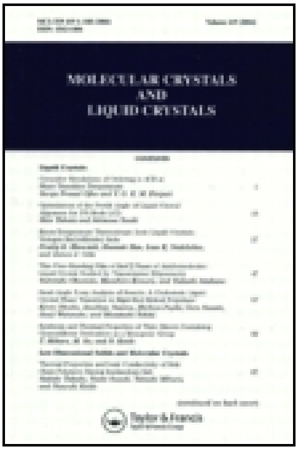

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Solid State Polymerization of Diacetylenes with Amide Groups

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Solid State Polymerization of Diacetylenes with Amide Groups

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*Two diacetylene derivatives (***1**, **2***) carrying amide groups were prepared in order to control their packing arrangements by intermolecular hydrogen bonds. 1, 6-Bis(4-acetamidomethylphenoxy)-2,4-hexadiyne* **1** *is a symmetric diamide, which showed no changes by annealing. p-N-acetyl(6-hydroxy-2,4-hexadiynenyloxy)benzylamine* **2** *with amide and alcohol groups showed photo and thermal reactivity. Compound* **2** *crystallized in the monoclinic* $P2_1/c$ *space group with* $a = 17.9162(3)$ Å, $b = 4.8646(2)$ Å, $c = 16.106(3)$ Å, $\beta = 105.19(1)^\circ$. *The molecules stacked one-dimensionally along the b axis and the intermolecular hydrogen bonds of the amide groups ran along the stacking axis. The hydroxyl group in the other end of the structure of* **2** *was also involved in polymeric hydrogen bonds, which also appear to play an important role in the molecular arrangement.*

Keywords: amide; crystal structure; hydrogen bond; polydiacetylene; solid-state polymerization

INTRODUCTION

Polydiacetylenes (PDAs), which have one-dimensional π-conjugated systems, are attractive from the viewpoint of their physical properties such as non-linear optics [1], conductivity [2] and magnetism [3]. It is

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Address correspondence to Dr. Tsunehisa Okuno, Department of Material Science and Chemistry, Wakayama University, 930 Sakaedani, Wakayama 640–8510, Japan. E-mail: okuno@sys.wakayama-u.ac.jp well-known that reactivity of solid-state polymerization of diacetylenes heavily depends on their crystal packings [4,5]. A schematic drawing of solid-state polymerization and its conditions of the molecular arrangement are shown in Figure 1. According to Baughman's criterion [5], polymerization can proceed when the stacking interval is from 4.8 Å to 5.6 Å, and the inclination angle between the molecular axis and the stacking one is from 40° to 50°. It is necessary to control the molecular arrangements in order to develop novel polydiacetylenes. Intermolecular hydrogen bonds are thought to be the most convenient interaction to control molecular arrangement.

There are many crystal engineering works for PDA systems. TCDU molecules [6] form intermolecular hydrogen bonds in urethane groups. The bonds proceed in the same direction to the stacking axis. *m*-AAPB molecules [2] also have the same hydrogen bond with TCDU. It is important in controlling molecular arrangement of diacetylenes that the hydrogen bonds run along the stacking axis.

Generally, intermolecular hydrogen bonds in an acetanilide moiety have a tendency to extend within the same plane to the phenyl rings because of π-conjugation. These bonds have low possibility to make appropriate one-dimensional stacks. However, the hydrogen bonds

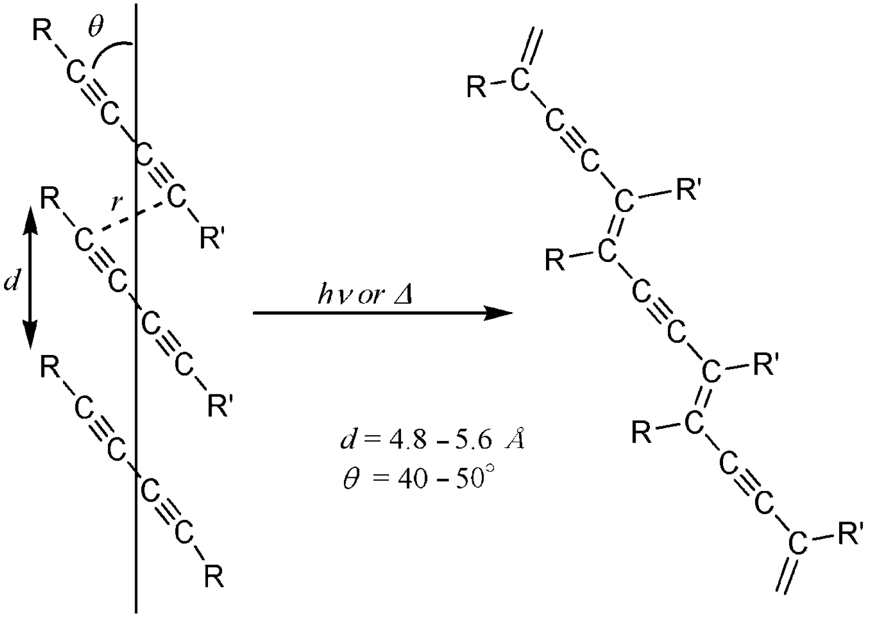
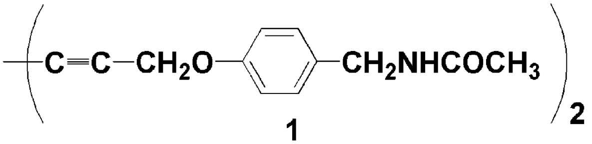


FIGURE 1 A schematic drawing of solid-state polymerization of diacetylenes.

in an acetylbenzylamine moiety, where a CH_2 group is inserted between the phenyl ring and the nitrogen atom, have a tendency to form the perpendicular bonds to the phenyl rings [7]. The bonds are very convenient to construct a one-dimensional arrangement. We wish to report here preparation, crystal structure and polymerization reactivity of diacetylene molecules (**1**, **2**) with amide groups.



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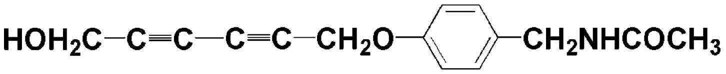

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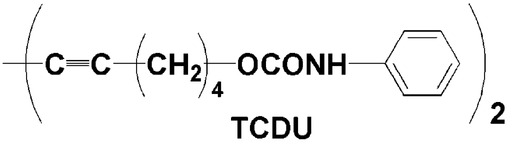
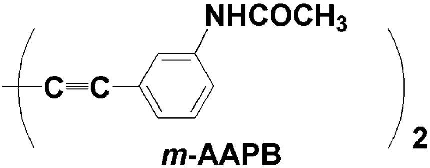


TCDU

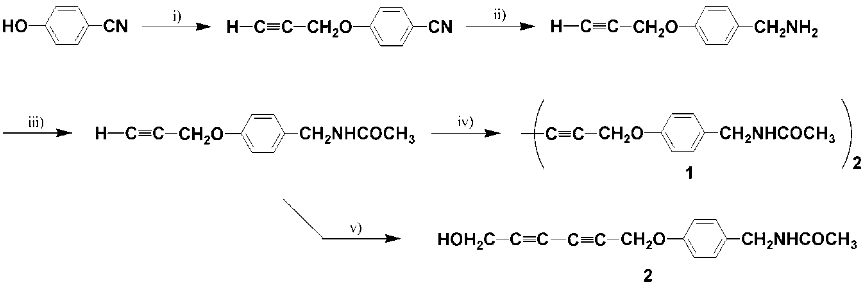


***m*-AAPB**

RESULTS AND DISCUSSION

Preparation of compound **1** and **2** was summarized in Scheme 1. Reaction between 4-cyanophenol and 3-bromo-1-propyne gave 4-(2-propynyloxy)benzonitrile [8]. The cyano group was transformed to an aminomethyl group by a reduction with lithium aluminum hydride. The amino group was allowed to react with acetic anhydride to give an amide group. Finally, this compound was coupled with itself to afford compound **1**, and coupled with 2-propyne-1-ol to give compound **2** [9].

Crystals with sufficient quality were obtained for compound **2**. Unfortunately, compound **1** did not give samples that were suitable



SCHEME 1 Syntheses of diacetylene derivatives **1** and **2**: (i) 3-Bromo-1-propyne, K_2CO_3/NMP (ii) $LiAlH_4$/THF (iii) $(CH_3CO)_2O$ (iv) O_2, CuCl, TMEDA/Acetone (v) 2-Propyne-1-ol, O_2, CuCl, TMEDA/Acetone.

for single crystal X-ray diffraction. Crystal data for compound **2** are summarized in Table 1 and Figure 2 shows its crystal structure. The aromatic, diyne and hydroxymethyl portions of the molecule fall in the same plane, which forms a dihedral angle of 79.4° [Fig. 2(a)] with the plane of the amide group.

Figure 2(b) shows the molecular stacking of compound **2**. The molecules stack along the *b* axis with a spacing of 4.85 Å. The inclination angle between the molecular axis and the *b* axis is ca. 48°.

TABLE 1 Crystal Data of Compounds **2**

	2
formula	$C_{15}H_{15}O_3N_1$
molar mass [g mol^{-1}]	257.29
crystal system	monoclinic
space group	$P2_1/c$
a [Å]	17.916(2)
b [Å]	4.8646(2)
c [Å]	16.106(3)
α[°]	90
β[°]	105.19(1)
γ[°]	90
Z	4
V [Å^3]	1349.6(7)
ρ_{calcd} [Mgm^{-3}]	1.266
no. of reflections	2780
no. of unique data	2682
$R1(I > 3\sigma(I)$, all data)	0.108, 0.253
$wR2(I > 3\sigma(I)$, all data)	0.142, 0.210
$Goof(I > 3\sigma(I)$, all data)	1.37, 1.25

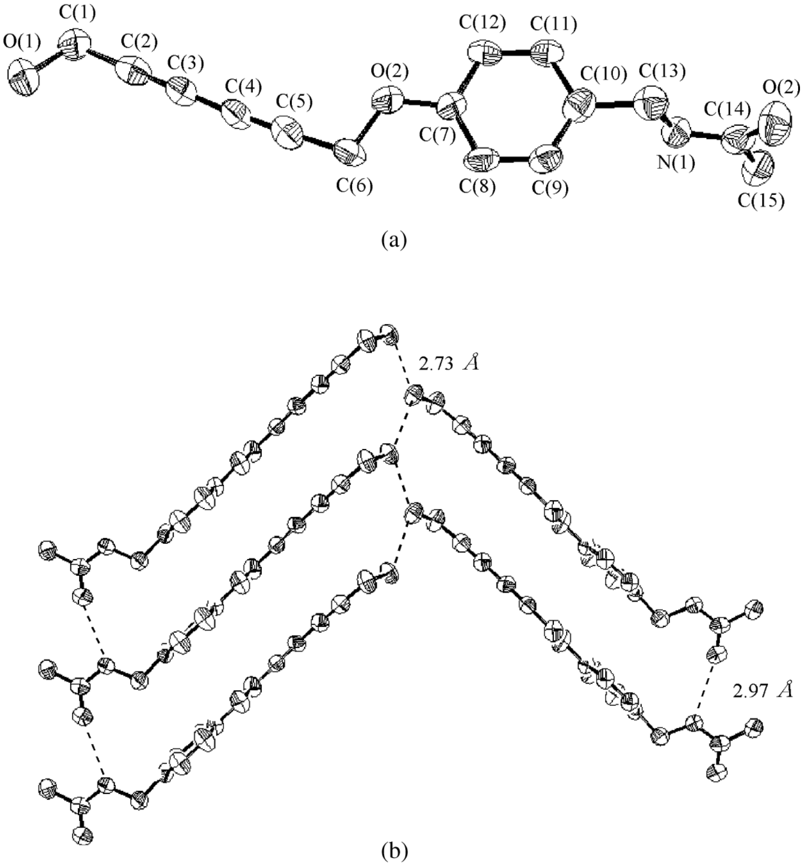


FIGURE 2 Crystal structure of the compound **2**: (a) Molecular structure (b) Molecular stacking along the *b* axis.

The interatomic distance between adjacent alkynes given by carbon C(2) of one molecule and C(5) of the other is 3.68 Å. This condition satisfies Baughman's criterion [5].

It is thought that there are two important interactions. One is the polymeric hydrogen bond formed by the hydroxyl groups, where the interatomic distance is 2.73 Å. The other is the one-dimensional hydrogen bond made by the amide groups, where the distance is 2.97 Å. These two interactions are thought to play a crucial role in fixing the molecular arrangements.

Compound **2** showed color changes by thermal annealing. The compound gradually turned blue by heating at 90°C. Finally it turned black and became insoluble. The surface of the compound also turned blue by UV irradiation. The electronic spectrum of the polymer showed a broad band around 620 nm, which was assigned to an excitonic transition [10]. On the other hand, compound **1** did not show polymerization reactivity by thermal annealing. The compound was also expected to form a one-dimensional stack with intermolecular hydrogen bonds in the amide groups. However, some significant structural differences must exist which may the stability of compound **1**.

In summary, we prepared two novel diacetylene derivatives (**1**, **2**), which carried amide groups in their side chains. Unfortunately, we could not analyze the crystal structure of compound **1** which did not show any thermal reactivity. However, we succeeded in crystal structural analysis of compound **2**, which showed solid-state polymerization reactivity. The intermolecular hydrogen bonds in the hydroxyl and amide groups were found to play a crucial role in forming the crystal packing. Especially, the intermolecular hydrogen bonds of amide groups which ran parallel to the stacking direction formed an ideal stacking for solid state polymerization of diacetylenes.

EXPERIMENTAL PART

General Procedure

Infrared spectra were recorded on a JASCO FT/IR-420 spectrometer with samples in compressed KBr discs. UV/Visible spectra were measured on a HITACHI U-2010 spectrometer. ^1H and ^{13}C NMR spectra were measured on a JEOL JNM-AL300. Tetramethylsilane was used for an internal standard. Melting points were measured on a Yanako Model MP and temperature was not corrected.

X-ray diffraction data were collected on RIGAKU AFC-5R automatic four-circle diffractmeter using graphite-monochromatic Mo Kα radiation. The crystal structure was solved by using Texsan. Anisotropic thermal parameters were introduced for all non-H atoms. Hydrogen atoms were not refined.

Synthesis

4-(2-Propynyloxy)benzonitrile [8]

To a solution of 4-cyanophenol (6.51 g, 54.7 mmol) and 3-bromo-1-propyne (7.80 g, 65.6 mmol) in 100 ml of *N*-methyl-2-pyrrodinone was added K_2CO_3(22.66 g, 164.0 mmol). The suspension was stirred for 3 hours at 85°C. It was poured into 500 ml of water to precipitate white powder. The precipitate was filtered off and recrystallized from hexane to give 7.52 g (yield 88%) of 4-(2-propynyloxy)benzonitrile. ^{1}H NMR (300 MHz, $CDCl_3$): δ2.56 (*s*, 1H), 4.75 (*s*, 2H), 7.03 (*d*, $J = 9.0$ Hz, Hz, 2H), 7.61 (*d*, $J = 9.0$ Hz, 2H), IR (cm^{-1}): 2128 ($\nu_{C\equiv C}$), 2222 ($\nu_{C\equiv N}$).

4-(2-Propynyloxy)benzylamine

A solution of 4-(2-propynyloxy)benzonitrile in THF (300 ml) was added dropwise to a suspension of $LiAlH_4$ (3.77 g, 99.3 mmol) in 100 ml of THF. The suspension was stirred for 24 hours at room temperature. It was poured into ice water and extracted with ether. The organic layer was washed with brine and dried over Na_2SO_4. After filtration, the filtrate was concentrated under a reduced pressure and dried *in vacuo*. The residue was purified by column chromatography (SiO_2, ethanol) to afford 8.71 g (66%) of colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ1.72 (*s*, 2 H), 2.52 (*t*, $J = 2.4$ Hz, 1H), 3.81 (*s*, 2 H), 4.68 (*d*, $J = 2.4$ Hz, 2H), 6.95 (*d*, $J = 6$ Hz, 2H), 7.24 (*d*, $J = 6$ Hz, 2H).

N-acetyl-4-(2-propynyloxy)benzylamine

A solution of 4-(2-propynyloxy)benzylamine (4.00 g, 24.8 mmol) in 18 ml(163.3 mmol) of acetic anhydride was stirred for 20 minutes at room temperature. The solution was poured into 50 ml of water and extracted with ether. The organic layer was washed with aqueous Na_2CO_3 (5%) and water, and dried over Na_2SO_4. After the removal of Na_2SO_4, the solution was evaporated under a reduced pressure. The residue was recrystallized from toluene to afford pale pink solid (3.02 g) in 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ2.01 (*s*, 3H), 2.52 (*t*, $J = 1.8$ Hz, 1H), 4.37 (*d*, $J = 5.7$ Hz, 2H), 4.68 (*d*, $J = 1.8$ Hz, 2H), 5.69 (*s*, 1H), 6.94 (*d*, $J = 8.4$ Hz, 2H), 7.23 (*d*, $J = 8.4$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ23.3, 43.2, 55.8, 75.6, 78.4, 115.1, 129.2, 131.3, 156.9, 169.8, IR (cm^{-1}) : 2127 ($\nu_{C\equiv C}$), 3235 (ν_{N-H}).

1, 6-Bis(4-acetamidomethylphenoxy)-2,4-hexadiyne(1) [9]

A suspension of CuCl (0.19 g, 1.93 mmol) in acetone (20 ml) was stirred under an argon atmosphere. After an addition of N, N, N', N'-tetramethylethylenediamine (0.070 ml, 0.82 mmol) to the suspension, it was stirred for 1 hour. The supernatant was added dropwise to an acetone solution of *N*-acetyl-4-(2-propynyloxy)benzylamine (2.78 g, 13.7 mmol) under an argon atmosphere. Then the solution was stirred for 3 days under an oxygen atmosphere to give white precipitate. It was filtered off and washed with acetone to afford 2.74 g (99%) of white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ2.01 (*s*, 3H), 4.37 (*s*, 2H), 4.68 (*s*, 2H), 5.69 (*s*, 1H), 6.94 (*d*, $J = 8.4$ Hz, 2H), 7.23 (*d*, $J = 8.4$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ23.3, 43.2, 56.2, 71.1, 74.5, 115.1, 129.3, 131.6, 156.7, 169.8. IR (cm^{-1}): 1628($\nu_{C=O}$), 2127 ($\nu_{C\equiv C}$), 3279 (ν_{N-H}).

p-N-acetyl(6-hydroxy-2,4-hexadiynenyloxy)benzylamine (2)

A suspension of CuCl (0.19 g, 1.93 mmol) in acetone (28 ml) was stirred under an argon atmosphere. After an addition of *N,N,N′,N′*-tetramethylethylenediamine (0.074 ml, 0.83 mmol) to the suspension, it was stirred for 1 hour. The supernatant was added dropwise to an acetone solution of *N*-acetyl-4-(2-propynyloxy)benzylamine (1.40 g, 6.89 mmol) and 2-propyne-1-ol (3.90 g, 68.9 mmol) under an argon atmosphere. Then the solution was stirred for 3 days under an oxygen atmosphere. It was poured into water and extracted with dichloromethane. The organic layer was washed with hydrochloric acid (4.0 M), aqueous Na_2CO_3 (5%) and water. It was dried over Na_2SO_4. After filtration, the filtrate was evaporated to dryness under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2-ethanol) and recrystallized from chloroform to give 0.94 g (39%) of white solid. mp. 118°C. ^1H NMR (300 MHz, $CDCl_3$): δ2.01 (*s*, 3H), 2.04 (*t*, $J = 3.3$ Hz, 1H), 4.32 (*d*, $J = 3.3$ Hz, 2H), 4.75 (*s*, 2H), 5.76 (*s*, 1H), 6.92 (*d*, $J = 8.6$ Hz, 2H), 7.21 (*d*, $J = 8.6$ Hz, 2H). ^{13}C NMR (75 MHz, DMSO): δ23.2, 42.1, 49.9, 56.3, 68.0, 71.1, 75.4, 81.5, 115.3, 129.2, 133.2, 156.4, 169.7. IR (cm^{-1}): 1631($\nu_{C=O}$), 3289 (ν_{N-H}).

Supplementary Data

Supplementary data are available, upon request, from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, quoting the deposition number 282617.

REFERENCES

[1] Hann, R. A. & Bloor, D. (1989). The Royal society of chemistry, special publication. *Organic Materials for Non-Linear Optics*, *69*.

[2] Matsuda, H., Nakanishi, H., Kato, S., & Kato, M. (1987). *J. Polym. Sci. Polym. Chem.*, *25*, 1663.

[3] (a) Izuoka, A., Okuno, T., & Sugawara, T. (1990). *The Physics and Chemistry of Organic Superconductors*, 428, Springer-Verlag; (b) Inoue, K., Koga, N., & Iwamura, H. (1991). *J. Am. Chem. Soc.*, *113*, 9803.

[4] (a) Wegner, G. (1971). *J. Polym. Sci. Polym. Lett. Ed.*, *9*, 133; (b) Enkelmann, V. (1984). *Advances in Polymer Science*, *63*, 91, Springer-Verlag and references cited therein.

[5] Boughman, R. H. (1974). *J. Polym. Sci. Polym. Phys. Ed.*, *12*, 1511.

[6] Gross, H., Sixl, H., Kröhnke, H., & Enkelmann, V. (1980). *Chem. Phys.*, *45*, 15.

[7] (a) Chekhlov, A. N., Berl, V. K., & Martynov, I. V. (1986). *Russ. Chem. Bull.*, 2446; (b) Luo, J. T. & Huang, W. Q. (2004). *Chinese J. Struc. Chem.*, *23*, 32; (c) Baures, P. W., Beatty, A. M., Dhanasekaren, M., Helfrich, B. A., Segarra, W. P., & Desper, J. (2002). *J. Am. Chem. Soc.*, *124*, 11315.

[8] Fomina, L., Vega, A., Fomine, S., Gavino, R., & Ogawa, T. (1996). *Macromol. Chem. Phys.*, *197*, 2653.
[9] Jones, G. E., Kendrick, D. A., & Holmes, A. B. (1993). *Organic Syntheses, Coll.*, *8*, 63.
[10] (a) Tokura, Y., Koda, T., Itsubo, A., Miyabayashi, M., Okuhara, K., & Ueda, A. (1986). *J. Chem., Phys.*, *85*, 99; (b) Okuno, T., Izuoka, A., Kume, K., Sato, N., & Sugawara, T. (1993). *Mol. Cryst. Liq. Cryst.*, *225*, 393.