Selenium-Containing Heterocycles from Isoselenocyanates: Base-Catalyzed Reaction of Malononitrile with Phenyl Isoselenocyanate and Bromoacetonitrile or α-Halogenated Ketones

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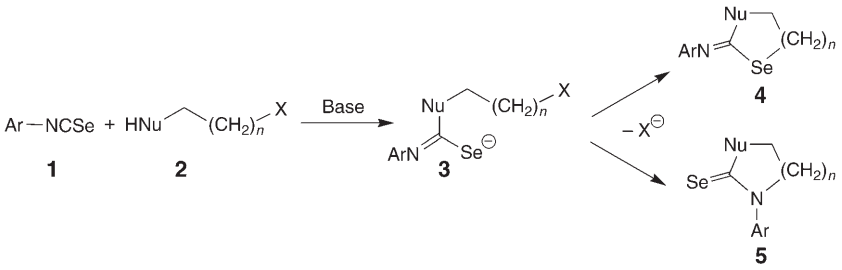
The reaction of phenyl isoselenocyanate (**1a**) with malononitrile (= propanedinitrile) in DMF in the presence of Et_3N leads to the intermediate ketene N,Se-hemiacetal **6a**, which can be trapped with bromoacetonitrile or α-halogenated ketones **12a** and **12b** (*Scheme 3*). The products are [(alkylseleno)-(phenylamino)methylene]malononitriles **10** and **13**, which are obtained in good yield. In the case of the (2-oxoalkyl)seleno derivatives **13**, they are in equilibrium with the cyclic hemiacetals **14**. Chemical and spectroscopic evidence for the structures of the new compounds are described. The structure of **14a** was established by X-ray crystallography.

1. Introduction. – In the last few years, it has been shown that isoselenocyanates **1** are versatile building blocks for the synthesis of selenium-containing heterocycles [1 – 4] and heterocyclic selones (see [5 – 6] and refs. cit. therein). For example, the reaction of **1** with nucleophiles of type **2**, which also bear an electrophilic group, in the presence of a base gave either Se-containing heterocycles **4** with an imino group or N-containing heterocycles **5** with a selenoxo group (*Scheme 1*). A likely intermediate is **3**, which undergoes a *5*- or *6-exo-tet* cyclization [7] *via* the Se- and N-atom, respectively.

Scheme 1



1 2 3 4 5

Recently, we have shown that 'three-component reactions' of **1**, cyanomethylene derivatives, and bis-electrophiles in the presence of a base yield 2-methylene-1,3-

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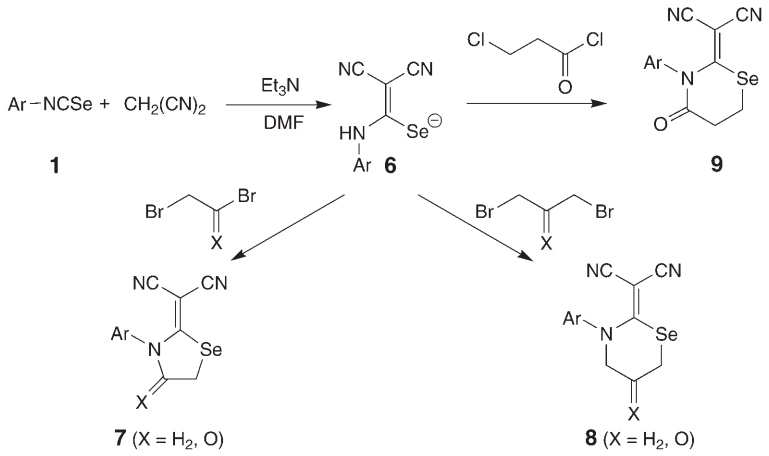
selenazolidine [8] and analogous 1,3-selenazinane (=tetrahydro-1*H*-1,3-selenazine) derivatives [9] (*Scheme 2*). For example, the reactions with 1,2-dibromoethane or 2-bromoacetyl bromide yield **7**, and the analogous reactions with 1,3-dibromopropane, 1,3-dichloroacetone, and 3-chloropropanoyl chloride, respectively, give the six-membered products **8**[2]) or **9**. The crucial intermediate of these reactions is the N,Se-hemiacetal **6**, which in all cases reacted with the bis-electrophilic reagent by double nucleophilic substitution.

Scheme 2



With the aim of further extending this concept, we carried out reactions of **1a** (Ar = Ph), malononitrile, and α-halogenated ketones or bromoacetonitrile.

2. Results and Discussion. – By following the previously described procedure [8][9], the intermediate **6a** was generated *in situ* by treatment of a mixture of malononitrile and phenyl isoselenocyanate (**1a**) in DMF with an equimolar amount of Et_3N at room temperature (*Scheme 3*). After reaction with bromoacetonitrile, a brownish solid was isolated. On the basis of the spectroscopic data, structure **10** was assigned to this product. Obviously, **6a** underwent an S_N2 reaction with bromoacetonitrile, but no subsequent cyclization to the expected (4-amino-1,3-selenazol-2(3*H*)-ylidene)malononitrile **11** occurred (*Scheme 3*). All attempts to obtain a cyclized product by treatment of **10** with different bases failed and led to the decomposition of **10**.

The CI-MS of **10** shows the base-peak at *m*/*z* 306, and the elemental analysis corresponds with the molecular formula $C_{12}H_8N_4Se$, *i.e.*, a product, which was formed by a substitution reaction of **6a** and bromoacetonitrile. According to the IR- and ^{13}C-NMR spectra, the product contains three CN groups (2212, 2201, and 2194 cm^{-1}, and δ(C) 115.1, 114.9, and 110.1, resp.). In the ^{1}H-NMR spectrum, a CH_2 group absorbs at δ(H) 4.38 as a *s*, and a broad *s* at δ(H) 13.85 can be attributed to a NH group.

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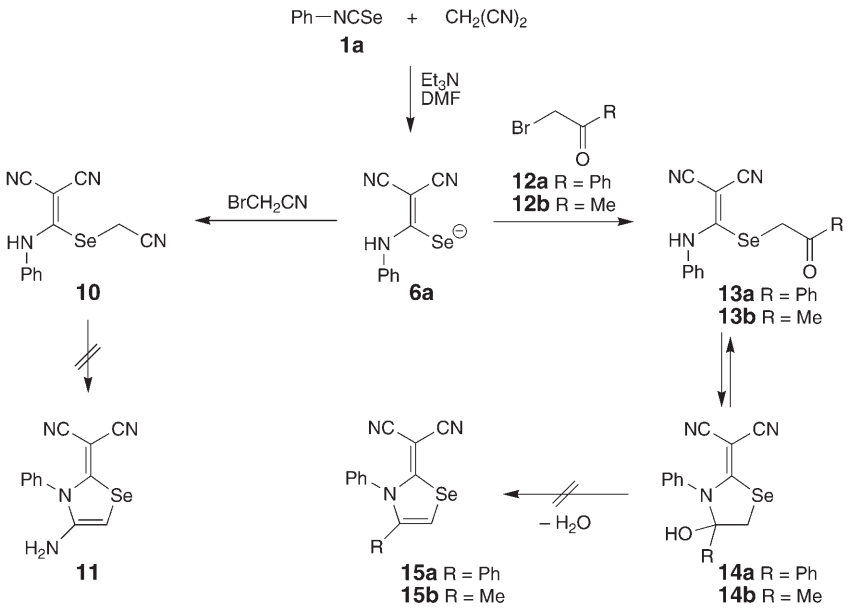
[2]) The crystal structure of **8** (Ar = 4-Cl–C_6H_4, X = O) [9] was established also by X-ray crystallography (see below, *Fig.* and *Table*).

Scheme 3



In the analogous reaction of **1a** with malononitrile and α-bromoacetophenone (**12a**) or α-bromoacetone (**12b**), respectively (*Scheme 3*), the products were isolated as pale yellow crystals. Their data were consistent with the products of a substitution reaction of the intermediate **6a** and the α-halogenated ketone **12**, but inconsistent with the desired products **15** (*Scheme 3*). The IR data excluded ketone derivatives **13**; however, the NMR and MS data were compatible with structures **13** and 1,3-selenazolidine derivatives **14**. Taking also the X-ray analyses (see below) into account, we propose that the products which were obtained from **1a**, malononitrile, and α-halogenated ketones **12** exist in the keto form **13** in solution but as the cyclic 'hemiacetal' **14** in the crystalline state. Again, treatment of **13a**/**14a** with a base did not result in the elimination of H_2O to give the desired compound **15a** but in the decomposition of the product.

In the IR spectrum (KBr), the products from **6a** and **12** show two signals for CN groups and a broad absorption at 3370–3400 cm^{-1}, but no C=O absorption. The ^{13}C-NMR spectra indicate clearly the presence of a C=O group (δ(C) 196.5 and 206.0 for the products from **12a** and **12b**, resp.). Furthermore, in the ^{1}H-NMR spectra, a *s* for a CH_2 group appears at δ(H) 3.69 and 3.64, respectively (δ(C) 34.2 and 36.7 in the ^{13}C-NMR spectra). The CI-MS and elemental analyses are in accordance with products **13** or 1,3-selenazolidines **14** but not with **15**.

Finally, the structure of **14a** was established by an X-ray crystal-structure determination (*Fig.*). In the crystal structure of **14a**, the five-membered ring has an envelope conformation with atom C(5) as the envelope flap. Most of the geometric parameters are similar to those of the previously described structures of (1,3-

selenazolidin-2-ylidene)malononitriles **7** and a (1,3-selenazinan-2-ylidene)malononitrile **9** [8][9]: the two CN groups are almost coplanar with the atoms Se(1), C(2), N(3), and C(6), the C(2)=C(6) bond is longer (1.389(3) Å) than a normal C=C bond, whereas the formal single bonds Se(1)–C(2), N(3)–C(2), C(6)–C(7), and C(6)–C(8) are short (1.894(2), 1.332(3), 1.424(3), and 1.428(3) Å, resp.). Furthermore, the bond angle C(2)–C(6)–C(8) is larger than normal at 125.9(2)°, whereas the angles C(2)–C(6)–C(7) and C(7)–C(6)–C(8) are small (117.7(2) and 116.4(2)°, resp.), *i.e.*, the CN(8) group is tilted away from the PhN(3) residue. The OH group forms an intermolecular H-bond with one of the cyano N-atoms of a neighboring molecule. These interactions link the molecules into extended chains, which run parallel to the [001] direction and can be described by a graph set motif [11] of C(8).

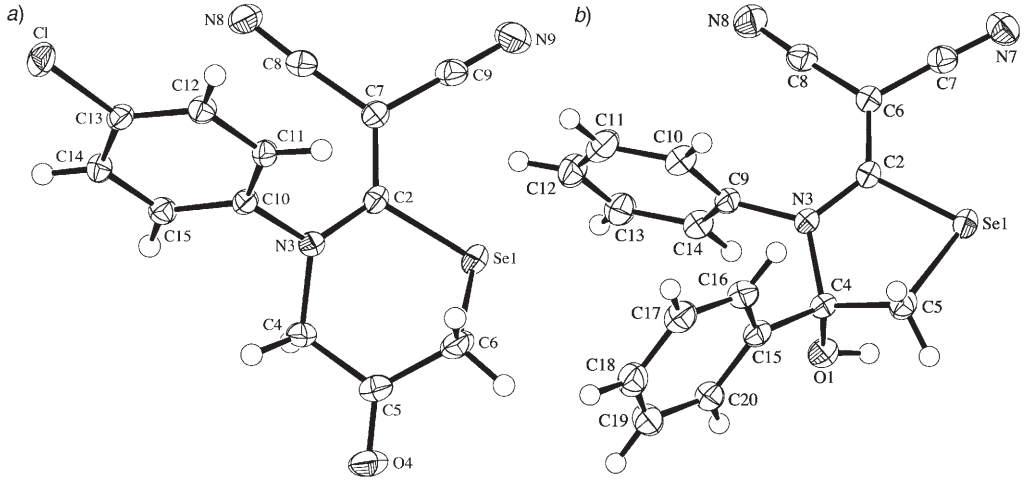


Figure. *ORTEP Plots* [10] *of the molecular structures of* a) **8** (Ar = 4-Cl–C_6H_4, X = O) *and* b) **14a**. Arbitrary atom numbering; 50% probability ellipsoids.

The heterocycle of **8** (Ar = 4-Cl–C_6H_4, X = O) [9] has a distorted screw-boat conformation as shown by its crystal structure (*Fig.*). The geometric parameters are again mostly similar to those of **7**, **9**, and **14** (*e.g.*, a long C(2)=C(7) bond (1.385(3) Å) and short Se(1)–C(2), N(3)–C(2), C(7)–C(8), and C(7)–C(9) bonds (1.890(2), 1.351(2), 1.432(3), and 1.427(3) Å, resp.), as well as a tilting of the CN(8) group away from the aromatic residue (the bond angle C(2)–C(7)–C(8) is 124.9(2)° and C(8)–C(7)–C(9) is 115.1(2)°). In contrast, however, the environment about the C=C bond is not planar, the plane defined by atoms C(7), C(8), and C(9) making an angle of 14.3(3)° with the plane defined by atoms N(3), C(2) and Se(1).

In conclusion, the three-component reaction of **1a**, malononitrile, and bromoacetonitrile or α-halogenated ketones leads to the acyclic adducts **10** and **13**, respectively, in good yield *via* the intermediate **6a**. The ketone derivatives of type **13** are in equilibrium with the 1,3-selenazolidine derivatives **14**, which can be isolated in the crystalline form.

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Experimental Part

1. *General*. See [12][13]. TLC: silica gel *60 F_{254}* plates (0.25 mm; *Merck*). Column chromatography (CC): silica gel *60* (0.040–0.063 mm; *Merck*). M.p.: *Büchi B-540* apparatus, in capillaries; uncorrected. IR Spectra: *Perkin-Elmer 1600 FT-IR* spectrophotometer; in KBr; ν in cm^{-1}. ^{1}H- (300 MHz) and ^{13}C-NMR (75.5 MHz) Spectra: *Bruker ARX-300* instrument; in $CDCl_3$; chemical shifts δ in ppm, *J* in Hz. CI-MS: *Finnigan SSQ-700* or *MAT-90* instrument; NH_3 as carrier gas; in *m*/*z*.

2. *Starting Materials*. Propanedinitrile (=malononitrile) and all halogenated compounds are commercially available (*Fluka*). Phenyl isoselenocyanate (**1a**) was prepared according to *Barton*'s procedure starting from formanilide [14], which is commercially available (*Fluka*, *Aldrich*).

3. Reaction of **1a***, Malononitrile, and a Halogenated Compound: General Procedure*. To a soln. of malononitrile (73 mg, 1.1 mmol) in DMF (10 ml), Et_3N (0.15 ml, 1.1 mmol) was added, and the mixture was stirred for 30 min at r.t. Then, **1a** (200 mg, 1.1 mmol) was added, and the mixture was stirred for 1 h at r.t. The halogenated compound (1.1 mmol) was added dropwise, the mixture stirred for 4 h, and the solvent evaporated. The crude product was purified by CC (hexane/AcOEt mixtures).

2-{[(Cyanomethyl)seleno](phenylamino)methylene}propanedinitrile (**10**). From **1a**, malononitrile, and bromoacetonitrile: 234 mg (74%) of **10**. Brownish crystals. M.p. 166–168° (AcOEt/hexane). IR (KBr): 2212*s*, 2201*s*, 2194*s*, 1596*w*, 1554*w*, 1523*s*, 1488*w*, 1454*m*, 1415*w*, 1388*w*, 1354*m*, 1212*w*, 1200*w*, 1166*w*, 1105*w*, 1054*w*, 1022*w*, 1008*w*, 912*w*, 905*w*, 888*w*, 754*w*, 736*w*, 705*w*, 698*m*. ^{1}H-NMR: 4.38 (*s*, CH_2); 7.40–7.45 (*m*, 2 arom. H); 7.50–7.57 (*m*, 3 arom. H); 13.85 (br. *s*, NH). ^{13}C-NMR: 29.1 (CH_2); 57.8 ($C(CN)_2$); 110.1, 114.9, 115.1 (3 CN); 128.9 (2 arom. CH); 129.4 (2 arom. CH); 130.8 (1 arom. CH); 134.8 (1 arom. C); 173.3 (CNSe). CI-MS: 306 (100, $[M(^{80}Se)+NH_4]^+$), 289 (10, $[M(^{80}Se)+1]^+$). Anal. calc. for $C_{12}H_8N_4Se$ (287.18): C 50.19, H 2.81, N 19.51; found: C 49.95, H 3.02, N 19.63.

2-{[(2-Oxo-2-phenylethyl)seleno](phenylamino)methylene}propanedinitrile (**13a**)*/2-(4-Hydroxy-3,4-diphenyl-1,3-selenazolidin-2-ylidene)propanedinitrile* (**14a**). From **1a**, malononitrile, and α-bromoacetophenone (**12a**): 326 mg (81%) of **14a**. Yellowish crystals. M.p. 155–157° (AcOEt/hexane). IR (**14a**; KBr): 3397*s*, 3055*w*, 2211*s*, 2196*s*, 1598*w*, 1554*w*, 1518*s*, 1490*m*, 1450*m*, 1421*w*, 1392*w*, 1346*m*, 1212*m*, 1198*w*, 1168*w*, 1105*w*, 1075*w*, 1031*w*, 1015*m*, 1003*w*, 984*w*, 931*w*, 907*w*, 852*w*, 764*w*, 737*w*, 707*w*, 694*m*. ^{1}H-NMR (**13a**): 3.69 (*s*, CH_2); 6.76 (*d*, $J=7.9$, 1 arom. H); 7.03 (*d*, $J=8.1$, 1 arom. H); 7.12–7.25 (*m*, 6 arom. H); 7.44 (*t*, $J=8.1$, 2 arom. H); 10.68 (br. *s*, NH). ^{13}C-NMR (**13a**): 34.2 (CH_2); 49.8 ($C(CN)_2$); 111.9, 118.2 (2 CN); 126.0 (1 arom. CH); 126.5 (2 arom. CH); 127.8 (2 arom. CH); 128.3 (2 arom. CH); 128.5 (2 arom. CH); 129.3 (1 arom. CH); 137.1, 139.6 (2 arom. C); 172.6 (CNSe); 196.5 (CO). CI-MS (**14a**): 385 (100, $[M(^{80}Se)+NH_4]^+$), 368 (10, $[M(^{80}Se)+1]^+$). Anal. calc. for $C_{18}H_{13}N_3OSe$ (366.28): C 59.02, H 3.58, N 11.47; found: C 58.91, H 3.58, N 11.47.

2-{[(2-Oxopropyl)seleno](phenylamino)methylene}propanedinitrile (**13b**)*/2-(4-Hydroxy-4-methyl-3-phenyl-1,3-selenazolidin-2-ylidene)propanedinitrile* (**14b**). From **1a**, malononitrile, and α-bromoacetone (**12b**): 221 mg (66%) of **14b**. Pale yellow crystals. M.p. 170–172° (AcOEt/hexane). IR (**14b**; KBr): 3371*s*, 2212*s*, 2197*s*, 1595*w*, 1507*s*, 1454*w*, 1428*w*, 1392*w*, 1348*m*, 1225*w*, 1181*w*, 1161*w*, 1105*w*, 1054*m*, 999*w*, 953*w*, 903*w*, 851*w*, 744*w*, 694*m*. ^{1}H-NMR (**13b**): 1.31 (*s*, Me); 3.64 (*s*, CH_2); 7.26–7.31 (*m*, 2 arom. H); 7.39–7.49 (*m*, 3 arom. H); 11.45 (br. *s*, NH). ^{13}C-NMR (**13b**): 25.8 (Me); 36.7 (CH_2); 47.7 ($C(CN)_2$); 112.0, 118.2 (2 CN); 129.0 (2 arom. CH); 129.7 (2 arom. CH); 130.0 (1 arom. CH); 136.5 (1 arom. C); 171.7 (CNSe); 206.2 (CO). CI-MS (**14b**): 323 (100, $[M(^{80}Se)+NH_4]^+$), 305 (31, $[M(^{80}Se)+1]^+$). Anal. calc. for $C_{13}H_{11}N_3OSe$ (304.21): C 51.33, H 3.64, N 13.81; found: C 51.28, H 3.71, N 13.68.

4. *X-Ray Crystal-Structure Determination* of **8** (Ar = 4-Cl–C_6H_4, X = O) *and* **14a** (see *Table* and *Fig.*)[3]). All measurements were made on a *Nonius-KappaCCD* diffractometer [15] by using graphite-

[3]) CCDC-647556 and -647557 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* http://www.ccdc.ac.uk/data_request/cif.

monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford-Cryosystems Cryostream-700* cooler. Data reduction was performed with HKL Denzo and Scalepack [16]. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method [17] was applied. Equivalent reflections were merged. Data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in the *Figure*. The structure of **8** (Ar = 4-Cl–C_6H_4, X = O) was solved by direct methods with SIR92 [18], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. The structure of **14a** was solved by heavy-atom *Patterson* methods [19], which revealed the position of the Se-atom. All remaining non-H-atoms were located in a *Fourier* expansion of the *Patterson* solution, which was performed by DIRDIF 94 [20]. Non-H-atoms were refined anisotropically. The hydroxy H-atom of **14a** was placed in the position indicated by a difference electron density map and its position was allowed to refine together with an isotropic displacement parameter. All remaining H-atoms and all H-atoms of **8** (Ar = 4-Cl–C_6H_4, X = O) were placed in geometrically calculated positions and refined with a riding model where each H-atom was assigned a

Table. *Crystallographic Data for Compounds* **8** (Ar = 4-Cl–C_6H_4, X = O) *and* **14a**

	8 (Ar = 4-Cl–C_6H_4, X = O)	**14a**
Crystallized from	MeCN	AcOEt/hexane
Empirical formula	$C_{13}H_8ClN_3OSe$	$C_{18}H_{13}N_3OSe$
M_r	336.58	366.22
Crystal color, habit	yellow, prism	colorless, prism
Crystal dimensions [mm]	$0.07 \times 0.20 \times 0.27$	$0.23 \times 0.23 \times 0.25$
Temperature [K]	160(1)	160(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
Z	4	8
Reflections for cell determination	18890	218336
2θ range for cell determination [°]	4–60	4–60
Unit cell parameters: a [Å]	9.9940(2)	33.263(1)
b [Å]	12.2053(2)	6.6722(2)
c [Å]	11.4240(2)	14.6996(4)
β [°]	111.419(1)	109.014(2)
V [Å^3]	1297.25(4)	3084.4(2)
D_x [g cm^{-3}]	1.723	1.577
μ(MoK_α) [mm^{-1}]	3.092	2.441
Scan type	ϕ and ω	ϕ and ω
$2\theta_{(max)}$ [°]	60	60
Transmission factors [min; max]	0.567; 0.811	0.498; 0.592
Total reflections measured	32822	37952
Symmetry-independent reflections	3786	4516
Reflections with $I > 2\sigma(I)$	3104	3627
Reflections used in refinement	3786	4516
Parameters refined	173	213
Final $R(F)$ ($I > 2\sigma(I)$ reflections)	0.0310	0.0410
$wR(F^2)$ (all data)	0.0754	0.0993
Weighting parameters [a; b][a]	0.0338; 0.7475	0.0479; 2.9032
Goodness of fit	1.046	1.102
Secondary extinction coefficient	0.0024(6)	0.0052(3)
Final Δ_{max}/σ	0.001	0.004
$\Delta\rho$ (max; min) [e Å^{-3}]	0.59; −0.68	0.61; −0.75

[a]) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$

fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom. The refinement of each structure was carried out on F^2 by using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were applied. Neutral-atom scattering factors for non-H-atoms were taken from [21a], and the scattering factors for H-atoms were taken from [22]. Anomalous dispersion effects were included in F_c [23]; the values for f' and f'' were those of [21b]. The values of the mass attenuation coefficients are those of [21c]. All calculations were performed with the SHELXL97 [24] program.

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