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The First Ammonium Aromatic Diselenoates: Stable Heavy Congeners of Aromatic Carboxylic Acid Salts

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Since the first synthesis[1] of sulfur isologues of aromatic carboxylic acid salts, that is, dithiobenzoic acid salts, many studies on their synthesis, reactions, and applications have been reported.[2] In contrast, the corresponding selenium isologues, that is, diselenoic acid salts, have been almost totally ignored until very recently. With regard to their aliphatic derivatives, Jensen proposed that zinc diselenoates are putative intermediates in the reaction of dialkylzinc with carbon diselenide.[3] Very recently, the inner salts with a diselenocarboxyl group were isolated as stable compounds and characterized.[4] Nevertheless, no examples of aromatic diselenoic acids and their salts have been reported.[5] We report here the first successful isolation and characterization of ammonium aromatic diselenoates.

The key starting materials, that is, aromatic diselenoic acid 2-(trimethylsilyl)ethyl esters **4** leading to ammonium diselenoates, were obtained as green or blue-green oils by reacting aluminum 2-(trimethylsilyl)ethyl selenolate **2** derived from the diselenide **1**[6] and *i*-Bu_2AlH with aromatic selenoic acid *O*-methyl esters **3** (Scheme 1).[7]

The oily esters **4** were unstable and decomposed to the corresponding selenoic acid esters ($ArCOSeCH_2CH_2SiMe_3$) under Ar within 12 h, even at −20 °C, except for 2-methylphenyl derivative **4b**.

The reaction of **4** with Me_4NF gave the corresponding ammonium aromatic diselenoates **5** as green solids in yields of 47−78% and in high purity.[8] Interestingly, the salt **5a** was more stable than the starting ester **4a**. For example, the salt **5a** could be handled in air without any appreciable change, although it decomposed when it was dissolved in CH_3CN and THF. Furthermore, the introduction of a methyl group to the ortho position of the aromatic ring increased the stability of the salt **5b**. No appreciable change was observed for **5b**, even when it was dissolved in CH_3CN at −20 °C.

The molecular structure of **5a** was determined by X-ray crystallography.[10] An ORTEP drawing of **5a** is shown in Figure 1.

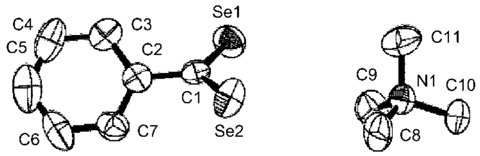
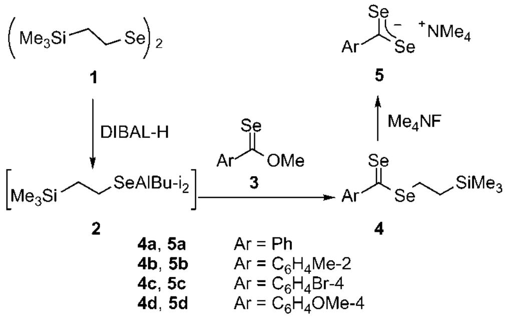


Figure 1. ORTEP representation of **5a**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Se1−C1, 1.828(4); Se2−Cl, 1.831(4); C1−C2, 1.482(5). Selected bond angles (deg): Se1−C1−Se2, 124.3(2); Se1−C1−C2, 118.0(3); Se2−C2, 117.7(3).

Scheme 1



This is the first X-ray molecular analysis of aromatic diselenoic acid salts. Several characteristic features can be noted. First, the distances between the selenium atoms and the hydrogen atoms of the ammonium ion are longer than the sum of the van der Waals radii of both atoms,[11] and no interaction was observed between the diselenocarboxyl and ammonium groups. Second, the salt **5a** is monomeric in the solid state. Third, the dihedral angle of the phenyl group and diselenocarboxyl group was 48.0(2)°, and the phenyl group does not appear to resonate with the diselenocarboxyl group. Fourth, the average length of the two C−Se bonds is 1.830(4) Å, which is closer to the lengths of ordinary C−Se double-bonds (1.74−1.80 Å)[12] than to those of C−Se single bonds (1.94 Å).[13]

Representative spectroscopic data for **4** and **5** are listed in Table 1.

In the ^{13}C NMR spectra, signals due to the selenocarbonyl carbon atoms in **4** were observed at 237 ± 5 ppm, whereas the corresponding signals in salts **5** were shifted to lower fields by 22.5 ± 0.5 ppm. Two resonances at about 900 and 1800 ppm in ^{77}Se NMR spectra were observed for the selenium atoms in C−Se single- and C═Se double-bonds in the case of **4**. Coupling constants typical of C−Se (172 ± 3 Hz) and C═Se (224 ± 1.2 Hz) bonds were also detected. On the other hand, only one signal appeared at 1360−1493 ppm, which is in the region of the signals for C═Se bonds,[14] when esters **4** were converted to salts **5**. Interestingly, the signals of **5** [δ_5(Se)] are linearly correlated to the signals of the C═Se groups of **4** [δ_4(Se)]:[15] $\delta_5(\mathrm{Se}) = 379.3 + 0.595 \times \delta_4(\mathrm{Se})$ ($r = 1.00$).

More importantly, the coupling constants between the selenium and carbon atoms in **5** were larger than 200 Hz, which indicates that both the carbon−selenium bonds in **5** possess a double-bond character. Thus, when the resonance hybrid **5** is depicted with three resonance forms **5I**−**5III**, the forms **5I** and **5III** contribute more to **5** than form **5II**, and the electrons are efficiently delocalized on the diselenocarboxyl group in **5**.[16,17]

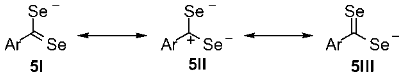


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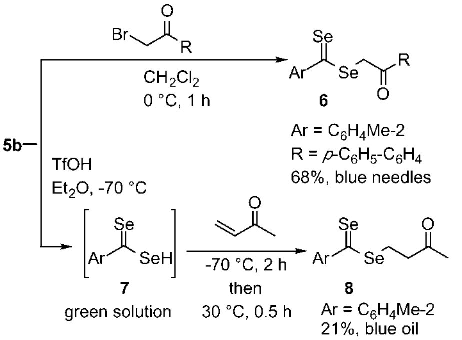
Table 1. Spectroscopic Data of Compounds **4** and **5**

cmpd	^{13}C NMR[a] δ [ppm]	^{77}Se NMR[a] δ [ppm]	$^{1}J_{Se-C}$[b] [Hz]	UV–vis [nm][c] π–π*	UV–vis [nm][c] n–π*
4a	236.9	897.9, 1770.2	171.9, 223.3	391	622
4b	241.5	954.6, 1846.7	174.5, 225.2	375	609
4c	234.2	901.3, 1798.1	171.6, 222.8	394	627
4d	233.9	863.4, 1652.4	169.2, 222.8	366	618
5a	259.3	1433.3	213.5	447 (423)[d]	684 (654)[d]
5b	263.6	1493.0	208.7	417 (385)[d]	634 (611)[d]
5c	256.1	1449.4	214.9	453 (433)[d]	670 (671)[d]
5d	256.6	1362.6	211.6	452 (448)[d]	690 (692)[d]

[a] $CDCl_3$ was used as a solvent for **4**, whereas CD_3CN and DMSO-d_6 were used for **5**. [b] The coupling constants were determined in the ^{13}C NMR spectra. [c] THF was used as a solvent. [d] The UV−vis spectra were measured in the solid state.

Scheme 2



The UV−visible spectra of **5** further support the double-bond character between the carbon atom and selenium atoms in **5**. For **4**, absorptions ascribed to $\pi-\pi^*$ and n−π^* transitions were seen at 366−394 and 609−627 nm, respectively. The corresponding absorptions for **5** were substantially shifted to a longer wavelength.

The suitability of ammonium diselenoate **5** as a starting material that could lead to a variety of compounds bearing a diselenocarboxyl group was demonstrated by the following reaction. First, alkylation of **5b** with *p*-phenylphenacyl bromide gave the corresponding phenacyl ester **6** as stable blue needles in 68% yield (Scheme 2).

Second, to generate diselenoic acids, TfOH or HCl/Et_2O solution was added to a THF-d_8 suspension of **5b** in an NMR tube at −70 °C. Insoluble salt **5b** quickly dissolved in THF-d_8, and the light green suspension quickly changed to green, which reflected the formation of diselenoic acid **7**; however, the low-temperature NMR spectra of the reaction mixture did not show signals that could be ascribed to **7**. To a homogeneous reaction mixture of TfOH with **5b** in Et_2O was added methyl vinyl ketone at −70 °C, and the mixture was stirred for 30 min at 30 °C to afford γ-oxabutyl diselenoate **8** as a labile blue oil in 21% yield. These results suggest that aromatic diselenoic acid **7**[18] is generated by the protonation of **5b** but easily decomposes.

In summary, we have succeeded in the first synthesis and structural analysis of ammonium aromatic diselenoates. The electronic properties of the selenocarboxyl group in ammonium salts **5** were also elucidated by analyzing various NMR and UV−visible spectra.

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Supporting Information Available: Experimental procedures, characterization data for **4**−**6**, **8**, crystallographic data, molecular orbital calculations of model compounds (PDF). An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Engelhardt, A.; Latschinoff, P. *Z. Chem.* **1868**, 455−460.

(2) (a) Scheithauer, S.; Mayer, R. In *Topics in Sulfur Chemistry*; Senning, A., Ed.; Georg Thime Publischers: Stuttgart, Germany, 1979; Vol. 4. (b) Mayer, R.; Scheithauer, S. In *Methoden der Organishen Chemie*; Falbe, J., Ed.; Georg Thime Verlag: Stuttgart, Germany, 1985; Band E5, Teil 2, pp 891−930. (c) Kato, S.; Murai, T. In *Supplement B: The Chemistry of Acid Derivatives*; Patai, S., Ed.; John Wiley & Sons: New York, 1992; Vol. 2, pp 803−847. (d) Murai, T.; Kato, S. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 5, pp 545−563.

(3) Jensen, K. A. *Q. Rep. Sulfur Chem.* **1970**, *5*, 45−52.

(4) Nakayama, J.; Kitahara, T.; Sugihara, Y.; Sakamoto, A.; Ishii, A. *J. Am. Chem. Soc.* **2000**, *122*, 9120−9126.

(5) The incorporation of a selenium atom into Mo and W carbyne complexes has been reported to result in the formation of Mo and W diselenoates, see: Gill, D. S.; Green, M.; Marsden, K.; Moore, I.; Orpen, A. G.; Stone, F. G. A.; Williams, I. D.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 1343−1347.

(6) 2-(Trimethylsilyl)ethaneselenol, or bis[2-(trimethylsilyl)ethyl] diselenide **1**, which was not previously known, was the key precursor to synthesize the esters **4**. Several attempts to prepare diselenide **1** failed. We finally realized the reproducible synthesis of **1** from Li_2Se_2 and in situ generated 2-(trimethylsilyl)ethyl bromide. For details, see the Supporting Information.

(7) (a) Murai, T.; Mizutani, T.; Kanda, T.; Kato, S. *J. Am. Chem. Soc.* **1993**, *115*, 5823−5824. (b) Murai, T.; Mizutani, T.; Kanda, T.; Kato, S. *Heteroat. Chem.* **1995**, *6*, 241−246.

(8) First, the tetrabutylammonium salt was prepared from ester **4a** with Bu_4NF in THF using a procedure to that used to prepare ammonium selenothioates.[9] However, the stability of the resulting salts was fairly low.

(9) Murai, T.; Kamoto, T.; Kato, S. *J. Am. Chem. Soc.* **2000**, *122*, 9850−9851.

(10) Crystal data of **5a**: See Supporting Information.

(11) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(12) Murai, T.; Kato, S. In *Topics in Current Chemistry*; Wirth, T. Ed.; Springer-Verlag: Berlin, 2000; Vol. 208, pp 177−199.

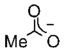
(13) Pauling, L. *The Chemical Bond;* Cornell University Press: Ithaca, NY, 1976; pp 135−155.

(14) (a) Duddeck, H. *Prog. Nucl. Magn. Reson. Spectrosc.* **1995**, *27*, 1. (b) Klapotke, T. M.; Broschag, M. *Compilation of Reported ^{77}Se NMR Chemical Shifts;* John Wiley & Sons: New York, 1996.

(15) The plot of δ_5(Se) against δ_4(Se) is shown in the Supporting Information.

(16) A resonance structure analogous to **5II** has been suggested to be important for acetate ion based on theoretical investigations. See: Wiberg, K. B. *J. Am. Chem. Soc.* **1990**, *112*, 4177−4182.

(17) Bond orders of three model compounds **9**−**11** were calculated at the B3LYP/6-311+G(d,p) level. The polar nature of the C═O group in **9** is evident, since the value is on the order of 1.25 for C═O. In contrast, the values are on the order of 1.81 for C═S in **10** and 1.78 for C═Se in **11**. This result suggests that the double bond character of the two carbon−selenium bonds in diselenoate ions is more important than that of the carbon−oxygen bonds in carboxylate ions. See the Supporting Information.



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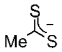

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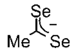

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(18) Theoretical studies on diselenoformic acid, see: Jemmis, E. D.; Giju, K. T.; Leszczynski, J. *J. Phys. Chem. A* **1997**, *101*, 7389−7395.

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