

## Strained Chlorocarbons. Structure of Perchlorotoluene, the Simplest Perchloroarylalkane

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(Received 5 February 1990; accepted 27 June 1990)

**Abstract.**  $C_7Cl_8$ ,  $M_r = 367.7$ , monoclinic,  $P2_1/c$ ,  $a = 10.312$  (9),  $b = 10.832$  (8),  $c = 11.449$  (9) Å,  $\beta = 112.96$  (6)°,  $V = 1177$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.07$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 19.9$  cm<sup>-1</sup>,  $F(000) = 712$ ,  $T = 291$  K,  $R = 0.039$  for 1386 observed reflections. The molecular and crystal structure of the highly strained molecule of perchlorotoluene is presented and discussed. The steric strain is due to interactions among the bulky Cl-atom substituents.

**Introduction.** Perchlorotoluene, synthesized by Ballester, Molinet & Castañer (1960), presents an abnormal UV-absorption spectrum principally consisting of a large bathochromic shift of its secondary band (Ballester & Castañer, 1960) and has a low thermal stability, *i.e.* it decomposes at temperatures around 473 K (Ballester, Molinet & Rosa, 1961). These facts have been accounted for by assuming a large steric strain in the molecule due to strong interactions between the trichloromethyl group and the two *ortho* Cl atoms, leading to the more probable conformation for the trichloromethyl group in which two Cl atoms are located on one side and the third on the other side of the mean plane of the aromatic ring. This arrangement, already observed in perchloro-*p*-xylene (Solans, Gali, Miravittles & Font-Altava, 1978) differs from that of the same group in the almost strain-free 2*H*,5*H*-octachloro-*p*-xylene, where one aliphatic Cl atom lies in the plane of the ring, *i.e.* facing the H atom, and the other two are located symmetrically above and below this plane (Silverman, Krukoniš & Yannoni, 1973).

However, since no single crystals of perchlorotoluene could be obtained at that time, the molecular structure of this compound could not be confirmed by X-ray diffraction methods. Recently, during the study of a new synthetic route to polychloro(trichloromethyl)benzenes (Riera, Castañer, Carilla & Robert 1989), single crystals of perchlorotoluene

were obtained and an X-ray structure determination has been undertaken.

**Experimental.** Colourless crystals obtained by very slow evaporation from an ethanolic solution. A fragment of a tabular crystal, dimensions 0.25 × 0.20 × 0.15 mm. Lattice parameters refined from 25 reflections in the range  $5 < \theta < 40^\circ$ . Enraf-Nonius CAD-4 diffractometer, Mo  $K\alpha$  radiation,  $\omega$  scan. 1751 independent reflections with  $(\sin \theta)/\lambda \leq 0.592$  Å<sup>-1</sup>,  $-10 \leq h \leq 10$ ,  $0 \leq k \leq 12$ ,  $0 \leq l \leq 12$ , 1386 with  $I \geq 2.5\sigma(I)$ . Three standard reflections checked every 50 measurements; no significant deviation.

The crystal structure was solved by multiresolution direct methods using the  $\Omega$ -tangent formula (Rius & Miravittles, 1989). Full-matrix least-squares refinement on  $F$  using *SHELX76* (Sheldrick, 1976),  $w = 1/(\sigma^2 + 0.00078F^2)$ ,  $R = 0.039$ ,  $wR = 0.042$ ,  $S = 0.92$  for 1386 observed reflections. Final  $(\Delta/\sigma)_{\max} = 0.26$ , max. and min. heights in final Fourier syntheses 0.37 and  $-0.39$  e Å<sup>-3</sup>. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

**Discussion.** Final atomic parameters and equivalent isotropic temperature coefficients are given in Table 1.\* Bond distances and bond angles are listed in Table 2. Numbering scheme and non-bonding interatomic distances are depicted in Fig. 1.

The molecule of perchlorotoluene presents severe steric strain due to interaction among the bulky Cl-atom substituents as indicated by the short distances between the aliphatic Cl(7*a*) and Cl(7*c*) atoms

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53335 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Refined atomic positional parameters ( $\times 10^4$ ) and equivalent isotropic temperature coefficients ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	$B_{\text{eq}}$
Cl(2)	7456 (1)	693 (1)	2009 (1)	4.79
Cl(3)	10623 (1)	706 (1)	2899 (1)	4.96
Cl(4)	12452 (1)	-1308 (1)	4685 (1)	5.57
Cl(5)	11060 (1)	-3334 (1)	5706 (1)	5.28
Cl(6)	7890 (1)	-3477 (1)	4845 (1)	4.57
Cl(7a)	5084 (1)	-1069 (1)	1147 (1)	4.93
Cl(7b)	5275 (1)	-1568 (1)	3653 (1)	5.12
Cl(7c)	5853 (1)	-3448 (1)	2081 (1)	4.53
C(1)	7682 (4)	-1567 (3)	3189 (3)	2.71
C(2)	8348 (4)	-567 (3)	2884 (3)	2.82
C(3)	9821 (4)	-488 (3)	3344 (3)	3.15
C(4)	10646 (4)	-1376 (4)	4165 (3)	3.44
C(5)	10023 (4)	-2291 (3)	4603 (3)	3.21
C(6)	8562 (4)	-2379 (3)	4146 (3)	2.98
C(7)	6091 (4)	-1865 (4)	2571 (4)	3.35

respectively). An additional consequence of these interactions is the loss of planarity of the toluene skeleton, as clearly evidenced by the out-of-plane deviations of the atoms (Fig. 2). These interactions are similar to those observed in perchloro-*p*-xylene (Solans *et al.*, 1978); however, a major difference between the two molecules has been found: while in perchloro-*p*-xylene the arrangement of the two  $\text{CCl}_3$  groups has one Cl atom with its torsion angle  $\text{C}(2)-\text{C}(1)-\text{C}(7)-\text{Cl}(7b)$  around  $90^\circ$ , i.e. it is practically equidistant to the two *ortho* Cl atoms, the arrangement in perchlorotoluene shows torsion angles  $\text{C}(2)-\text{C}(1)-\text{C}(7)-\text{Cl}(7b)$ ,  $\text{C}(6)-\text{C}(1)-\text{C}(7)-\text{Cl}(7b)$ ,  $\text{C}(2)-\text{C}(1)-\text{C}(7)-\text{Cl}(7a)$  and  $\text{C}(6)-\text{C}(1)-\text{C}(7)-\text{Cl}(7c)$  of  $-108.6(4)$ ,  $72.1(4)$ ,  $13.6(4)$  and  $-49.7(4)^\circ$ , respectively, quite different from the normal expected values of  $-90$ ,  $90$ ,  $30$  and  $-30^\circ$ ; also the distances  $\text{Cl}(2)\cdots\text{Cl}(7b) = 3.955(3)$  and

Table 2. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) with e.s.d.'s in parentheses

C(2)—Cl(2)	1.730 (3)	C(2)—C(1)	1.398 (5)
C(3)—Cl(3)	1.715 (4)	C(6)—C(1)	1.422 (5)
C(4)—Cl(4)	1.721 (4)	C(7)—C(1)	1.546 (5)
C(5)—Cl(5)	1.721 (4)	C(3)—C(2)	1.403 (5)
C(6)—Cl(6)	1.723 (3)	C(4)—C(3)	1.382 (5)
C(7)—Cl(7a)	1.777 (4)	C(5)—C(4)	1.378 (5)
C(7)—Cl(7b)	1.778 (4)	C(6)—C(5)	1.391 (5)
C(7)—Cl(7c)	1.791 (4)		
C(6)—C(1)—C(2)	116.3 (3)	C(4)—C(5)—Cl(5)	119.6 (3)
C(7)—C(1)—C(2)	125.8 (3)	C(6)—C(5)—Cl(5)	120.2 (3)
C(7)—C(1)—C(6)	117.9 (3)	C(6)—C(5)—C(4)	120.2 (3)
C(1)—C(2)—Cl(2)	123.6 (3)	C(1)—C(6)—Cl(6)	122.3 (3)
C(3)—C(2)—Cl(2)	115.0 (3)	C(5)—C(6)—Cl(6)	116.4 (3)
C(3)—C(2)—C(1)	121.3 (3)	C(5)—C(6)—C(1)	121.3 (3)
C(2)—C(3)—Cl(3)	120.7 (3)	Cl(7b)—C(7)—Cl(7a)	106.6 (2)
C(4)—C(3)—Cl(3)	119.1 (3)	Cl(7c)—C(7)—Cl(7a)	102.6 (2)
C(4)—C(3)—C(2)	120.1 (3)	Cl(7c)—C(7)—Cl(7b)	110.3 (2)
C(3)—C(4)—Cl(4)	120.1 (3)	C(1)—C(7)—Cl(7a)	117.0 (3)
C(5)—C(4)—Cl(4)	120.0 (3)	C(1)—C(7)—Cl(7b)	110.5 (3)
C(5)—C(4)—C(3)	119.8 (3)	C(1)—C(7)—Cl(7c)	109.5 (2)

and the aromatic Cl(2) and Cl(6) atoms, respectively (Fig. 1) (mean value  $2.996 \text{\AA}$ ). Almost identical distances between Cl atoms at analogous positions have been found in other perchloroaromatic compounds such as perchloro-*p*-xylene, perchlorobenzylidene-2,5-cyclohexadiene (Gali, Solans, Miravittles & Plana, 1978), octachloronaphthalene (Gafner & Herbstein, 1963), perchloro-1,2,3-triphenylbenzene (Gali, Solans, Miravittles, Font-Altaba & Armet, 1978), decachlorophenanthrene (Herbstein, Kapon & Merksamer, 1976) and decachloropyrene (Hazell & Jagner, 1976).

The interactions  $\text{Cl}(7a)\cdots\text{Cl}(2)$  and  $\text{Cl}(7c)\cdots\text{Cl}(6)$  cause the  $\text{C}(1)-\text{C}(2)-\text{Cl}(2)$  and  $\text{C}(1)-\text{C}(6)-\text{Cl}(6)$  angles to be significantly increased ( $123.6$ ,  $122.3^\circ$ ) and the  $\text{C}(2)-\text{C}(1)-\text{C}(6)$  ( $116.3^\circ$ ) and the  $\text{Cl}(7a)-\text{C}(7)-\text{Cl}(7c)$  ( $102.6^\circ$ ) angles to be decreased relative to their normal values ( $120$ ,  $120$ ,  $120$  and  $109^\circ$

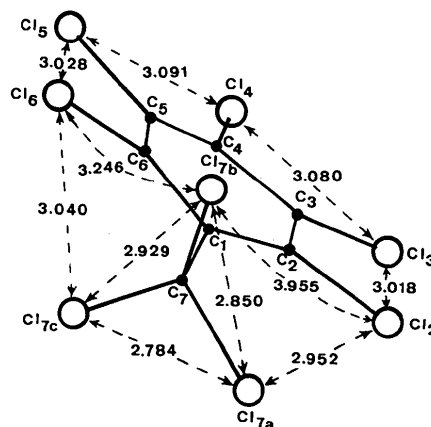


Fig. 1. Projection of the molecular structure of perchlorotoluene with atom numbering and non-bonding interatomic  $\text{Cl}\cdots\text{Cl}$  distances in  $\text{\AA}$  (e.s.d.'s  $0.003 \text{\AA}$ ).

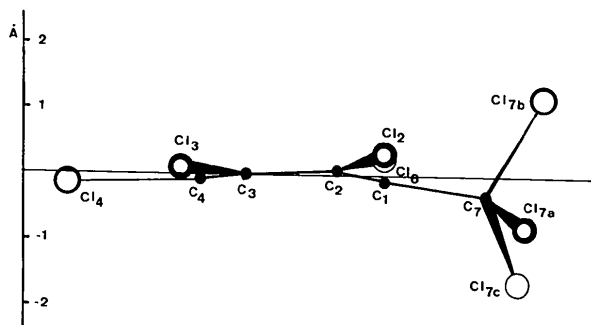


Fig. 2. Side projection of the molecular structure of perchlorotoluene showing the out-of-plane deviations of the atoms ( $\text{\AA}$ ):  $\text{C}(1) = -0.06$ ;  $\text{C}(2) = 0.04$ ;  $\text{C}(3) = 0.02$ ;  $\text{C}(4) = -0.04$ ;  $\text{C}(5) = 0.02$ ;  $\text{C}(6) = 0.04$ ;  $\text{C}(7) = -0.28$ ;  $\text{Cl}(2) = 0.30$ ;  $\text{Cl}(3) = 0.06$ ;  $\text{Cl}(4) = -0.13$ ;  $\text{Cl}(5) = 0.06$ ;  $\text{Cl}(6) = 0.04$ ;  $\text{Cl}(7) = -0.28$ ;  $\text{Cl}(2) = 0.30$ ;  $\text{Cl}(3) = 0.06$ ;  $\text{Cl}(4) = -0.13$ ;  $\text{Cl}(5) = 0.06$ ;  $\text{Cl}(6) = 0.25$ ;  $\text{Cl}(7a) = -0.79$ ;  $\text{Cl}(7b) = 1.20$ ;  $\text{Cl}(7c) = -1.64$ .

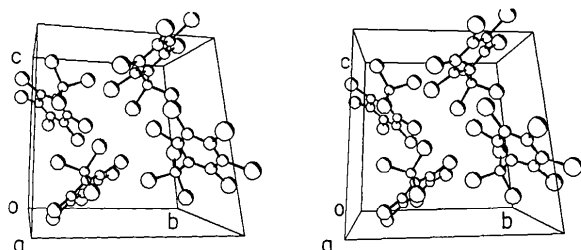


Fig. 3. Stereoview of the unit cell. Minimum intermolecular distance:  $\text{Cl}(7a)\cdots\text{Cl}(7a') = 3.455(3) \text{ \AA}$ .

$\text{Cl}(6)\cdots\text{Cl}(7b) = 3.246(3) \text{ \AA}$  are significantly different. This indicates a rotation of the  $\text{CCl}_3$  group of about  $18^\circ$  from the expected conformation, already observed in perchloro-*p*-xylene. This rotation is probably due to the molecular packing in the crystal. As can be seen in Fig. 3, the aliphatic Cl atoms form close-packed layers parallel to the (100) plane, while the molecular skeletons are normal to this plane.

The authors thank the 'Servei de Raigs-X del CSIC i la Generalitat de Catalunya' for the use of facilities enabling us to carry out the collection of

X-ray diffraction data, and the DGICYT of MEC (Spain) for financial support (project PB87-0388).

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*Acta Cryst.* (1991). **C47**, 629–632

## Structure and NMR Spectra of *N*-[2-( $\alpha$ -Hydrazonobenzyl)-3-benzofuranyl]-*p*-toluenesulfonamide

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(Received 20 February 1990; accepted 27 June 1990)

**Abstract.**  $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$ ,  $M_r = 405.48$ , monoclinic,  $P2_1/c$ ,  $a = 8.296(3)$ ,  $b = 26.859(8)$ ,  $c = 8.820(4) \text{ \AA}$ ,  $\beta = 99.53(1)^\circ$ ,  $V = 1938.3 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.389 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$ ,  $\mu = 1.87 \text{ cm}^{-1}$ ,  $F(000) = 848$ ,  $T = 293 \text{ K}$ ,  $R = 0.056$  for 2074 reflections with  $I \geq 3\sigma(I)$ . The  $\alpha$ -hydrazonobenzyl group has a *syn* configuration with respect to N(1). Two hydrogen bonds, involving N and O atoms, are present. In solution, the  $^1\text{H}$  mononuclear

NMR spectrum and two-dimensional homonuclear correlated spectroscopy experiments (COSY) confirm the presence of hydrogen bonding.

**Introduction.** The title compound was prepared by treatment of 2-benzoyl-3-*N*-(*p*-toluenesulfonyl)-benzofuran with hydrazines and was used as the starting material in the synthesis of derivatives with probable psychotropic activity.