

# Notes

Thermochromic Properties of Diphenyl  
Diselenide in Solution

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Figure 1. Absorption spectra of an  $8.9 \times 10^{-5}$  mol/L 1,2-ethanediol solution of diphenyl diselenide from 220 to 450 nm at (a) 10, (b) 50, and (c) 100 °C and (inset) a  $2.05 \times 10^{-3}$  mol/L solution from 280 to 500 nm at (a) 5, (b) 20, (c) 100, and (d) 180 °C.

Gaussian deconvolution of the short wavelength spectra revealed the presence of a prominent band at 241 nm ( $\epsilon = 1.69 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>) along with weaker bands (integrated areas <25% of that of the 241-nm band) at 254 and 276 nm, which appear as shoulders on the 241-nm peak. None of these three peaks appear to be very sensitive to temperature changes over the region studied. The longer wavelength spectra reveal the observed thermochromism to arise from an apparent broadening of the peak located at 332 nm ( $\epsilon = 1.0 \times 10^3$  L mol<sup>-1</sup> cm<sup>-1</sup>) at 20 °C. Due to the broadness and lack of definition of this peak, as well as the presence of significant absorption from the tails of the shorter wavelength bands, it was not possible to unambiguously demonstrate the presence of more than a single component band by Gaussian deconvolution. The single band centered at 332 nm was determined by Gaussian fitting to be about three times as broad and one fifth as large in area as the band centered at 241 nm.

A small degree of thermal instability at higher temperatures as well as changes in the dielectric constant of the solution with temperature could account for the lack of completely reproducible spectra and sharp isosbestic points. Measurements of the absorption spectrum from 280 to 550 nm following irradiation with white light over a period of 25 min indicated that significant

photochemical decomposition of the compound to yield colloidal selenium had occurred and could account for the lack of complete reproducibility in the absorption spectra. The lower temperature spectra shown in Figure 1 are in excellent agreement with literature reports of the room temperature spectra of diphenyl diselenide in ethanol<sup>9</sup> and heptane, methanol, and acetonitrile<sup>13</sup> solvents.

The three short wavelength bands located by Gaussian curve fitting procedures to lie at 241, 254, and 276 nm have been assigned previously to be due to transitions of electrons from the Se-localized FOMO of 4p lone pair character to  $\pi^*$  orbitals localized mainly on the phenyl rings.<sup>13</sup> As such these transitions can be considered to possess significant selenium to phenyl charge transfer character, in accord with calculations for dimethyl disulfide.<sup>12</sup> In contrast the long wavelength band at 332 nm was assigned, in accord with Bergson's model,<sup>11</sup> to Se-localized transitions from the HOMO to the  $\pi^*$ -Se LUMO.<sup>13</sup> These assignments appear to be reasonable.

Assuming the assignment for the long wavelength band is correct, the explanation for the observed thermochromism is relatively straightforward. At lower temperatures