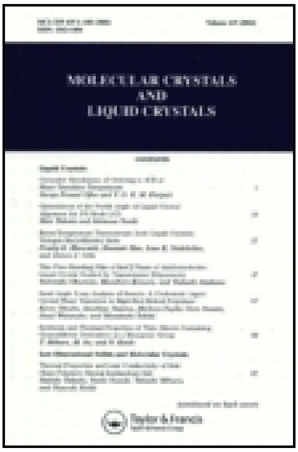

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Structure of Novel Symmetrical and Unsymmetrical Diacetylenes

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SYNTHESIS, POLYMERIZATION AND X-RAY STRUCTURE OF NOVEL SYMMETRICAL AND UNSYMMETRICAL DIACETYLENES

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Abstract Some preliminary solid-state properties of a new symmetrical diacetylene and an unsymmetrical derivative with toluene sulfonate side groups are reported. The unsymmetrical compound presents a stable non polymerizable form and a metastable polymerizable one.

INTRODUCTION

Diacetylenes are compounds, R_1-OCH_2-C≡C-C≡C-CH_2O-R_2, where R_1 is R_2 or different from R_2. Some of them, such as pTS (3) (where $R_1 = R_2 =$ p-CH_3-Ph-SO_2) and analogous compounds, undergo in crystalline state topochemically controlled solid-state polymerization, eventually yielding monocrystals of conjugated polymer chains extended along crystallographic directions[1]. Unsymmetrical compounds are a potential source of non-centrosymmetrical crystals with, eventually, non-linear optical properties[2].

In connection with our previous studies in this area[3,4,5,6], we report synthesis and X-ray structure of a new symmetrical derivative of hexa-2,4-diyne-1,6-diol (1) and m-CH_3-Ph-SO_2Cl, named di-mTS (4) which is not polymerizable, and an unsymmetrical diacetylene pTS-mTS (5) which combines the side group of pTS with that of di-mTS. Note that pTS exhibits an incommensurate phase in the range from ~ 155 to 195 K. Its low temperature structure is still monoclinic P $2_1/c$ (as at high temperature) with a doubling of the cell dimensions (Z = 4) and two inequivalent sites for each structural unit[10,11]. All these compounds are listed in table I.

TABLE I New diacetylenes (4)-(5) and related compounds

		R_1-OCH -C≡C-C≡C-OCH -R_2	
		R_1	R_2
HDD	(1)	H	H
	(2)	p-$CH_3C_6H_4$-SO_2	H
	(3)	p-$CH_3C_6H_4$-SO_2	p-$CH_3C_6H_4$-SO_2
di-mTS	(4)	m-$CH_3C_6H_4$-SO_2	m-CH_3-C_6H_4-SO_2
mTS-pTS	(5)	p-CH_3-C_6H_4-SO_2	m-CH_3-C_6H_4-SO_2

SYNTHESIS AND CRYSTALLIZATION

For the preparation of the symmetrical di-mTS (4), diol (1) was di-esterified in the presence of one equivalent of m-toluenesulfonyl chloride (liquid at room temperature) in ice-cooled acetone. Then an aqueous solution of NaOH was added dropwise. After separation of the resulting precipitate, the crude product was chromatographed over a silica gel column with dichloromethane/hexane (volume ratio 8:2) as the eluant. Crystals of (4) suitable for structural studies were grown from acetone at 4°C. They did not turn pink at room or at higher temperature, indicating that this compound does not polymerize.

For the preparation of the unsymmetrical pTS-mTS (5), diol (1) was first mono-esterified to give (2) (as indicated in reference 3) in presence of p-toluenesulfonyl chloride. Next (2), reaction with one equivalent of m-toluenesulfonyl chloride in ice-cooled acetone and dropwise addition of an aqueous solution of KOH yielded the diester (5). After filtration and separation by chromatography over silica gel with dichloromethane/diethyl ether (volume ratio 9:1) as the eluant, the final compound obtained was pale yellow. Sometimes it undercooled at room temperature.

Crystals of (5) suitable for structural studies were grown

- from acetone at 4°C yielding a stable form (5)a which gave small transparent, colourless, non-polymerisable crystals (melting point ≃ 69°C).
- from dichloromethane/ethanol (volume ratio 9:1) as the solvent, at about -5°C, yielding a metastable form (5)b which gave small transparent crystals (melting point ≃ 36°C). First these crystals

turned pink at room temperature (or at 0°C,not so rapidly). At the same time they changed slowly giving material which no longer diffracts after 24 hours at room temperature when studied on an x-ray diffractometer.

CRYSTAL STRUCTURE DETERMINATION OF DIACETYLENE (4) and (5)

Small plates of (4) and (5) (0,3 x 0,3 x 0,15 mm in size) were studied on an Enraf-Nonius CAD-4 automatic diffractometer and data were processed with a PDP8 computer. For the low-temperature structure determinations, the crystals were flushed with a stream of nitrogen gas. The unit cell parameters were determined from the angles of 25 strong reflections and the structures were solved by direct methods.

Symmetrical diacetylene di-mTS (4)

The structure at room temperature (T = 293 K) was monoclinic, space group $P2_1/c$, with four molecules in the unit cell. The lattice parameters are a = 11.514(6) Å ; b = 11.429(9) Å ; c = 16.184(4) Å ; β = 111.28(3)° ; V = 1984 $Å^3$.

The crystals do not show any phase transition from room temperature down to 130 K.

Figure 1 shows a drawing of the di-mTS molecule in the crystal with the atoms numbered. The plane of the figure contains the diacetylene rod, which is non-linear ; for example the angle between three adjacent carbons $C_1C_2C_3$ or $C_2C_1C_{11}$, is 177 to 178°. One of the side groups is folded towards the diacetylene rod. The $O_{11}S_{11}C_{14}$ angle is close to 104°. The $C_{12}C_{13}O_{11}$ is angle close to 110°.

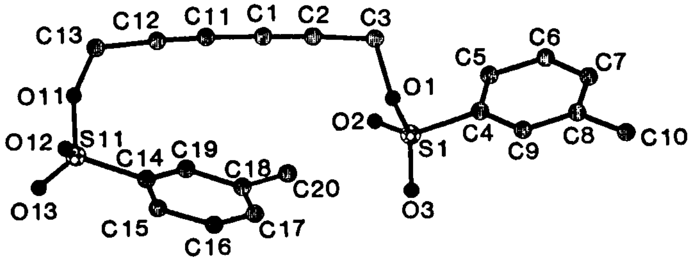

FIGURE 1 di-mTS molecule (4) 293 K structure with atom labelling

Figure 2 is a drawing showing the unit cell with the four molecules and the curvature of the diacetylene rods in perspective.

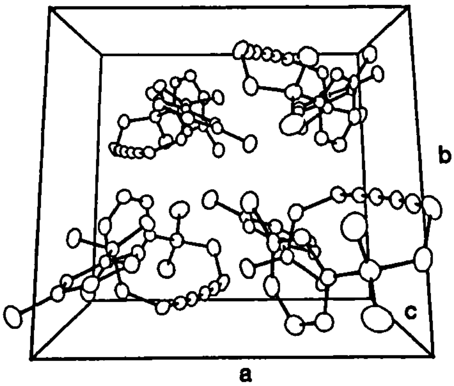

FIGURE 2 Drawing in perspective of the di-mTS unit cell

The half-folded molecule of di-mTS adapts in the crystal a conformation which prevents the close approach of the potentially reacting C atoms necessary for the polymerization of adjacent molecules, as is observed in pTS[1]. This explains the lack of solid-state reactivity of di-mTS. It is prevented by steric hindrance, as already observed in a series of sulfonate disubstituted diacetylenes[7] where the two lateral groups are folded back.

Unsymmetrical diacetylene pTS-mTS (5)

It had been previously indicated that crystalline pTS-mTS is polymorphic and presents a stable form, (5)a, and a metastable form (5)b.

The structure of (5)a at room temperature (T = 293 K) is monoclinic, space group $P\,2_1/c$, with four molecules in the unit cell. The lattice parameters are : a = 16.595(7) Å ; b = 7.65(1) Å ; c = 16.70(1) Å ; β = 110.21(3)° ; V = 1990 $Å^3$.

The crystals do not show any phase transition from room temperature down to 130 K.

Figure 3 shows the projection of the crystal structure on the plane containing the diacetylene rods and b axis, and Figure 4 shows the projection on plane (101) of the molecules of a row.

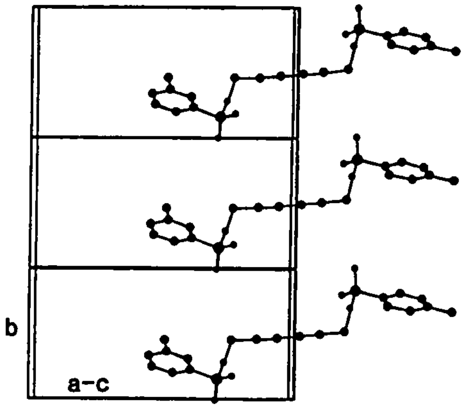

FIGURE 3 Crystal packing of (5)a in projection on the plane of the diacetylene stacks

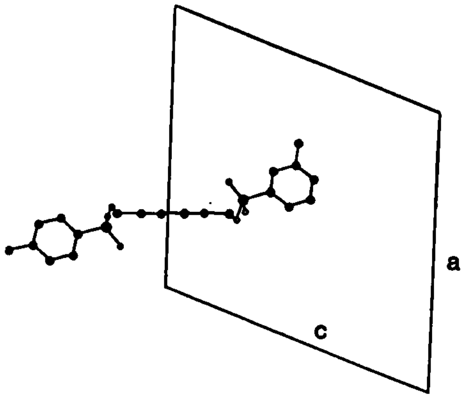

FIGURE 4 Projection of (5)a on plane (101)

It can be observed that the packing of the (5)a diacetylene molecules is similar to that of the symmetrical reactive pTS (3), but the solid state polymerization of pTS-mTS is prevented because the distance between diacetylene rods (d = b = 7.65 Å at 293 K) and their mean angle with b axis (φ = 85°) are too large compared to the corresponding packing parameters for pTS at 295 K[8] (d = b = 5.18 Å, φ = 45.6° and R = 3.64 Å, the distance between the reacting C atoms of adjacent molecules). This fulfills the geometrical criteria for polymerizability [9]. Separation R $\leqslant$ 4 Å, tested using crystal structure data for reactive and unreactive diacetylene monomers, is a good criteria for solid-state polymerization[1]. In the case of pTS-mTS, R is near 8 Å, much too large for reaction to occur.

The structure of (5)b (the metastable form of pTS-mTS) was resolved at T = 133 K and was monoclinic, space group P 2_1/c, with four molecules in the unit cell. The lattice parameters of the monomer are a = 14.752(8) Å ; b = 5.11(1) Å ; c = 26.01(2) Å ; β = 97.27(5)° ; V = 1946 Å^3.

The crystals do not show any phase transition from room temperature down to 130 K. It is interesting to compare those values to the lattice parameters of monomer pTS at T = 120 K (space group P 2_1/c, Z = 4) [10] : a = 14.745(7) Å ; b = 5.086(2) Å ; c = 25.738(12) Å ; β = 91.71(5)° ; V = 1929 Å^3.

Figure 5 shows the projection of the monomer structure of (5)b onto the plane of the diacetylene stacks which are extended along the crystallographic b axis. Figure 6 shows the projection on the (ac) plane of the molecules of a row.

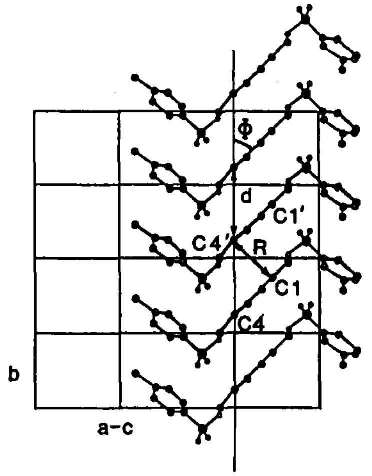

FIGURE 5 Crystal packing of (5)b in projection on the plane of diacetylene stack

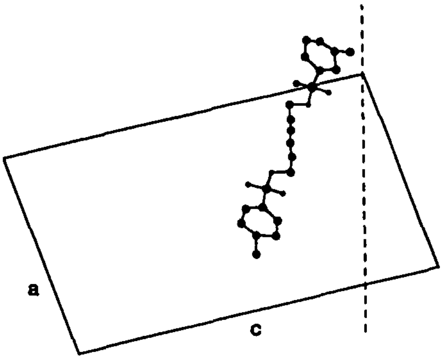

FIGURE 6 Projection on plane (101) of monomer (5)b (130 K structure)

The parameters of the unit cells of pTS and pTS-mTS at about the same temperature are very close. It is the same at room temperature for the b parameter, which is the packing direction of (3) and (5)b molecules. Thus crystalline conformation of pTS-mTS allows reactive packing of the monomer units. All the criteria for solid-state polymerization are satisfied ; the angle between diacetylene rods and b axis, $\varphi = 44°$, separation of the monomer units, $d = b$ axis, distance between potentially reactive carbons C_1-C'_4 of adjacent molecules $R \simeq 3.65$ Å (figure 5).

The observation that the crystals of pTS-mTS turn pink at room temperature or at 0°C indicates that this compound can polymerize. But, as at the same time the crystals change to a material which no longer diffracts after 24 hours at room temperature and become pale yellow in colour (much slower at 0°C or at lower temperature where the polymerization is almost prevented), the solid-state thermally induced reaction cannot be really observed. A study is in progress to try to promote X or γ-ray induced polymerization at sufficiently low temperature so as to prevent crystal change and damage.

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