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Naphthalene-1,2,3-Dithiazolyl and Its Selenium-Containing Variants

Richard T. Oakley,*,[†] Robert W. Reed,[†] Craig M. Robertson,[†] and John F. Richardson[‡]

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada, and
Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

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Synthetic routes to salts of the 3H-naphtho[1,2-*d*][1,2,3]dithiazolylium cation and its three selenium-containing variants (SSeN, SeSN, and SeSeN) are described. The most efficient and general method involves the intermediacy of bis-acetylated aminothiolates and aminoselenolates. These reagents react smoothly with sulfur and selenium halides to afford the desired ring closure products. Electrochemical reduction of the four cations indicates that corresponding radicals (SSN, SSeN, SeSN, and SeSeN) are stable in solution. The EPR spectra of all four have been recorded, and experimental spin distributions have been cross-matched with those obtained from DFT calculations. The selenium-containing radicals are thermally unstable at or slightly above room temperature, but the all-sulfur species has been isolated and characterized crystallographically. In the solid state, the radicals are associated into cofacial dimers which are closely linked to other dimers by intermolecular S---S, S---N, and C–H---aromatic ring interactions.

Introduction

Interest in the development of radical-based magnets[1,2] and conductors[3−5] has kindled the search for new molecular building blocks. From a structural perspective, however, understanding let alone controlling the way radicals interact in the solid state poses a major challenge. Crystal engineering[6] methods hold much appeal, and the use of supramolecular synthons[7] to dictate architecture has enjoyed a degree of success,[2a,8] but the task of establishing structure−property relationships remains largely empirical. The design of new materials thus begins with the identification and exploration of thermally stable radical systems that can be easily modified, both structurally and electronically.[9]

Within this context, 1,2,3-dithiazolyl (DTA) radicals have become appealing targets.[10] When first discovered, over 20 years ago, these compounds were little more than spectroscopic curiosities;[11,12] virtually nothing was known of their molecular or solid state properties. Recently, however, a few stable crystalline derivatives have been isolated, and trends

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* Author to whom correspondence should be addressed. E-mail: oakley@sciborg.uwaterloo.ca.

[†] University of Waterloo.

[‡] University of Louisville.

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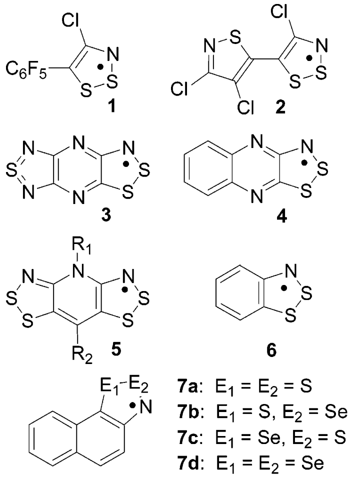
10.1021/ic048534e CCC: $30.25

Chart 1



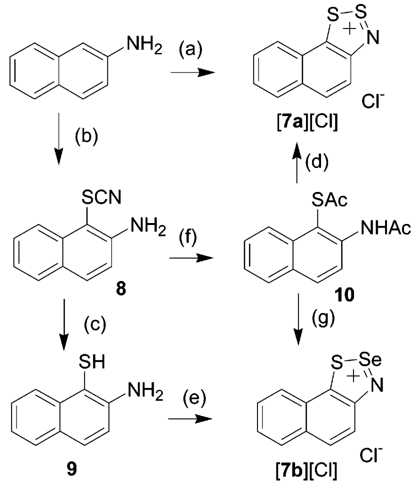
in solid-state structures and properties are emerging. Stability in simple monocyclic derivatives can be induced by the attachment of sterically bulky substituents, as in the pentafluorophenyl compound **1** (Chart 1),[13] or extremely electron-withdrawing substituents, as in the isothiazolo derivative **2**.[14] Fusion of electron-withdrawing heterocyclic groups, as in the dithiazolopyrazino compound **3**, can lead to remarkable thermal stability, although surprisingly the related quinoxaline system **4** is far less robust.[15] Resonance effects, as found in bis-DTA radicals **5**, not only improve stability but also afford materials with the favorable molecular properties for electronic conductivity.[5]

Aromatic 1,2,3-DTA radicals such as the benzene and naphthalene derivatives **6** and **7**, which were among the earliest to be observed by in situ EPR spectroscopy,[11,12] have hitherto eluded isolation. Even less is known of their selenium-containing variants. To learn more about these species, particularly methods to effect selenium incorporation, a factor crucial to the development of materials with improved conductivity, we have carried out a systematic investigation of the four possible S/Se radicals arising from the naphthalene-based framework **7**. New synthetic routes are reported, along with EPR spectroscopic and electrochemical data for all four compounds. X-ray structural results are provided for **7a** and [**7d**][$GaCl_4$].

Results

Synthesis. The preferred method for generating aromatic 1,2,3-dithiazolylium salts is the Herz cyclocondensation[16] of an aromatic amine with sulfur monochloride. In the case of 2-aminonaphthalene, the reaction (Scheme 1) leads exclusively to ring closure at the more reactive 1-position, affording [**7a**][Cl] in good yield; chlorination of the naphthalene framework is not observed. By contrast, the analogous reaction of 1-aminonaphthalene with sulfur halides[17] is inevitably accompanied by ring chlorination (at the 4-position).

Scheme 1 [a]



[a] (a) S_2Cl_2. (b) KSCN, Br_2. (c) S^{2-}, H_2O, H^+. (d) S_2Cl_2 or $SOCl_2$. (e) $SeCl_4$. (f) S^{2-}, H_2O, Ac_2O. (g) $SeOCl_2$.

Access to the mixed ring system **7b** requires a less direct approach. As a first step, we prepared the 2-amino-1-thiocyanate **8** by oxidative thiocyanation of 2-aminonaphthalene. Basic hydrolysis and acidification of **8** led to the aminothiol **9**, which could then be condensed with either sulfur monochloride or thionyl chloride to yield [**7a**][Cl], or with selenium tetrachloride to give the mixed S/Se salt [**7b**][Cl]. The aminothiol **9** is, however, an air-sensitive oil and not easily purified. We therefore developed a more convenient and easily handled intermediate by protecting both the amine and the thiol functionality of **9** with acetyl groups. Thus, when the intermediate thiolate obtained by the hydrolysis of **8** was quenched with acetic anhydride rather than acetic acid, the bis-N,S-acetyl derivative **10** was produced. This is an air-stable crystalline solid, which is much more easily purified and handled than the aminothiol **9**. It also reacts smoothly with both $SOCl_2$ and $SeOCl_2$ to afford [**7a**][Cl] and [**7b**][Cl], respectively.

To incorporate selenium at the 1-position of the naphthalene ring, and gain access to the frameworks of **7c** and **7d**, we prepared 2-aminonaphthalene-1-selenocyanate **11** by oxidative selenocyanation of 2-aminonaphthalene (Scheme 2). Based on our experience with the sulfur chemistry, and the success found with the bis-N,S-acetyl **10**, we moved directly to preparation of the corresponding selenium reagent. Thus, when 2-aminonaphthalene-1-selenocyanate **11** was hydrolyzed and the resulting selenolate quenched with a large excess of acetic anhydride, the bis-N,Se-acetyl derivative **12** was produced. Like its sulfur analogue **10**, compound **12**

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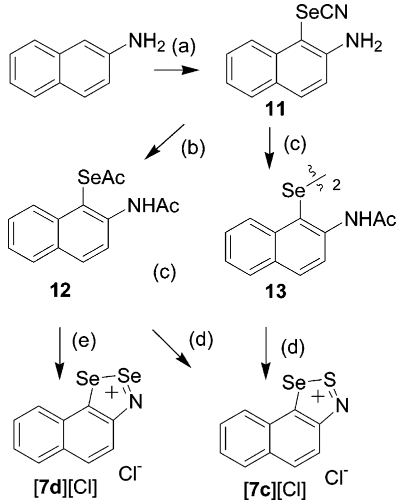
Scheme 2 [a]



[a] (a) KSeCN, Br_2. (b) S^{2-}, H_2O, xs Ac_2O. (c) S^{2-}, H_2O, Ac_2O, pH 7. (d) S_2Cl_2, DCE. (e) $SeOCl_2$, MeCN.

was stable in air and could be recrystallized from heptane. However, when the intermediate selenolate was quenched slowly with acetic anhydride, so that the pH was not allowed go below a value of 7, the N-acetyl diselenide **13** was produced. As expected, the reaction of either **12** or **13** with excess sulfur monochloride afforded [**7c**][Cl] in good yield, and treatment of **12** with $SeOCl_2$ at room temperature in MeCN provided the desired diselenazolylium chloride [**7d**][Cl] in good yield.

The insoluble chloride salts [**7a**−**d**][Cl] were readily converted, by treatment with $GaCl_3$ in MeCN, into the corresponding tetrachlorogallate salts, all of which were crystallized from chlorobenzene. Bulk conversion to the radicals **7a**−**d** was effected by chemical reduction of either the crude chloride salts with triphenylantimony or the tetrachlorogallate salts with decamethylferrocene. In the case of **7a**, the resulting radical was sufficiently thermally stable and volatile to allow its purification by vacuum sublimation. The selenium-containing radicals **7b**−**d**, however, were less thermally stable, and purification of these materials by either sublimation or recrystallization methods was unsuccessful. All of the radicals were nonetheless fully characterized by EPR spectroscopy and cyclic voltammetry.

Cyclic Voltammetry and EPR Spectra. As part of our ongoing investigations of the spin distributions in 1,2,3-DTA radicals and the effect of spin delocalization on their gas-phase disproportionation energies ΔH_{disp},[18] we have calculated, at the B3LYP/6-31G** level, their gas-phase ionization potentials (IP) and electron affinities (EA) of **7a**−**d**. We have also measured by cyclic voltammetry the half-wave potentials for their oxidation and reduction. The results are summarized in Table 1, along with similar data for related compounds.

While reduction of the cation to the radical, the +1/0 process, is electrochemically reversible, subsequent reduction of the radical to the anion, the 0/−1 process, is not. This is a common feature of 1,2,3-DTA radicals (although not observed in **3**) and reflects the ease of reductive cleavage of the S−S[19] (or S−N)[20] bond. From an energetic standpoint, the estimated gas-phase IP and EA values, as well as the experimental cell potentials E_{cell}, map well onto the previous data, the variations in each parameter reflecting the influence of the substituents on the DTA ring. Overall, it is apparent that the naphthalene framework in **7** serves as an effective reservoir for spin density, an observation supported by the B3LYP/6-31G** SOMOs (Figure 1). As a result, **7a**−**d** are all relatively soft;[21] that is, they have a low ΔH_{disp}, lower indeed than **3**, a feature which bodes well for these and related radicals in the design of molecular conductors, where a low disproportionation energy and cell potential are critical for promoting a low on-site Coulomb repulsion U,[22−24] the energetic barrier to charge transport.

The X-band EPR spectra of all four radicals **7a**−**d** have been recorded in CH_2Cl_2 at room temperature. The experimental g-values and hyperfine coupling constants derived by simulation are provided in Table 2, along with those obtained by calculation (B3LYP/6-31G**). Taken collectively, the data reveal a small but steady increase in g-value with increasing selenium content, as well as a general loss of resolution. Both effects can be attributed to the expected greater spin−orbit contribution of selenium. Thus, while the EPR signal of all four radicals is split into a three-line pattern arising from hyperfine coupling to the DTA nitrogen, only in the case of **7a** is additional fine structure discernible.

As can be seen in Figure 2, the spectrum of **7a** displays a rich overlay of hyperfine structure arising from coupling to the six distinct hydrogens on the naphthalene periphery. All six a_H values have been extracted by simulation, but given the similarity in the various a_H values in **7a** we have made no attempt to assign them to particular hydrogens. The value of a_N in **7a** is consistent with that seen for aromatic 1,2,3-dithiazolyls,[25] and there is a slight (but not steady) increase with selenium incorporation. Similar trends have been observed elsewhere and have been interpreted in terms of the electronegativity difference between S and Se.[26] In essence, selenium, being more electropositive than sulfur, appears to transfer spin density more strongly to nitrogen. These simple ideas are, however, not reflected by the results of spin density calculations (and the SOMO distributions),

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(18) ΔH_{disp} is the enthalpy change for the conversion of two gas-phase radicals R into a cation/anion pair, that is, $2R \rightleftarrows R^+ + R^-$, and accordingly is equal to the difference between the ionization potential (IP) and electron affinity (EA). The solution-based cell potential $E_{cell} = E_{1/2}(ox) - E_{1/2}(red)$ is the difference between the half-wave potentials for the oxidation and reduction processes.

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Table 1. Gas-Phase Ion Energetics (in eV), and Solution Half-Wave and Cell Potentials (V)

	compound								
	1	**2**	**3**	**4**	**6**	**7a**	**7b**	**7c**	**7d**
IP[a]		7.08	7.81	7.24	6.68	6.34	6.31	6.29	6.26
EA[a]		2.11	2.57	1.93	0.93	1.12	1.18	1.15	1.20
ΔH_{disp}[b]		4.97	5.23	5.32	5.74	5.22	5.13	5.15	5.06
$E_{1/2}(+1/0)$[c]	0.38	0.565	1.14		0.18	0.207	0.223	0.214	0.243
$E_{1/2}(0/-1)$[c]	-1.09^{e}	-0.39^{e}	0.15		-1.0^{e}	0.91^{e}	0.86^{e}	0.93^{e}	0.84^{e}
E_{cell}[c,d]	1.23^{f}	0.94^{f}	0.99		1.15^{f}	1.09^{f}	1.05^{f}	1.14^{f}	1.05^{f}

[a] ΔSCF values (in eV) from B3LYP/6-31G** calculations run with full optimization within C_s symmetry. [b] ΔH_{disp} = IP − EA. [c] In MeCN, ref SCE. [d] $E_{cell} = E_{1/2}(+1/0) - E_{1/2}(0/-1)$. [e] Irreversible behavior, E_{pc} value quoted. [f] E_{cell} estimated as $E_{pc}(+1/0) - E_{pc}(0/-1)$.

Table 2. EPR Data for **7a**−**d**

	compound			
	7a	**7b**	**7c**	**7d**
g-value	2.0081	2.0113	2.0190	2.027
a_N[a]	0.748	0.715	0.731	0.800
	(0.812)	(0.773)	(0.802)	(0.757)
ρ(N)[b]	0.414	0.416	0.406	0.407
$\rho(E_1)$[b]	0.139	0.139	0.142	0.144
$\rho(E_2)$[b]	0.216	0.201	0.217	0.206

[a] Experimental values in mT; computed values (in parentheses) from B3LYP/6-31G** calculations with full optimization in C_s symmetry. [b] B3LYP/6-31G** spin densities ρ over the three-atom sequence E_1E_2N (E = S or Se).

Table 3. Crystallographic Data

	[**7d**][$GaCl_4$]	**7a**
formula	$C_{10}H_6Cl_4GaNSe_2$	$C_{10}H_6NS_2$
fw	509.602	04.28
a, Å	7.790(4)	17.841(7)
b, Å	10.009(5)	8.702(3)
c, Å	10.109(5)	11.669(4)
α, deg	100.109(5)	90
β, deg	104.778(8)	104.286(6)
γ, deg	92.760(6)	90
V, $Å^3$	745.5(6)	1755.6(11)
ρ(calcd), g cm^{-3}	2.270	1.546
space group	$P\bar{1}$	$P2_1/c$
Z	2	8
temp, K	295(2)	293(2)
μ, mm^{-1}	7.429	0.548
λ, Å	0.71073	0.71073
data/restraints/parameters	3453/0/163	4040/0/283
solution method	Direct Methods	Direct Methods
R, R_w (on F^2)[a]	0.0444, 0.1002	0.0434, 0.0934

[a] $R = [\sum||F_o| - |F_c||]/[\sum|F_o|]$ for $I > 2\sigma(I)$; $R_w = \{[\sum w||F_o|^2 - |F_c|^2|^2]/[\sum(w|F_o|^4)]\}$.

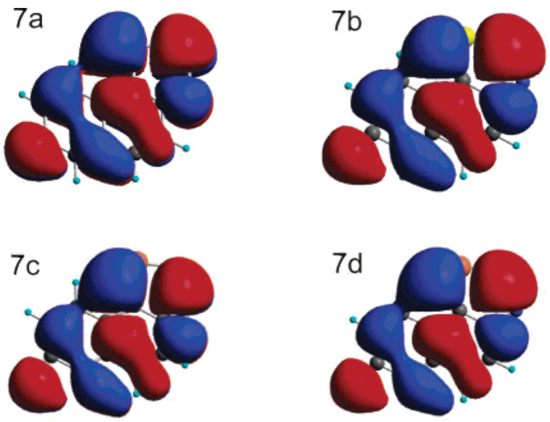

Figure 1. B3LYP/6-31G** SOMOs of radicals **7a**−**d**.

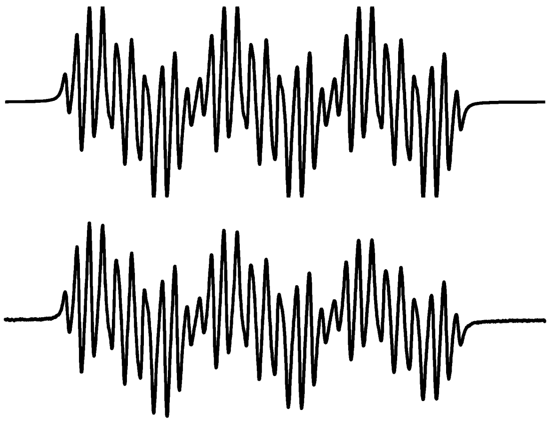

Figure 2. EPR spectrum (SW = 3 mT) of **7a** in CH_2Cl_2 (below) and simulation (above). Extracted a_H values: 0.178, 0.158, 0.014, 0.070, 0.069, 0.062 mT.

which indicate virtually no variation in the spin distribution as a result of S/Se exchange.

Crystal Structures. The crystal structures of the sulfur-based radical **7a** and the gallate salt of the selenium-based cation [**7d**][$GaCl_4$] have been determined by single-crystal X-ray diffraction at 293 K. Crystal data are compiled in Table 3, and ORTEP drawings of the molecular units, showing atom numbering, are illustrated in Figure 3. Summaries of pertinent intramolecular and intermolecular distances are provided in Table 4.

While we have been unable to characterize structurally the parent radical **7d**, the structure of [**7d**][$GaCl_4$] nonetheless represents the first structural characterization of a 1,2,3-diselenazole ring in any oxidation state. The crystal structure belongs to the triclinic space group $P\bar{1}$ and consists of [**7d**]$^+$ cations and [$GaCl_4$]$^-$ anions oriented so as to allow a pair of close intermolecular Cl---Se contacts. This kind of ion pairing is ubiquitous in related compounds.[27,28] In addition, there is a third contact (Cl3---Se1′) to the anion located above the molecular plane. At the molecular level, the structure holds few surprises; the internal Se−Se and Se−N bond lengths are consistent with those seen in, for example, structures of 1,2,3,5-diselenadiazolylium cations.[29]

The crystal packing of [**7d**][$GaCl_4$] is illustrated in Figure 4. The cations, which are planar to within 0.021(4) Å, adopt

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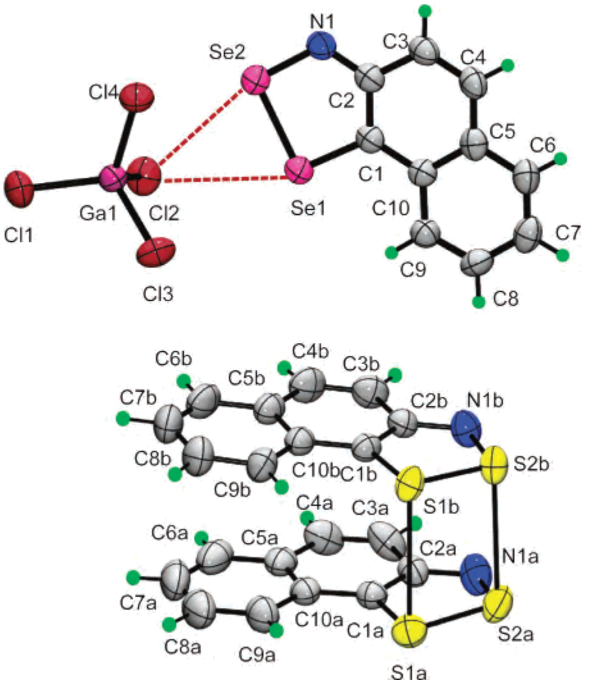

Figure 3. ORTEP drawings (50% probability ellipsoids) of [**7d**][GaCl$_4$] (above) and **7a** (below).

Table 4. Intra- and Intermolecular Distances (Å), ESDs in Parentheses

intramolecular		intermolecular	
[7d][GaCl$_4$]			
Se1−Se2	2.2900(12)	Se1---Cl2′	3.534(2)
Se2−N1	1.7667(4)	Se2---Cl2′	3.389(2)
Se1−C1	1.844(5)	Se1---Cl3′	3.578(4)
C1−C2	1.428(7)	Se2---N1′	2.874(4)
7a			
S1a−S2a	2.083(1)	S1a---S1b′	3.309(1)
S1b−S2b	2.081(1)	S2a---S2b′	3.053(1)
S2a−N1a	1.614(3)		
S2b−N1b	1.7617(2)	S2a---N1b′ (d1)	3.162(3)
S1a−C1a	1.740(3)	S2b---N2a′ (d2)	3.113(3)
S1b−C1b	1.732(3)	S2a---S2b′ (d3)	3.501(1)
C1a−C2a	1.410(3)	S2a---S1b′ (d4)	3.375(2)
C1b−C2b	1.402(3)	S1a---S2b′ (d5)	3.549(1)

a head-to-tail π-stacked arrangement running parallel to the x direction. The interplanar separation within the head-to-tail pairs is 3.513(5) Å, while that between the pairs is 3.383(6) Å. The π-stacked arrays of cations are linked by centrosymmetric pairs of Se2---N1′ contacts, thereby generating ribbons running along the y direction. These 4-center Se---N supramolecular synthons, which are common in diselenadiazolylium salts[29] and diselenadiazolyl radicals,[30] are likely to dominate the solid-state structures of reduced diselenazolyl materials, where ion pairing effects are no longer present.

The purely sulfur-based radical **7a** sublimes at 60 °C/10^{-2} Torr without decomposition to afford highly crystalline bronze blocks belonging to the monoclinic space group $P2_1/c$. The crystals, which are diamagnetic by EPR, consist of cofacial dimers of **7a**, with 4 dimers per unit cell linked by two long, albeit unequal (3.053(1) and 3.309(1) Å) interannular S−S bonds. This mode of association, which is so common in dithiadiazolyl chemistry,[31] has not hitherto been observed for 1,2,3-dithiazolyls. Indeed, the propensity for dimerization of 1,2,3-dithiazolyls seems to be less pronounced than it is for dithiadiazolyls. Thus, in the case of **2**, the room-temperature structure consists of undimerized π-stacks, as do all of the resonance-stabilized bis-dithiazolyls **5**. Dimerization is not, however, without precedent. In **1**, the sterically bulky C$_6$F$_5$-substituent causes the two rings to rotate about their respective midpoints so that only one long[32] S−S linkage (3.299(1) Å) remains, while in **3** an unusual head-to-tail mode of association is found. In all cases, however, dimerized or undimerized, the internal S−S, S−N, and S−C bonds show little variation; that is, association by whatever mode has very little effect on the electronic structures of the two halves. They are weakly associated π-radicals.

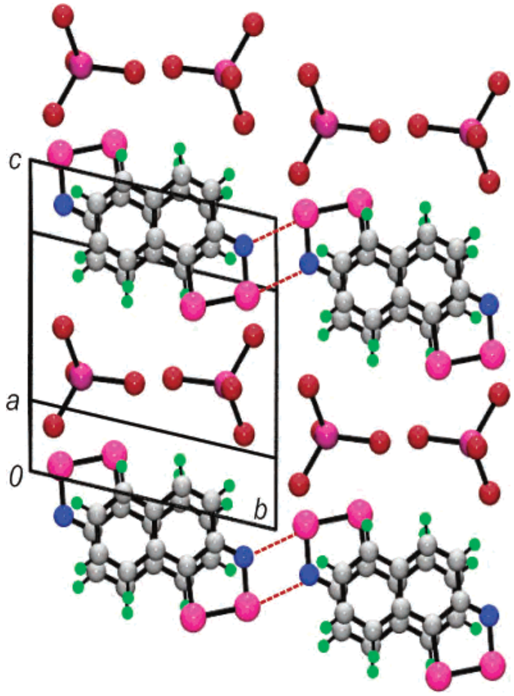

Figure 4. Packing of [**7d**][GaCl$_4$]. Intermolecular Se---N contacts are shown with dashed lines.

Dimers of **7a** do not form π-stacked arrays. Instead, they adopt the closed packed herringbone arrangement illustrated in Figure 5. This structure is reminiscent of that found for the naphthalene-based 1,3,2-dithiazolyl,[33] although in this latter case the radicals are not dimerized (at room temperature). Many polycyclic aromatics, for example, naphtha-

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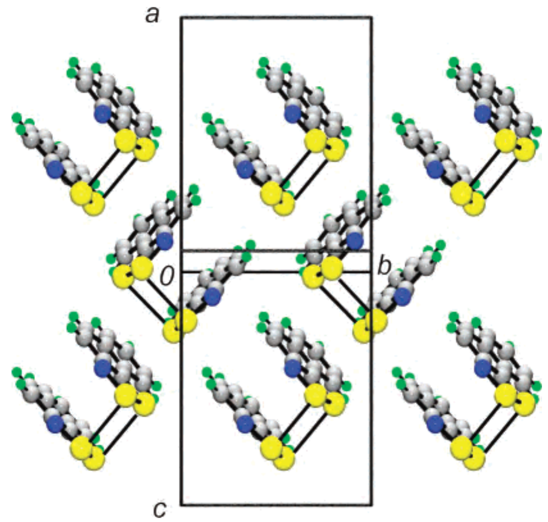

Figure 5. Herringbone packing of **7a**.

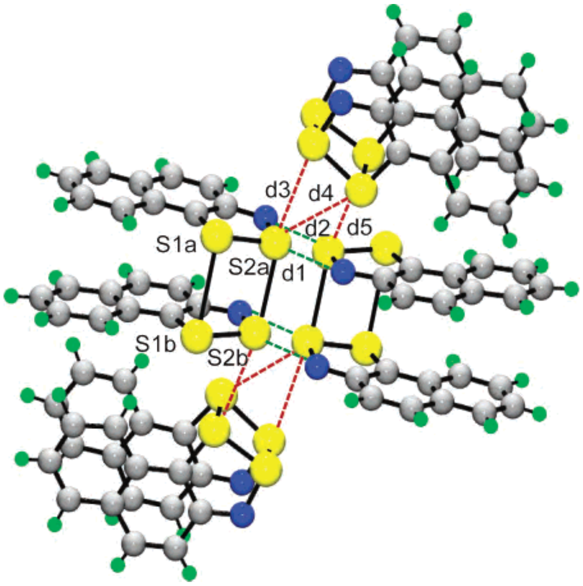

Figure 6. Interdimer contacts in **7a**. Intermolecular S---N and S---S contacts (dashed lines) are defined in Table 4.

lene[34] and anthracene,[35] adopt this type of packing, and the preference for it can be attributed to the opportunity that this geometry affords for the development of structure making "tilted T" CH---ring interactions.[36,37] By contrast, in radicals where the peripheral CH groups are replaced by N atoms, for example, **3**, the preference for close-packing is diminished, and a slipped π-stack structure prevails.

The herringbone arrangement also allows for a clustering of the radical heads so as to maximize S---S and S---N contacts. As shown in Figure 6, pairs of dimers are linked centrosymmetically by 4-center S---N interactions (d1, d2). Above and below these pairs are located two more dimers, linked by three close (d3, d4, and d5) contacts that are well within the van der Waals separation.[38]

Summary and Conclusion

Recent work on the use of resonance-stabilized bis(1,2,3-dithiazolyls) as building blocks for molecular conductors[5] has underscored the need for the development of materials with increased bandwidth, a feature necessary to offset the high on-site Coulomb repulsion energy intrinsic to a neutral radical material.[39] Replacement of sulfur by selenium represents an appealing solution to this dilemma, but methods for incorporation of selenium are rare.[40] The methodology demonstrated here for the naphthalene-based systems, based on the use of acetylated aminothiols and aminoselenols as synthetic intermediates, provides efficient access to all possible combinations of sulfur- and selenium-based cations [**7a**−**d**]$^+$. Within this manifold, we have been able to isolate and characterize the sulfur-based radical **7a**, but the corresponding selenium-based variants **7b**−**d** are less thermally stable. While design modifications are required to allow the isolation of functional materials, the synthetic procedure presented here should allow access to a wide range of selenium-containing rings.

Experimental Section

General Procedures and Starting Materials. The reagents sulfur monochloride, bromine, potassium thiocyanate, potassium selenocyanate, gallium trichloride, selenium, selenium dioxide, decamethylferrocene, and triphenylantimony were obtained commercially (all from Aldrich) and used as received. Selenium tetrachloride was prepared by direct chlorination of selenium,[41] and 2-aminonaphthalene[42] was prepared by a Bücherer reaction on 2-hydroxynaphthalene (Aldrich). The solvents were of at least reagent grade; acetonitrile (MeCN), dichloroethane (DCE), dichloromethane (DCM), and chlorobenzene were dried by distillation from P_2O_5. All reactions were performed under an atmosphere of dry nitrogen. Melting points are uncorrected. Infrared spectra (Nujol mulls, KBr optics) were recorded on a Nicolet Avatar FTIR spectrometer (at 2 cm^{-1} resolution). ^{1}H and ^{77}Se NMR spectra were run on a Bruker Avance 300 MHz NMR spectrometer. The latter were obtained operating in analogue mode, 256 transients, 30° pulse widths, and long relaxation delays (5−10 s); chemical shifts are referenced to external SeO_2 (saturated solution in D_2O) and reported relative to neat $Me_2Se(l)$ at 25 °C [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$ ppm].[43] Elemental analyses were performed by MHW Laboratories, Phoenix, AZ 85018.

Synthesis of 2-Aminonaphthalene-1-thiocyanate 8. Liquid bromine (7.77 g, 48.6 mmol) was added dropwise over a period of 20 min to a stirred solution of potassium thiocyanate (17.0 g, 176. mmol) and 2-aminonaphthalene (12.6 g, 88.1 mmol) in 600 mL of degassed methanol at −78 °C (EtOH/dry ice). The resulting pink slurry was stirred for an additional 30 min, and the mixture was poured onto 1 L of water. The off-white precipitate was filtered

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off and dried in vacuo. White needles of **8** were obtained by recrystallization from EtOH; yield 12.06 g (60.2 mmol, 68%); mp 152−154 °C (lit.[44] 150−154 °C). IR: 3466 (s), 3363 (s), 3189 (w), 3059 (w), 2154 (vs), 1624 (vs), 1559 (m), 1429 (s), 1398 (m), 1377 (m), 1293 (m), 1250 (m), 1210 (m), 1149 (s), 1031 (w), 978 (w), 867 (w), 821 (vs), 829 (s), 772 (s), 754 (s), 653 (m), 544 (w), 528 (w), 461 (m) $\mathrm{cm^{-1}}$.

Synthesis of 2-Aminonaphthalene-1-thiol 9. Thiocyanate **8** (5.0 g, 24.9 mmol) was added to solution of sodium sulfide nonahydrate (11.95 g, 50.0 mmol) in 250 mL of degassed water, and the slurry was heated at reflux for 2 h. The resulting yellow solution was filtered and neutralized with acetic acid to afford a yellow oil. The oil was extracted with 2 × 150 mL of DCM, and the extracts were washed with 2 × 150 mL of water and dried over magnesium sulfate. Removal of the solvent in vacuo gave a dark yellow air-sensitive oil[45] that was not subjected to further purification; yield 3.93 g (22.4 mmol, 90%). IR: 3226 (w), 3061 (m), 2522 (m), 1952 (w), 1829 (w), 1800 (w), 1612 (s), 1566 (s), 1526 (m), 1417 (s), 1339 (m), 1320 (w), 1281 (m), 1235 (w), 1202 (w), 1142 (w), 1123 (w), 1036 (w), 947 (w), 873 (w), 820 (m), 678 (w), 586 (w) $\mathrm{cm^{-1}}$.

Synthesis of *S*-[2-(Acetylamino)-1-naphthyl]ethanethiolate 10. Thiocyanate **8** (2.50 g, 12.4 mmol) was added to a solution of sodium sulfide nonahydrate (6.00 g, 24.8 mmol) in 200 mL of degassed water, and the mixture was gently heated to ca. 40 °C for 2 h. The solution was cooled and filtered, and excess acetic anhydride was added to the filtrate. The resulting white precipitate was filtered off, washed with water, and dried in vacuo; crude yield 2.39 g (9.22 mmol, 74%). White needles were grown from heptane; mp 153−154 °C. IR: 3336 (m), 1692 (s), 1620 (w), 1595 (w), 1566 (w), 1513 (w), 1497 (s), 1425 (m), 1376 (m), 1364 (w), 1327 (w), 1274 (m), 1229 (w), 1150 (w), 1121 (w), 1018 (w), 948 (m), 860 (w), 820 (m), 771 (w), 743 (m), 667 (w), 656 (w), 620 (m), 591 (w), 538 (w), 509 (w), 427 (w) $\mathrm{cm^{-1}}$. ^{1}H NMR (δ, $\mathrm{CDCl_3}$): 7.4−8.5 (m, 6H, aromatic), 2.49 (s, 3H, $\mathrm{NC(O)CH_3}$), 2.23 (s, 3H, $\mathrm{SC(O)CH_3}$). Anal. Calcd for $\mathrm{C_{14}H_{13}NO_2S}$: C, 64.84; H, 5.05; N, 5.40. Found: C, 64.75; H, 5.05; N, 5.27.

Synthesis of 3H-Naphtho[1,2-*d*][1,2,3]dithiazolylium Chloride [7a][Cl]. Method 1. Aminothiol **9** (4.00 g, 22.8 mmol) and $\mathrm{S_2Cl_2}$ (15.4 g, 0.114 mol) were added to 150 mL of degassed dichloroethane, and the mixture was heated at reflux for 1 h. The resulting red precipitate of [**7a**][Cl] was filtered off, washed with 2 × 75 mL of DCM, and dried in vacuo; yield 4.10 g (17.1 mmol, 75%). IR: 3069 (w), 1600 (m), 1492 (w), 1426 (w), 1333 (m), 1007 (w), 1150 (w), 1129 (w), 1042 (w), 972 (w), 882 (s), 821 (s), 765 (s), 729 (m), 564 (w), 542 (m), 494 (m), 412 (m) $\mathrm{cm^{-1}}$.

Method 2. Excess of $\mathrm{S_2Cl_2}$ (39.1 g, 0.290 mol) was slowly added to a solution of 2-aminonaphthalene (8.30 g, 58.0 mmol) in 150 mL of DCE, and the mixture was heated at reflux for 4 h. The resulting red precipitate of [**7a**][Cl] was filtered off, washed with 2 × 200 mL of DCM, and dried in vacuo; yield 7.52 g (31.3 mmol, 54%).

Method 3. Excess $\mathrm{S_2Cl_2}$ (1.30 g, 9.63 mmol) was added to a slurry of **10** (0.500 g, 1.93 mmol) in 50 mL of degassed MeCN. The clear red solution which formed was gently heated (ca. 40 °C) for 2 h, and the resulting red precipitate of [**7a**][Cl] was filtered off, washed with 3 × 50 mL of DCM, and dried in vacuo; yield 0.249 g (1.04 mmol, 54%).

Synthesis of 3H-Naphtho[1,2-*d*][1,2,3]dithiazolylium Tetrachlorogallate [7a][GaCl$_4$]. Gallium trichloride (1.90 g, 10.8 mmol) was added to a slurry of [**7a**][Cl] (2.37 g, 9.90 mmol) in 50 mL of MeCN. The resulting orange solution was stirred for 10 min and filtered, and the solvent was flash distilled to leave an orange solid that was recrystallized from chlorobenzene as dark red platelets of [**7a**][GaCl$_4$]; yield 3.32 g (7.97 mmol, 81%); dec >165 °C. IR: 3069 (w), 2725 (w), 2670 (w), 1602 (s), 1336 (w), 1165 (w), 1130 (w), 983 (w), 885 (s), 822 (s), 777 (m), 760 (m), 666 (m), 566 (w), 538 (m), 498 (w) $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{C_{10}H_6Cl_4GaNS_2}$: C, 28.88; H, 1.45; N, 3.37. Found: C, 29.07; H, 1.60; N, 3.14.

Synthesis of 3H-Naphtho[1,2-*d*][1,2,3]dithiazolyl 7a. Method 1. Decamethylferrocene (0.393 g, 1.20 mmol) and [**7a**][GaCl$_4$] (0.500 g, 1.20 mmol) were added to 15 mL of degassed MeCN, and the solution was cooled to −20 °C overnight. The resulting black precipitate of **7a** was filtered off and dried in vacuo. The crude radical (0.221 g, 1.08 mmol, 90%) was purified by vacuum sublimation in a three-zone temperature gradient furnace (90−30 °C/10^{-2} Torr) over a period of 3 days to give bronze blocks of **7a**, dec >120 °C. IR: 1603 (m), 1532 (w), 1495 (m), 1421 (m), 1326 (m), 1284 (w), 1250 (m), 1208 (m), 1183 (w), 1136 (m), 1126 (m), 1100 (w), 1081 (w), 1036 (m), 1014 (s), 966 (m), 856 (w), 888 (s), 817 (vs), 805 (s), 761 (m), 733 (s), 661 (s), 501 (m), 535 (m), 511 (m), 500 (s), 466 (s), 412 (m) $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{C_{10}H_6NS_2}$: C, 58.79; H, 2.96; N, 6.86. Found: C, 59.02; H, 3.15; N, 7.00.

Method 2. Triphenylantimony (1.55 g, 4.39 mmol) was added to a slurry of [**7a**][Cl] (1.41 g, 5.86 mmol) in 15 mL of MeCN, and the resulting mixture was stirred for 3 h, and then filtered and cooled to −20 °C overnight. The resulting black precipitate was filtered off and dried in vacuo. The crude radical (0.60 g, 52%) was sublimed as described above.

Synthesis of 3H-Naphtho[1,2-*d*][1,2,3]thiaselenazolylium Chloride [7b][Cl]. A solution of $\mathrm{SeOCl_2}$ was prepared in situ by gently warming a slurry of $\mathrm{SeO_2}$ (0.214 g, 1.93 mmol) and $\mathrm{SeCl_4}$ (0.426 g, 1.93 mmol) in 40 mL of MeCN until all solids dissolved. The mixture was cooled to room temperature, and **10** (0.500 g, 1.93 mmol) was added to give a clear red solution that was gently heated (ca. 40 °C) for 2 h. The resulting brown precipitate was filtered off, washed with 3 × 50 mL DCM, and dried in vacuo; yield 0.400 g (1.40 mmol, 72%). IR: 3064 (w), 3047 (w), 1602 (s), 1593 (m), 1422 (m), 1326 (w), 1294 (w), 1267 (m), 1161 (w), 1140 (m), 1129 (m), 1052 (w), 1021 (w), 968 (w), 951 (w), 870 (m), 814 (s), 783 (w), 748 (s), 703 (m), 662 (m), 537 (s), 412 (m) $\mathrm{cm^{-1}}$.

Synthesis of 3H-Naphtho[1,2-*d*][1,2,3]thiaselenazolylium Tetrachlorogallate [7b][GaCl$_4$]. Gallium trichloride (2.28 g, 12.9 mmol) was added to a slurry of [**7b**][Cl] (3.38 g, 11.8 mmol) in 50 mL of MeCN, and the resulting solution was filtered. The solvent was then flash distilled to leave a dark orange crystalline mass that was recrystallized from chlorobenzene as dark brown needles of [**7b**][GaCl$_4$]; yield 4.08 g (8.81 mmol, 74.3%); dec >182 °C. ^{77}Se NMR (δ, $\mathrm{CD_3CN}$): 1536. IR: 3065 (w), 3050 (w), 1598 (s), 1592 (s), 1485 (m), 1427 (w), 1343 (m), 1330 (m), 1292 (w), 1264 (m), 1145 (m), 1133 (m), 1046 (w), 1006 (w), 975 (w), 886 (m), 817 (vs), 782 (s), 764 (s), 663 (s), 536 (s), 509 (m), 500 (w), 431 (m), 411 (m) $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{C_{10}H_6Cl_4GaNSSe}$: C, 25.96; H, 1.31; N, 3.03. Found: C, 25.92; H, 0.96; N, 2.81.

Synthesis of 2-Aminonaphthalene-1-selenocyanate 11. Bromine (5.34 g, 33.4 mmol) was slowly added to a solution of potassium selenocyanate (9.62 g, 66.8 mmol) in 160 mL of degassed MeOH at −78 °C (EtOH/dry ice). To this mixture was slowly added a solution of 2-aminonaphthalene (4.79 g, 33.4 mmol) in 80 mL of cold MeOH. The resulting mixture was warmed to room temperature and quenched with 500 mL of water. The red precipitate (9.81 g) was filtered off and dried in vacuo. This crude product was extracted into 400 mL of EtOH, and the extract was hot filtered

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and concentrated to dryness to leave an orange solid that was recrystallized from DCE as orange needles of **11**; yield 5.78 g (23.4 mmol, 70%); dec >134 °C. IR: 3464 (s), 3368 (s), 3230 (w), 2149 (vs), 1629 (s), 1499 (s), 1377 (m), 1348 (m), 1293 (m), 1244 (w), 1211 (s), 1161 (m), 1145 (m), 1027 (w), 964 (w), 858 (w), 814 (vs), 643 (w), 545 (w), 501 (w) cm^{-1}. Anal. Calcd for $C_{11}H_8N_2Se$: C, 53.46; H, 3.26; N, 11.33. Found: C, 53.54; H, 3.47; N, 11.19.

Synthesis of Se-[2-(Acetylamino)-1-naphthyl]ethaneselenolate 12. Amino-selenocyanate **11** (2.45 g, 10.0 mmol) was added to a solution of sodium sulfide nonhydrate (4.78 g, 19.9 mmol) in 100 mL of degassed water, and the mixture was gently heated at 40 °C for 90 min. The resulting yellow solution was filtered and cooled to 0 °C, whereupon excess acetic anhydride (ca. 10 mL) was quickly added. The white precipitate so produced was filtered off and dried in vacuo; crude yield 2.79 g (9.11 mmol, 92%). White needles of **12** were grown from heptane; mp 116−117 °C. IR: 3323 (m), 2724 (w), 1712 (vs), 1696 (m), 1667 (vs), 1618 (m), 1595 (s), 1566 (s), 1515 (m), 1499 (s), 1407 (m), 1326 (s), 1279 (s), 1257 (m), 1227 (w), 1164 (w), 1149 (w), 1135 (w), 1102 (vs), 1032 (w), 1017 (w), 940 (m), 863 (m), 819 (vs), 767 (s), 742 (s), 668 (m), 638 (m), 576 (vs), 529 (m), 503 (m), 467 (w), 418 (m) cm^{-1}. ^1H NMR (δ, $CDCl_3$): 7.4−8.5 (m, 6H, aromatic), 2.49 (s, 3H, NC(O)CH_3), 2.23 (s, 3H, SeC(O)CH_3). Anal. Calcd for $C_{12}H_{11}NOSe$: C, 54.56; H, 4.20; N, 5.30. Found: C, 54.71; H, 4.28; N, 5.34.

Synthesis of *N*-(1-{[2-(Acetylamino)-1-naphthyl]diseleno}2-naphthyl)acetamide 13. Amino-selenocyanate **11** (1.00 g, 0.45 mmol) was added to a solution of sodium sulfide nonhydrate (1.95 g, 8.12 mmol) in 40 mL of degassed water, and the mixture was gently heated at 40 °C for 30 min. The resulting yellow solution was filtered and cooled to 0 °C, whereupon acetic anhydride (ca. 1.5 mL) was carefully added until a neutral pH was reached. The orange precipitate was filtered off, washed with water, and dried in vacuo; crude yield 1.20 g (2.28 mmol, 56%). Orange crystalline blocks of **13** were grown from DCE, mp 236−238 °C. IR: 3347 (m), 1686 (vs), 1615 (w), 1596 (m), 1561 (s), 1493 (s), 1428 (s), 1327 (s), 1327 (s), 1275 (m), 1253 (m), 1151 (w), 989 (w), 819 (s), 776 (m), 664 (w), 627 (w), 583 (m), 535 (w), 523 (w), 503 (w) cm^{-1}. ^1H NMR (δ, $CDCl_3$): 7.4−8.5 (m, 6H, aromatic), 1.34 (s, br, 3H, NC(O)CH_3). Anal. Calcd for $C_{24}H_{20}N_2O_2Se_2$: C, 54.91; H, 4.28; N, 4.57. Found: C, 55.14; H, 4.08; N, 4.73.

Synthesis of 3H-Naphtho[1,2-*d*][1,2,3]selenathiazolylium Chloride [7c][Cl]. Method 1. Sulfur monochloride (2.20 g, 16.3 mmol) was injected into a degassed solution of **12** (0.500 g, 1.63 mmol) in 20 mL of DCE, and the mixture was gently warmed for 4 h. The dark red precipitate of [**7c**][Cl] was filtered off, washed with 2 × 40 mL of DCE, and dried in vacuo; yield 0.235 g (0.820 mmol, 50%). IR: 1602 (s), 1427 (m), 1339 (m), 1326 (m), 1308 (w), 1263 (m), 1211 (w), 1166 (m), 1123 (m), 964 (m), 884 (s), 804 (s), 771 (m), 751 (m), 667 (w), 650 (w), 558 (w), 526 (m), 480 (m) cm^{-1}.

Method 2. Sulfur monochloride (1.28 g, 9.50 mmol) was injected into a degassed solution of **13** (0.500 g, 0.950 mmol) in 30 mL of DCE, and the resulting mixture was gently heated for 4 h. The dark red precipitate of [**7c**][Cl] was filtered off and washed with 2 × 40 mL of DCE and dried in vacuo; yield 0.264 g (0.921 mmol, 49%).

Synthesis of 3H-Naphtho[1,2-*d*][1,2,3]selenathiazolylium Tetrachlorogallate [7c][$GaCl_4$]. Gallium trichloride (0.202 g, 1.15 mmol) was added to a slurry of [**7c**][Cl] (0.274 g, 0.956 mmol) in 20 mL of MeCN, the resulting red solution was filtered, and the solvent was flash distilled from the filtrate to leave an orange crystalline mass. Bright red needles of [**7c**][$GaCl_4$] were grown from chlorobenzene; yield 0.265 g (0.574 mmol, 60%); dec > 120 °C. ^{77}Se NMR (δ, CD_3CN): 1399.9. IR: 1601 (s), 1488 (m), 1426 (m), 1329 (m), 1314 (w), 1260 (m), 1214 (w), 1164 (w), 1126 (w), 965 (w), 892 (s), 879 (m), 819 (s), 777 (s), 757 (m), 667 (w), 650 (w), 532 (m), 480 (w) cm^{-1}. Anal. Calcd for $C_{10}H_6Cl_4GaNSSe$: C, 25.96; H, 1.31; N, 3.03. Found: C, 26.15; H, 1.12; N, 3.22.

Synthesis of 3H-Naphtho[1,2-*d*][1,2,3]diselenazolylium Chloride [7d][Cl]. A solution of $SeOCl_2$ was prepared in situ by gently warming $SeCl_4$ (1.08 g, 4.90 mmol) and SeO_2 (0.544 g, 4.90 mmol) in 40 mL of degassed MeCN until all solids dissolved. The solution was cooled to room temperature, and **12** (1.50 g, 4.90 mmol) was added. The mixture was then stirred for 2.5 h, and the resulting brown precipitate was filtered off, washed with 3 × 40 mL of DCE, and dried in vacuo; yield 1.37 g (4.11 mmol, 84%). IR: 1601 (s), 1533 (w), 1420 (m), 1342 (m), 1306 (w), 1261 (m), 1217 (w), 1166 (m), 1145 (w), 1122 (m), 1041 (w), 996 (w), 965 (w), 874 (m), 804 (vs), 786 (m), 772 (m), 750 (m), 698 (m), 668 (w), 659 (w), 648 (w), 526 (m), 494 (w), 463 (m) cm^{-1}.

Synthesis of 3H-Naphtho[1,2-*d*][1,2,3]diselenazolylium Tetrachlorogallate [7d][$GaCl_4$]. Gallium trichloride (0.320 g, 1.82 mmol) was added to a slurry of [**7**][Cl] (0.500 g, 1.52 mmol) in 30 mL of MeCN. The resulting clear red solution was filtered, and the filtrate was flash distilled to leave a dark brown crystalline mass. Dark purple needles of [**7d**][$GaCl_4$] were grown from chlorobenzene; yield 0.526 g (1.03 mmol, 69%); dec > 120 °C. ^{77}Se NMR (δ, CD_3CN): 1561 (Se_1), 1324 (Se_2). IR: 2002 (w), 1842 (w), 1779 (w), 16.37 (w), 1599 (vs), 1483 (s), 1421 (s), 1410 (w), 1342 (m), 1328 (m), 1286 (w), 1259 (s), 1213 (w), 1167 (w), 1145 (m), 1128 (m), 1044 (w), 1002 (w), 979 (w), 881 (m), 814 (vs), 780 (s), 778 (s), 759 (s), 707 (s), 668 (w), 648 (m), 531 (m), 524 (m), 498 (w), 464 (m) cm^{-1}. Anal. Calcd for $C_{10}H_6Cl_4GaNSe_2$: C, 23.57; H, 1.19; N, 2.75. Found: C, 23.70; H, 1.30; N, 2.60.

Generation of Selenium-Based Radicals 7b−d. Bulk reduction of the gallate salts [**7b**−**d**][$GaCl_4$] with decamethylferrocene, as described above for [**7a**][$GaCl_4$], provided precipitates of the corresponding radicals **7b**−**d** in crude form. Attempts to purify these materials by recrystallization or sublimation were ineffective, inevitably leading to the extrusion of varying amounts of elemental selenium. For EPR purposes, the radicals were conveniently generated by in situ reduction of a slurry of the appropriate chloride salt [**7b**−**d**][Cl] with triphenylantimony in DCM.

Cyclic Voltammetry. Cyclic voltammetry was performed using a PINE bipotentiostat, model AFCClBP1, with scan rates of 50−100 mV s^{-1} on solutions of [**7a**−**d**][SbF_6] in MeCN (dried by distillation from P_2O_5) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate. Potentials were scanned with respect to the quasi-reference electrode in a single compartment cell fitted with Pt electrodes and referenced to the Fc/Fc^+ couple of ferrocene at 0.38 V vs SCE.[46] In all cases (**7a**−**d**), the $E_{pa}-E_{pc}$ separation of the reversible couple of [**7**]/[**7**]$^+$ was within 10% of that of the Fc/Fc^+ couple.

EPR Spectra. X-Band EPR spectra were recorded at ambient temperature using a Bruker EMX-200 spectrometer. In the case of **7a**, the pristine radical was dissolved in degassed DCM. The selenium-based materials **7b**−**d** were generated in situ as described above. Hyperfine coupling constants were obtained by spectral simulation using Simfonia[47] and WinSim.

Density Functional Calculations. The ion energetics data shown in Table 1 were obtained from ΔSCF calculations using the B3LYP

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(47) WinEPR Simfonia; Bruker Instruments, Inc., Billerica, MA.

method, as contained in the Gaussian 98W suite of programs.[48] Adiabatic (ΔSCF) ionization potential and electron affinity estimates were obtained from total electronic energy calculations using a 6-31G** basis set within the constraints of C_s symmetry. Full vibrational frequency calculations on the final geometries of the radical and cation confirmed that they were stationary points. In the case of the anion, there was one negative frequency, which may be interpreted in terms of an incipient cleavage of one of the E−N (E = S, Se) bonds.

X-ray Measurements. Samples were mounted on glass fibers with epoxy and centered on a Bruker P4/CCD diffractometer. The reflection data (Mo Kα) were processed using SAINT,[49] and the structures were solved by direct methods using SHELXS-90[50] and refined by least-squares methods on F^2 using SHELXL-97[51] incorporated in the SHELXTL[52] suite of programs. All non-hydrogen atoms were refined anisotropically; in the case of **7a**, the hydrogen atoms were located on difference maps and refined isotropically, while in [**7d**][$GaCl_4$] their position was fixed. Details of data collection and refinement are presented in Table 3.

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Supporting Information Available: Details of computational results on **7a**−**d**, and of X-ray crystallographic data collection and structure refinement for **7a** and [**7d**][$GaCl_4$], including tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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