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Crystal Structure of 2,4,6-Tri-*tert*-butylphenyltrichlorogermane and 2,4,6-Tri-*tert*-butylphenylgermane

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ABSTRACT: *Two organogermanium compounds, 2,4,6-(t-Bu)$_3$C$_6$H$_2$GeCl$_3$ (**1**) and 2,4,6-(t-Bu)$_3$C$_6$H$_2$GeH$_3$ (**2**), were prepared, and the structures were determined by X-ray crystallography. Compound **1** exhibits unusual structural parameters due to the strong repulsion of the bulky t-butyl substituents and GeCl$_3$ moiety; the benzene ring assumes a boat conformation, and the GeCl$_3$ group as well as the o-t-butyl groups stay significantly away from the benzene ring.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:238–243, 2001

INTRODUCTION

It has been recognized that the 2,4,6-tri-*tert*-butylphenyl group (denoted Mes* hereafter) is a promising protective moiety for conferring a kinetic stability on reactive species [1]. As for the group 14 elements, Ge and Sn, the following compounds have been thus synthesized: Mes$^*_2$Ge [2], Mes*Ge$=$S [2a], Mes*(Cl)Ge [3], and Mes$^*_2$Sn [4]. During the course of our investigation on the chemistry of germanium compounds having bulky substituents [5], we have become interested in the structures and electronic properties of the molecules of the type Mes*GeX$_3$ (X $=$ Cl, Br, I). We thought that these molecules should possess severe distortions in the structures due to the great steric repulsion between the Mes* groups and the GeX$_3$ moiety. In 1984, Richelme et al. reported the synthesis of Mes*GeCl$_3$ (**1**) and Mes*GeH$_3$ (**2**) [6], but the crystal structures of these compounds have not been provided so far. Here we report the crystal structures and electronic spectra of compounds **1** and **2**.

RESULTS AND DISCUSSION

Preparation of Mes*GeCl$_3$ (1) and Mes*GeH$_3$ (2)

Richelme et al. [6] obtained compound **1** from Ge(OMe)$_4$ in 15% overall yield via a three-step process: (1) preparation of Mes*Ge(OMe)$_3$ from Mes*Li and Ge(OMe)$_4$; (2) reduction to Mes*GeH$_3$ (**2**) with LiAlH$_4$; and (3) chlorination with CCl$_4$/AIBN to give **1**. However, we found that **1** can be prepared in one step by the reaction of Mes*Li and GeCl$_4$. Thus, Mes*Li was allowed to react with GeCl$_4$ at -15°C in THF, and the reaction mixture was stirred for 12 hours at room temperature. Workup afforded **1** in 13% isolated yield, and reduction of **1** with LiAlH$_4$ gave **2** in 95% yield (Scheme 1).

Crystal Structure of 1 and 2

The structures of both compounds were determined by X-ray crystallography. Crystallographic data are shown in Table 1. The selected bond lengths and angles for **1** are given in Table 2, and the ORTEP drawings are shown in Figure 1. Disorder was observed

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Dedicated to Prof. Naoki Inamoto for his outstanding contribution to the field of heteroatom chemistry.

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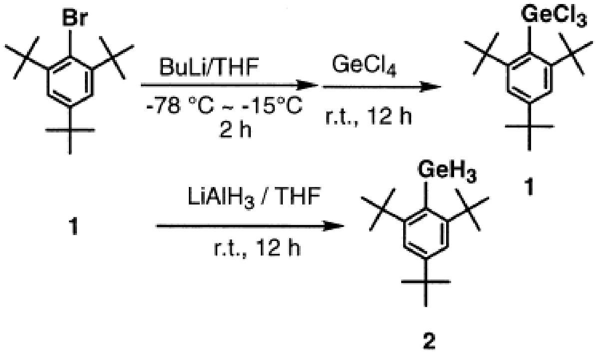


SCHEME 1

in the *t*-Bu group at 4-position of the benzene ring in **1**; two structures (**a** and **b**) were obtained, and the occupancy was 50% for structure **a** and 50% for structure **b**. Both molecules **a** and **b** assume highly deformed conformations. The benzene ring forms a boat conformation; the dihedral angles β and δ are 14.0 and 7.0°, respectively. Additionally, the $GeCl_3$ group deviates (α, 20.9°), and the *t*-Bu groups deviate 14.9° (γ, 2,6-positions) and 3.1° (ε, 4-position) from the benzene ring. Table 3 summarizes the angles α, β, γ, δ, and ε of **1** with those of selected compounds. For aryl compounds substituted with halosilyl or halogermyl groups that have not been reported to our best knowledge, we have listed examples of compounds with deformed benzene rings. The dihedral angles β and δ in **1** are smaller than those observed for the compound Mes_2^*Ge (angles β of 32.2° and 4.9° and angles δ of 7.8° and 0.5° [2b] and lie between those of 3-carboxy[7]paracyclophane [7] and 8-carboxy[6]cyclophane [8]. The hexa-substituted compound **3** is one of the examples having deformed benzene rings and show a similar feature [9]. Phosphorus compounds with Mes* group 4 show a similar trend, but the angle α of 4 is smaller than that of 1 [10]. It is interesting to note that all bond lengths including the Ge–C bond (1.98(2) Å) in **1** are within the normal values.

The structure of **2** is shown in Figure 2. Selected bond lengths and angles for **2** are given in Table 4. Interestingly, the benzene ring of **2** is planar, indicating that the steric effect of three chlorine atoms is significant. Compound **2** crystallizes in the $P2_1/m$ space group with two molecules in the unit cell. A symmetric axis passes through Ge, C(1), and C(4), and thus the benzene ring is planar and the Ge atom remains in the benzene ring plane. Bond lengths of **2** are all in the normal range, as in the case of **1**.

UV Spectra of Compounds 1 and 2

The large distortion of the benzene ring in **1** affects the electronic properties. The UV spectra of **1** and **2** in hexane are shown in Figure 3. In **1** and **2**, the lowest energy transitions occur at 308 and 279 nm, respectively, indicating that substitution with the chlorine atoms in **2** leads to a significant bathochromic shift of the electronic transition. However, no bathochromic shift was observed in the lowest energy transition between $PhGeCl_3$ (270 nm, ε 500) and $PhGeH_3$ (269 nm, ε 162) [11]. Furthermore, 1,3,5-tri-*t*-butylbenzene (Mes*H) shows absorption maxima at 268 shoulder (sh) and 261 nm [12]. We feel that the bathochromic shift observed for **1** relative to **2** and $PhGeCl_3$ may be attributable to the electronic perturbation of the benzene ring caused by the large distortion.

In summary, novel syntheses of Mes^*GeCl_3 **1** and Mes^*GeH_3 **2** were performed, and these compounds are now more accessible than previously. The structure analysis revealed the highly deformed structure of **1** and planar shape of **2**. Comparing UV spectra of **1** and **2** indicated that the large red shift of **1** is a result of the deformed benzene ring.

EXPERIMENTAL

All NMR spectra were recorded on a JEOL model α-500 (^1H, 500.0 MHz; ^{13}C, 125.7 MHz; ^{29}Si, 99.3 MHz). Chemical shifts are reported as δ units relative to $SiMe_4$ as an internal standard. For ^{29}Si NMR, $SiMe_4$ was used as an external standard. Mass spectrometry was performed on a JEOL JMS-D300 instrument. Infrared spectra were measured with a JASCO A-102 spectrometer. UV spectra were recorded with a JASCO Ubest-50 spectrometer.

*2,4,6-Tri-tert-butylphenyltrichlorogermane (**1**)*

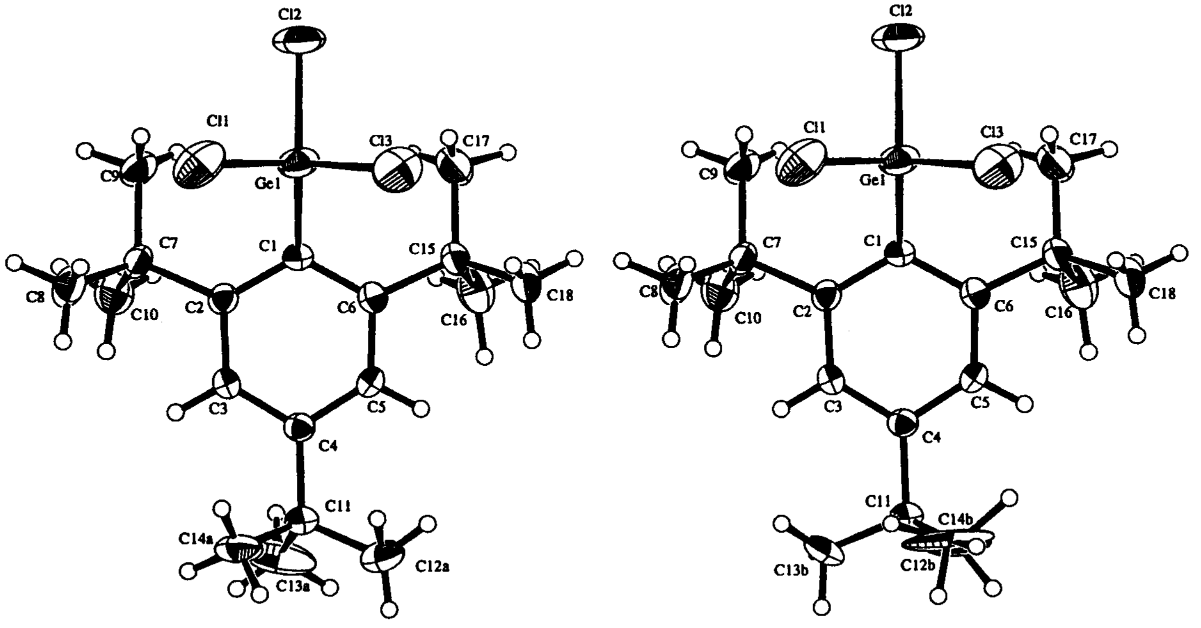
A solution of Mes*Br [13] (3.0 g, 9.2 mmol) in THF (30 mL) was cooled to −78°C, and BuLi (1.7 M, 6.3 mL) was added. The solution was gradually warmed to −15°C for 2 hours, then $GeCl_4$ (1.2 mL, 10.5 mmol) was added. After having been stirred for 12 hours at room temperature, the solvent was removed, hexane was added, and the precipitated salt was filtered off. Hexane was removed and the resulting solid was recrystallized from pentane to give 0.51 g (13%) of Mes^*GeCl_3 as colorless crystals, m.p. 143–144°C. ^1H NMR (C_6D_6): δ 1.08 (s, 9H), 1.49 (s, 18H), 7.40 (s, 2H). ^{13}C NMR (C_6D_6): δ 30.80, 33.10, 34.66, 40.33, 125.10, 128.29, 154.15, 159.01. IR (KBr): 2960, 1580, 1390, 1360, 1240, 880, 740 cm^{-1}. MS (70 eV) *m/z* (%): 424 (M^+, 6), 353 (35), 245 (79), 203 (51), 56 (100). UV (hexane) λ_{max} (ε) 308 nm (1500). Anal. Found: C, 50.76; H, 6.91%. Calcd for $C_{18}H_{29}Cl_3Ge$: C, 50.94; H, 6.89%.

TABLE 1 Summary of Crystal Data, Data Collection, and Refinement for **1** and **2**

	ArGeCl$_3$ *(***3***)*	*ArGeH*$_3$ *(***2***)*
	Crystal Data	
Formula	$C_{18}H_{29}Cl_3Ge$	$C_{18}H_{32}Ge$
Molecular weight	424.38	321.04
Crystal description	Colorless prisms	Colorless prisms
Crystal size, mm	0.6 × 0.5 × 0.15	0.2 × 0.2 × 0.2
Crystal system	Monoclinic	Monoclinic
Space group	$P\ 2_1/n$	$P\ 2_1/m$
a (Å)	9.759(1)	10.065(4)
b (Å)	11.678(2)	9.842(2)
c (Å)	19.092(2)	10.241(2)
β (°)	103.335(10)	113.82(2)
V (Å^3)	2117.2(5)	928.1(4)
Z	4	2
D_{calc} (g/cm^3)	1.331	1.149
	Data Collection	
Diffractometer	Rigaku AFC7S	Rigaku AFC7S
Radiation (λ, Å)	MoKα (0.71069)	CuKα (1.54178)
μ (cm^{-1})	18.20	21.17
2θ max (°)	55.0	120.2
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
Scan width, deg	$1.10 + 0.30 \tan \theta$	$0.89 + 0.30 \tan \theta$
No. of reflections measured	5399	1577
No. of independent reflections	5107	1485
No. of observed reflections ($\lvert F_0 \rvert \geq 3\sigma(F_0)$)	2158	551
	Refinement	
R	0.043	0.087
R_w	0.039	0.065
Weighting scheme	$w = 1/\sigma^2$ (F$_0$)	$w = 1/\sigma^2(F_0)$
S	1.65	4.55
$(\Delta/\sigma)_{max}$	0.23	0.06
$(\Delta\rho)_{max}$ (e Å^{-3})	0.36	0.43
$(\Delta\rho)_{min}$ (e Å^{-3})	−0.43	−0.53
No. of parameters	308	107

TABLE 2 Selected Bond Lengths (Å) and Angles (°) for **1**

		Bond Lengths			
Ge(1)–Cl(1)	2.139(2)	Ge(1)–Cl(2)	2.146(2)	Ge(1)–Cl(3)	2.137(2)
Ge(1)–C(1)	1.944(4)	C(1)–C(2)	1.412(6)	C(1)–C(6)	1.411(6)
C(2)–C(3)	1.390(6)	C(2)–C(7)	1.545(6)	C(3)–C(4)	1.378(6)
C(4)–C(5)	1.381(6)	C(4)–C(11)	1.534(6)	C(5)–C(6)	1.391(6)
C(6)–C(15)	1.548(6)				
		Bond Angles			
Cl(1)–Ge(1)–Cl(2)	103.82(8)	Cl(1)–Ge(1)–Cl(3)	97.84(8)		
Cl(1)–Ge(1)–C(1)	112.6(2)	Cl(2)–Ge(1)–Cl(3)	105.39(8)		
Cl(2)–Ge(1)–C(1)	123.2(2)	Cl(3)–Ge(1)–C(1)	110.7(1)		
Ge(1)–C(1)–C(2)	118.2(3)	Ge(1)–C(1)–C(6)	118.1(3)		
C(2)–C(1)–C(6)	119.4(4)	C(1)–C(2)–C(3)	117.5(4)		
C(1)–C(2)–C(7)	126.3(4)	C(3)–C(2)–C(7)	115.6(4)		
C(2)–C(3)–C(4)	123.4(5)	C(3)–C(4)–C(5)	116.4(4)		
C(3)–C(4)–C(11)	122.5(4)	C(5)–C(4)–C(11)	121.1(5)		
C(4)–C(5)–C(6)	123.6(5)	C(1)–C(6)–C(5)	117.3(4)		
C(1)–C(6)–C(15)	126.8(4)	C(5)–C(6)–C(15)	115.3(4)		



Molecular a

Molecular b

FIGURE 1 ORTEP drawing of $ArGeCl_3$ 1. Thermal ellipsoids are drawn in 30% probability level.

TABLE 3 Selected Bond Lengths (Å) and Angles (°) for **2**

		Bond Lengths			
Ge(1)–C(1)	1.98(2)	C(1)–C(2)	1.45(2)	C(1)–C(6)	1.43(2)
C(2)–C(3)	1.36(2)	C(2)–C(7)	1.50(2)	C(3)–C(4)	1.38(2)
C(4)–C(5)	1.40(2)	C(4)–C(10)	1.54(2)	C(5)–C(6)	1.38(2)
C(6)–C(13)	1.54(2)				
		Bond Angles			
Ge(1)–C(1)–C(2)	118(1)	Ge(1)–C(1)–C(6)	119(1)		
C(2)–C(1)–C(6)	121(1)	C(1)–C(2)–C(3)	115(1)		
C(1)–C(2)–C(7)	126(1)	C(3)–C(2)–C(7)	118(1)		
C(2)–C(3)–C(4)	124(1)	C(3)–C(4)–C(5)	119(1)		
C(3)–C(4)–C(10)	123(1)	C(5)–C(4)–C(10)	117(1)		
C(4)–C(5)–C(6)	121(1)	C(1)–C(6)–C(5)	117(1)		
C(1)–C(6)–C(13)	123(1)	C(5)–C(6)–C(13)	118(1)		

*2,4,6-Tri-tert-butylphenylgermane (***2***)*

An ether (15 mL) solution of Mes*$GeCl_3$ (0.45 g, 1.1 mmol) was added dropwise to an ether (10 mL) suspension of $LiAlH_4$ (0.14 g, 3.7 mmol) during 5 minutes at 0°C. The reaction mixture was stirred for 2 hours, then hydrolyzed carefully with dilute aqueous HCl and extracted with ether. The organic layer was separated and the water layer extracted twice with ether. The combined organic phase was dried with $MgSO_4$. Evaporation of the solvent yielded **2** (0.32 g, 95%) that was recrystallized from ethanol to give colorless needles. ^1H NMR (C_6D_6) δ 1.29 (s, 9H), 1.51 (s, 18H), 4.79 (s, 3H), 7.56 (s, 2H) ppm. ^{13}C NMR (C_6D_6) δ 31.4, 33.3, 34.9, 38.8, 122.3, 125.2, 150.4, 158.0 ppm. IR (KBr) ν 2860, 2100, 2050, 1600, 1360, 930, 850 cm^{-1}. MS (70 eV) m/z 320 (M^+, 3), 265 (11), 56 (100). UV (hexane) λ_{max} (ε) 279 nm (350).

X-Ray Crystallographic Analysis of 1

Colorless crystals of 2,4,6-tri-*tert*-butylphenyltrichlorogermane (**1**) was recrystallized by slow evaporation. A crystal specimen of dimensions 0.60 × 0.60 × 0.15 mm was sealed in a glass capillary and used for data collection on a Rigaku AFC7S diffractometer using graphite-monochromated MoKα radiation. Cell parameters were refined by the least-squares method using 25 reflections ($20.51 < 2\theta < 24.99°$). The space group $P2_1/n$ was uniquely determined from systematic absences ($h0l$: $h + l \neq 2n$; $0k0$:$k \neq 2n$). Intensity data were collected in the range of $3 < 2\theta < 55°$ by the $\omega - 2\theta$ scan technique at a temperature of 20 ± 1°C. Of the 5399 reflections that were collected, 5107 were unique ($R_{\text{int}} = 0.027$). The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. The linear absorption coefficient, μ, for MoKα radiation is 18.2 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.65 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved by use of SHELXS86 [14] and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, and the rest were included in fixed positions. The final cycle of full-matrix least-squares refinement was based on 2158 observed reflections ($|F_o| \geq 3\sigma(F_o)$) and 308 variable parameters and with unweighted and weighted factors of $R = 4.3\%$ and $R_w = 3.9\%$. All calculations were carried out on a SiliconGraphics INDY computer using the teXsan crystallographic software package [15]. Details of crystal data, data collection, and refinement are listed in Table 1.

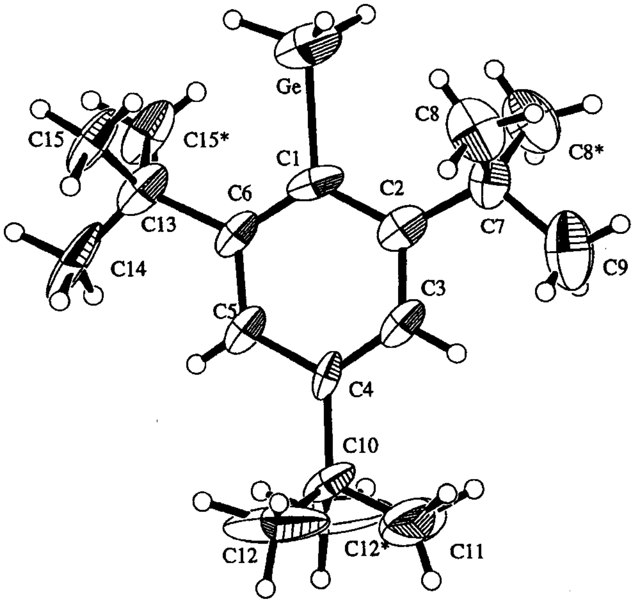
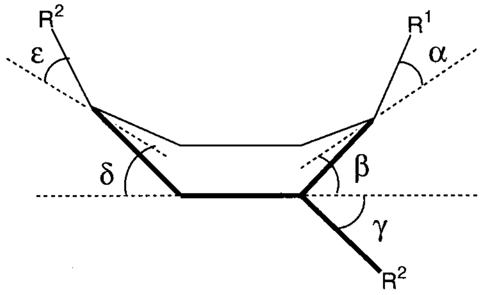


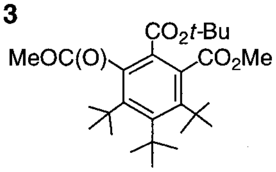
FIGURE 2 ORTEP drawing of ArGeH$_3$ 2. Thermal ellipsoids are drawn in 30% probability level.

TABLE 4 Deformation Angles



Run	Compounds	α	β	γ	δ	ε	Reference
1	**1**	14.0°	20.9°	14.8°/14.9°	7.0°	3.1°	This work
2	**2**	0°	0°	0°/0°	0°	0°	This work
3	Mes$^*_2$Ge (ring 1)	15.1°	32.2°	11.9°/13.9°	7.8°	1.0°	[2b]
4	Mes$^*_2$Ge (ring 2)	5.1°	4.9°	4.5°/6.0°	0.5°	1.2°	[2b]
5	3-Carboxy[7]paracyclophane	7.8°	15.2°	–	18.3°	5.7°	[7]
6	8-Carboxy[6]paracyclophane	20.2°	21.1°	–	20.3°	17.4°	[8]
7	**3**	16.4°	30.1°	–	11.6°	−2.9°	[9]
8	**4**	7.4°	13°	–	5.7°	−3.4°	[10]

3



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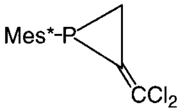

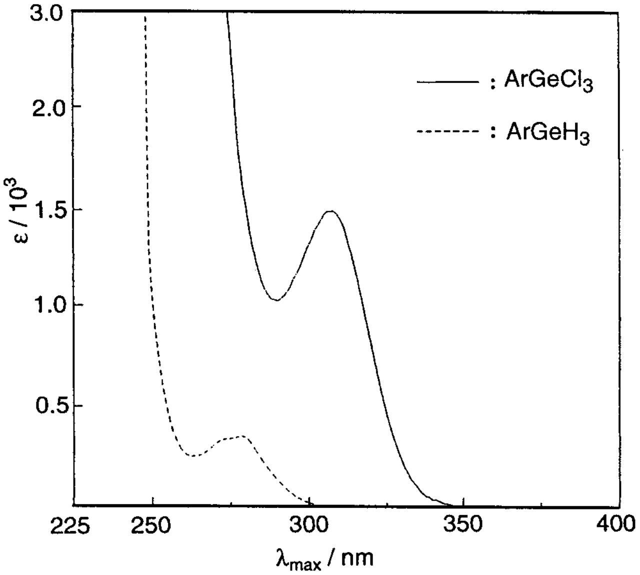

FIGURE 3 UV spectra of 1 and 2 in hexane.

X-Ray Crystallography of 2,4,6-Tri-tert-butylphenylgermane (2)

Colorless crystals of 2,4,6-tri-*tert*-butylphenylgermane (**2**) were obtained from an ethanol solution by slow evaporation. A crystal specimen of dimensions 0.20 × 0.20 × 0.20 mm was sealed in a glass capillary and used for data collection on a Rigaku AFC7S diffractometer using graphite-monochromated CuKα radiation. Cell parameters were refined by the least-squares method using 25 reflections ($42.20 < 2\theta < 56.01°$). The space group $P2_1/m$ was determined from systematic absences ($0k0$: $k \neq 2n$), packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure. Intensity data were collected in the range of $3 < 2\theta < 120.2°$ by the ω-2θ scan technique at a temperature of 20 ± 1°C. Of the 1577 reflections that were collected, 1485 were unique ($R_{\text{int}} = 0.142$). The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standard decreased by −9.6%. A polynomial correction factor was applied to the data to account for this phenomenon. The linear absorption coefficient, μ, for CuKα radiation is 21.2 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.66 to 1.15. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 8.65555×10^{-8}). The structure was solved by use of SHELXS86 [14] and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares refinement was based on 551 observed reflections ($|F_o| \geq 3\sigma(F_o)$) and 107 variable parameters and with unweighted and weighted factors of $R = 8.7\%$ and $R_w = 6.5\%$. All calculations were carried out on a SiliconGraphics INDY computer using the teXsan crystallographic software package [15]. Details of crystal data, data collection, and refinement are listed in Table 1.

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