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Stable 1*H*-Benzo[*c*]thio- and 1*H*-Benzo[*c*]selenophen-2-ium Tetrafluoroborates: Insight into Electronic Structures, Electrochemical Behavior, and Reactivity

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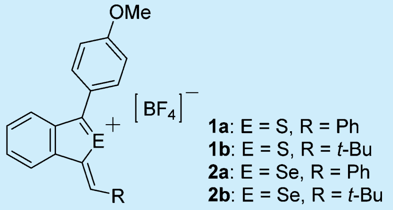
Supporting Information

ABSTRACT: The synthesis of 1*H*-benzo[*c*]thio- and 1*H*-benzo[*c*]selenophen-2-ium tetrafluoroborates by the reaction of triphenylcarbenium tetrafluoroborate with 1-ethylidene-1,3-dihydrobenzo[*c*]thiophene or 1-ethylidene-1,3-dihydrobenzo[*c*]selenophene, respectively, is reported. The electronic structure of these novel 1*H*-benzo[c]chalcogenophenium salts was examined on the basis of their electronic spectra, whereby transitions were assigned in agreement with theoretical calculations. Electrochemical measurements revealed irreversible one-electron reduction waves for these 1*H*-benzo[*c*]chalcogenophenium salts.



Benzothiophene and its selenium congener, benzoselenophene, represent one of the most fundamental classes of molecules in the field of organic chemistry. The chemistry of benzothiophenes in particular has received much attention, as they not only represent fascinating synthetic building blocks for new organosulfur compounds, but potentially also offer promise for functional electronic devices such as organic field-effect transistors or light-emitting devices.[1−7]

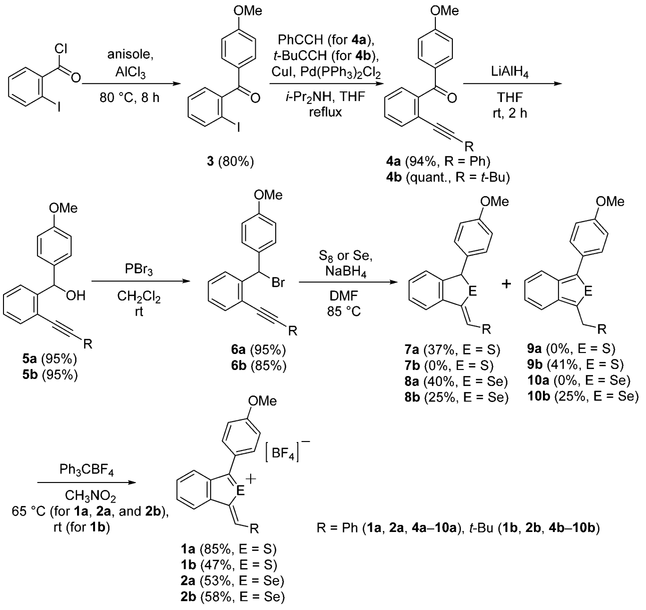
On the other hand, several papers have been published on the synthesis of *S*-alkyl- or *S*-arylthiophenium salts,[8−23] and some of these compounds have known to be present among electrophilic alkylation or arylation reagents toward aromatics and heteroaromatics. However, in contrast to the chemistry of benzothiophenes, synthetic investigations of thiophenium as well as selenophenium still remain limited.

As far as superior properties of organic electronic devices based on benzochalcogenophenes are concerned,[1,2,4−7] 1*H*-benzochalcogenophenium salts are promising candidates for molecular electronics. Disclosing their properties in photophysics and electrochemistry is extremely fascinating from the viewpoint of not only fundamental chemistry but also developing molecular electronics.

Herein, we present studies on (i) the synthesis of the novel 1-alkylidene-1*H*-benzo[*c*]thio- and 1-alkylidene-1*H*-benzo[*c*]selenophen-2-ium tetrafluoroborates **1a**−**2b**, (ii) their electronic structures probed by various experimental methods and theoretical calculations, (iii) their electrochemical properties, and (iv) reactivity toward 1,3-butadiene.

The synthetic strategy toward these novel 1-alkylidene-1*H*-benzo[*c*]chalcogenophen-2-ium salts was based on the synthesis of 1,3-dihydroisobenzochalcogephenes by intramolecular 5-*exo* cyclizations of 2-alkynylphenyl-(4-methoxyphenyl)-methanechalcogenolate, followed by hydride abstraction reactions with triphenylcarbenium salt. In order to gain synthetic access to **1a**−**2b**, we modified the synthetic procedure for 2-benzoselenopyrylium salts reported by Sashida and co-workers,[24,25] which is outlined in Scheme 1. A Friedel−Crafts acylation of anisole with 2-iodobenzoyl chloride furnished 2-iodobenzophenone **3** in 80% yield. A subsequent Sonogashira coupling of **3** with phenylacetylene or 2,2-dimethylbut-1-yne in the presence of copper iodide and a palladium catalyst afforded **4a** or **4b** in 94% or quantitative yield, respectively. Reduction of **4a** and **4b** with $LiAlH_4$ provided both **5a** and **5b** in 95% yields,

Scheme 1. Synthesis of 1*H*-Benzo[*c*]thio- and 1*H*-Benzo[*c*]selenophen-2-ium Tetrafluoroborates 1a−2b



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which reacted smoothly with PBr_3 at room temperature to afford the corresponding benzyl bromides **6a** and **6b** in 95% and 85% yields, respectively. Treatment of **6a** with NaSH or NaSeH followed by sequential cyclization reactions yielded the corresponding 1-benzylidene-3-(4-methoxyphenyl)-1,3-dihydroisobenzothiophene **7a** (37%) and selenophene **8a** (40%), respectively. The molecular structure of **8a** was confirmed by X-ray crystallographic analysis (Figure 1).[26] The corresponding 6-*endo*-cyclized products, 1*H*-isothio- and 1*H*-isoselenochromenes, were not detected in the reaction mixture, which is in sharp contrast to the results reported by Sashida and coworkers.[24,25] In the case of compound **6b**, the reaction with NaSH or NaSeH afforded benzo[*c*]thiophene **9b** in 41% yield and a 1:1 mixture of 1-alkylidene-1,3-dihydroisobenzoselenophene **8b** and benzo[*c*]selenophene **10b** in 50% total yield. In a final step, the reactions of **7a**, **8a**, and **8b** with $[Ph_3C][BF_4]$ in nitromethane furnished 1-benzylidene-1*H*-benzo[*c*]thiophenium and 1*H*-benzo[*c*]selenophenium tetrafluoroborates **1a**, **2a**, and **2b** in 85%, 53%, and 58% isolated yields, respectively. Hydride abstraction of benzo[*c*]thiophene **9b** using $[Ph_3C][BF_4]$ also proceeded in the formation of 1*H*-benzo[*c*]thiophenium tetrafluoroborate **1b** as orange crystals in 47% yield. Crystalline **1a**–**2b** do not show any signs of decomposition under atmospheric conditions and are moreover thermally stable under an inert atmosphere of argon (their melting or decomposition temperatures are shown in the SI).

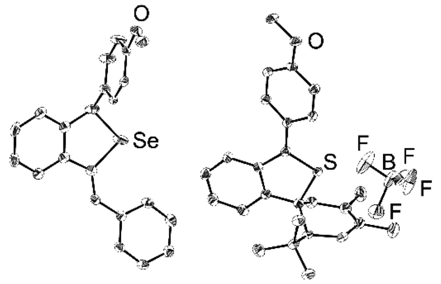

Figure 1. Molecular structure of **8a** (left) and **11b** (right) with thermal ellipsoid plots (50% probability). All hydrogen atoms are omitted for clarity.

The ^{1}H NMR spectra of **7a**, **8a**, and **8b** in $CDCl_3$ showed singlet signals at 5.93/7.15 ppm (**7a**), 6.11/7.56 ppm (**8a**), and 6.61/5.97 ppm (**8b**) for the H3 and H4 hydrogen atoms (Figure 2). In contrast, 1-alkylidene-1*H*-benzo[c]-chalcogenophenium tetrafluoroborates **1a**, **2a**, and **2b** revealed the corresponding singlet resonances for the H4 hydrogen atoms at 8.96, 8.97, and 8.30 ppm, respectively. The deshielded resonances of **1a**, **2a**, and **2b** relative to **7a**, **8a**, and **8b** can mostly likely be attributed to the character of the heterobutadiene subunit containing a sulfonium or selenonium cation.

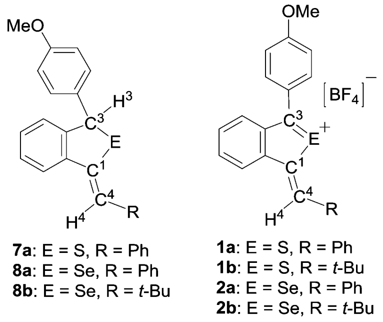

Figure 2. Chemical structures of compounds **7a**–**8b** as well as **1a**–**2b**.

The ^{13}C NMR spectra of **7a**, **8a**, and **8b** exhibited signals for the C3 carbon atoms at 55.3 ppm (**7a**), 52.0 ppm (**8a**), and 51.4 ppm (**8b**), the latter two of which exhibited satellite peaks ($^{1}J_{CSe}$ = 54.8 Hz for **8a**, $^{1}J_{CSe}$ = 54.7 Hz for **8b**) arising from coupling between carbon and selenium. Moreover, the characteristic signals at 144.4/130.0 ppm (**7a**) and 138.1/128.1 ppm (**8a**) were assigned to the C1 and C4 carbon atoms. In selenium analogue **8a**, these signals were accompanied by ^{77}Se satellites with $^{1}J_{CSe}$ = 112 Hz, $^{2}J_{CSe}$ = 11.7 Hz (for **8a**). Conversely, 1-alkylidene-1*H*-benzo[*c*]chalcogenophenium tetrafluoroborates **1a**, **2a**, and **2b** showed signals at 197.2, 212.6 ($^{1}J_{CSe}$ = 210 Hz), and 212.8 ppm ($^{1}J_{CSe}$ = 257 Hz), respectively. The $^{1}J_{CSe}$ coupling constants of **2a** and **2b** are larger than that of the corresponding monocyclic selenopyrylium tetrafluoroborate ($^{1}J_{CSe}$ = 155.4 Hz) and smaller than those of selenocarbonyl compounds such as $t\text{-}Bu_2C{=}Se$ ($^{1}J_{CSe}$ = 213.6 Hz) or selenofenchone ($^{1}J_{CSe}$ = 220.8 Hz).[27−29] However, it is comparable to those of selenoamides[30] and selenoesters ($^{1}J_{CSe}$ = 202−211 Hz),[27−29] suggesting a partial double-bond character for the C3−Se bond in **2a** and **2b**.

The ^{77}Se NMR spectra of **8a** and **8b** in $CDCl_3$ exhibited a doublet of doublets at 472.4 ppm (J_{HSe} = 13.7/13.4 Hz) and 531.5 ppm (J_{HSe} = 16.8/14.0 Hz), while **2a** and **2b** in CD_3CN showed only one doublet at 746.0 ppm ($^{3}J_{HSe}$ = 17.9 Hz) and 739.9 ppm ($^{3}J_{HSe}$ = 21.9 Hz), respectively. The observed chemical shift of **2a** and **2b** is characteristic for heterocycles containing a selenium atom, e.g., selenophene (δ_{Se} = 613),[31] and slightly upfield shifted relative to the parent selenopyrylium perchlorate (δ_{Se} = 976 in CF_3CO_2D),[32] selenopyrylium tetrafluoroborate (δ_{Se} = 975.7 in CD_3CN),[25] or 3-*tert*-butyl-2-benzoselenopyrylium tetrafluoroborate (δ_{Se} = 890 in CD_3CN).[25] Moreover, the chemical shift of the selenium analogues is low-field shift as compared with those of selenonium salts (δ_{Se} = 256 for $Me_3Se^{+}I^{-}$), selenonium ylides, and selenoamides. The coupling constants of **2a** ($^{3}J_{HSe}$ = 17.9 Hz) and **2b** ($^{3}J_{HSe}$ = 21.9 Hz) are slightly larger than those of previously reported heterocycles (2.3–16 Hz) and similar to those of compounds containing an $sp^2C{-}Se$ bond, e.g., PhSeSePh (19 Hz) or benzo[*b*]selenophene (21 Hz).[27] Accordingly, the multinuclear NMR analysis clearly confirmed their molecular structures of 1*H*-benzo[c]chalcogenophenium tetrafluoroborates **1a**–**2b** in solution.

In order to examine the electronic structure of **1a**–**2b**, their UV–vis absorption spectra were measured (Figure 3), and the

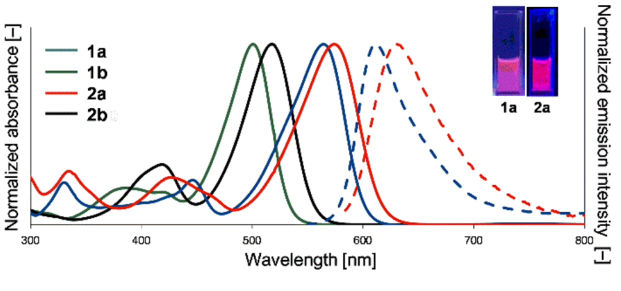

Figure 3. UV–vis absorption (solid line) and emission (broken line) spectra of 1-alkylidene-1*H*-benzo[c]chalcogenophenium tetrafluoroborates **1a**–**2b** in CH_2Cl_2 at room temperature. Inset: photographs of CH_2Cl_2 solution of **1a** and **2a** (concentration: 2.5×10^{-5} mol/L for **1a**, and 2.0×10^{-5} mol/L for **2a**) upon irradiation with UV light (365 nm).

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photophysical parameters are summarized in Table 1. Commensurate with the large absorption coefficients, the absorption maxima at 565 (**1a**), 572 (**2a**), 501 (**1b**), and 518 nm (**2b**) were assigned to the π−π^* electron transitions of the 1*H*-benzo[*c*]chalcogenophenium chromophore. The successively larger bathochromic shifts (**2a** > **1a**, **2b** > **1b**) indicate that the introduction of consecutively heavier group 16 atoms in the heterobutadiene system results in a decrease of the HOMO−LUMO energy gap.

Table 1. Photophysical and Electrochemical Data of 1-Alkylidene-1*H*-benzo[*c*]chalcogenophenium Tetrafluoroborates 1a−2b in CH_2Cl_2

compd	absorption λ (nm)	absorption ε (M^{-1} cm^{-1})	emission λ (nm)	Stokes shift (cm^{-1})	E_{pc}
1a	565	50600	612	1390	−0.55
2a	572	45300	631	1570	−0.39
1b	501	22100			−0.53
2b	518	29300			−0.51

Figure 3 shows the emission spectra of **1a** and **2a** in CH_2Cl_2, which exhibited emission maxima at 612 (**1a**) and 631 nm (**2a**).[33] The emission energies were found to decrease in the order **1a** > **2a**, whereby the Stokes shifts of **1a** and **2a** were found to be comparable.

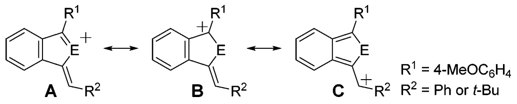
In order to gain further insight into the electronic structures of **1a**−**2b**, theoretical calculations were carried out on model compounds **1a′**−**2b′**, in which the tetrafluoroborate anions were omitted.[34,35] In **1a′**−**2b′**, the LUMO is delocalized over the entire molecular framework, whereas the HOMO is predominantly localized on the 1-alkylidene-1*H*-benzo[*c*]-chalcogenophenium moieties including the anisyl group (Figures S3−S6). An assignment of the absorption maxima in the UV−vis spectra was based on TD-DFT calculations of **1a′**−**2b′** at the B3LYP/6-311+G(d,p) level of theory. The lowest energy absorption maxima of **1a**−**2b** should accordingly be assigned to symmetry-allowed π−π^* electron transitions (HOMO−LUMO). The HOMO−LUMO transition energies of **1a′**−**2b′** are expected to decrease monotonically in the order **1a′** > **2a′**, **1b′** > **2b′** (Table 2), which is in good agreement with the experimentally observed results.

Table 2. Calculated Molecular Orbital Energy Levels and First Excited-State Energies for 1-Alkylidene-1*H*-benzo[*c*]chalcogenophenium Cations 1a′−2b′

compd	HOMO (eV)	LUMO (eV)	HOMO−LUMO (eV)	transition energy (eV) (λ (nm))	*f*
1a′	−9.28	−6.70	2.58	2.41 (514)	0.668
2a′	−9.25	−6.70	2.55	2.35 (528)	0.617
1b′	−9.56	−6.69	2.87	2.71 (458)	0.595
2b′	−9.50	−6.68	2.82	2.63 (472)	0.574

A natural population analysis[36] of **1a′**−**2b′** (Table S2) revealed charge values between +0.68 and +0.55 at the chalcogen atoms of **1a′**−**2b′**. The remaining nine carbon atoms in the 1-alkylidene-1*H*-benzo[*c*]chalcogenophenium framework exhibited merely small negative values (−0.20 to 0.00). The bond order analysis based on the Wiberg bond index[37] (Table S3) suggested bond order values of 1.30−1.35 and 1.63−1.74 for the C3−chalcogen and C1−C4 bonds in **1a′**−**2b′**, respectively. Taking these calculations into consideration, we draw the following conclusions for 1-alkylidene-1*H*-benzo[*c*]chalcogenophenium cations **1a′**−**2b′**: (i) structure A should be the dominant mesomeric resonance structure (Scheme 2), and (ii) cations **1a′**−**2b′** have striking features of *s-trans* heterodutadiene analogues containing sulfonium or selenonium.

Scheme 2. Conceivable Resonance Structures for 1-Alkylidene-1*H*-benzo[*c*]chalcogenophenium Cations 1a′−2b′



The electrochemical behavior of **1a**−**2b** was analyzed by cyclic and differential pulse voltammetry, and the corresponding voltammograms are shown in Figure 4. In CH_2Cl_2 at room temperature, irreversible one-electron reduction waves were observed for **1a**−**2b** between −0.39 and −0.55 V (all potentials vs Fc/Fc^+, Table 1), whereas no oxidation waves were observed during anodic sweeps. The observed trends are consistent with the theoretically calculated LUMO energy levels of **1a′**−**2b′** (Table 2).

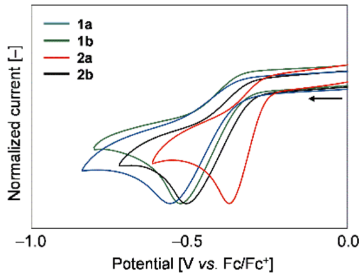
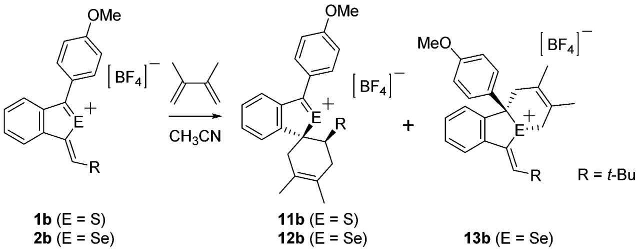


Figure 4. Cyclic voltammograms of **1a**−**2b** in $[(n\text{-Bu})_4N][PF_6]/CH_2Cl_2$ at room temperature (scan rate: 100 mV s^{-1}).

Finally, we have attempted Diels−Alder reactions of **1b** and **2b** with 2,3-dimethyl-1,3-butadiene in order to disclose their reactivity (Scheme 3). A solution of **1b** with dimethylbutadiene in acetonitrile at room temperature smoothly afforded **11b** in 91% isolated yield. The molecular structure of **11b** was determined by X-ray crystallographic analysis,[26] as shown in Figure 1, which clarified that Diels−Alder reaction of the *exo*-alkene subunit of **1b** proceeded. Compound **2b** was subjected to a Diels−Alder reaction, which generated not only *exo*-alkene adduct **12b** but also C═Se$^+$ adduct **13b** in total 78% yield in a ratio of 1:1. These results revealed novel reactivity of the 1-alkylidene-1*H*-benzo[*c*]chalcogenophenium fragment.

Scheme 3. Diels−Alder Reactions of 1b and 2b



In conclusion, we have successfully synthesized a series of the first stable 1-alkylidene-1*H*-benzo[*c*]chalcogenophen-2-ium tetrafluoroborates (**1a**−**2b**) and disclosed their photophysical properties as well as their electrochemical behavior. The selenium-containing heavy heterocycles **2a** and **2b** exhibit absorption and emission maxima at significantly longer wavelengths relative to sulfur derivatives **1a** and **1b**. Further research on the intriguing properties of **1a**−**2b** is currently in progress in our laboratory and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00716.

> Experimental procedure, characterization data, NMR spectra for all products, X-ray crystallographic analyses, and theoretical calculations for the model compounds (PDF)

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Notes

The authors declare no competing financial interest.

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