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Structural chemistry of organotin carboxylates

XIII *. Crystal structure of dicyclohexylammonium tri-n-butyltin 2-sulfobenzoate, $[(c\text{-}C_6H_{11})_2NH_2][^nBu_3Sn(O_2CC_6H_4\text{-}2\text{-}SO_3)]$

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Abstract

Two dicyclohexylammonium triorganotin 2-sulfobenzoates, $[(c\text{-}C_6H_{11})_2NH_2]^+$ $[R_3Sn(O_2CC_6H_4\text{-}2\text{-}SO_3)]^-$ ($R = {}^nBu$, Ph), have been prepared by treating bis(tri-n-butyltin)oxide or triphenyltin hydroxide in the appropriate stoichiometry with an equimolar mixture of 2-sulfobenzoic acid and dicyclohexylamine in ethanol. On the basis of Mössbauer and IR spectral evidence, the organotin compounds are shown to be benzoato esters in which the sulfonato group is coordinated intermolecularly to tin, whose geometry is inferred to be *trans*-R_3SnO_2 trigonal bipyramidal. In the crystal structure of $[(c\text{-}C_6H_{11})_2NH_2][^nBu_3Sn(O_2CC_6H_4\text{-}2\text{-}SO_3)]$, the anions are linked to form helical polymeric chains featuring *trans*-R_3SnO_2 trigonal bipyramidal Sn geometries. The Sn–O bond distances within the chain are inequivalent, with the Sn–O(carboxylato) distance of 2.169(6) Å significantly shorter than the Sn–O(sulfonato) distance of 2.575(6) Å; the O–Sn–O angle is 170.7(3)°. The $[(c\text{-}C_6H_{11})_2NH_2]$ cations are linked to the polymeric backbone via hydrogen bonding contacts.

Introduction

Bis(triorganotin)oxides and triorganotin hydroxides are known to condense with alkane- and arene-sulfonic acids to afford triorganotin sulfonates. These sulfonates, $[R_3SnOSO_2R']$, are sulfonate-bridged compounds in which the Sn atoms are five-coordinate such that the Sn atom geometry is based on a *trans*-C_3SnO_2 trigonal

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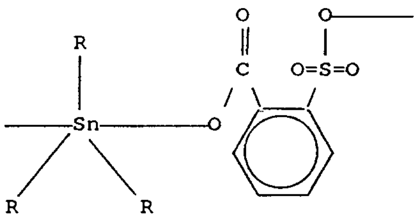
* For Part XII see ref. 1.

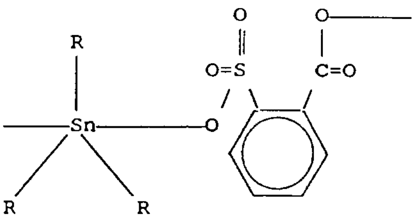
bipyramid, as evidenced by large (i.e. $\geqslant 4.0$ mm s^{-1}) tin-199*m* Mössbauer quadrupole splittings [2,3]. Within this class the tri-n-butyltin alkanesulfonates are believed to retain the five-coordinate geometry even in solution [3]. For the 2-carboxybenzenesulfonate compound, [$^{n}Bu_3Sn(OSO_2C_6H_4\text{-}2\text{-}CO_2H)$], the spectral data do not, however, allow an unambiguous structural assignment; either a monomeric tetrahedral or a monomeric *cis*-trigonal bipyramidal configuration is possible, both in the solid state and in solution [4]. This organotin sulfonate possesses a carboxylic acid function that can be deprotonated, using an amine, to yield an anionic organotin salt. Dicyclohexylamine has been used previously to prepare several triorganostannyl esters of dicarboxylic acids [5–7], and these studies have now been extended to include the anions derived from [$R_3Sn(OSO_2C_6H_4\text{-}2\text{-}CO_2H)$] ($R = {}^{n}Bu$, Ph).

Results and discussion

Triorganotin compounds, R_3SnX, show a propensity to achieve five-fold coordination and, whenever possible, invariably adopt a *trans*-R_3SnX_2 configuration in which the more electronegative X ligands occupy the axial sites, particularly when the anionic X residue can itself engage the Sn atom in auto-complexation [8]. Triorganotin carboxylates, for example, are typically coordination polymers as a result of carboxylate bridging [9,10]. As both uninegative CO_2 and SO_3 groups are present in the 2-sulfobenzoate dianion, at least four structural possibilities are conceivable for the resulting dicyclohexylammonium triorganotin 2-sulfobenzoates, assuming that intermolecular bridging is favoured over intramolecular coordination.



(I)



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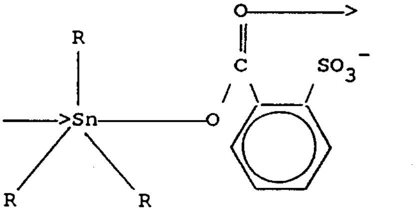

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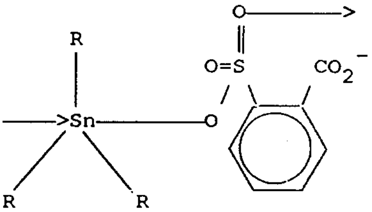

(IV)

The latter necessitates an axial–equatorial span of the 2-sulfobenzoate ligand, but steric strain in this configuration would be severe. The four structural possibilities I–IV are shown above.

The structures I and II are seemingly equivalent; however, in the *trans*-R_3SnO_2 motif the axial Sn–O bond distances are invariably inequivalent and thus structure I assumes the weaker, intermolecular Sn–O link is provided by the sulfonate residue, whereas in II the weaker link is provided by the carboxylate residue. Structures I and III are formally triorganotin benzoates, whereas II and IV are triorganotin benzenesulfonates. In III and IV, the doubly bonded carbonyl (III) or sulfonyl (IV) O atom participates in bridging.

The quadrupole splittings (QS) for the two $[(c\text{-}C_6H_{11})_2NH_2][R_3Sn(O_2CC_6H_4\text{-}2\text{-}SO_3)]$ compounds (R = ^{n}Bu, 3.48; R = Ph, 3.05 mm s^{-1}) are in the range commonly encountered and predicted for *trans*-trigonal bipyramidal triorganotin compounds [11]. The magnitudes of the splittings are similar to those of the dicyclohexylammonium salts of dicarboxylatotriorganostannyl anions [6], but are much smaller than those found for the neutral, five-coordinate triorganotin sulfonates [2,3]. The Mössbauer data suggest that I and III are the more likely structures for the $[(c\text{-}C_6H_{11})_2NH_2][R_3Sn(O_2CC_6H_4\text{-}2\text{-}SO_3)]$ (R = ^{n}Bu, Ph) compounds. In the infrared spectra, the asymmetric carbonyl stretch (R = ^{n}Bu, 1624; R = Ph, 1639 cm^{-1}) is shifted to lower wavenumbers with respect to ammonium hydrogen 2-sulfobenzoate (1728 cm^{-1}). The shift suggests the presence of a carboxylate ester linkage in both compounds. Since this shift is small, and the difference between the symmetric and asymmetric CO_2 stretching frequencies exceeds 200 cm^{-1} [12], the carboxylato group can be inferred to engage in monodentate bonding to the Sn atom (i.e. structure I). Corroborative support for sulfonate bridging could not, however, be obtained from the infrared spectra as the bonds in the sulfonyl region are overlapping. For the R = ^{n}Bu compound, single crystals were obtained and thus a single-crystal X-ray study was performed.

The crystallographic numbering scheme for the anion is shown in Fig. 1 and selected interatomic parameters are listed in Table 1. The crystal structure analysis shows the compound to be polymeric owing to the presence of a bridging 2-sulfobenzoato ligand which coordinates via one O atom of each of the carboxylate and sulfonate residues as shown in the lower view of Fig. 1. The helical, polymeric chain runs parallel to the crystallographic *b*-axis. The five-coordinate Sn atom geometry is based on a distorted trigonal bipyramid. The structure conforms to the *trans*-R_3SnO_2 structural motif such that the three organo substituents occupy positions in the trigonal plane and the two O atoms occupy the axial sites; the Sn atom lies 0.2042(6) Å out of the trigonal plane in the direction of the O(1) atom. The Sn–O bond distances are inequivalent with the Sn–O(1) bond distance, involving the carboxylate O atom, of 2.169(6) Å being substantially shorter than the Sn–O(5)′ (symmetry operation: $0.5-x$, $0.5+y$, $0.5-z$) distance, involving a sulfonate O atom, of 2.575(6) Å; the O(1)–Sn–O(5)′ angle is 170.7(3)°.

The O(2) atom of the carboxylate group is non-coordinating (Sn ··· O(2) 3.088(6) Å) and this is reflected in the C(1)–O(1) and C(1)–O(2) bond distances of 1.30(1) and 1.23(1) Å, respectively, indicating localization of π-electron density in the C(1)–O(2) bond. Similarly, the O(3) and O(4) atoms of the sulfonate group are not coordinated to the Sn atom. The S(1)–O bond distances fall in two classes with one distance being shorter (S(1)–O(3) 1.433(7) Å) than the other two (S(1)–O(4), O(5)

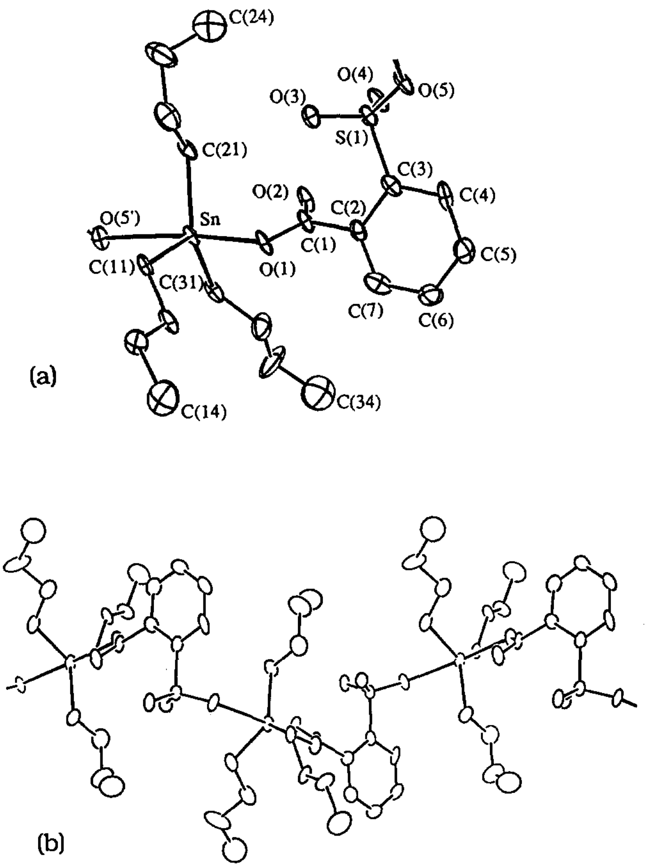

Fig. 1. (a) Molecular structure and crystallographic numbering scheme employed for the anion in $[(c\text{-}C_6H_{11})_2NH_2][^nBu_3Sn(O_2CC_6Hs_4\text{-}2\text{-}SO_3)]$. (b) Mode of association of the anions to generate the helical polymeric chain.

Table 1
Selected interatomic parameters (Å, deg) for $[(c\text{-}C_6H_{11})_2NH_2][^nBu_3Sn(O_2CC_6H_4\text{-}2\text{-}SO_3)]$

Sn–O(1)	2.169(6)	Sn–O(5)′ [a]	2.575(6)
Sn–C(11)	2.150(9)	Sn–C(21)	2.16(1)
Sn–C(31)	2.14(1)	S(1)–O(3)	1.433(7)
S(1)–O(4)	1.461(7)	S(1)–O(5)	1.467(7)
S(1)–C(3)	1.76(1)	O(1)–C(1)	1.30(1)
O(2)–C(1)	1.23(1)	C(1)–C(2)	1.50(1)
O(1)–Sn–O(5)′	170.7(3)	O(1)–Sn–C(11)	88.7(3)
O(1)–Sn–C(21)	100.0(3)	O(1)–Sn–C(31)	97.0(3)
O(5)′–Sn–C(11)	82.3(3)	O(5)′–Sn–C(21)	86.2(3)
O(5)′–Sn–C(31)	84.8(3)	C(11)–Sn–C(21)	115.0(4)
C(11)–Sn–C(31)	117.6(4)	C(21)–Sn–C(31)	124.7(4)
Sn–O(1)–C(1)	115.4(6)	O(1)–C(1)–O(2)	125.2(9)
O(1)–C(1)–C(2)	114.9(9)	O(2)–C(1)–C(2)	119.6(9)
Sn–O(5)′–S(1)′	131.5(3)	O(3)–S(1)–O(4)	113.7(4)
O(3)–S(1)–O(5)	115.3(4)	O(3)–S(1)–C(3)	105.9(4)
O(4)–S(1)–O(5)	110.2(4)	O(4)–S(1)–C(3)	106.8(4)
O(5)–S(1)–C(3)	104.0(4)		

[a] Primed atoms are related by the symmetry operation: 0.5 − x, 0.5 + y, 0.5 − z.

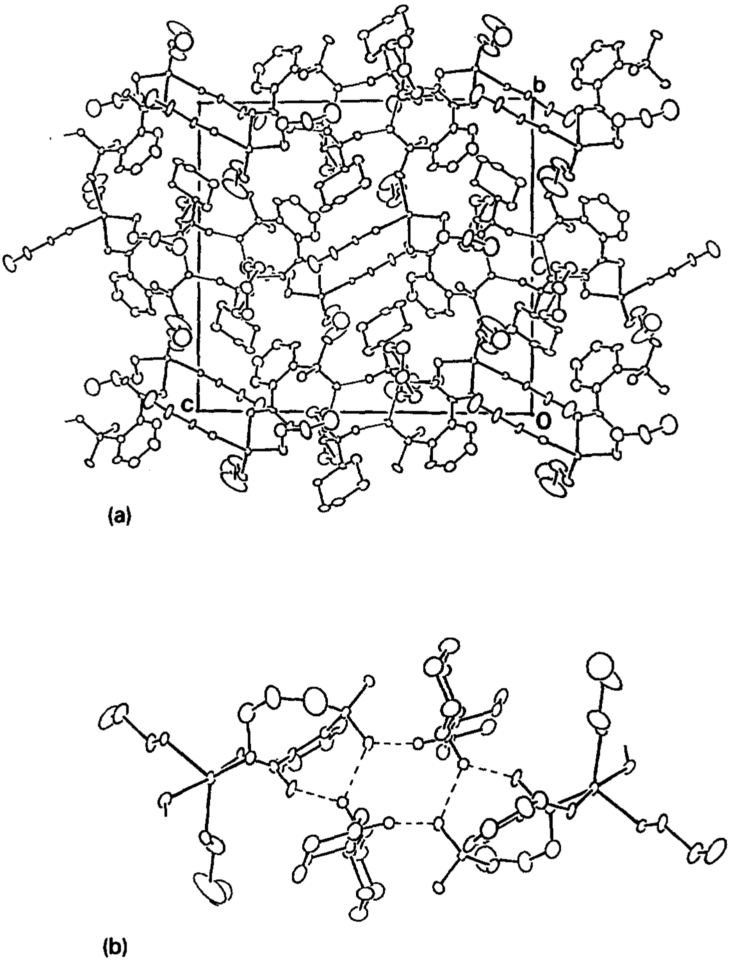

Fig. 2. (a) Unit cell contents for $[(c\text{-}C_6H_{11})_2NH_2][R_3Sn(O_2CC_6H_4\text{-}2\text{-}SO_3)]$ as viewed down the [100] direction. (b) Detail of the hydrogen bonding network in the lattice.

1.461(7), 1.467(7) Å). The elongation of the S(1)–O(5) bond is expected, owing to the close O(5)–Sn′ interaction of 2.575(6) Å, and the lengthening of the S(1)–O(4) bond may be related to the close hydrogen bonding contacts with the cation as described below.

The X-ray analysis of $[(c\text{-}C_6H_{11})_2NH_2][^nBu_3Sn(O_2CC_6H_4\text{-}2\text{-}SO_3)]$ shows that I is indeed the structure adopted in the solid state, in accord with the spectroscopic observations. While this structure is novel, it can be compared with another triorganotin carboxylate structure, namely $[Ph_3Sn(O_2CC_5H_4N)]_n$ [13]. This compound features a 3-pyridinecarboxylate ligand which, while uninegative, coordinates via one O atom and the pyridine N atom leading to a polymeric chain similar to that reported here, and to other *trans*-R_3SnO_2 compounds [9,10].

A [100] view of the unit cell contents of $[(c\text{-}C_6H_{11})_2NH_2][^nBu_3Sn(O_2CC_6H_4\text{-}2\text{-}SO_3)]$ is shown in Fig. 2; for reasons of clarity only the N-bound H atoms are shown. Associated with the helical polymeric chains, via hydrogen bonding contacts, are the $[(c\text{-}C_6H_{11})_2NH_2]^+$ cations as emphasized in the lower diagram in Fig. 2. In the lattice each $[(c\text{-}C_6H_{11})_2NH_2]^+$ cation links two $[^nBu_3Sn(O_2CC_6H_4\text{-}2\text{-}SO_3)]^-$ entities derived from adjacent polymeric chains thereby forming a tightly held, three-dimensional structure. Thus, the H(10)a atom forms two contacts with one anionic chain, one of 1.93(1) Å with the O(2)′ (symmetry operation: $0.5-x$, $-0.5+y$, $0.5-z$) atom of the carboxylate group and the other of 2.26(1) Å with the O(4)′ atom derived from the sulfonate group such that the N(10)–H(10)a ··· O(2)′ and N(10)–H(10)a ··· O(4)′ angles are 136(1) and 126(1)°, respectively. The H(10)b atom is linked to the O(4)″ (symmetry operation:) atom of a second polymeric chain such that the H(10)b ··· O(4)″ separation is 1.77(1) and N(10)–H(10)b ··· O(4)″ angle is 166(1)°. As shown in Fig. 2(b), these intermolecular hydrogen bonding contacts are situated about a crystallographic centre of inversion which results in the formation of six- and seven-membered rings.

In chloroform solution the polymeric chain breaks down into four-coordinate triorganotin anions as evidenced [14] from the magnitude of the one-bond coupling constant $^1J(^{119}Sn-^{13}C)$ of 355.3 Hz).

Experimental

Synthesis

$[(c\text{-}C_6H_{11})_2NH_2][^nBu_3Sn(O_2CC_6H_4SO_3)]$. One molecular equivalent of bis(tri-n-butyltin) oxide when added to two molar equivalents each of 2-sulfobenzoic acid * and dicyclohexylamine dissolved in a small volume of ethanol yielded

Table 2
Crystal data and refinement details for $[(c\text{-}C_6H_{11})_2NH_2][^nBu_3Sn(O_2CC_6H_4\text{-}2\text{-}SO_3)]$

Formula	$C_{31}H_{55}NO_5SSn$
Mol. wt.	672.5
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	14.445(9)
b, Å	14.904(5)
c, Å	16.723(13)
β, deg.	101.09(5)
V, Å^3	3533.0
Z	4
D_c, g cm^{-3}	1.264
$F(000)$	1416
μ, cm^{-1}	7.37
T, K	180
No. of data collected	3642
No. of unique data	3290
No. of unique reflections used with $I \geq 2.5\sigma(I)$	2273
R	0.058
g	0.0084
R_w	0.057
Residual ρ_{max}, e Å^{-3}	1.62 (near Sn)

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* Listed as 2-sulfobenzoic acid hydrate, $HO_3SC_6H_4CO_2H \cdot xH_2O$, in chemical catalogs; the value of x is most certainly 3 [15].

dicyclohexylammonium tri-n-butyltin 2-sulfobenzoate (> 90% yield), which was recrystallized from ethanol. *Anal.* Found: C, 55.00; H, 8.41; N, 2.07. $C_{31}H_{55}NO_5SSn$ calc.: C, 55,36; H, 8.25; N, 2.08%. Mössbauer (78 K) data: Isomer shift (IS) 1.43, Quadrupole splitting (QS) 3.48, Γ_1 0.93, Γ_2 0.91 mm s^{-1}. Infrared (Nujoll mull): CO_2 asymmetric 1624, symmetric 1251 cm^{-1}. Carbon-13 NMR in CDCl3 [δ in ppm (coupling constant ^1J in Hz)]: ^{n}Bu carbons C_1 16.4 (355.3), C_2 27.7 (18.8), C_3 27.0 (67.1), C_4 13.5 pp, (< 5 Hz); cyclohexyl carbons 24.6, 24.7, 28.6, 53.3; aromatic carbons 127.5, 128.3, 129.2, 134.5, 142.5 (overlapped); carboxyl carbon 173.9 ppm.

Table 3
Fractional atomic coordinates ($\times 10^5$ for Sn and $\times 10^4$ for remaining atoms) for $[(c\text{-}C_6H_{11})_2NH_2][^nBu_3Sn(O_2CC_6H_4\text{-}2\text{-}SO_3)]$

Atom	*x*	*y*	*z*
Sn	27229(5)	64342(4)	35551(4)
S(1)	1230(2)	3709(2)	1453(2)
O(1)	1885(5)	5219(4)	3485(4)
O(2)	1071(5)	5686(5)	2278(4)
O(3)	2148(4)	3976(4)	1877(4)
O(4)	797(5)	4342(4)	823(4)
O(5)	1167(5)	2793(4)	1125(4)
C(1)	1241(7)	5135(6)	2835(7)
C(2)	607(7)	4335(7)	2827(6)
C(3)	509(7)	3685(6)	2193(6)
C(4)	−176(7)	3018(7)	2157(6)
C(5)	−737(8)	2994(7)	2734(7)
C(6)	−630(9)	3603(8)	3365(7)
C(7)	47(9)	4259(8)	3398(7)
C(11)	3647(7)	5886(6)	4607(6)
C(12)	3110(7)	5558(7)	5261(6)
C(13)	3767(8)	5105(8)	5967(6)
C(14)	3207(9)	4746(10)	6597(8)
C(21)	3237(7)	6329(6)	2427(6)
C(22)	4026(9)	5662(9)	2465(7)
C(23)	4440(10)	5615(11)	1710(7)
C(24)	3801(11)	5336(12)	967(9)
C(31)	1648(7)	7345(7)	3762(6)
C(32)	762(8)	6938(8)	3971(9)
C(33)	53(11)	7667(12)	4120(14)
C(34)	−814(16)	7264(19)	4247(19)
N(10)	5041(6)	1204(5)	4213(5)
C(41)	5851(7)	1280(6)	3775(6)
C(42)	6318(7)	367(7)	3798(6)
C(43)	7155(8)	382(8)	3387(7)
C(44)	7872(8)	1070(8)	3793(8)
C(45)	7397(8)	2002(8)	3773(8)
C(46)	6563(7)	1994(7)	4166(7)
C(51)	4521(7)	2042(6)	4387(6)
C(52)	3755(7)	1767(7)	4810(7)
C(53)	3190(8)	2569(7)	5039(6)
C(54)	2801(8)	3118(7)	4266(7)
C(55)	3580(10)	3383(7)	3833(7)
C(56)	4144(8)	2580(6)	3608(6)

$[(c\text{-}C_6H_{11})_2NH_2][Ph_3Sn(O_2CC_6H_4SO_3)]$. The reaction of triphenyltin hydroxide, the acid and the amine in 1/1/1 molar amounts in ethanol gave dicyclohexylammonium triphenyltin 2-sulfobenzoate (> 90% yield), which was crystallized from ethanol. *Anal.* Found: C, 60.10; H, 5.91; N, 1.94. $C_{37}H_{43}NO_5SSn$ calc.: C, 60.66; H, 5.91; N, 1.91%. Mössbauer: IS 1.24, QS 3.05, Γ_1 0.83, Γ_2 0.85 mm s^{-1}. Infrared: CO_2 asymmetric 1639, symmetric 1256 cm^{-1}.

Crystallography

The intensity data set for $[(c\text{-}C_6H_{11})_2NH_2][^nBu_3Sn(O_2CC_6H_4\text{-}2\text{-}SO_3)]$ was measured at 180 K on an Enraf–Nonius CAD4F diffractometer fitted with graphite-monochromatized Mo-K_α radiation, $\lambda = 0.7107$ Å. The ω–2θ scan technique was employed to measure data to a maximum Bragg angle of 22.5°, and the data were corrected for Lorentz and polarization effects but not for absorption. Relevant crystal data are given in Table 2.

The structure was solved from the interpretation of the Patterson synthesis [16] and refined by a full-matrix least-squares procedure based on F [16]. All non-H atoms, with the exception of the C(34) atom, were refined with anisotropic thermal parameters and H atoms were included in the model at their calculated (C–H 0.97 Å) positions. The C(33)–C(34) bond distance was fixed at 1.50(2) Å owing to positional disorder associated with the terminal methyl group, C(34). After the inclusion of a weighting scheme of the form, $w = [\sigma^2(F) + g|F|^2]^{-1}$, the refinement was continued until convergence; final refinement details are listed in Table 3. The analysis of variance showed no special features indicating that an appropriate weighting scheme had been applied. Fractional atomic coordinates are listed in Table 3 and the numbering scheme employed is shown in Fig. 1 which was drawn with ORTEP [17] at 25% probability ellipsoids. Scattering factors were as incorporated in the SHELX76 program [16] and the refinement was performed on a SUN4/280 computer. Other crystallographic details (available from ERTT) comprise thermal parameters, H-atom parameters, all bond distances and angles, and tables of observed and calculated structure factors.

Acknowledgements

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