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## Conformational polymorphism of solid tetramesityldisilene Mes<sub>2</sub>Si=SiMes<sub>2</sub> (Raman, UV–vis, IR and fluorescence study)<sup>☆</sup>

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#### Abstract

Conformational polymorphism of solid tetramesityldisilene (1) has been studied by the methods of optical spectroscopy. The three known modifications of 1: orange unsolvated 1a and two 1:1 solvates with toluene (1b) and THF (1c) have been found to transform under specific conditions to a new, most thermodynamically stable polymorph, yellow unsolvated powder 1d. The latter has been characterized by the Raman, IR, UV-vis and fluorescence data. All forms of 1 exhibit Raman spectra differing in details, which reflect their different crystal and molecular structures. Unsolvated 1a and 1d differ significantly in electronic absorption and fluorescence emission. The yellow form 1d can be converted to the orange form 1a upon illumination with laser light in the region 514-457 nm. Similarity of the Raman and UV-vis spectra of 1d to those of the solutions of 1 provides some evidence for a quasi-*trans* conformation of 1d.  $\bigcirc$  2003 Elsevier Science B.V. All rights reserved.

Keywords: Disilene; Conformational polymorphism; Raman; UV-vis spectra; Fluorescence

### 1. Introduction

Tetramesityldisilene (1) was the first Si=Si doubly bonded compound to be synthesized [2] and is undoubtedly the best studied of disilenes [3–5]. Nevertheless, details of its structural and conformational behaviour are not completely understood. Three different crystalline forms

have been reported for this compound: an unsolvated modification **1a**, orange at room temperature and thermochromic, obtained from solution in hexane [6]; a yellow, crystalline 1:1 toluene solvate, (Mes<sub>4</sub>Si<sub>2</sub>·C<sub>7</sub>H<sub>8</sub>), **1b** [7]; and a similar solvate with one molecule of THF, (Mes<sub>4</sub>Si<sub>2</sub>·THF), **1c** [8]. Recently, formation of the fourth, unsolvated yellow form **1d** was described but briefly [1,9].

The X-ray data [6-8] show that both the crystal and the molecular structures of 1a-c differ in several respects (Table 1; Fig. 1). The C<sub>2</sub>Si=SiC<sub>2</sub> moiety is slightly distorted from planarity in all three forms, but differently, with the twisting and

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Compound	Space group	Site sym	Ζ	r(Si=Si), pm	Twist angle, $(^{\circ})^{a}$	Pyram. angle, $(^{\circ})^{b}$	Ring orient, $(^{\circ})^{c}$
1a Orange	<i>P</i> 2 <sub>1</sub> /c	C1-1	4	214.3	3	12, 14	42, 52, 67, 70
1b 1 · C <sub>7</sub> H <sub>8</sub>	$I4_1/a$	C <sub>2</sub> -2	8	216.0	12	18	35, 35, 78, 78
1c 1. THF	Ccca	C <sub>2</sub> -222	4	214.6	13	0	62.6

Table 1 X-ray data for conformational polymorphs of **1** 

<sup>a</sup> The dihedral angle between the C–Si–C and C'–Si'–C' planes.

<sup>b</sup> The angle between the C-Si-C plane and the Si-Si vector.

<sup>c</sup> The dihedral angle between the aromatic ring plane and the C–Si–Si plane.

pyramidalization both largest for **1b**. The aromatic rings are twisted out of this plane in all structures, giving a helical arrangement with all torsion angles different (42, 52, 67 and 70°) for **1a**, and all angles equal at  $62^{\circ}$  for **1c**. The aromatic rings are also

helically disposed in **1b**, but with the two of the *cis*-mesityl groups being more nearly coplanar  $(35^{\circ})$  and the other two more nearly orthogonal  $(78^{\circ})$ . There is no specific interaction between **1** and the solvent molecules in the solvates **1b**-c,



Fig. 1. Structures of 1a-d and conditions of their interconversions.

both being typical 'packing crystals' [10] where the role of the solvent molecule is simply to fill space in the loose crystal lattice. The three structures demonstrate that 1 enjoys considerable conformational flexibility. Distortions around the Si=Si double bond are consistent with theoretical (ab initio) calculations for H<sub>2</sub>Si=SiH<sub>2</sub> and Me<sub>2</sub>Si= SiMe<sub>2</sub> [11a], which predict a very flat potential energy surface for these model disilenes, with a difference of energy between the planar and distorted skeletons of only 1-2 kcal/mol. The results [11] suggest that the structures which will actually be found for disilenes with bulky substituents may well be strongly affected by substituent steric hindrance, crystal packing forces and other environmental effects.

Different conformations due to different mesityl ring orientations are also to be expected. Conjugation between the aromatic rings and the Si=Si double bond would be maximized in a fully coplanar conformation, but this is impossible sterically, so that twisting of the rings must take place. Fischer [12] has shown that in the related *trans*-diarylethylenes and similar compounds, almost isoenergetic rotamers are present.

The orange crystals of **1a** were found to exhibit reversible thermochromism, turning to pale yellow on cooling and to red on heating [6]. X-ray diffraction studies of **1a** carried out at 173 and 295 K showed that both crystal and molecular structures are experimentally equivalent at these two temperatures. This led to the suggestion that the thermochromism might result from a temperature redistribution of molecules among low-lying vibrational levels of the ground electronic state. No corresponding thermochromism was observed for the yellow crystals of **1b** or for solutions of **1**.

The aims of this work are as follows:

- to obtain and to compare in detail vibrational (Raman, IR) and electronic (UV-vis absorption, fluorescence emission) spectra of the reported modifications (1a-d) in order to find out how the small changes in their molecular and crystal structure affect their spectra;
- to study interconversions of modifications (1a-d);

- to try to propose a structure for the newly found form 1d which does not form single crystals suitable for X-ray diffraction study;
- 4) to investigate the temperature dependence of the electronic and vibrational spectra of **1a** in connection with the problem of its thermochromism.

### 2. Results

### 2.1. Interconversions of 1a-d

These interconversions as well as different structures of solid 1 are presented in Fig. 1. In the course of experimenting with the orange crystals 1a (in inert atmosphere or in high vacuum), we found that, when heated or sublimed or ground in a mortar, they easily transform to a yellow powder 1d whose UV band at  $\sim 425$  nm confirms it is also a disilene [2-5,13]. 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 proved by the complete coincidence of their Raman and UV-vis spectra. Numerous efforts to prepare a good crystal of unsolvated 1d for singlecrystal X-ray analysis were unsuccessful. Crystallization from solutions lead to formation of either 1a or the corresponding solvates, whereas sublimation of 1d resulted in a fine powder on a glass surface. It seems that 1d molecules are incapable of forming perfect crystals due to their particular shape incovenient for close packing (Aufbau principle of Kitaigorodsky [10]).

Unsolvated forms **1a** and **1d** were found to interconvert upon laser irradiation (in the course of obtaining Raman or fluorescence spectra), if 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, long exposure to the 514.5 nm laser beam produced a bright orange spot in the yellow sample of **1c** sealed in a capillary. The spot persisted when the capillary was removed from light. When exposed to light of the same wavelength but of higher intensity, the crystals of **1b**, sealed in vacuo in a quartz cell, on one occasion 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**.

### 2.2. Vibrational spectra of solid 1a-d

When examining vibrational spectrum of a disilene, a chemist is most interested in identification of the stretching vibration of the Si=Si bond, the so-called v(Si=Si). This problem was considered in detail in our previous papers [14] where the Raman and IR spectra of three disilenes were reported along with the results of normal coordinate analysis (NCA) for several disilene models.

Herewith we report the Raman spectra of four solid forms of 1 and of its solution in hexane. The results are presented in Figs. 2–4, 10–12, 15 and 16. IR spectra of unsolvated forms 1a and 1d are also given (Fig. 5).

Molecule 1 consists of 82 atoms and, formally speaking, its vibrational spectrum must have 240 fundamentals. However, vast experience in vibrational spectroscopy of organometallics suggests that internal vibrations of mesityl groups do not interact kinematically through the heavier silicon atoms, so that the frequencies of their similar vibrations should coincide, leading to a great simplification of the spectrum. Vibrational spectrum of mesitylene was investigated in detail in Ref. [15], and vibrational modes of a mesityl group attached to silicon atom were analyzed in terms of  $C_{\rm s}$  local symmetry in Ref. [14]. Most of the latter vibrations are situated in the region above 750  $cm^{-1}$ . Vibrations of the framework C<sub>2</sub>Si=SiC<sub>2</sub> should obey their own symmetry and their frequencies are anticipated in the region below 750  $cm^{-1}$ . However, some of the mesityl group modes are also situated in this region. For correct assignment of the bands observed, the results of normal coordinate calculations [14] appeared particularly useful.

The main result of the NCA obtained for the  $C_2Si=SiC_2$  moiety is that there is no normal mode in the spectrum of a disilene which is well-localized



Fig. 2. Raman spectra of solid 1a-d with 514.5 nm excitation at ambient temperature in the region 450–750 cm<sup>-1</sup>. (a) 1a; (b) 1b; (c) 1c; (d) 1d.

in the Si=Si bond. The Si=Si and Si-C internal stretching coordinates are heavily mixed. Their inphase combination results in a symmetric Raman active normal mode with frequency in the range 460–550 cm<sup>-1</sup> ( $v_1$ ) while their out-of-phase combination gives a symmetric Raman active normal mode near 700 cm<sup>-1</sup> ( $v_2$ ). Variation of the force constant  $F_{Si=Si}$  within reasonable limits does not alter this general conclusion. Particular contributions from the Si=Si and Si-C stretching coordinates to the eigenvectors of  $v_1$  and  $v_2$ , the normal modes of principal interest, depend on particular molecular structure and substituents but both contributions are always significant. Therefore, the assignment of the  $v_1$  mode as the v(Si=Si)stretch and of the  $v_2$  mode as the totally symmetric

Fig. 3. Evolution of the Raman spectrum of 1c sample in the process of its degradation in air (514.5 nm excitation; room temperature). (1) initial spectrum; (2-8) the process of degradation during 5 days; (9) Raman spectrum of Mes<sub>2</sub>Si(O)<sub>2</sub>Mes<sub>2</sub>.

 $v^{s}(Si-C)$  stretch is in essence arbitrary. The kinematic effect of the out-of-plane twisting of the SiC<sub>2</sub> fragment on the NCA results is small, with the biggest frequency shift in the spectrum being only 10 cm<sup>-1</sup>.

For mesityl substituted disilenes, the results of NCA [14] predict that the Raman active  $v_1$  mode, still being an in-phase combination of the Si=Si and Si-C stretching coordinates, also becomes mixed with symmetric angle deformations in mesityl group. The degree of the latter mixing (reflected by the eigenvector elements) depends strongly on the mutual orientation of the disilene and mesityl moieties. The more coplanar these fragments, the more coupled are their vibrations. At the same time, it is very important that the frequency of the  $v_1$  mode is not affected by this mixing. Therefore mesityl-containing disilenes with different ring orientations are expected to exhibit Raman bands, corresponding to the  $v_1$ 

Fig. 4. Raman spectra of solid **1a**-**d** in the low-frequency region; 514.5 nm excitation, ambient temperature. (a) **1a**; (b) **1b**; (c) **1c**; (d) **1d**.

mode, with similar frequencies but with different intensities, because the intensity depends on the mode eigenvector as well. In addition, NCA has also shown that two of the symmetric Raman active vibrations, localized in the mesityl group (the ring breathing and deformation modes,  $v_3$  and  $v_4$ , respectively), should fall in the same frequency range as  $v_1$ , 500–550 cm<sup>-1</sup>.

The Raman spectra of 1a-d (excited by the 514.5 nm line) in the diagnostic region 450–750 cm<sup>-1</sup> are presented in Fig. 2 and can be easily rationalized on the basis of the NCA results. All of the spectra exhibit a triplet in the region 500–550 cm<sup>-1</sup>, which is evidently an overlap of three lines, corresponding to  $v_1$ ,  $v_3$  and  $v_4$ . Contrary to the Raman spectra of E-tBuMesSi=SiMes(tBu) [14]







Fig. 5. IR spectra of **1a** and **1d** as mulls in degassed apiezon (Section 4). The bands of apiezon are marked by asterisks. Identity of the compounds was checked by the UV-vis band positions of the very same samples.

and of a Z-diaminodisilyldisilene [13], where the  $v_1$  mode manifests itself as a most intense line at about 530 cm<sup>-1</sup>, the Raman intensity of the  $v_1$  line for all polymorphs of 1 is medium, comparable with those of  $v_3$  and  $v_4$ . Which of these could be assigned as  $v_1$  will be discussed below. The assignment of the most intense line at about 680 cm<sup>-1</sup> to  $v_2$  is straightforward. Significant contribution from the Si=Si stretch to this so-called  $v^{s}(Si-C)$  mode is confirmed by gradual disappearance of this line in the process of degradation of the disilene in air with formation of Mes<sub>2</sub>Si(O)<sub>2</sub>SiMes<sub>2</sub> (Fig. 3) [16].

Precise frequency measurements performed in the Raman spectra of 1a-d (with accuracy  $\pm 0.5$  cm<sup>-1</sup>, using spectral slit width of 1 cm<sup>-1</sup> and

optimum registration conditions) revealed reliable differences between their band parameters. For instance, the frequencies of the  $v_2$  mode are 681, 676.5, 675, and  $\overline{674}$  cm<sup>-1</sup> for **1a**, **1b**, **1c** and **1d**, respectively. The half-width of these lines also varies within  $9-15 \text{ cm}^{-1}$ . The frequencies of the components of the triplet in the region 500-550  $cm^{-1}$  are close in value for all polymorphs (Fig. 2), whereas their intensities vary distinctly, each modification exhibiting its own characteristic pattern in this region. Also notable are different intensity ratios of the  $v_2$  line and the neighboring v(Si-C) line at 720 cm<sup>-1</sup> in the four spectra. All these observations are in good accord with the NCA results, mentioned above. The differences in the Raman spectra of 1a-d reflect their different molecular structures and allow their unambiguous identification by the Raman method.

The reason for the intensity redistributions in the Raman spectra under consideration is not only kinematic (different ring orientations in the molecules of **1a**-d leading to a change in the corresponding eigenvector elements) but also electronic. The change in the aromatic ring arrangements affects the degree of  $\pi-\pi$  conjugation in the molecule, which in its turn affects the Raman intensity of the  $v_1$ ,  $v_2$  and, possibly,  $v_3$  lines, since the Raman intensity of the appropriate lines is known to be very sensitive to conjugation [17–19].

There are also notable differences between the four forms of 1 in the low-frequency region of the Raman spectrum where the crystal lattice modes are situated (Fig. 4). These differences agree well with the X-ray data [6–8], which point to different crystal structures of 1a-c. From Fig. 4 it also follows that the crystal structure of 1d (which has not been characterized by the X-ray data) differs from those of 1a-c. Thus, the Raman data for 1d allow the conclusion that its crystal and molecular structure is distinct from those of 1a-c.

In the IR spectra of 1a-d, in contrast to the Raman spectra, the symmetric  $v_1-v_4$  modes manifest themselves as very weak features, if at all (Fig. 5). The IR spectra are strongly dominated by mesityl group vibrations and hence are not so informative. Anyway, there are some differences between the IR spectra of 1a and 1d, also in the diagnostic region below 750 cm<sup>-1</sup>.

# 2.3. Electronic absorption and fluorescence emission spectra

The UV-vis absorption spectrum of 1 was investigated in 3-Me-pentane at 77 K and in hexane solutions and was reported to contain a lowest-energy band at ~420 nm, assigned to the first  $\pi$ - $\pi$ \* transition localized in a Si=Si chromophore [2-5]. We obtained a band with a similar  $\lambda_{max}$  at about 425 nm for the solid sample of yellow unsolvated form 1d prepared as a thin film deposited on a cold target of the cryostat in vacuo (Fig. 6) or as a nujol mull (Fig. 7). The  $\lambda_{max}$  value of this band varies slightly with temperature, being 424 nm at -160 °C and 428 nm at 20 °C (Fig. 6).



Fig. 6. UV-vis absorption spectrum of solid 1d at various temperatures. The sample was obtained by sublimation on a quartz window in vacuum cryostat. (a) -160 °C; (b) -70 °C; (c) 20 °C.



Fig. 7. UV-vis absorption spectra of solid 1d and 1a as nujol mulls. All the intermediate curves belong to various mixtures of 1a and 1d obtained as a result of 1a grinding (see text).

As was said above, our first attempt to obtain the UV–vis spectrum of the solid **1a** by subliming the orange crystals in vacuo onto a cold window of the

cryostat, resulted in an excellent spectrum, but which was surprisingly that of 1d. However, different colors of **1a** and **1d** suggested that they should differ also in electronic absorption. Indeed, the UV-vis spectrum of real 1a exhibited a band at about 465 nm which is  $\sim 40$  nm red-shifted compared to that of 1d (Fig. 7). To obtain this result, it appeared necessary to prepare the sample without exposing the compound 1a to any mechanical or thermal stress. The best way was to put small crystals in nujol, apiezon or silicone grease in a dry box and just to slightly press this suspension between the quartz windows almost without grinding. Otherwise spectra of mixtures of 1a and 1d in various proportions are obtained, corresponding examples being given in Fig. 7.

As one might expect, we could not obtain reliable electronic absorption spectra of the solvates **1b** and **1c** because it was impossible to determine whether or not or to what extent the compounds have lost the solvents during sample preparation. It should be noted, however, that the compounds **1b**, **1c** and **1d** seem to be of the same color.

The fluorescence emission and excitation spectra for a solution of **1** were reported [2–5]. We recorded the fluorescence emission spectra excited by the 457.9 nm laser line for both **1a** and **1d** as solids (Fig. 8). The  $\lambda_{max}$  values of their broad bands differ significantly (~560 and ~515 nm, respectively) in good accord with the position of electronic absorption bands. A large Stokes shift points to a substantial geometry change upon excitation. Under prolonged illumination, **1d** 



Fig. 8. Fluorescence emission spectra of solid **1a** and **1d** excited by 457.9 nm line. Two lower curves demonstrate gradual transformation of **1d** into **1a** upon laser illumination.

slowly transformed into **1a**, this is clearly seen from the lower curves of Fig. 8.

# 2.4. Pre-resonance enhancement in the Raman spectra

As the disilenes absorb in the visible region 420-460 nm and as their lowest-energy electronic absorption band is largely due to a Si=Si  $\pi$ - $\pi$ \* transition, the Raman spectra of disilenes, provided they are excited by visible light, should exhibit pre-resonance enhancement of some lines. It could be expected that, as the excited light frequency approaches the disilene absorption band (Fig. 9), those normal modes which are vibronically active in this electronic transition should be most enhanced [17]. These are, above all, the  $v_1$ and v<sub>2</sub> modes, involving the Si=Si stretching coordinate. However, if the aromatic rings are in conjugation with the double bond, the totally symmetric modes of the rings could be also enhanced to some extent, depending on ring orientation [18]. The dependence of the Raman spectra of 1a-c on the exciting wavelength was investigated, using the laser lines with  $\omega = 457.9$ ; 514.5; 632.8; 647.1 and 1064 nm. The results obtained for 1a-c are similar; the examples are presented in Figs. 10 and 11.

Excitation dependence of the Raman spectrum of the THF solvate **1c** is given in Fig. 10. To eliminate the intensity increase due to the  $\omega^4$ scattering law, the spectra excited by different  $\omega$ were normalized so as to make the intensity of the line at 1380 cm<sup>-1</sup> approximately equal. The latter line corresponds to a  $\delta$ CH<sub>3</sub> mode, hardly sensitive to resonance. But the intensity of this feature is too small (Fig. 10) and therefore this normalization procedure does not allow strict quantitative measurements of line intensities, but only qualitative comparisons between the spectra.

If the Raman spectrum of **1c** is excited by the 1064 nm line in the near IR region, away from resonance (Fig. 9), then the most intense is the line of the aromatic ring stretching mode at 1600 cm<sup>-1</sup> (Fig. 10, curve 1). The intensity of the  $v_2$  line at approximately 680 cm<sup>-1</sup> in this spectrum is comparable with that of a mesityl mode at 1290 cm<sup>-1</sup>, while the diagnostic triplet in the region of



Fig. 9. Location of the absorption bands of 1a and 1d and of the laser lines applied for Raman excitation.



Fig. 10. Excitation dependence of the Raman spectrum of **1c**. (1) 1064 nm; (2) 647.1 nm; (3) 514.5 nm; (4) 457.9 nm.

500–550 cm<sup>-1</sup>, involving  $v_1$ , is of modest intensity. On approaching resonance, already with red



Fig. 11. Excitation dependence of the Raman spectrum of **1a**. (1) 1064 nm; (2) 632.8 nm; (3) 514.5 nm; (4) 457.9 nm.

(647.1 nm) excitation, a dramatic redistribution of the Raman intensities is observed (Fig. 10, curve 2), demonstrating evident pre-resonance enhancement of some lines, which regularly becomes greater with green and blue excitation (Fig. 10, curves 3 and 4). The most enhanced is evidently the line at approximately  $680 \text{ cm}^{-1}$  which dominates in the spectrum. This is one more strong piece of evidence of the complex origin of  $v_2$  with a substantial Si=Si stretch contribution. In the spectrum excited in the blue region, close to resonance, an overtone  $2v_2$  at ~1350 cm<sup>-1</sup> becomes noticeable, as is typical for pre-resonance Raman spectra [17]. Some other lines corresponding to mesityl group vibrations also exhibit intensity enhancement, but not so great as  $v_2$ . Analogous results in a limited region are presented in Fig. 11 for the orange form 1a. In the triplet at  $500-550 \text{ cm}^{-1}$  the most enhanced for all forms of 1 is the line at 540 cm<sup>-1</sup> (Figs. 10 and 11). This gives some reason to assign it to  $v_1$ .

It is notable that in the Raman spectra of the solvates **1b** and **1c** excited in the visible region, even the most intense lines of toluene and THF are not seen, because their intensities are thousands of times smaller than those of the pre-resonantly enhanced disilene lines. To detect the most intense lines of toluene or THF in the Raman spectra of **1b** or **1c** as weak features, excitation in the near infrared was needed.

# 2.5. On the structure of the unsolvated yellow form 1d

In spite of the fact that we have no X-ray data for 1d, there are some reasons to speculate about its structure. For disilenes of the type RR'Si=SiR'R, photochemical *cis-trans* isomerization in solution was shown to occur [20], the *trans* isomer being predominant under equilibrium conditions at room temperature. Of course, symmetrically substituted 1 cannot have real *cis-trans* isomers, but, by analogy, a similar equilibrium with predominance of a conformer, close to the *trans* one, seems likely in solution.



This assumption is confirmed by polarization measurements in the Raman spectrum of a solution of **1** in hexane. Only two Raman lines are observed in the v(Si-C) region, those at approximately 680 ( $v_2$ ) and 720 cm<sup>-1</sup>, both being polarized. This suggests C<sub>2h</sub> symmetry of the species predominant in solution, that is, a quasi-*trans* structure of this conformer.

It is important that the Raman pattern in the region  $500-550 \text{ cm}^{-1}$  for solid 1d is very close to that observed for a solution of 1 in hexane (Fig. 12). Moreover, the UV-vis spectrum of solid 1d is similar to those of 1 in solutions (the data on solution in hexane and 3-methylpentane are given in Refs. [2-5]; the UV-vis spectrum of solution of 1 in liquid Xe obtained at different temperatures is presented in Fig. 13). As both the Raman and UV-vis absorption as well as fluorescence emission spectra of solid 1d are similar to those observed for 1 in solution, we can tentatively suggest for 1d also a quasi-*trans* structure shown in Fig. 1.



Fig. 12. Comparison of the region  $500-550 \text{ cm}^{-1}$  of the Raman spectra of solid 1d (1) and of concentrated solution of 1 in hexane (2).



Fig. 13. UV-vis spectrum of solution of 1 in liquid Xe at various temperatures.

### 2.6. Thermochromism of 1a

First of all, we have investigated temperature dependence of the UV-vis spectrum of orange **1a**. Comparison of the spectra obtained at 20 and -180 °C is presented in Fig. 14. No real  $\lambda_{max}$  shift was observed (within the limits of experimental error) but the band narrowing is evident. The latter could be the origin of the thermochromism, human eyes being very sensitive to slight changes in this spectral region [21].



Fig. 14. UV-vis absorption spectrum of solid **1a** (suspension in silicone grease, without grinding). (1) room temperature; (2) -180 °C.

To study the possible vibrational origin of the thermochromism of 1a (see above), its Raman spectrum was obtained at different temperatures. It is evident that only depopulation of excited lowlying vibrational modes upon cooling could lead to the observed change in color. However, we investigated temperature dependence not only of the low-frequency spectral region, but also of the higher frequency region in order to obtain better resolution of overlapping bands. As could be expected, no substantial changes were found on cooling to -180 °C for intramolecular vibrations, only the usual band narrowing leading to a better resolution (Fig. 15), especially in the 500-550  $cm^{-1}$  triplet. It became evident that the middle peak of the triplet is the weakest one and thus cannot correspond to  $v_1$ . At low temperature, the left and the right peaks of the triplet split in two components each, probably due to Davydov (correlation field splitting) effect.

The low-frequency Raman region (Figs. 15 and 16) does exhibit some changes as the temperature decreases. Apart from regular band narrowing and shifts to higher frequencies, some redistributions of line intensities seem to occur below  $60 \text{ cm}^{-1}$  that could be possibly related to the presence of lattice hot bands in the room temperature spectrum.

However, all these results do not give a definite answer about the nature of thermochromism. The latter is a common phenomenon among disilenes (see Ref. 4, p. 241) and calls for further special investigation.

#### 3. Discussion

Thus, solid 1 exists as at least four forms differing in both crystalline and molecular structure: 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. Bernstein [22] uses a term 'conformational polymorphism' for this phenomenon, that is, existence of several forms of a conformationally flexible molecule (with energy difference between the conformers < 2 kcal/mol) depending on crystallization conditions. Our experience with a step-



Fig. 15. Temperature evolution of the Raman spectrum of **1a** in the region of intramolecular vibrations. (514.5 nm excitation). (1)  $20^{\circ}$ ; (2)  $-100^{\circ}$ ; (3)  $-140^{\circ}$ ; (4)  $-180^{\circ}$  °C.



Fig. 16. Temperature evolution of the Raman spectrum of **1a** in the low-frequency region (632.8 nm excitation). (1) 20 °C; (2) -180 °C.

by-step serendipitous finding of new conformational polymorphs of **1** (Refs. [1,2,6–9], and this paper) closely resembles the classical story about analogous forms of dimethylbenzylideneaniline, described vividly in Ref. [22].

Conformational polymorphism of **1** is evidently a result of interplay between the steric hindrance of the mesityl groups, the tendency of the whole molecule towards planarity which would maximize  $\pi-\pi$  conjugation, and crystal forces favoring close packing.

The facts that both the solvates as well as the orange form 1a easily convert to 1d clearly show that forms 1a-c are metastable while form 1d is the most stable thermodynamically. Modifications 1b-d can be converted to 1a, but only upon strong illumination.

It is notable that the bands in electronic absorption and fluorescence emission spectra of the orange form **1a** ( $\lambda_{max}$  at ~465 and 560 nm, respectively) are significantly red-shifted compared to those of the yellow 1d (  $\sim$  425 and  $\sim$  515 nm). It seems unreasonable to suppose that  $\pi - \pi$  conjugation is maximal for 1a. There is some evidence that the position of the low-energy UV band for disilenes (as well as for aryl-substituted ethylenes) is determined not only by degree of  $\pi - \pi$  conjugation with substituents, but also by distortion of the double bond plane, its twisting leading to a red shift ([4], p. 241). However, the distortion for orange **1a** is less than for yellow **1b** (Table 1), so this cannot be the explanation. The reason for the lower-energy absorption and emission of **1a** still remains a mystery.

### 4. Experimental

The synthesis of **1** was accomplished according to the method reported previously [2]. All experiments were carried out under high vacuum or strictly inert atmosphere to prevent sample oxidation, which was checked by the absence in the spectra of the bands corresponding to products of degradation.

To remove the solvents from solvates **1b** and **1c**, the substances put in quartz cells were heated in high vacuum ( $10^{-5}$  Torr) to ~ 60 and ~ 100 °C, respectively, because THF was lost more reluctantly. A yellow layer of **1d** sublimed on the upper part of the cell, while caked residue remained on the bottom.

For Raman and fluorescence studies, the samples were sealed in capillaries in vacuo or in an inert atmosphere. To obtain the UV-vis and IR spectra of solid orange **1a** was a difficult task. We used samples prepared in degased nujol, apiezon or silicone grease in an inert atmosphere almost without grinding because the latter procedure was found to lead to transformation of **1a** into **1d**. Analogous spectra of yellow unsolvated **1d** were obtained either for nujol or apiezon mulls or for thin solid films obtained by slow sublimation of the sample onto a cool quartz or CsI window of the cryostat in high vacuum. Sublimation of **1a** also results in **1d**.

The UV-vis spectra of solution of **1** in liquid Xe were obtained applying the technique proposed and elaborated by Bulanin [23]. A specially constructed high pressure (up to 60 atm) metal cell with quartz windows and optical path length 5 cm was used, which permitted to change the temperature of the solution within the interval from -80 to -5 °C. The temperature was maintained with accuracy  $\pm 1$  °C.

The UV-vis absorption spectra were recorded using a computerized Carl Zeiss M-40 and a Perkin-Elmer Lambda Array 3280 spectrophotometers. The IR spectra were obtained using a computerized Carl Zeiss M-82 and an IFS 113V Bruker FT spectrometers. To obtain the Raman and fluorescence spectra, a Jobin-Yvon HG2S, an U-1000 and a T-64000 laser Raman spectrometers were used. Various exciting lines in the visible region were applied, those of an  $Ar^+$  laser SP-2020, a  $Kr^+$  laser SP-165, and a He–Ne laser SP-124. Fourier-transform Raman spectra of 1a-c were recorded with a Bruker-88 spectrometer equipped with a FRA 106 FT Raman module.

For temperature measurements, various types of cryostats were applied, including a Meric 91 Arpagon and an Air Products cryogenic system DE 220.

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