

Raman and UV-VIS study of the conformational polymorphism of solid tetramesityldisilene $\text{Mes}_2\text{Si}=\text{SiMes}_2$

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All three modifications of tetramesityldisilene **1** reported to date (orange unsolvated **1a** and two yellow 1:1 solvates with toluene **1b** and THF **1c**) have been shown to readily transform to a new form, yellow unsolvated **1d**, for which a quasi-*trans* conformation with two mesityl rings nearly orthogonal and the other two nearly coplanar to the double bond plane, is tentatively proposed. Form **1d** appears to be the most stable conformational polymorph, but can be converted to the orange form upon illumination in the region 514–457 nm.

Tetramesityldisilene **1**, the first stable Si=Si doubly-bonded compound, was synthesized in 1981.¹ However, details of its structure and especially its conformation are not completely understood. Three different crystalline modifications of **1** have been reported to date and characterized by X-ray diffraction: an unsolvated orange modification **1a** obtained from solution in hexane,² and two yellow 1:1 solvates: **1b** with toluene³ and **1c** with THF,⁴ obtainable from the corresponding solutions. In this paper yet a fourth, unsolvated, yellow modification **1d** is reported and interconversions of **1a–d** are described.[†]

The X-ray data for **1a–c**, summarized in ref. 4, demonstrate that both the crystal and the molecular structures of **1a–c** differ significantly. The Si=Si moiety is slightly distorted from planarity in all three forms but in a different way. The aromatic rings are twisted out of the double bond plane in all structures but again, in quite different ways. In addition, there is no specific interaction between **1** and solvent molecules in the solvates **1b–c**, both being typical 'packing crystals'.⁵

Figure 1 presents the Raman spectra of solid samples of **1a–c** in the most informative region, *i.e.* 15–750 cm^{-1} .[‡] According to a recently published paper⁶ in which the normal vibrations of disilenes were analysed by normal coordinate analysis (NCA), the Si=Si stretching vibration $\nu(\text{Si}=\text{Si})$ is not localized, the Si=Si and Si–C stretching coordinates of the $\text{C}_2\text{Si}=\text{SiC}_2$ moiety being heavily mixed. Their in-phase combination (ν_1) results in a normal mode in the region 460–550 cm^{-1} while their out-of-phase combination (ν_2) gives a normal mode near 700 cm^{-1} . Particular contributions of the Si=Si and Si–C stretching coordinates to the eigenvectors of ν_1 and ν_2 , the modes of principal interest, depend on the particular molecular structure but both are always significant. Therefore, the assignment of the ν_1 mode to the $\nu(\text{Si}=\text{Si})$ stretch and of the ν_2 mode to the totally symmetric $\nu(\text{Si}-\text{C})$ stretch is in essence arbitrary. For mesityl-substituted disilenes, the results of NCA⁶ predict that two of the symmetric vibrations localized in the mesityl group should fall in the same frequency range as ν_1 , *i.e.* 500–550 cm^{-1} . In good accord with the data,⁶ Figure 1 demonstrates that the Raman spectra of **1a–c** all exhibit a triplet in the region 520–550 cm^{-1} , which is the result of superposition of three lines, corresponding to two mesityl vibrations and to ν_1 , as well as an intense line of ν_2 at *ca.* 680 cm^{-1} . However, the precise frequency values and intensity ratios for **1a–c** differ slightly but distinctly, in accord with their different molecular structures, allowing identification of each modification by its Raman spectrum.

[†] Experimental. The synthesis of **1** was accomplished according to the method reported previously.¹ All experiments were carried out in a high vacuum or in a strictly inert atmosphere to prevent sample decomposition. To control sample purity, the spectra of the products of degradation were specially studied.

[‡] For Raman studies, the samples were sealed in capillaries *in vacuo*. To record the Raman spectra, Jobin-Yvon HG2S and U-1000 laser Raman spectrometers were used, excited by the 514.5 nm line of an SP-2020 Ar⁺ laser.

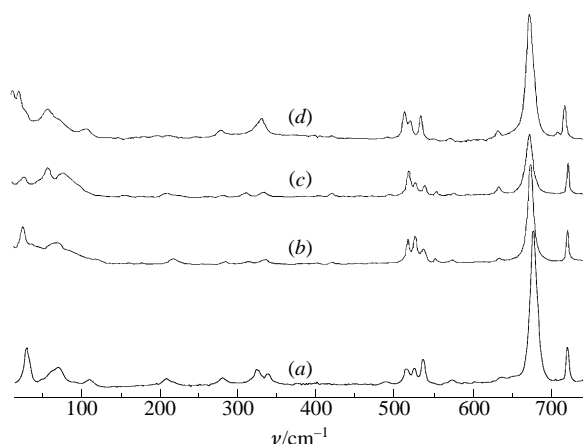


Figure 1 Raman spectra in the region 15–750 cm^{-1} of the four conformational polymorphs of solid $\text{Mes}_2\text{Si}=\text{SiMes}_2$ (solid samples sealed *in vacuo*), 514.5 nm excitation. (a) Orange crystals; (b) 1:1 toluene solvate; (c) 1:1 THF solvate; (d) unsolvated yellow form.

In the course of experimenting with the orange crystals **1a** (in an inert atmosphere or in a high vacuum) we found that, when slightly heated, sublimed or ground in a mortar, they readily transform to a yellow powder **1d** whose UV band at *ca.* 425 nm confirms that it is also a disilene.^{1,7} The same substance **1d** was obtained when solvates **1b** or **1c** were exposed to high vacuum and heated to remove the solvent. The identity of **1d**, obtained from unsolvated **1a** and from the solvates **1b–c**, was confirmed from its Raman and UV-VIS spectra.[§]

In the low-frequency region of the Raman spectra, 15–150 cm^{-1} , the crystal lattice modes are situated. This region demonstrates that the crystal structure of **1d** differs from those of **1a–c**. The Raman spectrum of **1d** in the region 450–750 cm^{-1} presented in Figure 1 resembles the spectra of **1a–c** but exhibits minor and quite expected changes in position and intensity of the diagnostic lines, allowing the conclusion that the molecular structure of **1d** also differs from those of **1a–c**.

The different colours of **1a** and **1d** suggest that they should also differ in electronic absorption. Indeed, the UV-VIS spectrum of solid **1a** exhibited a band at *ca.* 460 nm which is *ca.* 35 nm red-shifted compared to that of **1d** (see Figure 2). It is important to note that to obtain a real UV spectrum of **1a** one should not expose the sample to any mechanical or thermal stress, otherwise spectra of mixtures of **1a** and **1d** in various

[§] The UV-VIS spectra of solid **1a** and **1d** samples were obtained using Nujol, apiezon or silicone grease mulls or suspensions prepared in an inert atmosphere. The UV-VIS spectrum of **1d** was also obtained when either **1a** or **1d** were sublimed slowly onto the cooled quartz window of a cryostat in a high vacuum. The UV-VIS absorption spectra were recorded on Carl Zeiss M-40 and Perkin-Elmer Lambda Array 3280 spectrophotometers.

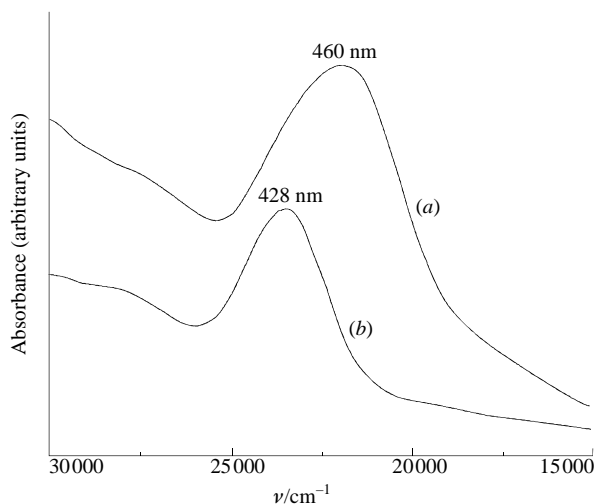


Figure 2 UV-VIS spectra of solid samples of $\text{Mes}_2\text{Si}=\text{SiMes}_2$: (a) orange crystals as an apiezon mull (almost without grinding); (b) unsolvated yellow form sublimed on a quartz window.

proportions are obtained. The best way is to simply press a small amount of **1a** in Nujol, apiezon or silicon grease between quartz plates in a dry box.

Unsolvated forms **1a** and **1d** were found to interconvert upon laser irradiation, provided the laser light density overcomes a certain threshold. Moreover, the yellow solvates **1b** and **1c** can also, sometimes, be converted to orange **1a**. For instance, prolonged exposure to a 514.5 nm laser beam produced an orange spot in the yellow sample of **1c** sealed in a capillary. The spot persisted when the capillary was removed from the light. When exposed to light of the same wavelength but of higher intensity, the crystals of **1b**, sealed *in vacuo* in a quartz cell, suddenly emitted a yellow 'cloud', a solid part of which settled on the upper wall of the cell, well separated from the initial crystals. According to the Raman spectrum, this solid film appeared to be a mixture of **1a** and **1d** with **1a** predominant.

Thus, solid **1** exists in at least four forms: two yellow crystalline 1:1 solvates with toluene and THF (**1b** and **1c**) and two solvent-free forms: orange crystals **1a** and a yellow powder **1d**. The spectral data reported here clearly show that the crystal and molecular structure of **1d** differ from those of **1a-c**.

Bernstein⁸ proposed the term 'conformational polymorphism' for an analogous phenomenon, *i.e.*, the existence of several forms of a conformationally flexible molecule, depending on crystallization conditions.

Theoretical (*ab initio*) calculations for model disilenes⁹ predicted a very flat molecular potential energy surface for the $\text{C}_2\text{Si}=\text{SiC}_2$ moiety. The existence of conformational polymorphs of **1** is evidently the result of interplay between the steric hindrance of the bulky mesityl groups, the tendency of the whole molecule towards planarity which would maximize π - π conjugation, and the crystal forces favouring close packing.

The fact that unsolvated **1a** as well as both solvates **1b** and **1c** readily convert to yellow form **1d** indicates that forms **1a-c** are metastable while form **1d** is the most thermodynamically stable.

In spite of the fact that we still have no X-ray data for **1d**, there are some reasons to speculate about its structure. For

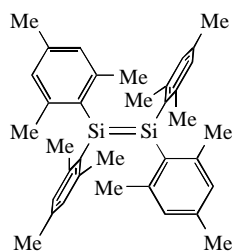


Figure 3 The structure proposed for the unsolvated yellow form of $\text{Mes}_2\text{Si}=\text{SiMes}_2$.

disilenes of the type $\text{RR}'\text{Si}=\text{SiR}'\text{R}$, photochemical *cis-trans* isomerization in solution was shown to occur,¹⁰ the *trans* isomer being predominant under equilibrium conditions. Of course, symmetrically substituted **1** cannot have real *cis-trans* isomers, but, by analogy, a similar equilibrium with predominance of the quasi-*trans* conformer seems likely in solution. This assumption is confirmed by our Raman polarization measurements for a solution of **1** in hexane,¹¹ because the selection rules observed for the conformer predominant in solution are consistent with C_{2h} symmetry, *i.e.*, with a quasi-*trans* structure of this conformer. As both the Raman and UV-VIS absorption spectra of solid **1d** are very similar to those of **1** in solution,^{1,7,11} we can also suggest for **1d** a quasi-*trans* structure shown in Figure 3.

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