

Short Note

2,4,6-Trimethylbenzyl Chloride (α^2 -Chloroisodurene)

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Abstract: The X-ray structure of the title compound has been determined and it is compared with those of other substituted benzyl chlorides reported previously. It has an atypically long CH₂–Cl bond.

Keywords: 2,4,6-trimethylbenzyl chloride; X-ray structure; C–Cl bond length

1. Introduction

The formation of 2,4,6-trimethylbenzyl chloride **1** by chloromethylation of mesitylene was first mentioned by Sommelet in 1913 [1], although no data were given for the product. Subsequent reports [2–5] described the stepwise development of this into a reliable synthetic procedure [6], with the product characterised by melting point and boiling point values. The compound has also been characterised by infrared [7], ¹H and ¹³C nuclear magnetic resonance [8], and nuclear quadrupole resonance [9] spectroscopy, as well as mass spectrometry [10]. However, as far as we are aware, its solid-state structure has not been examined, perhaps as a result of its waxy nature and low melting point of 37 °C. We report here the crystal and molecular structure of **1** as determined by single crystal X-ray diffraction and compare the result with those of similar benzylic chlorides that have been previously reported.

2. Results

Crystals suitable for diffraction were obtained from the inner surface of a commercial bottle (Lancaster Synthesis) that had been stored for >20 years, allowing slow sublimation. The resulting structure (Figure 1) shows two chemically equivalent but crystallographically independent molecules per asymmetric unit. As expected, there are no significant intermolecular interactions, and the shape of each molecule is determined largely by steric factors and, in particular, the presence of the 2,6-dimethyl substituents, which forces the CH₂Cl group to take up an orientation with C–Cl almost perpendicular to the plane of the benzene ring. The key geometric parameters for **1** are compared with those for a range of other crystallographically characterised benzyl chlorides (Figure 2) taken from the Cambridge Structural Database (CSD) and shown in Table 1. These included benzyl chloride itself **2**, which is a liquid at room temperature but whose structure was determined at 150 K, and seven further crystalline compounds containing a benzene ring and only CH₂Cl, Me, or Cl groups: the three isomeric bis(chloromethyl)benzenes or α, α' -dichloroxylenes **3–5**, 1,3,5-tris(chloromethyl)benzene or $\alpha, \alpha', \alpha''$ -trichloromesitylene **6**, and the hexasubstituted benzene derivatives **7–9**. The parameters examined are the length of the ring to CH₂ bond, the length of the CH₂ to Cl bond, the ring C to CH₂ to Cl angle, and finally the torsion angle between the plane of the benzene ring and the CH₂ to Cl bond.

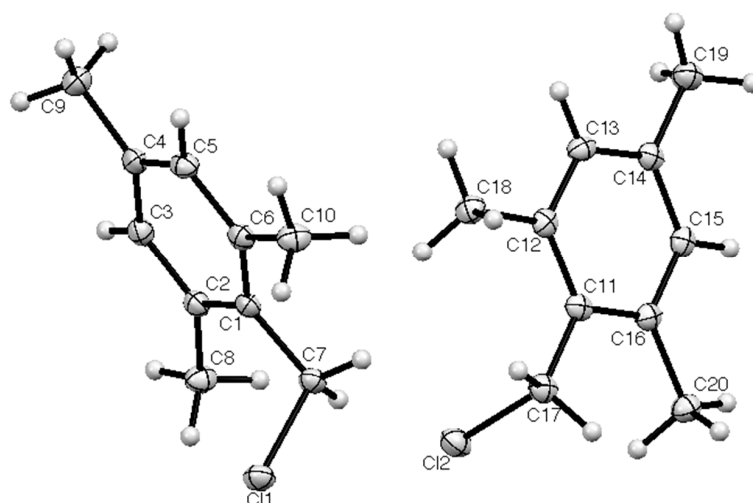


Figure 1. Molecular structures of **1** with anisotropic displacement ellipsoids drawn at 50% probability level.

Of the compounds examined, the molecules of **3**, **5**, **8**, and **9** lie on special positions that impose crystallographic symmetry on the molecule, thus exhibiting only one independent set of parameters for CH_2Cl , while the molecules of **4**, **6**, and **7** have all CH_2Cl groups with independent geometries; in addition **6**, similar to **1**, shows two independent molecules per asymmetric unit, thus giving rise to six sets of values.

While the length of the $\text{C}-\text{CH}_2$ bond does not vary significantly between any of the compounds, the same cannot be said for CH_2-Cl , where the values measured for the two molecules in our structure are significantly longer than most of the previously reported values. The value of the $\text{C}-\text{CH}_2-\text{Cl}$ angle also turns out to vary relatively little between the compounds, and although the first listed molecule of **1** has a high value of 112.3° , the difference from the normal range of $110\text{--}111.5^\circ$ is small. It is perhaps surprising to observe that the torsion angle between the plane of the aromatic ring and the $\text{C}-\text{Cl}$ bond is generally between 78° and 89° regardless of the position and nature of substituents present. Apart from a slightly lower value for two such bonds in one molecule of **6**, all the other values are in this range indicating that even in the absence of *ortho* substituents as in compound **1**, the favoured orientation in a benzyl chloride is to have the $\text{C}-\text{Cl}$ bond essentially perpendicular to the plane of the benzene ring.

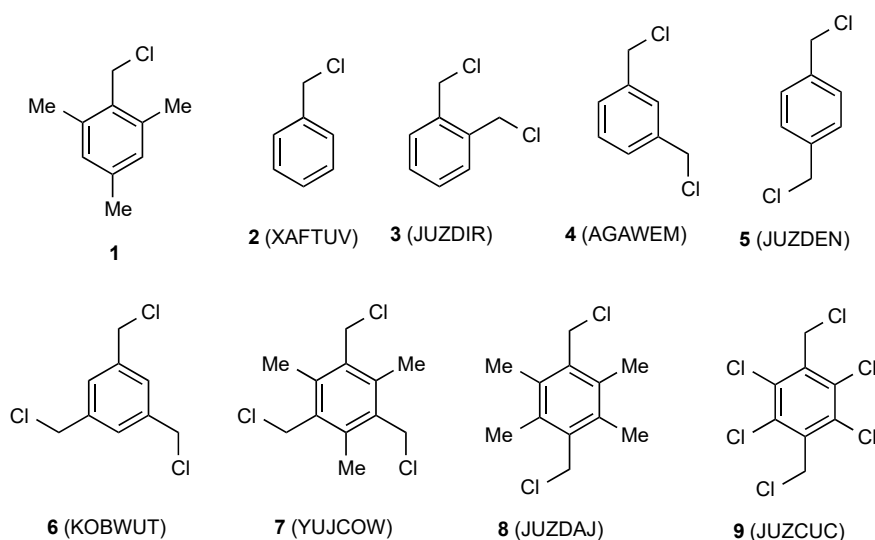


Figure 2. A survey of crystallographically characterised benzyl chlorides with CSD reference codes.

Table 1. Key geometric parameters for crystallographically characterised benzyl chlorides.

Compd	Length C–CH ₂ (Å)	Length CH ₂ –Cl (Å)	Angle C–CH ₂ –Cl°	Torsion Angle Ring/CH ₂ –Cl°	Reference
1	1.500(2)	1.831(1)	112.32(9)	85.50	this work
*	1.500(2)	1.829(1)	111.34(9)	85.51	
2	1.492(3)	1.801(3)	111.5(2)	78.38	[11]
3	1.498(6)	1.814(5)	111.5(3)	81.03	[12]
4	1.501(2)	1.811(1)	109.98(8)	78.49	[13]
	1.500(2)	1.815(1)	109.92(8)	83.52	
5	1.494(3)	1.805(3)	111.0(2)	86.06	[12]
6	1.498(3)	1.806(2)	110.6(2)	85.98	[14]
	1.494(3)	1.804(3)	110.5(2)	84.29	
	1.496(3)	1.793(2)	110.8(1)	82.11	
*	1.495(3)	1.805(2)	110.4(2)	77.48	
*	1.495(3)	1.804(2)	111.2(1)	68.88	
*	1.501(3)	1.790(2)	110.1(1)	82.60	
7	1.501(3)	1.814(3)	111.3(2)	84.31	[15]
	1.502(3)	1.815(2)	111.3(2)	86.53	
	1.504(5)	1.810(3)	109.8(2)	83.13	
8	1.493(5)	1.817(5)	111.3(3)	88.55	[12]
9	1.497(3)	1.796(3)	110.6(2)	81.11	[12]

* Values for second molecule in the asymmetric unit.

In summary, we obtained the X-ray crystal structure of 2,4,6-trimethylbenzyl chloride for the first time and found it to have two independent molecules per asymmetric unit both with a C–Cl bond length of 1.83 Å, which is slightly longer than for a range of comparable benzyl chloride structures previously reported.

3. Experimental

The structure was determined on a Rigaku XtalLAB P200 diffractometer using graphite monochromated Mo K α radiation $\lambda = 0.71075$ Å.

Crystal data for C₁₀H₁₃Cl, $M = 168.67$ g mol⁻¹, colourless prism, crystal dimensions 0.10 × 0.10 × 0.10 mm, triclinic, space group *P*-1, $a = 7.8666(9)$, $b = 10.2719(13)$, $c = 11.8789(15)$ Å, $\alpha = 87.557(9)$, $\beta = 77.371(8)$, $\gamma = 73.908(7)^\circ$, $V = 899.8(2)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.245$ g cm⁻³, $T = 93$ K, $R_1 = 0.0290$, $Rw_2 = 0.0890$ for 3040 reflections with $I > 2\sigma(I)$, and 205 variables, $R_{\text{int}} = 0.0494$, Goodness of fit on $F^2 = 1.063$. Data have been deposited at the Cambridge Crystallographic Data Centre as CCDC 2010796. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/getstructures>. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXL Version 2018/3 [16]). Hydrogen atoms were located from difference Fourier maps and refined at idealized positions riding on the carbon atoms with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ and C–H 0.95–0.99 Å. All CH₃ hydrogen atoms were allowed to rotate but not to tip.

Author Contributions: A.M.Z.S. collected the X-ray data and solved the structure; R.A.A. designed the experiments, analysed the data, and wrote the paper. All authors have read and agreed to the published version of the manuscript.

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