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# Preparations, crystal structures and DFT calculations of novel diacetylenes incorporating ynamine moieties

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HIGHLIGHTS

- ► Two diacetylene molecules were characterized by NMR and X-ray diffraction.
- ▶ The crystal structures were controlled by the intermolecular hydrogen-bondings.

▶ The molecular structures were compared with those obtained by DFT alculations.

#### ARTICLE INFO

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#### ABSTRACT

Two diacetylene molecules incorporating an ynamine moiety, 5-(diphenylamino)-2,4-pentadiyne-1-ol (1) and 6-(diphenylamino)-2-methylhexa-3,5-diyn-2-ol (2), were prepared and characterized by single crystal X-ray diffraction, <sup>1</sup>H and <sup>13</sup>C NMR. The crystal structures of 1 and 2 were solved successfully and were interpreted to be controlled mainly by the intermolecular hydrogen-bondings. The difference in the crystal structures between 1 and 2 was well explained by consideration of the steric repulsion with the methyl groups connected to the carbon atom adjacent to the hydroxyl group in 2. The steric effects of the methyl groups on intra and intercolumnar interaction were found to be important for designing molecular and crystal structures of diacetylene molecules. Although the geometries obtained by DFT calculations showed a good agreement on 2 except for the butadiynyl part, a significant difference was recognized at the environment around the nitrogen of 1. The difference could be explained by the effect of the crystal packing.

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# 1. Introduction

Polydiacetylenes (PDAs), which are obtained by solid-state polymerization of diacetylene derivatives [1,2], have been paid much attention from the viewpoint of physical properties originating in their one-dimensional  $\pi$ -conjugated systems. In order to improve their physical properties, expansion of  $\pi$ -conjugation has been thought to be effective. According to this strategy, introduction of aromatic groups [3–6] and/or hetero atoms [7–12] has been examined extensively.

Ynamines, where an acetylene group connects directly to a nitrogen atom, have been known unstable because of polymerization and hydrolysis. The instability of ynamines originates in high electron density owing to conjugation of  $\pi$ -electrons with a lone pair of a nitrogen atom. On the contrary, electron richness is thought to be suitable for enhancement of physical properties of PDAs. Several reactive diacetylene derivatives incorporating an

\* Corresponding author. E-mail address: okuno@center.wakayama-u.ac.jp (T. Okuno). ynamine moiety have been prepared and have given varieties of PDAs which carry amino groups as a pendant group, such as carbazol-9-yl [7,8], phenothiazin-10-yl [9] and diphenylamino groups [10–12].

While the reactivity in solid-state polymerization of diacetylene derivatives is known to depend heavily on the relative orientation of diacetylene monomers. The conditions of relative packing parameters [13] are given by stacking intervals (d = 4.4-5.9 Å) and inclination angles ( $\varphi = 36-51^{\circ}$ ) between the stacking axis and the diacetylene moiety as shown in Scheme 1. Therefore the correlation between chemical modifications and crystal packing becomes significantly important in order to establish the methodology for designing an appropriate one-dimensional stacking of diacetylenes.

In order to control the relative orientation of diacetylene monomers to the appropriate one-dimensional stack, amido, urethane and/or hydroxyl groups have been introduced in the side chain of the monomers [2]. When hydroxyl groups are introduced in the side chain, the molecules have a tendency to form one-dimensional columnar stacks with intercolumnar hydrogen-bondings.

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**Scheme 1.** General representation of solid-state polymerization of diacetylene monomers accompanied by the packing parameters.

DFT calculation is one of the most useful methods for molecular modeling. The calculation, however, has not been applied to diacetylene molecules yet because the modeling does not give the similar structure to the crystal structure in the case when the compounds have many flexible bonds or a hydrogen-bonding donor (or acceptor) group.

We wish to report the preparations and the crystal structures of 5-(diphenylamino)-2,4-pentadiyne-1-ol (1) and 6-(diphenylamino)-2-methylhexa-3,5-diyn-2-ol (2), where the diphenylamino and hydroxymethyl groups are connected to the both ends of the diacetylenes. The effects of methyl groups for the molecular structure and the crystal packing structure are discussed. And the crystal structures are also compared with those obtained by DFT method.

#### 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. Gel permeation chromatography (GPC) was performed on a JAI LC-918 equipped with JAIGEL-1H and -2H columns. <sup>1</sup>H and <sup>13</sup>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 <sup>13</sup>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.

X-ray crystallographic data were obtained by a RIGAKU Saturn 724+ CCD device using multi-layered mirror monochromatic Mo K $\alpha$  radiation at -180 °C. In compound **2**, Friedel pairs were merged because the molecule itself was achiral and because there were not any anomalous scattering effects. The structures were solved by a direct method (SIR 92) [14], and were refined by full-matrix leastsquares method (Shelx 97) [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 atom for  $C_{sp2}$ ) and  $1.5U_{eq}$  (parent atom for C<sub>sp3</sub>). The O-bound H atoms were obtained from a difference Fourier map and were not refined in 1. In 2, the isotropic thermal factor of the O-bound H atom was set at  $U_{i-}$  $_{so}(H) = 1.2 U_{eq}$  (parent atom) and the position of the atom was refined with the restraint on O-H range between 0.994 and 1.034 Å.





Table 1Crystal data and refinement details for 1 and 2.

Compounds	1	2
Empirical formula	C <sub>17</sub> H <sub>13</sub> O <sub>1</sub> N <sub>1</sub>	C <sub>19</sub> H <sub>17</sub> O <sub>1</sub> N <sub>1</sub>
Formula weight	247.30	275.35
Crystal system	Monoclinic	Orthorhombic
Crystal size	$0.14 \times 0.08 \times 0.04$	$0.10 \times 0.10 \times 0.04$
Crystal color	Colorless	Colorless
Space group	$P2_1/n$	$P2_{1}2_{1}2_{1}$
a (Å)	11.849(5)	5.836(2)
b (Å)	5.219(2)	12.054(4)
c (Å)	22.004(10)	21.913(8)
β (°)	104.957(7)	90.000
V (Å <sup>3</sup> )	1314.6(10)	1541.5(10)
Ζ	4	4
$Dx (Mg/m^3)$	1.249	1.186
$\mu$ (mm <sup>-1</sup> )	0.08	0.07
Theta range for data collection (°)	1.8-27.5	3.3–27.5
Limiting indices	$-14 \leqslant h \leqslant 15$ ,	$-7 \leqslant h \leqslant 7$ ,
	$-6 \leqslant k \leqslant 6$ , $-28 \leqslant l \leqslant 25$	$-15 \leqslant k \leqslant 15$ ,
		$-28 \leqslant l \leqslant 19$
Reflections collected/	10224/3028	128158/2048
unique	$(R_{int} = 0.0384)$	$(R_{int} = 0.0435)$
Reflections with	2259	1780
$I > 2\sigma(I)$		
Refined parameters/ restrains	224/0	257/1
Goodness of fit on $F^2$	1.099	1.073
$R_1(I > 2\sigma(I)), wR_2$ (all	0.0567, 0.145	0.0596, 0.162
data)		
Data completeness	0.998	0.990
Data/restrains/	3028/0/224	2048/1/257
parameters		
Max. and min.	0.993 and 0.997	0.995 and 0.997
transmission		
Largest diff. peak and	0.21 and -0.23	0.28 and -0.25
hole (e Å <sup>-3</sup> )		

#### 2.2. Preparation of N-phenyl-N-(1,2,2-trichlorovinyl)aniline

A solution of *N*,*N*-diphenylacetamide (3.00 g, 14.2 mmol) and phosphorus pentachloride (12.0 g, 57.5 mmol) in dry toluene (50 ml) was heated at 90 °C for 5 h under a nitrogen stream. The solution was poured into an ice water (100 ml), and the water layer was extracted with toluene (50 ml). The combined organic layer was washed with 5% sodium carbonate solution (50 ml). The organic layer was dried over anhydrous sodium sulfate, and concentrated after filtration. The residue was purified by column chromatography on a silica gel with hexane as an eluant to give 1.02 g (yield 24%) of *N*-phenyl-*N*-(1,2,2-trichlorovinyl)aniline as an yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.08 (d, 4H, <sup>3</sup>*J* = 8 Hz, C<sub>6</sub>H<sub>5</sub>–H2, H6); 7.12 (t, 2H, <sup>3</sup>*J* = 8 Hz, C<sub>6</sub>H<sub>5</sub>–H4); 7.32 (t, 4H, <sup>3</sup>*J* = 8 Hz, C<sub>6</sub>H<sub>5</sub>–H3, H5). Anal. Calc. for C<sub>14</sub>H<sub>10</sub>Cl<sub>3</sub>N<sub>1</sub>: C, 56.31; H, 3.38; N, 4.69. Found: C, 55.91; H, 3.36; N, 4.65.

Table 2 Selected experimental and calculated geometric parameters (Å,  $^{\circ}$ ) for crystal 1 and 2.

	Exp. (1)	Cal.	$\varDelta^a$	Exp. (2)	Cal. (2)	$\varDelta^a$
		(1)				
Bond distances (	Å)					
01–C17	1.419(3)	1.428	0.009	1.446(4)	1.440	-0.006
N1-C1	1.451(3)	1.436	-0.015	1.438(4)	1.437	-0.001
N1-C7	1.420(3)	1.435	0.015	1.424(4)	1.434	0.010
N1-C13	1.340(3)	1.335	-0.005	1.340(4)	1.335	-0.005
C1-C2	1.385(3)	1.397	0.012	1.389(5)	1.396	0.007
C1-C6	1.379(3)	1.398	0.019	1.397(4)	1.398	0.001
C2-C3	1.388(4)	1.392	0.004	1.381(5)	1.392	0.011
C3–C4	1.385(4)	1.393	0.008	1.394(5)	1.393	-0.001
C4–C5	1.373(3)	1.394	0.021	1.373(6)	1.394	0.021
C5-C6	1.390(4)	1.391	0.001	1.391(5)	1.391	0.000
C7–C8	1.388(3)	1.398	0.010	1.392(5)	1.399	0.007
C7–C12	1.400(3)	1.397	-0.003	1.394(5)	1.397	0.003
C8–C9	1.392(3)	1.391	-0.001	1.393(5)	1.391	-0.002
C9-C10	1.389(4)	1.394	0.005	1.393(5)	1.394	0.001
C10-C11	1.388(3)	1.393	0.005	1.388(5)	1.393	0.005
C11-C12	1.384(3)	1.392	0.008	1.390(5)	1.391	0.001
C13-C14	1.205(3)	1.215	0.010	1.205(4)	1.215	0.010
C14–C15	1.370(3)	1.357	-0.013	1.368(4)	1.358	-0.010
C15-C16	1.204(3)	1.212	0.008	1.207(4)	1.214	0.007
C16–C17	1.457(3)	1.452	-0.005	1.472(5)	1.469	-0.003
C17–C18	-	-	-	1.532(5)	1.540	0.008
C17-C19	-	-	-	1.518(5)	1.533	0.015
Bond angles (°)						
C1-N1-C7	121.53(14)	121.82	0.31	121.6(3)	121.91	0.3
C1-N1-C13	116.96(16)	118.99	2.03	118.1(3)	118.72	0.6
C7-N1-C13	121.47(17)	119.19	-2.28	120.1(3)	119.37	-0.7
N1-C13-C14	178.1(2)	179.70	1.6	178.7(4)	179.74	1.0
C13-C14-C15	177.89(18)	179.82	1.93	175.6(4)	179.75	4.2
C14-C15-C16	179.68(18)	179.89	0.31	177.6(4)	179.60	2.0
C15-C16-C17	176.58(18)	179.18	2.60	178.1(3)	178.79	0.7
01-C17-C16	110.33(15)	110.35	0.02	108.7(3)	110.49	1.8

<sup>a</sup> Differences between the calculated values and the observed ones.

#### 2.3. Preparation of N-ethynyl-N-phenylaniline

Butyllithium in hexane (5.4 ml, 8.6 mmol) was added dropwise to a solution of *N*-phenyl-*N*-(1,2,2-trichlorovinyl)aniline (1.00 g, 3.35 mmol) in dry tetrahydrofuran (60 ml) at -65 °C under an argon atmosphere. After the solution was stirred for 1 h, methanol (0.4 ml) was added to the solution. It was allowed to warm to -10 °C and was poured into water (20 ml). The water layer was extracted with ether (50 ml), and the combined organic layer was washed with saturated brine (30 ml), and dried over anhydrous sodium sulfate. After filtration, the solution was concentrated to give *N*-ethynyl-*N*-phenylaniline as brown oil. Since this compound was unstable, it was used to the following preparation without purification.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.89 (s, 1H, CH); 7.11 (tt, 2H, <sup>3</sup>*J* = 7.2 and <sup>4</sup>*J* = 1.5 Hz, C<sub>6</sub>H<sub>5</sub>-H4); 7.29 (dd, 4H, <sup>3</sup>*J* = 7.4 and <sup>4</sup>*J* = 1.4 Hz, C<sub>6</sub>H<sub>5</sub>-H2, H6); 7.34 (t, 4H, <sup>3</sup>*J* = 7.2 Hz, C<sub>6</sub>H<sub>5</sub>-H3, H5).

# 2.4. Preparation of 5-(diphenylamino)-2,4-pentadiyne-1-ol(1) [16]

After a suspension of cupper (I) chloride (0.38 g, 3.91 mmol) in acetone (6.9 ml) was degassed by argon bubbling for 30 min, N,N,N',N'-tetramethylethylenediamine (TMEDA) (0.19 ml, 1.29 mmol) was added to the suspension, and it was stirred for 30 min. The supernatant solution containing CuCl–TMEDA catalyst was transferred into a mixture of *N*-ethynyl-*N*-phenylaniline (0.65 g, 3.35 mmol) and 2-propyn-1-ol (1.1 ml, 18.3 mmol) in acetone at -20 °C. The solution was stirred for 14 h under an oxygen atmosphere. The solvent was evaporated, and the residue was extracted with chloroform. The solution was sushed with 5%



**Fig. 1.** The asymmetric unit of **1** with atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres.



**Fig. 2.** A view of the hydrogen-bonding interactions in **1**. [Symmetry codes: (i) -x + 3/2, y + 1/2, -z + 3/2; (ii) x, y + 1, z.]

#### Table 3

Hydrogen-bonding geometry	/ (Å,	°) for	crystal	<b>1</b> a	nd 2	2.
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D-H···A	d(D-H)	d(H…A)	d(D…A)	∠DHA
Crystal <b>1</b> O1 <sup>i</sup> –H1 <sup>i</sup> …O1	0.898	1.917	2.764(3)	157(3)
Crystal <b>2</b> 01–H1…01 <sup>iii</sup>	1.00(3)	2.33(4)	3.179(5)	142(4)
Symmetry codes: (i)	v + 3/2 + 1/2	$7 + 3/2 \cdot (iii)$	$v \pm 1/2 = v \pm 1/2$	7

Symmetry codes: (i) -x + 3/2, y + 1/2, -z + 3/2; (iii) x + 1/2, -y + 1/2, -z.

# Table 4

Stacking parameters of the diacetylene moieties (Å,  $^{\circ}$ ) for crystal 1 and 2.

Crystal <b>1</b>		Crystal <b>2</b>	
Stacking intervals	5.219(2)	Stacking intervals	5.836(2)
d(C13…C16 <sup>ii</sup> )	3.474(3)	d(C13…C16 <sup>iv</sup> )	5.332(5)
∠C13-C16-C16 <sup>ii</sup>	41.70(4)	∠C13–C16–C16 <sup>iv</sup>	63.18(7)

Symmetry codes: (ii) *x*, *y* + 1, *z*; (iv) *x* + 1, *y*, *z*.

ammonium hydroxide, and the water layer was extracted twice with chloroform. The combined organic layer was washed with water, and dried over anhydrous sodium sulfate. After the solvent



Fig. 3. Crystal packing structure of 1. Hydrogen atoms are omitted for clarity.



**Fig. 4.** The asymmetric unit of **2** with atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres.

was evaporated, the residue was purified by GPC to give 0.14 g (yield 70%) of **1** as a brown solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.71 (t, 1H, <sup>3</sup>*J* = 6.4 Hz, OH); 4.40 (d, 2H, <sup>3</sup>*J* = 6.4 Hz, CH<sub>2</sub>); 7.16 (tt, 2H, <sup>3</sup>*J* = 7.3 and <sup>4</sup>*J* = 1.4 Hz, C<sub>6</sub>H<sub>5</sub>–H4); 7.26 (dd, 4H, <sup>3</sup>*J* = 7.3 and <sup>4</sup>*J* = 1.4 Hz, C<sub>6</sub>H<sub>5</sub>–H2, H6); 7.35 (t, 4H, <sup>3</sup>*J* = 7.3 Hz, C<sub>6</sub>H<sub>5</sub>–H3, H5). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 51.95; 54.27; 71.35; 77.66; 80.29; 121.20; 124.96; 129.42; 142.17. IR (KBr): 3411, 2232, 2160 cm<sup>-1</sup>. Anal. Calc. for C<sub>17</sub>H<sub>13</sub>NO: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.46; H, 5.49; N, 5.65.

# 2.5. Preparation of 6-(diphenylamino)-2-methylhexa-3,5-diyn-2-ol(2)

After a suspension of cupper (I) chloride (0.29 g, 2.96 mmol) in acetone (8.3 ml) was degassed by argon bubbling for 30 min, TME-DA (0.15 ml, 1.01 mmol) was added to the suspension, and it was stirred for 45 min. The supernatant solution containing CuCl–TME-DA catalyst was transferred into a mixture of *N*-ethynyl-*N*-pheny-laniline (0.52 g, 2.69 mmol) and 2-methyl-3-butyn-2-ol (1.0 ml) in acetone at -20 °C. The solution was stirred for 18 h under an oxygen atmosphere. The solvent was evaporated, and the residue was extracted with dichloromethane. The solution was washed with 5% ammonium hydroxide, and the water layer was extracted twice with dichloromethane. The combined organic layer was washed with water, and dried over anhydrous sodium sulfate. After the solvent was evaporated, the residue was purified by column



Fig. 5. A view of the hydrogen-bonding interactions in 2. [Symmetry codes: (iii) x + 1/2, -y + 1/2, -z; (iv) x + 1, y, z.]



Fig. 6. Crystal packing structure of 2. Hydrogen atoms are omitted for clarity.

chromatography on a silica gel with dichloromethane as an eluant to give 0.31 g (yield 42%) of **2** as a white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.56 (s, 6H,  $2 \times CH_3$ ); 2.00 (s, 1H, OH); 7.15 (dt, 2H, <sup>3</sup>*J* = 7.3 and <sup>4</sup>*J* = 1.4 Hz, C<sub>6</sub>H<sub>5</sub>–H4); 7.26 (dd, 4H, <sup>3</sup>*J* = 7.3 and <sup>4</sup>*J* = 1.4 Hz, C<sub>6</sub>H<sub>5</sub>–H2, H6); 7.35 (t, 4H, <sup>3</sup>*J* = 7.3 Hz, C<sub>6</sub>H<sub>5</sub>–H3, H5). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 31.29; 53.91; 65.89; 67.64; 77.53; 86.12; 121.17; 124.86; 129.39; 142.21. IR (KBr): 3454, 2250, 2166 cm<sup>-1</sup>. Anal. Calc. for C<sub>19</sub>H<sub>17</sub>NO: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.70; H, 6.41; N, 5.17.

# 2.6. Computational methods

DFT calculations of **1** and **2** were performed using the Spartan 04 software [17] (Wavefunction, Inc.) with B3LYP 6-311G (d, p) level. The geometrical optimization was carried out without symmetry constraints, where the initial structures for calculations were set at those obtained by crystallographycal analyses.

# 3. Results and discussion

#### 3.1. Preparation of 1 and 2

Preparation of **1** and **2** is shown in Scheme 2. Treatment of N,N-diphenylacetamide with phosphorus pentachloride in dry toluene gave N-phenyl-N-(1,2,2-trichlorovinyl)aniline in 24% yield. Reaction of N-phenyl-N-(1,2,2-trichlorovinyl)aniline with n-BuLi afforded N-ethynyl-N-phenylaniline. Since this compound was unstable, it was used to the following preparation without purification. Hay coupling reaction between N-ethynyl-N-phenylaniline and the corresponding acetylenes gave **1** and **2** in 70% and 42% yield, respectively.

# 3.2. Crystal structure of 1 and 2

The single crystals of **1** and **2** suitable for X-ray crystallography were obtained by slow evaporation of chloroform and hexane, respectively. Crystal data and details of refinement for **1** and **2** 

are summarized in Table 1. Selected bond distances and angles of **1** and **2** are listed in Table 2.

Fig. 1 shows the crystal structure of **1**. The structure around the nitrogen (the N1/C1/C7/C13 plane; r.m.s. deviation = 0.007 Å) is planar. The dihedral angles of the plane with two phenyl groups (the C1–C6 plane and the C7–C12 plane) are 82.5(9)° and 7.05(9)°, respectively. It clearly shows that the C7–C12 phenyl group conjugates with acetylenic groups and the C1–C6 ring does not contribute to the  $\pi$ -conjugated system. The bond distances of N1–C1 and N1–C7 are 1.451(3) Å and 1.420(3) Å. The difference in the bond distances is thought to originate in  $\pi$ -conjugation. Such geometry is unusual for that of a diphenylamino group.

The bond length of N1–C13 is 1.340(3)Å, which is consistent with the reported lengths [7–12,18–21]. The distances of C13–C14, C14–C15 and C15–C16 are 1.205(3)Å, 1.370(3)Å and 1.204(3)Å, showing a clear bond alternation. The diacetylene group curves slightly, where the angles of N1–C13–C14, C13–C14–C15, C14–C15–C16 and C15–C16–C17 are  $178.1(2)^{\circ}$ ,  $177.89(18)^{\circ}$ ,  $179.68(18)^{\circ}$  and  $176.58(18)^{\circ}$ .

Fig. 2 shows the intermolecular interaction observed in 1. The molecules stack along the *b* axis making regular one-dimensional columns. The intermolecular polymeric O-H···O hydrogenbondings were recognized between the columnar stacks. The geometries of the hydrogen-bonding patterns are summarized at Table 3. The distance between O1 and O1<sup>i</sup> atoms [symmetry codes: (i) -x + 3/2, y + 1/2, -z + 3/2] is 2.764(3)Å and the angles of  $O1^{i}$ -H1<sup>i</sup>···O1 is 157(3)°. The stacking parameters of the diacetylene moieties are also listed in Table 4. Stacking intervals of the molecules **1** are 5.219(2)Å, and the inclination angle between the diacetylene moiety and the *b* axis (C13–C16–C16<sup>ii</sup> [symmetry codes: (ii) x, y + 1, z]) is 41.70(4)°. Intermolecular distance between C13 and the neighboring C16<sup>ii</sup> atom is 3.474(3) Å. These packing parameters satisfy the Baughman's condition for solid-state polymerization of diacetylenes. Fig. 3 shows the crystal packing structure of **1**. The one-dimensional columnar stacks fill in the crystal space capably. The inter-columnar interactions are not recognized except for the hydrogen-bonding.



Fig. 7. Optimized molecular structures of  $\mathbf{1}$  (a) and  $\mathbf{2}$  (b) with atom-numbering scheme.

Fig. 4 shows the crystal structure of **2**. The structure around the nitrogen (the N1/C1/C7/C13 plane; r.m.s. deviation = 0.018 Å) is planar. The dihedral angles of the plane with two phenyl groups (the C1–C6 plane and the C7–C12 plane) are 52.3(1)° and 23.5(1)°, respectively. In crystal **2**, both phenyl rings are found to contribute to the  $\pi$  conjugated system. The bond distances of N1–C1 (1.438(4) Å) and N1–C7 (1.424(4) Å) show a tendency to depend on the dihedral angles. The bond length of N1–C13 is 1.340(4) Å, which is consistent with the reported lengths. The distances of C13–C14, C14–C15 and C15–C16 are 1.205(4) Å, 1.368(4) Å and 1.207(4) Å, showing a clear bond alternation. The diacetylenic group curves slightly, where the angles of N1–C13–C14, C13–C14–C15, C14–C15–C16 and C15–C16–C17 are 178.7(4)°, 175.6(4)°, 177.6(4)° and 178.1(3)°.

Fig. 5 shows the intermolecular interaction observed at **2**. The molecules stack along the *a* axis making regular one-dimensional columns. The intermolecular polymeric O–H···O hydrogen-bonds were recognized between the columnar stacks. The geometries of the hydrogen-bonding patterns are summarized at Table 3. The distance between O1 and O1<sup>iii</sup> atoms [symmetry code: (iii) x + 1/2, -y + 1/2, -z.] is 3.179(5) Å and the angles of O1–H1···O1<sup>iii</sup> is

142(4)°. The stacking parameters of diacetylene moieties are also listed in Table 4. Stacking intervals of the molecules are 5.836(2) Å, and the inclination angle between the molecular axis and the *a* axis (C13–C16–C16<sup>iv</sup> [symmetry code: (iv) *x* + 1, *y*, *z*.]) is 63.18(7)°. Intermolecular distance between C13 and neighboring C16<sup>iv</sup> atom is 5.332(5) Å. These packing parameters do not satisfy the Baughman's condition. Fig. 6 shows the crystal packing structure of **2**. The one-dimensional columnar stacks fill in the crystal space capably. The intercolumnar interactions are not recognized except for the hydrogen-bondings.

The following is the difference in the molecular structures and crystal packings between **1** and **2**. The differences in the structures are recognized at around the N1 and the O1 atoms. Although the environment around the N1 atom is planar in both compounds, the dihedral angles of the N1/C1/C7/C13 planes with the two phenyl rings are significantly different. The perpendicular orientation of two phenyl rings in **1** is thought to be suitable for crystal packing judged by the rather high density.

The significant difference is also observed at the bond distance of O1-C17, where the distances of **1** and **2** are 1.419(3)Å and 1.446(4)Å, respectively. The geometry of the intermolecular hydrogen-bonding and the stacking parameters showed a significant difference. These differences are well explained by considering the bulkyness of methyl groups. A large stacking intervals and weak hydrogen-bonding of **2** suggest that the methyl groups prevent the tight stacking and the close contact between the hydrogen bonded oxygen atoms.

#### 3.3. Geometry optimization

The optimized molecular structures of **1**, **2** with their numbering schemes are shown in Fig. 7 in accordance with the atom numbering given in Figs. 1 and 4. The optimized structural parameters of **1** and **2** calculated using B3LYP functional with 6-311 G (d, p) basis set are listed and compared with the experimental ones in Table 2. In the case of **2**, the DFT calculation reproduced the crystal structure well except for C4–C5 bond and the diacetylene moiety. In the case of **1**, however, a significant difference was recognized at the dihedral angles around the N1/C1/C7/C13 plane in addition to the exceptions observed at **2**. Although we do not have any clear answers concerning shrinkage of C4–C5 bond, the difference in the remaining parts is thought to originate in the crystal packing.

Diacetylene moieties are known to bend easily by the effect of the crystal packing. This may be the reason that the calculation underestimated the C14–C15 bond lengths. The difference in the environment around the nitrogen atom is considered to be affected by the unusual structure of the diphenylamino group which is aforementioned in the crystal structure.

#### 4. Conclusions

We have succeeded in preparations and crystallographical analyses of the novel diacetylene compounds, **1** and **2**, where the molecules incorporate an ynamine moiety. The crystal structures of both compounds were interpreted to be controlled mainly by the intermolecular hydrogen-bondings. The difference in crystal structures between **1** and **2** was well explained by consideration of the steric repulsion with methyl groups connected to the carbon atom adjacent to the hydroxyl group. The unusual structure of the diphenylamino group in **1** was also interpreted as the effect of crystal packing. The steric effects of the methyl groups on intra and intercolumnar interaction should be important for designing molecular and crystal structures of diacetylene molecules. The DFT calculations could reproduce the crystal structures except for the parts which were easily affected by the crystal packing.

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## Appendix A. Supplementary material

The supplementary crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallography Data Centre, 12 Union road, Cambridge CB22 1EZ, UK (Fax: +44 1223 336 033); E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) and are available free of charge on request quoting the deposition number CCDC 871688 and CCDC 871689 for **1** and **2**, respectively. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012.07.003.

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