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Study on the crystal and molecular structure of triphenyl tin methacrylate: $(C_6H_5)_3SnOCOCCH_2CH_3$

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The crystal and molecular structure of $(C_6H_5)_3SnOCOCCH_2CH_3$ has been determined by a single crystal X-ray diffraction study. The crystal is monoclinic with space group $P2_1/c$, a = 11.902(3), b = 10.104(4), c = 16.721(2) Å, β = 97.56(1)°, V = 1930.4 Å^3, Z = 4 and D_c = 1.495 g/cm^3, $F(0,0,0)$ = 872, λ(Cu Kα) = 1.5418 Å. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures to an R factor of 0.060 based on 2157 independent reflections. The results showed that the Sn—O bond distance is 2.064(4) Å. The average Sn—C bond distance is 2.126 Å. There is a weak coordination through the O of the CO group of the methacrylate residue (Sn—O(2) 2.774(5) Å) except for four normal coordinations. The coordination number at the Sn^{4+} is 5.

Introduction

Organotin polymers such as poly (triphenyl tin methacrylate) are of practical importance, particularly for making antifouling paints for marine structures. Recently, it has been studied for organotin monomer in synthesis, purification, and copolymerization (Ghanem *et al.*, 1979, 1980, 1981; Messiha *et al.*, 1980). Up to now, however, to our knowledge, the crystal structure of triphenyl tin methacrylate has not been reported. We have synthesized the organotin monomer of triphenyl tin methacrylate and determined its X-ray single crystal structure.

Experimental

Fresh methylacrylic acid was slowly added to a benzene solution of Ph_3SnOH. After reaction for 3 hr under 25°C, white crystals of triphenyl tin methacrylate were obtained from the solution. A crystal of good quality was obtained by recrystallization from a 30–60°C petroleum ether. A single crystal with dimensions of 0.14 × 0.25 × 0.33 mm^3 was selected for the X-ray analysis. The crystal of triphenyl tin methacrylate is monoclinic, space group $P2_1/c$ with the cell constants: a = 11.903(3), b = 10.104(4), c = 16.721(2) Å, β = 97.56(1)°, V = 1930.4 A^3. D_c = 1.495 g/cm^3 and Z = 4, $F(000)$ = 872. Its molecular formula is $SnO_2C_{22}H_{20}$ and molecular weight is 434.6. Intensity data of 2157 independent reflections were collected in a range of $2° \leq \theta \leq 58°$ by using graphite-monochromated Cu Kα radiation (λ = 1.5418 Å) and a ω-2θ scan mode on an Enraf-Nonius CAD-4 four Circle Diffractometer. Three reflections ($0\bar{2}4$; $40\bar{3}$; $0\bar{4}2$) were measured every half and an hour and showed only random fluctuations, within 2% of their mean values during data collection; a linear correction was applied. All data were corrected by LP factor and absorption (transmission factors 0.391 to 0.561).

The structure was solved by the heavy-atom method. The atomic coordinates of tin were obtained by analyzing a Patterson function. The rest of the nonhydrogen atoms were revealed from successive difference Fourier maps. The structure was refined by block matrix least-squares

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with the positional and isotropic thermal parameters of all nonhydrogen atoms to R (= $\Sigma\|Fo| - |Fc\|/\Sigma|Fo|$) = 0.086, and then by full-matrix least-squares with anisotropic thermal parameters to R = 0.067. All hydrogen atoms were found from difference Fourier maps. Further full matrix least-squares refinements for anisotropic thermal parameters of all the nonhydrogen atoms and isotropic thermal parameters of all the hydrogen atoms using all independent reflections give the final R factor of 0.060 and Rw 0.066, where $Rw = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(F)$. The number of variables is 306. The maximum shift-over-error ratio in the last refinement cycle was less than 0.2. The final difference Fourier map showed no unusual features and the maximum height is 0.577 e $Å^{-3}$. All calculations were performed on a PDP11/44 computer with the SDP program package.

Results and discussion

The coordinates, main bond lengths, and bond angles of atoms are listed in Tables 1, 2, and 3, respectively. The molecular structure and its packing distribution in the cell are shown in Fig. 1 and Fig. 2, respectively.

The molecular structure consists of three $(C_6H_5)^-$ and one $(OCOCCH_2CH_3)^-$ and one tin atom. One carbon atom of every phenyl and one oxygen atom of methylacrylic acid formed a slightly distorted tetrahedron and the tin atom was located in the center of the tetrahedron. The results indicate that the distance from the tin atom to the carbon atom and to the oxygen atom are almost equal. The bond lengths and angles involving the tin ion are all normal. The Sn—O bond distance is 2.064(4) Å. This is shorter than the Sn—O bond distance, 2.201 Å, in $(CH_3)_2 \cdot (C_6H_5)SnOC(O)CH_3$ (Mostafa *et al.*, 1989). This is also shorter than those in other results (Huber *et al.*, 1989; Seik *et al.*, 1989). The average Sn—C bond distance is 2.126 Å. This is in agreement with the results (Huber *et al.*, 1989; Seik *et al.*, 1989). The average O—Sn—C bond angle is 106.3°. The average C—Sn—C bond angle is 112.1°. There is one crystallographically independent molecule of $(C_6H_5)_3SnOCOCCH_2CH_3$ in the asymmetric unit. The shortest nonbond distance Sn—Sn is 6.395(7) Å.

The atoms of methylacrylic acid form a very good plane (see Table 4). The largest deviation from the least-squares plane is 0.04 Å. The phenyl rings are very well defined with carbon–carbon distances for adjacent carbon atoms ranging from 1.340(11) to 1.412(9) Å (an

Table 1. Fractional atomic coordinates of atoms and their equivalent isotropic thermal parameters B_{eq}

Atom	x	y	z	B(A2)
Sn	0.26080(6)	0.01546(7)	0.07803(4)	3.43(1)
O1	0.5802(6)	0.4823(8)	0.3576(5)	4.6(2)
O2	0.6548(7)	0.6128(9)	0.2708(6)	5.5(2)
C1	0.575(1)	0.551(1)	0.2875(7)	4.7(3)
C2	0.465(1)	0.535(1)	0.2313(7)	4.6(3)
C3	0.377(1)	0.452(2)	0.256(1)	7.3(4)
C4	0.455(1)	0.614(2)	0.1601(9)	7.1(4)
C5	0.210(1)	0.710(1)	0.3444(8)	5.5(3)
C6	0.195(1)	0.629(1)	0.4113(7)	4.7(3)
C7	0.715(1)	0.390(1)	0.5243(7)	3.9(3)
C8	0.388(1)	0.676(1)	0.4721(8)	4.4(3)
C9	0.600(1)	0.255(1)	0.0949(8)	4.7(3)
C10	0.686(1)	0.275(1)	0.1569(8)	5.5(3)
C11	0.8703(9)	0.438(1)	0.3604(6)	3.2(2)
C12	0.905(1)	0.499(1)	0.2895(7)	4.4(3)
C13	0.002(1)	0.453(1)	0.2575(8)	5.3(3)
C14	0.062(1)	0.349(1)	0.2933(8)	4.9(3)
C15	0.971(1)	0.786(1)	0.1400(8)	5.0(3)
C16	0.933(1)	0.329(1)	0.3939(7)	4.3(3)
C17	0.2396(9)	0.217(1)	0.0419(7)	3.5(2)
C18	0.840(1)	0.796(1)	0.4257(8)	5.9(4)
C19	0.144(1)	0.428(1)	0.0480(8)	6.1(4)
C20	0.206(1)	0.477(1)	−0.0111(9)	6.0(3)
C21	0.721(1)	0.604(1)	0.047(1)	6.2(4)
C22	0.704(1)	0.728(1)	0.020(1)	5.7(3)

Table 2. Main bond lengths (Å)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Sn	O1	2.064(4)[a]	Sn	C7	2.140(6)
Sn	C11	2.109(6)	Sn	C17	2.128(6)
O1	C1	1.326(8)	O2	C1	1.197(9)
C1	C2	1.507(9)	C2	C3	1.432(12)
C2	C4	1.392(11)	C5	C6	1.388(10)
C5	C10	1.398(12)	C6	C7	1.412(9)
C7	C8	1.395(9)	C8	C9	1.374(10)
C9	C10	1.352(11)	C11	C12	1.411(8)
C11	C16	1.401(9)	C12	C13	1.397(10)
C13	C14	1.359(11)	C14	C15	1.358(11)
C17	C18	1.391(10)	C17	C22	1.393(10)
C18	C19	1.408(10)	C19	C20	1.373(12)
C20	C21	1.377(12)	C21	C22	1.340(11)

[a] Numbers in parentheses are estimated deviations in the least significant digits.

Table 3. Main bond angle (°)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	Sn	C7	95.0(2)	O1	Sn	C11	112.7(2)
O1	Sn	C17	111.2(2)	C7	Sn	C11	109.4(2)
C7	Sn	C17	112.2(2)	C11	Sn	C17	114.6(2)
Sn	O1	C1	106.5(4)	O1	C1	O2	121.3(6)
O1	C1	C2	113.7(7)	O2	C1	C2	124.9(7)
C1	C2	C3	120.0(7)	C1	C2	C4	114.2(8)
C3	C2	C4	125.6(8)	C6	C5	C10	119.8(7)
C5	C6	C7	119.3(7)	Sn	C7	C6	119.1(5)
Sn	C7	C8	121.5(5)	C6	C7	C8	119.4(7)
C7	C8	C9	119.7(7)	C8	C9	C10	121.6(8)
C5	C10	C9	120.2(8)	Sn	C11	C12	122.7(4)
Sn	C11	C16	119.9(5)	C12	C11	C16	117.2(6)
C11	C12	C13	120.2(7)	C12	C13	C14	120.6(7)
C13	C14	C15	120.8(8)	Sn	C17	C18	120.2(5)
Sn	C17	C22	121.8(5)	C18	C17	C22	117.7(6)
C17	C18	C19	119.6(8)	C18	C19	C20	119.5(8)
C19	C20	C21	120.6(8)	C20	C21	C22	119.4(9)
C17	C22	C21	122.8(8)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

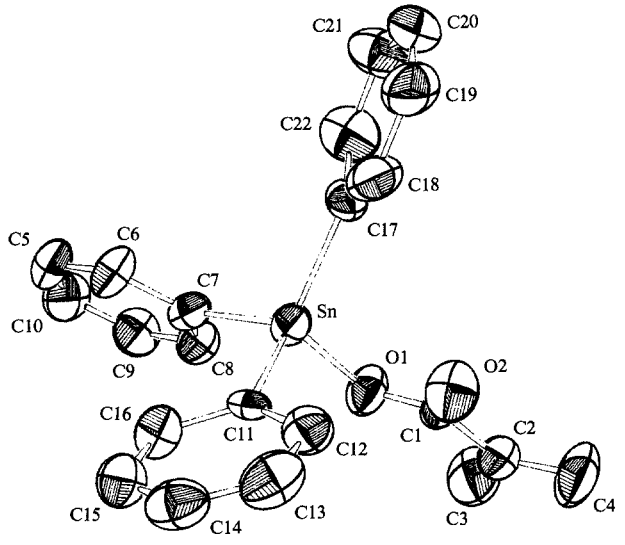

Fig. 1. The molecular structure of $(C_6H_5)_3SnOCOCCH_2CH_3$.

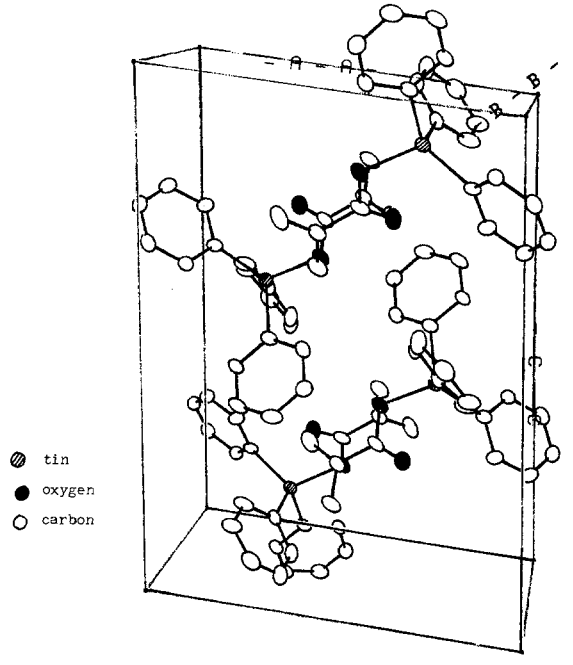

Fig. 2. The molecular packing diagram in cell.

average of 1.384 Å) and with C—C—C angles within a ring ranging from 117.2(6)° to 122.8(8)°, an average of 119.9°. The title compound, triphenyl tin methacrylate, is a discrete molecule with no close intermolecular contacts. We note that there is a weak coordination through the carbonyl oxygen atom (Sn—O(2) 2.774(5) Å) in addition to four normal coordinations. This contact raises the coordination number at the metal to five, a result which is readily rationalized in terms of the known propensity of diorganotin compounds to achieve higher coordination numbers whenever possible. A similar effect has been noted in bis(2-carbomethoxyethyl) chloro (quinolin-8-olato) tin(IV),

Table 4. Deviations (Å) of atoms from the least-squares plane[a]

Atom	O1	O2	C1	C2
Distance	−0.037(8)	0.042(9)	−0.013(12)	0.022(12)
Atom	C3	C4		
Distance	0.027(16)	−0.041(16)		
Constant	A	B	C	D
	0.4232	−0.7771	−0.4658	−3.8286

[a]The equation of the plane is the form: $A\,x + B\,y + C\,z - D = 0$.

$C_{17}H_{20}ClNO_5Sn$ (Sn—O 2.847(4) Å) (Seik *et al.*, 1989).

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Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication no. 63140 (12 pages).