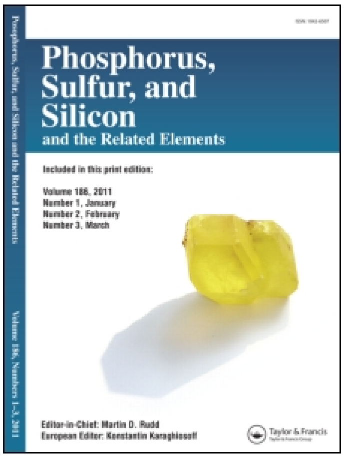

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

DISTORTION COORDINATE FOR NONRIGID FIVE-COORDINATED ANTIMONY. SYNTHESIS AND STRUCTURE OF OXYGEN- AND SULFUR-CONTAINING CYCLIC ORGANOSTIBORANES

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To cite this Article Holmes, Robert R. , Day, Roberta O. , Chandrasekhar, V. and Holmes, Joan M.(1995) 'DISTORTION COORDINATE FOR NONRIGID FIVE-COORDINATED ANTIMONY. SYNTHESIS AND STRUCTURE OF OXYGEN-AND SULFUR-CONTAINING CYCLIC ORGANOSTIBORANES', Phosphorus, Sulfur, and Silicon and the Related Elements, 99: 1, 13 — 27

To link to this Article: DOI: 10.1080/10426509508031333
URL: http://dx.doi.org/10.1080/10426509508031333

Phosphorus, Sulfur, and Silicon, 1995, Vol. 99, pp. 13–27
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DISTORTION COORDINATE FOR NONRIGID FIVE-COORDINATED ANTIMONY. SYNTHESIS AND STRUCTURE OF OXYGEN- AND SULFUR-CONTAINING CYCLIC ORGANOSTIBORANES[1,2]

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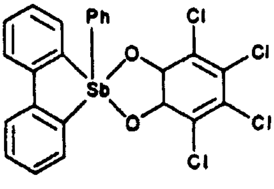
The monocyclic stiboranes $Ph_3Sb[S_2C_2(CN)_2]$ (**1**) and $Ph_3Sb(O_2C_6H_3\text{-}4\text{-}NO_2)$ (**3**) were synthesized by the reaction of Ph_3SbCl_2 with the disodium salt of maleonitriledithiol and by the reaction of 4-nitrocatechol in the presence of Et_3N, respectively. Reaction of *p*-tolylstibonic acid with pinacol gave the bicyclic stiborane $(Me_4C_2O_2)_2Sb(C_6H_4\text{-}p\text{-}Me)$ (**2**). Stiboranes **2** and **3** are new compounds. X-ray analysis revealed that **1** and **2** are trigonal bipyramidal while **3** is closer to a square-pyramidal structure. Molecules of **3** exist in the solid as weakly connected dimers, which accounts for its structural displacement toward the square pyramid. The distortion coordinate expressing solid-state nonrigidity is the Berry pseudorotational coordinate, the same as that found for pentacoordinated structures of other elements of main groups 4 (14) and 5 (15). However, lattice effects enter as a more important structural influence for some stiboranes. Stiborane **1** crystallizes in the monoclinic space group $P2_1/c$ with a = 9.844 (3) Å, b = 10.101 (2) Å, c = 20.537 (4) Å, β = 92.63 (2)°, and Z = 4. **2** crystallizes in the tetragonal space group $I\bar{4}2d$ with a = 23.787 (5) Å, c = 7.070 (1) Å, and Z = 8. **3** crystallizes in the monoclinic space group $P2_1/n$ with a = 10.131 (1) Å, b = 18.945 (5) Å, c = 10.788 (2) Å, β = 99.69 (1)°, and Z = 4. The final conventional unweighted agreement factors were 0.024 (**1**), 0.025 (**2**), and 0.032 (**3**).

INTRODUCTION

In the previous paper,[1b] we showed that, in the absence of lattice effects, the formation of the normally higher energy square-pyramidal structure for five-coordinated antimony compounds follows the same general criteria found for other group 4 (14^{39})[3–5] and 5 (15^{39})[6–8] elements in the pentacoordinated state.

Since lattice effects are more pronounced with antimony as the central element[9] and hence act as a complicating feature compared to the case for phosphorus or arsenic, it remains to establish how well a distortion coordinate between the trigonal bipyramid (TBP) and square or rectangular pyramid (RP) is followed and what influence substituent effects have in controlling structural distortions along this coordinate. For example, it is concluded[1b] that lattice effects are important in leading to the formation of square pyramids for $SbPh_5$[10] and the monohydrate composition $[Ph_3Sb(O_2C_6H_4)]_2 \cdot H_2O$.[11] This assertion is supported by the presence of trigonal-bipyramidal geometries in the cyclohexane solvate $SbPh_5 \cdot 0.5C_6H_{12}$,[12] the tolyl derivative $(p\text{-}CH_3\text{-}C_6H_4)_5Sb$,[13] and the chlorinated monocyclic $Ph_3Sb(O_2C_6Cl_4)$[1b] analogue to the monohydrate composition above.

Thus far, the square pyramid has been found in only one spirocyclic derivative, $(Cl_4C_6O_2)(C_{12}H_8)SbPh \cdot 0.25C_6H_6 \cdot 0.25CH_2Cl_2$.[1b] Ring unsaturation is present, and



like atoms are bound to antimony in each of the rings, a criterion found in forming square pyramids for phosphoranes[6,7] and arsoranes,[8] as well as five-coordinated anionic silicates,[3] germanates,[4] and stannates[5] isoelectronic with the group 5 elements.

It is necessary to explore a greater variety of stiboranes to define the form of the distortion coordinate for hypervalent antimony in the pentacoordinated state. With the realization that stiboranes are more fluxional or nonrigid entities than their phosphorus and arsenic counterparts,[9] one can expect more pronounced structural changes induced by substituent electronic and steric effects, as well as changes brought about by intermolecular effects caused by the less electronegative, more metallic character of antimony.

In this paper, we report the synthesis and structural determination of the dithiolato stiborane $Ph_3Sb[S_2C_2(CN)_2]$ (**1**), the pinacolato stiborane $(Me_4C_2O_2)_2Sb(C_6H_4\text{-}p\text{-}Me)$ (**2**), and the 4-nitrocatecholato derivative $Ph_3Sb(O_2C_6H_3\text{-}4\text{-}NO_2)$ (**3**).

The monocyclic derivatives **1** and **3**, having varying ring compositions, were chosen to provide comparison with the monohydrate stiborane $[Ph_3Sb(O_2C_6H_4)]_2 \cdot H_2O$ containing an unsubstituted catecholate ring. Since a dramatic structural change was encountered on going from antimony pentaphenyl[10] to the p-tolyl derivative $(p\text{-}MeC_6H_4)_5Sb$,[13] a comparison between the structure of the p-tolyl-containing compound **2** and that of the previously studied phenyl stiborane $(Me_4C_2O_2)_2SbPh$[14] should reveal if lattice effects are an important consideration here as well. Both contain the spirobis(pinacolato) ring system.

EXPERIMENTAL

Triphenylantimony dichloride (Alfa) was used as received. Triphenylantimony and antimony trichloride (Aldrich) were purified by sublimation before use. Pinacol was thoroughly dried under vacuum before use. The solvents were purified according to standard procedures.[15]

Proton NMR spectra were recorded on a Varian 300-MHz instrument operating in the FT-pulse mode. Chemical shifts were measured in ppm relative to tetramethylsilane as the internal standard.

Preparation of Triphenyl(maleonitrile-1,2-dithiolato)antimony(V), $Ph_3Sb[S_2C_2(CN)_2]$ (**1**). The disodium salt of maleononitriledithiol (1.10 g, 5.91 mmol), prepared according to the procedure of Holm and coworkers,[16] and triphenylantimony dichloride (2.51 g, 5.93 mmol) were taken in a two-necked round-bottomed flask under an atmosphere of argon.[17] Benzene (200 mL) was added to this mixture, and it was stirred for 48 h. Filtration of sodium chloride and removal of benzene in vacuo from the filtrate afforded a red-colored solid: 2.6 g, 89.7%.

The product was recrystallized from methylene chloride to yield red crystals: mp 176–180°C (lit.[17] mp 171–172°C). Anal. Calcd for $C_{22}H_{15}N_2S_2Sb$: C, 53.57; H, 3.07; N, 5.68. Found: C, 53.58; H, 3.03; N, 5.42. ^1H NMR ($CDCl_3$): 7.62 (m).

Preparation of p-Tolylbis(pinacolato)antimony(**V**), *$(Me_4C_2O_2)_2Sb(C_6H_4$-p-Me)* (**2**). *p*-Tolylstibonic acid[18] (0.75 g, 2.85 mmol) was taken as a suspension in dry benzene (70 mL). Pinacol (0.67 g, 5.67 mmol) was added to this suspension followed by 2,2-dimethoxypropane (0.90 g, 8.64 mmol). The reaction mixture was heated under reflux for 4 h and filtered to remove some insoluble material. The filtrate was stripped from its solvent, affording a semisolid. This was dissolved in a minimum amount of hot benzene (2 mL). Skelly B (a mixture of aliphatic hydrocarbons, 88–98°C fraction, Home Oil Co., Wichita, KS) was added (4 mL) until a slight turbidity appeared. The solution was kept at room temperature for crystallization. Fine needlelike crystals could be isolated, identified to be compound **2**. As these crystals were not suitable for single-crystal X-ray study, a second recrystallization from methylene chloride and Skelly B (1:1) was carried out at 0°C, now affording suitable single crystals: 0.76 g, 60%; mp 183–186°C. Anal. Calcd for $C_{19}H_{31}O_4Sb$: C, 51.26; H, 7.02. Found: C, 51.00; H, 7.16. ^1H NMR ($CDCl_3$): 7.45 (m, 4 H); 2.40 (s, 3 H); 1.30 (s, 6 H); 1.10 (s, 6 H).

Preparation of Triphenyl(4-nitrocatecholato)antimony(**V**), *$Ph_3Sb(O_2C_6H_3$-4-$NO_2)$* (**3**). Triphenylantimony dichloride (1.14 g, 2.79 mmol) was dissolved in benzene (200 mL), and 4-nitrocatechol (0.43 g, 2.77 mmol) was added to the mixture followed by triethylamine (0.56 g, 5.53 mmol). The reaction mixture was stirred at room temperature for 48 h. A precipitate had formed in the reaction mixture. It was filtered and dissolved in chloroform (100 mL), and the solution was washed with water (4 × 50 mL). The organic layer was separated and dried (Na_2SO_4). Removal of chloroform in vacuo afforded a yellow solid, which was recrystallized from a mixture of methylene chloride and Skelly B (1:2) at 5°C. Beautiful yellow crystals, identified to be compound **3**, were isolated: 0.7 g, 50%; mp 144–146°C. ^1H NMR ($CDCl_3$): 7.68 (m), 7.46 (m), 6.84 (m).

Crystallography. All X-ray crystallographic studies were done with an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda_{K\alpha 1}$ = 0.709 30 Å, $\lambda_{K\alpha 2}$ = 0.713 59 Å) at an ambient temperature of 23 ± 2°C. Details of the experimental and computational procedures have been described previously.[19] Crystals were mounted inside of thin-walled glass capillaries, which were sealed as a precaution against moisture sensitivity.

X-ray Crystallographic Studies for **1**. The crystal used for the X-ray study was cut from a large, bright red-orange, multifaceted, canoe-shaped crystal and had dimensions of 0.24 × 0.33 × 0.38 mm.

Crystal data: $Ph_3Sb[S_2C_2(CN)_2]$ (**1**), monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14),[20] a = 9.844 (3) Å, b = 10.101 (2) Å, c = 20.537 (4) Å, β = 92.63 (2)°, Z = 4, and $\mu_{MoK\bar{\alpha}}$ = 1.573 mm^{-1}. A total of 3572 independent reflections (+h, +k, ±l) was measured with use of the θ-2θ scan mode for 2° ≤ $2\theta_{MoK\bar{\alpha}}$ ≤ 50°. No corrections were made for absorption.

The structure was solved by using conventional Patterson and difference Fourier techniques and was refined by using full-matrix least squares.[21] The 27 independent non-hydrogen atoms were refined anisotropically. The 15 independent hydrogen atoms were included in the refinement as fixed isotropic scatterers with calculated coordinates that were updated as refinement converged so that the final C—H bond lengths were 0.98 Å. The final agreement factors[22] were R = 0.024 and R_w = 0.034 for the 3060 reflections having $I \geq 2\sigma_I$.

X-ray Crystallographic Studies for **2**. Conditions for data collection, solution, and refinement were the same as described for **1**, unless otherwise noted. The crystal used for the X-ray study was cut from a colorless rectangular-prismatic needle-shaped crystal and had dimensions of 0.18 × 0.25 × 0.35 mm.

Crystal data: $(Me_4C_2O_2)_2Sb(C_6H_4$-p-Me) (**2**), tetragonal, space group $I\bar{4}2d$ (D_{2d}^{12}, No. 122),[23] a = 23.787 (5) Å, c = 7.070 (1) Å, Z = 8, and $\mu_{MoK\bar{\alpha}}$ = 1.415 mm^{-1}. A total of 1007 independent reflections (+h, +k, +l for $|h| \geq |k|$) was measured.

The 14 independent non-hydrogen atoms were refined anisotropically. Coordinates for the 12 hydrogen atoms of the independent pinacol ligand were obtained from a difference Fourier synthesis, and these hydrogen atoms were included in the refinement as fixed isotropic scatterers. The two independent aromatic hydrogen atoms were treated in the same fashion as described for **1**. The three disordered methyl hydrogen atoms of the tolyl group were omitted from the refinement. The final agreement factors[22,24] were R = 0.025 and R_w = 0.036 for the 930 reflections having $I \geq 2\sigma_I$.

X-ray Crystallographic Studies for **3**. Conditions for data collection, solution, and refinement were the same as described for **1**, unless otherwise noted. The crystal used for the X-ray study was an irregular lump cut from an orange polycrystalline mass and had approximate dimensions of 0.25 × 0.33 × 0.33 mm.

Crystal data: $Ph_3Sb(O_2C_6H_3\text{-}4\text{-}NO_2)$ (**3**), monoclinic, space group $P2_1/n$ (alternate setting of $P2_1/c$ (C^5_{2h}, No. 14)[20]), a = 10.131 (1) Å, b = 18.945 (5) Å, c = 10.788 (2) Å, β = 99.69 (1)°, Z = 4, and $\mu_{MoK\bar{\alpha}}$ = 1.402 mm^{-1}. A total of 3580 independent reflections was measured.

The 30 independent non-hydrogen atoms were refined anisotropically. The 18 independent hydrogen atoms were treated as described for **1**. The final agreement factors[22] were R = 0.032 and R_w = 0.042 for the 2840 reflections having $I \gtrsim 2\sigma_I$.

RESULTS

The atom-labeling schemes for **1–3** are given in the ORTEP plots of Figures 1–3, respectively. Figure 4 shows an inversion-related molecule for **3**. Atomic coordinates are given in Tables I–III, while selected bond lengths and angles are given in Tables IV–VI. Thermal parameters, hydrogen atom parameters, additional bond lengths and angles, and deviations from selected least-squares mean planes are provided as supplementary material.

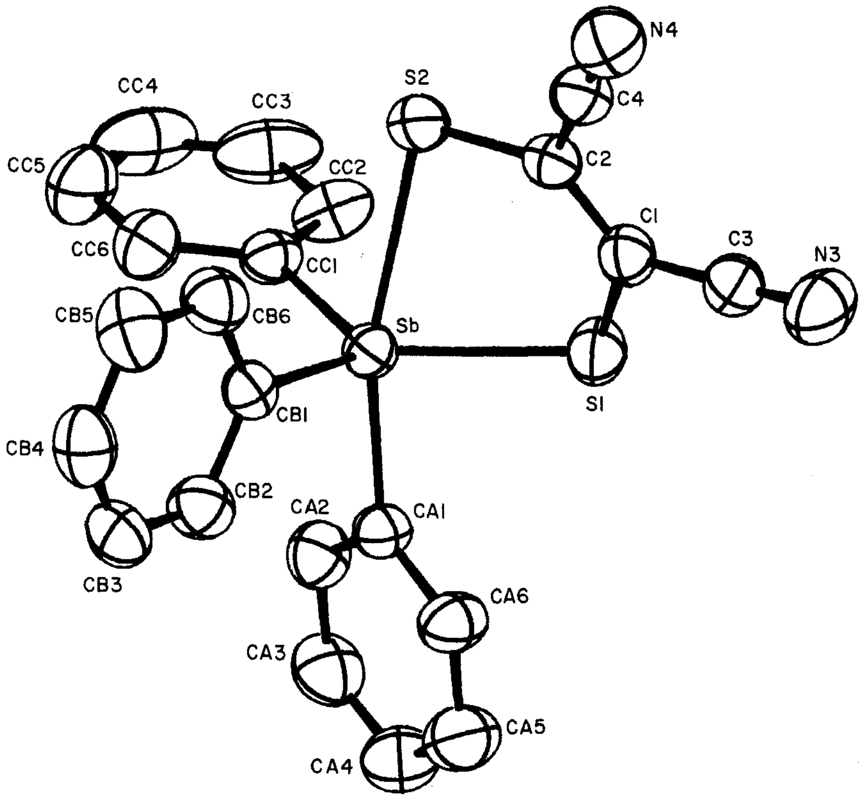


FIGURE 1 ORTEP plot of $Ph_3Sb[S_2C_2(CN)_2]$ (**1**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for purposes of clarity.

TABLE I

Atomic Coordinates in Crystalline $Ph_3Sb[S_2C_2(CN)_2]$ (1)[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Sb	1266.4 (2)	702.5 (2)	3446.8 (1)
S1	1903 (1)	−189 (1)	2383.8 (4)
S2	1604 (1)	2936 (1)	2760.1 (5)
N3	4990 (4)	268 (4)	1457 (2)
N4	4725 (4)	3954 (4)	1928 (2)
C1	2996 (3)	1043 (4)	2133 (2)
C2	2883 (4)	2346 (3)	2294 (2)
C3	4110 (4)	601 (3)	1762 (2)
C4	3905 (4)	3248 (4)	2096 (2)
CA1	954 (3)	−1328 (3)	3737 (2)
CA2	−275 (4)	−1700 (4)	3993 (2)
CA3	−488 (4)	−3004 (4)	4165 (2)
CA4	506 (5)	−3938 (4)	4084 (2)
CA5	1735 (5)	−3582 (4)	3842 (2)
CA6	1958 (4)	−2267 (4)	3665 (2)
CB1	2589 (3)	1358 (3)	4235 (2)
CB2	2875 (4)	488 (4)	4746 (2)
CB3	3655 (4)	901 (4)	5281 (2)
CB4	4167 (4)	2163 (5)	5307 (2)
CB5	3883 (4)	3033 (4)	4807 (2)
CB6	3089 (4)	2632 (4)	4266 (2)
CC1	−716 (3)	1455 (3)	3567 (2)
CC2	−1702 (4)	1280 (4)	3081 (2)
CC3	−3008 (4)	1744 (5)	3168 (3)
CC4	−3283 (5)	2365 (5)	3735 (4)
CC5	−2301 (6)	2567 (5)	4219 (3)
CC6	−979 (5)	2103 (5)	4138 (2)

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 1.

TABLE II

Atomic Coordinates in Crystalline $(Me_4C_2O_2)_2Sb(C_6H_4\text{-}p\text{-}Me)$ (2)[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Sb	−383.2 (2)	2500[c]	1250[c]
O1	−306 (2)	3321 (2)	1546 (6)
O2	43 (2)	2617 (1)	−1057 (7)
CT1	−1268 (3)	2500[c]	1250[c]
CT4	−2441 (4)	2500[c]	1250[c]
CT5	−3097 (3)	2500[c]	1250[c]
CT2	−1560 (2)	1999 (2)	1267 (12)
CT3	−2138 (2)	2003 (2)	1263 (13)
C1	122 (2)	3548 (2)	293 (9)
C2	88 (2)	3211 (2)	−1587 (10)
C11	−23 (3)	4180 (2)	42 (11)
C12	n83 (2)	3495 (3)	1269 (17)
C21	−436 (3)	3347 (3)	−2798 (11)
C22	609 (3)	3258 (3)	−2791 (11)

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 2. [c] Fixed.

TABLE III

Atomic Coordinates in Crystalline $Ph_3Sb(O_2C_6H_3\text{-}4\text{-}NO_2)$ (3)[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Sb	464.0 (3)	551.9 (1)	1876.4 (3)
O1	424 (3)	1393 (2)	634 (3)
O2	1530 (3)	171 (1)	578 (3)
O3	5348 (4)	1671 (2)	−2078 (4)
O4	5248 (4)	533 (2)	−1876 (5)
N	4815 (4)	1129 (3)	−1737 (4)
C1	1464 (4)	1362 (2)	18 (4)
C2	2082 (4)	705 (2)	−3 (4)
C3	3192 (4)	614 (2)	−576 (4)
C4	3640 (4)	1212 (3)	−1152 (4)
C5	3029 (5)	1859 (3)	−1166 (4)
C6	1934 (5)	1940 (2)	−574 (4)
CA1	454 (4)	−504 (2)	2561 (4)
CA2	1584 (4)	−926 (2)	2573 (4)
CA3	1651 (5)	−1579 (2)	3131 (4)
CA4	603 (5)	−1830 (2)	3673 (4)
CA5	−539 (5)	−1422 (2)	3653 (5)
CA6	−604 (4)	−750 (2)	3105 (4)
CB1	−1459 (4)	926 (2)	2118 (4)
CB2	−2338 (5)	1204 (2)	1142 (4)
CB3	−3582 (5)	1444 (3)	1334 (5)
CB4	−3934 (5)	1394 (3)	2521 (5)
CB5	−3035 (5)	1127 (3)	3514 (5)
CB6	−1783 (5)	901 (3)	3316 (4)
CC1	1921 (4)	1035 (2)	3244 (4)
CC2	2793 (5)	643 (3)	4092 (5)
CC3	3759 (5)	973 (4)	4972 (5)
CC4	3842 (6)	1700 (4)	5001 (5)
CC5	2982 (6)	2087 (3)	4171 (5)
CC6	2004 (6)	1766 (3)	3281 (5)

[a] Numbers in parentheses are estimated standard deviations..
[b] Atoms are labeled to agree with Figure 3.

TABLE IV

Selected Bond Lengths (Å) and Angles (deg) in $Ph_3Sb[S_2C_2(CN)_2]$ (1)[a]

type[b]	length	type	length
Sb–S1	2.469 (1)	Sb–CA1	2.162 (3)
Sb–S2·	2.689 (1)	Sb–CB1	2.136 3)
		Sb–CC1	2.119 (3)
type	**angle**	**type**	**angle**
S1–Sb–S2	78.45 (3)	S2–Sb–CC1	84.09 (9)
S1–Sb–CA1	86.71 (9)	CA1–Sb–CB1	100.1 (1)
S1–Sb–CB1	127.80 (9)	CA1–Sb–CC1	99.5 (1)
S1–Sb–CC1	120.4 (1)	CB1–Sb–CC1	109.5 (1)
S2–Sb–CA1	164.37 (9)	Sb–S1–C1	100.7 (1)
S2–Sb–CB1	92.98 (9)	Sb–S2–C2	96.5 (1)

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 1.

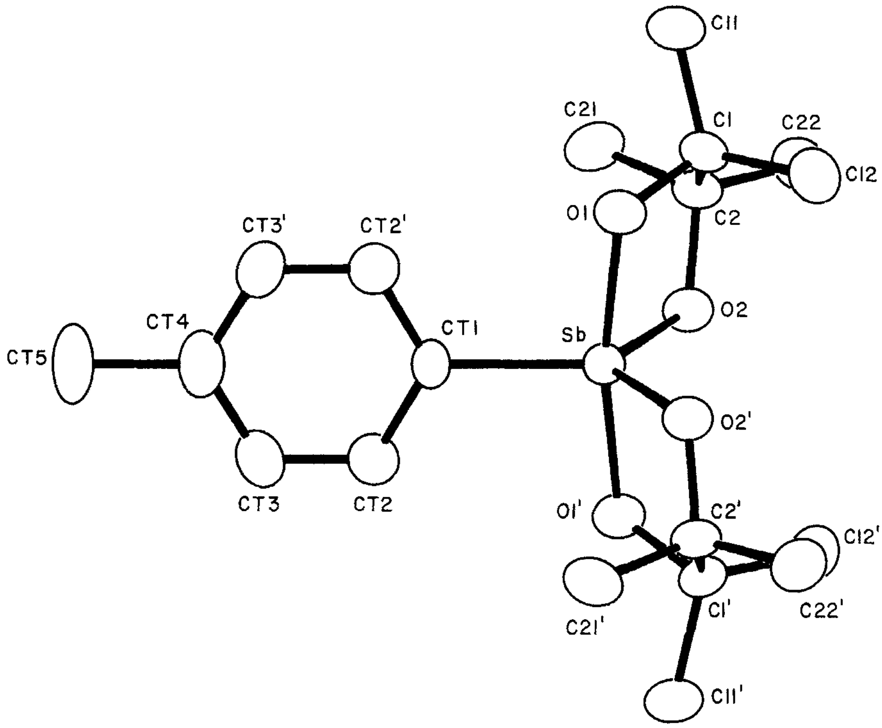


FIGURE 2 ORTEP plot of $(Me_4C_2O_2)_2Sb(C_6H_4\text{-}p\text{-}Me)$ (**2**) with thermal ellipsoids at the 50% probability level. Primed atoms are related to unprimed ones by x, $1/2 - y$, $1/4 - z$. Hydrogen atoms are omitted for purposes of clarity.

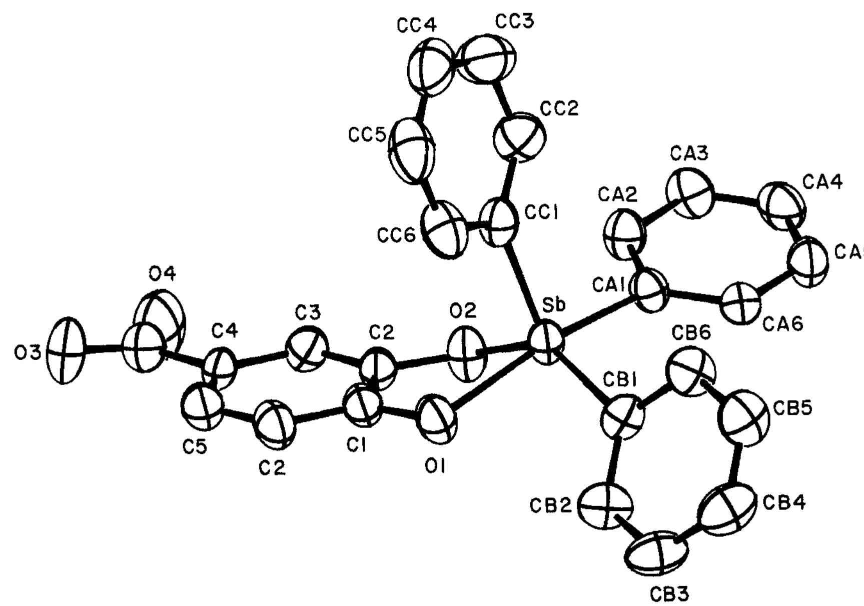


FIGURE 3 ORTEP plot of $Ph_3Sb(O_2C_6H_3\text{-}4\text{-}NO_2)$ (**3**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for purposes of clarity.

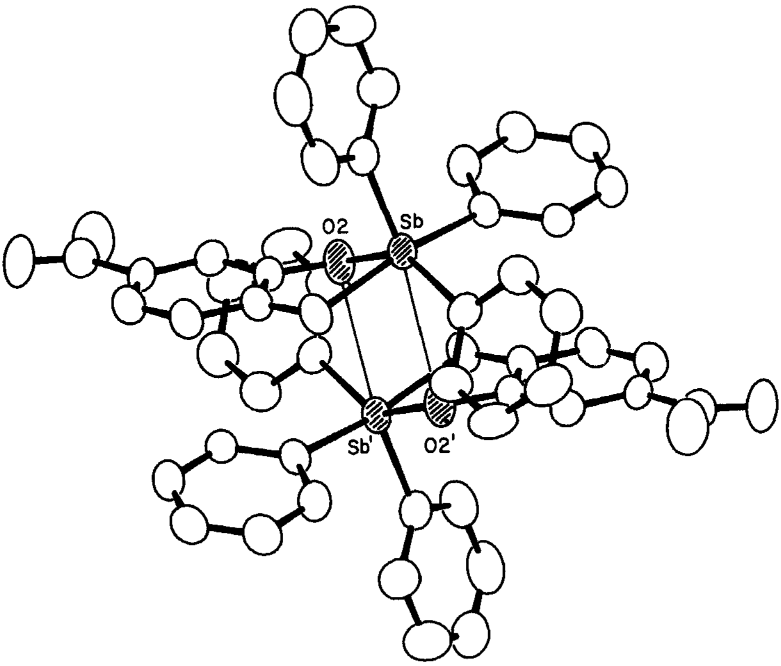


FIGURE 4 ORTEP plot of $Ph_3Sb(O_2C_6H_3\text{-}4\text{-}NO_2)$ (3) showing an inversion-related molecule (the prime indicates transformation by -x, -y, -z). The Sb—O interactions forming the weakly connected dimer are indicated by the narrow solid lines.

TABLE V

Selected Bond Lengths (Å) and Bond Angles (deg) for $(Me_4C_2O_2)_2Sb(C_6H_4\text{-}p\text{-}Me)$ (2)[a]

type[b]	length	type[b]	length
Sb–O1	1.972 (4)	Sb–CT1	2.105 (7)
Sb–O2	1.941 (5)		
type	**angle**	**type**	**angle**
O1–Sb–O1′	169.4 (2)	CT1–Sb–O2	121.5 (1)
O2–Sb–O2′	117.0 (2)	O1–Sb–O2	84.2 (2)
CT1–Sb–O1	95.3 (1)	O1–Sb–O2′	90.2 (2)

[a]Numbers in parentheses are estimated standard deviations.
[b]Atoms are labeled to agree with Figure 2.

DISCUSSION

Synthetic Routes

Stiboranes **2** and **3** represent new compounds. In the preparation of pentacoordinated mono-ring-containing triorganoantimony derivatives of the types **1** or **3**, applicable routes involve either an oxidative-addition reaction of R_3Sb^{III} with use of α-diketones containing electron-withdrawing groups[25] or a halide displacement reaction of R_3SbCl_2.[11] Both of these routes were illustrated in the accompanying paper.[1b] However, reaction of Ph_3SbCl_2 with 2,3-naphthalenediol in the presence

TABLE VI

Selected Bond Lengths (Å) and Angles (deg) in $Ph_3Sb(O_2C_6H_3\text{-}4\text{-}NO_2)$ (3)[a]

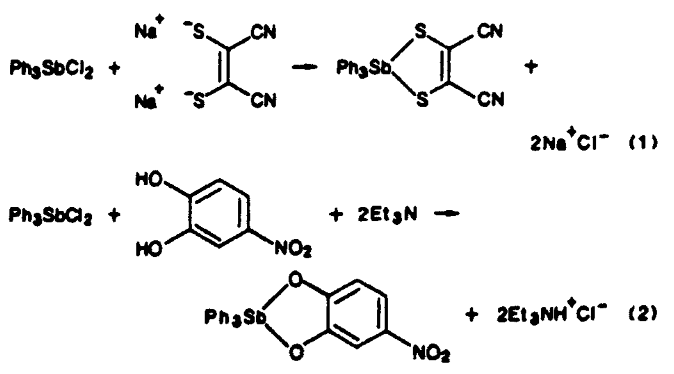
type[b]	length	type	length
Sb–O1	2.078 (3)	O1–C1	1.338 (5)
Sb–O2	2.039 (3)	O2–C2	1.360 (5)
Sb–CA1	2.132 (4)	C4–N	1.447 (5)
Sb–CB1	2.130 (4)	N–O3	1.245 (5)
Sb–CC1	2.112 (4)	N–O4	1.230 (6)

type	angle	type	angle
O1–Sb–O2	77.5 (1)	Sb–CB1–CB2	121.7 (3)
O1–Sb–CA1	160.3 (1)	Sb–CB1–CB6	117.9 (3)
O1–Sb–CB1	84.5 (1)	Sb–CC1–CC2	121.7 (3)
O1–Sb–CC1	93.1 (1)	Sb–CC1–CC6	119.0 (4)
O2–Sb–CA1	86.5 (1)	O1–C1–C2	116.7 (3)
O2–Sb–CB1	143.4 (1)	O1–C1–C6	123.5 (4)
O2–Sb–CC1	104.2 (1)	O2–C2–C1	115.8 (4)
CA1–Sb–CB1	102.2 (2)	O2–C2–C3	122.8 (8)
CA1–Sb–CC1	102.0 (3)	C4–N–O3	117.9 (5)
CB1–Sb–CC1	108.4 (2)	C4–N–O4	119.3 (4)
Sb–O1–C1	110.8 (2)	O3–N–O4	122.7 (5)
Sb–O2–C2	111.0 (3)	C3–C4–N	117.1 (4)
Sb–CA1–CA2	119.3 (3)	C5–C4–N	119.7 (4)
Sb–CA1–CA6	120.8 (3)		

[a]Numbers in parentheses are estimated standard deviations.
[b]Atoms are labeled to agree with Figure 3.

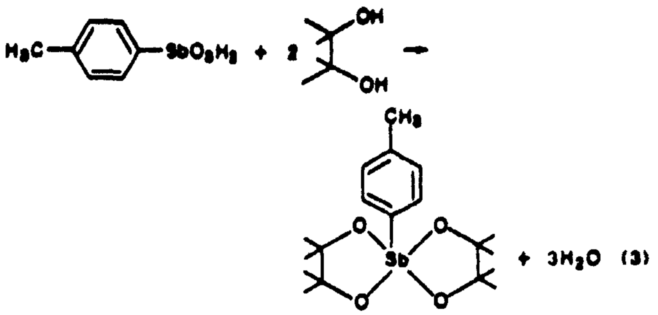
of Et_3N proved complicated and led to the chloride-containing hexacoordinated salt $[Ph_3Sb(Cl)(O_2C_{10}H_6)][Et_3NH]$[1b] instead of the expected pentacoordinated derivative.

This reaction, employed in the preparation of **1** and **3**, appears to follow the more conventional route, (eq 1 and 2, respectively). Following the reaction anal-



ogous to that expressed in eq 2, Hall and Sowerby[11] formed the hydrated complex $[Ph_3Sb(O_2C_6H_4)]_2 \cdot H_2O$ using catechol as the displacing reagent in the presence of ammonia. Crystallographic analysis[11] showed that the hydrate possessed both five- and six-coordinated antimony atoms.

In synthesizing the bicyclic stiborane **2**, reaction of *p*-tolyl-stibonic acid with pinacol was employed, analogous to the preparation of the related phenyl stiborane $(Me_4C_2O_2)_2SbPh$[14](eq. 3). Water is taken up by 2,2-dimethoxypropane with conversion to methanol and acetone. This route is analogous to the reaction in arsenic chemistry employing arylarsonic acids[8,26] to obtain five-coordinated derivatives containing a bicyclic framework.



2

Structural Details

The molecular geometry about the antimony atom in the thio-containing monocyclic stiborane **1** can be referred to a trigonal bipyramid having S1, CB1, and CC1 in equatorial positions and S2 and CA1 in axial positions. Distortions from the ideal trigonal-bipyramidal geometry are not extreme. They are in the anti-Berry direction frequently seen when angle deviations are modest.[5c] The axial bond Sb—S2 has a length of 2.689 (1) Å, which is considerably longer than the corresponding equatorial bond length (Sb—S1 = 2.469 (1) Å). The difference between axial and equatorial Sb—C bond lengths is much less pronounced. The axial bond, Sb—CA1, has a length of 2.162 (3) Å as compared to the average value of the equatorial Sb—C bond lengths of 2.128 (3) Å. The four atoms Sb, S1, CB1, and CC1 are not precisely coplanar. Rather, the Sb atom is displaced 0.197 Å out of the plane defined by the other three in a direction toward CA1. The eight atoms comprising the dithiodicyanoethylene ligand are coplanar to within ±0.037 Å. The Sb atom does not lie in this plane; the dihedral angle between this plane and the plane defined by Sb, S1, and S2 is 41.6°.

For the spirocyclic derivative **2**, the molecule has crystallographic C_2 symmetry with the atoms Sb, CT1, CT4, and CT5 lying on the twofold axis. The hydrogen atoms of the methyl group containing CT5 are therefore taken to be disordered about this axis. The geometry about the antimony atom is best described as trigonal bipyramidal with CT1, O2, and O2′ in equatorial positions and O1 and O1′ in axial positions. Deviations from the idealized trigonal-bipyramidal geometry follow a non-Berry coordinate. As the angle O1-Sb-O1′ decreases to 169.4 (2)°, from the idealized value of 180°, in a direction commensurate with distortion toward a rectangular pyramid with CT1 apical, the angle O2-Sb-O2′ also decreases from the idealized value of 120 to 117.0 (2)°, instead of increasing as would be required if the distortion was precisely on the Berry coordinate[27] toward the rectangular pyramid.

The four atoms comprising the equatorial plane are required by symmetry to be coplanar. The dihedral angle between this plane and the plane defined by the tolyl group is 79.8°. As expected, the axial Sb—O1 bond length (1.972 (4) Å) is somewhat longer than the equatorial Sb—O2 bond length (1.941 (5) Å). The five-membered ring formed by the atoms Sb, O1, O2, C1, and C2 is not planar. The atoms Sb, O1, O2, and C1 are coplanar to within ±0.097 Å, while C2 is displaced out of this plane in a direction toward the tolyl group. This arrangement serves to stagger the substituents with respect to the C1—C2 bond.

For the monocyclic derivative containing the nitrocatecholate ligand, **3**, the molecular geometry about the antimony atom lies on the Berry pseudorotation coordinate[27] connecting a trigonal bipyramid having CA1 and O1 in axial positions to a rectangular pyramid with CC1 in the apical position. With use of the dihedral angle method[7,28] to assess displacement, the geometry is displaced 67.8% (68.5% using unit vectors) from the trigonal bipyramid toward the rectangular pyramid. At first sight such a geometry for a species containing three acyclic substituents seems unusual in being displaced so far toward the rectangular pyramid. Examination of intermolecular contacts, however, shows that the molecules exist in the solid state as weakly connected dimers that act to promote opening of the O2—Sb—CB1 angle. As shown in Figure 4, inversion-related molecules are so disposed as to reflect weak Sb—O interactions. The distance between Sb and O2′ (or Sb′—O2) is 3.341 (3) Å, as compared to the van der Waals sum of 3.6 Å.[29] The closest intermolecular Sb—O contact for **2** is greater than 4 Å. The closest intermolecular Sb—S contact in **1** is 4.615 (1) Å compared to the van der Waals sum of 4.05 Å.

Distortion Coordinate and Structural Comparisons

With the availability of the structures of the ring-containing five-coordinated antimony compounds reported in the accompanying paper,[1b] $Ph_3Sb(O_2C_6Cl_4)$ (**4**), $(Cl_4C_6O_2)(C_{12}H_8)SbPh \cdot 0.25C_6H_6 \cdot 0.25CH_2Cl_2$ (**5**), and $[Ph_3Sb(Cl)(O_2C_{10}H_6)][Et_3NH]$ (**6**), and those reported here, **1–3**, sufficient examples exist to clearly outline the distortion coordinate followed by these nonrigid entities. The structures of three previously studied cyclic derivatives also are available, $Ph_3Sb(C_{12}H_8)$ (**7**),[30] $[Ph_3Sb(O_2C_6H_4)]_2 \cdot H_2O$ (**8**),[11] and $(Me_4C_2O_2)_2SbPh$ (**9**),[14] as well as those of six acyclic derivatives, $Ph_3Sb(NCO)_2$ (**10**),[31] $SbPh_5 \cdot 0.5C_6H_{12}$ (**11**),[12] Me_3SbF_2 (**12**),[32] $SbPh_5$ (**13**),[10] $Ph_3SbCl_2 \cdot SbCl_3$ (**14**),[33] and Ph_3SbCl_2 (**15**).[34]

A convenient measure of structural distortion for pentacoordinated molecules[28,35–37] is obtained by plotting the values of the trans basal angles θ_{15} and θ_{24} of the RP (which are axial and equatorial angles with reference to the TBP) vs. the dihedral angle δ_{24}.[37]

Figure 5 displays a θ vs. δ_{24} graph for the stiboranes that have been structurally characterized by X-ray analysis. These data are summarized in Table VII. The lines shown are determined by the θ values of 120 and 180° for the ideal trigonal bipyramid, which has δ_{24} = 53.1°, and the θ value of 150° for the "limiting" rectangular pyramid. It is seen that the Berry coordinate is well followed for the five-coordinated antimony compounds other than **1, 2, 4,** and **9,** which exhibit non-Berry type displacements, and **13,** whose structure is under strong lattice influences.

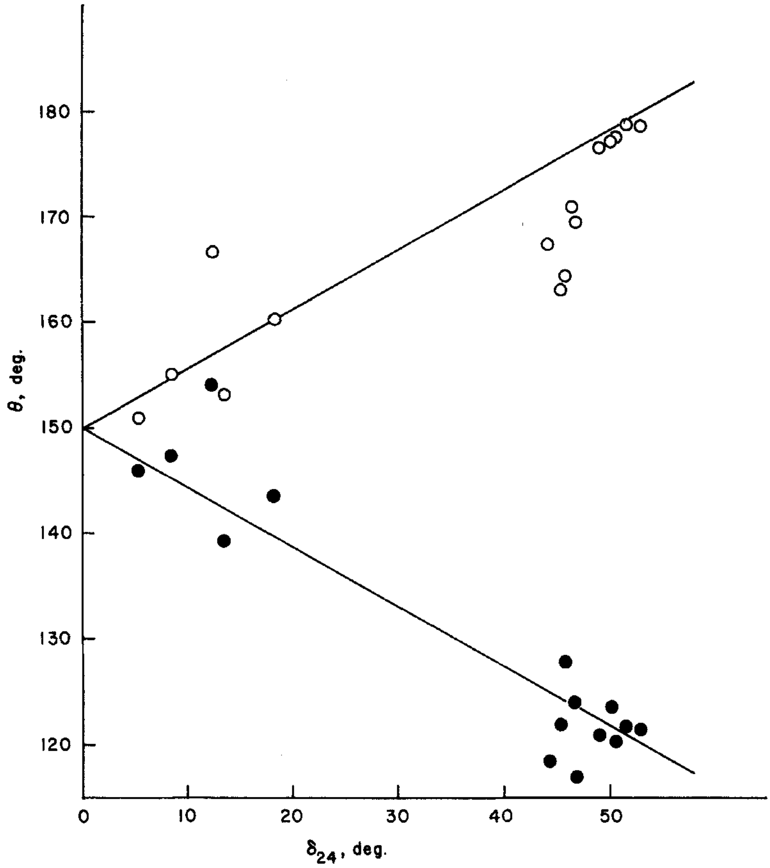


FIGURE 5 Variations of the axial angle θ_{15} (open circles) and equatorial angle θ_{24} (filled circles) vs. the dihedral angle δ_{24} as structural distortion for pentacoordinated antimony(V) compounds listed in Table VII proceeds along the Berry coordinate from a rectangular pyramid toward a trigonal bipyramid.

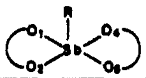
The former set of compounds are identified in Figure 5 by their δ_{24} values which lie in the range, 44.3–46.8°. A comparison of this type of plot for phosphoranes,[9,28,35] arsoranes,[8] and five-coordinated silicon[38] and germanium [4a] compounds indicates a similar scatter of points as well as a "limiting" rectangular pyramid with a trans basal θ angle near 150°.

However, a more even distribution of structural distortions between the trigonal bipyramid and rectangular pyramid is found for those elements, whereas for antimony, no examples with distortions midway between the two idealized five-coordinated geometries have been found thus far. Additional studies of examples with varying ligand construction should rectify this situation.

It is interesting that where lattice distortions have been indicated to be mild, as in the nitrocatecholate derivative **3** or in the hydrate **8**, structural displacements are along the Berry coordinate. In situations where intermolecular effects become more pronounced, as in **13** or **6**,[1b] considerable deviations from the C_{2v} coordinate are found. In these cases, positive deviations are present (see Table VII for the appropriate data for **6**).

TABLE VII

Axial and Equatorial Angles (θ, deg), Dihedral Angles (δ, deg), and Sb—O Bond Lengths (Å) for Pentacoordinated Antimony Compounds



compd no.	δ_{24}	θ_{15}	θ_{24}	Sb–O_{ax}[a]	Sb–O_{eq}[a]	Δ(ax–eq)	% TBP → RP[b]	ref[c]
10	52.8	178.6	121.4				1.6	31
11	51.5	178.7	121.7				4.1	12
14	50.5	177.3	120.3				5.1	33
12	50.2	177.0	123.5				11.3	32
2[d,e]	46.8	169.4	117.0	1.972 (1) (5)	1.941 (2) (4)	0.031	8.5	this work
15	49.1	176.5[h]	121.0[h]				15.0	34
7	46.5	170.8	123.9				15.8	30
4[e]	45.3	163.0	121.9	2.107 (1)	2.019 (4)	0.088	22.0	1b
1[e]	45.8	164.4	127.8				24.2	this work
9[d,e]	44.3	167.4	118.3	1.980 (1) (5)	1.950 (2) (4)	0.030	12.9	14
3	18.2	160.3	143.4	2.078 (1)	2.039 (2)	0.039	68.5	this work
5A[f]	5.2	151.0	145.9	2.055 (1)	0.027 (2)	0.028	88.9	1b
5B	13.5	153.1	139.3	2.067 (1)	2.032 (2)	0.035	72.6	1b
13	12.4	166.7	154.1				81.7	10
8	8.3	154.8	147.4	2.060 (1)	2.013 (2)	0.047	85.3	11
6[g]	2.8	166.7	162.7	2.050 (1)	2.052 (2)	−0.002		1b

[a] The numbers in parentheses are atom identifications relative to the figure given below the table heading. [b] Based on unit bond distances. [c] These are references to the X-ray studies. [d] Compounds **2** and **9** contain a crystallographic two-fold axis about antimony. [e] These compounds have non-Berry type distortions. [f] There are two independent molecules per unit cell for **5**. [g] Not included in Figure 5 since it is pseudooctahedral. [h] These are calculated values from atomic coordinates given in *ref* 34.

Although the Sb—O axial ring bond distances are longer than Sb—O equatorial values, no systematic change toward equality in these two types of distances is observed (Table VII) as the structural displacement increases toward the RP. An average difference of about 0.04 Å is maintained. However, this range of Sb—O axial ring bond lengths is 1.97–2.11 Å compared to a somewhat lower range for the corresponding Sb—O equatorial bond lengths, 1.94–2.05 Å. These ranges are larger than observed for related M—O bond lengths in phosphoranes, arsoranes, and five-coordinated silicates, perhaps expected due to the large size of antimony and presumably weaker M—O bond present relative to the other series studied.

Conclusion

In general, solid-state five-coordinated antimony structures lie along the Berry pseudorotational coordinate. Considerable deviation from this coordinate is present only when strong intermolecular effects are indicated (as in **6** and **13**). It is apparent that lattice effects enter as an important factor influencing stiborane structures, more so than with other five-coordinated derivatives of elements in groups 4 and 5.[3-5,7-9]

ACKNOWLEDGEMENT

The support of this research by the National Science Foundation (Grant No. CHE85040737) is gratefully acknowledged. We also thank the University of Massachusetts Computing Center for generous allocation of computer time.

Supplementary Material Available: Thermal parameters, hydrogen atom parameters, additional bond lengths and angles (Tables S1–S3, respectively, for **1**, Tables S4–S6 for **2**, and Tables S7–S9 for **3**), and deviations from least-squares mean planes (Tables S10–S12 for **1–3**, respectively) (13 pages);

listings of observed and calculated structure factor amplitudes for **1–3** (27 pages). Ordering information is given on any current masthead page.

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