Wybrzeże Wyspińskiego 27, 50370 Wrocław, Poland* and G. P. CHARBONNEAU,* Y. DELUGEARD and L. TOUPET, *Groupe de Physique Cristalline, ERA au CNRS n° 015, Université de Rennes, campus de Beaulieu, 35042 Rennes CEDEX, France*

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Abstract

C_6HCl_5S , monoclinic, $P2_1/c$, $a = 8.16$ (2), $b = 3.85$ (1), $c = 16.65$ (3) Å, $\beta = 116.7$ (3)°, $Z = 2$, $D_c = 2.01$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 1.686$ mm⁻¹. The structure was refined to an *R* value of 0.061 for 1193 reflexions. The molecules are situated on centres of symmetry in the unit cell. The substituents of the benzene ring are equivalent and were represented in the refinement by pseudo-atoms with scattering factors f_{sub} equal to $(5f_{\text{Cl}} + f_{\text{S}})/6$.

Introduction

Many penta- and hexasubstituted benzenes exhibit disordered structures in the crystalline state at room temperature (Tulinsky & White, 1958; Charbonneau, 1968; Fourme, Renaud & André, 1972; Messager & Blot, 1971). This work was conducted as part of an extensive study of disorder of substituted benzenes.

Pentachlorothiophenol (PCTP) was investigated by Brot & Darmon (1966) by means of NMR and dielectric methods. They found two types of reorientation movements in solid PCTP: reorientation of the proton in the SH group active above 100 K and reorientation of the whole molecule about its pseudo-hexagonal axis, active above 150 K. On the

other hand, PCTP displays the presence of a weak λ anomaly of the C_p curve in the temperature range 200–250 K (Radomska, 1978). Moreover, it is known that PCTP and the high-temperature phase of pentachlorophenol (Wojcik & Rohleder, 1976) form solid solutions over the whole concentration range (Radomski, Gola & Radomska, 1975). All this suggests that the high-temperature phase of PCTP may be disordered in a similar manner to that of pentachlorophenol. Commercial PCTP was purified by repeated sublimation under vacuum and by crystallization from CCl_4 . Pale-yellow single crystals were grown by slow evaporation from a CCl_4 solution. A needle of approximate dimensions $0.10 \times 0.10 \times 5$ mm was used for data collection. The lattice constants and space group were determined from Weissenberg photographs. Intensity data were collected on an Enraf–Nonius three-circle automatic diffractometer with Zr-filtered Mo $K\alpha$ radiation (scan range: 1.20°). Two control reflexions were measured after every 50 reflexions and their intensities showed no unusual fluctuations or decay with time. Absorption effects were neglected but corrections for the change in the column of the crystal bathed by the X-ray beam were applied to the measured intensities; 1193 independent reflexions were used in the structure determination.

Space-group requirements fix the positions of the two molecules at centres of symmetry, resulting in the apparent centrosymmetry of the molecules and the equivalence of the six substituents of the benzene. Since PCTP is isomorphous with dichlorodurene (Messager & Blot, 1971) these coordi-

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Table 1. Fractional coordinates ($\times 10^4$) and isotropic temperature factors, with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
C(1)	620 (4)	1390 (7)	-593 (2)	2.2 (1)
C(2)	1825 (4)	971 (8)	317 (2)	2.4 (1)
C(3)	1221 (4)	-401 (8)	913 (2)	2.4 (1)
X(1)	1390 (1)	3046 (2)	-1325 (1)	3.8 (1)
X(2)	4089 (1)	2222 (3)	713 (1)	3.9 (1)
X(3)	2730 (1)	-949 (3)	2035 (1)	4.0 (1)

* X represents a substituent equivalent to (5Cl + S)/6.

nates were used as initial values in the refinement with the program *ORFLS* (Busing, Martin & Levy, 1962). Scattering factors for the six equivalent substituents were taken to be $f_{\text{sub}} = (5f_{\text{Cl}} + f_{\text{S}})/6$ where f_{Cl} and f_{S} are the atomic scattering factors for Cl and S respectively. The final $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.061$, and $R_w = |\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2|^{1/2} = 0.056$. * The weight, w , for each reflexion was $w = 1/\sigma^2(|F_o|)$ with $\sigma^2(|F_o|) = (1/N)(F_o^2/4I^2) \{CN + (B_1/4) + (B_2/4) + (I^2/400)\}$. CN is the total number of counts collected during the scan, B_1 and B_2 are the background counts, I is the net intensity and N is the number of cycles of measurements for the reflexion.

Discussion

The final atomic coordinates are given in Table 1. Bond lengths and angles, shown in Fig. 1, agree well with the expected values, particularly with those observed in hexachlorobenzene (Brown & Strydom, 1974). The three carbon-substituent distances are not significantly different and must be assumed as identical. Moreover, it should be noted that they are intermediate between those of C-Cl and C-S bonds. The molecule is approximately planar, the largest deviation being 0.02 Å.

The PCTP structure is statistically disordered and is isomorphous with the high-temperature phases of other hexa-substituted benzenes: pentachlorophenol (Wojcik & Rohleder, 1976), chloromethylbenzenes (Charbonneau, 1968;

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34893 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

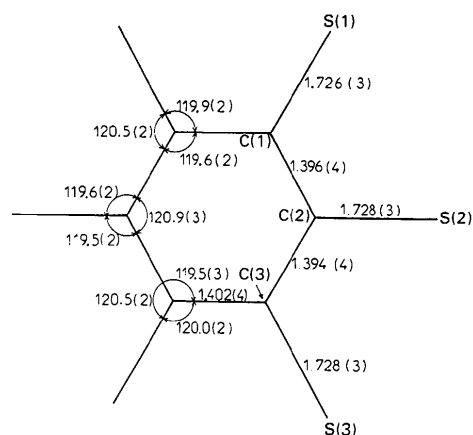


Fig. 1. Bond lengths (Å) and angles (°) of the pentachlorothiophenol molecule. Estimated standard deviations are given in parentheses.

Messenger & Blot, 1971; Fourme, Renaud & André, 1972) and bromochlorobenzene (Khotsyanova, Babushkina & Semin, 1968).

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