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The Crystal and Molecular Structure of 2-Chloro-4-*tert*-butyl-6-methylthiacyclohexane Sulphoxide

By Francis Robert and Sylvie Gauchotte

Laboratoire de Chimie des Métaux de Transition, Equipe de Recherche associée au CNRS n° 608,
4 place Jussieu, 75230 *Paris CEDEX* 05, *France*

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$C_{10}H_{19}SOCl$ is orthorhombic, space group *Pbcn*, with $a = 20{\cdot}124\ (5)$, $b = 12{\cdot}921\ (3)$, $c = 9{\cdot}238\ (2)$ Å, $Z = 8$. The structure was refined to a final *R* of 0·078 for 1274 counter reflexions. The O atom is in the axial position. The weak ring distortion is related to the twist of the *tert*-butyl group.

Introduction

Having solved the structure of 2-chloro-4-*tert*-butylthiacyclohexane sulphoxide (CTTH, Robert, 1977) we report the structure of 2-chloro-4-*tert*-butyl-6-methylthiacyclohexane sulphoxide. Our goal is to obtain information on conformational differences, if any, of the thiacyclohexane ring. Since the O atom in CTTH is equatorial and because NMR shows an axial O atom in the title compound it is interesting to look for distortion differences in the ring.

During this work we will refer to force-field calculations of 4-*tert*-butylcyclohexane (Altona & Sundaralingam, 1970, hereinafter AS, 1970) and to two X-ray investigations: *cis*-4-*tert*-butylcyclohexane-1-carboxylic acid (van Koningsveld, 1972) and 2b *seq cis*-1-phenyl-4-*tert*-butylcyclohexanecarboxylic acid (Mallissard, Sicsic, Welvart, Chiaroni, Riche & Pascard-Billy, 1974) referred to respectively as BCA and PBCA.

Experimental

The description by Bory, Lett, Moreau & Marquet (1973) of halogenation of sulphoxides shows the high stereoselectivity of these reactions. This stereoselectivity has been used to isolate the title compound.

Table 1. *Crystal data*

Formula	$C_{10}H_{19}SOCl$
M_r	222·5
Density	$D_c = 1·232$, $D_m = 1·20$ g cm^{-3}
Space group	*Pbcn*
Orthorhombic cell	$a = 20·124$ (5), $b = 12·921$ (3), $c = 9·238$ (2) Å $Z = 8$, $V = 2402$ Å^3
Linear absorption coefficient	$\mu = 40·67$ cm^{-1} ($\lambda = 1·5418$ Å)
Crystal size	0·4 × 0·2 × 0·2 mm
$F(000)$	960

The crystals are colourless prisms. The space group corresponding to the systematic absences $0kl$ with $k = 2n + 1$, $h0l$ with $l = 2n + 1$, $hk0$ with $h + k = 2n + 1$ is *Pbcn*. The lattice constants were refined from eight high-Bragg-angle reflexions. Crystal data are summarized in Table 1. A crystal was mounted with **a** parallel to the φ axis of a CAD-3 Enraf–Nonius automated diffractometer. Background counting time was taken equal to peak counting time and attenuation filters were introduced to operate in the linear part of the counter and to maintain a constant counting rate. The scan speed was equal to $\frac{1}{6}°$ s^{-1}. The θ–2θ scan mode was used up to $\theta = 66°$ to collect 2165 independent reflexions with Cu $K\alpha$ Ni-filtered radiation at room temperature. 1274 reflexions with $I > 3\sigma(I)$, based on counting statistics, were considered as observed. The decrease of 12% of the intensity of two standard reflexions was interpreted as a slow sublimation of the crystal. This phenomenon was also observed for CTTH. The intensities were corrected for the Lorentz–polarization factor but not for absorption. The scale and overall thermal ($B = 5·8$ Å^2) factors were deduced from a Wilson plot.

Structure determination and refinement

The structure was solved by direct methods. The 400 reflexions with $E > 1·28$ were used with *MULTAN* (Germain, Main & Woolfson, 1971). The E map computed from the best set of phases led to the coordinates of all the non-hydrogen atoms. A first isotropic least-squares refinement gave $R = \Sigma||F_o| - |F_c||/\Sigma |F_o| = 0·17$ which fell to 0·11 with anisotropic thermal parameters.

At this stage a difference synthesis showed all the H atoms in their expected positions. Refinement of their coordinates led to $R = 0·08$ with isotropic thermal parameters equal to those of their attached C atom. A weighting scheme, $w = (12·9 + 259·7F_o)^{-1}$, applied in the last cycles led to a final R of 0·078 and R_w $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}\}$ of 0·094.

All calculations were performed on an IBM 370-168 computer with local versions of *ORFLS* (Busing, Martin & Levy, 1962) for full-matrix least-squares calculations, *GEST* (De Rango, Tsoucaris, Zelwer & Baudour, 1964) for Fourier syntheses and NRC programs (Ahmed, Hall, Pippy & Huber, 1966) for geometrical calculations. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The anomalous dispersion of the Cl and S atoms was ignored.

Table 2. *Fractional atomic coordinates* (× 10^4)

Estimated standard deviations (× 10^4) are in parentheses.

	x	y	z
Cl	964 (1)	10734 (2)	6242 (3)
S	2197 (1)	9610 (1)	5993 (2)
O	2173 (2)	9264 (4)	7512 (5)
C(2)	1343 (3)	9665 (5)	5353 (8)
C(3)	975 (3)	8690 (5)	5687 (7)
C(4)	1232 (3)	7756 (4)	4824 (6)
C(5)	1965 (3)	7587 (4)	5192 (7)
C(6)	2409 (3)	8508 (5)	4859 (7)
C(7)	812 (3)	6752 (5)	5014 (6)
C(8)	897 (4)	6281 (7)	6495 (8)
C(9)	1010 (4)	5981 (6)	3853 (9)
C(10)	75 (3)	7009 (6)	4773 (9)
C(11)	3145 (3)	8243 (7)	5149 (12)

Table 3. *Hydrogen atom coordinates* (× 10^3) *and their e.s.d.'s* (× 10^3) *in parentheses*

	x	y	z
H(21)	139 (3)	984 (5)	411 (8)
H(31)	557 (4)	876 (5)	558 (7)
H(32)	99 (3)	855 (5)	673 (7)
H(41)	120 (3)	794 (5)	366 (8)
H(51)	212 (3)	691 (5)	449 (8)
H(52)	202 (3)	738 (5)	633 (7)
H(61)	235 (4)	877 (6)	377 (8)
H(81)	65 (4)	564 (6)	655 (8)
H(82)	79 (4)	683 (6)	734 (9)
H(83)	131 (4)	603 (6)	661 (8)
H(91)	141 (4)	580 (6)	403 (9)
H(92)	79 (4)	518 (6)	398 (8)
H(93)	95 (4)	640 (5)	285 (9)
H(101)	−10 (3)	734 (5)	576 (7)
H(102)	−1 (3)	734 (5)	377 (7)
H(103)	−13 (3)	634 (5)	460 (7)
H(111)	337 (4)	879 (6)	481 (9)
H(112)	325 (4)	767 (6)	422 (9)
H(113)	315 (4)	810 (6)	632 (9)

Atomic parameters are listed in Tables 2 and 3.*

Description of the structure

Atomic numbering and bond distances are shown in Fig. 1. As for CTTH (Robert, 1977) the ring is in the

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32743 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

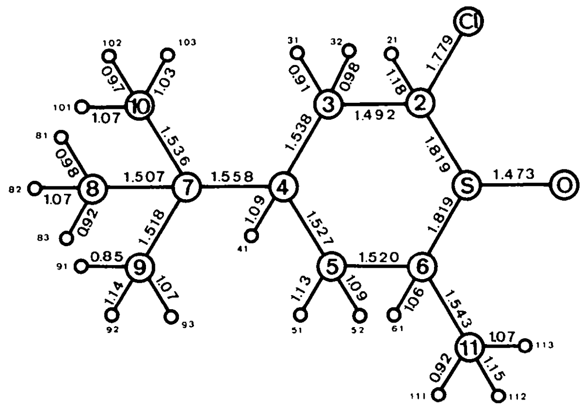

Fig. 1. Atomic numbering and bond distances (Å). The e.s.d.'s are less than 0·009 Å for C–C, C–S, C–Cl, S–O bonds and 0·06 Å for C–H bonds.

Table 4. *Bond angles* (°)

The e.s.d.'s in parentheses refer to the last decimal place.

O–S–C(2)	106·9 (3)	H(51)–C(5)–C(6)	109 (4)
O–S–C(6)	108·5 (3)	H(51)–C(5)–H(52)	110 (5)
C(2)–S–C(6)	93·7 (3)	H(52)–C(5)–C(4)	111 (4)
S–C(2)–C(3)	111·7 (5)	H(52)–C(5)–C(6)	109 (4)
S–C(2)–Cl	106·5 (4)	H(61)–C(6)–C(5)	112 (4)
Cl–C(2)–C(3)	110·3 (5)	H(61)–C(6)–S	105 (4)
C(2)–C(3)–C(4)	112·8 (5)	H(61)–C(6)–C(11)	110 (4)
C(3)–C(4)–C(5)	108·9 (5)	H(81)–C(8)–C(7)	109 (5)
C(3)–C(4)–C(7)	114·3 (5)	H(82)–C(8)–C(7)	112 (4)
C(5)–C(4)–C(7)	112·4 (5)	H(83)–C(8)–C(7)	111 (5)
C(4)–C(5)–C(6)	114·2 (5)	H(81)–C(8)–H(82)	116 (6)
C(5)–C(6)–C(11)	110·9 (6)	H(81)–C(8)–H(83)	99 (7)
C(5)–C(6)–S	111·0 (4)	H(82)–C(8)–H(83)	109 (7)
C(11)–C(6)–S	107·3 (5)	H(91)–C(9)–C(7)	108 (6)
C(4)–C(7)–C(8)	112·1 (5)	H(92)–C(9)–C(7)	114 (4)
C(4)–C(7)–C(9)	108·9 (5)	H(93)–C(9)–C(7)	104 (4)
C(4)–C(7)–C(10)	109·2 (5)	H(91)–C(9)–H(92)	95 (7)
C(8)–C(7)–C(9)	110·2 (6)	H(91)–C(9)–H(93)	113 (7)
C(8)–C(7)–C(10)	109·1 (6)	H(92)–C(9)–H(93)	121 (6)
C(9)–C(7)–C(10)	107·0 (5)	H(101)–C(10)–C(7)	106 (4)
H(21)–C(2)–S	104 (3)	H(102)–C(10)–C(7)	111 (4)
H(21)–C(2)–Cl	109 (3)	H(103)–C(10)–C(7)	105 (4)
H(21)–C(2)–C(3)	114 (3)	H(101)–C(10)–H(102)	122 (5)
H(31)–C(3)–C(2)	112 (4)	H(101)–C(10)–H(103)	111 (5)
H(31)–C(3)–C(4)	111 (4)	H(102)–C(10)–H(103)	100 (5)
H(31)–C(3)–H(32)	100 (6)	H(111)–C(11)–C(6)	105 (5)
H(32)–C(3)–C(2)	110 (4)	H(112)–C(11)–C(6)	101 (4)
H(32)–C(3)–C(4)	110 (4)	H(113)–C(11)–C(6)	102 (4)
H(41)–C(4)–C(3)	108 (4)	H(111)–C(11)–H(112)	97 (6)
H(41)–C(4)–C(5)	107 (4)	H(111)–C(11)–H(113)	119 (7)
H(41)–C(4)–C(7)	105 (4)	H(112)–C(11)–H(113)	129 (6)
H(51)–C(5)–C(4)	104 (4)		

Table 5. *Equation of mean least-squares plane and deviation of atoms from this plane* (Å)

An asterisk denotes atoms not included in the calculation of the plane.

C(2)	0·010 (7)	S*	−1·001 (1)
C(3)	−0·009 (6)	O*	−2·311 (4)
C(5)	0·008 (7)	C(4)*	0·704 (6)
C(6)	−0·008 (7)	C(7)*	0·842 (6)

$$-0\cdot2603X - 0\cdot0671Y - 0\cdot9632Z + 6\cdot3151 = 0$$

Table 6. *Torsion angles* (°) *of some 4-tert-butylcyclohexane and 4-tert-butylthiacyclohexane derivatives*

Torsion angle	*a*	*b*	*c*	*d*		*e*
6–1–2–3	−51·4	−55·6	−53	−59·0	−58·9	−61·0
2–1–6–5	52·9	57·0	53	60·7	59·8	58·8
1–2–3–4	54·4	54·3	57	63·4	63·9	67·7
1–6–5–4	−57·1	−57·7	−57	−66·7	−65·9	−65·2
2–3–4–5	−55·9	−52·7	−56	−58·8	−58·3	−59·9
3–4–5–6	57·2	54·8	56	60·2	59·1	59·0
Mean	54·8	55·4	55·3	60·4	61·0	61·9

References: (*a*) van Koningsveld (1972). (*b*) Altona & Sundaralingam (1970). (*c*) Mallissard, Sicsic, Welvart, Chiaroni, Riche & Pascard-Billy (1974). (*d*) Robert (1977). (*e*) This work.

expected chair conformation. The O atom is in the axial position. The methyl is *cis* to the Cl atom. Bond angles are listed in Table 4.

Thiacyclohexane ring

Deviations of C(2), C(3), C(5), C(6) from their mean plane (Table 5) are not significant, but they may be due to the asymmetric distortion of the ring related to the twist of the *tert*-butyl group (see below). Table 6 compares the torsion angles of the ring for AS (1970), PBCA, BCA, CTTH and for this work. The mean torsion angles are around 55·2° for cyclohexane rings but around 61·1° for heterocyclic compounds such as thiacyclohexane. Bucourt & Hainaut (1965) have already computed a mean value of 54·5° for cyclohexane rings. AS (1970) noticed that the small C–X–C angle [here C(2)–S–C(6) is 93·7°] has a puckering effect on the ring and predicted in that situation torsion angles greater than 60°.

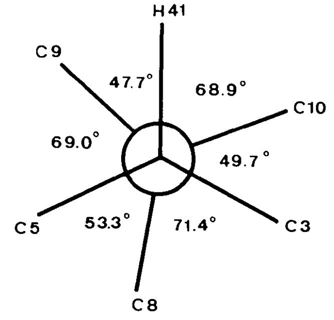

Fig. 2. Newman projection through C(4)–C(7).

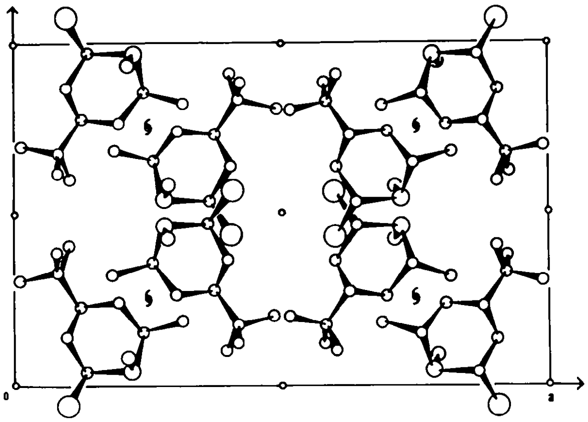

Fig. 3. Projection of the structure along **c**.

tert-Butyl group

Fig. 2 is the Newman projection through C(4)–C(7). The *tert*-butyl group is twisted away from the staggered position by about 10°. This value is greater than for PBCA (6°), BCA (6°), BCA (8°), and CTTH (8 and 6°).

Sulphoxide group

The O atom is axial. C(2)–S and C(6)–S bonds are equal (1·819 Å). The S–O distance is 1·473 Å. All these values are similar to those in other sulphoxides (Robert, 1977).

The crystal packing is governed by van der Waals contacts (Fig. 3).

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The Crystal and Molecular Structure of Triaqua[2,6-bis(2'-pyridyl)-4-(2'-pyridinio)-1,3,5-triazine]nickel(II) Bromide Monohydrate

By G. A. Barclay, R. S. Vagg and E. C. Watton

School of Chemistry, Macquarie University, North Ryde, NSW 2113, *Australia*

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$[C_{18}H_{13}N_6(H_2O)_3Ni]^{3+}.3Br^-.H_2O$ is monoclinic, space group $P2_1$, with a = 12·06 (4), b = 11·23 (4), c = 8·95 (2) Å, β = 96·5 (2)°, Z = 2. The structure was refined to R 0·069 for 1363 photographic intensities. The Ni atom is at the centre of a distorted octahedron of three water molecules [av. Ni–O 2·07 (2) Å] and three N atoms of the tridentate ligand. The bond from the metal atom to the central triazine ring of the ligand molecule [Ni–N 1·97 (2) Å] is significantly shorter than those to the two outer pyridyl rings [av. Ni–N 2·15 (2) Å]. The N atom of the pyridyl ring which is not coordinated to the Ni atom is protonated; all four aromatic rings of the ligand are coplanar. There is evidence for the existence of a network of hydrogen bonds between the pyridinium ion, the Br^- ions and the water molecules.

Introduction

2,4,6-Tris(2'-pyridyl)-1,3,5-triazine (tpt) (I) has been shown to act primarily as a tridentate ligand, similar to 2,2',2''-terpyridine, in forming complexes with bivalent Ni (Vagg, Warrener & Watton, 1967), Co (Vagg, Warrener & Watton, 1969; Goodwin, Sylva, Vagg & Watton, 1969) and the lanthanides (Durham, Frost &