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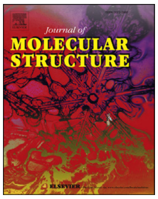

Preparations, crystal structures and DFT calculation of diacetylene derivatives carrying nicotinic esters

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Novel three diacetylene derivatives **1**–**3**, which carry a pyridine ring as a pendant group, have been successfully prepared and crystallographically analyzed. In compound **1**, the molecular stacks form a layered structure within the *ac* plane. In **2**, the molecules make a columnar stack along the *a* axis. In **3**, the molecules have a dimeric form and the dimers make a one-dimensional stack along the *b* axis.

The all compounds make a columnar stack, but conformation at nicotinic ester part is found to have a crucial role for molecular arrangement. The *gauche* conformation at nicotinic ester part (**1** and **2**) makes an intermolecular p–p interaction between the pyridine groups. This interaction between the stacks prevents an independent molecular stack in **1**, and the interaction within the stack in **2** makes larger inclination angles than the ideal one for solid-state polymerization of diacetylenes. The *anti* conformation in **3**, caused by N-H···N hydrogen-bonded dimer, makes it enable to stack one-dimensionaly with a moderate inclination angle, which is favorable for the polymerization.

1. Introduction

Polydiacetylenes (PDAs), which are classified into conjugated polymers [1,2], have attracted not only from their physical properties originating from one-dimensional π-conjugated systems such as non-linear optics [3] or conductivity [4–6], but also from application to chemosensors [7]. PDAs are prepared by solid-state-polymerization of diacetylene monomers, where relative orientation of monomers is quite important for the polymerization [8] because molecular motions are restricted in their crystals. Many PDAs have a $-(CH_2)_n-$ side chain adjacent to the backbone in order to reduce lattice strain caused by the solid-state polymerization. However, *gauche* or pseudo *gauche* conformation of the side chain frequently prevents suitable molecular orientation for the polymerization. Examples of the polymerization in gauche conformer are limited to some diacetylenes [9].

Pyridines have a large variety of chemical modification such as oxidation, protonation or N-alkylation [10]. Pyridines can also work as ligands for metal complexes or hydrogen-bond acceptors in supramolecular complexes [11]. PDAs carrying pyridyl pendant groups promise to give novel functional materials. Few PDAs carrying a pyridyl unit, however, have been reported as a single component judged by their crystal packing structures. While Lauher et al. have proposed several crystal designs for arranging pyridine-containing diacetylene derivatives by utilizing template molecules [12,13].

We report herein preparation and crystal structures of novel three pyridine-containing diacetylenes and discuss their molecular structures based on intermolecular interactions and DFT calculation.

2. Experimental

2.1. General procedure

All chemicals were purchased from Kanto Chemical Co. Ltd. or Tokyo Kasei Kogyo Co. Ltd. and were used without further purification. Compound **1** was prepared according to the literature [12]. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM–ECA–400 spectrometer in a deuterated solvent (chloroform-*d*) with tetramethylsilane as an internal standard. All ^{13}C NMR spectra were obtained with complete proton decoupling. IR spectra were recorded on a JASCO FT/IR–420 spectrometer by using a KBr pellet. Elemental analysis was performed on a J-SCEINCE LAB MICRO CORDER JM10.

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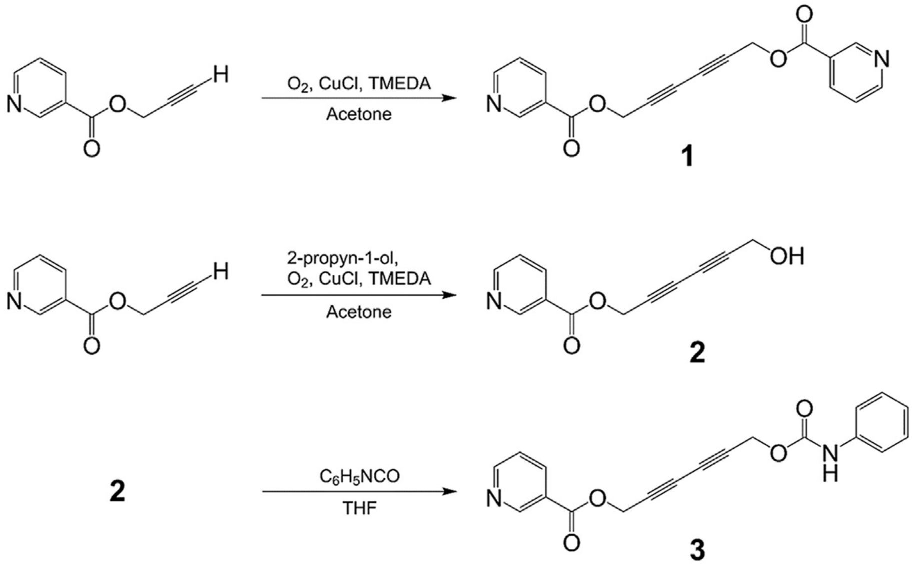

Scheme 1. Preparation of **1**, **2** and **3**.

2.2. Crystallographical analysis

X-ray crystallographic data of **1**–**3** were obtained by a RIGAKU Saturn 724 + CCD device using multi-layered mirror monochromatic Mo $K\alpha$ radiation at 93 K. The structures were solved by a direct method (SHELXD) [14] and were refined by full-matrix least-squares method (SHELXL97) [15]. The positions of non-H atoms were obtained from difference Fourier maps and were refined anisotropically. The C-bound H atoms were obtained by calculation and were refined as riding on their parent C atoms. $U_{iso}(H)$ values of the H atoms were set at $1.2U_{eq}$ (parent C atoms). The N-bound and O-bound H atoms were obtained from difference Fourier maps and were refined isotropically.

2.3. DFT calculations

DFT calculations were performed on the GAMESS software [16,17] with B3LYP 6-31G (d,p) level. The geometrical optimization was carried out in C1 symmetry, where the initial structures for calculations were set at those obtained by crystallographical analyses or by calculations of RHF 6-31G(d) level.

2.4. Materials

2.4.1. Preparation of 6-hydroxyhexa-2,4-diyn-1-yl nicotinate (**2**)

After a suspension of cupper chloride (I) (1.34 g, 13.5 mmol) in acetone (55 mL) was degassed by argon bubbling for 30 min,

Table 1
Crystal data and refinement details for **1**, **2** and **3**.

Compounds	1	2	3
Empirical formula	$C_{18}H_{12}N_2O_4$	$C_{12}H_9NO_3$	$C_{19}H_{14}N_2O_4$
Formula weight	320.30	215.21	334.33
Crystal system	*Monoclinic*	*Monoclinic*	*Monoclinic*
Crystal size (mm)	0.10 × 0.08 × 0.01	0.15 × 0.12 × 0.01	0.12 × 0.08 × 0.01
Crystal color	Colorless	Colorless	Colorless
Space group	$C2/c$	$P2_1/n$	$P2_1/c$
a (Å)	6.751(3)	4.0658(11)	17.263(7)
b (Å)	18.919(7)	28.023(7)	4.8799(17)
c (Å)	11.543(4)	8.993(3)	20.084(9)
α (°)	90	90	90
β (°)	94.130(5)	90.773(6)	110.268(6)
γ (°)	90	90	90
V (Å^3)	1470.5(10)	1024.5(5)	1587.1(11)
Z	4	4	4
Dx (Mg/m^3)	1.447	1.395	1.399
μ (mm^{-1})	0.104	0.102	0.100
Theta range for data collection (°)	2.2–31.3	2.3–31.2	1.9–31.1
Limiting indices	$-8 \le h \le 7$, $-22 \le k \le 21$, $-13 \le l \le 13$	$-4 \le h \le 4$, $-33 \le k \le 32$, $-10 \le l \le 10$	$-22 \le h \le 21$, $-5 \le k \le 6$, $-24 \le l \le 26$
Reflections collected/unique	4952/1291 ($R_{int} = 0.056$)	6412/1773 ($R_{int} = 0.024$)	12235/3631 ($R_{int} = 0.038$)
Reflections with $I > 2\sigma(I)$	981	1455	2636
Refined parameters/restrains	109/0	149/0	230/0
Goodness of Fit on F^2	1.05	1.10	1.07
R_1, wR_2	0.043, 0.105	0.041, 0.109	0.051, 0.130
Data completeness	0.998	0.986	0.993
Data/restrains/parameters	1291/0/109	1772/0/149	3631/0/230
Max. and min. transmission	0.999 and 0.995	0.999 and 0.989	0.999 and 0.992
Largest diff. peak and hole (eÅ^{-3})	0.20 and −0.20	0.24 and −0.18	0.24 and −0.25