

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.

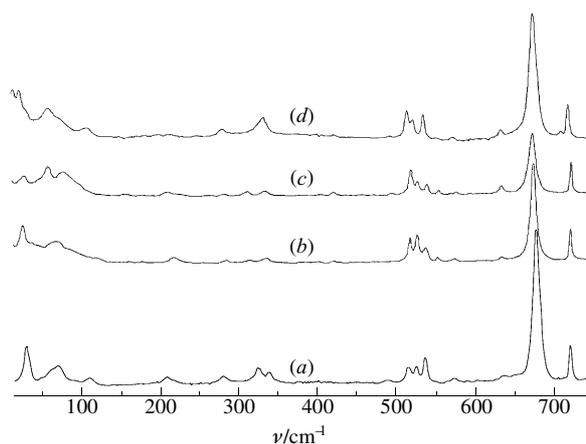


Figure 1 Raman spectra in the region 15–750 cm^{-1} of the four conformational polymorphs of solid $\text{Mes}_2\text{Si}=\text{SiMes}_2$ (solid samples sealed *in vacuo*), 514.5 nm excitation. (a) Orange crystals; (b) 1:1 toluene solvate; (c) 1:1 THF solvate; (d) unsolvated yellow form.

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.

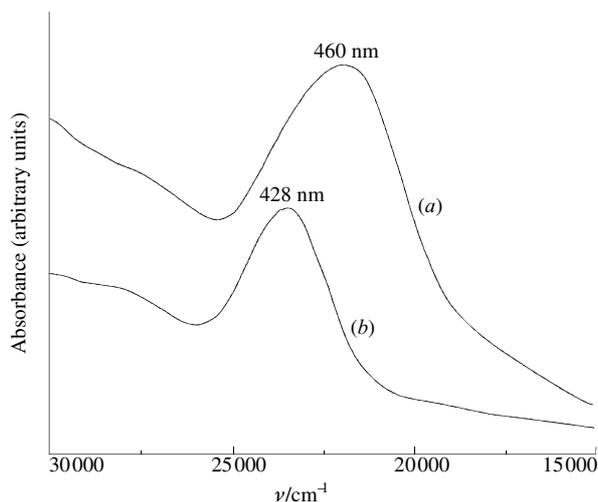


Figure 2 UV-VIS spectra of solid samples of $\text{Mes}_2\text{Si}=\text{SiMes}_2$: (a) orange crystals as an apiezon mull (almost without grinding); (b) unsolvated yellow form sublimed on a quartz window.

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 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

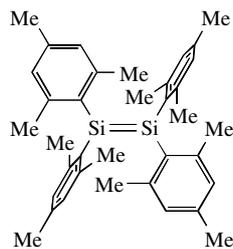


Figure 3 The structure proposed for the unsolvated yellow form of $\text{Mes}_2\text{Si}=\text{SiMes}_2$.

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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