# Conformational Polymorphism of Mechanochromic 5,6-Di(*p*-chlorobenzoyl)-1,3,4,7-tetraphenylbenzo[*c*]thiophene

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X-Ray crystallographic analyses show that mechanochromic polymorphs of 5,6-di(*p*-chlorobenzoyl)-1,3,4,7-tetraphenylbenzo[*c*]thiophene originate from different *syn*- and *anti*-arrangements of two vicinal carbonyl groups.

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Recently, in the field of material sciences interests in molecular crystals have grown significantly.[1,2] Polymorphism of organic molecules[3] finds its origin in the different mode of molecular packing in crystalline states. A free C-C bond rotation in a molecule in solution is frozen in a crystal and may lead to more than one conformer, thus giving rise to various "conformational" polymorphs.[4]

The present communication reports on a novel conformational polymorphism of mechanochromic 5,6-di(*p*-chlorobenzoyl)-1,3,4,7-tetraphenylbenzo[*c*]thiophene (**1**).[5]

Depending upon the solvent and the conditions of crystallization, **1** crystallizes in many forms with various colors from pale yellow to dark orange. Pale yellow crystal **1-A**, yellow crystal **1-S** and/or dark orange crystal **1-SW** were obtained from acetonitrile. Under strictly anhydrous conditions for the recrystallization, **1-A** was predominantly formed, while **1-SW** was mainly formed from wet acetonitrile. Also, wet ethanol and wet 2-propanol gave **1-SW**, while dry methanol, ethanol, 2-propanol, *n*-butanol yielded **1-A**. Colorless crystals **1-AW** were obtained when any form of crystal of **1** was heated at 100 °C in ethylene glycol.

Elemental analysis of the four crystals revealed that **1-AW** and **1-SW** are 0.5 hydrate of **1**, while **1-A** and **1-S** contain no molecules of solvation.

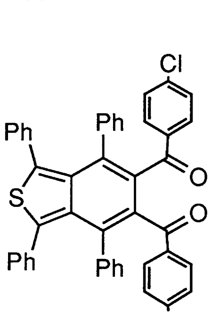
Intrigued as to the origin of the polymorphism of **1**, X-ray crystallograhic analyses[6] were carried out to reveal a remarkable difference in the intramolecular arrangement among **1-A**,[7] **1-S**[8], and **1-SW**[9,10] (Figure 1); the rotation of the two C-C single bonds connecting the two *p*-chlorobenzoyl groups with the aromatic line, is frozen in different ways; in **1-A**, the oxygen atoms of the two *p*-chlorobenzoyl groups take positions on different sides of the molecular plane (*anti*-conformation) while they are on the same side (*syn*-conformation) in **1-S** and **1-SW**.

The stereoviews of **1-A**, **1-S**, and **1-SW**[10] are shown in Figures 2-4. The intermolecular arrangements of **1-S** and **1-SW** are quite different. In **1-S**, the two oxygen atoms of the two *p*-chlorobenzoyl-moieties of each molecule are on reverse sides of the plane formed by the two benzo[*c*]thiophene rings. The *p*-chlorobenzoyl oxygen atoms are situated on the same side of the plane formed by the benzo[*c*]thiophene rings in **1-SW**.

The different colors of the crystals, pale yellow **1-A** and light yellow **1-S** may be related to the conformation of the phenyl rings and the *p*-chlorobenzoyl groups[11]. The dihedral angles between the central ring and the plane of the carbonyl groups of the *p*-chlorobenzoyl groups are smaller in **1-A** (56° and 56°) than in **1-S** (62° and 68°). However the *p*-chlorophenyl rings of **1-A** is less planar than those of **1-S** as is shown in the angles between the plane of the carbonyl groups and *p*-chlorophenyl rings (29° and 26° in **1-A** and 9° and 17° in **1-S**). Crystals **1-S** show smaller dihedral angles (61°, 65°, 64°, and 67°) between the benzothiophene ring and the four phenyl rings than **1-A** (70°, 70°, 68°, and 70°). These facts indicate a more effective delocalization of pi-electrons in **1-A** than in **1-S**. In **1-SW**, the dihedral angles (61°, 63°, 67° and 73°) between the central ring and the phenyl rings are close to those of **1-S**, except for the largest one. The two *p*-chlorobenzoyl groups of **1-SW** are connected to the central ring with the dihedral angle of 58° and 72°, respectively. Thus, the deep colorization of hydrate **1-SW** may not be explained in terms of the intramolecular arrangement only and be attributable to an intermolecular one in the crystals.

The FT-IR spectra of crushed samples of **1-A** and **1-AW** show one C=O band (1660 $cm^{-1}$ and 1666 $cm^{-1}$, respectively) while **1-S** and **1-SW** exhibit two C=O bands (1680 and 1666 $cm^{-1}$ and 1674 and 1652 $cm^{-1}$, respectively). Although the crystal structure of **1-AW** has not yet been determined, the two *p*-chlorobenzoyl groups are tentatively deduced to be in an *anti*-conformation.

Crystals **1-A**, **1-SW**, and **1-AW** are mechanochromic and



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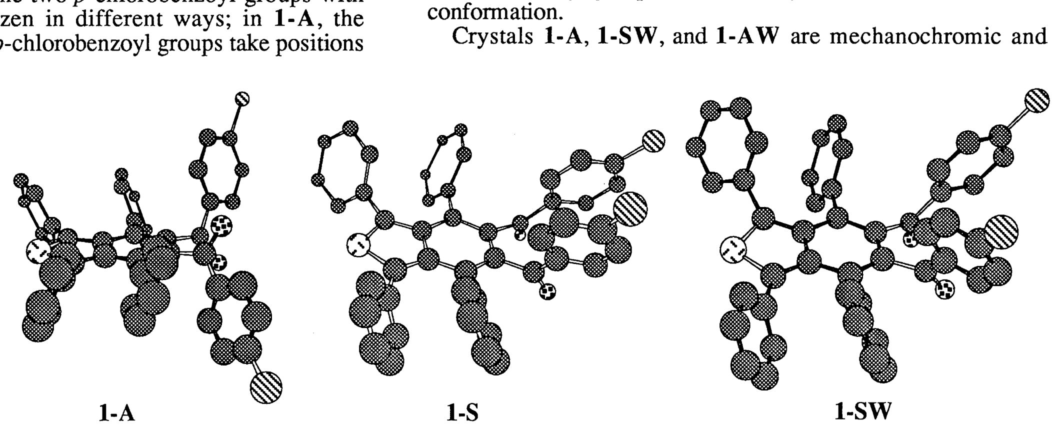

**1-A** **1-S** **1-SW**

**Figure 1.** X-Ray structure of **1-A, 1-S, 1-SW.**

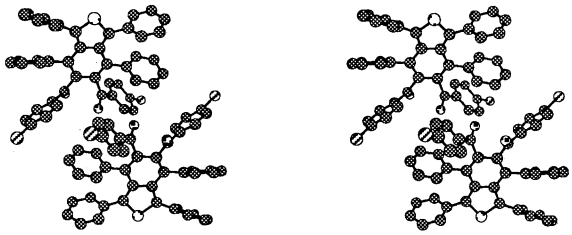

**Figure 2**. stereoview of **1-A**.

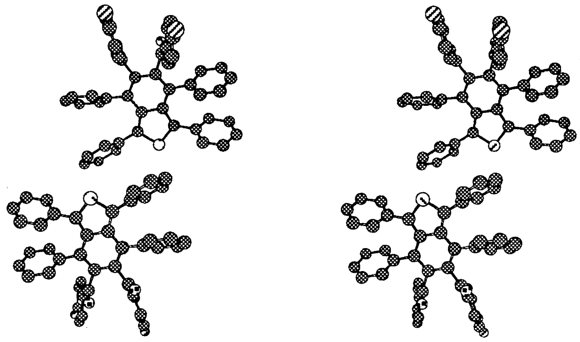

**Figure 3**. stereoview of **1-S**.

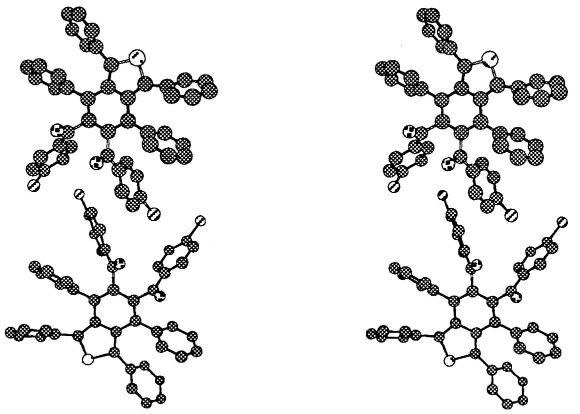

**Figure 4**. stereoview of **1-SW**.

exhibit a reversible color-change, though their behavior is different. Under irradiation of a UV lamp (365 nm), pale yellow **1-A** shows blue fluorescence (460 nm) while the fluorescence of the dark orange **1-SW** is yellow-green (504 nm). On grinding or crushing, **1-A** and **1-SW** change their colors to green with green fluorescence, while colorless **1-AW** with blue fluorescence change its colors to yellow-green with yellow-green fluorescence. The original colors can be restored either on exposure to a solvent vapor or on washing with a solvent. Light yellow **1-S** is also mechanochromic, changing the color to yellow with yellow-green fluorescence, although the color change is not as distinct as for **1-A**, **1-SW**, and **1-AW**. Crystals **1-S**, and **1-SW** gives different X-ray powder diffraction patterns before and after the grinding, suggesting the presence of unknown polymorphs of **1**, while no significant change could be observed in the pattern of **1-A**, and **1-AW**.

## References and Notes

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5 Compound **1** was prepared according to a method reported previously. M. P. Cava, M. A. Sprecker, and W. R. Hall, *J. Am. Chem. Soc.*, **96**, 1817 (1974).

6 Crystallograhic analysis of **1**. Data were collected on an Enraf-Nonius CAD4 diffractometer, ω-2θ scan type, graphite-monochromated CuKα radiation, $\lambda = 1.54184$ Å. The crystals of **1-A**, **1-S**, and **1-SW** did not show any significant decay during the data collection. Positional parameters were determined by direct methods using SIR 88[12] and were reflected by full-matrix least-squares calculations with all nonhydrogen atoms treated anisotropically and hydrogen atoms treated isotropically using the scheme $w = 4F_0{}^2/\sigma^2(F_0{}^2)^2$ to give the final residuals.

7 Crystal data of **1-A**: pale yellow prisms, $C_{46}H_{28}Cl_2O_2S$, Mw = 715.70, triclinic, $P_1$, a = 12.960 (1), b = 14.390 (1), c = 12.236 (1) Å, $\alpha = 113.21$ (1), $\beta = 93.91$ (1), $\gamma = 114.91$ (1)°, V = 1825.6 Å$^3$, Z = 2, $D_{calc} = 1.30$ g·cm$^{-3}$. Of 6532 independent reflections collected in the range $2.5 < \theta < 65°$, 5118 with $I_0 > 3\sigma(I_0)$ were taken as observed. R = 0.050 and $R_w = 0.069$.

8 Crystal data of **1-S**: light yellow prisms, $C_{46}H_{28}Cl_2O_2S$, Mw = 715.70, triclinic, $P_1$, a = 11.384 (2), b = 15.803 (2), c = 10.994 (2) Å, $\alpha = 98.58$ (1), $\beta = 111.06$ (2), $\gamma = 74.79$ (2)°, V = 1777.7 Å$^3$, Z = 2, $D_{calc} = 1.34$ g·cm$^{-3}$. Of 6277 independent reflections collected in the range $2.5 < \theta < 65°$, 5142 with $I_0 > 3\sigma(I_0)$ were taken as observed. R = 0.052 and $R_w = 0.082$.

9 Crystal data of **1-SW**: dark orange prisms, $C_{46}H_{28}Cl_2O_2S\cdot0.5H_2O$, Mw = 724.81, monoclinic, $P2_1$, a = 18.402 (2), b = 6.361 (1), c = 15.539 (2) Å, $\beta = 91.26$ (1), V = 1818.5 Å$^3$, Z = 2, $D_{calc} = 1.31$ g·cm$^{-3}$. Of 6447 independent reflections collected in the range $2.5 < \theta < 65°$, 4502 with $I_0 > 3\sigma(I_0)$ were taken as observed. R = 0.064 and $R_w = 0.078$.

10 The water molecule in **1-SW** is omitted in Figures 1 and 4.

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