N2—O21	1.217 (3)	N3—C4	1.443 (3)
N2—O22	1.218 (3)		
C1—N1—C8	122.0 (2)	N1—C1—C2	123.6 (2)
C1—N1—C7	118.6 (2)	C6—C1—C2	115.3 (2)
C8—N1—C7	115.7 (2)	C13—C8—C9	119.2 (3)
O21—N2—O22	123.9 (2)	C13—C8—N1	120.4 (2)
O32—N3—O31	122.9 (3)	C9—C8—N1	120.3 (3)
N1—C1—C6	121.1 (2)		

All H atoms were found on successive Fourier difference maps. All non-H atoms were refined anisotropically. Atoms H6 and H9 were refined riding on their parent C atoms.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4-*PC Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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α-Phase *p*-Dichlorobenzene at 293 K

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Abstract

The α-phase structure of the title compound, $C_6H_4Cl_2$, has been accurately redetermined at room temperature. Comparison with 100 K data shows that all different shortest intermolecular contacts ($Cl\cdots Cl$, $Cl\cdots C$, $Cl\cdots H$, $C\cdots C$, $C\cdots H$, $H\cdots H$) undergo thermal expansion. A three-centred hydrogen-bonding geometry is considered for some $Cl\cdots H$ contacts.

Comment

As a part of a study on molecular miscibility, some temperature–composition phase diagrams of *para*-disubstituted benzenes $X—C_6H_4—Y$ (X, Y = Cl, Br, I, Me) have been studied (Haget *et al.*, 1984; Bonpunt *et al.*, 1991; Calvet *et al.*, 1995). In order to define the factors determining the existence of mixed crystals, it is important to know the crystal structure (packing) of the components. Some of them have been known for a long time: *p*-dichlorobenzene (α-phase at room temperature: Croatto, Bezzi & Bua, 1952; α-phase at 133 K, metastable: Frasson, Garbuglio & Bezzi, 1959; α-phase at 100 K, metastable: Wheeler & Colson, 1976; β-phase: Housty & Clastre, 1957; β-phase at 100 and 300 K, metastable: Wheeler & Colson, 1976; γ-phase at 100 K: Wheeler & Colson, 1975; high-pressure phase: Sankaran, Sharma, Sikka & Chidambaram, 1986); *p*-dibromobenzene (Bezzi & Croatto, 1942; Croatto & Bezzi, 1949); *p*-diiodobenzene (α-phase: Hendricks, Maxwell, Mosley & Jefferson, 1933; Struchkov & Dun-Chai, 1959; Hinchliffe, Munn, Pritchard & Sunpicer, 1985; Alcobé *et al.*, 1994; β-phase at 333 K: Alcobé *et al.*, 1994); *p*-bromochlorobenzene (Hendricks, 1933; Klug, 1947); and *p*-iodotoluene (Ahn, Soled & Carpenter, 1972). We present here a more precise determination

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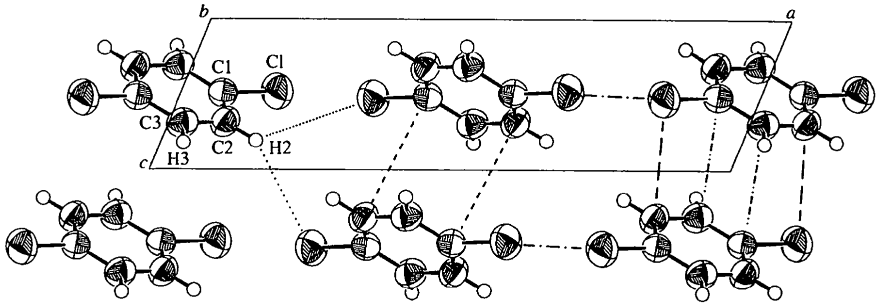
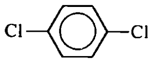


Fig. 1. View of the crystal packing projected in the (010) plane showing the atomic numeration. Shortest Cl···Cl, Cl···C, Cl···H and C···C intermolecular contacts are included. Their distances are given in Table 2.

of the *p*-dichlorobenzene, (I), α-phase structure at room temperature than that made by Croatto *et al.* (1952) and a comparison of intermolecular distances with those found in the structure determined at 100 K by Wheeler & Colson (1976).



(I)

Given three different atoms (Cl, C and H), six types of interatomic contacts can be considered. The shortest intermolecular contacts of each type for the 100 and 293 K structures are included in Table 2. A view of the crystal packing projected in the (010) plane shows several of these contacts (Fig. 1). The shortest Cl···Cl contacts have been considered responsible for the formation of molecular sheets which are stacked optimizing C···C contacts in the β-phase (Sarma & Desiraju, 1985).

Thermal expansion is observed for all contacts collected in Table 2, H···H being the greatest. These thermal expansions do not reflect the macroscopic dilatation anisotropy [maximum and minimum thermal expansion coefficients are $\alpha_1 = 1.2 \times 10^{-4}$ K^{-1} and $\alpha_3 = 2.1 \times 10^{-6}$ K^{-1} (Wheeler & Colson, 1976)]. This behaviour is due to, among others factors, the fact that none of the shortest contacts collected in Table 2 have the minimum thermal expansion direction. This direction lies in the (010) plane making an angle of 29° with the **a** direction (7° with **a***).

It is interesting to analyse in more detail the effect of the temperature on the H···Cl contacts which are the principal contributors to the potential energy (Bandoli, Clemente, Croatto & Panattoni, 1970). The temperature modifies the H···Cl distances but does not affect the angles around the H atoms (Table 2). These H···Cl contacts present a geometry which satisfies the requirements usually considered for the three-centred hydrogen bonding (Jeffrey & Saenger, 1991): C2—H2 is bonded to two Cl atoms (Table 2 and Fig. 1) in such a way that the H atom lies in the plane of C2 and the two Cl atoms [the deviation of H2 from the C2—Cl($\frac{1}{2}-x, \frac{1}{2}+y, 1-z$)—Cl($\frac{1}{2}-x, \frac{1}{2}+y, 2-z$) plane is 0.040 (4) Å]. The H3 atom also has two chlorine contacts but is slightly displaced from the C3—Cl($x, 1+y, z$)—Cl($x, 1+y, 1+z$) plane [0.279 (4) Å]. A Cambridge Structural Database (Allen & Kennard, 1993) search reveals that this geometry is very common in the structures of chlorinated compounds. About two thousand structures show C_{sp^2}—H intermolecularly bonded to two Cl—C with H···Cl distances below 4.0 Å and the sum of three angles around H in the 350–360° range. These contacts are observed even in the presence of other stronger intermolecular hydrogen bondings. The H···Cl distance distribution in these type of contacts begins at 2.6 Å, raises sharply to the maximum, located near 3.2 Å, and decreases smoothly (Fig. 2). Two of the H···Cl distances found in the *p*-dichlorobenzene α-phase are slightly shorter than the distribution maximum but the other two are near it (Table 2).

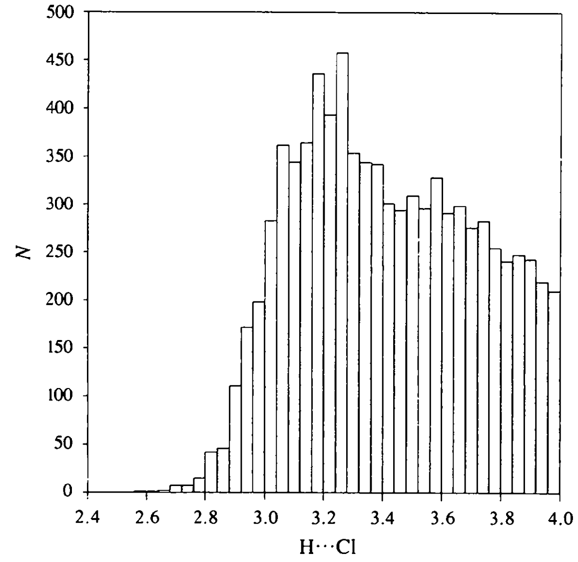


Fig. 2. H···Cl distance distribution in C—Cl···H···Cl—C bifurcated contacts (H bonded to C_{sp^2}). H-atom positions have been normalized (C—H distance 0.93 Å).

Experimental

Single crystals were obtained by slow sublimation over a few weeks at room temperature of the commercial product (purity greater than 99%). For the diffraction measurements, a crystal was mounted in a sealed capillary to prevent its sublimation.

Crystal data

$C_6H_4Cl_2$
$M_r = 146.99$
Monoclinic
$P2_1/a$
$a = 14.762\ (3)$ Å
$b = 5.832\ (2)$ Å
$c = 4.039\ (2)$ Å
$\beta = 112.78\ (2)°$
$V = 320.6\ (2)$ Å^3
$Z = 2$
$D_x = 1.523$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8$–$12°$
$\mu = 0.891$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.3 × 0.2 × 0.2 mm
Colourless

Data collection

Philips PW-1100 diffractometer
ω–2θ scan
Absorption correction: none
430 measured reflections
430 independent reflections
427 reflections with $I > 2\sigma(I)$

$\theta_{max} = 25.01°$
$h = -17 \rightarrow 16$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 4$
3 standard reflections
  frequency: 120 min
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.136$
$S = 1.069$
430 reflections
39 parameters
H atoms riding (see below)
$w = 1/[\sigma^2(F_o^2) + (0.0961P)^2 + 0.1088P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.037$

$\Delta\rho_{max} = 0.349$ e Å^{-3}
$\Delta\rho_{min} = -0.287$ e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.12 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cl—C1	1.744 (4)	C1—C2	1.374 (5)
C1—C3^{i}	1.367 (5)	C2—C3	1.370 (5)
C3^{i}—C1—C2	121.0 (3)	C3—C2—C1	119.3 (3)
C3^{i}—C1—Cl	119.4 (3)	C1^{i}—C3—C2	119.8 (4)
C2—C1—Cl	119.6 (3)		

Symmetry code: (i) $-x, 1 - y, 1 - z$.

Table 2. *Shortest intermolecular distances at 100 K ($d_{100\,K}$, Å) and 293 K ($d_{293\,K}$, Å) with their thermal expansions [$(\Delta d/d)/\Delta T\ 10^4$, K^{-1}]*

For Cl···H interactions, angles around H at 100 ($\Phi_{100\,K}$, °) and 293 K ($\Phi_{293\,K}$, °) are included. $\Delta d = d_{293\,K} - d_{100\,K}$, $d = (d_{293\,K} + d_{100\,K})/2$, $\Delta T = 193$ K. In the 293 K structure, the C—H length has been fixed at 0.93 Å. For comparison, the H-atom positions of the 100 K structure have been recalculated for giving the same bond length. In the 293 K structure the next longer distances for Cl···Cl, Cl···C, H···C and H···H interactions are 4.039 (3), 3.769 (5), 3.427 (6) and 3.034 (6) Å, respectively; in the case of the C···C interactions, the two distances given in the table are equal within the s.u. and the next one is 3.691 (6) Å; in addition to the H···Cl interactions cited in the table, there are two distances shorter than 4 Å: 3.628 (5) and 3.656 (5) Å.

	$d_{100\,K}$	$d_{293\,K}$	$(\Delta d/d)/\Delta T\ 10^4$
H3···H3^{i}	2.704 (7)	2.895 (6)	3.52 (15)
H3···C3^{ii}	3.175 (6)	3.288 (6)	1.81 (15)
C1···C2^{iii}	3.516 (6)	3.614 (6)	1.40 (10)
C1···C3^{iii}	3.557 (6)	3.620 (6)	0.93 (10)
Cl···C2^{iii}	3.653 (4)	3.716 (4)	0.88 (10)
Cl···Cl^{iv}	3.729 (2)	3.806 (2)	1.04 (5)
H2···Cl^{iv}	3.107 (5)	3.199 (5)	1.50 (10)
H2···Cl^{v}	3.015 (4)	3.064 (4)	0.83 (10)
H3···Cl^{vi}	3.150 (4)	3.261 (4)	1.81 (10)
H3···Cl^{vii}	3.283 (5)	3.352 (5)	1.09 (10)
	$\Phi_{100\,K}$	$\Phi_{293\,K}$	
C2—H2···Cl^{iv}	131.3 (4)	130.8 (4)	
C2—H2···Cl^{v}	148.5 (4)	148.6 (4)	
Cl^{iv}···H2···Cl^{v}	79.8 (1)	80.3 (1)	
C3—H3···Cl^{vi}	154.1 (4)	156.3 (4)	
C3—H3···Cl^{vii}	108.3 (4)	109.7 (4)	
Cl^{vi}···H3···Cl^{vii}	75.2 (1)	75.3 (1)	

Symmetry codes: (i) $-x, 2 - y, 2 - z$; (ii) $-x, 2 - y, 1 - z$; (iii) $x, y, -1 + z$; (iv) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, 2 - z$; (vi) $x, 1 + y, 1 + z$; (vii) $x, 1 + y, z$.

H atoms were placed in calculated positions using a riding model, with a fixed C—H distance (0.93 Å) and an overall isotropic factor refined.

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *PLUTON93* (Spek, 1993). Software used to prepare material for publication: *PARST95* (Nardelli, 1995).

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1,1,1-Trifluoro-3-phenyl-2-butyl *p*-Nitrobenzoate

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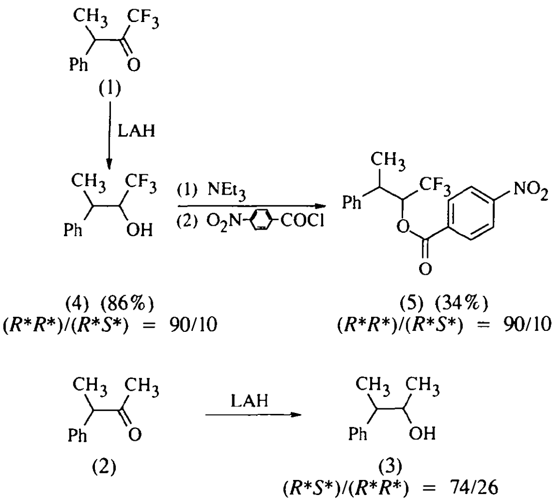
Abstract

The reduction of the trifluoromethylated ketone, 1,1,1-trifluoro-3-phenyl-2-butanone, (1), or its hydrogenated homologue, 3-phenyl-2-butanone, (2), with lithium aluminium hydride (LAH) gave 1,1,1-trifluoro-3-phenyl-2-butanol, (4), or 3-phenyl-2-butanol, (3), respectively, as a mixture of the (R^*R^*)/(R^*S^*) isomers. The title compound, $C_{17}H_{14}F_3NO_4$, (5), was obtained by a benzoylation reaction of the major diastereoisomer of (4). The *threo*-(R^*R^*) configuration is clearly evidenced in the crystal structure of (5). So, in the reduction of (1) or (2), the *threo* isomer is the major product. It is noteworthy that the presence of the CF_3 group enhances the diastereoselectivity of the reduction reaction.

Comment

The introduction of one or more F atoms in organic compounds results in changes in their chemical reactivity. Many research groups have explored the reactivity of trifluoromethylated ketones (Begue & Bonnet-Delpon, 1991; McClinton & McClinton, 1992). It has been recognized that the CF_3 group behaves as though it is bulkier than an isopropyl group (Bott, Field & Sternhell, 1980). Bearing in mind the steric size of the CF_3 group and its electronic influence, we believe that the diastereoselectivity of the reduction reaction would be altered by the introduction of a trifluoromethyl group.

During the course of our studies (Félix, Laurent & Mison, 1995), we were interested in the diastereoselectivity of the reduction of ketone (1) with LAH. It is known that the reduction of ketone (2) with LAH leads preferentially to the formation of the *threo*-(R^*R^*) isomer of alcohol (3) (Cram & Abdelhafez, 1952). The same conditions (large excess of LAH) were used to reduce ketones (1) and (2) (Félix *et al.*, 1995), and we observed a greater diastereoselectivity in the case of the formation of alcohol (4) with respect to alcohol (3) [(R^*S^*)/(R^*R^*) 74/26].



Analysis of the ^1H, ^{13}C and ^{19}F NMR spectra allowed us to determine the ratio of the two isomers of the benzoylated derivative (5) of alcohol (4), but did not allowed determination of the (R^*R^*)/(R^*S^*) configuration of the major isomer of (5). We therefore undertook the single-crystal X-ray structure analysis of this isomer. An *ORTEP* (Johnson, 1965) plot of (5) with the numbering system is shown in Fig. 1. It is clear that the major isomer of (5) has a *threo*-(R^*R^*) configuration. This is in agreement with the literature (Ramachandran, Teodorovic & Brown, 1993).