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Enhanced Nucleophilicity of Tris-(2,6-dimethoxyphenyl)bismuthane as Studied by X-ray Crystallography, ^{17}O NMR Spectroscopy and Theoretical Calculations. X-Ray Molecular Structure of Tris-(2,6-dimethoxyphenyl)bismuthane and of Trimesitylbismuthane

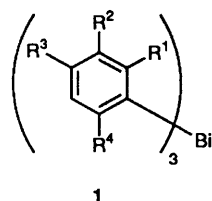
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In marked contrast to previously studied triarylbi-muthanes, tris-(2,6-dimethoxyphenyl)bismuthane **1f** showed itself to be a nucleophile strong enough to react with some activated alkyl halides *via* the probable formation of a bismuthonium intermediate. On the basis of X-ray crystallographic and ^{17}O NMR studies, as well as theoretical considerations, the origin of this uniqueness has been attributed to the through-space interaction between the bismuth centre and neighbouring oxygen atoms working favourably toward the stabilization of the bismuthonium intermediate.

In the area of heteroatom chemistry, much attention has been paid to special effects due to *ortho*-methoxy and -amino substituents on the pnictogenide centre in arylpnictogenides.¹ However, the origin of such special effects has not yet been well clarified. In the preceding paper,² we have reported the excellent properties of tris-(2,6-dimethoxyphenyl)bismuthane **1f** as a selective activating agent of primary carboxylic acids for reactions with amines and alcohols to give amides and esters in non-aqueous, neutral media. Such an especial high reactivity of the bismuthane **1f** is on the lines of the special effects denoted above. In this accompanying paper, we provide the first indirect evidence for the formation of a bismuthonium compound from the interaction of triarylbi-muthanes **1** with an activated alkyl halide. The origin of the marked difference in nucleophilicity between compound **1f** and previously studied triarylbi-muthanes has been extensively examined by X-ray structure analysis, ^{17}O NMR spectrometry and theoretical considerations based on PM3 and *ab initio* calculations, the results of which are a subject of the present short paper.



- 1a**; $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$
b; $\text{R}^1 = \text{OMe}, \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$
c; $\text{R}^1 = \text{R}^3 = \text{R}^4 = \text{H}, \text{R}^2 = \text{OMe}$
d; $\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{H}, \text{R}^3 = \text{OMe}$
e; $\text{R}^1 = \text{R}^3 = \text{OMe}, \text{R}^2 = \text{R}^4 = \text{H}$
f; $\text{R}^1 = \text{R}^4 = \text{OMe}, \text{R}^2 = \text{R}^3 = \text{H}$
g; $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{OMe}, \text{R}^4 = \text{H}$
h; $\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{H}, \text{R}^3 = \text{Me}$
i; $\text{R}^1 = \text{R}^3 = \text{R}^4 = \text{Me}, \text{R}^2 = \text{H}$

Results and Discussion

Prolonged heating of phenacyl bromide **2** with the bismuthane **1f** in benzene at reflux temperature afforded 2,6-dimethoxybenzyl phenyl ketone **5** in 91% yield. Tris-(2-methoxyphenyl)-, tris(4-methoxyphenyl)- and tris-(2,3,4-trimethoxyphenyl)-bismuthane **1b**, **1e** and **1g** all afforded poor yields of similar arylation products while triphenylbismuthane **1a** and tris-(3-methoxyphenyl)bismuthane **1c** produced no corresponding products (Table 1). A plausible reaction pathway is depicted in Scheme 1. The arylation product **5** could arise either from the bismuthonium compound **3** *via* ligand coupling³ or from the bismuthonium ylide **4** according to the known reaction mode.⁴ We favour the latter mechanism at present, since the epoxides **6** were formed in good yields in the presence of aromatic aldehydes.

Table 1 Reaction of triarylbi-muthanes Ar_3Bi with phenacyl bromide and the calculated ΔH_f -values for the formation of triarylmethyl-bismuthonium ions Ar_3MeBi^+

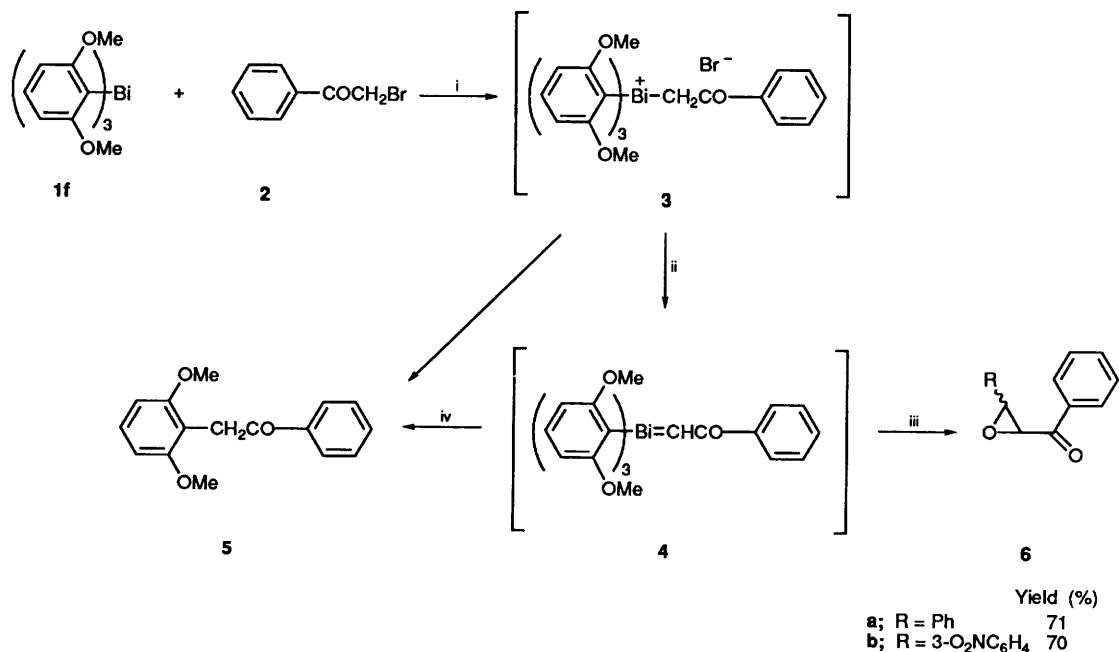
Bismuthane Ar_3Bi 1	Yield of ketone 5 (%)	Calculated ΔH_f for Ar_3BiMe^+ formation ^a (kcal mol ⁻¹) ^b
1a	0	34.9
1b	6	38.2
1c	0	36.4
1d	0	34.4
1e	Trace	39.5
1f	91	43.2
1g	8	36.1
1i		37.8

^a PM3 method in MOPAC ver. 6.01⁷ was used for the estimation of ΔH_f -values for the reaction $\text{Ar}_3\text{Bi} + \text{Me}^+ = \text{Ar}_3\text{MeBi}^+ + \Delta H_f$.
^b 1 cal = 4.184 J.

To the best of our knowledge, compound **1f** is the first example of a triarylbi-muthane that reacts directly with alkyl halides. In order to gain an insight into the origin of this notably enhanced nucleophilicity of the bismuthane **1f**, and also to obtain a guide principle for designing more highly nucleophilic bismuthanes, we examined its molecular structure by X-ray crystallography. ORTEP drawings of compound **1f** and **1i** are shown in Figs. 1 and 2 and selected atomic distances and bond angles are tabulated in Table 2. Two noteworthy features are: (1) the bond angles C–Bi–C (101.4°, 95.7°, 101.2°) are significantly larger as compared with those of tris-(4-methylphenyl)bismuthane **1h** (94.8°, 93.9°, 95.3°);⁵ (2) atomic distances between the oxygen and bismuth atoms (2.98–3.41 Å) are longer than the ordinary covalent O–Bi bond lengths (2.08–2.80 Å),⁶ but considerably shortened as compared with the sum of estimated Van der Waals radii (> 3.60 Å),[†] suggesting the operation of a strong interaction between both heteroatom species.

At first sight, the first feature (1) may be taken to indicate that the electronic configuration of bismuthane **1f** differs from the $6s^2-6p^3$ configuration of bismuthane **1h** and that the lone pair of electrons in the former compound tends to

[†] Since an established value is not available for the Van der Waals radius of the bismuth atom, we assumed it to be not less than the value for antimony (2.10 Å).



Scheme 1 Reagents and conditions: i, PhH, reflux, 3 days; ii, DBU, reflux, 1 day; iii, RCHO; iv, reflux

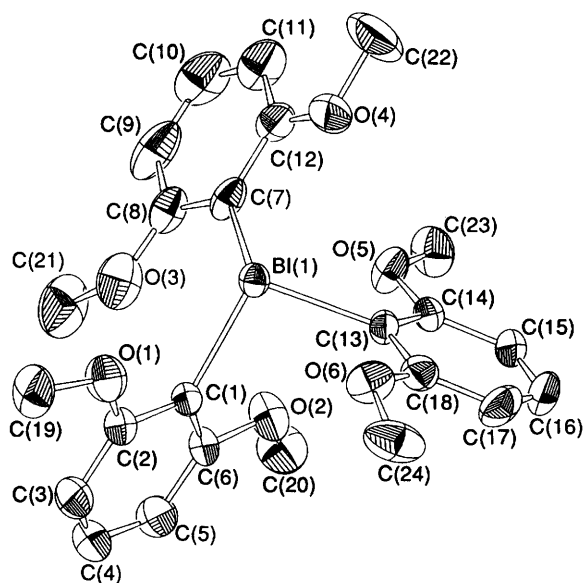


Fig. 1 An ORTEP drawing of bismuthane **1f** with the atomic-numbering scheme

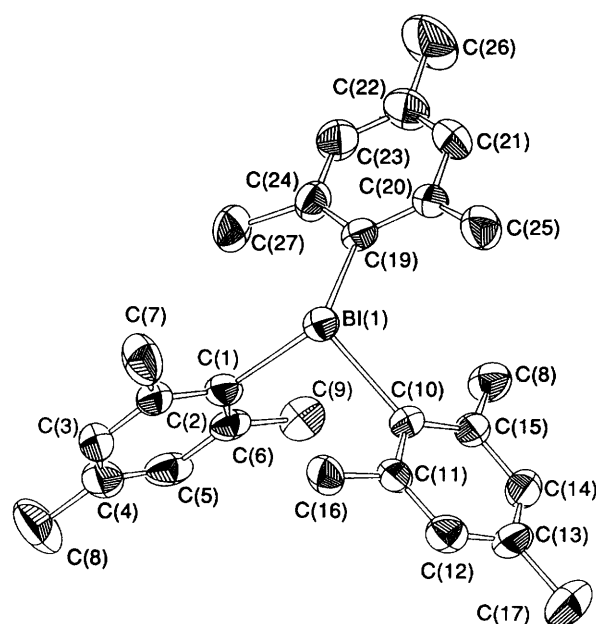


Fig. 2 An ORTEP drawing of bismuthane **1i** with the atomic-numbering scheme

gain more p-character through the increased sp^3 hybridization by enlargement of the bond angles. However, this idea was ruled out because bismuthane **1i** of lower nucleophilicity was found by the X-ray crystallography study to possess even larger bond angles: 94.7° , 107.0° and 107.6° (Table 2). A theoretical study by PM3 calculations⁸ also supported the idea that the s-character of the lone pair of electrons does not decrease in compound **1f** as compared with the parent **1a** (see Table 4, below).

The second feature (2) may be attributed to electron donation from the oxygen atoms of the methoxy groups to the bismuth centre *via* through-space interaction. If such is the case, the electron density on the bismuth atom would be expected to be significantly increased in compound **1f** as compared with **1a**. The most reliable method for estimating the increase in electron density is to measure the ^{209}Bi NMR spectrum of these bismuth compounds. In practice, however, the numerical assignment of the ^{209}Bi chemical shifts proved to be quite difficult for triarylbismuthanes because of the intrinsically broad linewidth

of their absorption peaks. Therefore, the ^{17}O NMR spectrum of bismuthanes **1b–1d** and **1f** were measured to estimate the relative difference in electron densities of the oxygen atoms in these compounds (Table 3). As anticipated, the ^{17}O resonance of bismuthane **1f** appeared at significantly lower field (δ_{O} 102.7) as compared with other bismuthanes **1b–1d** (δ_{O} 85.3–92.7), endorsing the postulate of diminished electron density at the oxygen atoms of **1f**. The decrease in electron density at the oxygen atoms, however, does not always mean there is a corresponding increase at the bismuth atom. We have estimated the electron density on the bismuth atom by calculation, since no appropriate measures are available at present to determine it experimentally. As is apparent from Table 2, the PM3-optimized structures for compounds **1f** and **1i** are sufficiently similar to those determined by X-ray crystallography that we may safely regard the values obtained by calculation as a

Table 2 Observed and calculated atomic distances (Å) and bond angles for bismuthanes **1f** and **1i** with estimated deviations in parentheses

	Bismuthane 1f		Bismuthane 1i		
	X-ray	PM3 ^a	X-ray	PM3 ^a	
<i>Bond length</i>					
Bi-C(1)	2.253(7)	2.274	Bi-C(1)	2.31(1)	2.266
Bi-C(13)	2.256(7)	2.275	Bi-C(10)	2.32(1)	2.258
Bi-C(7)	2.278(8)	2.273	Bi-C(19)	2.31(1)	2.264
Bi-O(1)	3.11	3.16			
Bi-O(2)	3.33	3.42			
Bi-O(3)	3.39	3.39			
Bi-O(4)	3.05	3.15			
Bi-O(5)	3.41	3.38			
Bi-O(6)	2.98	3.17			
<i>Bond Angle</i>					
C(1)-Bi-C(7)	101.4(3)	101.6	C(1)-Bi-C(10)	94.7(4)	98.4
C(1)-Bi-C(13)	95.7(3)	103.8	C(1)-Bi-C(19)	107.0(4)	108.7
C(7)-Bi-C(13)	101.2(3)	105.2	C(10)-Bi-C(19)	107.6(4)	108.3

^a MOPAC Ver. 6.01.⁷ Fully optimized with no symmetry specifications.**Table 3** ¹⁷O NMR chemical shifts of bismuthanes **1b-1d** and **1f**, and calculated charges on oxygen atoms

Compound	Chemical shift ^a (ppm)	Δ^b (ppm)	Calculated charges on oxygen	
			PM3 ^c	<i>ab initio</i> ^d
Anisole	87.99		-0.1892	-0.5159
1,3-Dimethoxybenzene	88.66		-0.1884	-0.5138
1b	92.66	4.67	-0.2012 ^e	-0.2392 ^e
1c	85.33	-2.66	-0.1951 ^e	-0.2459 ^e
1d	~90 ^f	2	-0.1929 ^e	-0.2453 ^e
1f	102.66	14.67	-0.1972 ^e	-0.2290 ^e

^a Chemical shifts were measured in CDCl₃, using methanol as internal standard (δ_{O} 6.00 ppm from H₂O). ^b Difference in chemical shift from those of the corresponding aromatic ethers. ^c PM3 method in MOPAC ver. 6.01.⁷ ^d RHF/LANL2DZ in Gaussian 92.⁹ ^e Averaged value of the three or six oxygen atoms. ^f Owing to low solubility of this compound, the chemical shift could not be determined accurately.**Table 4** Calculated charges in Pn atoms and estimated s-character of a lone pair of electrons of Ar₃Pn

Pn	Calculated charges on Pn		Estimated s-character (%) ^b	
	Ar = Ph	Ar = 2,6-DMP ^a	Ar = Ph	Ar = 2,6-DMP ^a
P	+0.6718 ^b	+0.8048 ^b	53.2	55.1
As	+0.6014 ^b	+0.6941 ^b	54.4	55.7
Sb	+0.7837 ^b	+0.9984 ^b	71.0	73.1
Bi	+0.7569 ^b +0.2492 ^c	+0.7995 ^b +0.3872 ^c	76.3	77.2

^a 2,6-DMP = 2,6-dimethoxyphenyl. ^b PM3 method in MOPAC ver. 6.01.⁷ ^c RHF/LANL2DZ in Gaussian 92.⁹

reliable basis for the following discussions. Electron densities at pnictogen atoms (Pn) of compound types Ar₃Pn were calculated for the cases Ar = phenyl and 2,6-dimethoxyphenyl, respectively (Table 4). Contrary to our expectation, all calculated charges at Pn atoms have been found to be more positive for tris-(2,6-dimethoxyphenyl) derivatives than for the unsubstituted parent compounds. That is, the calculated electron density at the bismuth atom of compound **1f** is lower than that of its parent **1a**. The electron-electron repulsion between the bismuth and oxygen atoms might be responsible for the diminished electron densities at those element atoms in **1f**. Judging from the ¹⁷O NMR chemical shifts, the oxygen atoms of 2,6-dimethoxy compound **1f** are more positive than those of 2-methoxy compound **1b**, which is consistent with *ab initio* calculations (Table 3). The methoxy group of compound **1b** can be distanced from the bismuth atom by distorting its C-C-Bi

bonds to some extent; in contrast, the 2-methoxy group of compound **1f** can release hardly any steric repulsion between these atoms in such a way because of the existence of the 6-methoxy group on the opposite side of the aryl ring. As a result, electron-electron repulsion between the bismuth and oxygen of compound **1f** is more significant than that of compound **1b**, which causes the lower ¹⁷O NMR chemical shifts of the former bismuthane.

Since the above mentioned results led us to the conclusion that the enhanced nucleophilicity of compound **1f** as compared with other triarylbismuthanes cannot reasonably be explained by the simple ground-state properties of these compounds, our attention was then turned to the intermediate or transition state of the reaction. The formation energy (ΔH_f) of the triaryl-methylbismuthonium cation Ar₃MeBi⁺, which may be regarded as a model system for the probable intermediate for the

condensation reaction shown in Scheme 1, was calculated for a series of triarylbi-muthanes **1a–1g** and **1i** (Table 1). The methylbismuthonium cation derived from bismuthane **1f** is the most exothermic among the eight compounds examined; it is 3.7 kcal mol⁻¹ more exothermic than the analogous ion derived from bismuthane **1e**, thus revealing the significant contribution of the *ortho* methoxy groups toward the stabilization of the bismuthonium cation. The special role of the *ortho* methoxy groups may be well recognized from the higher ΔH_f -value of bismuthane **1b** compared with those of isomeric compounds **1c** or **1d**; only those triarylbi-muthanes having an *ortho* methoxy group afforded the arylation products, though the yields were quite low (Table 1). The interaction between the oxygen atom of the *ortho* methoxy group and the bismuth atom in the methylbismuthonium cation can be represented by the presence of non-zero bond orders of 0.013–0.015. Calculated charges at the bismuth centre of the respective bismuthonium cations are 0.9802 for **1a**, 0.9941 for **1e** and 0.9611 for **1f**; the charge of the methylbismuthonium cation derived from compound **1f** is considerably lower compared with those of the other two bismuthonium cations, which may be taken to reflect the relief of positive charge by the through-space interaction described above.

On the basis of the above considerations, we may conclude that the bismuthane **1f** can behave as a strong nucleophile because of the stabilization of the corresponding onium form through the interaction between the *ortho* methoxy groups and the bismuth centre, and that the relative nucleophilicity of bismuthanes can be predicted by calculating the ΔH_f -values for the onium formation. Since the nucleophilic bismuthanes are promising precursors for more general types of bismuthonio ylides, a study directed toward those compounds is underway in our laboratory.

Experimental

Tris(methoxyphenyl)bismuthanes were prepared by the arylation of bismuth(III) chloride with the corresponding arylmagnesium bromides or aryllithiums. IR spectra were determined on a Hitachi 260-10 spectrophotometer. ¹H and ¹⁷O NMR spectra were determined on a JEOL JMN-GX 270 instrument for solutions in CDCl₃, using tetramethylsilane and methanol as the respective internal standards for proton and oxygen-17.

Typical Procedure for Reaction of Tris-(2,6-dimethoxyphenyl)bismuthane 1f with Phenacyl Bromide.—A mixture of triarylbi-muthane **1f** (620 mg, 1 mmol), phenacyl bromide **2** (199 mg, 1 mmol) and benzene (10 cm³) was heated and stirred under reflux under argon. After 3 days, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (152 mg, 1 mmol) was added and the mixture was stirred for an additional day under the same conditions, during the course of which time the starting materials disappeared completely. The reaction was quenched by the addition of dil. hydrochloric acid and the organic phase was extracted with diethyl ether (20 cm³ × 2). The combined extracts were washed successively with saturated aq. sodium hydrogen carbonate and brine, dried with sodium sulfate, and evaporated to leave a residue, which was chromatographed on silica gel with hexane-dichloromethane (1:0 to 1:1) or hexane-chloroform (1:0 to 1:1) as eluent to give 2,6-dimethoxybenzyl phenyl ketone **5** as crystals (235 mg, 92%), m.p. 103–104 °C; δ_H 3.76 (6 H, s, MeO), 4.32 (2 H, s, CH₂) and 6.47–7.98 (8 H, m, ArH); ν_{\max} (KBr) cm⁻¹ 1700 (CO); *m/z* 256 (15%, M⁺) (Found: C, 74.6; H, 6.3. C₁₆H₁₆O₃ requires C, 74.6; H, 6.3%).

Crystallographic Analyses of Bismuthanes 1f and 1i.—**Bismuthane 1f.** A crystal of dimensions 0.250 × 0.250 × 0.500 mm was used for X-ray crystallography.

Crystal data. C₂₄H₂₇BiO₆, M = 620.45. Monoclinic, *a* = 8.007(1), *b* = 20.920(4), *c* = 14.6228(8) Å, β = 101.644(7), *V* = 2399.0(6) Å³ (by least-squares refinement using the setting angles of 25 carefully centred reflections in the range of 118.37 < 2 θ < 119.67°, λ = 1.541 78 Å), space group *P*₂₁/*n*, *Z* = 4, *D*_c = 1.718 g cm⁻³, prisms. Intensity data were recorded on a Rigaku AFC5R diffractometer with graphite-monochromated Cu-K α radiation and a 12 kW rotating anode generator using the ω -2 θ scan technique to a maximum 2 θ -value of 122.9°. Scans of (1.05 + 0.30 tan θ)° were made at a speed of 16.0 deg min⁻¹ (in ω). Of the 4141 reflections which were collected, 3840 were unique (*R*_{int} = 0.029). The linear absorption coefficient for Cu-K α was 146.9 cm⁻¹. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.61 to 1.00. Data were corrected for Lorentz polarization and absorption effects. A correction for secondary extinction was applied (coefficient = 0.48068 × 10⁻⁵). The structure was solved by a combination of the Patterson method and direct methods.¹⁰ The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3245 observed reflections [*I* > 3.00 σ] and 323 variable parameters and converged with unweighted and weighted agreement factors of *R* = 0.035 and *R*_w = 0.046. The weighting scheme, *w* = 1/ σ^2 (*F*_o), was employed. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.90 and -1.54 e Å⁻³, respectively. Neutral atom-scattering factors were taken from Cromer and Waber.¹¹ Anomalous dispersion effects were included in *F*_{calc}.¹² The values for $\Delta f'$ and $\Delta f''$ were those of Cromer.¹³ All calculations were performed on a VAX station 3200 computer using the TEXSAN¹⁴ crystallographic software package from the Molecular Structure Corporation. The ORTEP¹⁵ program was used to obtain Fig. 1. Full details of crystal data, fractional atomic co-ordinates, bond lengths, bond angles, hydrogen co-ordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Bismuthane 1i.¹⁶ A crystal of dimensions 0.230 × 0.200 × 0.200 mm was used for X-ray crystallography.

Crystal data. C₂₇H₃₃Bi, M = 566.54. Monoclinic, *a* = 12.456(4), *b* = 11.49(1), *c* = 16.882(6) Å, β = 99.15(3)°, *V* = 2386(3) Å³ (by least-squares refinement using the setting angles of 24 carefully centred reflections in the range 35.91 < 2 θ < 41.00°, λ = 0.710 69 Å), space group *P*₂₁/*n*, *Z* = 4, *D*_c = 1.577 g cm⁻³, prisms. Intensity data were recorded on Rigaku AFC5R diffractometer with graphite-monochromated Mo-K α radiation and a 12 kW rotating anode generator using the ω -2 θ scan technique to a maximum 2 θ -value of 55.0°. Scans of (0.84 + 0.30 tan θ)° were made at a speed of 8.0 deg min⁻¹ (in ω). Of the 5998 reflections which were collected, 5743 were unique (*R*_{int} = 0.044). Data were corrected for Lorentz polarization and absorption effects. The structure was solved by a combination of the Patterson method and direct methods.¹⁰ The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3397 observed reflections [*I* > 3.00 σ] and 253 variable parameters and converged with unweighted and weighted agreement factors of *R* = 0.038 and *R*_w = 0.064. The weighting scheme, *w* = 1/ σ^2 (*F*_o), was employed. Neutral atom-scattering factors were taken from Cromer and Waber.¹¹ Anomalous dispersion effects were included in *F*_{calc}.¹² The values for $\Delta f'$ and $\Delta f''$ were those of Cromer.¹³ All calculations were performed on a VAX station 3200 computer using the TEXSAN¹⁴ crystallographic software package from the Molecular Structure Corporation. The ORTEP¹⁵ program was used to obtain Fig. 2. Full details of crystal data, fractional atomic co-ordinates, bond lengths, bond angles, hydrogen co-ordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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