N1—C2	1.392 (14)	C4—C5	1.357 (15)
N1—C6	1.43 (2)	C5—C6	1.43 (2)
N1—C1	1.462 (14)		
N7—Au—P	177.5 (2)	C5—N7—Au	126.9 (7)
C10—P—C16	105.1 (5)	C8—N9—C4	102.2 (9)
C10—P—C17	106.3 (6)	O2—C2—N3	121.3 (11)
C16—P—C17	102.2 (6)	O2—C2—N1	121.8 (11)
C10—P—Au	112.8 (4)	N3—C2—N1	116.8 (10)
C16—P—Au	115.9 (4)	C5—C4—N3	122.7 (10)
C17—P—Au	113.4 (4)	C5—C4—N9	110.4 (10)
C2—N1—C6	127.1 (9)	N3—C4—N9	126.9 (10)
C2—N1—C1	115.2 (10)	C4—C5—N7	108.3 (10)
C6—N1—C1	117.6 (9)	C4—C5—C6	123.1 (13)
C2—N3—C4	119.7 (9)	N7—C5—C6	128.6 (12)
C2—N3—C3	119.7 (10)	O6—C6—C5	129.7 (19)
C4—N3—C3	120.4 (10)	O6—C6—N1	119.9 (14)
C8—N7—C5	103.9 (10)	C5—C6—N1	110.3 (10)
C8—N7—Au	129.1 (8)	N7—C8—N9	115.2 (11)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1194). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3,5-Dimethoxycarbonyl-2,6-dimethyl-4-(2-nitrosophenyl)pyridine and Dichlorobis[3,5-dimethoxycarbonyl-2,6-dimethyl-4-(2-nitrophenyl)pyridine]copper(II)

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Abstract

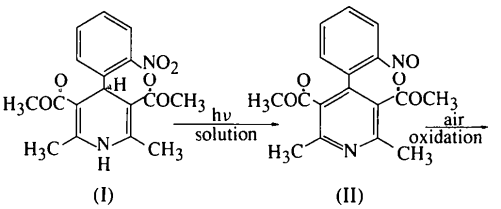
Two decomposition products of the calcium channel blocker nifedipine {the title compounds dimethyl 2,6-dimethyl-4-(2-nitrosophenyl)pyridine-3,5-dicarboxylate, $C_{17}H_{16}N_2O_5$, and dichlorobis[dimethyl 2,6-dimethyl-4-(2-nitrophenyl)pyridine-3,5-dicarboxylate-*N*]copper(II), $[CuCl_2(C_{17}H_{16}N_2O_6)_2]$}, have been found to exist in the solid state, with approximately perpendicular orientations of the pyridine and phenyl rings. Unlike in the parent compound, the ester groups are not coplanar with their pyridine ring, but the nitro and nitroso substituents are coplanar with their respective phenyl rings.

Comment

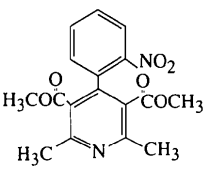
Nifedipine [3,5-dimethoxycarbonyl-2,6-dimethyl-4-(2-nitrophenyl)-1,4-dihydropyridine], (I), is an important calcium-channel antagonist of the dihydropyridine type, known to interact with the α_1 moiety of L-type calcium channels, regulating excitation–contraction coupling of cardiovascular tissues, *i.e.* the smooth muscle of the veins and arteries. Compounds of this class are currently being used in the treatment of a variety of cardiovascular disorders such as angina and hypertension (Triggle, Langs & Janis, 1989; Hurwitz, Partridge & Leach, 1991).

Nifedipine, like most derivatives of the 1,4-dihydropyridine class, undergoes photodecomposition processes. This reaction has been reported to be extremely wavelength sensitive and two decomposition products have been identified by spectroscopic methods. Exposure to UV radiation appears to cause aromatization of the dihydropyridine ring and reduction of the nitro group

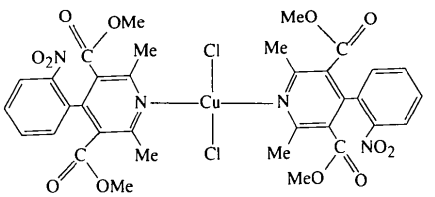
to a nitroso moiety, *i.e.* forming compound (II). Daylight and air oxidation lead to reoxidation of the nitroso group to a nitro function, *i.e.* forming compound (II*a*). The existence of these decomposition products has led to concern about shelf-life, packaging and potency (Núnez-Vergara, Sunkel & Squella, 1994; Sadana & Ghogare, 1991; Hayase, Itagaki, Ogawa, Akutsu, Inagaki & Abiko, 1994).



(I) (II)



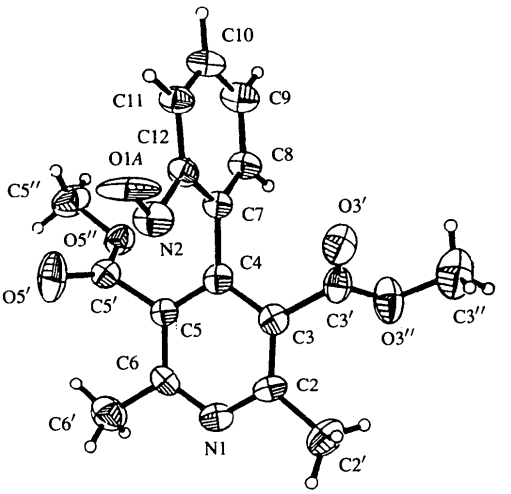
(II*a*)



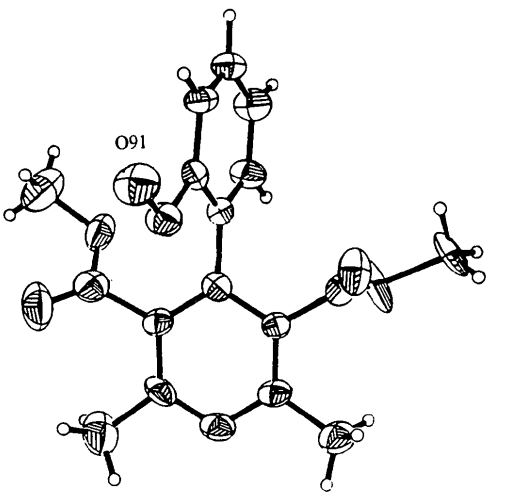
(III)

Calcium antagonistic activity of the 1,4-dihydropyridine family is influenced by (*a*) the presence of the 1,4-dihydropyridine moiety, (*b*) alkyl groups (preferably methyl) substituted at the 2 and 6 positions, (*c*) ester groups at the 3 and 5 positions, (*d*) an aryl (phenyl) substituent at position 4 and (*e*) N—H at position 1. Oxidation of the 1,4-hydropyridine ring to pyridine is reported to diminish activity significantly (Triggle, Langs & Janis, 1989; Morad, Goldmann & Trentham, 1983; Loev, Goodman, Snader, Tedeschi & Macko, 1974; Janis, Silver & Triggle, 1987).

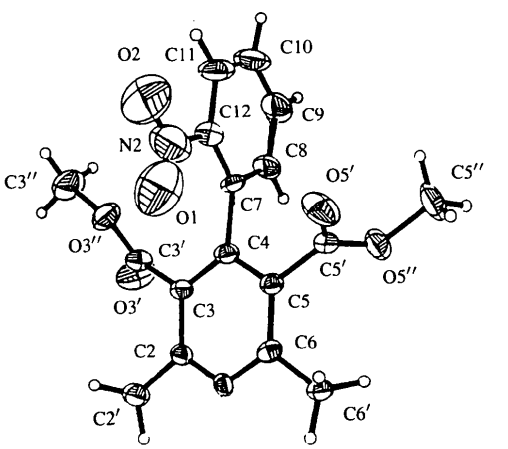
The three-dimensional conformation of these compounds is also important. In all of the 1,4-dihydropyridine-ring-containing nifedipine derivatives examined by single-crystal X-ray diffraction (Triggle, Langs & Janis, 1989; Mehdi & Ravikumar, 1992), the 1,4-dihydropyridine ring exhibits a boat conformation with the N atom at the prow and the phenyl ring in an axial position at the bow. Structure–activity studies have demonstrated that flattening of the boat conformation correlates with increased activity, presumably due to the concurrent change in position of the phenyl ring. When the plane of the phenyl ring is perpendicular to the plane of the base of the boat, *i.e.* the plane formed by atoms C2, C3, C5 and C6 of the non-aromatic ring,



(*a*)



(*b*)



(*c*)

Fig. 1. Projection views of (*a*) molecule *A* and (*b*) molecule *B* of compound (II) (atom numbers for molecule *B* are the same as those of *A* but with the number 9 prefixed to each), and (*c*) the 2,6-dimethyl-3,5-dimethoxycarbonyl-4-(2-nitrophenyl)pyridine ligand of compound (III). Ellipsoids are shown at the 50% probability level.

activity increases (Loev, Goodman, Snader, Tedeschi & Macko, 1974; Triggle, Schefter & Triggle, 1980).

The majority of the more than 30 crystal structures of members of the nifedipine family show the ester groups to have the C=O group coplanar with the C=C bond of the 1,4-dihydropyridine ring (Triggle, Langs & Janis, 1989).

In nifedipine itself, the carbonyl of the ester group attached to C3 is antiperiplanar (*ap*) to the C2=C3 bond, whereas the carbonyl of the ester group at C5 is synplanar (*sp*) to the C5=C6 bond. Thus, the carbonyl groups of the ester functions do not point in the same direction. It is thought that only the *sp* conformation of the ester group permits hydrogen bonding to the carbonyl O atom as an acceptor group (Triggle, Schefter & Triggle, 1980; Langs, Strong & Triggle, 1990).

The decomposition products, which lack the hydrogen-bonding N—H donor group, are reported to lose their activity (Morad, Goldmann & Trentam, 1983). However, various studies of nifedipine derivatives which have an aromatic pyridine ring in place of the 1,4-dihydropyridine ring do not show a complete loss of activity (Loev, Goodman, Snader, Tedeschi & Macko, 1974). Thus, it was of interest to examine the solid-state structures of the two decomposition products of nifedipine, (II) and (II*a*), to observe the change in conformation of the two-ring system and the change in position of the ester groups at positions 3 and 5 upon decomposition.

Compound (II) was isolated from solvent as green–yellow needles. Compound (III) was produced as a yellow oil which failed to crystallize and was isolated as a coordination complex of copper(II) (Fig. 2). Both decomposition products show the plane of the aryl ring to be approximately perpendicular to the plane of the pyridine ring. This is best described by analysis of the torsion angles about C4—C7 [C3—C4—C7—C8 81.6 (8) and 74.4 (9)° in molecules *A* and *B*, respectively, of compound (II), 90.2 (10)° in compound (III)]. In the parent compound, the related angle between the plane of the aryl ring and the plane of the base of the boat of the 1,4-dihydropyridine ring is less than 90°. Perpendicularity of the phenyl ring to the plane of the base of the boat will result in a C5—C4—C7—C8 torsion angle of 60°. The observed angle is 49.2°. With aromatization of the pyridine ring, the boat is completely flattened and atom C4 is sp^2 hybridized, causing the aromatic ring to extend further out into space.

The nitroso and nitro substituents at the 2 position of the aryl ring of compounds (II) and (III), respectively, are coplanar with the aromatic phenyl rings to which they are respectively attached [deviations 0.018 in (II), 0.014 Å in (III)]. In nifedipine, the nitro group is rotated away from coplanarity with the phenyl ring by approximately 37° (Triggle, Schefter & Triggle, 1980).

The spatial arrangements of the methoxycarbonyl groups at C3 and C5 are also different. Both (II) and (III) have methoxycarbonyl groups in non-coplanar positions with respect to the pyridine ring, presumably in order to minimize the steric interactions with the phenyl substituent. In the two molecules in the asymmetric unit of compound (II), one has a C2—C3—C3′—O3′ angle of −126.3 (8)° and a C6—C5—C5′—O5′ angle of 65.1 (10)°, whereas the corresponding angles for the second molecule are −98.4 (9) and 40.2 (12)°. Both show carbonyl groups projecting in the same spatial direction relative to the plane of the pyridine ring. Compound (III) has a C2—C3—C3′—O3′ torsion angle of −101.2 (11)° and a C6—C5—C5′—O5′ angle of −54.2 (13)°. However, the carbonyl groups point in opposite directions with respect to the plane of the pyridine ring.

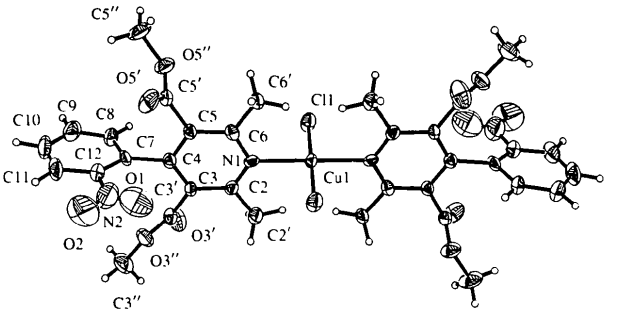


Fig. 2. Projection view of compound (III) with ellipsoids shown at the 50% probability level.

Thus, the decomposition products show the appropriate conformation of the two rings that is associated with activity (*i.e.* approximately perpendicular), but decomposition has caused pronounced changes in the orientation of the ester groups and the nitroso or nitro functional groups.

Aromatization of the 1,4-dihydropyridine ring results in the loss of the H atom from N1, removing any possibility of a hydrogen-bonding interaction with the receptor site. However, the rotation of the ester groups at positions 3 and 5 of (II) and (III) out of conjugation with the π bonds of the ring may permit increased hydrogen bonding to these groups.

Experimental

Compound (II) was prepared by slow evaporation of a solution of 20 mg of nifedipine in 10 ml of ethanol in ultraviolet light. Light-green needle-like crystals were formed. Compound (III) was prepared by slow evaporation of a solution of 20 mg of nifedipine in 10 ml of ethanol with copper(II) chloride (9.8 mg, 1:1) in an open container in the presence of fluorescent light. Dark purple crystals were produced after several weeks.

Compound (II)

Crystal data

$C_{17}H_{16}N_2O_5$
$M_r = 328.3$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$P2_1/c$
a = 18.171 (4) Å
b = 7.157 (1) Å
c = 26.165 (5) Å
β = 90.20 (3)°
V = 3402.6 (13) Å^3
Z = 8
D_x = 1.282 Mg m^{-3}

Cell parameters from 46 reflections
θ = 4.38–12.37°
μ = 0.096 mm^{-1}
T = 298 K
Needle
0.4 × 0.2 × 0.1 mm
Green

Data collection

Syntex $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
7522 measured reflections
5831 independent reflections
1328 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.084
θ_{max} = 25°
$h = -1 \rightarrow 19$
$k = -1 \rightarrow 8$
$l = -31 \rightarrow 31$
3 standard reflections monitored every 97 reflections
intensity decay: 3.7%

Refinement

Refinement on F^2
$R(F)$ = 0.063
$wR(F^2)$ = 0.158
S = 0.694
5795 reflections
461 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0268P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -1.272$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Extinction was refined but was insignificant
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
N1	0.2852 (3)	−0.1787 (8)	0.0848 (2)	0.061 (2)
C2	0.3300 (3)	−0.0918 (10)	0.0523 (2)	0.052 (2)
C2′	0.3326 (3)	−0.1806 (9)	0.0005 (2)	0.083 (2)
C3	0.3726 (3)	0.0585 (10)	0.0668 (2)	0.053 (2)
C3′	0.4241 (4)	0.1545 (10)	0.0296 (3)	0.066 (2)
O3′	0.4883 (2)	0.1801 (8)	0.03731 (15)	0.088 (2)
O3′′	0.3876 (2)	0.2127 (8)	−0.0108 (2)	0.096 (2)
C3′′	0.4316 (4)	0.2938 (11)	−0.0510 (2)	0.123 (3)
C4	0.3715 (3)	0.1225 (9)	0.1177 (2)	0.055 (2)
C5	0.3225 (3)	0.0309 (9)	0.1508 (2)	0.048 (2)
C5′	0.3181 (3)	0.0904 (11)	0.2059 (3)	0.054 (2)
C5′′	0.2796 (3)	0.3342 (9)	0.2607 (2)	0.095 (3)
O5′	0.3384 (3)	−0.0012 (8)	0.2409 (2)	0.115 (2)
O5′′	0.2867 (2)	0.2539 (7)	0.2100 (2)	0.0704 (14)
C6	0.2818 (3)	−0.1207 (10)	0.1329 (3)	0.055 (2)
C6′	0.2298 (3)	−0.2199 (9)	0.1683 (2)	0.091 (2)
C7	0.4183 (3)	0.2808 (10)	0.1360 (2)	0.047 (2)
C8	0.3990 (3)	0.4600 (10)	0.1288 (2)	0.058 (2)
C9	0.4400 (4)	0.6035 (10)	0.1489 (2)	0.075 (2)
C10	0.5028 (4)	0.5665 (10)	0.1773 (3)	0.070 (2)
C11	0.5239 (3)	0.3854 (10)	0.1846 (2)	0.063 (2)
C12	0.4830 (3)	0.2433 (10)	0.1639 (2)	0.054 (2)
N2	0.5020 (3)	0.0504 (9)	0.1690 (2)	0.081 (2)
O1*A*†	0.5649 (17)	0.019 (3)	0.1865 (14)	0.115 (11)
O1*B*†	0.5550 (22)	0.026 (4)	0.1929 (15)	0.156 (14)
N91	0.0632 (4)	0.2394 (8)	−0.0383 (2)	0.071 (2)
C92	0.0034 (4)	0.3288 (10)	−0.0554 (2)	0.060 (2)
C92′	−0.0674 (3)	0.2501 (9)	−0.0354 (2)	0.086 (2)
C93	0.0064 (3)	0.4696 (10)	−0.0901 (2)	0.052 (2)
C93′	−0.0625 (4)	0.5461 (12)	−0.1138 (3)	0.062 (2)
C93′′†	−0.1711 (14)	0.720 (4)	−0.1023 (9)	0.096 (10)
C93*X*†	−0.1492 (19)	0.796 (5)	−0.1132 (12)	0.142 (15)
O93′	−0.0845 (2)	0.5016 (7)	−0.1544 (2)	0.089 (2)
O93′′†	−0.090 (3)	0.659 (8)	−0.0784 (15)	0.124 (14)
O93*X*†	−0.100 (3)	0.6788 (6)	−0.0900 (14)	0.090 (10)
C94	0.0739 (4)	0.5358 (10)	−0.1080 (2)	0.053 (2)
C95	0.1370 (4)	0.4472 (10)	−0.0896 (2)	0.059 (2)
C95′	0.2129 (5)	0.4977 (14)	−0.1100 (3)	0.076 (3)
C95′′	0.2871 (4)	0.7447 (12)	−0.1359 (2)	0.138 (4)
O95′	0.2583 (3)	0.3847 (10)	−0.1222 (2)	0.126 (3)
O95′′	0.2208 (3)	0.6802 (9)	−0.1111 (2)	0.089 (2)
C96	0.1295 (4)	0.2991 (11)	−0.0556 (2)	0.068 (2)
C96′	0.1932 (4)	0.1850 (12)	−0.0359 (2)	0.133 (4)
C97	0.0749 (3)	0.6917 (10)	−0.1452 (2)	0.050 (2)
C98	0.0605 (4)	0.8694 (11)	−0.1304 (3)	0.074 (2)
C99	0.0592 (4)	1.0135 (10)	−0.1652 (3)	0.080 (2)
C910	0.0735 (3)	0.9826 (10)	−0.2163 (3)	0.068 (2)
C911	0.0855 (3)	0.8038 (10)	−0.2323 (2)	0.061 (2)
C912	0.0881 (3)	0.6577 (10)	−0.1976 (2)	0.051 (2)
N92	0.1012 (3)	0.4688 (9)	−0.2111 (2)	0.070 (2)
O91	0.1145 (3)	0.4430 (7)	−0.2563 (2)	0.098 (2)

† Molecule *A* has 50/50 disorder in the position of the O atom of the nitroso group (O1*A* and O1*B*). Molecule *B* has 50/50 disorder of the methoxy O atom and the CH_3 group of one ester group (O93′′, C93′′ and O93*X*, C93*X*).

Table 2. *Selected geometric parameters* (Å, °) *for* (II)

N1—C6	1.326 (7)	N91—C96	1.358 (7)
N1—C2	1.332 (7)	N91—C92	1.338 (7)
C2—C3	1.378 (7)	C92—C93	1.357 (7)
C2—C2′	1.500 (7)	C92—C92′	1.500 (7)
C3—C4	1.408 (7)	C93—C94	1.397 (7)
C3—C3′	1.518 (8)	C93—C93′	1.501 (8)
C3′—O3′	1.197 (7)	C93′—O93′	1.176 (6)
C3′—O3′′	1.315 (7)	C93′—O93′′	1.33 (5)
O3′′—C3′′	1.446 (6)	C93′—O93*X*	1.33 (5)
C4—C5	1.406 (7)	C93′′—O93′′	1.65 (5)
C4—C7	1.495 (8)	C93*X*—O93*X*	1.36 (5)
C5—C6	1.394 (7)	C94—C95	1.394 (7)
C5—C5′	1.506 (7)	C94—C97	1.481 (8)
C5′—O5′	1.183 (7)	C95—C96	1.391 (8)
C5′—O5′′	1.307 (7)	C95—C95′	1.525 (9)
C5′′—O5′′	1.453 (6)	C95′—O95′	1.199 (8)
C6—C6′	1.503 (7)	C95′—O95′′	1.315 (8)
C7—C8	1.343 (7)	C95′′—O95′′	1.445 (7)
C7—C12	1.407 (7)	C96—C96′	1.506 (8)
C8—C9	1.373 (7)	C97—C98	1.355 (8)
C9—C10	1.385 (7)	C97—C912	1.413 (7)
C10—C11	1.365 (8)	C98—C99	1.376 (8)
C11—C12	1.370 (7)	C99—C910	1.381 (7)
C12—N2	1.429 (8)	C910—C911	1.364 (8)
N2—O1*B*	1.16 (3)	C911—C912	1.386 (7)
N2—O1*A*	1.25 (3)	C912—N92	1.418 (7)
		N92—O91	1.221 (5)
C6—N1—C2	119.3 (6)	C92—N91—C96	117.4 (6)
N1—C2—C3	122.2 (6)	N91—C92—C93	122.9 (6)
N1—C2—C2′	113.6 (6)	N91—C92—C92′	113.7 (6)
C3—C2—C2′	124.1 (7)	C93—C92—C92′	123.3 (7)
C2—C3—C4	120.3 (6)	C92—C93—C94	121.0 (6)
C2—C3—C3′	121.6 (6)	C92—C93—C93′	120.8 (6)
C4—C3—C3′	118.0 (6)	C94—C93—C93′	118.0 (6)
O3′—C3′—O3′′	125.2 (7)	O93′—C93′—O93′′	131.7 (18)
O3′—C3′—C3	124.3 (7)	O93′—C93′—C93	123.7 (7)
O3′′—C3′—C3	110.4 (6)	O93′′—C93′—C93	104.5 (18)
C3′—O3′′—C3′′	115.6 (5)	C93′—O93′′—C93′′	103.5 (24)
C3—C4—C5	116.2 (6)	C95—C94—C93	116.8 (6)
C3—C4—C7	122.6 (6)	C95—C94—C97	123.9 (6)
C5—C4—C7	121.2 (6)	C93—C94—C97	119.3 (6)
C6—C5—C4	119.5 (6)	C96—C95—C94	119.1 (6)
C6—C5—C5′	120.8 (6)	C96—C95—C95′	119.6 (7)
C4—C5—C5′	119.5 (6)	C94—C95—C95′	121.0 (6)
O5′—C5′—O5′′	124.5 (7)	O95′—C95′—O95′′	126.1 (9)
O5′—C5′—C5	124.5 (7)	O95′—C95′—C95	123.9 (9)

O5''—C5'—C5	110.9 (6)	O95''—C95'—C95	110.0 (8)
C5'—O5''—C5''	118.1 (5)	C95'—O95''—C95''	114.8 (7)
N1—C6—C5	122.4 (6)	N91—C96—C95	122.8 (6)
N1—C6—C6'	117.9 (7)	N91—C96—C96'	113.4 (7)
C5—C6—C6'	119.6 (6)	C95—C96—C96'	123.7 (7)
C8—C7—C12	118.2 (6)	C98—C97—C912	118.2 (6)
C8—C7—C4	122.1 (6)	C98—C97—C94	121.1 (6)
C12—C7—C4	119.7 (6)	C912—C97—C94	120.7 (6)
C7—C8—C9	121.3 (6)	C97—C98—C99	121.1 (6)
C8—C9—C10	120.5 (7)	C98—C99—C910	121.2 (7)
C11—C10—C9	119.1 (7)	C911—C910—C99	118.5 (6)
C10—C11—C12	119.9 (6)	C910—C911—C912	120.8 (6)
C11—C12—C7	121.0 (6)	C911—C912—N92	124.1 (6)
C11—C12—N2	123.3 (6)	C911—C912—C97	120.0 (6)
C7—C12—N2	115.7 (6)	N92—C912—C97	115.9 (6)
O1A—N2—C12	115.5 (12)	O91—N92—C912	114.8 (6)

Compound (III)

Crystal data

$[CuCl_2(C_{17}H_{16}N_2O_6)_2]$
$M_r = 823.1$
Monoclinic
$P2_1/n$
$a = 13.184$ (3) Å
$b = 7.768$ (2) Å
$c = 17.736$ (4) Å
$\beta = 91.50$ (3)°
$V = 1815.8$ (7) Å^3
$Z = 2$
$D_x = 1.506$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 27 reflections
$\theta = 5.37$–$8.56°$
$\mu = 0.817$ mm^{-1}
$T = 298$ K
Chunk
0.3 × 0.2 × 0.2 mm
Purple

Data collection

Siemens $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XEMP*; Sheldrick, 1993)
$T_{min} = 0.72$, $T_{max} = 0.78$
4231 measured reflections
3211 independent reflections
1262 observed reflections [$F > 10.0\sigma(F)$]

$R_{int} = 0.070$
$\theta_{max} = 30.0°$
$h = -1 \rightarrow 15$
$k = -1 \rightarrow 9$
$l = -21 \rightarrow 21$
3 standard reflections monitored every 97 reflections
intensity decay: 3%

Refinement

Refinement on F
$R = 0.058$
$wR = 0.071$
$S = 1.70$
3211 reflections
242 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.0008F_o^2]$
$(\Delta/\sigma)_{max} = 0.014$

$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ e Å^{-3}
Extinction was refined but was insignificant
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (III)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Cu1	0	0	0	0.041 (1)
Cl1	−0.1450 (2)	0.1416 (3)	0.0165 (1)	0.066 (1)
N1	−0.0012 (4)	0.069 (1)	−0.1111 (4)	0.039 (2)
C2	−0.0505 (6)	−0.029 (1)	−0.1624 (5)	0.040 (3)
C2'	−0.0997 (7)	−0.193 (1)	−0.1338 (5)	0.053 (3)
C3	−0.0540 (6)	0.018 (1)	−0.2384 (4)	0.039 (3)
C4	−0.0068 (6)	0.166 (1)	−0.2615 (5)	0.045 (3)
C5	0.0419 (6)	0.269 (1)	−0.2084 (4)	0.037 (3)
C5'	0.0879 (8)	0.436 (1)	−0.2308 (6)	0.052 (4)
C5''	0.2004 (10)	0.570 (1)	−0.3108 (8)	0.107 (6)
O5'	0.0654 (7)	0.572 (1)	−0.2048 (5)	0.061 (4)
O5''	0.1555 (5)	0.417 (1)	−0.2823 (4)	0.072 (3)
C6	0.0418 (6)	0.219 (1)	−0.1328 (5)	0.042 (3)
C6'	0.0921 (7)	0.326 (1)	−0.0705 (5)	0.060 (4)
C7	−0.0173 (7)	0.219 (1)	−0.3432 (5)	0.048 (3)
C8	−0.0988 (8)	0.327 (1)	−0.3643 (6)	0.068 (4)
C9	−0.1165 (10)	0.371 (1)	−0.4385 (8)	0.087 (6)
C10	−0.0491 (13)	0.309 (2)	−0.4918 (7)	0.099 (6)
C11	0.0317 (11)	0.210 (1)	−0.4743 (6)	0.081 (5)
C12	0.0418 (8)	0.167 (1)	−0.3991 (5)	0.060 (4)
N2	0.1249 (17)	0.064 (2)	−0.3867 (10)	0.130 (9)
O1	0.1451 (13)	0.016 (2)	−0.3364 (12)	0.178 (9)
O2	0.1807 (10)	0.004 (2)	−0.4326 (9)	0.182 (7)
O3''	−0.2068 (5)	−0.0587 (9)	−0.2975 (4)	0.073 (3)
O3'	−0.0697 (6)	−0.191 (1)	−0.3368 (4)	0.088 (3)
C3'	−0.1103 (8)	−0.094 (1)	−0.2959 (5)	0.050 (4)
C3''	−0.2676 (8)	−0.15 (1)	−0.3562 (7)	0.103 (6)

Table 4. *Selected geometric parameters* (Å, °) *for* (III)

Cu1—Cl1	2.232 (2)	C5''—O5''	1.43 (1)
Cu1—N1	2.041 (7)	C6—C6'	1.52 (1)
N1—C2	1.34 (1)	C7—C8	1.41 (1)
N1—C6	1.36 (1)	C7—C12	1.34 (1)
C2—C2'	1.52 (1)	C8—C9	1.37 (1)
C2—C3	1.40 (1)	C9—C10	1.40 (2)
C3—C4	1.36 (1)	C10—C11	1.34 (2)
C3—C3'	1.52 (1)	C11—C12	1.38 (1)
C4—C5	1.38 (1)	C12—N2	1.37 (2)
C4—C7	1.51 (1)	N2—O1	0.99 (2)
C5—C5'	1.49 (1)	N2—O2	1.20 (2)
C5—C6	1.40 (1)	O3''—C3'	1.30 (1)
C5'—O5'	1.20 (1)	O3''—C3''	1.48 (1)
C5'—O5''	1.30 (1)	O3'—C3'	1.19 (1)
Cl1—Cu1—N1	90.7 (2)	N1—C6—C6'	116.3 (7)
N1—Cu1—Cl1'	89.3 (2)	C5—C6—C6'	122.2 (8)
Cu1—N1—C6	120.4 (5)	C4—C7—C8	117.8 (8)
C2—N1—C6	119.5 (7)	C4—C7—C12	126.2 (9)
N1—C2—C2'	116.7 (7)	C8—C7—C12	116.0 (9)
N1—C2—C3	120.8 (8)	C7—C8—C9	120.8 (10)
C2'—C2—C3	122.4 (8)	C8—C9—C10	117.9 (12)
C2—C3—C4	120.2 (8)	C9—C10—C11	123.6 (12)
C2—C3—C3'	120.2 (8)	C10—C11—C12	114.8 (12)
C4—C3—C3'	119.6 (7)	C7—C12—C11	126.8 (11)
C3—C4—C5	119.0 (8)	C7—C12—N2	122.3 (11)
C3—C4—C7	118.8 (8)	C11—C12—N2	110.9 (12)
C5—C4—C7	122.0 (8)	C12—N2—O1	123.7 (21)
C4—C5—C5'	120.3 (8)	C12—N2—O2	128.0 (17)
C4—C5—C6	118.9 (8)	O1—N2—O2	108.1 (22)
C5'—C5—C6	120.7 (8)	N2—O1—O2	39.9 (15)
C5—C5'—O5'	124.2 (10)	N2—O2—O1	32.0 (12)
C5—C5'—O5''	112.4 (9)	C3'—O3''—C3''	115.3 (8)
O5'—C5'—O5''	123.5 (11)	C3—C3'—O3''	110.9 (8)
C5'—O5''—C5''	116.9 (9)	C3—C3'—O3'	123.8 (9)
N1—C6—C5	121.5 (8)	O3''—C3'—O3'	125.2 (9)

Symmetry code: (i) $-x, -y, -z$.

A scan width of 0.6° above $K\alpha_1$ and 0.6° below $K\alpha_2$, a variable scan rate and background counts on each side of every scan were used. Refinement was by full-matrix least-squares methods. Compound (II) crystallizes with two molecules per asymmetric unit, each of which displays a disordered substituent.

For both compounds, data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1995); molecular graphics: *SHELXS*86.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1185). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[4-Chloro-3-(2-nitrophenylthio)butyl]triphenylstannane

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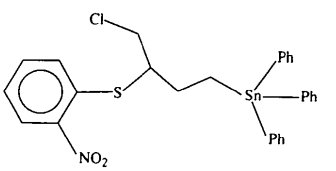
Abstract

The Sn atom in $[Sn(C_6H_5)_3(C_{10}H_{11}ClNO_2S)]$ has slightly distorted tetrahedral geometry; a weak intramolecular S···O interaction exists as shown by the S···O distance of 2.610 (5) Å and the C—S···O angle of 177.5 (3)°.

Comment

The crystal structure determination of the addition product of $Ph_3SnCH_2CH_2CH{:}CH_2$ and 2-$O_2NC_6H_4SCl$ reveals it to be $Ph_3SnCH_2CH_2CH(SC_6H_4NO_2\text{-}2)CH_2Cl$, (I), the anti-Markownikov adduct. This corrects an earlier assignment of the structure, based on the ^1H NMR spectrum, as $Ph_3SnCH_2CH_2CH(Cl)CH_2SC_6H_4NO_2$-2 (Wigzell & Wardell, 1982). The geometry about the Sn atom in (I) is slightly distorted tetrahedral, with C—Sn—C valence angles ranging from 107.2 (1) to 115.5 (2)°. There are no short Sn···Cl or Sn···S contacts.



(I)

As found for a number of aryl and alkyl 2-nitroaryl sulfides, there is a weak intramolecular S···O interaction within (I) in the solid state; the nitro group is nearly coplanar with the atoms in the SC_6H_4 moiety: the O(10)—N(8)—C(7)—C(6) torsion angle is 3.6 (7)°. The S(5)···O(10) separation in (I) is 2.610 (5) Å, which is less than the sum of the van der Waals radii (3.25 Å). The C(4)—S(5)···O(10) angle is 177.5 (3)°. Crystallographically determined values of S···O distances and C—S···O angles in other 2-nitroaryl sulfides are: 2.656 (1) Å and 171.7° in 2-$O_2NC_6H_4SC_6H_4NO_2$-2 (Kucsman, Kapovits, Parkanyi, Argay & Kalman, 1984); 2.715 (8) Å and 178.2 (3)° in $Ph_3SnCHClCH_2SC_6H_3Me$-4-NO_2-2 and 2.655 (5) Å and 172.7 (3)° in $Ph_3SnCH(SCN)CH_2SC_6H_4NO_2$-2 (Howie, Wardell, Zanetti, Cox & Doidge-Harrison, 1992). As shown by electron diffraction, the S···O interactions in 2-nitroaryl sulfides can persist in the gas phase; for example, values of S···O and C—S···O in gaseous 2-$O_2NC_6H_4SMe$ were determined to be 2.769 (9) Å and

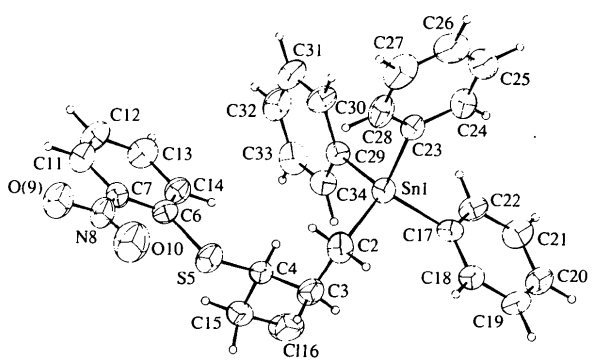


Fig. 1. View of a molecule of (I) indicating non-H-atom labelling. Displacement ellipsoids are at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.