

the corresponding ethoxymethyl derivatives **13** were isolated (63–82%) along with minor amounts (5–7%) of the symmetrical dimer **14**. Interestingly, these reactions also proceed at ambient temperatures but at a slower rate. For example, a solution of **10a** in absolute ethanol stirred at room temperature for 24 h resulted in **13a** and **14a** in 45% and 22% yields, respectively.

These data agree with the proposed *o*-quinone methides **11** as intermediates. In this regard, the alkoxyquinones are envisaged to arise via Michael addition of ethanol to the enone followed by oxidation of the resulting hydroquinone.<sup>10</sup> The dimer **14** could result from a number of possible pathways, but an attractive possibility involves Diels–Alder dimerization of the *o*-quinone methides **11** to the corresponding spiropyrans.<sup>11</sup> The symmetrical dimer, in its half-reduced oxidation state, would then result directly from an intramolecular elimination. Subsequent oxidation of this would then give the symmetrical diquinone dimer **14**.

Further evidence for the *o*-quinone methide intermediate comes from the observations that **10a** gave the hydroquinone **12a** (85%) in refluxing glacial acetic acid/sodium acetate and that this hydroquinone gave a similar product distribution as observed for **10a** when subjected to refluxing ethanol. Thus, the conversion of **10a** and **12a** to **13a** and **14a** strongly suggests the *o*-quinone methide **11a** as a common transient intermediate.

Additional studies illustrating the synthetic utility of the ((trimethylsilyl)methyl)quinone/*o*-quinone methide conversion are given in Scheme IV. Thermolysis of **10a** in 5% aqueous acetonitrile followed by oxidative workup afforded three products: the alcohol **15** (12%), the xanthen derivative **16** (22%), and the ethylene dimer **14a** (46%). The xanthen derivative is viewed as arising from the Diels–Alder cycloaddition of the quinone **10a** with the *o*-quinone methide **11a**.<sup>12</sup> Interestingly, the amount of water had a dramatic effect on the product distribution. For example, when 10% rather than 5% aqueous acetonitrile was employed, a 67% yield of **14a** and 18% of **15** were isolated. Only traces of **16** were detected. These results are consistent with a mechanism in which water functions as the reagent to induce *o*-quinone methide formation (Scheme I, NuH = H<sub>2</sub>O).<sup>13</sup> At low water concentration (5%), the concentration of the *o*-quinone methide is also low, and thus it is easily intercepted by an unreacted quinone in a Diels–Alder cycloaddition to give **16**. As the water concentration is increased (10%) so follows the *o*-quinone methide concentration, and dimerization as described previously takes place to give **14a**.

Finally, an example of Diels–Alder trapping of the *o*-quinone methide is illustrated by the synthesis of **17**. That is, generation of the *o*-quinone methide in 10% aqueous acetonitrile in the presence of excess *n*-butyl vinyl ether gave the chromanol **17** in 72% yield.<sup>14,15</sup>

In conclusion, the most significant aspects of this study include the following: (a) ((trimethylsilyl)methyl)-1,4-benzoquinones **1** function as excellent precursors to *o*-quinone methide intermediates **3**; (b) the *o*-quinone methides **3** do not undergo tautomerization, which suggests that ketonization is slower than nucleophilic addition; (c) the position of the trimethylsilyl group in **1** dictates the specific quinone methide formed; and (d) the conversion of

**1** to **3** can be accomplished under mild and neutral conditions and thus allows the synthetic utilization of these reactive electrophilic intermediates.

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**Supplementary Material Available:** A table of spectroscopic data (IR, MS, <sup>1</sup>H and <sup>13</sup>C NMR) for compounds **6–17** (2 pages). Ordering information is given on any current masthead page.

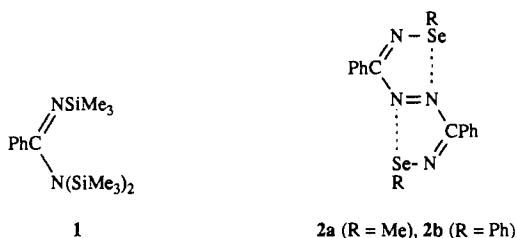
## Synthesis and Structure of Azo Dyes with Short, Intramolecular Selenium–Nitrogen Contacts

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Recently there has been considerable interest in the synthesis and structures of both organic and inorganic selenium–nitrogen (Se–N) compounds. Some important milestones include the structural characterization of (a) dimers of the cyclic seven- $\pi$ -electron radicals 1,2,4,6-selenatriazinyl, (Ph<sub>2</sub>C<sub>2</sub>N<sub>3</sub>Se)<sub>2</sub>,<sup>1</sup> 1,2,3,5-diselenadiazolyl, (PhCN<sub>2</sub>Se<sub>2</sub>)<sub>2</sub>,<sup>2</sup> and 1,2,4-triseleno-3,5-diazolium, (Se<sub>3</sub>N<sub>2</sub><sup>+</sup>)<sub>2</sub>,<sup>3</sup> and (b) metal complexes of the acyclic, binary Se–N anions, Se<sub>3</sub>N<sup>-</sup> and Se<sub>2</sub>N<sub>2</sub><sup>-</sup>.<sup>4,5</sup> We have prepared eight-membered 1,5-P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub> rings by the cyclocondensation reaction of Ph<sub>2</sub>P(NSiMe<sub>3</sub>)[N(SiMe<sub>3</sub>)<sub>2</sub>] with organoselenium trichlorides.<sup>6</sup> In an attempt to obtain the unknown 1,5-C<sub>2</sub>N<sub>4</sub>Se ring, we have found that the reaction of PhC(NSiMe<sub>3</sub>)[N(SiMe<sub>3</sub>)<sub>2</sub>] (**1**) with RSeCl<sub>3</sub> (R = Me, Ph) unexpectedly produces the intensely colored diazenes **2a** and **2b** rather than the expected eight-membered ring. The X-ray structure of **2a** reveals a nearly planar structure in which the hypervalent selenium atoms are connected by short, intramolecular contacts (ca. 2.65 Å) to one nitrogen of the azo group. A better synthesis of **2b** (and its sulfur analogue) involves the reaction of **1** with 3 mol of PhECl (E = S, Se).



**2a** (R = Me), **2b** (R = Ph)

The dark red azo compound **2a** was obtained in 44% yield by the slow addition of **1** to an equimolar amount of MeSeCl<sub>3</sub> in acetonitrile at 23 °C.<sup>7,8</sup> An X-ray structural analysis confirmed

(10) Subjecting **10a** to isopropyl alcohol (10 h, reflux) furnished the corresponding isopropoxymethylquinone and **14a** in 67% and 10% yields, respectively (oxidative workup). Analogously, the reaction of **10a** in *tert*-butyl alcohol (44 h) gave 45% of the *tert*-butoxymethylquinone and 22% of **14a**.

(11) For examples of the formation of unsymmetrical *o*-quinone methide dimers see: (a) Chauhan, M. S.; Dean, F. M.; Matkin, D.; Robinson, M. L. *J. Chem. Soc., Perkin Trans. 1* 1973, 120–125. (b) Chauhan, M. S.; Dean, F. M.; McDonald, S.; Robinson, M. S. *J. Chem. Soc., Perkin Trans. 1* 1973, 359–363.

(12) For examples of similar dimerizations see: (a) Smith, L. I.; Tess, R. W. H.; Ulyot, G. E. *J. Am. Chem. Soc.* 1944, 66, 1320–1323. (b) Chandrasenan, K.; Thomson, R. H. *J. Chem. Soc. C* 1966, 123–124. (c) References 2d and 2e.

(13) Heating **10a** in dry benzene at reflux for 90 h gave >98% of recovered starting material.

(14) A 74% yield of **17** was obtained when **12a** was heated in refluxing acetonitrile in the presence of excess *n*-butyl vinyl ether.

(15) For trapping of *o*-quinone methides in Diels–Alder reactions, see: (a) Bolon, D. A. *J. Org. Chem.* 1970, 35, 3666–3670. (b) References 1 and 11a.

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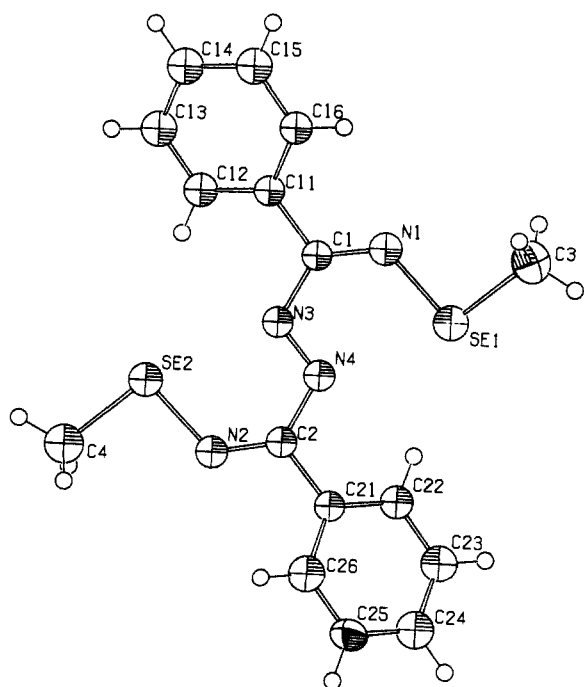
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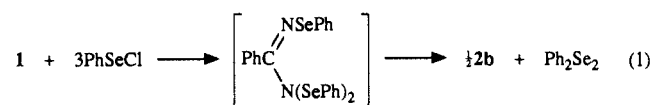
**Figure 1.** ORTEP plot for *trans*-MeSeN(Ph)CN=NC(Ph)NSeMe (**2a**); selected bond lengths (Å) and bond angles (deg): C(3)–Se(1), 1.934 (5); Se(1)–N(1), 1.817 (3); N(1)–C(1), 1.274 (5); C(1)–C(11), 1.484 (5); C(1)–N(3), 1.433 (5); N(3)–N(4), 1.263 (4); N(4)–C(2), 1.421 (5); C(2)–C(21), 1.476 (5); C(2)–N(2), 1.290 (5); N(2)–Se(2), 1.813 (3); Se(2)–C(4), 1.939 (5); Se(1)–N(4), 2.648 (3); Se(2)–N(3), 2.648 (4); C(3)–Se(1)–N(1), 93.0 (2); Se(1)–N(1)–C(1), 125.1 (3); N(1)–C(1)–N(3), 126.2 (3); N(1)–C(1)–C(11), 119.8 (4); N(3)–C(1)–C(11), 114.0 (3); C(1)–N(3)–N(4), 113.1 (3); N(3)–N(4)–C(2), 113.6 (2); N(4)–C(2)–C(21), 114.2 (3); N(4)–C(2)–N(2), 127.1 (3); C(21)–C(2)–N(2), 118.7 (4); C(2)–N(2)–Se(2), 124.0 (3); N(2)–Se(2)–C(4), 92.3 (2).

structure **2a**.<sup>9</sup> The molecular geometry and atomic numbering scheme are shown in Figure 1. The molecule forms a nearly planar SeNCNNCNSe chain in which an azo group is bonded in a *trans* fashion to the C(Ph)NSeMe substituents.<sup>10</sup> The phenyl groups attached to C(11) and C(21) are out of this plane by ca. 22° and 35°, respectively. There are short, intramolecular contacts between the selenium atoms and one of the nitrogen atoms of the azo group, i.e., Se(1)–N(4) and Se(2)–N(3), of ca. 2.65 Å (cf. 3.5 Å for the sum of the van der Waals radii for Se and N).<sup>11</sup> This "hypervalence" enforces a *syn* configuration with respect to the C=N bond.<sup>12</sup> The N=N bond distance of 1.263 (4) Å (cf.  $|d(\text{N}=\text{N})| = 1.24\text{--}1.26$  Å for simple aromatic azo compounds or diazenes with C=O groups bound to N=N)<sup>13</sup> and the unequal

C–N bond lengths of ca. 1.43 and 1.28 Å indicate only modest delocalization between the azo group and its substituents. The Se–N bond lengths of ca. 1.815 Å imply a low  $\pi$ -bond order.<sup>14,15</sup> Thus structure **2a** represents a reasonable approximation of the bonding. This model is reminiscent of the structures of trithia-pentalene analogues<sup>16</sup> except that the long Se–N bonds in **2a** are separated by an N=N group rather than a single (S, Se, or Te) atom. There are no significant intermolecular Se–N or Se–Se contacts.

The dark blue derivative **2b** may also be prepared by the reaction of **1** with PhSeCl<sub>3</sub> (1:1 molar ratio) in acetonitrile, but a better synthesis (55% yield) involves the reaction of **1** with 3 mol of PhSeCl in CH<sub>2</sub>Cl<sub>2</sub> for 3 h at 23 °C.<sup>7,17</sup> Diphenyl diselenide was isolated in quantitative yield according to eq 1.

*trans*-PhSN(Ph)CN=NC(Ph)NSPh (**3**), the sulfur analogue of **2b**, was obtained in 56% yield by the reaction of **1** with 3 mol of PhSCL.<sup>8,18</sup>



In azo dyes the  $n \rightarrow \pi^*$  transition of the N=N group, e.g.,  $\lambda_{\text{max}}$  443 nm ( $\epsilon = 5 \times 10^2$ ) in *trans*-azobenzene, is partially or totally obscured by the batho- and hyperchromically displaced  $\pi \rightarrow \pi^*$  band, which is responsible for the intense color of these compounds.<sup>19</sup> The high intensity ( $\epsilon \geq 10^4$ ) and low energy ( $\lambda_{\text{max}}$  500–550 nm) of the visible absorption band of **2a**, **2b**, and **3** indicate that it is also due to a  $\pi \rightarrow \pi^*$  transition, but the identification of the chromophore must await more detailed investigations of the nature of the Se–N interaction.

Compound **2b** is more easily reduced electrochemically than aromatic diazenes. It undergoes a reversible, one-electron reduction in acetonitrile at –0.51 V vs SCE (cf.  $E_{1/2} = -1.41$  V for *trans*-azobenzene in acetonitrile)<sup>20</sup> to give the corresponding anion radical ( $\lambda_{\text{max}}$  478 nm), which has a lifetime of <10 s in solution at room temperature.

In summary, we have prepared a structurally unusual class of selenium-containing azo dyes. The nature of the selenium hypervalency, the source of the chromophore, and the mechanism of their formation are under investigation. The ligand properties of these new compounds also merit attention.

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**Supplementary Material Available:** A listing of atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, bond distances, bond angles and torsion angles for non-hydrogen atoms, and experimental details for the X-ray analysis of **2a** (4 pages); a listing of structure factor amplitudes for **2a** (34 pages). Ordering information is given on any current masthead page.

(7) Compound **2a** forms dark maroon rectangular crystals [from CH<sub>2</sub>Cl<sub>2</sub>–pentane (4:1) at 0 °C], mp 123–5 °C. <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  8.25 (m) and 7.51 (m) (C<sub>6</sub>H<sub>5</sub>, 10 H), 2.31 (s, CH<sub>3</sub>, 6 H). <sup>2</sup>J (<sup>77</sup>Se–<sup>1</sup>H) = 14.1 Hz. UV–visible (in CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  532, 502 ( $\epsilon \sim 1.0 \times 10^4$  L mol<sup>–1</sup> cm<sup>–1</sup>), 472 nm.

(8) Satisfactory, C, H, and N analyses were obtained for **2a**, **2b**, and **3**.

(9) X-ray analysis: Compound **2a** crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c*, with  $a = 10.026$  (1) Å,  $b = 7.4129$  (7) Å,  $c = 22.351$  (2) Å,  $\beta = 98.344$  (9)°,  $V = 1643.6$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.706$  g cm<sup>–3</sup>, and  $Z = 4$ . Data were collected on an Enraf–Nonius CAD4 diffractometer at 25 °C. Of the 4796 unique data collected with Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å), the 2139 with  $I > 3\sigma(I)$  were used in the least-squares refinement to yield  $R = 3.8\%$ ,  $R_w = 2.3\%$  after an absorption correction was applied.

(10) The individual five-membered rings Se(1)–N(1)–C(1)–N(3)–N(4) and Se(2)–N(2)–C(2)–N(3)–N(4) are planar to within 0.075 (4) and 0.028 (4) Å, respectively, with N(3) and N(4) showing the largest deviation from planarity. The dihedral angles for N(4)–N(3)–C(1)–N(1) and N(3)–N(4)–C(2)–N(2) are –10.2 (5) and 3.4 (5)°, respectively.

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(12) Related structures involving intramolecular Se–O contacts of 2.6–2.7 Å have been reported. (a) Atkinson, A.; Brewster, A. G.; Ley, S. V.; Osborn, R. S.; Rogers, D.; Williams, D. J.; Woode, K. A. *J. Chem. Soc., Chem. Commun.* 1977, 325. (b) Tomoda, S.; Iwaoka, M. *J. Chem. Soc., Chem. Commun.* 1990, 231.

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(15) The average Se–N bond distance in diaminoselanes, R<sub>2</sub>NSe<sub>x</sub>NR<sub>2</sub> ( $x = 2\text{--}4$ ), is 1.843 (2) Å. Foss, O.; Janickis, V. *J. Chem. Soc., Dalton Trans.* 1980, 628.

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(17) Compound **2b** forms dark purple microcrystals (from hexane), mp 110 °C. UV–visible (in CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  553 ( $\epsilon = 1.3 \times 10^4$  L mol<sup>–1</sup> cm<sup>–1</sup>), 580 nm (sh).

(18) Compound **3** forms purple-brown microcrystals (from 3:1 CHCl<sub>3</sub>–pentane), mp 165 °C. UV–visible (in CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  537 nm ( $\epsilon = 1.7 \times 10^4$  L mol<sup>–1</sup> cm<sup>–1</sup>).

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