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SELENIUM-CONTAINING HETEROCYCLES FROM ISO-SELENOCYANATES: SYNTHESIS OF 2-ARYLAMINO-SELENAZOLO[5,4-*b*]PYRIDINES

Plamen K. Atanassov,[1] Anthony Linden, and Heinz Heimgartner*

Institute of Organic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland; E-mail: heimgart@oci.unizh.ch

Abstract – The reaction of 3-amino-2-chloropyridine (**4**) with aryl isoselenocyanates (**2a**-**d**) in refluxing 2-propanol gave the hydrochlorides of 2-arylaminoselenazolo[5,4-*b*]pyridines (**7a**-**d**) in good yield. The free bases (**8a**-**d**) were obtained after treatment with aqueous NaOH and recrystallization. A reaction mechanism *via* the intermediate selenourea derivatives (**5**) is most likely. The structure of the 2-phenylamino derivative (**8a**) has been established by X-Ray crystallography.

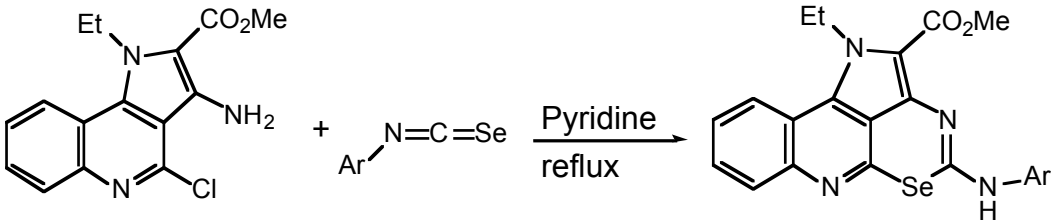
INTRODUCTION

The current interest in selenium-containing heterocycles is a result of their chemical properties[2] and biological activities.[3,4] Numerous recent papers deal with the pharmaceutical potential of selenium compounds,[5] and therefore, new efficient syntheses are an attractive goal of chemical research.[6] The main drawbacks of some syntheses are the toxicity of selenium reagents and the instability of some intermediates.

With the aim of using less toxic, conveniently accessible, and safely handlable selenium reagents for the synthesis of selenium-containing heterocycles, we have investigated reactions involving different isoselenocyanates. For example, the reaction of aroyl isoselenocyanates with ethyl diazoacetate led to 1,2,3-selenadiazoles,[7] and *N*-arylimidoyl isoselenocyanates were transformed into 2-amino-1,3-selenazoles[8] and 6*H*-5,1,3-benzoselenadiazocine derivatives,[9] whereas *N*-(4-nitro-benzyl)benzimidoyl isoselenocyanates, on treatment with triethylamine, gave the corresponding bis(2,4-diarylimidazole-5-yl) diselenides.[10]

Recently, we have shown that the reaction of aryl isoselenocyanates (**2**) with methyl 3-amino-4-chloro-1-ethylpyrrolo[3,2-*c*]quinoline-2-carboxylate (**1**) in boiling pyridine gives 1*H*-1,3,6-triazaaceanthrylene derivatives (**3**) (*Scheme 1*).[11] The formation of **3** can be rationalized *via* an intermediate selenourea derivative and cyclization by nucleophilic aromatic substitution of chloride by the selenium atom.

Scheme 1



1 **2** **3**

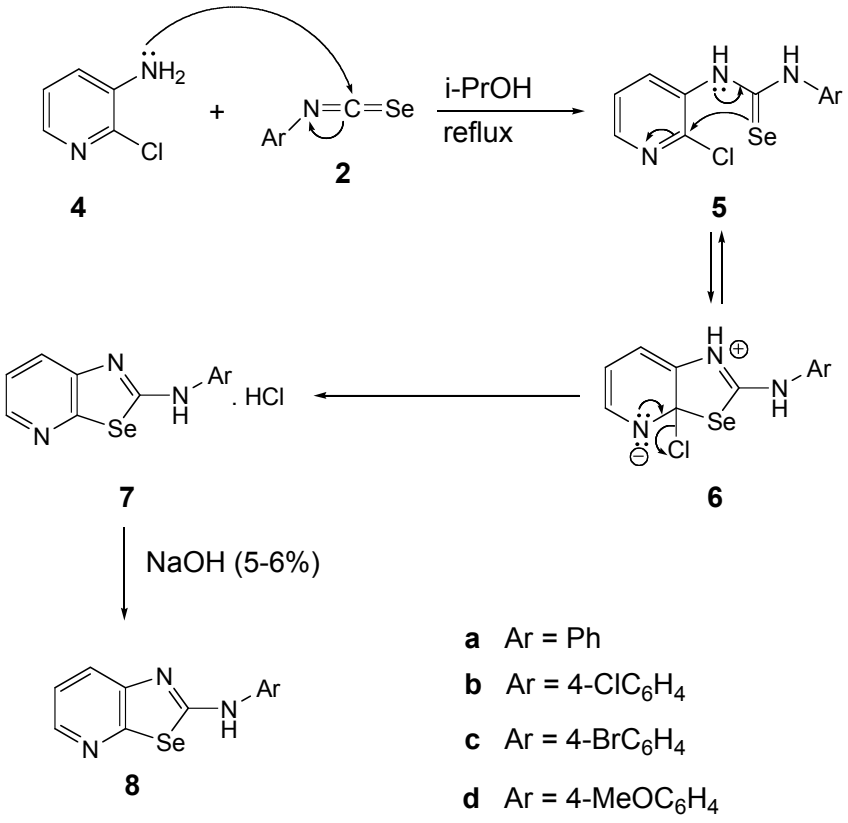
In the present paper, we report the analogous reaction of aryl isoselenocyanates (**2**) with 3-amino-2-chloropyridine (**4**). The latter has been used by *Altland* and *Molander* in reactions with isothiocyanates, which leads to 2-amino-1,3-thiazolo[5,4-*b*]pyridines.[12]

RESULTS AND DISCUSSION

To a stirred solution of 3-amino-2-chloropyridine (**4**) in dry 2-propanol, 1.1 equivalent of freshly prepared aryl isoselenocyanate (**2a**-**d**) was added at room temperature. The aryl isoselenocyanates of (**2**) could be prepared easily from the corresponding *N*-arylformamides by treatment with phosgene and selenium powder according to a protocol of *Barton* et al.[13] Heating of the solution of **2** and **4** in 2-propanol under reflux led to the formation of a yellowish solid. After 4 h, the mixture was cooled to room temperature and the 2-arylaminoselenazolo[5,4-*b*]pyridine hydrochlorides (**7a**-**d**) were isolated by filtration in 59-73% yield (*Scheme 2*). The free bases (**8a**-**d)** were obtained after treatment of the hydrochlorides with 5-6% aqueous NaOH at ambient temperature. After stirring the suspension for 15 min, the solid was filtered, washed with cold water, and recrystallized from ethyl acetate to give **8a**-**d** in quantitative yield.

The structures of the obtained products were established on the basis of their spectroscopic data and elemental analysis. In the case of **8a**, an X-Ray crystal structure determination was carried out, which confirmed the proposed structure (*Figure 1*).

Scheme 2



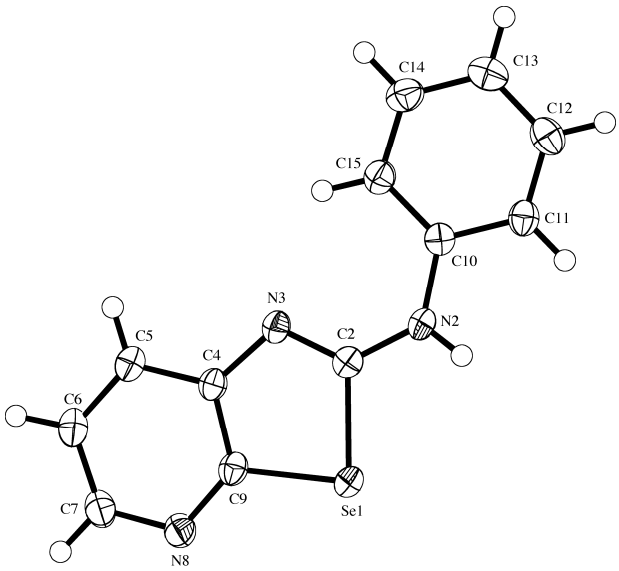


Figure 1. ORTEP plot[14] of the molecular structure of one of the two symmetry-independent molecules of **8a** (arbitrary numbering of atoms; 50% probability ellipsoids)

There are two symmetry-independent molecules, A and B, of **8a** in the asymmetric unit. The conformations of the two molecules are very similar and differ primarily in the orientation of the phenyl substituent, which in molecule B is twisted approximately 18° with respect to its orientation in molecule A. The fused heterocyclic system is planar and the phenylamino group is almost coplanar with the ring system (torsion angles for molecule A: N(3)-C(2)-N(2)-C(10) -0.5(4)°, C(2)-N(2)-C(10)-C(11) -174.0(2)°). The exocyclic N(2) atom also has a planar environment, and the similarity of the C,N-bond lengths (C(2)-N(2) 1.349(3) Å, C(2)-N(3) 1.292(3) Å) indicates a significant delocalization of the lone electron pair. The NH group of molecule A forms an intermolecular hydrogen bond with the N-atom of the six-membered ring of a neighboring molecule B. In turn, molecule B forms the same type of intermolecular hydrogen bond with a different molecule A. These interactions link the molecules in an ···A···B···A···B··· sequence into infinite zig-zag chains which run parallel to the *x*-axis and have a binary graph set motif[15] of $C_2^2(12)$ (*Figure 2*).

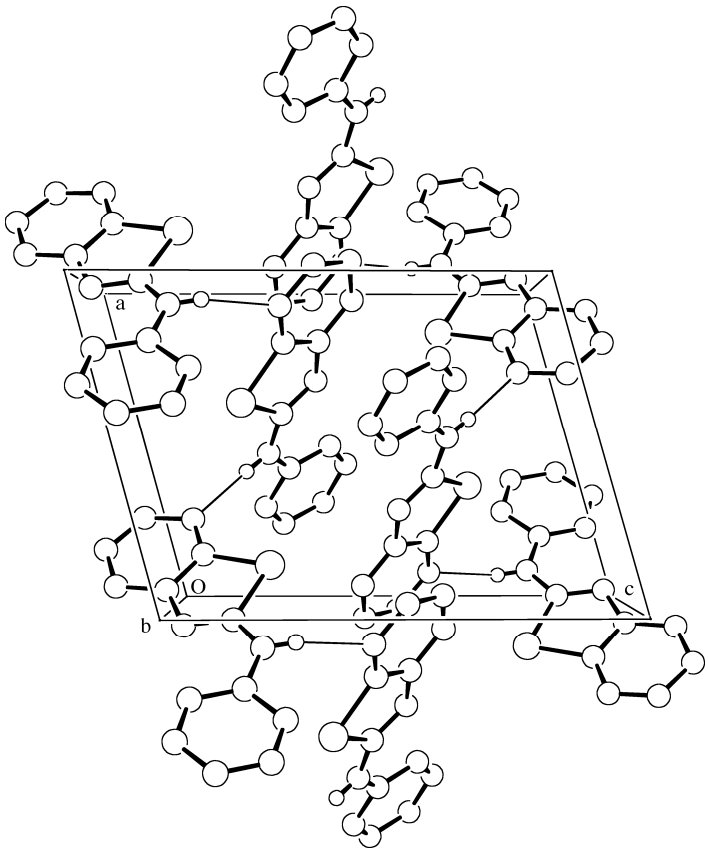


Figure 2. Molecular packing of **8a** projected down the *b*-axis showing the hydrogen bonded chains (uninvolved H-atoms omitted for clarity)

In conclusion, we have shown that **4** reacts with aryl isoselenocyanates (**2**) to give 2-arylaminoselenazolo[5,4-*b*]pyridines (**8**) in good yields. The ring closure of the proposed intermediate selenourea derivative (**5**) takes place by nucleophilic attack of the selenium atom at C(2) of the 2-chloropyridine residue and substitution of Cl^-. Therefore, aryl isoselenocyanates (**2**) are useful precursors for the preparation of selenaheterocycles. They are less toxic, relatively stable, safe and easy to handle, and can be synthesized conveniently.

EXPERIMENTAL

General remarks. See ref.[7] IR spectra in KBr (cm^{-1}), NMR spectra at 300 (^1H) and 75.6 (^{13}C) MHz in d_6-DMSO (ppm), and CI-MS with NH_3 (*m*/*z* (rel.%)).

Starting materials. 3-Amino-2-chloropyridine (**4**) was commercially available (*Fluka*). *N*-(4-Chlorophenyl)- and *N*-(4-bromophenyl)formamides were prepared from the respective aniline (0.02 mol) and 95% formic acid (40 mL).[16] The solution was heated to reflux for 30 min and evaporated to dryness under vacuum. The residue was dissolved in ether and washed with diluted acetic acid (5%), water, and aqueous $NaHCO_3$ solution (5%). The aqueous layer was extracted with ether, the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. The products were recrystallized from water.

N-(4-Methoxyphenyl)formamide was prepared analogously using *p*-anisidine (616 mg, 5 mmol) and formic acid (10 mL). After evaporation to dryness, the residue was dissolved in ethyl acetate, washed with aqueous $NaHCO_3$ solution (5%), and rinsed with water. The organic layer was dried ($MgSO_4$), the solvent was evaporated, and the crude product was used without further purification.

Synthesis of aryl isoselenocyanates. General procedure (cf. ref.[13]). In a 3-neck flask equipped with a magnetic stirrer and an addition funnel, *N*-arylformamide (4.84 g, 40 mmol) was dissolved in absolute toluene (100 mL). This solution was cooled in an ice bath and stirred under argon. Then, triethylamine (16.2 g, 160 mmol) and selenium powder (4.74 g, 60 mmol) were added to the stirred solution. The addition funnel was charged with 30 g (60 mmol) of phosgene as 20% solution in toluene. The phosgene solution was added slowly to the stirred suspension (kept in an ice-bath) over 30 min while an exothermic reaction took place. After

complete addition, the suspension was heated to reflux. The progress of the reaction was followed by TLC. Typically, 8-10 h reflux was required for the completion of the reaction. The mixture was filtered and washed with several portions of toluene. The filtrate was concentrated and chromatographic workup (SiO_2, hexane) afforded the corresponding aryl iso-selenocyanate. Yield of phenyl isoselenocyanate (**2a**): 3.24 g (44.6%). Clear, pale yellow oil.

Synthesis of 2-aminoselenazolo[5,4-*b*]pyridines. General procedure. To a stirred solution of 3-amino-2-chloropyridine (**4**) in dry 2-propanol (10 mL) at rt, 1.1 equivalents of freshly prepared aryl isoselenocyanate (**2**) were added. The mixture was heated to reflux for 4 h and the formation of a yellowish solid was observed. The solution was cooled to rt, the solid 2-aminoselenazolo[5,4-*b*]pyridine hydrochloride (**7**) was filtered, and stirred in aqueous NaOH solution (5-6%) for 15 min. Then, the solid (**8**) was filtered and recrystallized from ethyl acetate.

*2-(Phenylamino)selenazolo[5,4-*b*]pyridine* (**8a**). From 0.6 g (3.30 mmol) of phenyl iso-selenocyanate (**2a**) and 0.42 g (3.27 mmol) of **4**: 0.7 g (69.3%) hydrochloride (**7a**); mp 303-307°C. 0.61 g (69.3%) **8a** after treatment with NaOH. Pale gray crystals; mp 160.1-161.2°C. IR: 3248*w*, 3193*w*, 3073*w*, 3049*w*, 2997*w*, 2922*m*, 2847*w*, 1622*m*, 1608*s*, 1590*s*, 1556*s*, 1496*s*, 1445*s*, 1379*s*, 1318*m*, 1242*m*, 1207*s*, 1183*m*, 1151*m*, 1124*m*, 1113*m*, 1088*m*. ^{1}H-NMR: 10.66 (*s*, PhN*H*); 8.21-8.18(*m*, 1 arom. H); 7.87-7.79 (*m*, 3 arom. H); 7.42-7.32 (*m*, 3 arom. H); 7.11-7.06 (*m*, 1 arom. H). ^{13}C-NMR: 161.5, 159.0, 148.6, 140.2 (4*s*, 4 arom. C); 142.9, 129.0, 125.9, 122.7, 121.5, 118.3 (6*d*, 8 arom. CH). CI-MS: 276 (100, $[M+1]^+$). Anal. Calcd for $C_{12}H_9N_3Se$: C, 52.57; H, 3.31; N 15.33. Found: C, 52.54; H, 3.27; N, 15.38.
Crystals suitable for an X-Ray crystal-structure determination were grown from ethyl acetate.

*2-[(4-Chlorophenyl)amino]selenazolo[5,4-*b*]pyridine* (**8b**). From 0.66 g (3 mmol) of 4-chloro-phenyl isoselenocyanate (**2b**) and 0.35 g (2.72 mmol) of **4**: 0.69 g (73.0%) hydrochloride (**7b**); mp 286-290°C. 0.6 g (73.0%) **8b** after treatment with NaOH. Pale gray crystals; mp 276.0-277.0°C. IR: 3254*w*, 3188*w*, 3104*w*, 3034*m*, 2971*m*, 2922*m*, 2853*m*, 2794*w*, 1622*s*, 1586*s*, 1552*s*, 1524*s*, 1488*s*, 1453*m*, 1403*s*, 1378*s*, 1314*s*, 1303*s*, 1287*m*, 1246*s*, 1208*s*, 1154*m*, 1119*m*, 1097*m*. ^{1}H-NMR: 10.77 (*s*, PhN*H*); 8.22-8.20 (*m*, 1 arom. H); 7.88-7.81 (*m*, 3 arom. H); 7.45-7.33 (*m*, 3 arom. H). ^{13}C-NMR: 161.2, 158.9, 148.4, 139.0, 126.0 (5*s*, 5 arom. C); 143.1, 128.8, 126.1, 121.8, 119.6 (5*d*, 7 arom. CH). CI-MS: 310 (100, $[M+1]^+$). Anal. Calcd for $C_{12}H_8N_3ClSe$: C, 46.70; H, 2.61; N, 13.62. Found: C, 46.64; H, 2.71; N, 13.72.

*2-[(4-Bromophenyl)amino]selenazolo[5,4-*b*]pyridine* (**8c**). From 0.42 g (1.6 mmol) of 4-bromophenyl isoselenocyanate (**2c**) and 0.20 g (1.55 mmol) of **4**: 0.42 g (71.0%) hydrochloride (**7c**); mp 288.0-289.1°C. 0.38 g (71.0%) **8c** after treatment with NaOH. Pale gray crystals; mp 284.1°-285.0°C. IR: 3444*w* (br), 3256*m*, 3187*m*, 3101*m*, 3037*m*, 2970*m*, 2983*m*, 2853*m*, 2790*w*, 1621*m*, 1581*s*, 1550*s*, 1525*s*, 1485*s*, 1453*m*, 1397*m*, 1378*m*, 1340*w*, 1315*m*, 1302*m*, 1287*m*, 1245*s*, 1208*s*, 1175*m*, 1153*m*, 1118*m*, 1111*w*, 1094*w*. ^{1}H-NMR: 10.78 (*s*, PhN*H*); 8.22-8.20 (*d*-like, 1 arom. H); 7.88-7.87 (*d*-like, 1 arom. H); 7.86-7.76 (*d*-like, 2 arom. H); 7.57-7.54 (*d*-like, 2 arom. H); 7.38-7.34 (*m*, 1 arom. H). ^{13}C-NMR: 161.2, 159.0, 148.4, 139.4, 114.0 (5*s*, 5 arom. C); 143.2, 131.7, 126.2, 121.6, 120.1 (5*d*, 7 arom. CH). CI-MS: 354 (100, [*M*+1]$^+$). Anal. Calcd for $C_{12}H_8N_3BrSe$: C, 40.82; H, 2.28; N, 11.90. Found: C, 40.92; H, 2.20; N, 11.92.

*2-[(4-Methoxyphenyl)amino]selenazolo[5,4-*b*]pyridine* (**8d**). From 0.66 g (3.11 mmol) of 4-methoxyphenyl isoselenocyanate (**2d**) and 0.35 g (2.72 mmol) of **4**: 0.55 g (59.3%) hydrochloride (**7d**); mp 270.0-271.0°C. 0.49 g (59.3%) **8d** after treatment with NaOH. Pale gray crystals; mp 163.0-164.0°C. IR: 3224*w*, 3166*m*, 3103*w*, 3051*w*, 3030*w*, 3000*w*, 2963*m*, 2838*s*, 1621*s*, 1580*s*, 1558*s*, 1542*s*, 1511*s*, 1460*s*, 1413*m*, 1376*s*, 1346*m*, 1299*m*, 1287*s*, 1272*s*, 1246*s*, 1216*m*, 1206*s*, 1178*s*, 1111*s*. ^{1}H-NMR: 10.48 (*s*, PhN*H*); 8.16-8.14 (*d*-like, 1 arom. H); 7.79-7.76 (*d*-like, 1 arom. H); 7.70-7.64 (*d*-like, 2 arom. H); 7.33-7.29 (*m*, 1 arom. H); 7.00-6.94 (*d*-like, 2 arom. H); 3.76 (*s*, MeO). ^{13}C-NMR: 161.9, 155.2, 148.9, 133.6 (4*s*, 5 arom. C); 142.5, 125.4, 121.4, 120.3, 114.2 (5*d*, 7 arom. CH); 55.2 (*q*, MeO). CI-MS: 306 (100, [*M*+1]$^+$). Anal. Calcd for $C_{13}H_{11}N_3OSe$: C, 51.33; H, 3.54; N, 13.81. Found: C, 51.27; H, 3.76; N, 13.86.

X-Ray Crystal-Structure Determination of **8a** (see *Table 1* and *Figure 1*).[17] All measurements were made on a *Nonius KappaCCD* diffractometer[18] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream* 700 cooler. The data collection and refinement parameters are given in *Table 1* and views of the molecules are shown in *Figure 1*. Data reduction was performed with *HKL Denzo* and *Scalepack*.[19] The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method[20] was applied. The structure was solved by direct methods using SIR92,[21] which revealed the positions of all non-hydrogen atoms. There are two symmetry-independent molecules in the asymmetric unit. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher symmetry space group using the program PLATON,[22]

Table 1: *Crystallographic Data of Compound (**8a**)*

Crystallized from	EtOAc
Empirical formula	$C_{12}H_9N_3Se$
Formula weight [g mol^{-1}]	274.12
Crystal color, habit	colorless, prism
Crystal dimensions [mm]	0.17 × 0.25 × 0.27
Temperature [K]	160(1)
Crystal system	triclinic
Space group	$P\bar{1}$
Z	4
Reflections for cell determination	26683
2θ range for cell determination [°]	4 – 60
Unit cell parameters:	
a [Å]	8.9774(1)
b [Å]	10.4223(2)
c [Å]	11.9741(2)
α [°]	92.2273(9)
β [°]	105.2188(8)
γ [°]	93.1052(8)
V [Å^3]	1077.84(3)
D_x [g cm^{-3}]	1.689
μ(Mo$K\alpha$) [mm^{-1}]	3.454
Scan type	ω and φ
$2\theta_{(max)}$ [°]	60
Transmission factors (min; max)	0.472; 0.565
Total reflections measured	29955
Symmetry independent reflections	6303
Reflections with $I > 2\sigma(I)$	5125
Reflections used in refinement	6303
Parameters refined	298
Final: $R(F)$ [$I>2\sigma(I)$ reflections]	0.0339
$wR(F^2)$ (all data)	0.0865
Weights: $w = [\sigma^2(F_o^2) + (0.0437P)^2 + 0.4215P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$	
Goodness of fit	1.038
Secondary extinction coefficient	0.0062 (9)
Final Δ_{max}/σ	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.64; -0.95

but none could be found. The non-hydrogen atoms were refined anisotropically. The amine H-atoms were placed in the positions indicated by a difference electron density map and their positions were allowed to refine together with individual isotropic displacement parameters. All remaining H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom. Refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied. Neutral atom scattering factors for non-hydrogen atoms were taken from ref.[23a], and the scattering factors for H-atoms were taken from ref.[24] Anomalous dispersion effects were included in F_c;[25] the values for f' and f'' were those of ref.[23b] The values of the mass attenuation coefficients are those of ref.[23c] All calculations were performed using *SHELXL97*.[26]

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