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X-Ray Crystallographic Analysis and Differential Scanning Calorimetry of Two Polymorphic Forms of 2,6-Diphenyl-1,4-dithiin

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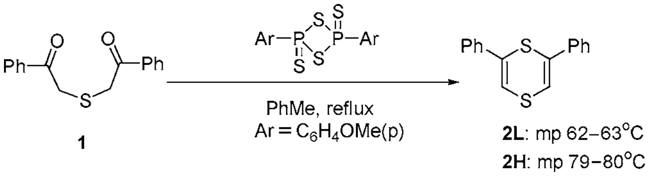
ABSTRACT: *2,6-Diphenyl-1,4-dithiin* **2** *exists in the two polymorphic forms. The dithiin* **2L**, *mp 62–63°C, was assigned as the metastable form, while the dithiin* **2H**, *mp 79–80°C, was assigned as the stable form, mainly on the basis of differential scanning calorimetry (DSC) analysis. X-Ray crystallographic analysis showed that the largest difference in the molecular structure between* **2L** *and* **2H** *is found in the coplanarity between the benzene ring and the double bond part of the dithiin ring; the benzene ring and the double bond are nearly coplanar for* **2L**, *whereas these are far from being coplanar for* **2H**. © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:424–427, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20035

INTRODUCTION

2,6-Diphenyl-1,4-dithiin (**2**) was found to exist in two polymorphic forms. Here we report the results of X-ray crystallographic analysis and differential scanning calorimetry (DSC) of these two polymorphic forms.

Two decades ago, we developed a general synthesis of 1,4-dithiins [1,2]. Thus, for example, sulfuration of diphenacyl sulfide (**1**), easily obtainable by treatment of phenacyl bromide or chloride with $Na_2S \cdot 9H_2O$, with Lawesson's reagent provides the 1,4-dithiin **2** in good yield [1].



We also investigated the thermolysis of **2** and the related 1,4-dithiins that result in the formation of thiophenes with extrusion of a sulfur atom [3,4]. During these studies, we observed the following. At the early stage of these studies, the 1,4-dithiin **2**, synthesized by the above method, melted at 62–63°C [1]. However, during the thermolysis study we obtained the dithiin **2**, which had a melting point of 79–80°C [3]. Since then, we obtained only the high melting point dithiin **2H**. The low melting point dithiin **2L** never formed despite repeated syntheses or recrystallizations. Although at that time we thought that the difference of the melting point is attributed to a polymorphism [3], we could not pursue these phenomena in detail because of the nonavailability of **2L**. Recently, we have reinvestigated the synthesis of **2** and obtained **2L** again, thus enabling us to report the results described below.

RESULTS AND DISCUSSION

First of all we should mention that no differences are found between **2L** and **2H** in their solution spectra

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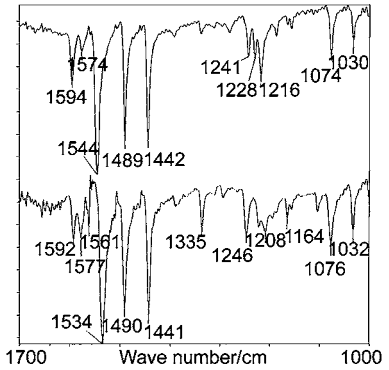

FIGURE 1 IR spectra of **2L** and **2H** for KBr disk.

such as ^{1}H NMR, ^{13}C NMR, and UV–Vis spectra, but many differences are found in the IR spectra when they were taken for KBr disk (Fig. 1), thus indicating that these two are polymorphic forms and not isomers. In addition, once we had **2L** in hand, we were able to convert **2H** to **2L** by using a piece of the crystals of **2L** as the seed of crystallization. Conversion of **2L** to **2H** was also possible in a similar way.

Molecular structures of **2L** and **2H**, which were viewed from two different directions, are shown in Figs. 2 and 3, respectively, along with the relevant bond lengths and angles. Reportedly, the 1,4-dithiin ring, including that of the parent compound [5], exists in a boat conformation in the crystalline state [6]. The present analyses revealed that both **2L** and **2H** also adopt boat conformations with flap and boat angles summarized in Table 1. The largest difference in the molecular structure between **2L** and **2H** is found in the coplanarity between the benzene ring and the double bond part of the dithiin ring. For **2L**, the benzene ring and the double bond are nearly coplanar, with small torsion angles of 11.8(2)° and −5.4(2)° for C_4—C_3—C_7—C_8 and C_5—C_6—C_{13}—C_{14}, respectively. On the other hand, the benzene ring and the double bond in **2H** are far from being coplanar, with torsion angles of 39.7(3)° and −26.7(3)° for C_4—C_3—C_7—C_8 and C_5—C_6—C_{13}—C_{14}, respectively.

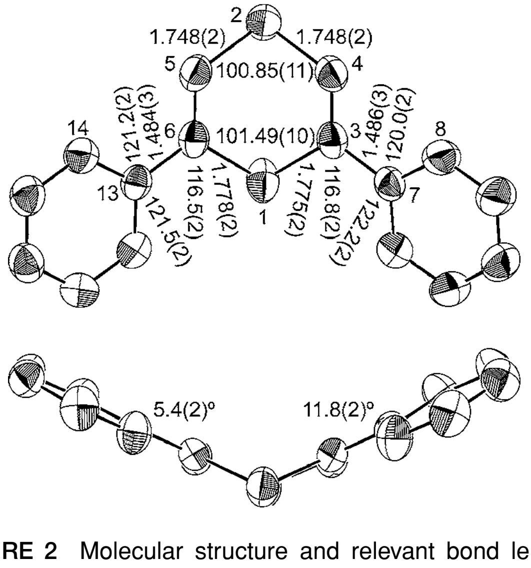

FIGURE 2 Molecular structure and relevant bond length, bond angle, and dihedral angle data of **2L**.

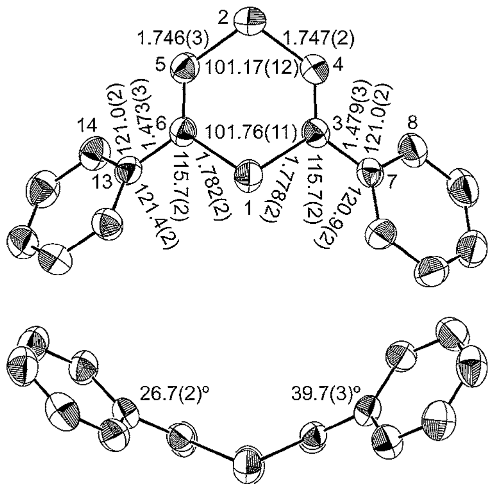

FIGURE 3 Molecular structure and relevant bond length, bond angle, and dihedral angle data of **2H.**

The molecular structure **2A** in Fig. 4 shows the optimized (energy-minimized) conformation of the dithiin obtained by DFT MO calculations (B3LYP/6-311+G(2d,p) level). The calculations were also carried out by input of the geometric parameters obtained by X-ray analysis of **2L** and **2H**. The use of the geometric parameters of **2L** and that of **2H** both led to the same structure **2B** (Fig. 5). These show that the calculated molecular structures well agree with that of **2H** and not of **2L** (see also Table 1). Thus, although it is not adequate to extrapolate the results of calculations on a single molecule to the molecule

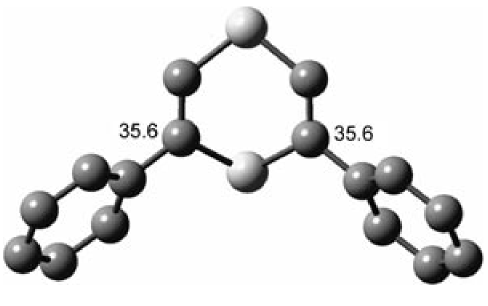

FIGURE 4 Calculated optimized structure **2A** of 2,6-diphenyl-1,4-dithiin (B3LYP/6-311+G(2d,p) level).

TABLE 1 Flap Angle and Boat Angle Data of **2L**, **2H**, **2A**, and **2B**

	Plane	**2L**	**2H**	**2A**	**2B**
Flap angle (°)[a]	S1–C3–C4/S1–C6–C5	127.9(3)	130.8(3)	132.8	132.8
	S2–C5–C6/S2–C4–C3	133.9(3)	136.8(3)	150.2	149.2
Boat angle (°)[b]	C3–S1–C6/C3–C4–C6	142.4(3)	145.1(3)	141.0	141.1
	C3–S1–C6/C3–C6–C5	142.9(3)	145.1(3)	156.8	157.1
	C4–S2–C5/C3–C4–C5	149.8(3)	151.7(3)		
	C4–S2–C5/C4–C5–C6	149.3(3)	151.8(3)		

[a] The flap angle is defined as the angle between two S—C—C planes.
[b] The boat angle is defined as the angle between a C—S—C plane and the plane of the olefinic carbon atoms.

in the crystals, it would be safe to say that the dithiin molecules in **2H** are adopting the energy-minimized conformation.

Figures 6 and 7 show the molecular packing diagrams of **2L** and **2H**, respectively. Both **2L** and **2H** are yellow monoclinic needles that belong to the space group of $P2_{1/c}$. The crystals of the former have a slightly larger density (1.362 g cm^{-3}) than those of the latter (1.360 g cm^{-3}). This will originate from fact that the conformation of the dithiin molecule in **2L** is more compact than that of **2H** because the benzene ring and the double bond are coplanar for **2L**.

Both experimental findings and calculations described above imply that **2H** is the stable form, and thus **2L** is the metastable one. In order to obtain more rigid experimental evidence for this, **2L** and **2H** were subjected to DSC analysis. Figures 8 and 9 show DSC curves of **2L** and **2H**, respectively. **2L** melted at 63.4°C with a ΔH_m [heat of fusion (melting)] of 20.9 kJ mol^{-1} (77.7 mJ mg^{-1}), while **2H** melted at 77.5°C with a ΔH_m of 24.6 kJ/mol (91.5 mJ mg^{-1}). Therefore, ΔH_m of **2H** is greater than that of **2L** by 3.7 kJ mol^{-1}, thus providing clear evidence that **2H** is the stable form.

In conclusion, we uncovered that **2** exists in two polymorphic forms, the metastable form **2L** and the stable form **2H**.

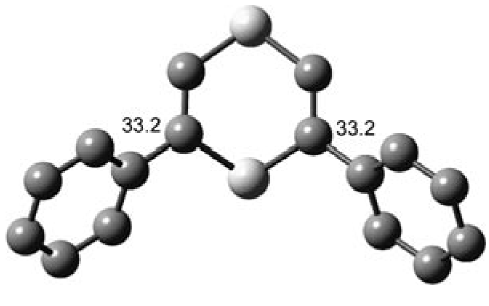

FIGURE 5 Calculated optimized structure **2B** of 2,6-diphenyl-1,4-dithiin obtained on the basis of the geometric parameters of the X-ray analyses (B3LYP/6-31G(d) level).

EXPERIMENTAL

*Preparation of the Low Melting Point 2,6-Diphenyl-1,4-dithiin (**2L**)*

A mixture of 1.15 g (4.3 mmol) of diphenacyl sulfide and 2.70 g (9.1 mmol) of Lawesson's reagent in 20 mL of toluene was heated at reflux for 1.5 h. The resulting organge mixture was cooled to room temperature and the insoluble materials were removed by filtration. The filtrate was washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel with CH_2Cl_2/hexane (1:10) as the eluent to give 1.05 g (91%) of 2,6-diphenyl-1,4-dithiin as an orange solid. Crystallization of the solid from MeOH gave 0.86 g (74%) of single crystals of the low melting point dithiin **2L** (mp 62–63°C), which are suitable for X-ray crystallographic analysis.

The single crystals of the high melting point dithiin **2H**, synthesized by us previously, were suitable enough for X-ray crystallographic analysis.

Spectroscopic Data of **2L** *and* **2H**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (s, 2H), 7.31–7.39 (m, 6H), 7.63–7.65 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 118.3, 127.0, 128.6, (accidental overlap of two peaks), 137.1, 139.2; ^{13}C NMR (100.6 MHz, C_6D_6) δ 118.9, 127.2, 128.6, 128.7, 137.4, 138.8; UV/Vis (hexane) λ_{max} (ε)

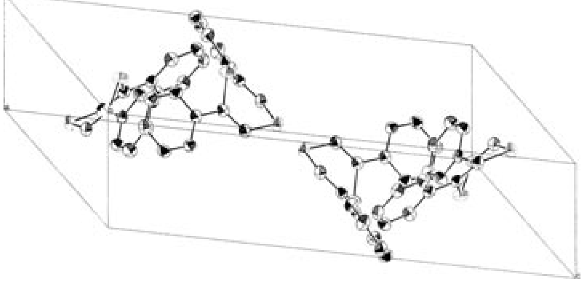

FIGURE 6 Molecular packing diagram of **2L**.

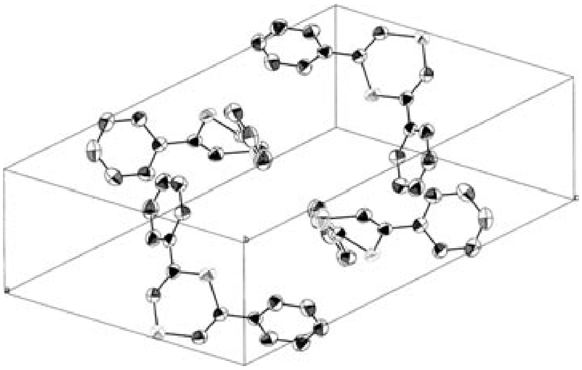

FIGURE 7 Molecular packing diagram of **2H**.

245.5 (29400), 309 nm (7700); MS (EI, 70 eV) *m/z* 268 (M^+); IR, see Fig. 1.

X-Ray Crystallographic Data

2L: $C_{16}H_{12}S_2$, $F_w = 268.40$, monoclinic, $a = 13.503(1)$, $b = 5.570(1)$, $c = 21.130(2)$ Å, $\beta = 94.98(1)^\circ$, $V = 1308.8(2)$ Å^3, space group $P2_1/c$, $Z = 4$, $D = 1.362$ g/cm^3, yellow needles, μ (Mo-$K\alpha$) $= 0.384$ mm^{-1}, $R_1 = 0.0548$ [$I > 2\sigma(I)$], $wR_2 = 0.1444$ (all data), GOF = 0.957.

2H: $C_{16}H_{12}S_2$, $F_w = 268.40$, monoclinic, $a = 11.624(1)$, $b = 6.085(1)$, $c = 19.220(2)$ Å, $\beta = 105.440(5)^\circ$, $V = 1310.41(13)$ Å^3, space group $P2_1/c$, $Z = 4$, $D = 1.360$ g/cm^3, yellow needles, μ (Mo-$K\alpha$) $= 0.383$ mm^{-1}, $R_1 = 0.0439$ [$I > 2\sigma(I)$], $wR_2 = 0.1059$ (all data), GOF = 0.942.

DSC Analysis

The DSC curves were determined over a temperature range of 45–90°C by raising temperature at the rate of 2°C min^{-1}. The average values of three scans were given. Each scan was carried out by using 3–4 mg of samples.

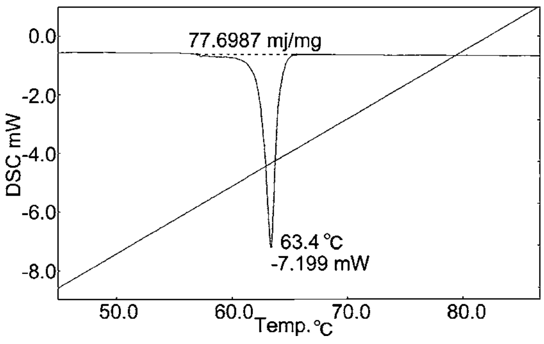

FIGURE 8 DSC curve of **2L**.

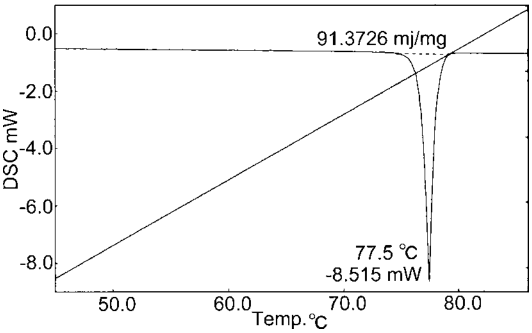

FIGURE 9 DSC curve of **2H**.

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