

Substitution at the chiral bismuth center of optically pure diastereomeric iodobismuthanes bearing an intramolecular Bi–N coordination bond. Inversion of the configuration by aryl-Grignard reagents

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Abstract

Optically pure diastereomeric iodobismuthanes **3a** and **3b** underwent the substitution at the chiral bismuth center by 4-methylphenyl- and 4-chlorophenylmagnesium bromide to give bismuthane **4a** and **4b** as a single diastereomer, respectively. Each reaction was highly stereoselective. Comparison of **4a** with **4b** by ¹H-NMR spectrum revealed that the chemical shifts of the aromatic ring protons are quite different from each other due to the anisotropic effect of the ferrocenyl group, which reflects the difference of the configuration around the chiral bismuth center. The differential ¹H-NMR NOE experiments of **4a** and **4b** provided a critical evidence for the configuration in each compound. The X-ray crystallographic study of **4** demonstrated that the substitution proceeds with inversion of the configuration at the chiral bismuth center. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Bismuth; Optically pure bismuthane; Chiral ferrocenyl group; Intramolecular coordination; Substitution; Inversion; Grignard reagent

1. Introduction

Although a number of compounds bearing an optically active heteroatom center of the Group 15 elements have been reported, the research is limited to phosphorus, arsenic and antimony [1–3]. To our knowledge, no such examples of bismuth appeared. Recently, we have first succeeded in the synthesis of an optically pure diastereomeric iodobismuthane **3a** by using intramolecular Bi–N coordination and the planar chirality of ferrocene, and characterized the structure by X-ray crystallography [4]. This paper describes the substitution at the chiral bismuth center of optically pure iodobismuthanes **3** by aryl-Grignard reagents.

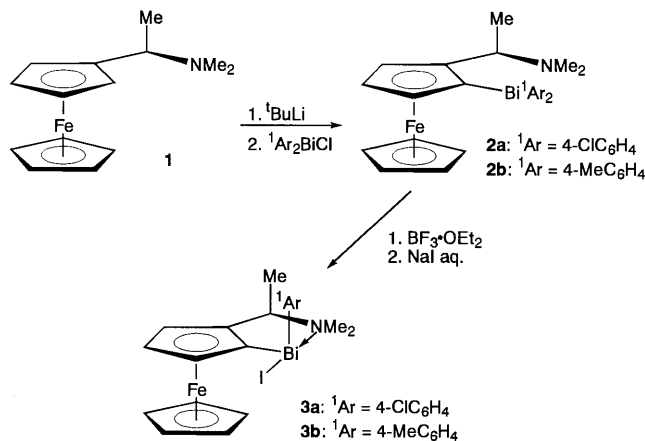
2. Results and discussion

Optically pure iodobismuthanes **3** were synthesized in two steps by using diastereoselective ortholithiation of (*R*)-(+)–*N,N*-dimethyl-1-ferrocenylethylamine (**1**), as shown in Scheme 1 [4]. The small C–Bi–C bond angle (ca. 93°) enhances the repulsive interaction between the *endo* aromatic substituent and the ferrocene moiety, so that *exo* isomers **3** form exclusively.

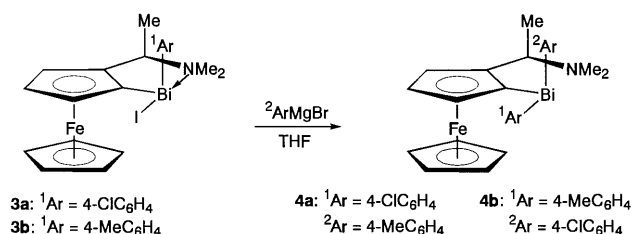
Iodobismuthane **3a** underwent substitution at the chiral bismuth center by 4-methylphenylmagnesium bromide to give bismuthane **4a** as a single diastereomer (Scheme 2). A similar reaction of **3b** with 4-chlorophenylmagnesium bromide afforded only bismuthane **4b**. Each reaction was highly stereoselective, which suggests that the substitution proceeds via a single route. These diastereomers did not suffer at all from thermal epimerization in refluxing toluene, but underwent disproportionation to **2a** or **2b** when purified

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Scheme 1.



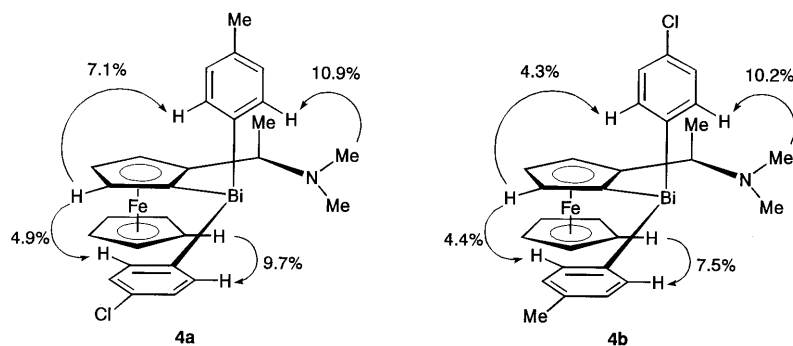
Scheme 2.

by chromatography on silica gel (hexane–ethyl acetate).

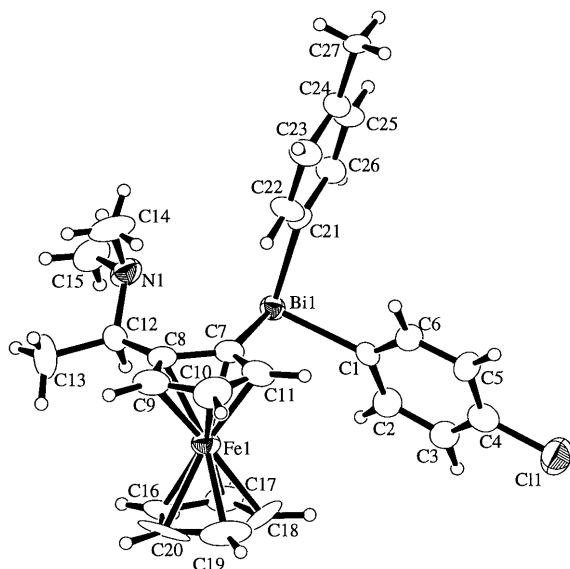
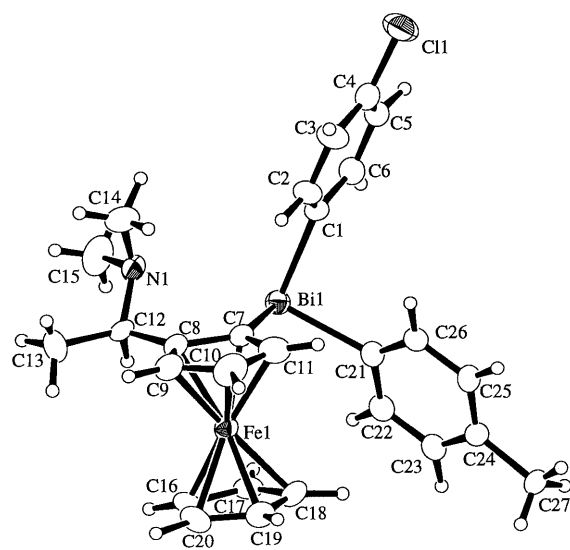
The ¹H-NMR spectral study of **3** and **4** provided some structural findings about the difference of the conformation between these bismuthanes. The proton signals of the Me₂N group in **4** appeared as a sharp singlet like **1** although those in **3** were observed as two very broad singlets which coalesced at 40°C. This suggests that the vertex inversion at the nitrogen atom which is followed by rotation about the CH(Me)–N bond of 180° takes place rapidly in **4** due to the lowered Lewis acidity of the bismuth atom relative to **3**. The signal due to the proton adjacent to the bismuth atom in the C₅H₃ ring of **4** appeared at an upfield region (ca. 0.3 ppm) compared with those due to the other two

protons in this ring. Furthermore, the proton signals of the C₅H₅ ring in **4** were observed at an upfield region (ca. 0.3 ppm) compared with those in **3**. These findings show that both the C₅H₃ ring proton and the C₅H₅ ring protons in **4** suffer from upfield shift by the ring current of one of the aryl groups at the chiral bismuth center. Thus, the aryl groups of **4** possess an axial–equatorial orientation relative to the ferrocene axis, and furthermore, the rotation of the Bi–C(cyclopentadienyl) bond toward the reverse side of the adjacent side chain in the ferrocenyl group is considered to be present. The ¹H-NMR spectra of **4a** and **4b** are quite different from each other in the chemical shifts of the aryl ring protons, which reflects the difference of the configuration around the chiral bismuth center between these diastereomers. If the ring protons of the axial aryl group appear at an upfield region compared with those of the equatorial one due to the anisotropic effect of the C₅H₃ ring, this may infer the orientation of the aryl groups in **4a** and **4b**. Such an effect is actually observed in 2-[2-(diphenylphosphino)ferrocenyl]oxazoline, where the two phenyl groups at the phosphorus atom have been revealed to possess axial–equatorial orientation by X-ray crystallography [5]. Thus, comparison of chemical shifts of the aryl ring protons revealed that the upfield shift of proton signals of the 4-methylphenyl group and that of the 4-chlorophenyl group were observed in **4a** and **4b**, respectively, which is suggestive of the axial orientation of the aryl group in the respective diastereomers.

The differential ¹H-NMR NOE experiments of **4a** and **4b** afforded reliable and critical evidence for the configuration around the chiral bismuth center of each diastereomer. The result is consistent with that estimated from the anisotropic effect. As shown in Scheme 3, two key NOEs were observed very clearly, i.e. between the proton signals of the equatorial aryl group and those of the C₅H₅ ring (9.7 and 7.5% in **4a** and **4b**, respectively) and, furthermore, between the proton signals of the axial aryl group and those of the Me₂N group (10.9 and 10.2% in **4a** and **4b**, respectively). These results manifest that the respective diastereomer



Scheme 3.

Fig. 1. ORTEP drawing of **4a**.Fig. 2. ORTEP drawing of **4b**.

has the opposite configuration around the chiral bismuth center.

An X-ray crystallographic study demonstrated that the structure of **4a** and **4b** is in accord with that estimated by the NOE experiments (Figs. 1 and 2). Thus, the substitution at the chiral bismuth center by the aryl-Grignard reagents was revealed to proceed with inversion of the configuration. The reaction is considered to take place via the following pathway, that is, the intramolecular bismuth–nitrogen coordination bond of **3** is first cleaved by the coordination of the Me₂N group with the aryl-Grignard reagent, which attacks the chiral bismuth center from the back of the bismuth–iodine bond to give **4** as a single diastereomer. Cleavage of the bismuth–nitrogen coordination bond

by the aryl-Grignard reagents is considered to take place easily as judged from the behavior of the Me₂N group in the ¹H-NMR spectra of **3** [4]. Coordination-mediated substitution by a nucleophile is reported in the spirophosphorane bearing a Me₂NCH₂CH₂O group as a substituent at the phosphorus center, where this group captures *n*-butyllithium as a nucleophile through the chelation of the lithium cation to undergo nucleophilic substitution with retention of configuration [6]. Unlike **3a**, the Me₂N group is not coplanar with the C₅H₃ ring in **4** and the intramolecular Bi–N distances [3.25(1) and 3.208(9) Å in **4a** and **4b**, respectively] (Table 2) are much longer than that of **3a** [2.71(1) Å] [4] although they are within the sum of the van der Waals radii (3.66 Å). This is consistent with the difference of behavior of the Me₂N group between **3** and **4** in the ¹H-NMR spectrum. Each equatorial aryl group of **4a** and **4b** faces the iron atom rather than the C₅H₃ ring proton, which is responsible to the observation of the ferrocenyl proton signals in an upfield region. Another

Table 1
Crystal and structure determination data for **4a** and **4b**

Compound	4a	4b
Formula	C ₂₇ H ₂₉ BiClFeN	C ₂₇ H ₂₉ BiClFeN
Formula weight	667.81	667.81
<i>a</i> (Å)	6.514(2)	6.453(3)
<i>b</i> Å	10.273(2)	20.679(3)
<i>c</i> Å	19.379(6)	9.729(2)
β (°)	97.95(5)	103.61(2)
<i>V</i> (Å ³)	1284.4(6)	1261.8(6)
Crystal color and shape	Yellow and prismatic	Yellow and prismatic
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ (# 4)	<i>P</i> 2 ₁ (# 4)
<i>Z</i>	2	2
<i>F</i> (000)	648.00	648.00
<i>D</i> _{calc} (g cm ⁻³)	1.727	1.758
Crystal dimensions (mm)	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.10
μ (cm ⁻¹)	75.11	76.45
Collection range (°)	2 θ _{max} = 54.9	2 θ _{max} = 55.0
Scan rate (° min ⁻¹)	16.0	16.0
Scan width (°)	1.15 + 0.30 tan θ	1.10 + 0.30 tan θ
Number of unique reflections	3118	4477
Number of observed data	3653 [<i>I</i> > 3.00 σ (<i>I</i>)]	4546 [<i>I</i> > 3.00 σ (<i>I</i>)]
Number of variables	282	281
Range of transmission factors	0.8517–0.9980	0.9055–0.9998
<i>R</i> ^a	0.040	0.042
<i>R</i> _w ^a	0.049	0.050
Maximum peak in final Fourier map (e Å ⁻³)	2.98	1.85
Minimum peak in final Fourier map (e Å ⁻³)	–0.58	–3.64
Goodness of fit	1.08	1.22

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$; $w = 1 / \sigma^2(F_o) = [\sigma^2(F_o) + (p^2/4)F_o^2]^{-1}$.

Table 2
Selected bond lengths (Å) and angles (°) for **4a** and **4b** with estimated S.D. values in parentheses

4a		4b	
<i>Bond lengths</i>			
Bi(1)–C(1)	2.27(1)	Bi(1)–C(1)	2.27(1)
Bi(1)–C(21)	2.25(1)	Bi(1)–C(21)	2.29(1)
Bi–C(7)	2.24(1)	Bi(1)–C(7)	2.22(1)
Bi⋯N(1)	3.25(1)	Bi⋯N(1)	3.208(9)
<i>Bond angles</i>			
C(1)–Bi(1)–C(7)	93.0(5)	C(1)–Bi(1)–C(7)	94.8(4)
C(1)–Bi(1)–C(21)	94.0(4)	C(1)–Bi(1)–C(21)	93.6(4)
C(7)–Bi(1)–C(21)	94.3(5)	C(7)–Bi(1)–C(21)	92.3(4)
Bi(1)–C(7)–C(8)	122.6(10)	Bi(1)–C(7)–C(8)	123.1(8)
Bi(1)–C(7)–C(11)	129(1)	Bi(1)–C(7)–C(11)	130.8(8)

structural feature of these diastereomers lies in the bismuth–carbon bond length. Among the three bismuth–carbon bonds in each diastereomer, the following relation is found to hold; Bi(1)–C(Ar_{eq}) > Bi(1)–C(Ar_{ax}) > Bi(1)–C(ferrocenyl). The elongation of the Bi(1)–C(Ar_{eq}) bond compared with the Bi(1)–C(Ar_{ax}) one probably associates with the intramolecular coordination of the Me₂N group. This is suggested by the fact that the Bi(1)–C(Ar_{eq}) bond lengthens with decreasing intramolecular Bi–N distance. The shortest Bi(1)–C(ferrocenyl) bond length is ascribable to the effect of the bidentate ferrocenyl group. The Bi(1)–C(ferrocenyl) bond is observed to become shorter with decreasing intramolecular Bi–N distance. This tendency is also the case for **3a** where the Bi(1)–C(ferrocenyl) bond length and the intramolecular Bi–N distance are 2.19(1) and 2.71(1) Å, respectively.

The values of the specific rotation $[\alpha]_{\text{D}}^{23}$ (*c* 1.0, CHCl₃) in **4a** and **4b** are –378 and –412, respectively, which are similar to those of **2** ($[\alpha]_{\text{D}}^{23}$ –330 [4]) and –391° for **2a** and **2b**, respectively) but smaller than those of **3** ($[\alpha]_{\text{D}}^{23}$ –546 [4] and –494° for **3a** and **3b**, respectively). The difference of the value between **4a** and **4b** reflects that of the configuration at the chiral bismuth center.

3. Experimental

All reactions were carried out under argon. Diethyl ether and THF were distilled from calcium hydride under nitrogen before use. Bismuth(III) chloride was purified by refluxing with thionyl chloride. ¹H-NMR spectra were recorded in CDCl₃ on a Bruker Avance 400S (400 MHz) spectrometer with tetramethylsilane as an internal standard. Optical rotations were taken with SEPA–300 (HORIBA) in solution in a 1-dm cell.

3.1. Synthesis of *{(S)-2-[(R)-1-(dimethylamino)ethyl]ferrocenyl}bis(4-methylphenyl)bismuthane (2b)*

According to the literature method [4], to a solution of **1** (0.51 ml; 2 mmol) in diethyl ether (10 ml) was added at ice bath temperature *tert*-butyllithium (2.1 mmol), and the mixture was stirred at room temperature (r.t.) for 2 h. To a suspension of the lithium compound thus obtained was added at ice bath temperature an ethereal suspension of chlorobis(4-methylphenyl)bismuthane (ca. 2 mmol), and the resulting mixture was stirred for 15 min. After the addition of brine (5 ml), the mixture was diluted with ethyl acetate (10 ml) and the insoluble polymeric substances were filtered off. The organic layer was separated and evaporated under reduced pressure to leave a brown oil, which was crystallized from MeOH to give the pure product as orange crystals (705 mg, 54% yield). M.p. 142–144°C. ¹H-NMR: δ 1.16 (3H, d, *J* = 6.7 Hz, Me), 1.83 (6H, s, Me₂N), 2.28 (3H, s, Me), 2.33 (3H, s, Me), 3.96 (1H, m, C₅H₃), 3.98 (5H, s, C₅H₅), 4.03 (1H, q, *J* = 6.7 Hz, MeCH), 4.21 (2H, m, C₅H₃), 7.09 (2H, d, *J*_{AB} = 7.9 Hz, ArH), 7.19 (2H, d, *J*_{AB} = 7.9 Hz, ArH), 7.61 (2H, d, *J*_{AB} = 7.9 Hz, ArH), 7.75 (2H, d, *J*_{AB} = 7.9 Hz, ArH). $[\alpha]_{\text{D}}^{23}$ –391 (*c* 1.0, CHCl₃). Anal. Calc. for C₂₈H₃₂BiFeN: C, 51.95; H, 4.98; N, 2.16. Found: C, 51.75; H, 4.82; N, 1.98%.

3.2. Synthesis of *exo-4-methylphenyl}{(S)-2-[(R)-1-(dimethylamino)ethyl]ferrocenyl}iodobismuthane (3b)*

According to the literature method [4], to a solution of compound **2b** (314 mg; 0.5 mmol) in CH₂Cl₂ (20 ml) was added dropwise at ice bath temperature boron trifluoride–diethyl etherate until **2b** was consumed (checked by TLC), and the mixture was stirred at r.t. for 1 h. After the addition of brine (5 ml), the mixture was diluted with ethyl acetate (10 ml) and the organic layer was separated and evaporated under reduced pressure to leave a brown oil. Recrystallization from ethyl acetate gave the pure product as orange crystals (286 mg, 91% yield). M.p. 195–198°C (dec.). ¹H-NMR: δ 1.12 (3H, d, *J* = 6.7 Hz, Me), 1.60 (3H, br s, MeN), 2.29 (3H, s, Me), 2.60 (3H, br s, MeN), 4.23 (1H, q, *J* = 6.7 Hz, MeCH), 4.25 (5H, s, C₅H₅), 4.31 (1H, m, C₅H₃), 4.43 (1H, m, C₅H₃), 4.82 (1H, m, C₅H₃), 7.26 (2H, d, *J*_{AB} = 7.9 Hz, ArH), 8.10 (2H, d, *J*_{AB} = 7.9 Hz, ArH). $[\alpha]_{\text{D}}^{23}$ –494 (*c* 1.0, CHCl₃). Anal. Calc. for C₂₁H₂₅BiFeIN: C, 36.92; H, 3.69; N, 2.05. Found: C, 36.71; H, 3.50; N, 1.96%.

3.3. Synthesis of *(4-chlorophenyl){(S)-2-[(R)-1-(dimethylamino)ethyl]ferrocenyl}(4-methylphenyl)-(S)-bismuthane (4a)*

To a solution of compound **3a** (194 mg; 0.3 mmol) in THF (5 ml) was added dropwise at ice bath tempera-

ture 4-methylphenylmagnesium bromide in THF (5 ml) until **3a** was consumed (checked by TLC). The reaction was quenched by the addition of brine (3 ml) and the organic layer was evaporated under reduced pressure to afford crude compound **4a**. Recrystallization from MeOH gave pure product as orange crystals (138 mg, 69% yield). M.p. 123–125°C. ¹H-NMR: δ 1.14 (3H, d, $J = 6.7$ Hz, Me), 1.81 (6H, s, Me₂N), 2.28 (3H, s, Me), 3.89 (1H, m, C₅H₃), 3.99 (5H, s, C₅H₅), 4.01 (1H, q, $J = 6.7$ Hz, MeCH), 4.24 (2H, m, C₅H₃), 7.11 (2H, d, $J_{AB} = 7.3$ Hz, MeArH), 7.31 (2H, d, $J_{AB} = 7.3$ Hz, ClArH), 7.59 (2H, d, $J_{AB} = 7.3$ Hz, MeArH), 7.77 (2H, d, $J_{AB} = 7.3$ Hz, ClArH). $[\alpha]_D^{23} = -378$ (c 1.0, CHCl₃). Anal. Calc. for C₂₇H₂₉BiClFeN: C, 48.56; H, 4.38; N, 2.10. Found: C, 48.40; H, 4.22; N, 2.02%.

3.4. Synthesis of (4-chlorophenyl){(S)-2-[(R)-1-(dimethylamino)ethyl]ferrocenyl}(4-methylphenyl)-(R)-bismuthane (**4b**)

To a solution of compound **3b** (188 mg; 0.3 mmol) in THF (5 ml) was added dropwise at ice bath temperature 4-chlorophenylmagnesium bromide in THF (5 ml) until **3b** was consumed (checked by TLC). The reaction was quenched by the addition of brine (3 ml) and the organic layer was evaporated under reduced pressure to afford crude compound **4b**. Recrystallization from MeOH gave pure product as orange crystals (111 mg, 56% yield). M.p. 125–126°C. ¹H-NMR: δ 1.15 (3H, d, $J = 6.7$ Hz, Me), 1.81 (6H, s, Me₂N), 2.28 (3H, s, Me), 3.96 (1H, m, C₅H₃), 4.00 (5H, s, C₅H₅), 4.01 (1H, q, $J = 6.7$ Hz, MeCH), 4.24 (2H, m, C₅H₃), 7.23 (2H, d, $J_{AB} = 7.3$ Hz, MeArH), 7.25 (2H, d, $J_{AB} = 7.3$ Hz, ClArH), 7.65 (2H, d, $J_{AB} = 7.3$ Hz, ClArH), 7.72 (2H, d, $J_{AB} = 7.3$ Hz, MeArH). $[\alpha]_D^{23} = -412$ (c 1.0, CHCl₃). Anal. Calc. for C₂₇H₂₉BiClFeN: C, 48.56; H, 4.38; N, 2.10. Found: C, 48.44; H, 4.30; N, 2.01%.

3.5. X-ray crystal structure analyses of **4a** and **4b**

All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71069$ Å). The data were collected at 296 K using the ω - 2θ scan technique. Three standard reflections were monitored every 150 reflections and a linear correction factor was applied to the data correction for **4a**. Reflection data were corrected for Lorentz-polarization and absorption (by ψ -scan method) effects. The weighting scheme was based on counting statistics and included a factor ($p = 0.050$) to down-weight the intense reflections. The structure of **4a** and **4b** was solved by direct methods with SIR-92 [7] and expanded using Fourier techniques [8]. The non-hydrogen atoms were refined anisotropically. Neutral-atom scattering factors were taken from Cromer and Waber [9]. Anomalous dispersion effects were included in F_{calc}

[10]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [11]. The values for the mass attenuation coefficients are those of Creagh and Hubbel [12]. All calculations were carried out on a Silicon Graphics Indigo2 workstation with the TEXSAN program [13]. Perspective drawings were drawn by using the ORTEP program [14]. The chirality has been determined by refinement of the Flack parameter. The chirality test was also examined by the R factor for the inverted structure. The R factors for the corresponding enantiomeric structure were 0.068 and 0.072 for **4a** and **4b**, respectively (Table 1).

4. Supplementary material

Complete lists of bond lengths and angles, hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (nos. CCDC 141120 and 141121). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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