Selenophen-2-yl-Substituted Thiocarbonyl Ylides – at the Borderline of Dipolar and Biradical Reactivity

by **Grzegorz Mlostoń***[a]), **Katarzyna Urbaniak**[a]), **Anthony Linden**[b]), and **Heinz Heimgartner***[b])

[a]) University of Łódź, Department of Organic and Applied Chemistry, Tamka 12, PL-91-403 Łódź (phone: +48-42-6355761; fax: +48-42-6655162; e-mail: gmloston@uni.lodz.pl)

[b]) University of Zürich, Department of Chemistry, Winterthurerstrasse 190, CH-8057 Zürich (phone: +41-44-6354282; fax: +41-44-6356812; e-mail: heinz.heimgartner@chem.uzh.ch)

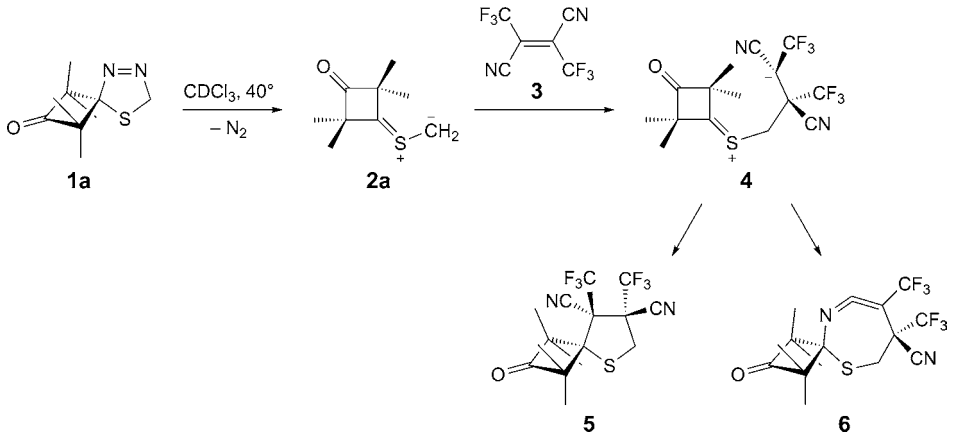
Dedicated to Professor *Christian Robl*, Friedrich-Schiller-Universität Jena, on the occasion of his 60th birthday

The reactions of aryl (selenophen-2-yl) thioketones with CH_2N_2 occur with spontaneous elimination of N_2, even at low temperature (−65°), to give regioselectively sterically crowded 4,4,5,5-tetrasubstituted 1,3-dithiolanes and/or a novel type of twelve-membered dithia-diselena heterocycles as dimers of the transient thiocarbonyl *S*-methanides. The ratio of these products depends on the type of substituent located at C(4) of the phenyl ring. Whereas the formation of the 1,3-dithiolanes corresponds to a [3+2] cycloaddition of an intermediate thiocarbonyl ylide with the starting thioketone, the twelve-memberd ring has to be formed *via* dimerization of the 'thiocarbonyl ylide' with an extended biradical structure.

Introduction. – The [3+2] cycloadditions belong to the most important reactions, which are of interest for both practical applications and development of reaction-mechanism concepts. Especially important are synthetic methods applied for preparations of diverse heterocyclic products [1]. In addition to the classical series of reactive 1,3-dipolar species presented in the historical reviews by *Huisgen* [2], the S-centered 1,3-dipoles, such as thiocarbonyl *S*-imides [3a], thiocarbonyl *S*-oxides [3a], thiocarbonyl *S*-sulfides [3b], and especially thiocarbonyl ylides [3c], have been studied extensively in recent decades. One of the most characteristic features of [3+2] cycloadditions is the concertedness of the creation of two new σ-bonds in the course of the formation of five-membered heterocycles. However, in the case of the sterically crowded thiocarbonyl ylide **2a**, the reaction with electron-deficient alkenes, such as (*E*)-1,2-bis(trifluoromethyl)ethene-1,2-dicarbonitrile (**3**) or dimethyl dicyanofumarate (dimethyl (*E*)-2,3-dicyanobut-2-enedioate), follows a stepwise mechanism *via* a zwitterionic intermediate of type **4** [4][5] (*Scheme 1*).

The stepwise mechanism was evidenced by the loss of stereospecifity, *i.e.*, the formation of two stereoisomeric thiolanes of type **5** (CF_3 groups replaced by COOMe) in the case of dimethyl dicyanofumarate [4], and the isolation of the seven-membered ketenimine **6** [5] or its derivatives obtained *via* its trapping with MeOH or H_2O in the case of **3a** [4][5]. The reactive thiocarbonyl ylide **2a** can be generated conveniently *via* thermal cycloreversion of the 2,5-dihydro-1,3,4-thiadiazole derivative **1a** [5], which is available by treatment of 2,2,4,4-tetramethyl-3-thioxocyclobutan-1-one with CH_2N_2 [6]. However, in the case of aromatic thioketones, 1,3,4-thiadiazoles of type **1** are

Scheme 1. *Stepwise Reaction of a Sterically Crowded Thiocarbonyl Ylide* **2a** *with Electron-Deficient 1,2-Bis(trifluoromethyl)ethene-1,2-Dicarbonitrile* (**3a**)

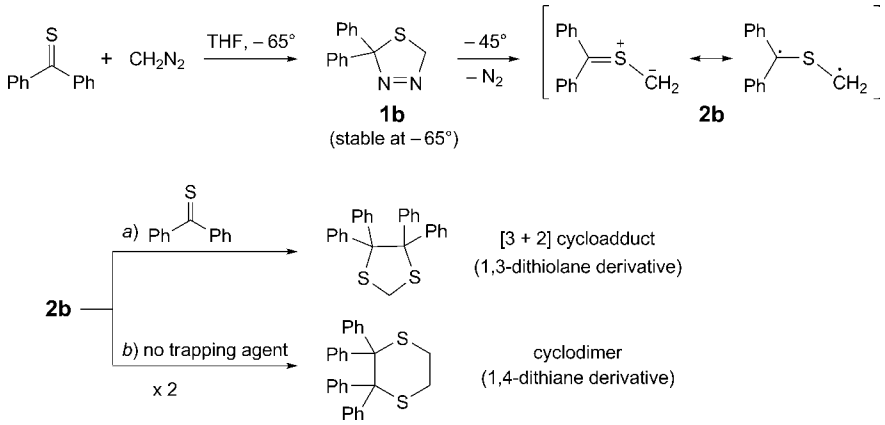


stable below $-60°$, and the corresponding thiocarbonyl ylides are generated *in situ* at *ca.* $-40°$ [7].

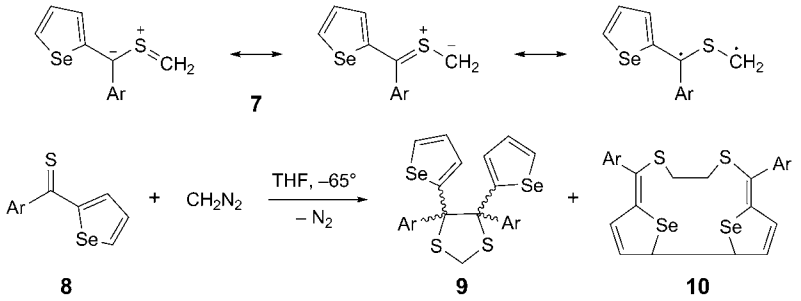
An alternative mechanism for stepwise [3 + 2] cycloadditions was postulated by *Firestone* [8], and, in that case, 1,3-biradicals were proposed to appear as reactive intermediates. However, the experimental evidence for this mechanism is vague, and, to the best of our knowledge, the addition of a nitrone with substituted 1,3-dienes, leading to a seven-membered heterocycle along with the expected five-membered isoxazolidines, is the only example supporting the intermediacy of a biradical species [9]. In the case of thiocarbonyl ylides, intermediate biradicals were postulated for the formation of 1,3-dithiolanes based on computational studies [10a,b]. Moreover, the biradical mechanism was postulated for the formation of sterically crowded 1,3-dithiolanes, derived from hetaryl thioketones and cycloaliphatic thioketone *S*-methanides [10c]. In addition, the head-to-head dimerization of *S*-methanides derived from bisaryl thioketones, like thiobenzophenone *S*-methanide (**2b**), leading to 1,4-dithianes, could be explained *via* an intermediate biradical species [11] (*Scheme 2*).

Results and Discussion. – In our ongoing studies on reactions with aryl and hetaryl thioketones, we focused our attention on the generation of *S*-methanides of type **7** derived from aryl (selenophen-2-yl) and di(selenophen-2-yl) thioketones **8** (*Scheme 3*). Unexpectedly, the treatment of **8a** (Ar^1 = Ph) with CH_2N_2 led to immediate evolution of N_2, irrespective of the reaction temperature. The experiments performed at 20°, 0°, and even $-65°$ afforded the same mixture of isomeric, sterically crowded 4,4,5,5-tetrasubstituted *cis*- and *trans*-1,3-dithiolanes **9a** as major products. The structures of these compounds were elucidated on the basis of the ^{13}C-NMR spectra, in which diagnostic signals of the CH_2 groups appeared at 30.3 and 31.0 ppm, respectively [10b]. However, the ^{1}H-NMR analysis of the mixture obtained with **8a** revealed that, along with isomeric dithiolanes **9a**, another minor product with characteristic *multiplet*s at 2.63–2.69 and 4.62–4.67 ppm was present. After separation of the mixture, this substance was obtained as slightly colored (beige) crystals. The ^{13}C-NMR spectrum

Scheme 2. *Generation of Thiobenzophenone* S-*Methanide* (**2b**) *and Its Behavior:* a) *in the Presence of Thiobenzophenone*; b) *in the Absence of a Trapping Agent*



Scheme 3. *Se-Containing Thiocarbonyl Ylides Disclosing the Nature of the Biradical Species*



exhibited ten signals; two of them, located at 29.3 and 60.6 ppm were attributed to CH_2 (sp^3) and CH (sp^3) groups, respectively. The ESI-HR-MS indicated a dimeric structure for the intermediate thiocarbonyl ylide **7a**. However, the spectroscopic data did not correspond to the structure of the corresponding 1,4-dithiane, which could be expected as a product of typical head-to-head dimerization of bis(arylthiocarbonyl) *S*-methanides [11] (*Scheme 2*).

Finally, the structure of the new cyclodimer of the thiocarbonyl ylide **7a** was established by X-ray crystallography as the hitherto unknown twelve-membered macrocycle **10a** (*Fig.*).

It is worth mentioning that the analogous reaction with phenyl (thiophen-2-yl) thioketone led exclusively to a *ca.* 1:1 mixture of isomeric 1,3-dithiolanes of type **9** [13]. This observation implies that the presence of a selenophen-2-yl substituent would be prerequisite for the formation of the dimer of type **10**. To assess the influence of substituents in the Ar ring of **8**, a series of experiments with 4-substituted phenyl analogs of **8a** was performed (*Table 1*). The obtained results revealed that electron-withdrawing substituents in the starting thioketone favor the formation of the dimer **10**.

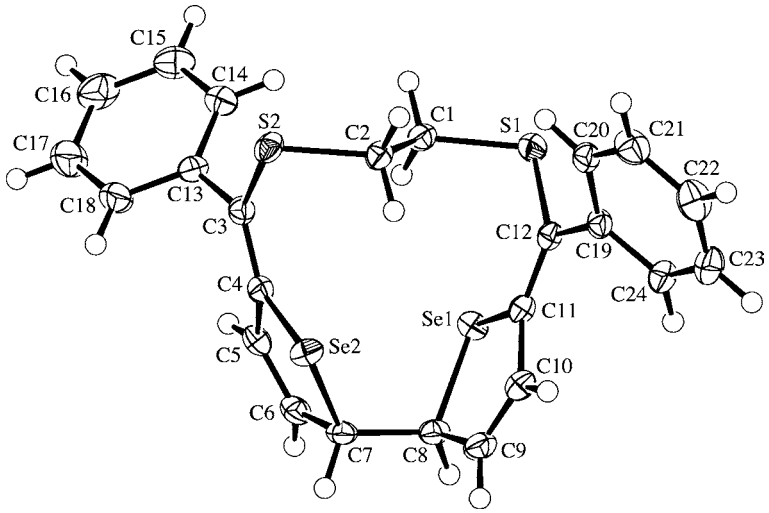


Figure. *ORTEP Plot* [12] *of the molecular structure of* **10a** (50% probability ellipsoids; arbitrary numbering of the atoms)

Table 1. *Reactions of Aryl (Selenophen-2-yl) Thioketones* **8** *with* CH_2N_2 *in THF at* $-65°$

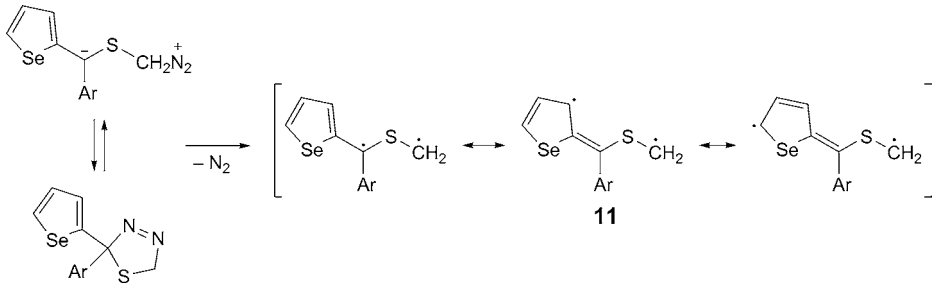
Entry	Thioketone **8**	Ar[1]	Products (Yield [%])[a])	
			9[b])	**10**
1	**8a**	Ph	**9a** (52)	**10a** (19)
2	**8b**	4-MeO–C_6H_4	**9b** (71)	**10b** (traces)[c])
3	**8c**	4-Me–C_6H_4	**9c** (72)	**10c** (traces)[c])
4	**8d**	4-Cl–C_6H_4	**9d** (traces)[c])	**10d** (16)
5	**8e**[d])	4-O_2N–C_6H_4	–	**10e** (53)
6	**8f**	4-F_3C–C_6H_4	**9f** (major)[c])	**10f** (traces)[c])
7	**8g**	Selenophen-2-yl	**9g** (65)	**10g** (traces)[c])

[a]) Yield of isolated product. [b]) Approximately 1:1 mixtures of *cis*- and *trans*-isomers. [c]) Not isolated; detected by ^{1}H-NMR in the crude mixture. [d]) Reaction carried out at $-85°$.

Remarkably, in the case of **8e** with the 4-nitrophenyl group, the reaction performed at $-85°$ occurred with vigorous evolution of N_2, and the dimer **10e** was obtained as the sole product according to ^{1}H-NMR analysis. Similarly, the 4-CF_3-substituted thioketone **8f** yielded under the same conditions the dimer **10f** and only traces of the corresponding dithiolanes **9f** (*Table 1*). On the other hand, the same reaction with **8b** and **8c**, which bear electron-donating substituents, gave predominantly mixtures of isomeric 1,3-dithiolanes **9b** and **9c**, respectively, and only traces of the corresponding dimers **10** were detected. Finally, the reaction with the symmetric di(selenophen-2-yl) thioketone (**8g**) furnished 1,3-dithiolanes as the major products [13], but traces of the unstable dimer **10g** could also be identified in the crude mixture.

These results indicate that the observed [6 + 6] dimerization of aryl (selenophen-2-yl) thiocarbonyl *S*-methanides **7** is favored by the presence of electron-withdrawing

Scheme 4. *Delocalized Biradical Intermediate*



substituents in the phenyl ring. In our opinion, this type of dimerization of a thiocarbonyl ylide occurs *via* the intermediate delocalized biradical **11** (*Scheme 4*). Apparently, the dimerization is initiated by the formation of the CH_2–CH_2 bond, and subsequent interaction of the radical centers in the α-positions of the selenophene rings. It seems likely that the reaction of CH_2N_2 with hetaryl thioketones **8** under the applied conditions occurs without the formation of a corresponding 4,5-dihydro-1,3,4-thiadiazole of type **1**, which may exist in the solution at a very low temperature. The observed spontaneous elimination of N_2 at low temperatures differs significantly from reactions of CH_2N_2 with diaryl and cycloaliphatic thioketones.

Conclusions. – The present study shows that the *in situ*-generated aryl (selenophen-2-yl) thiocarbonyl ylides **7** undergo either dimerization to give **10**, or the competitive reaction with the starting thioketone **8** to yield 1,3-dithiolanes **9** in a regioselective manner. The formation of **10** establishes the intermediacy of a delocalized biradical **11**. The yield of **10** depends on the substitution of the phenyl ring in the starting thioketone. The competitive formation of 4,4,5,5-tetraaryl-/hetaryl-substituted 1,3-dithiolanes **9** can be proposed to occur also *via* biradical intermediates as suggested by computational studies [10a].

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Experimental Part

1. *General.* Column chromatography (CC): silica gel (70–230 mesh; *Merck*). M.p.: *MEL-TEMP. II* (*Aldrich*); uncorrected. IR Spectra: *NEXUS* FT-IR instrument; in KBr; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker Avance III* instrument (at 600 and 150 MHz, resp.) using the solvent signal as reference; in $CDCl_3$; δ in ppm, J in Hz. The majority of the ^{13}C signals were assigned with the aid of DEPT spectra. HR-ESI-MS: *Bruker maXis* spectrometer in the Laboratory of Mass Spectrometry of the University of Zurich, *Finnigan MAT 59* in the Laboratory of Mass Spectroscopy in CBMiM PAN Łódź, and *Maldi SYNAPT G2-S HDMS* in the Laboratory of the Institute of Organic Chemistry PAN Warsaw. Elemental analyses: in the Laboratory of the Faculty of Chemistry, University of Łódź; in %

2. *Starting Materials.* All solvents and reagents are commercially available and were used as received. Thioketones **8** were obtained from the corresponding ketones [13] and *Lawesson*'s reagent [14] in boiling toluene or benzene.

3. *Reaction of Thioketones with CH_2N_2.* A soln. of the corresponding thioketone **8** (1 mmol) in dry THF (1 ml) was added dropwise to a magnetically stirred soln. of CH_2N_2 in Et_2O at $-65°$ according to a known procedure [11]. For the most reactive *4-nitrophenyl selenophen-2-yl thioketone* (**8f**), the reaction with CH_2N_2 was performed at $-85°$. Under these conditions, decolorization of the thioketone soln. was observed immediately after addition of each portion. Pure products were isolated by CC or by crystallization.

3.1. *Reaction with Phenyl Selenophen-2-yl Thioketone* (**8a**). *4,5-Diphenyl-4,5-di(selenophen-2-yl)-1,3-dithiolane* (**9a**; 1:1 mixture of *cis*- and *trans*-isomer). Purified by CC (petroleum ether/CH_2Cl_2 3:2). Yield: 135 mg (52%). Beige crystals. M.p. 162° (dec.; crystallization from hexane/CH_2Cl_2). IR (KBr): 3050*m*, 2920*m*, 1628*m*, 1577*m*, 1487*s*, 1419*m*, 1282*m*, 1229*s*, 1187*m*, 1157*m*, 1031*m*, 792*m*, 752*m*, 696v*s*. ^{1}H-NMR: 3.85, 3.97 (*AB*, J = 9.2, CH_2 of *cis*-isomer); 4.02 (*s*, CH_2 of *trans*-isomer); 6.89 (*d*, J = 3.9, 2 arom. H); 7.04 (*dd*, J = 5.6, 4.5, 2 arom. H); 7.01–7.13 (*m*, 6 arom. H); 7.19–7.22 (*m*, 8 arom. H); 7.25 (*d*, J = 7.2, 2 arom. H); 7.47 (*d*, J = 7.9, 4 arom. H); 7.49 (*d*, J = 7.9, 4 arom. H); 7.91 (*d*, J = 5.7, 2 arom. H); 7.95 (*d*, J = 5.7, 2 arom. H). ^{13}C-NMR (mixture of *cis*- and *trans*-isomer): 30.3, 31.0 (2 CH_2), 126.5, 127.3, 127.4, 127.5, 127.9, 128.0, 130.6, 130.9, 132.3, 132.4, 132.7, 132.9 (32 arom. CH); 132.7, 141.2, 142.2, 157.6 (8 arom. C). HR-ESI-MS: 517.919210 (M^+, $C_{23}H_{18}S_2Se_2^+$; calc. 517.918183).

(5Z,11Z)-6,11-Diphenyl-7,10-dithia-15,16-diselenatricyclo[10.2.1.1^{2,5}]hexadeca-3,5,11,13-tetraene (**10a**). Isolated by CC (petroleum ether (PE)/CH_2Cl_2 1:1). Yield: 50 mg (19%; partial dec. during CC). Beige crystals. M.p. >180° (dec.; crystallization from hexane/CH_2Cl_2). IR (KBr): 3026*s*, 2951*s*, 1625*s*, 1587*s*, 1533*s*, 1486*s*, 1439*s*, 1390*m*, 1362*m*, 1244*s*, 1226*s*, 1154*s*, 1138*s*, 1122*s*, 1075*s*, 1027*s*, 900*s*, 741v*s*, 730*s*, 709v*s*, 696v*s*. ^{1}H-NMR: 2.63–2.69 (*m*, CH_2S); 4.62–4.67 (*m*, CH_2S); 4.82–4.83 (*m*, 2 CHSe); 6.21 (*dd*, J = 6.5, 2.8, 2 CH=); 6.61 (*dd*, J = 6.5, 1.0, 2 CH=); 7.29–7.31 (*m*, 2 arom. H); 7.35–7.38 (*m*, 4 arom. H); 7.47–7.50 (*m*, 4 arom. H). ^{13}C-NMR: 29.3 (2 CH_2S); 60.6 (2 CHSe); 127.5, 128.2, 129.8, 134.5, 139.1 (10 arom. CH, 4 CH=); 123.7, 141.7, 150.3 (2 arom. C, 2 C=C). HR-ESI-MS: 531.9344 (M^+, $C_{24}H_{20}S_2Se_2^+$; calc. 531.9337).

3.2. *Reaction with 4-Methoxyphenyl Selenophen-2-yl Thioketone* (**8b**). *4,5-Bis(4-methoxyphenyl)-4,5-di(selenophen-2-yl)-1,3-dithiolane* (**9b**; 1:1 mixture of *cis*- and *trans*-isomer). Isolated by CC (PE/CH_2Cl_2 3:2). Yield: 205 mg (71%). Pale-yellow crystals. M.p. >183° (dec.; crystallization from hexane/CH_2Cl_2). IR (KBr): 3054*m*, 2927*m*, 1604*m*, 1577*m*, 1507v*s*, 1440*m*, 1294*m*, 1254v*s*, 1231*m*, 1184*m*, 1032*m*, 799*m*, 767*m*, 688*s*. ^{1}H-NMR: 3.76, 3.78 (2*s*, 2 MeO); 3.85, 3.95 (*AB*, J = 9.2, CH_2 of *cis*-isomer); 3.98 (*s*, CH_2 of *trans*-isomer); 6.62 (*d*, J = 8.7, 2 arom. H); 6.69 (*d*, J = 8.8, 4 arom. H); 6.92 (*d*, J = 3.6, 4 arom. H); 7.01–7.03 (*m*, 2 arom. H); 7.05–7.07 (*m*, 2 arom. H); 7.21 (*d*, J = 3.6, 2 arom. H); 7.31 (*d*, J = 5.2, 4 arom. H); 7.34 (*d*, J = 8.8, 4 arom. H); 7.88 (*d*, J = 5.7, 2 arom. H); 7.91 (*d*, J = 5.7, 2 arom. H). ^{13}C-NMR (mixture of *cis*- and *trans*-isomer): 30.1, 31.0 (2 CH_2); 55.2 (4 MeO); 111.7, 112.6, 129.7, 128.0, 131.8, 131.9, 132.1, 132.2, 132.3, 132.7 (28 arom. CH); 133.0, 134.1, 134.4, 158.2, 158.6, 158.9 (12 arom. C). HR-ESI-MS: 577.9413 (M^+, $C_{25}H_{22}O_2S_2Se_2^+$; calc. 577.9378).

(5Z,11Z)-6,11-Bis(4-methoxyphenyl)-7,10-dithia-15,16-diselenatricyclo[10.2.1.1^{2,5}]hexadeca-3,5,11,13-tetraene (**10b**). Detected in traces in the crude mixture; could not be isolated in pure form. ^{1}H-NMR (selected signals): 2.62–2.67 (*m*, CH_2S); 4.63–4.67 (*m*, CH_2S); 4.83–4.84 (*m*, 2 CHSe).

3.3. *Reaction with 4-Methylphenyl Selenophen-2-yl Thioketone* (**8c**). *4,5-Bis(4-methylphenyl)-4,5-di(selenophen-2-yl)-1,3-dithiolane* (**9c**; 1:1 mixture of *cis*- and *trans*-isomer). Isolated by CC (PE/CH_2Cl_2 3.5:1.5). Yield: 195 mg (72%). Pale-yellow crystals. M.p. >166° (dec.; crystallization from hexane/CH_2Cl_2). IR (KBr): 3024*m*, 2915*m*, 1626*m*, 1508*s*, 1441*m*, 1230*s*, 1193*m*, 1020*m*, 797*m*, 761*m*, 688v*s*. ^{1}H-NMR: 2.38, 2.40 (2*s*, 2 Me); 3.81, 3.93 (*AB*, J = 9.2, CH_2 of *cis*-isomer); 3.99 (*s*, CH_2 of *trans*-isomer); 6.88 (*d*, J = 3.7, 2 arom. H); 6.90 (*d*, J = 8.1, 4 arom. H); 6.97 (*d*, J = 8.1, 4 arom. H); 7.01 (*dd*, J = 5.6, 3.9, 2 arom. H); 7.05 (*dd*, J = 5.6, 3.9, 2 arom. H); 7.15 (*d*, J = 3.7, 2 arom. H); 7.30 (*d*, J = 8.3, 4 arom. H); 7.34 (*d*, J = 8.3, 4 arom. H); 7.87 (*d*, J = 5.6, 2 arom. H); 7.91 (*d*, J = 5.6, 2 arom. H). ^{13}C-NMR (mixture of *cis*- and *trans*-isomer): 20.9, 21.0 (2 CH_2); 30.1, 30.9 (4 Me); 127.2, 127.9, 128.0, 128.1, 130.5, 130.8, 131.8, 132.1, 132.3, 132.8 (28 arom. CH); 136.9, 137.6, 138.0, 139.2, 158.3 (12 arom. C). HR-ESI-MS: 545.9515 (M^+, $C_{25}H_{22}S_2Se_2^+$; calc. 545.9493). Anal. calc for $C_{25}H_{22}S_2Se_2$ (544.49): C 55.15, H 4.07, S 11.78; found: C 55.36, H 4.48, S 11.71.

(5Z,11Z)-6,11-Bis(4-methylphenyl)-7,10-dithia-15,16-diselenatricyclo[10.2.1.1^{2,5}]hexadeca-3,5,11,13-tetraene (**10c**). Traces, detected and identified spectroscopically in the crude mixture. ^{1}H-NMR (selected signals): 2.63–2.68 (*m*, CH_2S); 4.65–4.69 (*m*, CH_2S); 4.85–4.88 (*m*, 2 CHSe).

3.4. *Reaction with 4-Chlorophenyl Selenophen-2-yl Thioketone* (**8d**). *4,5-Bis(4-chlorophenyl)-4,5-di(selenophen-2-yl)-1,3-dithiolane* (**9d**; 1:1 mixture of *cis*- and *trans*-isomer). Traces, detected and identified by ^{1}H-NMR in the crude mixture. ^{1}H-NMR: 3.85, 3.99 (*AB*, *J* = 9.2, CH_2 of *cis*-isomer); 4.03 (*s*, CH_2S of *trans*-isomer).

(5Z,11Z)-6,11-Bis(4-chlorophenyl)-7,10-dithia-15,16-diselenatricyclo-[10.2.1.1^{2,5}]hexadeca-3,5,11,13-tetraene (**10d**). Isolated by CC (PE/CH_2Cl_2 1:1; partially decomposed during chromatographic purification). Yield: 50 mg (16%). Pale-brown crystals. M.p. >174° (dec.; crystallization from hexane/CH_2Cl_2). IR (KBr): 3028*m*, 2954*m*, 1630*m*, 1565*m*, 1533*s*, 1482v*s*, 1419*s*, 1395*s*, 1341*m*, 1238*s*, 1222*m*, 1161*s*, 1140*m*, 1120*m*, 1087*m*, 1011*s*, 900*s*, 762v*s*, 722*s*, 674*s*. ^{1}H-NMR: 2.61–2.67 (*m*, CH_2S); 4.57–4.62 (*m*, CH_2S); 4.86–4.87 (*m*, 2 CHSe); 6.25 (*dd*, *J* = 6.6, 2.7, 2 CH=); 6.56 (br. *d*, *J* = 6.6, 2 CH=); 7.31, 7.41 (*AB*, *J* = 8.5, 8 arom. H). ^{13}C-NMR: 29.2 (2 CH_2S); 60.6 (2 CHSe); 128.4, 131.1, 134.2, 139.7 (8 arom. H, 4 CH=); 122.3, 133.4, 140.0, 150.8 (4 arom. C, 2 C=C). HR-ESI-MS: 599.8564 (M^+, $C_{24}H_{18}Cl_2S_2Se_2^+$; calc. 599.8557).

3.5. *Reaction with 4-Nitrophenyl Selenophen-2-yl Thioketone* (**8e**). *(5Z,11Z)-6,11-Bis(4-nitrophenyl)-7,10-dithia-15,16-diselenatricyclo[10.2.1.1^{2,5}]hexadeca-3,5,11,13-tetraene* (**10e**). Yield: 165 mg (53%). Yellow crystals. M.p. >230° (dec.; crystallization from hexane/CH_2Cl_2). IR (KBr): 3058*m*, 2954*m*, 1628*m*, 1587*m*, 1527*m*, 1422*m*, 1301*vs*, 1237*m*, 1198*m*, 1108*m*, 1078*m*, 846*s*, 769*s*, 715*m*, 618*m*. ^{1}H-NMR: 2.68–2.72 (*m*, CH_2S); 4.56–4.61 (*m*, CH_2S); 4.94–4.95 (*m*, 2 CHSe); 6.39 (*dd*, *J* = 6.6, 2.8, 2 CH=); 6.60 (br. *d*, *J* = 6.6, 2 CH=); 7.65, 8.23 (*AB*, *J* = 8.7, 8 arom. H). ^{13}C-NMR: 32.1 (2 CH_2S); 63.5 (2 CHSe); 123.7, 129.9, 131.0, 139.0 (8 arom. CH, 4 CH=); 142.0, 143.1, 149.4, 149.9 (4 arom. C, 2 C=C). HR-ESI-MS: 621.90329 (M^+, $C_{24}H_{18}N_2O_4S_2Se_2^+$; calc. 621.90395).

3.6. *Reaction with Selenophen-2-yl 4-(Trifluoromethyl)phenyl Thioketone* (**8f**). The cyclodimer *(5Z,11Z)-6,11-Bis[4-(trifluoromethyl)phenyl]-7,10-dithia-15,16-diselenatricyclo[10.2.1.1^{2,5}]hexadeca-3,5,11,13-tetraene* (**10f**) was obtained only as a mixture with ketone $R^1C(O)R^2$ (R^1 = 4-$CF_3C_6H_4$, R^2 = selenophen-2-yl) and identified by NMR spectroscopy. All attempts to isolate **10f** in a pure form, either chromatographically or by crystallization, were unsuccessful.

3.7. *Reaction with Di(selenophen-2-yl) Thioketone* (**8g**). *4,4,5,5-Tetra(selenophen-2-yl)-1,3-dithiolane* (**9g**). Isolated by CC (PE/CH_2Cl_2 3:2). Yield: 200 mg (65%; undergoes partial decomposition during chromatographic purification). Beige crystals. M.p. >170° (dec.; crystallized from hexane/CH_2Cl_2). IR (KBr): 3087*m*, 3053*m*, 1631*m*, 1437*m*, 1412*m*, 1328*m*, 1230*s*, 1128*m*, 1101*m*, 1056*m*, 1022*m*, 846*m*, 733*m*, 687v*s*. ^{1}H-NMR: 4.13 (*s*, CH_2); 7.12 (*dd*, *J* = 5.8, 4.0, 4 arom. H); 7.21 (*dd*, *J* = 4.0, 1.0, 4 arom. H); 7.98 (*dd*, *J* = 5.8, 1.0, 4 arom. H). ^{13}C-NMR: 30.9 (CH_2); 60.0 (2 C_q); 128.2, 132.6, 133.8 (12 arom. CH); 152.5 (4 arom. C). HR-ESI-MS: 625.71826 (M^+, $C_{19}H_{14}S_2Se_4^+$; calc. 625.720434).

(5Z,11Z)-6,11-Bis(selenophen-2-yl)-7,10-dithia-15,16-diselenatricyclo[10.2.1.1^{2,5}]hexadeca-3,5,11,13-tetraene (**10g**). Observed as a minor product in the crude reaction mixture (^{1}H-NMR). This product completely decomposed during attempted purification by CC or crystallization. ^{1}H-NMR (selected signals: 2.63–2.69 (*m*, CH_2S); 4.54–4.61 (*m*, CH_2S); 4.86–4.87 (*m*, 2 CHSe).

4. *X-Ray Crystal-Structure Determination of* **10a** (*Table 2* and *Fig.*)[1]. A crystal of **10a** suitable for a low-temperature X-ray structure determination was obtained from hexane/CH_2Cl_2. All measurements were made on an *Agilent Technologies SuperNova* area-detector diffractometer [15] using MoK_α radiation (λ 0.71073 Å) from a microfocus X-ray source and an *Oxford Instruments Cryojet XL* cooler. Data reduction was performed with *CrysAlisPro* [15]. The intensities were corrected for *Lorentz* and polarization effects, and an empirical absorption correction using spherical harmonics [15] was applied. Equivalent reflections were merged. The data collection and refinement parameters are given in *Table 2*, and a view of the molecule is shown in the *Figure*. The structure was solved by direct methods using *SHELXS-2013* [16], which revealed the positions of all non-H-atoms. The non-H-atoms were refined

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[1]) CCDC-1035301 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre*, *via* www.ccdc.cam.ac.uk/data_request/cif.

Table 2. *Crystallographic Data for Compound* **10a**

Crystallized from	hexane/CH_2Cl_2
Empirical formula	$C_{24}H_{20}S_2Se_2$
Formula weight [g mol^{-1}]	530.34
Crystal color, habit	yellow, prism
Crystal dimensions [mm]	$0.10 \times 0.10 \times 0.23$
Temp. [K]	160(1)
Crystal system	monoclinic
Space group	*C*2/*c*
Z	8
Reflections for cell determination	12146
2θ Range for cell determination [°]	5 – 61
Unit cell parameters:	
a [Å]	26.2131(5)
b [Å]	14.4025(3)
c [Å]	12.0823(2)
β [°]	99.6333(18)
V [Å^3]	4497.17(15)
D_x [g cm^{-3}]	1.566
μ(MoK_α) [mm^{-1}]	3.480
Scan type	ω
$2\theta_{(max)}$ [°]	60.7
Transmission factors (min; max)	0.711; 1.000
Total reflections measured	28288
Symmetry-independent reflections	6258
Reflections with $I > 2\sigma(I)$	5019
Reflections used in refinement	6258
Parameters refined	253
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0265
$wR(F^2)$ (all data)	0.0628
Weights:	$w = [\sigma^2(F_o^2) + (0.027P)^2 + 2.909P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$
Goodness of fit	1.042
Final Δ_{max}/σ	0.002
$\Delta\rho$ (max; min) [e Å^{-3}]	0.51; -0.33

anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent atom. The refinement of the structure was carried out on F^2 by using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was not applied. There are two voids of 174 Å^3 per unit cell, which join together into channels running parallel to [001]. The SQUEEZE routine [17] of the PLATON program [18] indicated *ca.* 10 e per cavity, which would correspond to a H_2O molecule. However, neither inclusion of a H_2O molecule, even with partial occupancy, nor refinement with the data generated by SQUEEZE yielded any improvement in the results, so the original reflection data and the solvent-free model were retained for the final refinements. The maximum residual electron-density peak is only 0.55 e Å^{-3}, so if solvent is present in the channels, it is diffuse. Neutral atom-scattering factors for non-H-atoms were taken from [19a], and the scattering factors for H-atoms were taken from [20]. Anomalous dispersion effects were included in F_c [21]; the values for f' and f'' were those of *Creagh* and *McAuley* [19b]. The values of the mass attenuation coefficients are those of *Creagh* and *Hubbel* [19c]. The SHELXL-2013 program [22] was used for all calculations.

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