The 2 mL of distillate containing the methanol was injected onto the gas chromatography column in five successive injections (approximately 30 s apart). The column temperature was 80 °C; the helium flow was 90 cm^3/min. Methanol eluted first with a retention time of nearly 15 min; the water, which was not collected, had a retention time of nearly 35 min. The methanol was collected in a U-tube equipped with two vacuum stopcocks (2 mm bore), a 12/30 standard tapered inner ground glass joint on one end, and a 10/30 inner joint on the other. A pretrap was attached to the gas chromatograph on one end and to the U-tube on the other. The pretrap was immersed in an ice–salt bath.

In subsequent steps both portions were treated identically. The aqueous solution containing a small amount of methanol was carefully fractionally distilled. The first 2 mL of distillate, containing all of the methanol, was subjected to gas chromatography. The methanol was collected and transferred to the pyrolysis apparatus described by Borowitz et al.[18]

For the ether oxygen isotope effects this methanol was pyrolyzed at 1360 °C. It was determined by Fourier transform infrared analysis of the volatile pyrolysis products that CO was the only product of the pyrolysis under these conditions. Repeated measurement of the oxygen isotopic composition of a standard sample of methanol by this procedure gave consistent results. At lower temperatures substantial amounts of CO_2 and other volatile products were produced and isotope ratio analysis of the CO produced gave erratic results.

For the carbonyl carbon and carbonyl oxygen isotope effects the pyrolysis was conducted in the presence of an approximately twofold excess of H_2O. Under these conditions CO_2 is the only product of the pyrolysis.

Hydrazinolysis. The procedure in the hydrazinolysis experiments was basically the same as that in the hydrolysis experiments. The same quantities and ester concentrations were used. Complete reaction in the 100% reaction samples was achieved by conducting the hydrazinolysis at pH 13. The isotope ratios for these samples were, as expected, the same as those observed in the 100% reaction samples in the alkaline hydrolysis.

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Naphtho[1,8-*c,d*:4,5-*c′,d′*]bis[1,2,6]selenadiazine

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Abstract: The synthesis and chemical and physical properties of the title compound (**1**) are reported. With one notable exception the spectroscopic properties of naphtho[1,8-*c,d*:4,5-*c′,d′*]bis[1,2,6]selenadiazine (**1**) closely resemble those observed for naphtho[1,8-*c,d*:4,5-*c′,d′*]bis[1,2,6]thiadiazine (**2**). In particular, the compounds show ^1H NMR chemical shifts of δ 5.91 (**1**) and 4.74 (**2**) in dimethyl-d_6 sulfoxide. The discrepancy in the ^1H NMR chemical shifts of **1** and **2** is ascribed to differences in the magnitude of the induced paramagnetic ring currents. Theoretical analysis of these results leads to two important conclusions: (1) The magnitude of paramagnetic ring currents in structurally similar molecules is primarily determined by the spectrum of orbital energies and, in particular, the HOMO–LUMO energy gap. (2) The difference between the nitrogen–chalcogen resonance integrals in **1** and **2** is the dominant factor in determining the relative magnitude of the HOMO–LUMO energy gaps (and thus the intensity of the paramagnetic ring currents). Evidence is presented to show that the most important excitation for the development of the paramagnetic ring current in **1** and **2** is from the HOMO (B_{1u}) to the LUMO (A_u), whereas the long-wavelength band in the electronic spectrum involves the HOMO (B_{1u}) → second LUMO (B_{2g}) transition.

We report here the preparation and properties of naphtho[1,8-*c,d*:4,5-*c′,d′*]bis[1,2,6]selenadiazine (**1**), the first member of that class of compounds containing the $=N-Se-N= \leftrightarrow -N=Se=N$ linkage in a six-membered ring. By analogy with the previously prepared naphtho[1,8-*e,d*: 4,5-*c′,d′*]bis[1,2,6]thiadiazine (**2**),[2] we expected **1** to exhibit the

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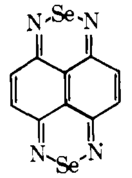

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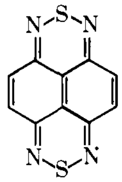


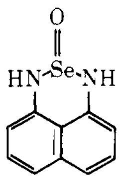
2

stability normally associated with compounds of aromatic character and at the same time to possess unusual physical properties suggestive of antiaromaticity.

Results and Discussion

The title compound could not be prepared by the Sachs' procedure.[3] Sachs had reported the synthesis of naphtho[1,8-*c,d*][1,2,6]selenadiazine (**3**) by reaction of 1,8-diaminonaphthalene with SeO_2 in dilute acetic acid. When we attempted to reproduce his results, we obtained an uncharacterizable material. However, when 1,8-diaminonaphthalene was allowed to react with $SeOCl_2$ in the presence of triethylamine, a product was isolated (51% yield) whose elemental analysis was correct for the selenoxide (**4**). All the methods of dehydration (P_2O_5/tetrachloroethylene, polyphosphoric acid, $POCl_3$/pyridine, sublimation from Al_2O_3) that were tried failed to yield the desired naphtho[1,8-*c,d*]-[1,2,6]selenadiazine (**3**). The fact that **3** could not be prepared by the same routes as **5**[4] may suggest that d-orbital participation and/or zwitterionic structures (as in **5a** and **5b**; see also ref 4 and 5) do not represent viable bonding alternatives for the selenium compound. We therefore turned our attention to **1**, which of course, does not necessarily require the contribution of such configurations.

3



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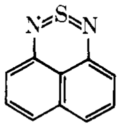
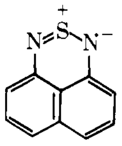


5a



5b

The title compound was prepared by treating a slurry of the "tin double salt" of 1,4,5,8-tetraaminonaphthalene[6] in dry CH_2Cl_2 with triethylamine and then with $SeOCl_2$ in an argon atmosphere. Recrystallization of the crude product afforded ~15% yield of metallic green needles.

With one notable exception (see below), the spectroscopic properties of **1** closely resemble those observed for **2**. The electronic spectra for **1** and **2** are compared in Figure 1. The long-wavelength band is red-shifted by 27 nm in the selenium compound. The IR spectrum of **1** also bore a remarkable similarity to that of **2**. The ESR spectrum of the radical cation of **1** consisted of nine lines ($g = 2.0178$), which we interpret as arising from coupling with 4 equivalent nitrogens ($a_N = 1.47$ G). We have been unsuccessful in preparing the anion radical of **1**.

Solubility problems have precluded examination of the electrochemistry and the ^{13}C NMR behavior of **1**. The FT proton NMR spectrum of **1** in dimethyl-d_6 sulfoxide showed a singlet at δ 5.91, which may be compared with the value of δ 4.74 obtained for **2** in the same solvent. A remote substituent effect of this order of magnitude is unprecedented in the chemistry of sulfur and selenium.

The high-field chemical shift observed for **2** was previously interpreted in terms of an induced paramagnetic ring current.[2] Theoretical support for this proposition was obtained from London-McWeeny[7] ring curent calculations, and a similar analysis has been carried out for **1** (Table I). The first two entries in the table show that the calculations faithfully reproduce the experimental trend, for the magnitudes of the paramagnetic ring currents in **1** are computed to be less than half that of **2**, even though the HMO parameters[8,9] for sulfur and selenium are very similar. Entries three and four in Table I are of illustrative value and demonstrate the sensitivity of the ring currents to the Coulomb (α) and resonance (β) integrals. If we consider **1**, then it is apparent that an increase in α to the value for α_S brings about a further decrease in the magnitude of the ring current, whereas increasing β to the β_{N-S} value leads to the largest paramagnetic ring current. Thus, while the two effects oppose one another, *the difference between the nitrogen-chalcogen resonance integrals in **1** and **2** is the dominant factor in determining the magnitude of the paramagnetic ring currents.*

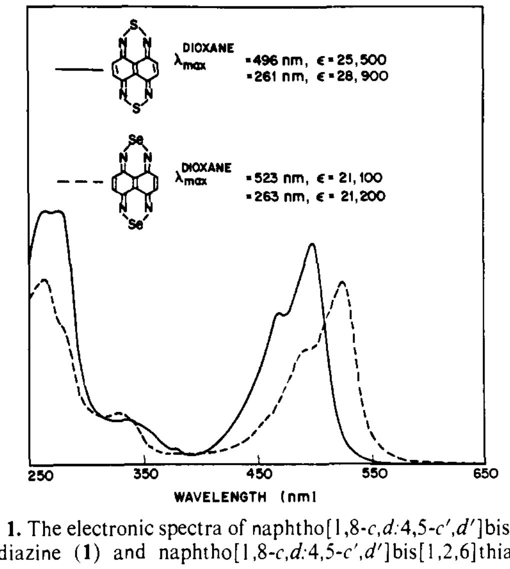
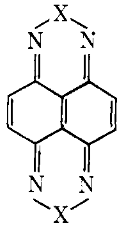


Figure 1. The electronic spectra of naphtho[1,8-*c,d*:4,5-*c′,d′*]bis[1,2,6]-selenadiazine (**1**) and naphtho[1,8-*c,d*:4,5-*c′,d′*]bis[1,2,6]thiadiazine (**2**).

Table I. Calculated Ring Currents (as a Ratio to the Benzene Value)



molecule	X	α_X^a	β^a_{N-X}	naphthalene rings	peri rings
1	Se	$\alpha + 1.04\beta$	0.6β	−0.353	−0.936
2	S	$\alpha + 1.1\beta$	0.7β	−0.935	−2.056
		$\alpha + 1.1\beta$	0.6β	−0.286	−0.803
		$\alpha + 1.04\beta$	0.7β	−1.143	−2.453

[a] Parameters taken from ref 8.

In an effort to further analyze the origins of the differing ring current intensities in **1** and **2** in terms of their electronic structure, we have carried out an additional series of calculations[7] (Table II). These calculations do not apply to true quantum mechanical systems; nevertheless, we felt they would be useful in illustrating the relative importance of the "wave function" and the "orbital energies" (insofar as they are separable), in influencing paramagnetic ring currents. The first two entries are for calculations which use the orbital energy spectrum from the pyrene dianion (**6**) together with the wave functions for **1** and **2**; clearly the large energy gap between the

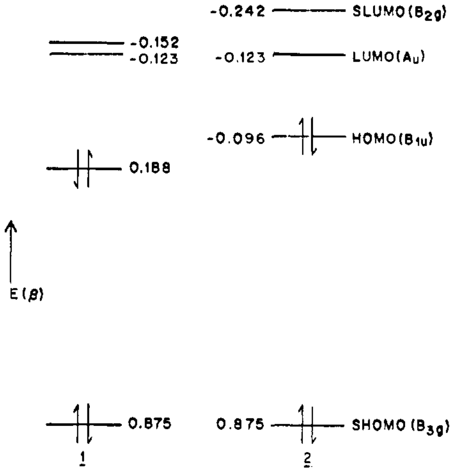


Figure 2. Calculated HMO orbital energy scheme for **1** and **2** (the level ordering is the same for both compounds).

Table II. Hypothetical Calculated Ring Currents[a] (as a Ratio to the Benzene Value)

eigenvectors	eigenvalues	HOMO-LUMO energy gap	naphthalene rings	peri rings
1	**6**	0.434β	0.088	0.732
2	**6**	0.434β	−0.136	0.703
6	**1**	0.311β	−2.176	−2.099
6	**2**	0.219β	−3.432	−2.670

[a] These systems do not fulfill certain quantum mechanical laws.

occupied and unoccupied MOs quenches the paramagnetism. The remaining two entries reverse this selection, and it may be seen that the paramagnetism is greatly enhanced as the highest occupied MO-lowest unoccupied MO (HOMO-LUMO) gap is contracted. This is to be expected, of course, from the form of the paramagnetic term in the ring current theory.[7,12] Clearly, *the magnitude of paramagnetic ring currents in structurally similar molecules is primarily determined by the spectrum of orbital energies, and in particular the HOMO-LUMO energy gap.*

Given the fact that both theory (Figure 2) and experiment suggest that the HOMO-LUMO separation is considerably smaller in **2** than **1**, the observation that **1** exhibits the longest wavelength electronic absorption spectrum (Figure 1) requires some examination. In both **1** and **2** (point group D_{2h}) the HOMO is of B_{1u} symmetry, whereas the LUMO is A_u; the HOMO → LUMO transition is therefore of symmetry $A_g \rightarrow B_{1g}$, which is electric dipole forbidden and is presumably not observed in the electronic spectra of **1** and **2**. This transition is magnetic dipole allowed and will certainly make a very large contribution to the paramagnetism of **1** and **2** (Table II). The next smallest energy gap between the occupied and vacant π-electron MOs (after the HOMO-LUMO pair) is associated with the HOMO-second (S) LUMO separation in **1** and **2**. The SLUMO is of B_{2g} symmetry; thus the HOMO → SLUMO transition is $A_g \rightarrow B_{3u}$, which is electric dipole allowed, and it is presumably this transition which is responsible for the long-wavelength band in **1** and **2**. The calculated energy difference between the HOMO and SLUMO pair is about 0.34β in both **1** and **2**, whereas the long-wavelength transition energy has values of 2.37 (**1**) and 2.50 eV (**2**). Considering the simplicity of the HMO model and the neglect of electron repulsion, the agreement is quite acceptable.

Experimental and Calculational Section

HMO wave functions were calculated with the parameterization of Atherton and co-workers:[8] $\alpha_N = \alpha + 0.7\beta$, $\alpha_S = \alpha + 1.1\beta$, $\alpha_{Se} = \alpha + 1.04\beta$, $\beta_{C-N} = 0.7\beta$, $\beta_{N-S} = 0.7\beta$, and $\beta_{N-Se} = 0.6\beta$. The ESR spectrum of the radical cation was obtained by bubbling a small amount of bromine through a solution of **1** in nitrobenzene.[13] Mass spectra were obtained by Gollob Analytical Service, Inc.

Preparation of Naphtho[1,8-*c,d*:4,5-*c′,d′*]bis[1,2,6]selenadiazine (1). To a slurry of the "tin double salt" of 1,4,5,8-tetraaminonaphthalene[2,6] (0.71 g, 1 mmol) in 50 mL of dry CH_2Cl_2 magnetically stirred under nitrogen was added triethylamine (1.67 mL, 1.21 g, 12 mmol). The mixture was stirred at room temperature and soon became dark. $SeOCl_2$ (0.27 mL, 0.664 g, 4 mmol) was added dropwise, and the mixture was stirred for 3 h at room temperature. The dark solid product which had formed was collected by filtration, washed with CH_2Cl_2 and CS_2, and dried under nitrogen; crude weight, 0.6 g. The material was recrystallized from 1,2-dichloroethane, and gave 50 mg of metallic green needles (15% yield); mp > 400 °C.

The NMR spectrum in Me_2SO-d_6 consisted of a singlet at δ 5.91. The MS showed a molecular ion at *m/e* 340 (base peak) together with the isotope pattern expected for a molecule containing two selenium atoms. The IR spectrum (CsI) gave rise to lines at 1610 (m), 1403 (m), 1325 (w), 1241 (w), 1137 (s), 1100 (m), 972 (m), 948 (w), 828 (vs), 765 (s), 745 (s), 738 (s), 657 (s), 615 (w), 492 (s), 455 (va), 363 (s), 298 (s) cm^{-1}. The UV spectrum (dioxane) exhibited the following $\lambda_{max}(\epsilon)$ 263 (21 200), 280 (sh) (15 500), 328 (5780), 341 (sh) (4580), 490 (sh) (13 100), and 523 (21 100) nm. Anal. Calcd for $C_{10}H_4N_4Se_2$: C, 35.53; H, 1.19; N, 16.57. Found: C, 35.81; H, 1.49; N, 16.42.

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