Synthesis and Trapping of Transient 1,2-Diselones To Yield 1,4-Diselenin Derivatives: Calculated Structures of 1,2-Diselones, 1,2-Diselenetes and Their Sulfur Analogues

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Abstract: Two conceptually different routes to transient 1,2-diselones are reported: 1) via ring fragmentation of the 1,4,2-diselenazine system **6**, and 2) by the tributylphosphane-induced depolymerisation of the shelf-stable organoselenium polymer **15**. Evidence for the intermediacy of 1,2-diselone species **7** and **16** is provided in both cases by in situ trapping with dimethyl acetylenedicarboxylate (DMAD) to yield 1,4-diselenin derivatives. The route via **15** is especially expedient and trapping of **16** is efficient. Subsequent reactions of adduct **17** afford [1,2-ethanediylbis(diphenylphosphane)][5,6-bis(methoxycarbonyl)-1,4-diselenin-2,3-dithiolato]nickel(IV) (**20**). Theoretical calculations at Hartree–Fock (HF) and Møller–Plesset electron-correlated levels (MP2) suggest that the cyclic 1,2-diselenete structure **7c** is significantly more stable than the acyclic 1,2-diselone structure **7a**. For the bicyclic system **16**, the difference in energy between the cyclic and acyclic structures is considerably reduced due to the conformational rigidity imposed by the fused 1,3-dithiole ring. In contrast, the acyclic structures of the 1,2-dithione analogues **13a** and **25a** are computed to be more stable than their corresponding cyclic 1,2-dithiete structures **13c** and **25c**.

Keywords: ab initio calculations · Diels–Alder reactions · 1,4-diselenin · 1,2-diselone · rearrangements

Introduction

The synthesis of unusual organoselenium heterocycles, especially by cycloaddition chemistry of reactive N=Se[1] and C=Se[2] bonds, has recently attracted attention. However, in contrast to the well-documented synthesis of 1,4-dithiins by Diels–Alder reactions of 1,2-dithiones,[3] prior to our investigations no examples of 1,2-diselones as 4π components in Diels–Alder reactions had been reported.[4] This is primarily due to the very limited number of methods which are available for the synthesis of C=Se bonds. (The selenium analogues of P_4S_{10} and Lawesson's reagent are very unstable and/or difficult to handle).[5] Moreover, $R_2C{=}Se$ units are less stable than their $R_2C{=}S$ counterparts, although selenoketones and selenoaldehydes are known to participate readily as 2π components in Diels–Alder reactions.[2a, 2c]

Results and Discussion

Synthesis: In considering suitable precursors to 1,2-diselone species, we drew on our recent experience of generating 1,2-dithiones by thermally induced fragmentation of 1,4,2-dithiazine derivatives.[6, 7] The unknown 1,4,2-diselenazine ring system was, therefore, an attractive target.[8] The stable 1,3-diselenolium cation salt **1** was available as an appropriate starting material.[9] Dropwise addition of aqueous ammonia to a mixture of cation salt **1** and an excess of iodine in acetonitrile at room temperature, led to the formation of the stable hydrazone derivative **3** (90% yield) (Scheme 1) presumably resulting from nitrogen insertion into the exocyclic carbon–nitrogen bond in intermediate **2**; none of the desired ring-expanded product **6** was detected in the reaction mixture. However, the reaction followed a different course when the order of addition of iodine and ammonia was reversed (i.e. iodine was added to a mixture of **1** and ammonia): under these conditions, the major product was the target 1,4,2-diselenazine derivative **6** (ca. 40% yield) alongside the hydrazone derivative **3** (ca. 20% yield). When ammonia and iodine were added simultaneously to a solution of **1** in acetonitrile, compound **6** was not observed: instead, the product mixture contained hydrazone **3** (16%), dimethylcyanamide **8** (5%) and 2,3,5,6-tetramethyl-1,4-diselenin **9** (5%) (Scheme 1).

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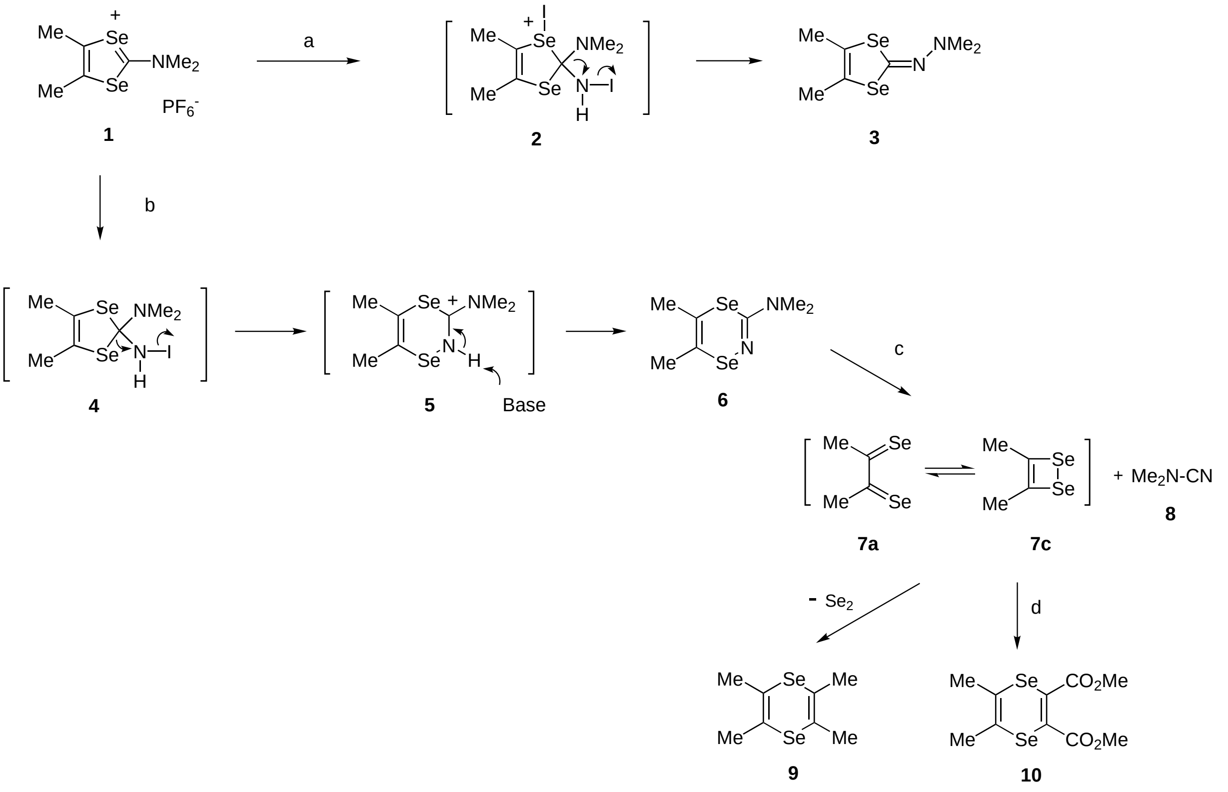


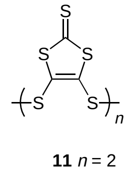
Scheme 1. Generation and trapping of intermediate 7. a) I_2, then NH_4OH (aq.), MeCN, 20 °C; b) NH_4OH (aq.) then I_2, MeCN, 20 °C; c) NH_4OH (aq.) and I_2 added simultaneously, MeCN, 20 °C; d) DMAD, 20 °C.

It is clear, therefore, that, unlike the analogous reactions of 1,3-dithiolium salts,[6] the products obtained from reaction of **1** with the iodine/ammonia system are very sensitive to the reaction conditions. A possible mechanism which accounts for the formation of these various products is shown in Scheme 1. The key step in the synthesis of the 1,4,2-diselenazine ring system **6** is formation of the selenium–nitrogen linkage, which most likely occurs by nucleophilic displacement of iodide ion from an intermediate adduct, such as **4**, formed from **1** and the NH_3/I_2 reagent. Cation **5** would then be deprotonated to afford the product **6**. The formation of hydrazone derivative **3**, which is favoured by the presence of an excess of iodine in the initial reaction mixture, could proceed via intermediate **2**, where the nucleophilicity of the selenium atoms has been reduced by a prior reaction of the 1,3-diselenole ring with iodine, for which there is precedent with inorganic selenium-containing heterocycles.[10]

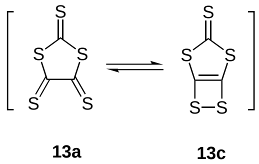
The formation of products **8** and **9**, albeit in very low yield, was significant as it gave us the first indication that an intermediate 1,2-diselone **7** may have been generated by in situ fragmentation of the 1,4,2-diselenazine ring **6**: compound **9** could be derived from **7** either by loss of one selenium atom followed by dimerisation,[11] or, less likely, by initial dimerisation of **7** to yield an eight-membered ring structure,[12] which could then lose two selenium atoms to afford **9**. Strong evidence to support the intermediacy of **7** was provided by a subsequent trapping experiment using dimethyl acetylenedicarboxylate (DMAD) as the dienophile. Addition of DMAD to a solution of **6** in acetonitrile at −5 °C resulted in no reaction; however, when the temperature of this mixture was raised to 20 °C, the novel 1,4-diselenin derivative **10** was isolated in 10% yield, after chromatographic separation from the unidentified decomposition products of **6**. Compound **6** is stable at −5 °C for several weeks (^1H NMR evidence) although upon storage at 20 °C it decomposes over a few days to yield a complex mixture of unidentified products, and this decomposition is greatly accelerated by addition of a mixture of ammonia and iodine (i.e. the conditions of its formation in Scheme 1).

The above route to 1,2-diselones has clear limitations: 1) the synthesis of the starting diselenolium salt **1** is not straightforward (it requires the use of hydrogen selenide) and 2) the instability of the 1,4,2-diselenazine system **6** (which contrasts markedly with the good shelf-stability of analogous 1,4,2-dithiazine derivatives)[6] presents practical difficulties in its purification and its controlled decomposition to 1,2-diselones. We, therefore, sought an entirely different approach to 1,2-diselone intermediates, and hence 1,4-diselenin derivatives, which would circumvent these problems.

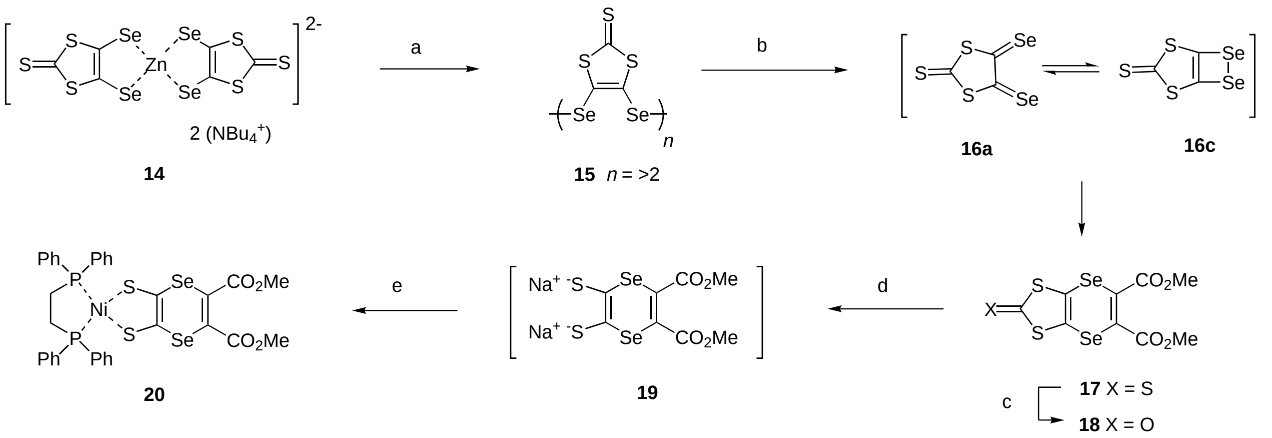
The synthesis of a range of 1,4-dithiins by Diels–Alder reactions of either the dimer **11**[13] or the oligomer/polymer **12**[14] of the C_3S_5 unit[15] has been previously reported, with the exocyclic 1,2,4-trithione **13** presumed to be the reactive



11 $n = 2$
12 $n = >2$



13a **13c**



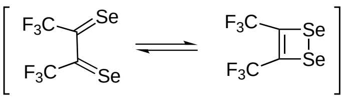
Scheme 2. Generation and trapping of intermediate **16**. a) Iodine (2.1 equiv), ethanol/acetone −50 to 20 °C; b) *n*Bu$_3$P (cat), DMAD (2 equiv), CH$_2$Cl$_2$, 20 °C; c) Hg(OAc)$_2$, CHCl$_3$/CH$_3$COOH (3:1 v/v), 20 °C; d) NaOMe (2 equiv), MeOH, 20 °C; e) NiCl$_2$(dppe), 20 °C.

intermediate species. We therefore investigated the exocyclic selenium-containing analogue of polymer **12** as a possible precursor to a diselone. The starting material for this route was the salt (NBu$_4$)$_2$[Zn(dsit)$_2$] (dsit = 1,3-dithiole-2-thione-4,5-diselenolate) (**14;** Scheme 2)[16] which was easily prepared on a multi-gram scale employing the more reactive red form of selenium.[16c] Oxidation of **14** with iodine in ethanol/acetone at −50 °C smoothly afforded, in excellent yield, a highly insoluble, air-stable compound, which analysed as (C$_3$S$_3$Se$_2$)$_n$, consistent with the oligomeric/polymeric structure **15**. The analysis and reactivity of this material were unchanged by storage in a sealed container at 20 °C for at least three months. The generation and reactivity of species **16** is shown in Scheme 2.

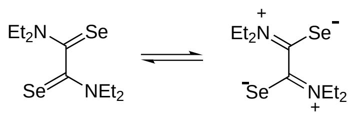
Treatment of **15** with tributylphosphane in dichloromethane at 20 °C in the presence of excess DMAD afforded the bicyclic 1,4-diselenin derivative **17** in 57 % yield, possibly via the intermediacy of the highly reactive 1,2-diselone **16**. Alternatively, the reacting species could be a tributylphosphane complex of **16**, or a selenide anion could attack DMAD in a Michael fashion, to produce an intermediate carbanion, and then **17**. The use of tributylphosphane to depolymerise **15** was vastly preferable to the usual method employed for the sulfur analogue (C$_3$S$_5$)$_n$ **12**, which is heated in a solvent such as benzene, toluene, dioxane or chlorobenzene:[14] using these thermal conditions with **15** led to poor yields of adduct **17**, which was contaminated with a variety of unidentified products. The fused trithiocarbonate group of **17** is suitable for further synthetic transformations: conversion of the thione group into the oxo derivative **18** proceeded almost quantitatively on reaction with mercuric acetate in a mixture of chloroform and acetic acid.[17] Subsequent ring opening of the 1,3-dithiol-2-one unit of **18** was achieved by reaction with sodium methoxide in anhydrous methanol: the intermediate disodium salt of 5,6-bis(methoxycarbonyl)-1,4-diselenin-2,3-dithiolate (**19**) thereby formed was not isolated: it was allowed to react in situ with [NiCl$_2$(dppe)] (dppe = 1,2-(Ph$_2$P)$_2$C$_2$H$_4$) to afford the dark green dithiolene complex **20** in 66 % yield, the structure of which followed from elemental analysis and ^{1}H NMR spectroscopy. The analogous complexation of 1,4-dithiin-2,3-dithiolene units with nickel species has been previously reported both by Rauchfuss et al.[13] and Bereman et al.[18] but, to our knowledge, the 1,4-diselenin-2,3-dithiolene system is new.[19]

Theoretical studies

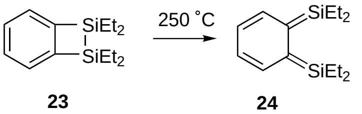
Whether 1,2-diselones exist as the acyclic diselone structure or as the cyclic 1,2-diselenete structure is a matter of interest which has received very scant attention in the literature. Electron diffraction experiments[20] clearly revealed that the cyclic 1,2-diselenete **21c** is favoured over the acyclic diselone structure **21a** in the case of F$_3$CC(Se)-C(Se)-CF$_3$. In the ground state the push–pull α-diselenoamide system **22** is best represented by the canonical structure **22′** (NMR and X-ray evidence).[21] Similar considerations of the relative energies of cyclic and acyclic structures stabilities pertain for certain organosilicon species: benzodisilacyclobutene **23** is a rather stable compound, which, however, can be involved in a



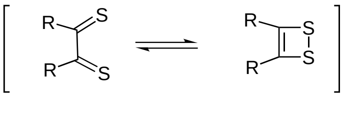
21a **21c**



22 **22'**



23 **24**



25a R = CH$_3$ **25c** R = CH$_3$
26a R = CF$_3$ **26c** R = CF$_3$

number of reactions at >250 °C producing *o*-quinodisilane **24** as a reactive intermediate species.[22] We, therefore, performed theoretical calculations on selenium compounds **7**, **16** and **21** as well as their sulfur analogues **25**, **13** and **26** by ab initio methods (HF, MP2).

Hartree–Fock calculations (HF/6-311++G**) show that cyclic diselenete **21c** is more stable (by 29.43 kcal mol^{-1}; Table 1) than the acyclic diselone **21a** which is in agreement with previous experimental data.[20] The calculated Se1–Se4 bond length in **21c** (2.370 Å; Figure 1) corresponds well to the electron diffraction data (2.367 Å[20]), whereas the calculated C2–C3 distance (1.324 Å) is shorter by 0.039 Å than the experimental value (1.363 Å). The latter results from a difference in the calculated and experimental Se1-C2-C3-Se4 dihedral angles (0.0° and 11.3°, respectively). A more accurate estimation of the total energies for **21a** and **21c** at the electron-correlated MP2 level (single point calculations for HF-optimised geometries) decreases their difference (ΔE_{a-c} = 20.25 kcal mol^{-1}) but the cyclic structure is still more stable. Similarly, for sulfur analogues **26a** and **26c** both HF level calculations and the addition of MP2 energies (single point) showed that cyclic structure **26c** more stable than acyclic structure **26a** (by +9.53 and +3.24 kcal mol^{-1}, respectively; Table 1, Figure 1) although the difference in the energies ΔE_{a-c} (**26**) is smaller than for the selenium analogue **21**.

Table 1. Total energies (E) for selenium-containing compounds **21**, **7**, **16** and their sulfur analogues **26**, **25**, **13**, and the differences in the energies for acyclic and cyclic structures (ΔE_{a-c}), from ab initio calculations at Hartree–Fock and electron-correlated Møller–Plesset (MP2) levels.

Method	E (acyclic) [au]	E (cyclic) [au]	ΔE_{a-c} [kcal mol^{-1}]
	21a	**21c**	**21a–21c**
HF/6-311+G*	−5547.84217	−5547.88907	+29.43
MP2/6-311++G**//HF/6-311++G**	−5549.86462	−5549.89690	+20.25
	26a	**26c**	**26a–26c**
HF/6-311+G*	−1543.33329	−1543.34847	+9.53
MP2/6-311++G**//HF/6-311++G**	−1545.36696	−1545.37213	+3.24
	7a	**7c**	**7a–7c**
HF/6-311G**	−4954.54519	−4954.56883	+14.83
HF/6-311++G**	−4954.54696	−4954.57136	+15.31
MP2/6-311++G**//HF/6-311++G**	−4955.38170	−4955.39942	+11.12
MP2/6-311++G**	−4955.38399	−4955.40258	+11.67
	25a	**25c**	**25a–25c**
HF/6-31G*	−949.95122	−949.94715	−2.55
HF/6-31++G**	−949.96433	−949.96103	−2.07
MP2/6-31++G**//HF/6-31++G**	−950.77707	−950.76895	−5.09
HF/6-311++G**	−950.03665	−950.03300	−2.29
MP2/6-311++G**//HF/6-311++G**	−950.88269	−950.87436	−5.23
	16a	**16c**	**16a–16c**
HF/6-311G*	−6105.74291	−6105.75611	+8.28
MP2/6-311G*//HF/6-311G*	−6106.80035	−6106.80067	+0.20
HF/6-311+G*	−6105.74920	−6105.76316	+8.76
MP2/6-311+G*//HF/6-311+G*	−6106.81378	−6106.81439	+0.38
MP2/6-311+G*	−6106.81573	−6106.81706	+0.83
	13a	**13c**	**13a–13c**
HF/6-31G*[a]	−2101.09731	−2101.07661	−12.99
MP2/6-31G*//HF/6-31G*[a]	−2102.18179	−2102.15268	−18.27
HF/6-311+G*	−2101.23641	−2101.21649	−12.50
MP2/6-311+G*	−102.31095	−2102.28340	−17.29

[a] Calculations were performed using HyperChem 5.02 (for Windows) software; other calculations were performed with Gaussian 94 software (see Experimental Section).

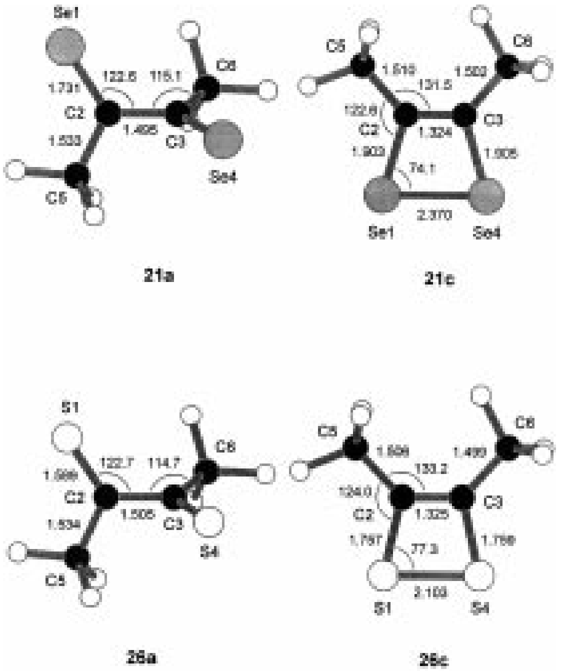


Figure 1. Geometry-optimised structures **21a, 21c, 26a** and **26c** (HF/6-311+G*); small open circles are fluorine atoms, C–F 1.303–1.316 Å. **21a**: Se1-C2-C3-Se4 101.2°, Se1-C2-C3-C6 77.1°; **26a**: S1-C2-C3-S4 102.0°, S1-C2-C3-C6 76.1°.

For compound **7**, the cyclic structure (**7c**) is more stable than the acyclic structure (**7a**), although the difference ΔE_{a-c} (**7**) is about half that of ΔE_{a-c} (**21**) at the corresponding levels of theory (HF or MP2; Table 1). The transformation of **6** into **10** almost certainly proceeds via **7a** as an intermediate in the [4+2] cycloaddition reaction with DMAD. However, formation of **9** could be interpreted in terms of a [4+2] hetero Diels–Alder reaction[23] between **7a** and **7c** followed by extrusion of two selenium atoms. The calculated relatively small difference in energies for **7a** and **7c** (ΔE_{a-c}(MP2) = +11.67 kcal mol^{-1}) suggests this is a realistic possibility. For compounds **7a** and **7c** full MP2 geometry optimisation was also performed and the results show only minor changes in the value of ΔE_{a-c} from MP2 single point energies for HF-optimised geometries (by 0.55 kcal mol^{-1}) confirming the adequate estimations of ΔE_{a-c} from MP2 (single point) calculations for **21** and **26**. HF calculations for the sulfur analogue **25** show that in this case acyclic structure **25a** becomes somewhat more stable (−2 to −5 kcal mol^{-1} depending on the level of calculation; Table 1) than cyclic structure **25c**. Generally, a similarity of conformations for cyclic structures (**7c, 21c, 25c, 26c**) and for acyclic structures (**7a, 21a, 25a, 26a**) is observed (Figure 1 and 2), for example, dihedral angles Se-C-C-Se (S-C-C-S) are about 0° and 100–160° for cyclic and acyclic structures, respectively.

Structures **16a** and **16c** and their sulfur analogues **13a** and **13c** (Figure 3) are more rigid molecules due to the fused five-membered 1,3-dithiole ring. Stabilisation of acyclic (**16a**, **13a**) versus cyclic (**16c, 13c**) structures would, therefore, be expected. Indeed, in the sequences **21**→**7**→**16**, and

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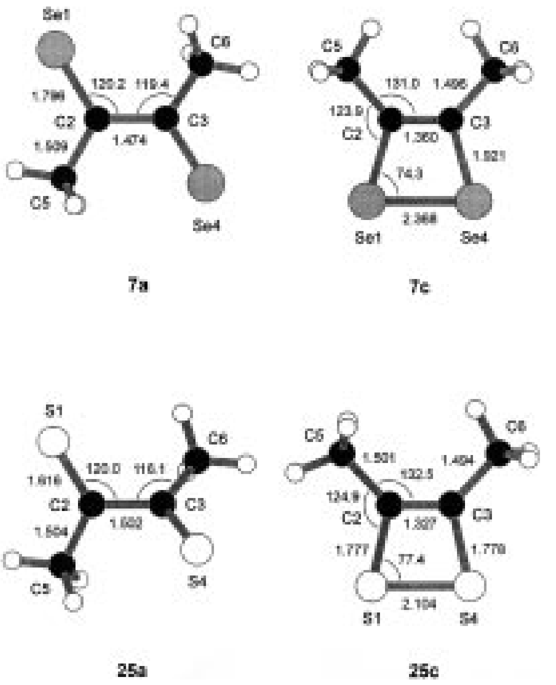

Figure 2. Geometry-optimised structures **7a** and **7c** (MP2/6–311 + G*), **25a** and **25c** (HF/6–311 + + G**); small open circles are hydrogen atoms, C–H 1.080–1.095 Å. **7a**: Se1-C2-C3-Se4 158.6°, Se1-C2-C3-C6 19.7°; **25a**: S1-C2-C3-S4 119.6°, S1-C2-C3-C6 59.4°.

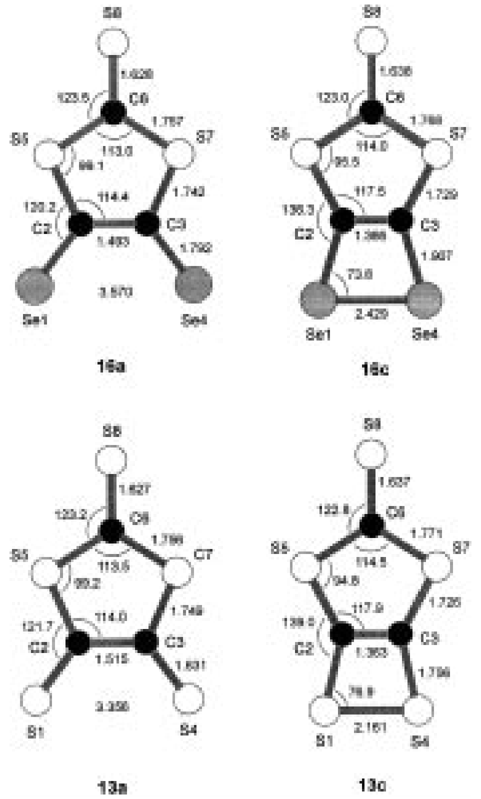

Figure 3. Geometry-optimised structures **16a, 16c, 13a** and **13c** (MP2/6–311 + G*).

26 →**25** →**13**, ΔE_{a-c} decreases (i.e., stabilisation of acyclic structures) and for **16** the acyclic and cyclic structures are of similar stability (the difference in energies $\Delta E_{a-c} = +0.83$ kcal mol^{-1} at the MP2 level; Table 1). So, from theoretical calculations (MP2) one can conclude that compound **16** can exist either as the acyclic (**16a**) or the cyclic (**16c**) structure. Increasing the stability of the acyclic structure for **16** as compared to **7** (ΔE_{a-c}(**16**) = +0.83 kcal mol^{-1}; ΔE_{a-c}(**7**) = +11.67 kcal mol^{-1}; Table 1) may be a contributing factor in the experimental observation of an increased yield in the reaction with DMAD (10 % for **6** →[**7a**] →**10** and 57 % for **15** →[**16a**] →**17**). The Se–Se distance in **16c** (2.429 Å) is somewhat longer than in **7c** (2.401 Å) (experimental X-ray Se–Se bond lengths vary from 2.315–2.361 Å[24]), whereas the C–Se bond lengths in **16c** are lower than in **7c** (1.907 and 1.921 Å, respectively; Figure 2 and 3) (experimental X-ray C(sp^2)–Se bond lengths are 1.882–1.902 Å[24]). Undoubtedly, both these changes are due to the effect of the annelated dithiole ring. For the sulfur analogue, computations show that acyclic structure **13a** is much more stable (by 17.29 kcal mol^{-1} at MP2/6-311 + G*) than cyclic structure **13c**, which is consistent with the results obtained by a number of research groups considering **13a** (and not **13c**) as a reactive intermediate formed from **11** and **12**.[13, 14]

Conclusion

In this work we have established two very different routes to 1,2-diselones with evidence for the intermediacy of species **7** and **16** being provided in both cases by the first in situ trapping reactions with DMAD to yield 1,4-diselenin derivatives. The route via the shelf-stable oligomeric/polymeric precursor **15** is especially expedient and trapping of **16** is efficient. We have demonstrated a new approach to highly-functionalised derivatives of the rare 1,4-diselenin ring system, and the products obtained offer scope for subsequent organic and organometallic reactivity. Theoretical calculations suggest that cyclic 1,2-diselenete structures are of lower energy than 1,2-diselone tautomers, whereas the acyclic structures of dithione analogues are of lower energy than the corresponding 1,2-dithiete structures.

Experimental Section

General details: ^{1}H NMR spectra were obtained on a Varian 400 spectrometer at 399.96 MHz; ^{13}C NMR spectra were obtained on a Varian 400 spectrometer at 100.58 MHz. Mass spectra were recorded on a VG7070E spectrometer operating at 70 eV. Infra-red spectra were recorded on a Perkin-Elmer 1615 FTIR operated from a Grams Analyst 1600. Elemental analyses were performed on a Carlo-Erba Strumentazione instrument. Melting points were obtained on a Kofler hot-stage microscope apparatus and are uncorrected. All reagents were of commercial quality and solvents were dried, where necessary, using standard procedures. All reactions were performed under an inert atmosphere of argon which was pre-dried by passing through phosphorus pentoxide.

Computational procedure: The computations were carried out using ab initio methods with the Gaussian 94[25] program; in some cases the HyperChem 5.02 package of programs[26] was also employed. Berni and Polak–Ribiere algorithms were used for geometry optimisations with Gaussian 94 and HyperChem 5.02, respectively. The geometries of compounds **7**, **13**, **16**, **21**, **25** and **26** were fully optimised at the Hartree–Fock level of theory using the 6-311 basis set (for comparison, compounds **13** and **25** were also optimised using the 6-31 basis set) supplemented by *d*-polarisation and diffuse functions on heavy atoms, as well as *p*-polarisation and diffuse functions on hydrogens (for **7**). In addition, for more accurate estimations of energies for acyclic versus cyclic structures the geometries of compounds **7**, **13** and **16** were fully optimised at the electron-correlated second-order Møller–Plesset level [MP2(full)]; for compounds **21**, **25** and **26** single-point calculations of MP2 energies were carried out for HF-optimised geometries. Spin-restricted formalism was used in all cases for both HF and MP2 calculations.

4,5-Dimethyl-1,3-diselenol-2-one *N*,*N*-dimethylhydrazone (3): To a mixture of cation salt **1**[9] (50 mg, 0.12 mmol) and iodine (46 mg, 0.18 mmol) in acetonitrile (100 mL) at 20 °C was added aqueous ammonia (5 mL). [**Caution**! Iodine/ammonia mixtures can be explosive]. The mixture slowly decolourised from black to orange-yellow and was then left to stir for 2 h. The mixture was poured into water (200 mL) and extracted with dichloromethane (2 × 50 mL). The organic extracts were dried ($MgSO_4$) and the solvent removed in vacuo to afford compound **3** (30 mg, 90 %) as a yellow solid m.p. 71–74 °C. ^1H NMR ($CDCl_3$): $\delta = 2.30$ (6H, s), 3.20 (6H, s); ^{13}C NMR ($CDCl_3$): $\delta =$ 20.39, 22.79, 41.58, 128.84, 135.84, 164.14; MS (EI): *m/z*: 284 (^{80}Se, 60 %) 269, 268, 214 (100 %) and 134; HRMS calcd. for $C_7H_{12}N_2Se_2$ 283.9331, found 283.9344; elemental analysis (%) calcd: C 29.80, H 4.29, N 9.93; found: C 29.50, H 4.40, N 10.34.

3-Dimethylamino-5,6-dimethyl-1,4,2-diselenazine (6): Salt **1** (150 mg, 0.36 mmol) was dissolved in acetonitrile (25 mL) containing aqueous ammonia (2 mL) at 20 °C. Iodine (138 mg, 0.54 mmol) was added. After stirring for 10 min, the mixture was poured into water (150 mL) and extracted with dichloromethane (3 × 50 mL). The organic extracts were combined, dried ($MgSO_4$), and the solvent removed in vacuo to yield an orange oil. Column chromatography on silica (eluent hexane:dichloromethane (2:1 v/v)) separated compound **6** as an unstable yellow oil (ca. 100 mg, 40 %) from compound **3** (20 %). Data for **6**: ^1H NMR ($CDCl_3$): $\delta =$ 2.31 (3H, s), 2.32 (3H, s), 3.32 (6H, s); ^{13}C NMR ($CDCl_3$): $\delta = 20.11$, 22.78, 41.65, 128.87, 135.55, 164.01; MS (CI): *m/z*: 285 (^{80}Se, 25 %), 204 (100 %); HRMS calcd. for $C_7H_{12}N_2Se_2$ 283.9331, found 283.9333.

2,3,5,6-Tetramethyl-1,4-diselenin (9): When ammonia (2 mL) and iodine (138 mg, 0.54 mmol) were added simultaneously to a solution of **1** (150 mg, 0.36 mmol) in acetonitrile under conditions described for the preparation of **6**, the products isolated were: hydrazone **3** (16 %), dimethylcyanamide **8** (5 %), and 2,3,5,6-tetramethyl-1,4-diselenin (**9**) as a yellow oil (10 mg, 5 %). Data for **9**: ^1H NMR ($CDCl_3$): $\delta = 2.10$ (6H); HRMS calcd. for $C_8H_{12}Se_2$ 267.9286, found 267.9286.

Dimethyl 5,6-dimethyl-1,4-diselenin-2,3-dicarboxylate (10): To a solution of **6** (50 mg, 0.12 mmol) in anhydrous acetonitrile (50 mL) at 20°C was added dimethyl acetylenedicarboxylate (69 mg, 0.48 mmol). The mixture was stirred for 16 h under argon, whereupon dichloromethane (20 mL) and silica gel (5 g) were added and the solvent was removed in vacuo to afford a slurry. Repeated column chromatography on silica gel using hexane:dichloromethane (3:1 v/v followed by 2:1 v/v) as the eluent furnished compound **10** (4.5 mg, 10 %) as a white solid; m.p. 102–104 °C; ^1H NMR ($CDCl_3$): $\delta = 3.85$ (6H, s) and 2.20 (6H, s); MS (EI) *m/z*: 355 (^{80}Se, 45 %), 263 (100 %), 214 (65 %) and 160 (20 %); HRMS calcd. for $C_{10}H_{12}O_4Se_2$ 355.9065, found: 355.9071.

Poly[seleno(2-thioxo-1,3-dithiol-4,5-diyl)seleno] (15): To a solution of zincate salt **14**[16c] (7.2 g, 6.37 mmol) in Analar acetone (30 mL) at −50 °C was added a solution of iodine (3.0 g, 13 mmol) in anhydrous ethanol (100 mL) with vigorous stirring over 30 min. The temperature was maintained at −50 °C for a further 15 min before being allowed to warm to 20 °C where it was maintained for 30 min. On completion of the reaction, the mixture was filtered and the solid obtained washed successively with water (3 × 250 mL), ethanol (250 mL) and diethyl ether (2 × 200 mL). The resultant brown solid was dried under high vacuum and afforded 3.25 g (87 %) of **15** as a highly insoluble powder. $(C_3S_3Se_2)_n$ (%): calcd: C 12.42; found: C 12.75.

Dimethyl 2-thioxo[1,4]diselenino[2,3-*d*]-1,3-dithiole-5,6-dicarboxylate (17): To a solution of polymer **15** (0.5 g) in anhydrous dichloromethane (20 mL) was added tri-*n*-butylphosphane (0.01 mL, catalytic; freshly distilled). The resultant suspension gradually changed to a brown solution over 10 min, whereupon dimethyl acetylenedicarboxylate (0.48 g, 0.4 mL, 3.4 mmol) was added in one portion and the mixture stirred at 20 °C for 16 h. Dichloromethane (200 mL) was added and the mixture was washed with water (2 × 100 mL) and brine (100 mL). The organic phase was dried ($MgSO_4$) and the solvent removed in vacuo to afford a yellow-brown solid. Column chromatography on silica gel using hexane:dichloromethane (1:1 v/v) as eluent separated a fast-running yellow product, which was recrystallised from methanol to give **17** (0.42 g, 57 %) as a yellow solid, m.p. 215–217 °C; ^1H NMR ($CDCl_3$): $\delta = 3.86$ (6H, s); ^{13}C NMR ($CDCl_3$): $\delta = 53.72$, 125.30, 136.15, 163.12, 216.32; MS (CI): *m/z*: 435 (^{80}Se, 25 %), 58 (100 %); IR (KBr): $\tilde{\nu}_{max} = 1723$, 1703, 1574, 1248 and 1049 cm^{-1}; $C_9H_6O_4S_3Se_2$ (%): calcd: C 25.00, H 1.40; found: C 25.28, H 1.45.

Dimethyl 2-oxo[1,4]diselenino[2,3-*d*]-1,3-dithiole-5,6-dicarboxylate (18): To a solution of thione **17** (0.43 g, 1 mmol) in acetic acid:chloroform (1:3 v/v, 40 mL) was added mercury(II) acetate (1.5 g, 5 mmol). The resultant suspension was stirred for 12 h at 20 °C, thence it was filtered, diluted with dichloromethane (100 mL), and washed successively with water (3 × 50 mL), 10 % aq. $NaHCO_3$ (2 × 50 mL) and brine (50 mL). The organic phase was dried ($MgSO_4$) and the solvent removed in vacuo to afford **18** (0.38 g, 93 %) as a white solid, m.p. 192–194 °C; ^1H NMR ($CDCl_3$): $\delta = 3.86$ (6H, s); ^{13}C NMR ($CDCl_3$): $\delta = 53.76$, 116.30, 135.75, 163.38, 194.46; MS (CI): *m/z*: 436 (^{80}Se, MNH_4^+, 100 %); IR (KBr): $\tilde{\nu}_{max} = 1732$, 1704, 1652, 1572, 1438, 1254 cm^{-1}; $C_9H_6O_5S_2Se_2$ (%): calcd. C 25.97, H 1.45; found C 26.03, H 1.41.

[1,2-Ethanediylbis(diphenylphosphane)][5,6-bis(methoxycarbonyl)-1,4-diselenin-2,3-dithiolato]nickel(IV) (20): To a solution of **18** (80 mg, 0.19 mmol) in anhydrous methanol (10 mL) was added sodium methoxide (20 mg, 0.38 mmol). The resultant solution turned orange over about 30 min, indicating the formation of dithiolate species **19** whereupon $[NiCl_2(dppe)]$ (dppe = $1,2-(Ph_2P)_2C_2H_4$) (100 mg, 0.19 mmol) was added in one portion. The solution rapidly turned green and was stirred for 16 h at 20 °C before the resultant solid was recovered by filtration. Recrystallisation of the solid from hot acetonitrile afforded **20** (105 mg, 66 %) as bright green crystals, m.p. > 250 °C; ^1H NMR ($[D_6]$DMSO): $\delta = 3.56$ (4H, t, $J =$ 7.8 Hz), 3.66 (6H, s), 7.55 (12H, m), 7.69 (8H, m); IR (KBr): $\tilde{\nu}_{max} = 1721$, 1566, 1434, 1242 cm^{-1}; $C_{34}H_{30}O_4P_2NiS_2Se_2$ (%): calcd: C 48.31, H 3.58; found: C 48.09, H 3.50.

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