Crystal structure of (2*S*,4*S*,7*S*)-7,7-dichloro-4-(1-chloro-1-methyl-ethyl)-1-(2,2,2-trichloroethyl)bicyclo[4.1.0]heptane, $C_{12}H_{16}Cl_6$

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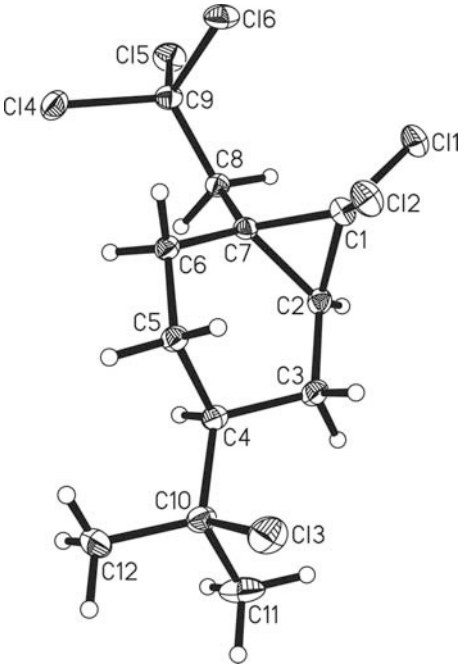

Abstract

$C_{12}H_{16}Cl_6$, orthorhombic, $P2_12_12_1$ (no. 19), a = 6.0742(3) Å, b = 9.7189(6) Å, c = 26.700(1) Å, V = 1576.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.019, $wR_{ref}(F^2)$ = 0.045, T = 200 K.

Source of material

A mixture of 1 g (7.34 mmol) of β-pinene and 1 mL (7.11 mmol) of triethylamine in 15 mL of carbon tetrachloride was added to 1.1 g (8.09 mmol) of $ZnCl_2$ in 15 mL of water. The mixture was stirred at room temperature. When the reaction was achieved, the reaction mixture was diluted with 25 mL of water, extracted with carbon tetrachloride (3 × 10 mL), dried over Na_2SO_4. After concentration to dryness, 3 g (14.7 mmol) of potassium *tert*-butanolate and 0.02 g (0.1 mmol) of benzyltriethylammonium chloride in 10 mL of carbon tetrachloride was added. The mixture was stirred for 10 min, and 0.8 mL (9.8 mmol) of chloroform was added dropwise (30 min). The mixture was stirred for 8 h at room temperature and hydrolysed by addition of 30 mL of water. The organic layer was extracted with dichloromethane (3 × 10 mL), dried over Na_2SO_4 and evaporated under vacuum. The title compound was isolated by column chromatography on silica gel using hexane as eluent (yield 90 %). The structure of the title molecule was confirmed using ^{1}H and ^{13}C NMR sperctroscopy.

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The ^{1}H NMR data indicate the presence of a cyclopropanic proton at 0.9 ppm and a CH_2CCl_3 as a singlet at 2.1 ppm. In ^{13}C NMR, the CCl_3 group gives rise to a signal at 99 ppm, CCl_2 group appears at 69 ppm, and the CCl group at 62.2 ppm.

Experimental details

The absolute configuration of the title compound was confirmed by refinement of the Flack parameter [x = 0.01(4)].

Discussion

The enormous importance of chlorinated cyclopropanes, in various scientific fields, lies in their diverse biological pyrethroid activity [1-3] and their usefulness as valuable building blocks in organic synthesis [4]. In the course of our research programs aimed at the synthesis of natural chlorinated compounds [5-8], we report here the structure of a new organic chlorinated monoterpene.

The X-ray single crystal structure analysis permits us to assign the absolute configuration of C2, C4 and C7. The analysis clearly shows the compound to be (2*S*,4*S*,7*S*)-7,7-dichloro-4-(1-chloro-1-methyl-ethyl)-1-(2,2,2-trichloroethyl)bicyclo[4.1.0]heptane. The seven-membered ring adopts a conformation with cyclopropane ring bent away from the C4 fragment (angle between the planes defined by C1, C2, C7 and C6, C7, C2, C3: 68.63(8)°). The examination of the cyclopropyl moiety indicates that the ring is unsymmetrical, with unequal C—C bond lengths. The C1—C2 bond length is 1.499(2) Å, while C1—C7 with 1.517(2) Å and C2—C7 with 1.544(2) Å are longer. The bond angles within the three-membered ring reflect the difference observed between bond lengths, with the smallest angle at C7 (∠(C1–C7–C2) 58.64(9)). The C—Cl bond length of the cyclopropane ring (d(C1—Cl1) = 1.766(1) Å and d(C1—Cl2) = 1.755(2) Å) are in the expected range, as in the Cl1–C1–Cl2 angle of 109.99(8)°.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.14 × 0.22 × 0.47 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.70 cm^{-1}
Diffractometer, scan mode:	STOE IPDS II, ω
$2\theta_{max}$:	53.36°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	24353, 3339
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3116
$N(param)_{refined}$:	163
Programs:	SHELXS-97 [9], SHELXL-97 [10]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*a*	0.0343	0.2881	0.5914	0.029
H(3A)	4*a*	0.4297	0.2344	0.5443	0.033
H(3B)	4*a*	0.2098	0.1450	0.5384	0.033
H(4)	4*a*	0.3053	0.0166	0.6104	0.028
H(5A)	4*a*	0.6839	0.1899	0.6135	0.029
H(5B)	4*a*	0.6683	0.0515	0.6458	0.029
H(6A)	4*a*	0.3985	0.1349	0.6954	0.028
H(6B)	4*a*	0.5573	0.2642	0.6887	0.028
H(8A)	4*a*	0.0039	0.2045	0.6937	0.027
H(8B)	4*a*	–0.0465	0.3579	0.6759	0.027
H(11A)	4*a*	0.3094	–0.0266	0.4996	0.075
H(11B)	4*a*	0.2555	–0.1532	0.5359	0.075
H(11C)	4*a*	0.4522	–0.1647	0.4963	0.075
H(12A)	4*a*	0.7373	–0.1244	0.6122	0.068
H(12B)	4*a*	0.7133	–0.2244	0.5649	0.068
H(12C)	4*a*	0.5180	–0.2135	0.6049	0.068

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*a*	0.2968(2)	0.4097(1)	0.61857(6)	0.0244(7)	0.0227(6)	0.0304(7)	0.0003(5)	0.0003(6)	0.0024(6)
C(2)	4*a*	0.1959(2)	0.2807(1)	0.59801(5)	0.0230(7)	0.0258(7)	0.0238(7)	–0.0001(6)	–0.0044(5)	0.0015(5)
C(3)	4*a*	0.3157(2)	0.1829(2)	0.56302(5)	0.0291(8)	0.0307(7)	0.0214(7)	0.0003(6)	–0.0028(6)	–0.0020(6)
C(4)	4*a*	0.4248(2)	0.0642(1)	0.59135(5)	0.0243(7)	0.0246(7)	0.0214(6)	–0.0029(6)	0.0010(5)	–0.0014(5)
C(5)	4*a*	0.5807(2)	0.1259(2)	0.63020(5)	0.0240(7)	0.0271(7)	0.0225(7)	0.0015(6)	–0.0019(5)	–0.0024(5)
C(6)	4*a*	0.4528(2)	0.2032(1)	0.67087(5)	0.0238(7)	0.0245(7)	0.0209(7)	0.0006(6)	–0.0027(5)	–0.0014(5)
C(7)	4*a*	0.2579(2)	0.2901(1)	0.65400(5)	0.0218(7)	0.0192(6)	0.0223(6)	–0.0018(5)	–0.0026(6)	–0.0019(5)
C(8)	4*a*	0.0681(2)	0.2978(1)	0.69066(5)	0.0214(7)	0.0230(7)	0.0237(7)	–0.0029(5)	–0.0014(6)	–0.0007(5)
C(9)	4*a*	0.1181(3)	0.3505(2)	0.74357(6)	0.0273(7)	0.0272(7)	0.0265(7)	–0.0006(6)	0.0026(6)	–0.0039(6)
C(10)	4*a*	0.5319(3)	–0.0454(2)	0.55743(5)	0.0325(8)	0.0286(8)	0.0240(7)	–0.0029(6)	0.0041(6)	–0.0025(6)
C(11)	4*a*	0.3732(4)	–0.1025(2)	0.51888(7)	0.048(1)	0.054(1)	0.048(1)	–0.001(1)	–0.0039(9)	–0.0296(9)
C(12)	4*a*	0.6343(4)	–0.1624(2)	0.58753(7)	0.072(1)	0.0283(8)	0.0352(8)	0.0140(9)	0.0090(9)	–0.0004(7)
Cl(1)	4*a*	0.12619(7)	0.55663(4)	0.62060(2)	0.0355(2)	0.0256(2)	0.0423(2)	0.0066(2)	0.0016(2)	0.0052(2)
Cl(2)	4*a*	0.56827(6)	0.45794(4)	0.60445(2)	0.0276(2)	0.0292(2)	0.0462(2)	–0.0058(2)	0.0068(2)	0.0057(2)
Cl(3)	4*a*	0.75787(8)	0.03420(5)	0.52246(2)	0.0436(2)	0.0492(2)	0.0392(2)	–0.0013(2)	0.0191(2)	0.0002(2)
Cl(4)	4*a*	0.25696(7)	0.22922(4)	0.78243(1)	0.0437(2)	0.0416(2)	0.0230(2)	0.0093(2)	–0.0015(2)	–0.0011(1)
Cl(5)	4*a*	–0.13878(7)	0.38643(4)	0.77399(2)	0.0348(2)	0.0410(2)	0.0391(2)	0.0039(2)	0.0127(2)	–0.0063(2)
Cl(6)	4*a*	0.27725(7)	0.50318(4)	0.74191(1)	0.0395(2)	0.0326(2)	0.0376(2)	–0.0114(2)	–0.0003(2)	–0.0107(2)

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