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Thia- and selenaheterocycles by a four-component reaction using elemental sulfur and selenium

Plamen K. Atanassov[a]; Anthony Linden[a]; Heinz Heimgartner[a]
[a] Institute of Organic Chemistry, University of Zürich, Zürich, Switzerland

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RESEARCH ARTICLE

Thia- and selenaheterocycles by a four-component reaction using elemental sulfur and selenium

PLAMEN K. ATANASSOV, ANTHONY LINDEN and HEINZ HEIMGARTNER*

Institute of Organic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

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The course of the four-component reactions of (2-benzimidazolyl) acetonitrile, carbondisulfide, isothiocyanate, and sulfur and selenium, respectively, is quite different. Whereas in the case of sulfur a tetracyclic [1,3]thiazolo[4′,5′:4,5]pyrimido[1,6-*a*]benzimidazol-2(3*H*)-thione is formed, a zwitterionic 7-(benzimidazolium-2-yl)-[1,2]thiaselenolo[2,3-*b*][1,2,4]thiaselenazole-6-thiolate (an azaselenadithiapentalene) is the product in the case of selenium. The structures of the products have been established by X-ray crystallography, and reaction mechanisms for their formation are proposed.

Keywords: Four-component reactions; Isoselenocyanates; Isothiocyanates; Selenaheterocycles; Thiaheterocycles

1. Introduction

Nowadays it is well known that selenium is an important trace element for bacteria as well as for animals and human beings [1, 2], and organoselenium compounds are an important class of biologically active products [3–5]. For example, the selenoenzyme glutathione peroxidase (GP_x) is an antioxidant, which catalyzes the reduction of harmful peroxides in biological systems [6–10]. In the last 20 years, a series of organoselenium compounds, *e.g.*, selenaheterocycles, have been described as GP_x mimics (cf. ref. [11–15]). Nevertheless, the synthesis of selenaheterocycles is much less developed than that of sulfur analogues. One drawback is the use of toxic selenium reagents, which are often difficult to handle, and the low stability of some intermediates and products.

With the aim of using conveniently accessible [16, 17], relatively stable, and less toxic isoselenocyanates as building blocks (see also ref. [18]), we have prepared a series of selenium-containing four- [19, 20], five- [21–26], six- [27, 28], seven- [29], and eight-membered [30] heterocycles. In some cases, the reactions were carried out analogously to those with isothiocyanates, and the reactivity of the two heterocumulenes was observed to be very similar. On

*Corresponding author. Email: heimgart@oci.unizh.ch

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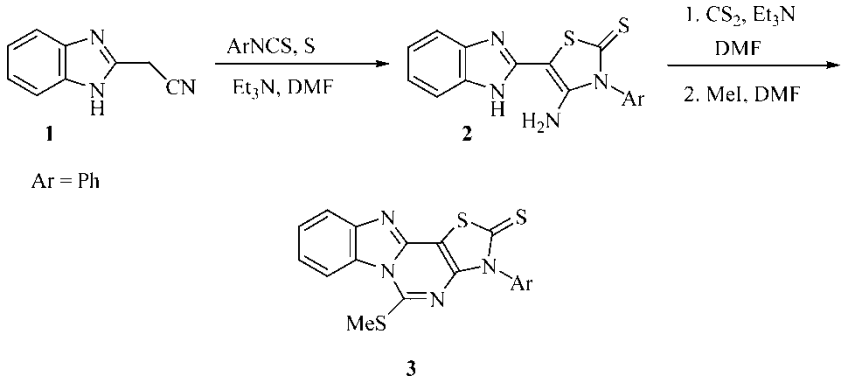


1 2 3

SCHEME 1

the other hand, heterocyclic selones undergo oxidative dimerization to give diselenides much faster than the corresponding thiones [24, 26].

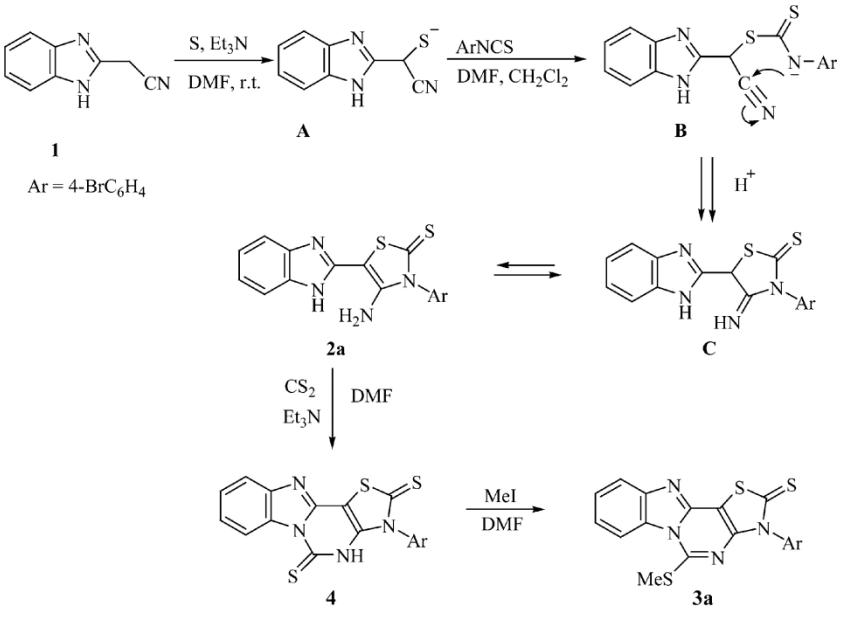
Recently, Ivachtchenko *et al.* [31] reported on the four-component reaction of (2-benzimidazolyl) acetonitrile (**1**) with sulfur, aryl isothiocyanates, and carbon disulfide, which had been described previously by Badawey *et al.* [32]. After methylation, tetracyclic products of type **3** were obtained [31] (scheme 1). As the authors did not disclose any spectroscopic data for **3**, we wanted to verify their results and to extend the reaction to selenium analogues.

2. Results and discussion

With the goal of obtaining crystalline products, which are suitable for X-ray crystal-structure determination, we used 4-bromophenyl isothiocyanate instead of the unsubstituted phenyl isothiocyanate as a reagent. Furthermore, we modified some reaction conditions because we obtained much lower yields than described in ref. [31]. First, **1** was treated with sulfur and triethylamine in DMF at room temperature, whereby the color of the solution changed to deep red. Then, a solution of 4-bromophenyl isothiocyanate in DMF/CH_2Cl_2 was added slowly, and the mixture was heated to 60 °C. The crude product was recrystallized from DMF/2-propanol yielding 41.7% of **2a** (m.p. 245–246 °C). A likely reaction mechanism for the formation of **2** is shown in scheme 2: addition of sulfur to the anion of **1** leads to the thiolate **A**, which reacts with the isothiocyanate to give **B**. Ring closure by nucleophilic attack of the N-atom at the nitrile group gives **C**, which undergoes a tautomerization to yield **2a**.

Treatment of **2a** with carbon disulfide in DMF under reflux led to a crystalline condensation product, for which we propose structure **4** (see refs. [31, 32]). Following the procedure described in ref. [31], the product was reacted with methyl iodide in DMF and the final product was recrystallized from DMF/ethanol to give **3a** in 50.8% yield with respect to **2a** (scheme 2). The molecular structure of **3a** was established by X-ray crystallography (figure 1), which confirmed the proposed structure of **3** [31]. The heterocyclic core of the molecule of **3a**, together with the fused benzene ring, is almost planar. The maximum deviation of the 16 atoms of the polycyclic ring from their mean plane is 0.102(2) Å for atom N(3). On the other hand, the 4-bromophenyl substituent is twisted significantly out of the heterocyclic plane, with the dihedral angle between the two planar systems being 56.80(8)°.

All attempts to repeat the reaction by using selenium instead of sulfur or 4-bromophenyl isoselenocyanate instead of the corresponding isothiocyanate failed to give a product analogous



SCHEME 2

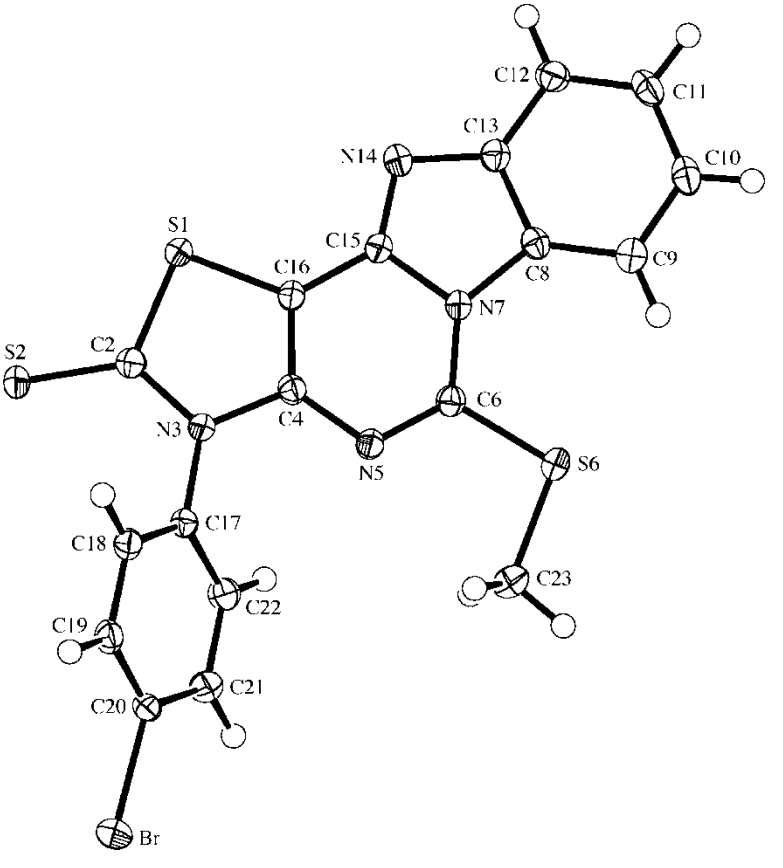
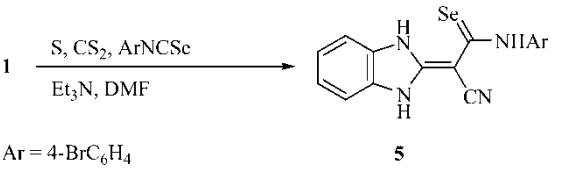


Figure 1. ORTEP-Plot [33] of the molecular structure of **3a** (arbitrary numbering of the atoms; 50% probability ellipsoids).

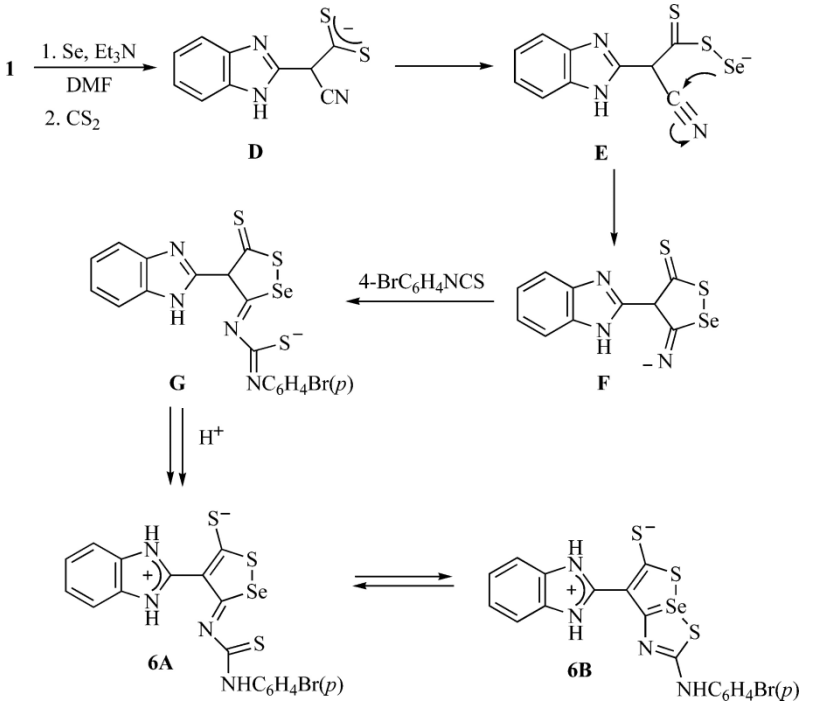


SCHEME 3

to **4**. From the mixture of **1** with sulfur, carbon disulfide, and 4-bromophenyl isoselenocyanate, only 2-(1*H*-1,3-benzimidazol-2-yl)-*N*-(4-bromophenyl)-2-cyanoselenoacetamide (**5**), which is the adduct of **1** and 4-bromophenyl isoselenocyanate, was obtained (scheme 3). This product was isolated in 50.5% yield when **1** and 4-bromophenyl isoselenocyanate in DMF/CH_2Cl_2 were reacted at room temperature.

Therefore, we modified the reaction conditions again. Finally, a one-pot reaction of **1**, selenium and triethylamine in DMF, and subsequent addition of carbon disulfide and 4-bromophenyl isothiocyanate led to a 1:1:1:1-adduct in 45.6% yield. Recrystallization of the material gave crystals suitable for X-ray crystallography, which proved structure **6** (scheme 4) for the adduct (figure 2).

The asymmetric unit in the crystal structure of **6** contains one molecule of each of the Se-heterocycle, water, and DMF. The heterocyclic product is a zwitterion with a terminal sulfide and a protonated benzimidazole residue. The heterocyclic core of **6** can be represented best by a superimposition of the formulae **6A** and **6B** (for similar structures see ref. [21] and literature cited therein). The lengths of the two Se–S bonds differ by approximately 0.32 Å and



SCHEME 4

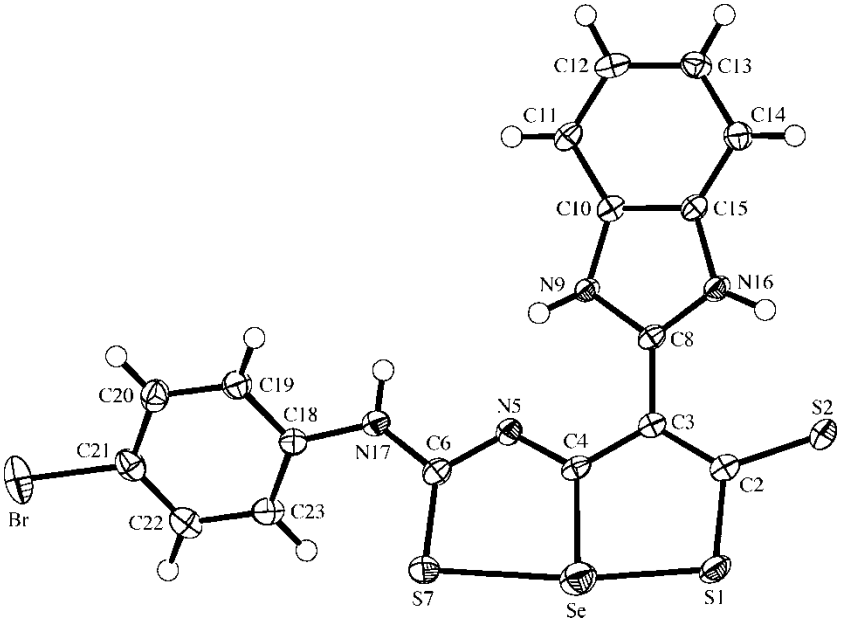


Figure 2. ORTEP-Plot [33] of the molecular structure of **6** (arbitrary numbering of the atoms; 50% probability ellipsoids; solvent molecules not shown).

the bond lengths within the fused, almost planar, core heterocyclic system indicate a significant delocalization of π-electrons (table 1). The maximum deviation of the eight ring atoms of this system from their mean plane is 0.075(4) Å for atom C(3). The attached atoms S(2), C(8), C(18), and N(17) also deviate only slightly from this plane (0.202(1), −0.275(4), 0.198(5) and 0.121(4) Å, respectively). Furthermore, the benzimidazole ring is only slightly twisted out of the plane of the heterocyclic core, with the dihedral angle between the two planar systems being 10.5(1)°. By contrast, the plane of the 4-bromophenyl ring deviates significantly from the core plane, with the dihedral angle between the ring planes being 43.3(2)°.

Table 1. Selected bond lengths (Å) and angles (°) for **6**.

Se-C(4)	1.891(4)	N(9)-C(8)	1.355(5)
Se-S(1)	2.265(1)	N(16)-C(8)	1.347(6)
Se-S(7)	2.584(1)	N(17)-C(6)	1.349(6)
S(1)-C(2)	1.720(5)	N(17)-C(18)	1.414(6)
S(2)-C(2)	1.714(5)	C(2)-C(3)	1.406(6)
S(7)-C(6)	1.686(5)	C(3)-C(4)	1.436(6)
N(5)-C(4)	1.306(6)	C(3)-C(8)	1.455(6)
N(5)-C(6)	1.362(6)		
C(4)-Se-S(1)	88.3(1)	S(2)-C(2)-S(1)	114.0(2)
C(4)-Se-S(7)	83.0(1)	C(2)-C(3)-C(4)	120.1(4)
S(1)-Se-S(7)	170.22(5)	N(5)-C(4)-C(3)	121.4(4)
C(2)-S(1)-Se	98.3(2)	N(5)-C(4)-Se	121.9(3)
C(6)-S(7)-Se	89.1(2)	N(17)-C(6)-S(7)	124.1(4)
C(4)-N(5)-C(6)	122.1(4)	N(5)-C(6)-S(7)	123.9(3)
C(6)-N(17)-C(18)	129.2(4)	C(3)-C(4)-Se	116.6(3)
C(3)-C(2)-S(2)	129.8(3)	N(17)-C(6)-N(5)	112.0(4)
C(3)-C(2)-S(1)	116.2(3)		

In the crystal structure of **6**, two intramolecular hydrogen bonds link the NH groups, HN(9) and HN(16), of the benzimidazole to N(5) of the 1,2,4-selenathiazole and the exocyclic S-atom, respectively. These interactions each have a graph set motif [34] of S(6) (figure 3). These amine groups actually form bifurcated hydrogen bonds, with the second interaction being with the O-atoms of the water and DMF molecules, respectively. The third amine group also forms an intermolecular hydrogen bond with the O-atom of the water molecule. Thus the water molecule is accepting two hydrogen bonds from the same molecule of **6**. Together with the intramolecular interaction emanating from N(9), this creates a six-membered loop with a graph set motif of $R_2^2(6)$. The water molecule donates intermolecular hydrogen bonds to the O-atom of a DMF molecule and to the exocyclic S-atom in another molecule of **6**. The exocyclic S-atom is an acceptor of two hydrogen bonds, as is the O-atom of the DMF molecule. The hydrogen-bonding interactions link two pairs of molecules of the Se-compound and water into a centrosymmetric dimer, which has a graph set motif of $R_4^4(16)$. These dimers are then linked by two sets of bridges via the O-atoms of DMF molecules into extended columns, which run parallel to the [100] direction. The repeating unit of the chain consists of one S^- atom from a molecule of the Se-compound, one DMF molecule and one water molecule and can be described by the graph set motif of C_3^2 (6) if an intramolecular hydrogen bond is included in the pattern.

A reaction mechanism for the formation of **6** is proposed in scheme 4. Addition of the anion of **1** to carbon disulfide yields **D**, which then reacts with selenium to give intermediate **E**. Ring closure of the latter (→**F**), addition of 4-bromophenyl isothiocyanate (→**G**), and cyclization could lead to the final product, the zwitterion **6** via tautomerization and protonation.

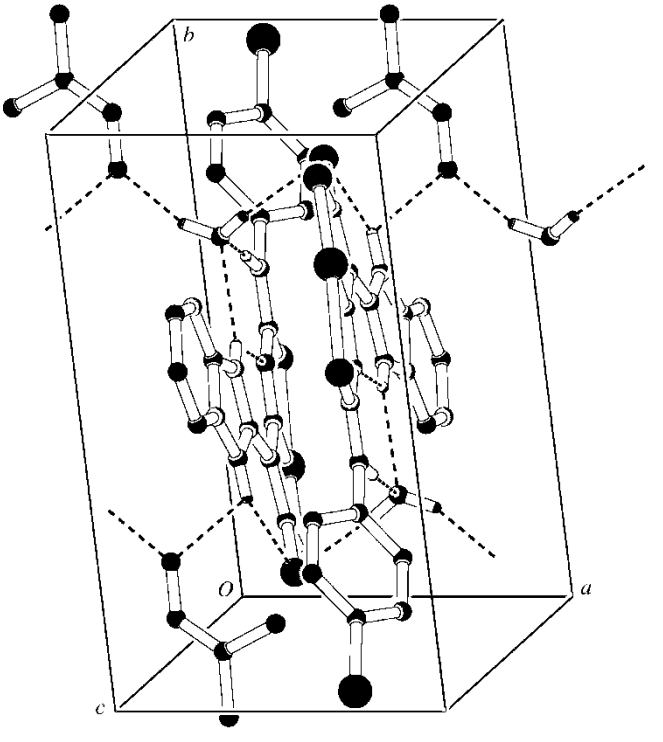


Figure 3. Crystal packing of **6** · DMF · H_2O showing the H-bonding interactions (uninvolved H-atoms omitted for clarity).

In conclusion, the reactions of **1**, aryl isothiocyanate, and carbon disulfide with sulfur and selenium, respectively, showed remarkable differences. Whereas in the case of sulfur, the proposed structure **3** [31] and, therefore, of compound **4** [31, 32] was established unambigously, a different product, *i.e.* the zwitterion **6**, was formed in the case of selenium. This difference is surprising, as in many reactions sulfur and selenium compounds behave similarly. In the last few years, we have shown that isoselenocyanates are very useful building blocks for the preparation of selenaheterocycles. But the present study shows that the reaction course may be quite different, leading to different product types and, therefore, a better knowledge of the reactivity of isoselenocyanates in comparison with their sulfur analogues is necessary.

3. Experimental

3.1 *General*

See ref. [21]. Melting points were determined on a Mettler-FP-5 or Büchi-510 apparatus and are not corrected. IR spectra in KBr (cm^{-1}), ^1H (300 MHz) and ^{13}C NMR spectra (75.6 MHz) in $CDCl_3$ (ppm); ^{13}C-signal multiplicity from DEPT spectra; significant peaks of CI and ESI-MS (m/z (rel. %)).

3.2 *Starting materials*

4-Bromophenyl isothiocyanate, (2-benzimidazolyl) acetonitrile (**1**), carbon disulfide, Se-powder and S-powder were purchased by Fluka AG. 4-Bromophenyl isoselenocyanate was prepared according to ref. [16].

3.3 *Synthesis of 3-(4-bromophenyl)-5-(methylsulfanyl)-[1,3]thiazolo[4′,5′:4,5]-pyrimido [1,6-a][1,3]benzimidazole-2(3H)-thione (3a)*

3.3.1 Preparation of 4-amino-5-(1H-1,3-benzimidazol-2-yl)-3-(4-bromophenyl)-1,3-thiazole-2(3*H*)-thione (2a). To a solution of **1** (1.57 g, 10 mmol) and sulfur (0.32 g, 10 mmol) in DMF (3 ml), Et_3N (1.5 ml) was added under stirring. A solution of 4-bromophenyl isothiocyanate (2.14 g, 10 mmol) in CH_2Cl_2/DMF was added slowly, the stirred mixture was heated to 60 °C for 1 h and then poured into water. The precipitate was filtered and recrystallized from DMF/2-propanol. Yield: 1.68 g (41.7%) of **2a**. M.p. 245.1–246.2 °C. ^1H NMR (DMSO-d_6): 12.45 (broad s, NH); 7.85, 7.42 (AA′BB′, J = 8.6 Hz, 4 arom. H); 7.48 (broad s, NH_2); 7.16–7.11 (m, 4 arom. H). ^{13}C NMR (DMSO-d_6): 184.37 (s, C=S); 162.20, 147.04, 146.49, 134.52, 123.45 (5 s, 6 C); 133.05, 131.22, 121.54 (3 d, 8 arom. CH); 80.65 (s, C). ESI-MS: 405 (100, $[M(^{81}Br)+1]^+$), 403 (92, $[M(^{79}Br)+1]^+$).

3.3.2 Preparation of 3-(4-bromophenyl)-[1,3]thiazolo[4′,5′:4,5]pyrimido[1,6-*a*][1,3] benzimidazole-2,5(3*H*,4*H*)-dithione (4). A mixture of **2a** (2.0 g, 5 mmol), triethylamine (2 ml), and carbon disulfide (2 ml) was heated under reflux, while DMF (2 ml) was added dropwise. The resulting solution was heated under reflux for 1.5 h, cooled to room temperature, concentrated in vacuo, and the residue was treated with ethanol. The solid material was recrystallized from DMF/ethanol to give 1.5 g (68.2%) of **4**. M.p. 241.1–242.5 °C. CI-MS (i-butane): 447 (14), 446 (22), 445 (100, $[M(^{81}Br)-1]^+$), 444 (20), 443 (87, $[M(^{79}Br)-1]^+$), 404 (32), 402 (29).

3.3.3 Preparation of 3a. To a stirred solution of **4** (0.5 g, 1.12 mmol) in DMF (6 ml) at room temperature, methyl iodide (1 ml) was added. After 1 h, the mixture was treated with water (80–100 ml), and the precipitate was recrystallized from DMF/ethanol. Yield: 0.38 g (74.5%) of **3a**. M.p. 281.4–281.7 °C. IR: 1638*s*, 1581*s*, 1531*m*, 1490*m*, 1479*m*, 1464*s*, 1446*s*, 1410*w*, 1325*s*, 1305*m*, 1253*s*, 1234*s*, 1184*s*, 1156*w*, 1088*w*, 1063*m*, 1027*w*, 1013*m*. ^{1}H NMR (DMF-d_7): 8.48 (d, $J = 8.3$ Hz, 1 arom. H); 7.95, 7.72 (AA′BB′, $J = 8.7$ Hz, 4 arom. H+1 H); 7.68 (t, $J = 8.3$ Hz, 1 arom. H); 7.59 (t, $J = 8.4$ Hz, 1 arom. H); 2.63 (s, Me). ^{13}C NMR (DMF-d_7): 188.17 (s, C=S); 157.09, 156.68, 148.90, 146.03, 143.42, 136.08, 128.68, 123.66 (8 s, 8 arom. C); 133.20, 131.81, 127.51, 123.43, 120.08, 116.04 (6 d, 8 arom. CH); 14.73 (q, Me). CI-MS (i-butane): 463 (14), 462 (25), 461 (100, $[M(^{81}Br)+1]^+$), 460 (42), 459 (89, $M(^{79}Br)+1]^+$), 458 (21). Calcd (%) for $C_{18}H_{11}BrN_4S_3$ (459.41): C 47.06, H 2.41, N 12.20; found: C 46.73, H 2.67, N 12.21.

Recrystallization from DMF gave crystals suitable for the X-ray crystal-structure determination.

3.4 *Synthesis of 2-(1*H*,3*H*-1,3-benzimidazol-2-yliden)-*N*-(4-bromophenyl)-2-cyanoselenoacetamide (5)*

To a stirred solution of **1** (0.39 g, 1.9 mmol) in absolute DMF, triethylamine (5 equiv.) was added. After 3 min, a solution of 4-bromophenyl isoselenocyanate (0.5 g, 1.9 mmol) in DMF/dichloromethane (1:1, 3 ml), was slowly added and the mixture stirred at room temperature for 1.5 h. The solution was concentrated in vacuo, methanol was added, and a yellow-orange solid was formed. After filtration, the product was recrystallized from DMF/methanol to give 0.4 g (50.6%) of **5**. M.p. 244.3–246.0 °C. IR: 3421*w*, 3013*w*, 2983*m*, 2685*m*, 1621*s*, 1601*s*, 1578*m*, 1522*s*, 1482*m*, 1454*m*, 1428*s*, 1380*s*, 1251*m*, 1162*m*, 1070*m*, 1021*m*, 1008*m*. ^{1}H-NMR (DMSO-d_6): 12.8 (broad s, NH); 8.80 (broad s, NH); 8.36 (d, $J = 7.8$ Hz, 1 arom. H); 7.65–7.55 (m, 3 arom. H); 7.01 (BB′ of AA′BB′, $J = 8.6$ Hz, 2 arom. H); 7.37, 7.23 (2 t-like, $J \approx 8$ Hz, 2 arom. H). ^{13}C-NMR (DMSO-d_6): 177.14 (s, C=Se); 149.98, 147.07, 145.93, 143.43, 131.23, 117.35, 116.56 (7 s, 7 C); 132.25, 124.86, 123.01, 122.75, 117.49, 115.62 (6 d, 8 arom. CH). CI-MS (i-butane): 423 (5), 422 (5), 421 (27), 420 (8), 419 (36), 418 (8), 417 (19), 416 (5), 415 (6), 342 (17), 341 (92), 340 (22), 339 (94), 338 (5), 158 (100). Calcd (%) for $C_{16}H_{11}BrN_4Se$ (418.15): C 45.96, H 2.65, N 13.40; found C 45.74, H 2.88, N 13.77.

3.5 *Synthesis of 7-(3*H*-1,3-benzimidazol-2-yl)-2-(4-bromoanilino)-2*H*-[1,2]thiaselenolo [2,3-*b*][1,2,4]thiaselenazole-6-thiolate (6)*

To a solution of 1 (0.79 g, 5 mmol) and selenium (0.40 g, 5 mmol) in DMF (2 ml) was added triethylamine (1 ml). The mixture was stirred at r.t. for 3 min, then, carbon disulfide (0.7 ml) was added and the mixture was stirred for an additional 3 min. A solution of 4-bromophenyl isothiocyanate (1.07 g, 5 mmol) in DMF/dichloromethane (1:1, ca. 5 ml) was added slowly, the mixture stirred at r.t. for 1.5 h and concentrated in vacuo. The residue was treated with ethanol and the product was recrystallized from DMF/ethanol. Yield: 1.2 g (45.6%). M.p. 260.7–261.0 °C. IR: 3316*m*, 1610*s*, 1576*m*, 1557*s*, 1500*s*, 1478*s*, 1394*s*, 1326*m*, 1345*s*, 1290*s*, 1244*m*, 1220*m*, 1170*s*, 1135*m*, 1068*m*, 1023*m*, 1010*m*. ^{1}H-NMR (DMF-d_7): 15.11, 14.79 (2 br. s, 2 NH); 11.59 (br. s, ArNH); 8.02–7.52 (m, 8 arom. H). ^{13}C-NMR (DMF-d_7): 182.82 (s, C=S); 147.89, 139.69, 139.50, 132.00, 130.06, 129.80, 126.62, 118.07 (8 s, 9 C); 132.61, 125.93, 125.14, 114.46 (4 d, 8 arom. CH). CI-MS (NH_3): 494 (22), 493 (13), 492 (28), 491 (13), 490 (14), 448 (14), 447 (27), 446 (100), 445 (69), 444 (91), 443 (44), 366 (13), 307 (24),

306 (12), 265 (58), 200 (16). Calcd (%) for $C_{17}H_{11}BrS_3Se$ (526.36): C 38.79, H 2.11, N 10.64; found: C 38.39, H 2.39, N 10.88.

Recrystallization from DMF gave crystals suitable for the X-ray crystal-structure determination.

3.6 *X-ray crystal-structure determination of 3a and 5 (see table* 2 *and figures* 1 *and* 2*)*

All measurements were made on a Nonius KappaCCD diffractometer [35] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack [36]. The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method [37] was applied. Equivalent reflections were merged. Data collection and refinement parameters are given in table 2, and views of the molecules are shown in

Table 2. Crystallographic Data for Compounds **3a** and **6**.

	3a	**6**
Crystallized from	DMF	AcOEt
Empirical formula	$C_{18}H_{11}BrN_4S_3$	$C_{17}H_{11}BrN_4S_3Se \cdot C_3H_7NO \cdot H_2O$
Formula weight [g mol^{-1}]	459.40	617.39
Crystal color, habit	yellow, needle	yellow, prism
Crystal dimensions [mm]	0.05 × 0.10 × 0.30	0.10 × 0.17 × 0.27
Temperature [K]	160(1)	160(1)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Z	4	2
Reflections for cell determination	38361	18556
2θ range for cell determination [°]	4–60	4–60
Unit cell parameters		
a[Å]	4.0411(1)	7.1471(1)
b[Å]	19.8593(4)	12.6103(3)
c[Å]	21.4327(4)	13.4765(4)
α[°]	90	99.178(1)
β[°]	93.266(1)	101.772(1)
γ[°]	90	96.861(1)
V[Å^3]	1717.25(6)	1159.22(5)
D_x [g cm^{-3}]	1.777	1.769
μ(Mo$K\alpha$) [mm^{-1}]	2.776	3.642
Scan type	ϕ and ω	ϕ and ω
$2\theta_{(max)}$[°]	60	60
Transmission factors (min; max)	0.631; 0.895	0.545; 0.698
Total reflections measured	45540	31319
Symmetry independent reflections	4990	6749
Reflections with $I > 2\sigma(I)$	3794	5097
Reflections used in refinement	4990	6749
Parameters refined; restraints	236; 0	311; 5
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0377	0.0623
$wR(F^2)$ (all data)	0.0937	0.2039
Weights:[a] a; b	0.0468; 0.6467	0.1054; 5.3394
Goodness of fit	1.047	1.049
Final Δ_{max}/σ	0.004	0.002
$\Delta\rho$(max; min) [e Å^{-3}]	0.54; −0.64	1.39; −2.72

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

*CCDC-258493-258494 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.cam.ac.uk/data_request/cif.

figures 1 and 2. The structures were solved by direct methods using SIR92 [38], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. For **5**, the H-atoms of the amine groups and the water molecule 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, while restraining the O–H and N–H bond lengths tightly to 0.84 and 0.88 Å, respectively. The remaining H-atoms for **5** and all of the H-atoms for **3a** 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 ($1.5U_{eq}$ for the Me group in **3a**). Refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was not applied. Neutral atom scattering factors for non-H-atoms were taken from ref. [39], and the scattering factors for H-atoms were taken from ref. [42]. Anomalous dispersion effects were included in F_c [43]; the values for f' and f'' were those of ref. [40]. The values of the mass attenuation coefficients are those of ref. [41]. All calculations were performed using the SHELXL97 [44] program.

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