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THE CRYSTAL STRUCTURE OF TRIPHENYLALLYLTIN

PAOLO GANIS

Dipartimento di Chimica, Universita' di Napoli, via Mezzocannone, 4, 80134 Napoli (Italia)

DONATELLA FURLANI, DANIELE MARTON, GIUSEPPE TAGLIAVINI *,

Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Universita' di Padova, Via Marzolo, 1, 35131 Padova (Italia)

and GIOVANNI VALLE

Centro di Ricerche sui biopolimeri del C.N.R., Via Marzolo, 1, 35131 (Padova) (Italia)

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Summary

The crystal structure of $(C_6H_5)_3SnCH_2CH{=}CH_2$ has been determined. The asymmetric unit consists of two molecules of triphenylallyltin having virtually the same conformation. Their geometrical parameters exclude p_π–d_π bonding between the metal and the allyl double bond, and seem to be in a better agreement with a σ–π conjugation effect.

Introduction

Unsaturated derivatives of organometallics have attracted considerable interest in the last few years as synthetic reagents in a number of addition, substitution and rearrangement reactions [1–3]. Particular attention has been given to unsaturated compounds bearing $R_nM{-}CH_2$ substituents, where M is a Group IV metal or Hg [4–6].

The electronic interactions which take place in the $MCH_2CH{=}CH_2$ moieties, i.e. the so called β-effect, have been extensively studied by chemical [7,8], physicochemical and theoretical methods [9–13] and have been copiously reviewed [4,14]. In brief, they are regarded as involving three components: (a) the inductive effect, (b) p_π–d_π bonding, and (c) σ–π conjugation. However the conclusions reached in the literature are often in conflict with each other [14]; most authors contest the relevance, or even the existence of a p_π–d_π bonding [9–11,15], and emphasize the predominance of the hyperconjugation effect [16].

We have been working for some time on the use of organotin unsaturated derivatives as synthons in organic chemistry [17–25]; problems arising from our

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studies and the lack of X-ray structural data stimulated us to determine crystal structures for some such derivatives in order to provide more complete information for settling the argument. We report below the crystal structure analysis of triphenylallyltin, $(C_6H_5)_3SnCH_2CH=CH_2$, the first for an allyltin derivative.

Experimental

Triphenylallyltin: crystal and intensity data

Triphenylallyltin was prepared as previously reported [26]. Well formed needle-shaped crystals, suitable for X-ray analysis were obtained from ethanol, m.p. 73°C (Lit. 73.5–74.5°C [26]).

$C_{21}H_{20}Sn$; M.W. 391.1; orthorhombic, a 34.720(12), b 32.254(12), c 6.537(3) Å; U 7320.5 Å^3, D_m 1.41 g cm^{-3}; Z 16; D_c 1.42 g cm^{-3}; $F(000)$ 3136; λ(Mo-K_α) 0.7107 Å; μ(Mo-K_α) 14.07 cm^{-1}; space group *Pcab*.

A selected crystal (~ 0.35 × 0.35 × 0.60 mm) was mounted on a Philips PW 1100 computer controlled four-circle diffractometer with graphite monochromator. Standard centering and auto-indexing procedures [27] indicated a primitive orthorhombic lattice. The orientation matrix and accurate unit cell dimensions were determined from a least square fit of 25 symmetry-related reflections ($10° \leqslant 2\vartheta \leqslant 23°$). Intensity data were collected at 24°C using the ϑ–2ϑ scan method; two standard reflections, monitored every 150 reflection measurements, fluctuated within ±2% of their mean value. Empirical absorption correction was applied by a pseudo-ellipsoidal treatment of intensities of selected strong reflections measured at various azimutal angles [28–30]. The intensities were then corrected for Lorentz and polarization factors and scaled to give 1404 independent F_{hkl} values for $I > 2\sigma(I)$.

Solution and refinement of the structure

The asymmetric unit consists of two independent molecules of triphenylallyltin, the positions of its two tin atoms were determined from a three-dimensional Patterson synthesis. All the carbon atoms were located from subsequent Fourier maps and refined anisotropically. The hydrogen atoms (excluding those of the allyl groups) were located from the final difference Fourier synthesis, they were included in the calculations but not refined. Blocked-cascade least squares refinements were used; they converged to the conventional R index of 0.037. The final difference map showed residual peaks (< 0.6 e Å^{-3}) of electron density in the neighbourhood of one $CH=CH_2$ group; these peaks arise from the high thermal motion of the terminal $CH=CH_2$ group * and probably from some kind of conformational disorder, but could certainly be neglected because of its very low occupancy factor. The weighting scheme used in the final calculations was of the form $W^{-1} = a_i|F_0|^i$. The a_i parameters were calculated using the program PESO [31]. Scattering factors for the atoms were taken from Cromer and Waber [32], the scattering factor for the tin atoms was corrected for the real and imaginary parts of anomalous dispersion using Cromer's values [33]. All computations were carried out on a CDC Cyber 76 computer using the programs of ref. 34. The positional parameters of the non-hydrogen atoms are listed in Table 1, the atom-numbering scheme being shown in Fig. 1.

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* See the U_{ij} values in Table 4 of the supplementary data available from the authors.

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) WITH THE ESTIMATED DEVIATIONS IN PARENTHESES

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Sn	3725(0)	4317(0)	4260(2)	Sn′	1201(0)	6938(0)	5020(2)
C(1)	4045(6)	4700(6)	6324(35)	C(1)′	0813(6)	7245(6)	3022(35)
C(2)	4444(7)	4718(8)	6160(43)	C(2)′	0731(7)	7675(7)	3418(40)
C(3)	4658(7)	4954(7)	7414(34)	C(3)′	0480(8)	7876(7)	2100(58)
C(4)	4485(8)	5199(7)	8920(43)	C(4)′	0334(7)	7688(8)	0323(49)
C(5)	4085(8)	5190(7)	9145(38)	C(5)′	0419(7)	7282(8)	−0014(36)
C(6)	3863(7)	4937(6)	7807(35)	C(6)′	0662(7)	7065(6)	1322(37)
C(7)	3307(7)	4689(8)	2678(33)	C(7)′	0884(6)	6462(6)	6568(31)
C(8)	3285(7)	5109(9)	2805(38)	C(8)′	0499(6)	6396(7)	6272(35)
C(9)	3023(7)	5333(6)	1767(46)	C(9)′	0297(7)	6116(7)	7380(48)
C(10)	2797(7)	5145(9)	0327(37)	C(10)′	0472(11)	5868(7)	8816(52)
C(11)	2823(6)	4732(7)	−0014(41)	C(11)′	0865(9)	5936(7)	9162(37)
C(12)	3078(7)	4495(6)	1181(38)	C(12)′	1081(6)	6227(7)	8110(34)
C(13)	3418(7)	3860(7)	6127(40)	C(13)′	1645(5)	6643(7)	3216(31)
C(14)	3621(7)	3579(8)	7287(44)	C(14)′	1658(6)	6201(6)	3104(33)
C(15)	3431(11)	3300(8)	8576(40)	C(15)′	1926(8)	6023(6)	1853(34)
C(16)	3025(9)	3310(9)	8606(43)	C(16)′	2192(6)	6260(9)	0824(39)
C(17)	2826(7)	3593(9)	7406(47)	C(17)′	2189(7)	6693(8)	0962(35)
C(18)	3027(8)	3860(8)	6191(39)	C(18)′	1910(6)	6867(8)	2184(35)
C(19)	4092(7)	4048(9)	1900(44)	C(19)′	1425(6)	7364(7)	7298(35)
C(20)	4340(9)	3744(8)	2590(52)	C(20)′	1712(13)	7626(12)	6582(63)
C(21)	4695(7)	3688(9)	2905(46)	C(21)′	2063(8)	7669(7)	6496(39)

Tables of thermal factors, hydrogen atom coordinates, and lists of the structure factors are available from the authors.

Description of the structure and discussion

The most relevant structural parameters of the two independent molecules **A** and **B** of triphenylallyltin forming the asymmetric unit are listed in Table 2. Both **A** and **B** show almost undistorted tetrahedral coordination about the tin atoms, with the phenyl groups nearly in the same paddle wheel conformation. The most interesting feature concerns the allyl groups. For **A** and **B** the CH_2–CH= bonds are respectively

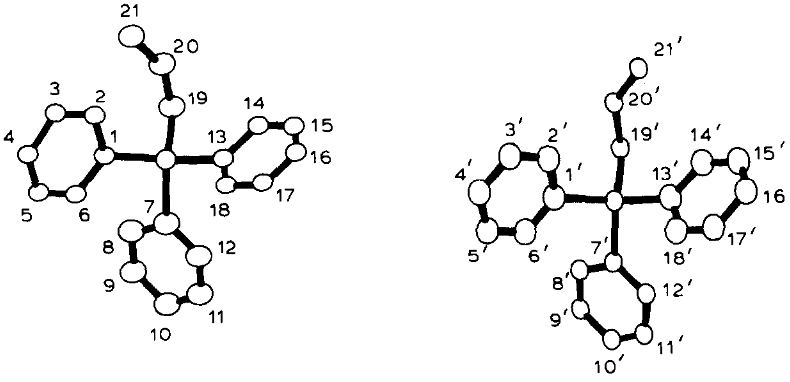

Fig. 1. Labelling scheme for the structural unit of triphenylallyltin.

TABLE 2

SELECTED STRUCTURAL PARAMETERS FOR TRIPHENYLALLYLTIN, WITH ESTIMATED STANDARD DEVIATIONS

	Molecule **A**	Molecule **B**
Bond lengths (Å)		
Sn–C(1)	2.14(1)	2.12(1)
Sn–C(7)	2.15(1)	2.14(1)
Sn–C(13)	2.19(2)	2.16(1)
Sn–C(19)	2.18(1)	2.18(2)
C(19)–C(20)	1.37(3)	1.39(3)
C(20)–C(21)	1.26(3)	1.23(3)
Bond angles (°)		
C(1)–Sn–C(19)	112(1)	111(1)
C(1)–Sn–C(7)	109(1)	107(1)
C(1)–Sn–C(13)	107(1)	109(1)
C(7)–Sn–C(19)	106(1)	108(1)
C(7)–Sn–C(13)	108(1)	108(1)
C(13)–Sn–C(19)	114(1)	113(1)
Sn–C(19)–C(20)	115(2)	114(1)
C(19)–C(20)–C(21)	140(3)	143(3)
Torsion angles (°)		
Sn–C(19)–C(20)–C(21)	|108|	|97|

1.37 and 1.39 Å, the $CH=CH_2$ double bonds 1.26 and 1.23 Å, the bond angles CH_2–$CH=CH_2$ 140 and 143°, and the torsion angles about the single bond CH_2–$CH=$ |108°| and |97°|. Thus the structures of the allyl groups in **A** and in **B** can be regarded as virtually identical within the standard deviations. Both the CH_2–$CH=$ and $CH=CH_2$ bonds are significantly shortened (about 0.08 and 0.10 Å, respectively) with respect to normal values for single and double bonds, and the bond angle CH_2–$CH=CH_2$ is larger than the normal value of about 20°. These effects could be artefacts of possible conformational disorder and of the evident high libration of the $CH=CH_2$ groups, but it is notable that molecules **A** and **B**, even though independent, have identical geometry. Moreover, the torsion angle about CH_2–$CH=$ is almost the same as that predicted by theoretical calculations [4,15] for the lowest energy conformation, which also affords the maximum amount of σ–π conjugation. We do not believe that all these features are merely coincidental.

The distance of the middle point of the double bond from tin is about 3.5 Å, and so p_π–d_π bonding between the metal and the allyl double bond is impossible.

Further evidence also supports the hypothesis of a hyperconjugative effect. The stretching vibration of the C=C double bond in triphenylallyltin, either in the solid state (1623 cm^{-1}, KBr discs) [35] or in solution (1620 cm^{-1} in DMSO and 1624 cm^{-1} in CH_2Cl_2) [36] are very similar. These values are approximatively the same, or only slightly increased in the series of $Bu_{3-n}(CH_2=CHCH_2)SnCl_n$ ($n = 0$–3) [17,18,37] and allylsilanes, allylgermanes and allylstannanes [14,38], where the substituents on the metal vary even more markedly in their potential inductive effects. These observations and those made recently for the reactivity of a number of allyl- and crotyl-tin compounds, for which the reactive site is the allyl carbon in γ position [17–25], suggest that σ–π conjugation, as first postulated by Eaborn and Parker [16],

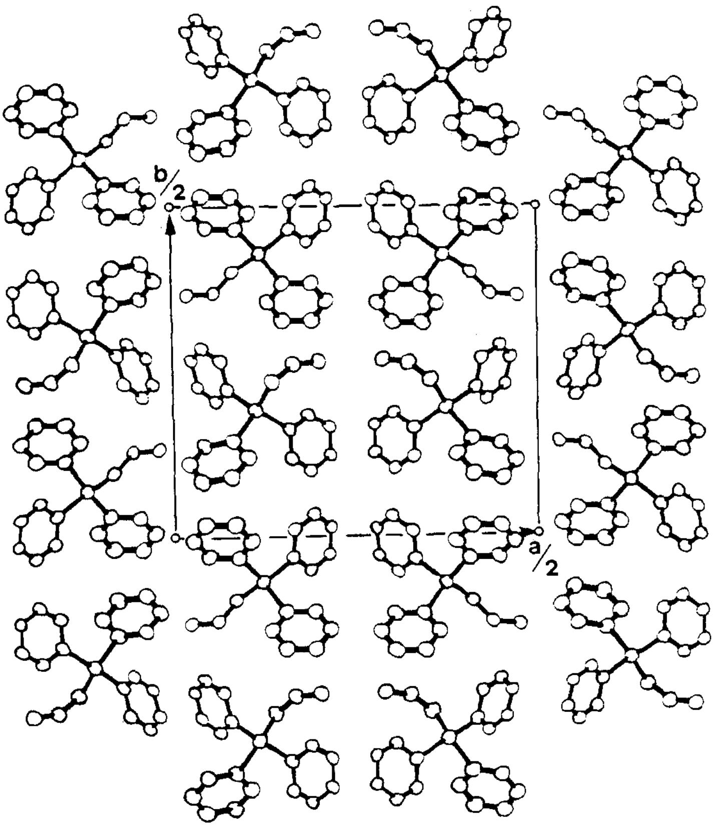

Fig. 2. Packing of the molecules of triphenylallyltin viewed along the *c* axis.

and later by others [39,40], probably plays the most important role in determining the electronic charge distribution in the allyl group.

Figure 2 shows the mode of packing of the molecules as viewed along the *c* axis. With respect to the substituents, considering phenyl and allyl groups of the same steric influence, the packing resembles a pseudo tetragonal arrangement.

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