

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

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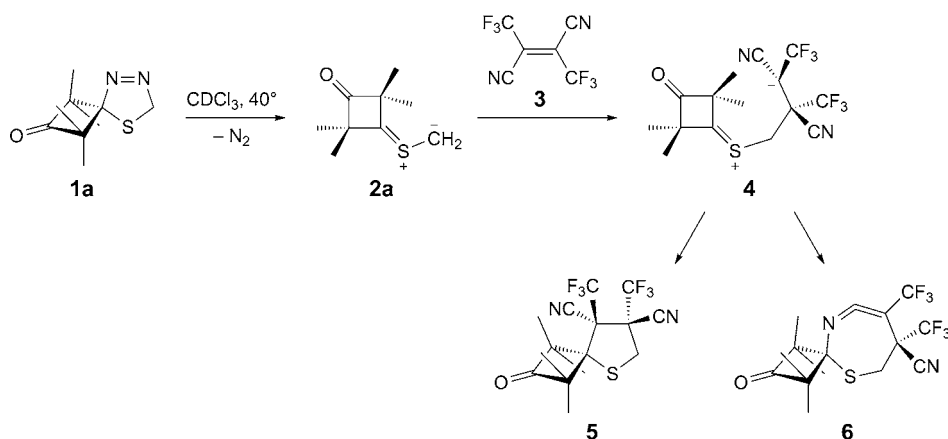
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Dedicated to Professor *Christian Robl*, Friedrich-Schiller-Universität Jena, on the occasion of his 60th birthday

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-member 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*).

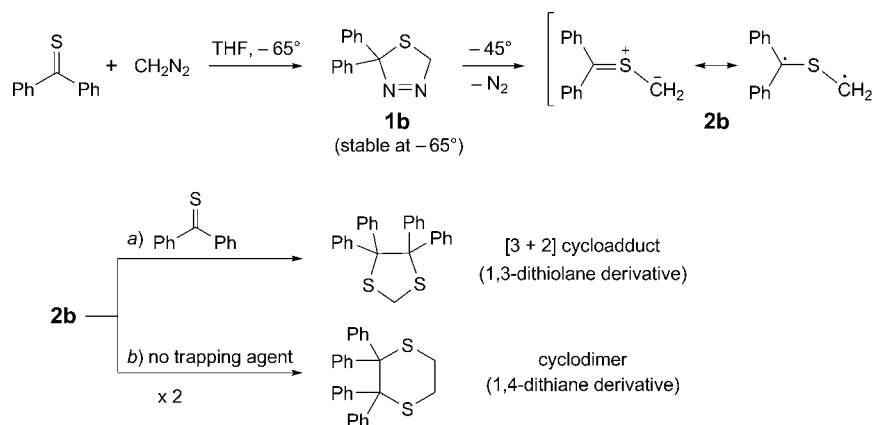
The stepwise mechanism was evidenced by the loss of stereospecificity, *i.e.*, the formation of two stereoisomeric thiolanes of type **5** (CF_3 groups replaced by COOMe) in the case of dimethyl dicyanofumarate [4], and the isolation of the seven-membered ketenimine **6** [5] or its derivatives obtained *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**)

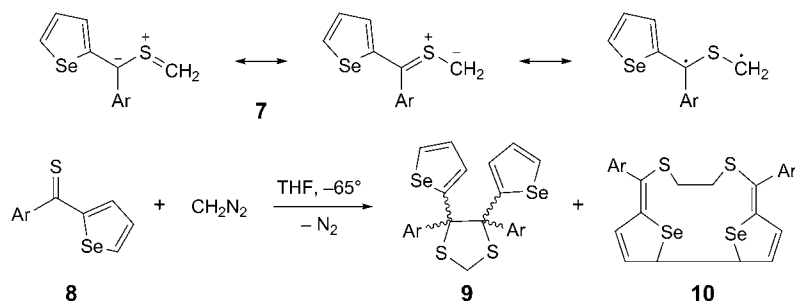
stable below -60° , and the corresponding thiocarbonyl ylides are generated *in situ* at *ca.* -40° [7].

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 nitron 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** ($\text{Ar}^1 = \text{Ph}$) 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 ^1H -NMR analysis of the mixture obtained with **8a** revealed that, along with isomeric dithiolanes **9a**, another minor product with characteristic *multiplets* 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 I). The obtained results revealed that electron-withdrawing substituents in the starting thioketone favor the formation of the dimer **10**.

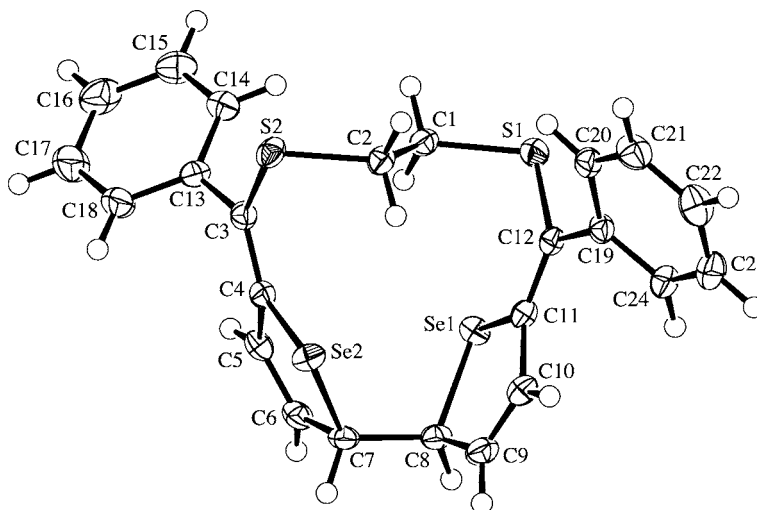


Figure. ORTEP Plot [12] of the molecular structure of **10a** (50% probability ellipsoids; arbitrary numbering of the atoms)

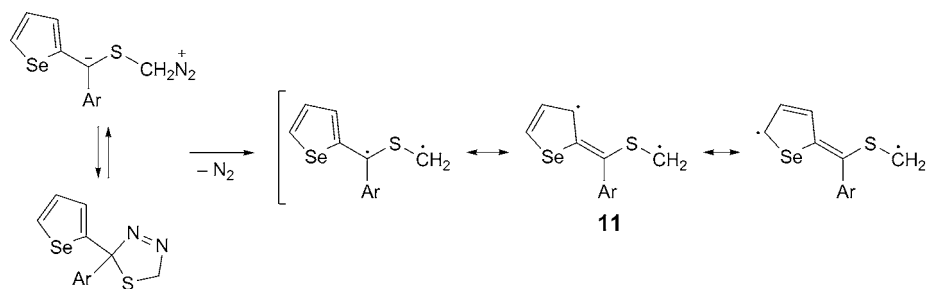
Table 1. Reactions of Aryl (Selenophen-2-yl) Thioketones **8** with CH_2N_2 in THF at -65°

Entry	Thioketone 8	Ar ¹	Products (Yield [%]) ^a	
			9 ^b	10
1	8a	Ph	9a (52)	10a (19)
2	8b	4-MeO-C ₆ H ₄	9b (71)	10b (traces) ^c
3	8c	4-Me-C ₆ H ₄	9c (72)	10c (traces) ^c
4	8d	4-Cl-C ₆ H ₄	9d (traces) ^c	10d (16)
5	8e ^d	4-O ₂ N-C ₆ H ₄	–	10e (53)
6	8f	4-F ₃ C-C ₆ H 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 ¹H-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 ¹H-NMR analysis. Similarly, the 4-CF₃-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 $\text{CH}_2\text{-CH}_2$ 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 CH₂N₂*. A soln. of the corresponding thioketone **8** (1 mmol) in dry THF (1 ml) was added dropwise to a magnetically stirred soln. of CH₂N₂ in Et₂O at –65° according to a known procedure [11]. For the most reactive *4-nitrophenyl selenophen-2-yl thioketone* (**8f**), the reaction with CH₂N₂ 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/CH₂Cl₂ 3:2). Yield: 135 mg (52%). Beige crystals. M.p. 162° (dec.; crystallization from hexane/CH₂Cl₂). IR (KBr): 3050m, 2920m, 1628m, 1577m, 1487s, 1419m, 1282m, 1229s, 1187m, 1157m, 1031m, 792m, 752m, 696vs. ¹H-NMR: 3.85, 3.97 (AB, *J* = 9.2, CH₂ of *cis*-isomer); 4.02 (s, CH₂ 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). ¹³C-NMR (mixture of *cis*- and *trans*-isomer): 30.3, 31.0 (2 CH₂), 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*⁺, C₂₅H₁₈S₂Se₂⁺; calc. 517.918183).

(5*Z*,11*Z*)-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)/CH₂Cl₂ 1:1). Yield: 50 mg (19%; partial dec. during CC). Beige crystals. M.p. > 180° (dec.; crystallization from hexane/CH₂Cl₂). IR (KBr): 3026s, 2951s, 1625s, 1587s, 1533s, 1486s, 1439s, 1390m, 1362m, 1244s, 1226s, 1154s, 1138s, 1122s, 1075s, 1027s, 900s, 741vs, 730s, 709vs, 696vs. ¹H-NMR: 2.63–2.69 (m, CH₂S); 4.62–4.67 (m, CH₂S); 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). ¹³C-NMR: 29.3 (2 CH₂S); 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*⁺, C₂₄H₂₀S₂Se₂⁺; 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/CH₂Cl₂ 3:2). Yield: 205 mg (71%). Pale-yellow crystals. M.p. > 183° (dec.; crystallization from hexane/CH₂Cl₂). IR (KBr): 3054m, 2927m, 1604m, 1577m, 1507vs, 1440m, 1294m, 1254vs, 1231m, 1184m, 1032m, 799m, 767m, 688s. ¹H-NMR: 3.76, 3.78 (2s, 2 MeO); 3.85, 3.95 (AB, *J* = 9.2, CH₂ of *cis*-isomer); 3.98 (s, CH₂ 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). ¹³C-NMR (mixture of *cis*- and *trans*-isomer): 30.1, 31.0 (2 CH₂); 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*⁺, C₂₅H₂₂O₂S₂Se₂⁺; calc. 577.9378).

(5*Z*,11*Z*)-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. ¹H-NMR (selected signals): 2.62–2.67 (m, CH₂S); 4.63–4.67 (m, CH₂S); 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/CH₂Cl₂ 3.5:1.5). Yield: 195 mg (72%). Pale-yellow crystals. M.p. > 166° (dec.; crystallization from hexane/CH₂Cl₂). IR (KBr): 3024m, 2915m, 1626m, 1508s, 1441m, 1230s, 1193m, 1020m, 797m, 761m, 688vs. ¹H-NMR: 2.38, 2.40 (2s, 2 Me); 3.81, 3.93 (AB, *J* = 9.2, CH₂ of *cis*-isomer); 3.99 (s, CH₂ 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). ¹³C-NMR (mixture of *cis*- and *trans*-isomer): 20.9, 21.0 (2 CH₃); 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*⁺, C₂₅H₂₂S₂Se₂⁺; calc. 545.9493). Anal. calc for C₂₅H₂₂S₂Se₂ (544.49): C 55.15, H 4.07, S 11.78; found: C 55.36, H 4.48, S 11.71.

(5*Z*,11*Z*)-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. ¹H-NMR (selected signals): 2.63–2.68 (*m*, CH₂S); 4.65–4.69 (*m*, CH₂S); 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 ¹H-NMR in the crude mixture. ¹H-NMR: 3.85, 3.99 (*AB*, *J* = 9.2, CH₂ of *cis*-isomer); 4.03 (*s*, CH₂S of *trans*-isomer).

(5*Z*,11*Z*)-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/CH₂Cl₂ 1:1; partially decomposed during chromatographic purification). Yield: 50 mg (16%). Pale-brown crystals. M.p. > 174° (dec.; crystallization from hexane/CH₂Cl₂). IR (KBr): 3028*m*, 2954*m*, 1630*m*, 1565*m*, 1533*s*, 1482*vs*, 1419*s*, 1395*s*, 1341*m*, 1238*s*, 1222*m*, 1161*s*, 1140*m*, 1120*m*, 1087*m*, 1011*s*, 900*s*, 762*vs*, 722*s*, 674*s*. ¹H-NMR: 2.61–2.67 (*m*, CH₂S); 4.57–4.62 (*m*, CH₂S); 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). ¹³C-NMR: 29.2 (2 CH₂S); 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*⁺, C₂₄H₁₈Cl₂S₂Se₂⁺; calc. 599.8557).

3.5. Reaction with 4-Nitrophenyl Selenophen-2-yl Thioketone (**8e**). (5*Z*,11*Z*)-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/CH₂Cl₂). 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*. ¹H-NMR: 2.68–2.72 (*m*, CH₂S); 4.56–4.61 (*m*, CH₂S); 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). ¹³C-NMR: 32.1 (2 CH₂S); 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*⁺, C₂₄H₁₈N₂O₄S₂Se₂⁺; calc. 621.90395).

3.6. Reaction with Selenophen-2-yl 4-(Trifluoromethyl)phenyl Thioketone (**8f**). The cyclodimer (5*Z*,11*Z*)-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 R¹C(O)R² (R¹ = 4-CF₃C₆H₄, R² = 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/CH₂Cl₂ 3:2). Yield: 200 mg (65%; undergoes partial decomposition during chromatographic purification). Beige crystals. M.p. > 170° (dec.; crystallized from hexane/CH₂Cl₂). 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*, 687*vs*. ¹H-NMR: 4.13 (*s*, CH₂); 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). ¹³C-NMR: 30.9 (CH₂); 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*⁺, C₁₀H₁₄S₂Se₂⁺; calc. 625.720434).

(5*Z*,11*Z*)-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 (¹H-NMR). This product completely decomposed during attempted purification by CC or crystallization. ¹H-NMR (selected signals): 2.63–2.69 (*m*, CH₂S); 4.54–4.61 (*m*, CH₂S); 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/CH₂Cl₂. 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

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 ₂ Cl ₂
Empirical formula	C ₂₄ H ₂₀ S ₂ Se ₂
Formula weight [g mol ⁻¹]	530.34
Crystal color, habit	yellow, prism
Crystal dimensions [mm]	0.10 × 0.10 × 0.23
Temp. [K]	160(1)
Crystal system	monoclinic
Space group	C2/c
Z	8
Reflections for cell determination	12146
2θ Range for cell determination [°]	5–61
Unit cell parameters:	
<i>a</i> [Å]	26.2131(5)
<i>b</i> [Å]	14.4025(3)
<i>c</i> [Å]	12.0823(2)
β [°]	99.6333(18)
<i>V</i> [Å ³]	4497.17(15)
<i>D_x</i> [g cm ⁻³]	1.566
μ(MoK _α) [mm ⁻¹]	3.480
Scan type	<i>ω</i>
2θ _(max) [°]	60.7
Transmission factors (min; max)	0.711; 1.000
Total reflections measured	28288
Symmetry-independent reflections	6258
Reflections with <i>I</i> > 2σ(<i>I</i>)	5019
Reflections used in refinement	6258
Parameters refined	253
Final <i>R</i> (<i>F</i>) [<i>I</i> > 2σ(<i>I</i>) reflections]	0.0265
<i>wR</i> (<i>F</i> 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
Δρ (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 $\sum w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was not applied. There are two voids of 174 Å³ 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 H₂O molecule. However, neither inclusion of a H₂O 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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