

Notes

Thermochromic Properties of Diphenyl Diselenide in Solution

H. Kunkely, A. Vogler,* and J. K. Nagle*[†]

Institut für Anorganische Chemie,
Universität Regensburg, Universitätstrasse 31,
D-93040 Regensburg, Federal Republic of Germany

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Introduction

Diphenyl diselenide was first reported to exhibit thermochromism more than 60 years ago,¹ forming a yellow solution in methylbenzene at room temperature which becomes orange upon heating. To our knowledge no subsequent reports on the solution thermochromism of dialkyl or diaryl diselenides have appeared, although a bright yellow to orange thermochromic change was reported to accompany the solid-to-liquid phase transition for dimethyl diselenide.² The behavior of dimethyl diselenide in this regard is in sharp contrast to the situation for distibines and dibismuthines which undergo blue shifts upon melting.^{2–5}

As predicted by Pauling⁶ and confirmed shortly thereafter by X-ray crystallography,⁷ diphenyl diselenide exhibits a nearly 90° dihedral angle between the two CSeSe planes. A red shift of the lowest UV band of various diselenides, R₂Se₂, as the dihedral angle is torsionally distorted from 90° due to structural variations in R has been observed.^{8–10} Bergson has proposed a simple orbital overlap model for diselenides and disulfides¹¹ which accounts for the nearly 90° bond angle in diphenyl diselenide as well as the red shift in the lowest UV band of the distorted diselenides.

In its simplest form Bergson's model attributes the Se–Se bonding in diselenides to Se 4p–4p atomic orbital overlaps in which any 4s involvement is neglected. In this model the highest occupied molecular orbitals (HOMOs) correspond to lone pairs of electrons located in Se 4p atomic orbitals, and the lowest unoccupied molecular orbital (LUMO), σ^*_{SeSe} , is the antibonding counterpart to the bond formed between the Se atoms. Any torsional distortions from 90° about the C₂ molecular symmetry axis are predicted to lead to a splitting of the degenerate HOMOs so that the HOMOs in the distorted

diselenides will lie at higher energy than in the undistorted case, while the energy of the LUMO is predicted to remain nearly constant. Bergson's model has received considerable support from electronic structure calculations on both disulfides^{12–14} and diselenides.¹³

In this contribution we present the results of a study of the absorption spectrum of diphenyl diselenide in 1,2-ethanediol as a function of temperature and demonstrate how Bergson's model can be used to explain the observed solution thermochromism. Although the original observation was made in methylbenzene, the higher boiling point and greater ultraviolet transparency of 1,2-ethanediol make it a more suitable solvent for more thorough spectroscopic studies of the thermochromic behavior of diphenyl diselenide. To our knowledge there have been no reports of analogous spectral effects for disulfides, probably because they absorb only in the ultraviolet region of the spectrum.

Experimental Section

Materials. Diphenyl diselenide (Aldrich) was used as received. Acetonitrile, methylbenzene, and 1,2-ethanediol were all spectrograde solvents.

Absorption Spectra. Absorption spectra were measured with an 8452 A Hewlett-Packard diode array spectrophotometer. All solvents were saturated with argon. Diphenyldiselenide was found to obey the Lambert–Beer law in the concentration range from $\approx 10^{-4}$ to 10^{-1} mol/L. 1,2-Ethanediol was used for measurements of thermochromism because of its transparency in the UV region and because it does not boil below 196 °C. Temperature-dependent spectra were obtained in a thermostated cell. The reversibility was checked by measuring spectral changes upon both heating and cooling of the cell.

Data Analysis. Digital spectral files were imported into the Spectra Calc (Galactic Industries) computer program for analysis. The observed spectra could be reproduced as the sums of individual Gaussian bands located at different wavelengths. They were resolved into their component bands by least-squares data fitting with either the Data Fit 1.10 (part of the Square Tools 2.0 data package for Spectra Calc available from Spectrum Square Associates) or Curve Fit routines in Spectra Calc.

Results and Discussion

Figure 1 shows the absorption spectrum from 220 to 450 nm of an 8.9×10^{-5} mol/L solution of diphenyl diselenide in 1,2-ethanediol at 10, 100, and 180 °C and from 280 to 500 nm of a 2.05×10^{-3} -mol/L solution at 5, 20, 100, and 180 °C. Nearly identical spectra are obtained by either heating cold solutions to high temperatures or by cooling hot solutions to low temperatures, and nearly isobestic points are seen at 308 and 380 nm. The integrated areas of the spectra from 214 to 550 nm were determined to vary by less than 2% over the temperature range from 20 to 180 °C, in accord with theoretically calculated oscillator strengths for dihydrogen disulfide¹² (such calculations for diselenides apparently have not been reported).

[†] Fulbright Scholar on sabbatical leave from the Department of Chemistry, Bowdoin College, Brunswick, ME 04011.

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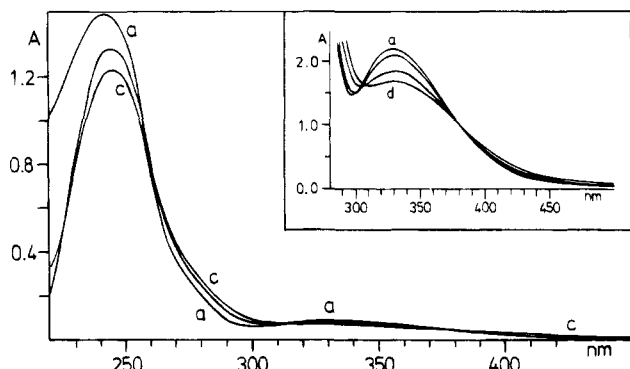


Figure 1. Absorption spectra of an 8.9×10^{-5} mol/L 1,2-ethanediol solution of diphenyl diselenide from 220 to 450 nm at (a) 10, (b) 50, and (c) 100 °C and (inset) a 2.05×10^{-3} mol/L solution from 280 to 500 nm at (a) 5, (b) 20, (c) 100, and (d) 180 °C.

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 $^{-1}$ cm $^{-1}$) 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 $^{-1}$ cm $^{-1}$) 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 isobestic 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 ethanol⁹ and heptane, methanol, and acetonitrile¹³ 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 HOMO of 4p lone pair character to π^* orbitals localized mainly on the phenyl rings.¹³ As such these transitions can be considered to possess significant selenium to phenyl charge transfer character, in accord with calculations for dimethyl disulfide.¹² In contrast the long wavelength band at 332 nm was assigned, in accord with Bergson's model,¹¹ to Se-localized transitions from the HOMO to the $\sigma^*_{\text{Se-Se}}$ LUMO¹³. 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 or in the solid form, vibrational motions resulting in torsional distortions about the 90° dihedral angle between the Se-Se-C planes are relatively restricted compared to the situation at higher temperatures. According to the Bergson model¹¹ such torsional distortions will split the symmetry-degenerate HOMOs found at 90° into π -bonding and antibonding combinations, thereby effectively broadening the observed peak at higher temperatures and leading to the observed thermochromism. There should be a statistical distribution of molecules with 90° dihedral angle variations, the extent of such variations increasing with increasing temperature and effectively lowering the HOMO-LUMO energy gap.

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