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Metalorganic diazoalkanes

XX *. Crystal structure of trimethyltin diazoacetic ester, $Me_3SnC(N_2)CO_2Et$ **

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Abstract

$Me_3SnC(N_2)CO_2Et$ was obtained as a yellow, crystalline compound, m.p. 30 °C from the reaction of Me_3SnNEt_2 with $HC(N_2)CO_2Et$, and its structure determined by X-ray diffractometry. The $Me_3SnC(N_2)CO_2Et$ molecules have a plane of symmetry, the diazoacetic ester group being fixed in the *Z*-(1)-conformation. The CNN group is almost linear (177.5(7)°) and has bond lengths (C–N 131.7(8) and N–N 111.9(9) pm) comparable with those in other metalorganic diazoalkanes. As in $Me_3PbC(N_2)CO_2Et$, the oxygen atom of the carbonyl group is weakly coordinated to the tin atom of a neighbouring molecule: Sn–O 312.5(5) pm, C–O–Sn 180.0°.

Introduction

There have been only a few reports of X-ray structural studies on metal derivatives of diazoalkanes. We present below the results of the first such study of a tin diazoalkane.

Results and discussion

The diazoalkanes $Me_3MC(N_2)CO_2Et$ with M = Sn [1] or Pb [2] are easily obtained by the amine elimination procedure:

$$Me_3MNR^1R^2 + HC(N_2)CO_2Et \rightarrow Me_3MC(N_2)CO_2Et + HNR^1R^2$$

$$(M = Sn;\ R^1 = R^2 = Me, Et;\ M = Pb;\ R^1 = R^2 = SiMe_3)$$

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* Final communication in the series "Metalorganic Diazoalkanes" ("Metallorganische Diazoalkane"); for Part XIX see ref. 2.

** Dedicated to Prof. K. Dimroth on the occasion of his 80th birthday.

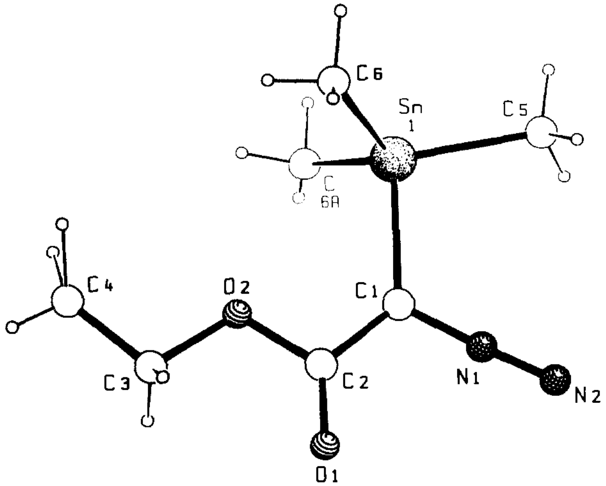

Fig. 1. SCHAKAL drawing [14] of a molecule $Me_3SnC(N_2)CO_2Et$ in the crystal.

On the basis of spectroscopic data mainly those for IR/RE, NMR (^1H, ^{13}C, ^{15}N, ^{119}Sn) and ^{119}Sn-Mössbauer spectra [2], we concluded that in solid Me_3Sn-$C(N_2)CO_2Et$ the molecules have a trigonal bipyramidal configuration at tin with carbonyl oxygen atoms interlinking neighbouring molecules in the crystal, as found previously for, e.g., solid $Me_3PbC(N_2)CO_2Et$ [2]. Diazoacetic ester in the liquid phase from $-50\,°C$ to $+20\,°C$ is present as 2 conformational isomers, *Z*-(1) and *E*-(1), with an estimated activation barrier for interconversion of only 36–48 kJ/mol (calculated value: 56 kJ/mol), a value significantly lower [3] than that for diazo ketones, for which values of 60–72 kJ/mol have been reported [4].

An X-ray crystal structure determination on $Me_3SnC(N_2)CO_2Et$ revealed (Fig. 1) that all the atoms except the methyl group at C(6) and two H-atoms at C(5) lie in the mirror plane of the space group $P2_1/m$. As in the other metalorganic di-

Table 1

Molecular parameters (bond lengths [pm], bond angles [°]) obtained from X-ray data for metalorganic diazoalkanes and the parent CH_2N_2 (gas phase)

Compound	M–C	C–N	N–N	M–C–N [H–C–N]	C–N–N	Lit.
CH_2N_2		132	112	[116.5]	180.0	[6]
$Ph_3Si(Ph)CN_2$	188.2(1)	128.0(1)	113.0(1)	115.3(1)	178.1(1)	[7]
$Ph_3Ge(Ph)CN_2$		isostructural to Si				
$Hg[CN_2CO_2R]_2$ ($R = t$-C_4H_9)	213(3)	125(4)	115(5)	118(1)	178(5)	[8]
$Hg[CN_2CO_2Et]_2$	201(1)	131(2)	108(2)	124(1)	175(2)	[9]
$Me_3PbCN_2CO_2Et$	227.0	133.0	117.0	116.3(1)	174.3(3)	[2]
$Me_3SnCN_2CO_2Et$	214.2(6)	131.7(8)	111.9(9)	118.2(4)	177.5(7)	this work
$[Ph_3P]_2Pd(Cl)[CN_2CO_2Et]$	201.5(1)	127.5(1)	116.0(1)	121.7(8)	177.2(1)	[10]
$[Bu_3P]_2Pd[CN_2CO_2Et]_2$	207.8(6)	127.9(8)	113.0(1)	119.5(5)	176.3(8)	[10]
$RhICH_3(PMe_3)_3[CN_2SiMe_3]$	210(2)	130(3)	109(3)	119(2)	175(2)	[11]

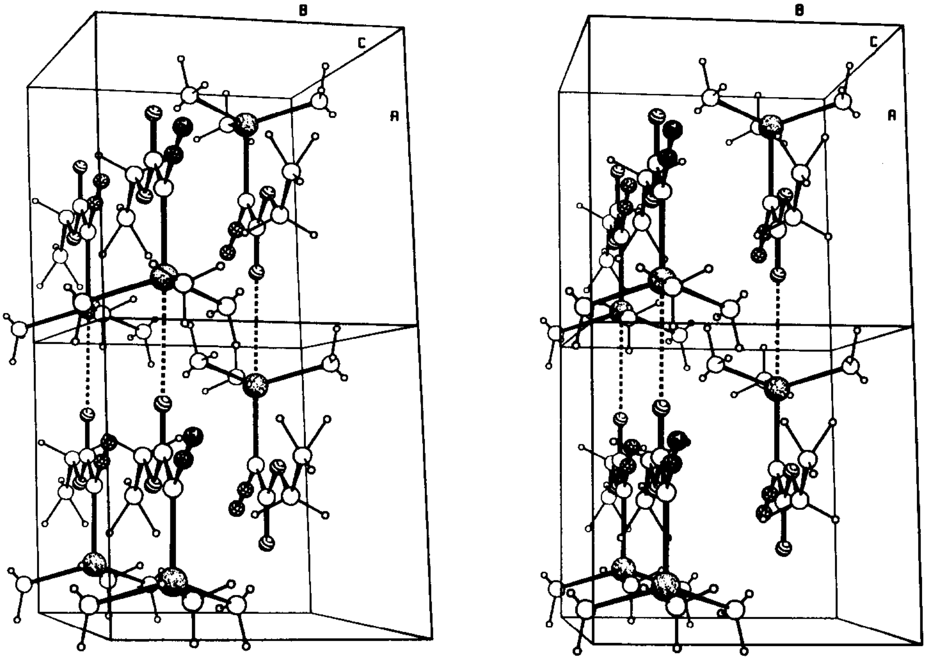

Fig. 2. Stereo view of two unit cells showing the chains formed by weak Sn · · · O contacts.

Table 2

Crystal data and details of crystallographic study

Crystal data	
Formula, M_r	$C_7H_{14}N_2O_2Sn$, 276.89
Absorption μ [cm^{-1}]	22.6, emp. correction (ψ-Scans)
Space group	$P2_1/m$, $Z = 2$
Lattice constants	$a = 745.4(2)$
[pm]	$b = 744.5(3)$ $\beta = 99.73(2)^\circ$
	$c = 1022.4(3)$
Temperature [K]	208
Density [$g\ cm^{-3}$]	$d_c = 1.644$
Data collection	
Diffractometer	4-circle, CAD4 (Enraf–Nonius)
Radiation	Mo-K_α, graphite monochromator
Scan-width (ω-mode)	$(1.1 + 0.35\mathrm{tg}\theta)^\circ$ and additional 25% before and after each reflection for background measurement
Measuring time	variable, max. 25 s/reflection
Measuring range	θ: 2–22°, $\pm h + k + l$
Reflections total	1493
uniques/with $F_o > 3\sigma$	753/745
Parameters	95
Residuals R	0.0289
R_w	0.0397 ($w = 1/\sigma^2(F_o)$)
Goodness of fit S	3.719

Table 3

Fractional coordinates and isotropic equivalent temperature factors U_{eq} [10^{-20} m^2]

Atom	x	y	z	U_{eq}
Sn1	0.83769(5)	0.75000(0)	0.19827(3)	0.0332(2)
O1	0.2630(6)	0.75000(0)	0.2542(4)	0.052(2)
O2	0.5319(6)	0.75000(0)	0.3944(4)	0.042(1)
N1	0.4492(7)	0.75000(0)	0.0507(6)	0.061(2)
N2	0.3765(9)	0.75000(0)	−0.0545(7)	0.107(4)
C1	0.5416(8)	0.75000(0)	0.1725(5)	0.041(2)
C2	0.4259(7)	0.75000(0)	0.2726(5)	0.037(2)
C3	0.4322(9)	0.75000(0)	0.5044(6)	0.048(2)
C4	0.575(1)	0.75000(0)	0.6295(7)	0.056(3)
C5	0.8819(9)	0.75000(0)	−0.0036(6)	0.054(3)
C6	0.9134(7)	0.9912(8)	0.3043(5)	0.054(2)

azoacetic esters listed in Table 1 the diazo ester groups adopt only the *Z*-(1) conformation in the crystal.

In the crystal the $Me_3SnC(N_2)CO_2Et$ molecules are packed in parallel layers (Fig. 2); there is additional weak intermolecular coordination between the carbonyl oxygen atoms of one molecule and the tin atom of the neighbouring molecule generated by translation along the *a*-axis. The Sn · · · O distance of 312.5(5) pm is much smaller than the Van der Waals contact distance of 382 pm: as a consequence, the angles C(1)–Sn–Me are smaller (average 103.1°) and the angle Me–Sn–Me larger (average 115°) than the tetrahedral angle of 109.5° (Tab. 4). This bonding mode confirms our conclusion [5] that five coordinate tin atoms are present in the solid state.

The tin–carbon bond distances are quite normal, with Sn–C(1) 217.8(6) pm somewhat longer than the mean Sn–methyl carbon distance of 213.1 pm. Bond distances in the diazo part of the molecule are similar to those in CH_2N_2 (determined in the gas phase) [6]: as in this molecule, the C(1)–N(1) bond length of

Table 4

Bond lengths [pm] and angles [°] in $Me_3SnC(N_2)CO_2Et$ [a]

Sn1–C1	217.8(6)	C1–Sn1–C5	101.6(2)
Sn1–C5	214.4(6)	C1–Sn1–C6	103.8(2)
Sn1–C6	212.5(6)	C5–Sn1–C6	114.9(2)
C1–N1	131.7(8)	C6–Sn1–C6′	115.4(2)
N1–N2	111.9(9)	Sn1–C1–N1	118.2(4)
C1–C2	144.6(8)	Sn1–C1–C2	128.9(4)
C2–O1	119.6(7)	C1–N1–N2	177.5(7)
C2–O2	135.8(7)	N1–C1–C2	113.0(5)
O2–C3	144.9(8)	C1–C2–O1	126.9(5)
C3–C4	151.7(10)	C1–C2–O2	108.9(5)
Sn1 · · · O1″	312.5(5)	O1–C2–O2	124.2(5)
		C2–O2–C3	114.6(5)
Sn1 · · · O1″–C2″	180.0(5)	O2–C3–C4	106.0(5)
C1–Sn1 · · · O1″	176.5(2)		

[a] Symmetry operations: ′ x, $1.5 - y$, z; ″ $1 + x$, y, z.

131.7(8) pm (for the lead compound the corresponding distance is 133 pm) is short and comparable with that of a carbon–nitrogen double bond (132 pm), while the N(1)–N(2) bond length of 111.9(9) pm (for Pb 117 pm) is consistent with nitrogen–nitrogen triple bond character. The diazo group shows relatively high anisotropic thermal parameters, with a maximum displacement for N(2) in the *b*-direction, perpendicular to the mirror plane ($U_{22} = 0.24(1)$ Å^2). Thus, the bond lengths are probably slightly underestimated. A librational analysis led to minor corrections within the esd for the bond lengths (N(1)–N(2) = 112.7 pm).

Structure determination

A yellow crystal was mounted on a 4-circle-diffractometer (Table 2). The monoclinic cell dimensions were determined from 25 strong reflections. From the systematic absence $0k0$: $k = 2n + 1$ the space group was judged to be $P2_1/m$ or $P2_1$. The structure determination was begun with the centrosymmetric choice $P2_1/m$, and this was confirmed by the subsequent results. The structure was solved by Patterson methods [12] and subsequent difference Fourier syntheses and refined by least square methods using anisotropic temperature factors for all non-H-atoms [13]. All the H-atoms were located and refined (except for those at C5 which were kept at riding positions) with isotropic temperature factors. The atomic coordinates are shown in Table 3 and the bond lengths and angles in Table 4 *.

Acknowledgements

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