



# Conformational polymorphs and solid-state polymerization of 9-(1,3-butadiynyl)carbazole derivatives

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## ABSTRACT

The novel diacetylenes, 9-(5-(4-nitrophenoxy)penta-1,3-diyne-1-yl)-9H-carbazole (**1**) and 4-((5-(9H-carbazol-9-yl)penta-2,4-diyne-1-yl)oxy)benzotrile (**2**), were prepared and characterized by crystallographic analyses. Compound **1** gave two conformational polymorphs, **1**-(I) and **1**-(II), whose differences were concluded to originate in intermolecular interactions among nitrophenyl groups. Crystal **1**-(I) and **2** had suitable molecular arrangements for solid-state polymerization and polymerized by thermal annealing to give crystalline polydiacetylenes (PDAs). While an arrangement of **1**-(II) was unsuitable for the polymerization. The PDAs showed broad absorption from UV to near IR region (ca. 900 nm), suggesting effective expansion of  $\pi$ -conjugated system by carbazolyl groups.

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## 1. Introduction

Polymorphs [1–3], which are often obtained in organic solids, give different properties on electric conductivity [4,5], magnetism [6] or solid-state reactivity [7]. Therefore control of molecular arrangements, namely control of polymorphs, is one of the most important subjects in materials chemistry.

A Charge transfer complex of 4,4',5,5'-tetramethyl- $\Delta^{2,2'}$ -bis-1,3-diselenole (TMTSF) and tetracyanoquinodimethane (TCNQ) is one of the most famous complexes in conducting materials, and it has two polymorphs [8,9]. One forms segregated stacks and shows metallic conductivity. The other makes mixed stacks and acts as a semiconductor. In a case of magnetic materials, *p*-nitrophenyl nitronyl nitroxide (NPNN) forms four crystal polymorphs [10–13], and only the  $\beta$ -phase shows ferromagnetism [14].

In a case of solid-state reactions, [2 + 2] cycloaddition of (*E*)-3-(2-ethoxyphenyl)acrylic acid [15] is known as a typical example whose reactivity and selectivity depend on molecular arrangements [16,17]. The compound gives three polymorphs,  $\alpha$ ,  $\beta$  and  $\gamma$ -phase. Photodimerization proceeds on  $\alpha$  and  $\beta$ -phase, affording syn head-to-tail and syn head-to-head products, respectively, while  $\gamma$ -phase does not show any reactivities.

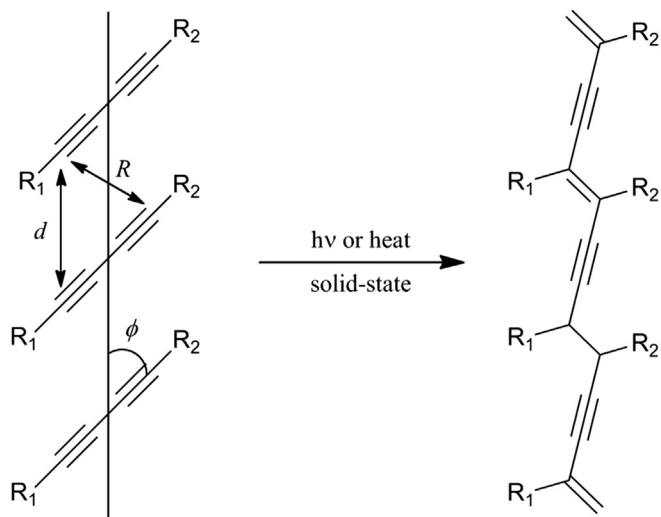
Reactivity in solid-state polymerization of diacetylene derivatives is also known to depend heavily on their molecular arrangements [18,19]. Baughman et al. studied many crystal packings of diacetylenes and found out condition for the polymerization [20]. They interpreted crystal packing in terms of stacking intervals (*d*) and inclination angles ( $\varphi$ ) of diacetylene moiety with their stacking axis. The condition for the polymerization was concluded that molecular stacking satisfied both limitations of  $d = 3.8\text{--}6.8 \text{ \AA}$  and  $\varphi = 30\text{--}65^\circ$  (Scheme 1).

Total of ninety four polymorphs for diacetylene derivatives have been reported on the Cambridge Crystallographic Data Centre (CCDC) [21,22], involving pseudo-polymorphs, cyclic compounds and tetraynes. Only a few cases were recognized that polymorphs involve reactive and non-reactive diacetylenes. In the first example reported by Hanson [23], both polymorphs could not polymerize under ambient pressure, but one of polymorphs gave PDAs under high pressure. In another example reported by Hocek et al. [24], one of polymorphs is supposed to form a suitable molecular arrangement for solid-state polymerization, but the solid-state reactivity was not discussed. Boughman's work [25] and a recent Lauher's work [26] can satisfy above condition.

In this study, we report preparations of novel diacetylene, **1** and **2**, which carry both a carbazolyl group and an acceptor unit as a substituent. Compound **1** gives two conformational polymorphs, **1**-(I) and **1**-(II), by recrystallization from different solutions, and they showed different reactivity in the solid state. Polymerization of **2** is

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**Scheme 1.** Schematic presentation for solid-state polymerization of diacetylenes.

also discussed based on its crystal structure in comparison with the structure of **1**-(I). To the best of our knowledge, this study is the third report which treats difference in solid-state polymerization reactivity of diacetylenes under ambient pressure between polymorphs.

## 2. Experimental

### 2.1. General procedure

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL JNM-ECA-400 spectrometer in chloroform-*d* with tetramethylsilane as an internal standard. IR spectra were recorded on a JASCO FT/IR-6100 spectrometer by using a KBr pellet. UV–Vis–NIR spectra in solid state were measured on a HITACHI U-3900 spectrometer equipped with an integrating sphere attachment. Elemental analyses were carried out on a J-SCEINCE LAB MICRO CORDER JM10. Differential scanning calorimetric (DSC) measurements were performed on a SHIMADZU DSC-50 calorimeter. Powder X-ray diffraction (PXRD) data were recorded on a RIGAKU MiniFlex II diffractometer with a monochromatic Cu K $\alpha$  radiation at ambient temperature.

Single crystals of **1** and **2** with sufficient quality for X-ray crystallographic analyses were obtained by slow evaporation from an acetonitrile solution for **1**-(I), an acetone solution for **1**-(II), or a dichloromethane solution for **2**. X-ray crystallographic data of **1**-(I), **1**-(II) and **2** were obtained at  $-180$  °C by a RIGAKU VariMax with RAPID with a multi-layer mirror monochromatic Cu K $\alpha$  radiation, a RIGAKU R-AXIS RAPID II with a graphite monochromatic Mo K $\alpha$  radiation and a RIGAKU RAXIS-RAPID with a graphite monochromatic Cu K $\alpha$  radiation, respectively. In **1**-(II), Friedel pairs were merged because the molecule itself was achiral and because there were not any anomalous scattering effects. All structures were solved by a direct method (SHELXS97) [27], and refined by full-matrix least-squares method (SHELXL97) [27]. The positions of all non-H atoms were obtained from differential Fourier maps and refined anisotropically. All H atoms were placed at ideal positions (Csp<sup>2</sup>-H = 0.95 Å; methylene Csp<sup>3</sup>-H = 0.99 Å) and were treated as riding on their parent C atoms with  $U_{iso}(H) = 1.2U_{eq}(C)$ .

The DFT calculations of **1** and **2** were performed on Spartan 04 software (Wavefunction, Inc.) [28] with B3LYP 6-31G(*d*) level. Crystal structures of **1** and **2** were used as initial structures.

### 2.2. Materials

All chemicals were purchased from Kanto Chemical Co. Ltd. or Sigma Aldrich Co. Ltd. and used without further purification. 9-Ethynyl-9*H*-carbazole [29], 4-(2-propynyloxy)nitrobenzene and 4-(2-propynyloxy)benzonitrile [30] were prepared according to the reported methods.

#### 2.2.1. 9-(5-(4-Nitrophenoxy)penta-1,3-diyne-1-yl)-9*H*-carbazole (**1**) [31]

After a suspension of copper (I) chloride (0.37 g, 3.6 mmol) in acetone (6.5 ml) was degassed by argon bubbling for 30 min, TMEDA (185  $\mu$ l, 1.2 mmol) was added to the suspension. It was stirred for 30 min, and the supernatant solution was transferred into a mixture of 9-ethynyl-9*H*-carbazole (0.61 g, 3.2 mmol) and 4-(2-propynyloxy)nitrobenzene (3.61 g, 20.4 mmol) in acetone (30 ml) at room temperature. The solution was stirred for 1 day under an oxygen atmosphere. After removal of the solvent, the residue was extracted with dichloromethane (250 ml). The solution was washed with 5% ammonium hydroxide (100 ml), and the water layer was extracted twice with dichloromethane (100 ml). The combined organic layer was washed with water (200 ml) and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was purified by column chromatography on a silica gel with a mixed solvent of *n*-hexane and ethyl acetate (10:1 *v/v*) as an eluent, and recrystallized from acetonitrile to give 0.28 g (yield 24%) of **1** as a white powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.26 (d,  $J = 9.2$  Hz, 2H), 7.99 (d,  $J = 7.8$  Hz, 2H), 7.64 (d,  $J = 7.8$  Hz, 2H), 7.50 (t,  $J = 7.8$  Hz, 2H), 7.36 (t,  $J = 7.8$  Hz, 2H), 7.10 (d,  $J = 9.2$  Hz, 2H), 5.02 (s, 2H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 162.29, 142.16, 140.09, 127.07, 125.92, 123.82, 123.10, 120.54, 114.98, 111.64, 77.46, 72.88, 68.85, 61.20, 57.16 ppm. IR (KBr pellet, cm<sup>-1</sup>): 2241 and 2178 ( $\nu_{C\equiv C}$ ), 1513 and 1343 ( $\nu_{NO_2}$ ). Elemental Anal. Calcd for C<sub>23</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>: C, 75.40; H, 3.85; N, 7.65. Found: C, 75.33; H, 3.91; N, 7.64.

#### 2.2.2. 4-((5-(9*H*-Carbazol-9-yl)penta-2,4-diyne-1-yl)oxy)benzonitrile (**2**) [31]

The compound **2** was prepared by a similar procedure to **1** with 9-ethynyl-9*H*-carbazole (1.20 g, 6.30 mmol) and 4-(2-propynyloxy)benzonitrile (4.95 g, 31.5 mmol). The crude material was purified by column chromatography to give 1.07 g (yield 49%) of **2** as a white powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.99 (d,  $J = 7.9$  Hz, 2H), 7.65 (d,  $J = 7.9$  Hz, 2H), 7.64 (d,  $J = 8.5$  Hz, 2H), 7.50 (t,  $J = 7.9$  Hz, 2H), 7.36 (t,  $J = 7.9$  Hz, 2H), 7.09 (d,  $J = 8.5$  Hz, 2H), 4.97 (s, 2H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 160.63, 140.11, 134.05, 127.06, 123.81, 123.08, 120.53, 118.97, 115.63, 111.63, 105.01, 77.66, 72.68, 68.72, 61.22, 56.81 ppm. IR (KBr pellet, cm<sup>-1</sup>): 2241 and 2175 ( $\nu_{C\equiv C}$ ), 2223 ( $\nu_{C\equiv N}$ ). Elemental Anal. Calcd for C<sub>24</sub>H<sub>14</sub>N<sub>2</sub>O: C, 83.22; H, 4.07; N, 8.09. Found: C, 83.28; H, 4.19; N, 8.00.

#### 2.2.3. Solid-state polymerization of **1** and **2**

Solid-state polymerization of the monomers **1**-(I) and **2** was carried out by thermal annealing in an electric oven. The powdered monomers were sealed into glass tubes with exchange gas of argon.

## 3. Results and discussion

The diacetylene derivatives **1** and **2** were prepared by Hay coupling reactions [31] of 9-ethynyl-9*H*-carbazole with excess of 4-(2-propynyloxy)nitrobenzene and 4-(2-propynyloxy)benzonitrile, respectively, as shown in Scheme 2.

The diacetylene derivative **1** gave two conformational polymorphs, **1**-(I) and **1**-(II). Polymorph **1**-(I) was obtained as pale blue platelet crystals by recrystallization from an acetonitrile solution,

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