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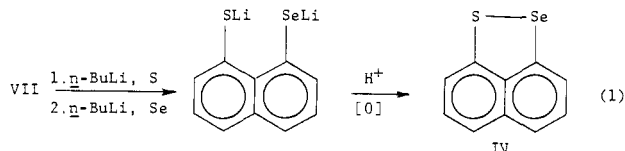
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Peri-Bridged Naphthalenes. 2. Unsymmetrical Diatomic Chalcogen Bridges¹

Sir:

In a previous communication,² we reported that 1,8-dithionaphthalene reacts with elemental sulfur, selenium, and tellurium to yield naphtho[1,8-*cd*]-1,2-dithiole (I), naphtho[1,8-*cd*]-1,2-diselenole (II) and naphtho[1,8-*cd*]-1,2-ditellurole (III), respectively. These compounds are good electron donors and are of particular interest in the formation of "one-dimensional" charge-transfer complexes. We now wish to report the synthesis of the three unsymmetrical members of this series: naphtho[1,8-*cd*]-1,2-selenathiole (IV), naphtho[1,8-*cd*]-1,2-tellurathiole (V), and naphtho[1,8-*cd*]-1,2-telluraselenole (VI). The methodology employed is illustrated by the preparation of the hitherto unknown naphtho[1,8-*cd*]-1,2-selenathiole (IV) in 24% yield from the sequential reaction of 1,8-dibromonaphthalene (VII) with 1



equiv of *n*-butyllithium, 1 equiv of elemental sulfur, a 2nd equiv of *n*-butyllithium, and 1 equiv of elemental selenium (eq 1). The crude product is isolated as a dark red solid by column chromatography on silica gel using hexane as eluent. Analysis of unpurified IV by GLC and TLC revealed that it contained I and II with the former being the major impurity. When the order of addition of sulfur and selenium is reversed, the results are qualitatively similar: IV is the major product in 29% yield, again accompanied by I and II, although in this case the latter is the major impurity. The formation of these symmetrical by-products probably results from the reaction of the chalcogens with 1,8-dithionaphthalene. Naphtho[1,8-*cd*]-1,2-selenathiole is a dark red crystalline solid (mp 121–122 °C) whose spectral properties³ resemble those of the previously synthesized, symmetrical chalcogen-bridged naphthalenes.² The characteristic ion intensity ratios of the molecular ion cluster of IV in its 70-eV mass spectrum provide good support for its composition (Table A).

The crystal structure of IV has been determined by x-ray diffraction.⁴ Crystals of IV belong to the monoclinic space group $P2_1/c$ with $a = 15.417$ (6) Å, $b = 4.244$ (2) Å, $c = 16.596$ (7) Å, and $\beta = 129.11$ (6)°. Density measurements indicated four molecules per unit cell or one per asymmetric unit. All unique data with $2\theta \leq 114^\circ$ were collected on a Syntex $P2_1$ diffractometer using monochromated $\text{Cu K}\alpha$ (1.54178 Å) radiation. A total of 1331 reflections was surveyed, and, after correction for Lorentz, polarization, and

Table A. Intensity Ratios of the Molecular Ion Clusters^{a-c}

Compound	IV	V	VI
232	2 (2)	280 7 (7)	324 1 (1)
233	0 (0)	281 2 (3)	325 1 (1)
234	19 (18)	282 14 (13)	326 5 (5)
235	18 (17)	283 22 (21)	327 6 (5)
236	49 (49)	284 56 (55)	328 20 (19)
237	7 (8)	285 8 (7)	329 16 (15)
238	100 (100)	286 93 (91)	330 40 (40)
239	12 (12)	287 11 (11)	331 27 (27)
240	22 (23)	288 100 (100)	332 83 (81)
241	3 (3)	289 12 (12)	333 23 (21)
242	1 (1)	290 5 (5)	334 100 (100)
			335 12 (11)
			336 76 (77)
			337 8 (9)
			338 12 (13)
			339 1 (1)

^a m/e intensity observed (calculated). ^b The observed spectra were obtained on an AEI MS-902 instrument. ^c The calculated mass spectra were obtained by use of the MASH computer program, which is a local version of ISOW developed by W. A. G. Graham, University of Alberta, and modified by R. C. Winterton, and R. S. Weber, Cornell University.

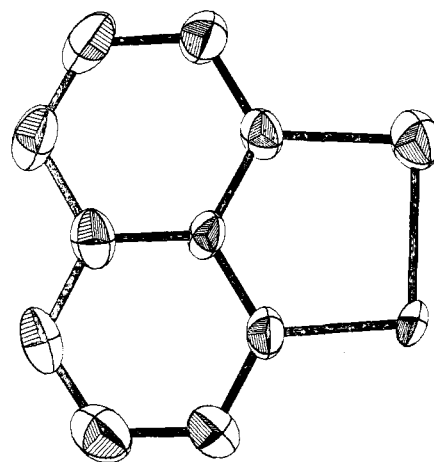
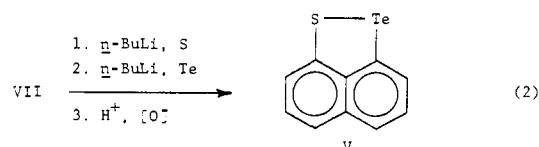


Figure 1. A computer-generated drawing of a single molecule of naphtho[1,8-*cd*]-1,2-selenathiole. Thermal ellipsoids are drawn at the 50% probability level.

background effects, 1076 (81%) were used in the final refinements ($F_o^2 \geq 3\sigma(F_o^2)$). The selenium atom was located using a three-dimensional Patterson synthesis and the nonhydrogen atoms were located on subsequent selenium-phased electron density syntheses. Full-matrix least-squares refinement, with anisotropic temperature factors for the nonhydrogen atoms and omitting hydrogen atoms, has converged to a standard crystallographic residual of 0.078.

Computer generated drawings of the final x-ray model and the extended structure are presented in Figures 1 and 2. The compound is planar and bond angles and distances are in good agreement with accepted values. From the Patterson map and refinement, there is no evidence of disorder with respect to the dichalcogen bridge; indeed the 4.244-Å stacking along the *b* axis (with 25° tilt) is such that the chalcogen atoms form linear chains along the stacking direction.

As summarized in eq 2, VII reacts sequentially with *n*-



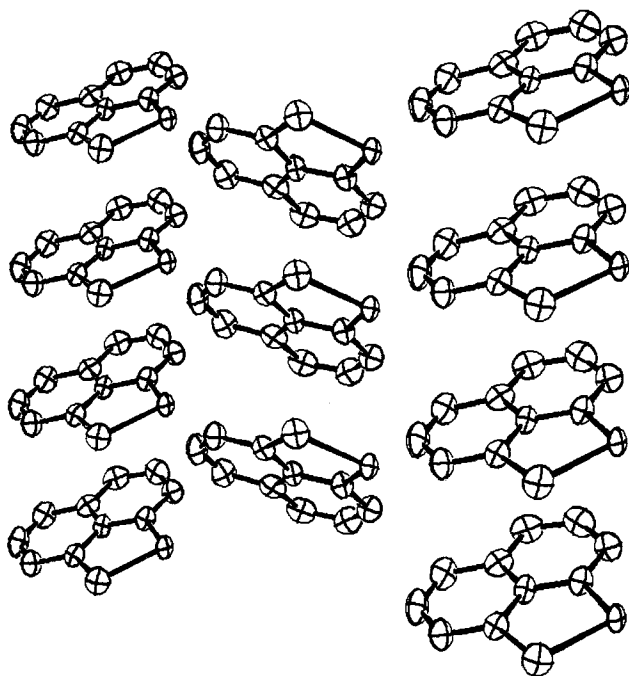
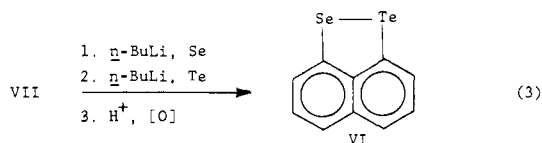


Figure 2. A computer-generated drawing of the extended structure of naphtho[1,8-*cd*]-1,2-selenathiole.

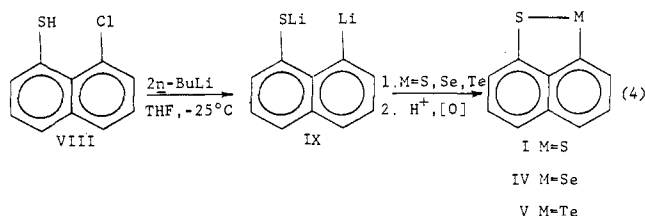
butyllithium, sulfur, and then *n*-butyllithium and tellurium, to give naphtho[1,8-*cd*]-1,2-tellurathiole (V) as bronze filaments (mp 214–216 °C), although in only 2% yield. The spectral properties of V,⁵ as well as the ion intensity ratios of the parent molecular ion (Table A), are consistent with the proposed structure.

The reaction of VII with *n*-butyllithium, selenium, *n*-butyllithium, and tellurium gives naphtho[1,8-*cd*]-1,2-tellura-selenole (VI) as shiny black flakes (mp 193–195 °C) in 4% yield (eq 3). The structure of VI is once again confirmed by its



spectral properties⁶ and its mass spectrum (Table A).

While the above-described reactions provided initial samples of the desired heterocycles, we considered it important to improve the syntheses to obtain a better supply of these compounds for further study. One solution, which allows efficient synthesis of IV and V, as well as of I, is outlined in eq 4. 8-Chloro-1-naphthalenethiol (VIII)⁷ is treated with 2 equiv of



n-butyllithium in tetrahydrofuran solution at –25 °C, to generate an intermediate dilithio salt (IX), which, after reaction with elemental sulfur and subsequent workup, gives I in 44% yield. Under analogous conditions, treatment of IX with elemental selenium gives IV in 65% yield, while reaction of IX

with elemental tellurium allows the isolation of a 60% yield of V.

From the results obtained above, it appears that 8-chloro-1-naphthalenethiol undergoes halogen-metal exchange readily. This is unusual, since aryl chlorides are not normally good substrates for halogen-metal exchange reactions.^{8,9} When 1-chloronaphthalene or 1-thiomethyl-8-chloronaphthalene are subjected to reaction conditions identical with those under which VIII is efficiently converted to IX, they are recovered unchanged. This suggests that the lithium thiolate in one peri position of naphthalene facilitates the exchange of the chlorine in the other peri position.

Like their symmetrical relatives,² the unsymmetrically bridged naphthalenes reported here are good electron donors; they form charge-transfer complexes both with 7,7,8,8-tetracyanoquinodimethane and iodine. The solid-state properties of these complexes will be reported elsewhere. We are now engaged in a study of the chemical properties of these novel heterocyclic systems.

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Supplementary Material Available: Tables of atomic fractional coordinates, interatomic distances, bond angles, thermal parameters, and a listing of the observed and calculated structure factor amplitudes (9 pages) is included. Ordering information is given on any current masthead page.

References and Notes

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- Anal. Calcd for C₁₀H₆SSe: C, 50.64; H, 2.55; S, 13.52; Se, 33.30. Found: C, 50.58; H, 2.53; S, 13.55; Se, 33.64. IR (KBr): 3007 (w), 1900 (w), 1739 (w), 1594, 1533 (s), 1478, 1407, 1342 (s), 1188 (s), 1135, 1033, 955, 945, 863 (s), 778 (s), 736 (s) cm⁻¹. ¹H NMR spectrum (CDCl₃): m, extending from δ 7.1 to 7.6. Mass spectrum *m/e* (rel intensity): 238 (100%, M⁺, Table A), 158 (11), 126 (4), 114 (4), 113 (3).
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- Anal. Calcd for C₁₀H₆STe: C, 42.02; H, 2.11. Found: C, 42.06; H, 2.00. IR (KBr): 3007 (w), 1904 (w), 1531 (s), 1480 (s), 1410, 1342, 1201 (s), 1146, 1036, 963, 941, 879, 853, 786 (s), 741 (s) cm⁻¹. ¹H NMR (Me₂SO-*d*₆): m, extending from δ 7.1 to 7.9. Mass spectrum *m/e* (rel intensity): 288 (100%, M⁺, Table A), 158 (65), 126 (10), 114 (23), 113 (12).
- IR (KBr): 3020 (w), 1913 (w), 1756 (w), 1597, 1534 (s), 1478 (s), 1414, 1345, 1198, 1140, 1040, 950, 888, 844, 790 (s), 747 (s) cm⁻¹. ¹H NMR (CDCl₃/CS₂): m, extending from δ 7.1 to 7.9. Mass spectrum *m/e* (rel intensity): 334 (M⁺, 100%, Table A), 208 (8), 207 (6), 206 (46), 204 (24), 126 (73). High resolution mass spectrum: calcd for most abundant molecular ion of C₁₀H₆SeTe, 333.8681; found, 333.8679.
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