

## Absorption and Emission of Germylenes (Germanediyls); Their Complexation

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Germylenes,  $R_2Ge$ : ( $R = Me$  or  $Ph$ ), show broad electronic absorption bands with  $\lambda_{max}$  in the region of 416–464 nm, weak fluorescence peaks in the region of 620–651 nm at 77 K, and a large Stokes shift, attributed to a conformational change in the C–Ge–C bond angle between the ground and the lowest excited singlet states; UV–VIS spectra provide evidence for the interaction of dimethylgermylene with the  $\pi$ -system of arylated germanium precursors.

The spectroscopic characterization of germylenes, analogues of carbenes and silylenes, has been the subject of considerable interest in recent years.<sup>1</sup> We herein describe the first report of the fluorescence spectra of the simple diorganogermylenes,  $R_2Ge$ : ( $R = Me$  or  $Ph$ ), in 3-methylpentane (3-MP) at 77 K, and spectroscopic evidence for dimethylgermylene complex formation with the  $\pi$ -system of arylated germanium precursors.

The known precursors of simple germylenes (permethylated polygermanes<sup>2,3</sup> and arylated germanium compounds<sup>4,5</sup>) were photolysed with a 110 W low-pressure Hg arc lamp (spiral type) in 3-MP at 77 K to give the corresponding germylenes. The photogenerated germylene residue appeared as a polymer, and was trapped with appropriate agents (2,3-dimethylbuta-1,3-diene and  $CCl_4$ ) to give the expected products [1,1,3,4-tetramethyl-1-germacyclopent-3-ene<sup>4</sup> and trichloromethyl dimethylchlorogermane, ( $CCl_3Me_2GeCl$ ), respectively].<sup>6,7</sup>

In 3-MP at 77 K diorganogermylenes showed absorption bands with  $\lambda_{max}$  in the range 416–436 nm for  $Me_2Ge$ :, at 456 nm for  $PhMeGe$ :, and at 462 nm for  $Ph_2Ge$ ;; and weak fluorescence peaks around 620–630 nm for  $Me_2Ge$ :, at 645 nm for  $PhMeGe$ :, and at 651 nm for  $Ph_2Ge$ :. The UV–VIS absorption and fluorescence spectra of  $Me_2Ge$ :, generated by the photolysis of  $Me[Me_2Ge]_5Me$ , in 3-MP at 77 K shown in Fig. 1 are typical. The UV–VIS absorptions due to  $R_2Ge$ :. were not observed when the matrix was warmed to its softening point. The fluorescence excitation spectra of  $R_2Ge$ :. followed the shape of the absorption bands. The absorption and emission data of diorganogermylenes ( $R_2Ge$ :) observed in this study are summarized in Table 1, together with results reported by other groups.<sup>7–9</sup>

The absorption bands in the region of 416–462 nm for  $R_2Ge$ :. observed in this study are due to the  $S_1$ – $S_0$  transition. Emissions with peaks in the 620–651 nm region were observed in 3-MP at 77 K. The fluorescence excitation spectra coincided with the absorption spectra of germylenes. There is a good mirror-image relationship between the absorption and emission spectra with a Stokes shift of 6285–7909  $cm^{-1}$ . We therefore conclude that the emission of germylenes in the

region of 620–651 nm corresponds to the  $S_1$ – $S_0$  radiative transition. The 0–0 transition energies for the germylenes are estimated to be 197–215  $kJ mol^{-1}$  from the positions of the absorption and emission peaks. The singlet excited state ( $S_1$ ) and triplet ground state ( $T_0$ ) of  $Me_2Ge$ :. are theoretically predicted to lie 213 and 57  $kJ mol^{-1}$  above the  $S_0$  ground state, respectively.<sup>10</sup> The huge Stokes shift of 6285–7909  $cm^{-1}$  for the germylenes is attributed to a change in the C–Ge–C bond angle between the lowest excited singlet state and the ground state and confirms theoretical expectation.<sup>10</sup> The change of the C–Ge–C bond angle for the germylenes increases in the order:  $Ph_2Ge$ :. <  $PhMeGe$ :. <  $Me_2Ge$ :. 3-MP solutions of  $R_2Ge$ :. ( $R = Ph$  or  $Me$ ) show no EPR signal, supporting a singlet ground state for  $R_2Ge$ :.

A careful examination of the UV data for  $R_2Ge$ :. (Table 1) shows that the absorption bands ( $\lambda_{max}$ ) of  $Me_2Ge$ :. generated from permethylated polygermanes  $\{[Me_2Ge]_6$  (dodecamethylcyclohexagermane) and  $Me[Me_2Ge]_5Me\}$  are blue-shifted compared with those of  $Me_2Ge$ :. obtained from  $\pi$ -system-substituted organogermanium compounds.<sup>7–9</sup> The observed blue shifts for  $Me_2Ge$ :. are probably due to the

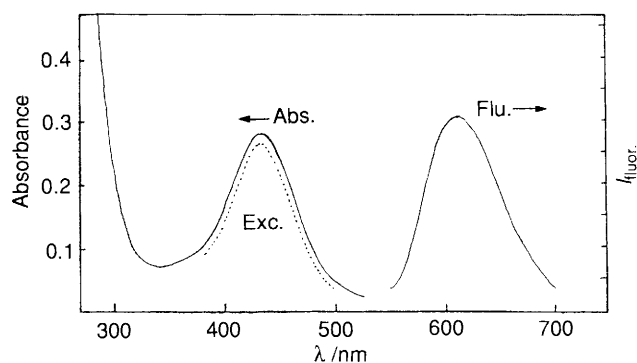


Fig. 1 Absorption, fluorescence and excitation spectra of dimethylgermylene obtained from  $Me[Me_2Ge]_5Me$  by UV irradiation in 3-MP at 77 K

**Table 1** Absorption and emission spectral data of germylenes in 3-MP at 77 K

R <sub>2</sub> Ge:	Precursor	λ/nm			Stokes shift/ cm <sup>-1</sup>	Remarks
		Abs.	Fluor.	Exc.		
Me <sub>2</sub> Ge:	[Me <sub>2</sub> Ge] <sub>6</sub>	430	630	430	7382	This work
Me <sub>2</sub> Ge:	Me[Me <sub>2</sub> Ge] <sub>5</sub> Me	436	628	440	7012	This work
Me <sub>2</sub> Ge:	(PhMe <sub>2</sub> Ge) <sub>2</sub> GeMe <sub>2</sub>	422	623	445	7645	This work
Me <sub>2</sub> Ge:	Me <sub>2</sub> Ge(SePh) <sub>2</sub>	420				7
Me <sub>2</sub> Ge:	Trigermacyclo- heptadiene	420				8
Me <sub>2</sub> Ge:	7-Germanorborna- diene	{416 420}	620	445	7909	This work 9
PhMeGe:	(Me <sub>3</sub> Ge) <sub>2</sub> GePhMe	456	645	455	6426	This work
Ph <sub>2</sub> Ge:	(Me <sub>3</sub> Ge) <sub>2</sub> GePh <sub>2</sub>	462	651	463	6285	This work

interaction of the vacant orbital of Me<sub>2</sub>Ge: with the π system of the arylated germanium compound precursors. The electronic environment of Me<sub>2</sub>Ge: appears to affect the nature of its interaction with the donor molecule. Thus, the degree of dimethylgermylene complex formation with donor molecules depends upon the strength of their π-donor properties. The fluorescence excitation spectra of Me<sub>2</sub>Ge: obtained from permethylated polygermanes perfectly followed the shape of the absorption bands of Me<sub>2</sub>Ge:, whereas the spectra for Me<sub>2</sub>Ge: obtained from arylated germanium compounds were red-shifted. The shift between the excited spectra and absorption spectra also supports the interaction of Me<sub>2</sub>Ge: with the π-system.

To confirm the stability of dimethylgermylene complex formation with π-systems, we irradiated Me[Me<sub>2</sub>Ge]<sub>5</sub>Me and [Me<sub>2</sub>Ge]<sub>6</sub> in a matrix [3-MP–isopentane (IP), 4:1] containing benzene or naphthalene. The absorption band at 436 nm due to free Me<sub>2</sub>Ge: was gradually blue-shifted (from 436 to 423 nm) with increasing concentration of benzene (molar ratio of benzene to Me[Me<sub>2</sub>Ge]<sub>5</sub>Me = 0–10:1) in the matrix. Similar phenomena were also observed in the absorption band of Me<sub>2</sub>Ge: (from 435.5 to 422.5 nm) obtained from Me[Me<sub>2</sub>Ge]<sub>5</sub>Me in a matrix containing naphthalene (molar ratio of naphthalene to Me[Me<sub>2</sub>Ge]<sub>5</sub>Me 0–2:1) and in the reaction of [Me<sub>2</sub>Ge]<sub>6</sub> with benzene or naphthalene.

Although the spectroscopic characterization of diarylgermylene complexes with heteroatom-containing substrates has been reported by Satgé and coworkers,<sup>11</sup> and Ando and coworkers,<sup>1b</sup> the present report provides the first examples of the formation of dimethylgermylene complexes with the π-system of the germylene precursors.

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