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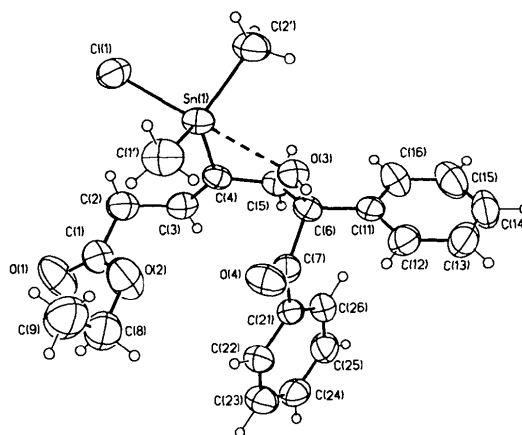

Fig. 1. General view (*SHELXTL-Plus* graphic) of the molecule, showing the atom-numbering scheme. Anisotropic ellipsoids represent 50% probability boundaries. H atoms are represented as spheres of arbitrary radii.

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Structure of Ethyl (Z)-4-(Chlorodimethylstannyl)-6-hydroxy-7-oxo-6,7-diphenyl-3-heptenoate

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Fig. 2. Stereoscopic view (*SHELXTL-Plus* graphic) of the unit cell.

Abstract

The atoms bound to Sn form a distorted trigonal bipyramid with the three C atoms in the equatorial [Sn—C 2.113(6), 2.122(5), 2.144(4) Å; C—Sn—C 116.8(2), 116.4(2), 118.0(2)°] and Cl and O in the apical positions [Sn—Cl 2.460(2), Sn—O 2.575(3) Å; Cl—Sn—O 172.53(9)°]. The remaining bond angles around Sn are in the range 70.7(2)–102.8(1)°.

Comment

The structure determination of the title compound was undertaken to confirm the presence of an intramolecular coordination between the Sn atom and the hydroxy group indicated by multinuclear NMR measurements. The Sn centre has a distorted trigonal bipyramidal environment. A similar coordination in the liquid phase has been demonstrated for other lone-pair-possessing nuclei (Jastrzebski, 1991) such as nitrogen (Jurkschat, Tzschach, Meunier-Piret & Van Meerssche, 1985; van Koten, Jastrzebski, Noltes, Verhoeckx, Spek & Kroon, 1980) and oxygen (Abbas & Poller, 1974; Kuivila, Dixon, Maxfield, Scarpa, Topka, Tsai & Wursthorn, 1975).
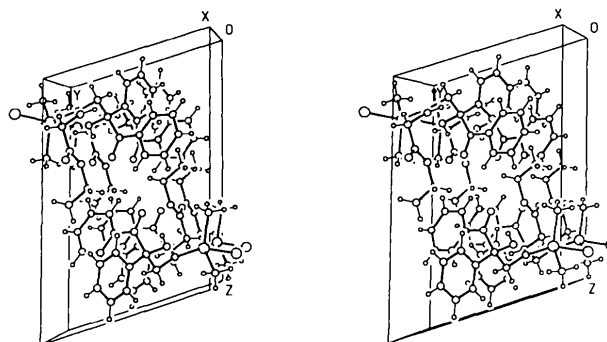
Experimental

Crystal data

$C_{23}H_{27}ClO_4Sn$	$Z = 2$
$M_r = 521.61$	$D_x = 1.455$ Mg m^{-3}
Triclinic	Mo $K\alpha$ radiation
$P\bar{1}$	$\lambda = 0.71073$ Å
$a = 8.321$ (3) Å	Cell parameters from 24
$b = 10.271$ (3) Å	reflections
$c = 15.313$ (4) Å	$\theta = 8.1$–14.6°
$\alpha = 71.59$ (2)°	$\mu = 1.21$ mm^{-1}
$\beta = 84.88$ (2)°	$T = 293$ (1) K
$\gamma = 73.50$ (2)°	0.36 × 0.22 × 0.12 mm
$V = 1190.6$ (7) Å^3	Colourless

Data collection

Nicolet *R3m*/V diffractometer	2573 observed reflections
$\theta/2\theta$ scans	[$F > 4.0\ \sigma(F)$]
Absorption correction:	$R_{int} = 0.035$
empirical	$\theta_{max} = 22.5$°
$T_{min} = 1.00,\ T_{max} = 0.94$	$h = -9 \rightarrow 9$
6405 measured reflections	$k = -12 \rightarrow 12$
3124 independent reflections	$l = 0 \rightarrow 17$

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Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.001$
Final $R = 0.0323$	$\Delta\rho_{max} = 0.3$ e Å^{-3}
$wR = 0.0388$	$\Delta\rho_{min} = -0.6$ e Å^{-3}
$S = 0.8672$	Atomic scattering factors
2573 reflections	from International Tables
263 parameters	for X-ray Crystallogra-
Only H-atom U's refined	phy (1974, Vol. IV, Table
Calculated weights	2.2B)
$w=1/[\sigma^2(F)+0.000841F^2]$	

Data collection: Nicolet R3m/V software, release 4.11. Cell refinement: Nicolet R3m/V software. Data reduction: Nicolet R3m/V software. Program(s) used to solve structure: Patterson function with SHELXTL-Plus (Sheldrick, 1987). Program(s) used to refine structure: SHELXTL-Plus. Software used to prepare material for publication: PARST (Nardelli, 1983), EUCLID (Spek, 1982), MISSYM (Le Page, 1987), PCK83 (Williams, 1984).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sn(1)	0.10700 (4)	0.02614 (3)	0.83256 (2)	0.0493
Cl(1)	−0.0483 (2)	−0.1549 (1)	0.89348 (9)	0.0686
O(1)	−0.4958 (5)	0.2184 (5)	0.6462 (3)	0.0941
O(2)	−0.2497 (5)	0.2641 (5)	0.6242 (3)	0.0939
O(3)	0.2430 (4)	0.2345 (3)	0.7811 (2)	0.0483
O(4)	0.1051 (4)	0.3955 (4)	0.6270 (2)	0.0655
C(1)	−0.3700 (7)	0.2200 (6)	0.6768 (4)	0.0592
C(1')	0.1755 (8)	−0.0060 (6)	0.7032 (4)	0.0751
C(2)	−0.3298 (6)	0.1702 (6)	0.7774 (4)	0.0613
C(2')	0.2940 (7)	−0.0538 (5)	0.9361 (4)	0.0673
C(3)	−0.2383 (6)	0.2573 (5)	0.8062 (3)	0.0527
C(4)	−0.0789 (6)	0.2201 (5)	0.8315 (3)	0.0431
C(5)	−0.0067 (6)	0.3232 (5)	0.8558 (3)	0.0470
C(6)	0.1281 (5)	0.3663 (5)	0.7855 (3)	0.0439
C(7)	0.0497 (6)	0.4472 (5)	0.6885 (3)	0.0474
C(8)	−0.269 (1)	0.3086 (8)	0.5236 (4)	0.0971
C(9)	−0.188 (1)	0.1885 (8)	0.4884 (5)	0.1086
C(11)	0.2274 (6)	0.4541 (5)	0.8116 (3)	0.0490
C(12)	0.3303 (6)	0.5179 (5)	0.7454 (4)	0.0609
C(13)	0.4292 (7)	0.5931 (6)	0.7667 (5)	0.0736
C(14)	0.4234 (8)	0.6061 (6)	0.8525 (5)	0.0797
C(15)	0.3214 (8)	0.5443 (7)	0.9189 (5)	0.0841
C(16)	0.2237 (7)	0.4678 (6)	0.8989 (4)	0.0685
C(21)	−0.0858 (6)	0.5842 (5)	0.6685 (3)	0.0458
C(22)	−0.1714 (6)	0.6273 (5)	0.5859 (3)	0.0566
C(23)	−0.2949 (7)	0.7554 (6)	0.5594 (4)	0.0682
C(24)	−0.3330 (7)	0.8413 (6)	0.6167 (4)	0.0690
C(25)	−0.2481 (7)	0.7999 (5)	0.6991 (4)	0.0656
C(26)	−0.1251 (6)	0.6715 (5)	0.7250 (3)	0.0541

Table 2. Geometric parameters (Å, °)

Sn(1)—Cl(1)	2.460 (2)	C(6)—C(11)	1.538 (8)
Sn(1)—O(3)	2.575 (3)	C(7)—C(21)	1.494 (6)
Sn(1)—C(1')	2.113 (6)	C(8)—C(9)	1.47 (1)
Sn(1)—C(2')	2.122 (5)	C(11)—C(12)	1.390 (7)
Sn(1)—C(4)	2.144 (4)	C(11)—C(16)	1.384 (8)
O(1)—C(1)	1.190 (8)	C(12)—C(13)	1.40 (1)
O(2)—C(1)	1.319 (7)	C(13)—C(14)	1.36 (1)
O(2)—C(8)	1.473 (7)	C(14)—C(15)	1.38 (1)
O(3)—C(6)	1.436 (5)	C(15)—C(16)	1.39 (1)
O(4)—C(7)	1.216 (6)	C(21)—C(22)	1.389 (7)
C(1)—C(2)	1.498 (8)	C(21)—C(26)	1.391 (8)
C(2)—C(3)	1.506 (9)	C(22)—C(23)	1.386 (7)
C(3)—C(4)	1.329 (7)	C(23)—C(24)	1.39 (1)
C(4)—C(5)	1.508 (8)	C(24)—C(25)	1.386 (9)
C(5)—C(6)	1.542 (6)	C(25)—C(26)	1.386 (6)
C(6)—C(7)	1.553 (6)		
C(2')—Sn(1)—C(4)	116.8 (2)	O(3)—C(6)—C(11)	108.3 (4)
C(1')—Sn(1)—C(4)	116.4 (2)	O(3)—C(6)—C(7)	107.7 (4)
C(1')—Sn(1)—C(2')	118.0 (2)	C(7)—C(6)—C(11)	109.7 (4)
O(3)—Sn(1)—C(4)	70.7 (2)	O(4)—C(7)—C(6)	117.1 (4)
O(3)—Sn(1)—C(2')	82.0 (2)	C(6)—C(7)—C(21)	122.9 (4)
O(3)—Sn(1)—C(1')	87.4 (2)	O(4)—C(7)—C(21)	120.0 (4)
Cl(1)—Sn(1)—C(4)	102.8 (1)	O(2)—C(8)—C(9)	110.1 (5)
Cl(1)—Sn(1)—C(2')	98.3 (2)	C(6)—C(11)—C(16)	122.9 (5)
Cl(1)—Sn(1)—C(1')	98.9 (2)	C(6)—C(11)—C(12)	118.3 (4)
Cl(1)—Sn(1)—O(3)	172.53 (9)	C(12)—C(11)—C(16)	118.7 (5)
C(1)—O(2)—C(8)	118.8 (5)	C(11)—C(12)—C(13)	120.7 (5)
Sn(1)—O(3)—C(6)	112.2 (3)	C(12)—C(13)—C(14)	119.8 (6)
O(1)—C(1)—O(2)	122.7 (5)	C(13)—C(14)—C(15)	120.3 (7)
O(2)—C(1)—C(2)	113.1 (5)	C(14)—C(15)—C(16)	120.5 (6)
O(1)—C(1)—C(2)	124.3 (5)	C(11)—C(16)—C(15)	120.0 (5)
C(1)—C(2)—C(3)	114.4 (4)	C(7)—C(21)—C(26)	124.2 (4)
C(2)—C(3)—C(4)	127.8 (5)	C(7)—C(21)—C(22)	116.6 (4)
Sn(1)—C(4)—C(3)	126.9 (4)	C(22)—C(21)—C(26)	119.2 (5)
C(3)—C(4)—C(5)	120.6 (5)	C(21)—C(22)—C(23)	121.0 (5)
Sn(1)—C(4)—C(5)	112.3 (3)	C(22)—C(23)—C(24)	119.2 (5)
C(4)—C(5)—C(6)	110.8 (4)	C(23)—C(24)—C(25)	120.4 (6)
O(3)—C(6)—C(5)	105.4 (4)	C(24)—C(25)—C(26)	119.9 (5)
C(5)—C(6)—C(11)	114.8 (4)	C(21)—C(26)—C(25)	120.3 (5)
C(5)—C(6)—C(7)	110.6 (4)		

A solution of benzil (13 mmol) in methylene chloride (20 ml) was cooled to 195 K under argon. $BF_3.Et_2O$ (3.8 ml, 30 mmol) was added over 5 min, followed by a solution of distannylalkene (13 mmol) in methylene chloride (20 ml) over 15 min. After 0.5 h the mixture was allowed to warm to room temperature and stirred for another 3 h at this temperature. The solution was poured into 200 ml of a saturated solution of NH_4Cl in water, the organic layer was separated, the aqueous layer extracted twice with 40 ml diethyl ether, the organic layers dried over Na_2SO_4 and the solvents removed under reduced pressure. The remaining solid was recrystallized from CCl_4 to obtain suitable crystals of the title compound. The crystal was mounted on the tip of a glass fibre with shellac adhesive. ω-scans of low-order reflections along the three crystal axes showed acceptable mosaicity. Six standard reflections (100, 050, 003, $\overline{1}00$, $0\overline{5}0$, $00\overline{3}$) monitored every 150 min showed insignificant intensity variation. H atoms were placed in geometrically calculated positions (C—H 0.96 Å). The correctness of the space-group choice was checked using MISSYM.

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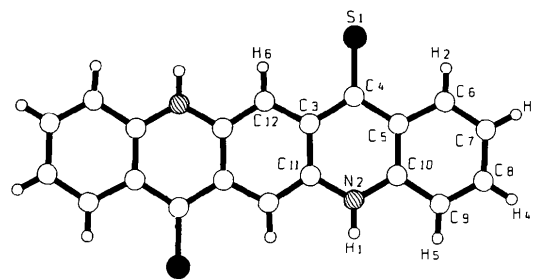
Fig. 1. Chemical structure of DTQ showing the numbering of the non-H atoms used in Tables 1 and 2.

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Structure of 5,7,12,14-Tetrahydroquinolino-[2,3-*b*]acridine-7,14-dithione

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Abstract

The molecule of the title compound, commonly called dithioquinacridone, belongs to point group $\bar{1}$ (C_i) and is planar. The maximal deviation from the best plane through the molecule is less than 0.04 (1) Å. In the crystal alternating molecules lie in the same plane and are stacked along the *b* axis at an inclination angle of 42.4 (2)°, in such a way that the molecular planes in the different columns are nearly perpendicular. The two sorts of stacking columns bond together, along a direction perpendicular to the stacking axis, through intermolecular hydrogen bonding between the NH group and the S atom. One molecule is hydrogen-bonded to four neighbouring molecules lying in the other columns.

Comment

5,7,12,14-Tetrahydroquinolino[2,3-*b*]acridine-7,14-dithione, commonly called dithioquinacridone (DTQ shown in Fig. 1), is a thionated derivative of linear *trans*-unsubstituted quinacridone (QA) which is known as a pigment of outstanding light, heat and chemical fastness. Several colours of QA pigments are available, depending on the polymorphic forms, although their detailed structures have not yet been

clarified (Koyama, Scheel & Laves, 1966; Ohmasa & Süsse, 1976; Lincke, 1980).

DTQ has recently attracted attention because of its near-IR absorption which is applicable to GaAs-diode laser printers (Rochat, Jaffe & Mizuguchi, 1988) and to information storage systems (Mizuguchi & Rochat, 1990). The near-IR absorption is, however, only available when the evaporated film of DTQ is exposed to the vapours of certain organic solvents. This vapour treatment brings about a rearrangement of molecules (phase transition) to give an intense near-IR absorption. The present structure determination has been undertaken in order to gain more insight into the correlation between crystal structures and optical properties.

DTQ was prepared from commercially available unsubstituted quinacridone by using a Lawesson's reagent as the thionation agent (Rochat, Jaffe & Mizuguchi, 1988). The single crystal was grown from the vapour phase using an apparatus which has been described previously (Mizuguchi, 1981). DTQ was sublimated at about 633 K, and the argon flow rate was controlled to 13 mm^3 s^{-1} using a mass flow meter (F-100/200, Bronkhorst BV).

The atomic positional and equivalent isotropic displacement parameters are listed in Table 1. Table 2 details the interatomic distances and bond angles together with their e.s.d.'s. The molecule is entirely planar with the exception of the S atoms which lie slightly out of plane by 0.04 (1) Å. It should be noted that the bonds C3—C4 and C4—C5 are significantly longer than aromatic C—C bonds, whereas the bonds C11—N2 and N2—C10 are shorter. Furthermore, the bonds C6—C7, C7—C8 and C8—C9 at the corner of the phenyl ring are slightly shorter than the bonds C5—C6, C5—C10 and C9—C10.

Fig. 2 shows the stereodiagram of the crystal structure of DTQ. Alternating molecules lie in the same plane and are stacked along the *b* axis at an inclination angle of 42.4 (2)°, in such a way that the molecular planes in the different columns are nearly perpendicular. The two sorts of stacking columns bond together, along a direction perpendicular to the stacking axis, through intermolecular bonding