Route towards diselenadiazafulvalenes

Zdenko Časar,[a] Patricia Bénard-Rocherullé,[b] Alenka Majcen-Le Maréchal[c] and Dominique Lorcy*[a]

[a] Synthèse et Electrosynthèse Organiques, UMR CNRS 6510, Université de Rennes 1 35042, Rennes cedex, France. E-mail: Dominique.Lorcy@univ-rennes1.fr
[b] Chimie du solide et inorganique moléculaire, UMR CNRS 6511, Université de Rennes 1 35042, Rennes cedex, France
[c] University of Maribor, Smetanova 17 2000, Maribor, Slovenija

The first diselenadiazafulvalene has been chemically synthesised and electrochemically characterised, it presents similar air sensitiveness to its sulfur analogue and affords a spiroamide derivative upon oxidation as confirmed by its crystal structure.

Among the numerous π-donor molecules described in the literature as precursors of organic materials various heterocyclic derivatives have been studied, mainly conjugated frameworks including sulfur atoms, such as tetrathiafulvalene (TTF).[1] Several modifications of the TTF skeleton have been performed, for example replacement of two sulfur atoms by nitrogen atoms has led to dithiadiazafulvalene (DTDAF) derivatives which have recently attracted attention owing to their high electron donating properties.[2] DTDAFs present the disadvantage of being air-sensitive in the neutral form but they can be trapped *in situ* by organic or inorganic acceptors and form molecular materials.[3] As the physical properties of organic materials are close-knit to molecular assembly, it was thus of interest to replace the sulfur atoms by selenium atoms, in order to increase the interactions between the donor cores. Otherwise diselenadiazafulvalene (DSeDAF) should exhibit properties close to DTDAF. Herein, we report the synthesis and the electrochemical behaviour of the first DSeDAF, namely benzo-DSeDAF, starting from selenazole moieties.
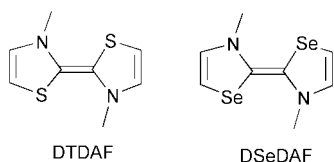

Compared to the chemistry carried out on 1,3-thiazole ring systems, 1,3-selenazole derivatives have been scarcely studied recently. Indeed, and as pointed out by Bogert *et al.*, selenazole derivatives are rather more difficult to prepare and less stable than their sulfur analogues.[4] Our approach for the synthesis of the 1,3-selenazole core consists of the preparation of bis(*o*-nitrophenyldiselenide) **1** starting from *o*-nitroaniline.[5]

We improved the chemical pathway to prepare benzo-1,3-selenazole-2(3*H*)-thione **2** by reaction of bis(*o*-nitrophenyldiselenide) **1** with sodium hydrosulfide in basic medium followed by the addition of carbon disulfide as described in Scheme 1.[6] Alkylation of **2** in the presence of base and methyl iodide led to 2-methylthiobenzo-1,3-selenazole **3**.[7] Preparation of the sulfur analog of **4**, the 3-alkylbenzo-1,3-thiazole-2(3*H*)-thione by rearrangement of 2-alkylthiobenzo-1,3-thiazole in the presence of a catalytic amount of iodine has been described.[8] Thus, we investigated the possibility of forming 3-methylbenzo-1,3-selenazole-2(3*H*)-thione **4** using the same strategy starting from **3**. Heating a mixture of **3** with iodine at 200–220 °C gave **4** in 67% yield (Scheme 1). Selenazole-2(3*H*)-thione **4** does not undergo intermolecular coupling by treatment with tertiary phosphorus derivatives. Therefore, we converted **4**,
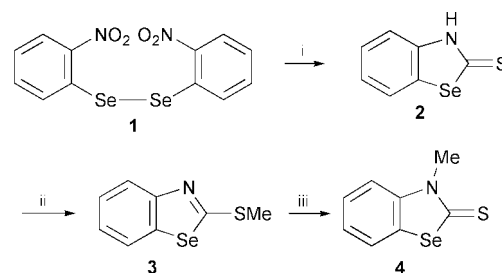
Scheme 1 *Reagents and conditions*: i, NaSH, NaOH, CS_2, H_2O, reflux, 90%; ii, MeI, NEt_3, CH_2Cl_2, rt, 93%; iii, I_2, 200–220°C, 67%.

in the presence of boron trifluoride diethyl etherate and triethyl orthoformate into 2-alkylthiobenzo-1,3-selenazolium salts **5**, following literature precedent for thiazole derivatives.[2] Another method for the preparation of this salt **5** utilises the alkylation of **3** with methyl iodide (Scheme 2).
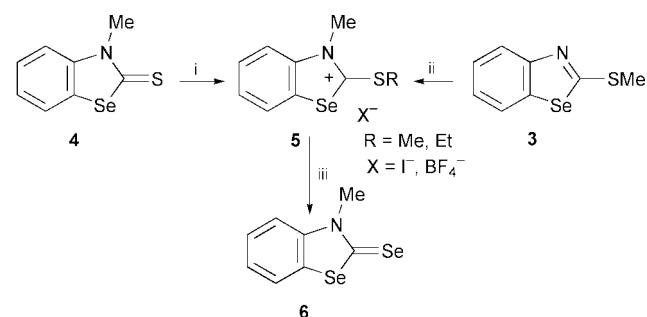
Scheme 2 *Reagents and conditions*: $BF_3·Et_2O$, $CH(OEt)_3$, $CHCl_3$, reflux, 97%; ii, MeI, reflux, 81%; iii, NaHSe, EtOH, rt, 95%.

Then, we treated 2-alkylthiobenzo-1,3-selenazolium salts **5** with sodium hydrogen selenide and we isolated the 3-methylbenzo-1,3-selenazole-2(3*H*)-selone **6**.† Coupling of **6** in the presence of triethyl phosphite in refluxing toluene under an inert atmosphere afforded DSeDAF **7**. Formation of this novel π-donor molecule can be observed by the important change of colour of the medium, due to the formation of a conjugated framework (Scheme 3).

Presence of electroactive species can be confirmed by cyclic voltammetry directly on the medium where the donor was formed.[9] Therefore after the chemical coupling of **6** in the presence of triethyl phosphite we added, under inert atmosphere, a degassed solution of tetrabutylammonium hexafluorophosphate in CH_2Cl_2 and we performed electrochemical investigations. Two reversible monoelectronic waves are observed at low potentials on the cyclic voltammogram and are associated with the redox behaviour of the DSeDAF formed in the medium. They correspond respectively to the formation of the radical cation and dication of **7** ($E_{pa1} = -0.07$ V and $E_{pa2} = +0.09$ V *vs* SCE) and indicate an extremely good donor character of benzo-DSeDAF. These oxidation potentials are

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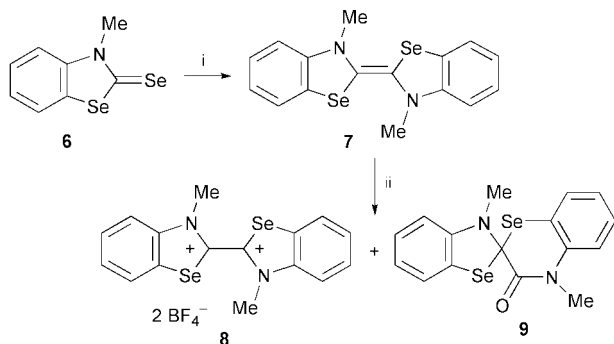
Scheme 3 *Reagents and conditions*: i, P(OEt)$_3$, toluene, reflux; ii, AgBF$_4$, THF, rt.

slightly higher than the one observed for the benzo-DTDAF[10] also obtained *in situ* following the same experimental procedure (E_{pa1} = −0.15 V and E_{pa2} = +0.05 V *vs* SCE). In order to prepare the dicationic salt of benzo-DSeDAF, chemical oxidation was performed by adding a solution of AgBF$_4$ in the medium where **7** was formed. The first dicationic, benzo-DSeDAF **8**, was obtained as its BF$_4$ salt together with a minor amount of a neutral compound (Scheme 3). ^{1}H NMR data and X-ray crystal structure determination of the latter proved this compound to be the spiroamide **9**.‡ As shown Fig. 1, the 4-methylbenzo-2*H*-1,4-selenazin-3(4*H*)-one ring is folded along the Se2–C4 vector, where the angle between the planes formed by Se2, C3, C7, N2, C4 and Se2, C1, C4 is 122.3 (2)° and N2 lies 0.200(3)Å from the first plane. The benzoselenazole system is not planar owing to a slight fold along the Se1–N1 vector leading to a torsion angle of 155.3(3) ° between the two planes formed by Se1, C2, C6, N1 and Se1, C1, N1, respectively.

The behavior of **7** is closely related to what was observed with its sulfur analogue the benzo-DTDAF. Indeed, in the presence of air benzo-DTDAF is easily oxidised and converted
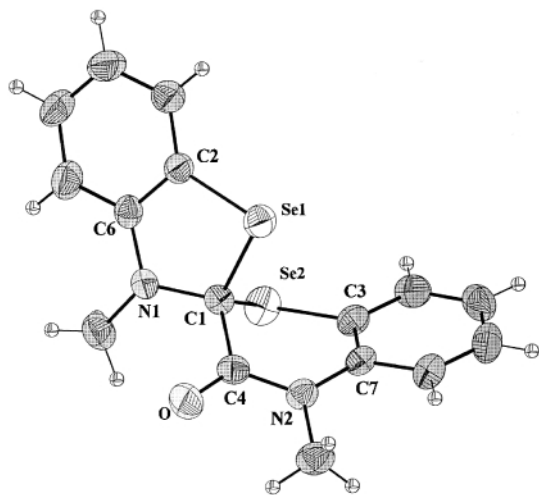
into the spiro amide derivative or further into a ten-membered ring compound.[11–13]

In summary, a novel heterocyclic donor has been synthesised, namely the benzo-DSeDAF, opening a route to a new family of π-donor molecules. This derivative exhibits similar redox behaviour and air-sensitivity to its sulfur analogue. Work is currently in progress in order to trap this derivative with appropriate acceptors and to analyse the potentialities of this new type of donor.

Notes and references

† Selected data for **6** (which was prepared in a scale up to 1.2 g): yellow crystals, mp 100 °C; δ_H(CDCl$_3$) 3.97 (s, 3H), 7.28–7.69 (m, 4H); Elemental analysis: calcd.for C$_8$H$_7$NSe$_2$: C, 34.93; H, 2.57; N, 5.09. Found: C, 35.08; H, 2.55; N, 4.72%; for **8**: colorless powder, δ_H(CD$_3$CN) 4.12 (s, 6H), 7.78–8.55 (m, 8H); for **9**: colorless crystals, mp 193 °C; δ_H(CDCl$_3$) 3.07 (s, 3H), 3.47 (s, 3H), 6.51–6.63 (m, 1H), 6.70–6.83 (m, 1H), 6.95–7.41 (m, 6H).

‡ Crystal data for compound **9** C$_{16}$H$_{14}$N$_2$OSe$_2$, *M* = 408.21, monoclinic, space group *P*2$_1$/*c*, *a* = 5.883(5), *b* = 15.922(5), *c* = 16.188(5) Å, *β* = 98.954(5)°, *U* = 1497.8(14) Å^3, *Z* = 4, *T* = 293(2) K, *μ*(Mo-Kα) = 4.94 mm^{-1}, D_c = 1.810 g cm^{-3}, 19344 reflections measured, of which 4370 independent (R_{int} = 0.0911) R_f = 0.054 [2906 data, *I* > 2σ(*I*)], *wR*(*F*^{2}) = 0.148. The largest residual density peak (1.45 e Å^{-3}) is located close to the Se2 atom (0.94 Å). CCDC 164964. See http://www.rsc.org/suppdata/cc/b1/b101757h/ for electronic files in .cif or other format.

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Fig. 1 Molecular structure of spiroamide **9** (50% displacement ellipsoids).