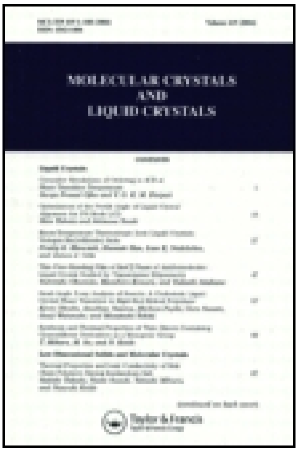

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Crystal Structure and Solid State Reactivity of Unsymmetrically Aryl-Substituted Diacetylene

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Novel unsymmetrically aryl-substituted diacetylene derivative (**1**), 4′-(5″-hydroxy-1″,3″-pentadiynyl)benzylidene-*p*-anisidine, was prepared. Reactivity of polymerization of **1** in the solid state was discussed based on its crystal structure revealed by an X-ray diffraction method.

INTRODUCTION

Growing interest in physical properties of polydiacetylenes, such as nonlinear optics,[1] magnetism,[2] conductivity[3] etc., prompts us to prepare unsymmetrically aryl-substituted polydiacetylenes, because nonlinear optical susceptibility should be enhanced by introducing an aryl group attached directly to the acetylenic moiety.[4] Unsymmetrical (head-to-tail) substitution pattern in polydiacetylenes is also crucial in realizing a high spin ground state based on a topochemical requirement of spin correlation in a conjugated π-system.[2] Such polydiacetylenes ought to be obtainable by "head-to-tail" 1,4-addition of the corresponding unsymmetrical monomer, if favorable molecular arrangement of monomers is realized in crystals. Successful examples, however, are very limited even on aryl substituted symmetrical diacetylene derivatives,[5] excepting some specific cases where the desirable stacking is achieved by the aid of such substituents as trifluoromethyl or amide groups. Aiming to solve the problem more generally, we have prepared aryl diacetylene derivatives **1**, where an aryl group is incorporated in a benzylideneaniline moiety as a mesogenic core.[6] Because mesogenic groups are supposed to stack in the same direction due to intermolecular forces, the resulting molecular packing in crystals may induce monomers to react in a head-to-tail, 1,4-addition manner. In the present paper, we discuss reactivity in polymerization of diacetylene **1** based on its crystal structure revealed by an X-ray diffraction method and propose one of the methodologies to prepare unsymmetrical polydiacetylenes from the aspect of crystal engineering.

EXPERIMENTAL PART

Preparation of Diacetylene 1

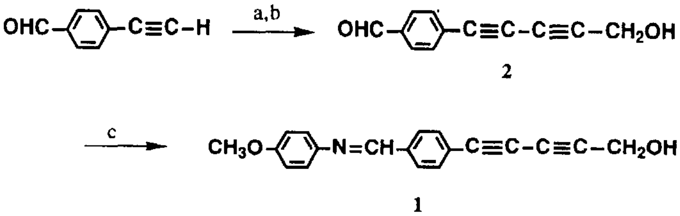
The preparation of diacetylene **1** was shown in Scheme 1.[7] To a solution of 34 mg of CuCl and 170 mg of $NH_2OH \cdot HCl$ in 40 ml of $EtNH_2aq$ (30%) was slowly added 4.28 g of powdered 4-ethynyl benzaldehyde[8] at 0°C. After a mixture was stirred for 30 min at 0°C, a solution of 5.35 g of 3-bromopropargyl alcohol in 10 ml of methanol was added dropwise to the reaction pot at 0°C. After the mixture was stirred for 20 hours, the solution was poured into water and extracted by dichloromethane. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under a reduced pressure. The residue was dissolved in 300 ml of ethanol and 50 ml of 1N HCl was added. The solution was refluxed for 3 hours. After removal of ethanol, precipitates were extracted by dichloromethane, washed with water, dried over $MgSO_4$, concentrated under a reduced pressure. The residue was recrystallized from benzene to give yellow powders of 4-(5′-hydroxy-1′,3′-pentadiynyl)benzaldehyde(**2**) in 52% yield. A 100 ml solution of 720 mg of **2** and 500 mg of p-anisidine in chloroform was stirred for 24 hours at room temperature in the presence of molecular sieves (3A). After filtering the solution, the solvent was removed under a reduced pressure. The residue was recrystallized from chloroform to give yellow powders of 4′-(5″-hydroxy-1″,3″-pentadiynyl)benzylidene-*p*-anisidine (**1**) in 50% yield. ^1H NMR ($CDCl_3$) δ = 3.84 (3H, s, $—OCH_3$), 4.44 (2H, s, $—C{\equiv}C—CH_2$), 6.94, 7.25 (4H, d, ArH, J = 8.8 Hz), 7.58, 7.85 (4H, d, ArH, J = 8.4 Hz), 8.50 (1H, s, —CH = N—); IR (KBr): 1620.5 ($\nu_{C=N}$), 2233.9 ($\nu_{C\equiv C}$), 3145.6 (ν_{OH}) cm^{-1}; Found: C, 78.64; H, 5.30; N, 5.11%, Calcd; C, 78.87; H, 5.26; N, 4.84%.

Instrumental and Measurements

^1H NMR and solid state ^{13}C NMR were measured on a JEOL GSH-270 spectrometer. UV/Vis and IR spectra were recorded on a Shimadzu UV-3101PC and Perkin Elmer FT-IR 1640 spectrometer, respectively. Photolysis was performed on a compaction sample diluted with KBr by using a high pressure mercury lamp through a pyrex filter.

X-ray Crystal Structure Analysis of Diacetylene 1

Monomer crystal was grown by slow evaporation from a solution of methanol. X-ray intensity data were collected on a Rigaku AFC-5 four-circle diffractometer at



SCHEME 1 (a) $Br\text{-}C{\equiv}C—CH_2OH/CuCl$, $NH_2OH \cdot HCl/EtNH_2aq$, (b) 1N HCl/EtOH, and (c) *p*-anisidine/$CHCl_3$

room temperature using graphite-monochromatized Mo Kα radiation. A total of 4036 reflections were collected (h, k, $\pm$ l) in the range of 3° $< 2\theta <$ 50°, 2330 reflections having $|F_0| \geqq 3\sigma(F_0)$ were used for analysis. Structure was solved by direct methods using *SAPI 85*, block diagonal least-squares refinement (*UNICS III*). The positions of the H atoms were obtained from a ΔF map. Anisotropic thermal parameters were introduced for all non-H atoms. H atoms were not refined. Space group was $P2_1$ with a = 22.190(4), b = 14.187(1), c = 4.797(1)Å, β = 92.81(1)°, V = 15.09.4(4)Å^3, Z = 4, FW = 289.33, d_{obs} = 1.25, d_{calcd} = 1.28, final R = 0.056.

RESULTS AND DISCUSSION

Crystal Structure of Diacetylene 1

The positional and thermal parameters are listed in Table I. The crystal structure of the diacetylene **1** with the space group of $P2_1$ is characterized as follows (Figure 1). Two independent molecules in the unit cell are related by a pseudo inversion symmetry. Chirality of the molecule is derived from axial asymmetry of twisted benzene rings in the benzylideneaniline moiety. A dihedral angle of two phenyl rings is about 30°. The hydoxyl and methoxyl groups are situated in an *anti* orientation with respect to the long molecular axis. Two independent monomers are hydrogen-bonded between the hydroxyl group and the imino nitrogen at two sites (C=N . . . HO) each other: intermolecular distance (2.84 Å) between the hydrogen-bonded oxygen and nitrogen atoms is the same in both sites. Diacetylene **1** stacks in a column with an interval of 4.80 Å along the c axis, and the molecular axis is inclined to the stacking axis by 54°, the mesogenic cores being located in the same direction. The distance between potentially reacting carbons C(2) and C(5′) is 3.96 Å within the stack. According to Baughman's criterion,[9] these packing parameters are favorable to 1,4-addition. This characteristic crystal structure is thought to be realized by an electronic effect of the mesogenic group. The hydroxymethyl group, which is bent against the long axis of the rod like molecule, also plays a role to prevent the molecule from slipping along this direction.[10]

Polymerization of Diacetylene 1

When the dispersed sample in a KBr pellet was irradiated at room temperature by a high pressure mercury lamp through a pyrex filter, the color of the sample changed from yellow to greenish blue. UV spectra of diacetylene monomer **1** and the photopolymerized sample are shown in Figure 2. In the spectrum of the polymer, a broad absorption band which can be assigned to an excitonic transition is observed with a maximum at 630 nm. Thus the polymer may be classified to have a "blue phase" of polydiacetylene. The observation of the exciton band suggests that the structure of the obtained polymer has a reasonable regularity along the extended π skeleton.[11] The conversion of the monomer became saturated at the limit of 20% determined by the decrease of an intensity of the $\nu_{C\equiv C}$ band. The low conversion may be derived from insufficient photolysis caused by a filtering effect of the product formed on the surface of crystals.

TABLE I

Atomic coordinates and equivalent anisotropic thermal parameters for diacetylene **1**; $B_{eq} = (4/3)\ \Sigma\ \beta_{ij}a_ia_j$

Atom	x	y	z	Beq(Å^2)
O(1)	0.0342(2)	0.1158(2)	0.5829(9)	5.2(1)
C(1)	0.0829(3)	0.0894(4)	0.7548(11)	5.3(2)
C(2)	0.1400(2)	0.0850(4)	0.6142(11)	4.4(1)
C(3)	0.1834(2)	0.0824(4)	0.4779(11)	4.3(1)
C(4)	0.2350(2)	0.0831(4)	0.3203(11)	4.4(1)
C(5)	0.2772(2)	0.0806(4)	0.1727(11)	4.6(1)
C(6)	0.3268(2)	0.0880(4)	-0.0028(11)	4.5(1)
C(7)	0.3623(2)	0.0088(4)	-0.0570(12)	4.8(2)
C(8)	0.4106(2)	0.0169(3)	-0.2200(12)	4.3(1)
C(9)	0.4208(2)	0.1005(3)	-0.3706(10)	3.8(1)
C(10)	0.3859(2)	0.1780(3)	-0.3169(12)	4.8(1)
C(11)	0.3411(2)	0.1727(3)	-0.1271(12)	4.6(1)
C(12)	0.4707(2)	0.1079(3)	-0.5558(11)	4.0(1)
N(1)	0.4881(2)	0.1818(3)	-0.6664(8)	4.1(1)
C(13)	0.5407(2)	0.1822(3)	-0.8271(9)	3.8(1)
C(14)	0.5464(2)	0.2508(4)	-1.0260(10)	4.0(1)
C(15)	0.5969(3)	0.2580(4)	-1.1792(10)	4.8(1)
C(16)	0.6440(3)	0.1954(4)	-1.1289(11)	5.0(2)
C(17)	0.6412(2)	0.1233(4)	-0.9237(11)	4.5(1)
C(18)	0.5904(2)	0.1212(3)	-0.7744(10)	3.9(1)
O(2)	0.6948(2)	0.2060(3)	-1.2892(8)	5.4(1)
C(19)	0.7437(2)	0.1446(4)	-1.2409(14)	6.0(2)
O(3)	0.4661(2)	0.3764(3)	-0.5760(8)	5.5(1)
C(20)	0.4157(3)	0.4015(4)	-0.7603(13)	5.6(2)
C(21)	0.3593(3)	0.4054(4)	-0.6091(12)	5.2(2)
C(22)	0.3147(3)	0.4081(4)	-0.4801(12)	5.0(2)
C(23)	0.2660(2)	0.4119(4)	-0.3170(12)	4.8(1)
C(24)	0.2242(2)	0.4107(4)	-0.1751(11)	4.8(1)
C(25)	0.1739(2)	0.4072(4)	0.0106(11)	4.2(1)
C(26)	0.1385(3)	0.4844(4)	0.0609(12)	5.1(2)
C(27)	0.0935(2)	0.4786(4)	0.2569(11)	4.6(1)
C(28)	0.0794(2)	0.3911(4)	0.3691(11)	4.4(1)
C(29)	0.1161(3)	0.3130(4)	0.3109(12)	5.3(2)
C(30)	0.1642(2)	0.3206(4)	0.1427(12)	5.1(2)
C(31)	0.0290(2)	0.3910(4)	0.5607(11)	4.5(1)
N(2)	0.0113(2)	0.3104(3)	0.6672(8)	4.1(1)
C(32)	-0.0409(2)	0.3121(4)	0.8275(10)	4.2(1)
C(33)	-0.0866(2)	0.3754(4)	0.7816(12)	5.0(2)
C(34)	-0.1398(2)	0.3665(4)	0.9320(11)	4.5(1)
C(35)	-0.1450(2)	0.2993(3)	1.1298(10)	4.0(1)
C(36)	-0.0975(2)	0.2366(4)	1.1823(11)	4.6(1)
C(37)	-0.0454(2)	0.2410(4)	1.0303(11)	4.8(1)
O(4)	-0.1932(2)	0.2850(3)	1.2830(8)	5.6(1)
C(38)	-0.2439(3)	0.3518(4)	1.2430(13)	5.7(2)

Diacetylene **1** turns out to have a nematic phase at temperature higher than 148°C, judged by DSC measurements and by direct observation under a microscope. The monomer **1** exhibits thermal reactivity as well both in the crystal and in the nematic phases. A pattern of 1,4-addition in the polymers is strongly suggested by solid state ^{13}C NMR (CP/MAS) spectra. Namely, resonance lines assignable to the backbone carbons of polydiacetylenes are observed at 115, 130 ppm[12] at the expense of signals of acetylenic carbons 71, 76, 79, 86 ppm of the monomer. The thermally formed polymers, however, does not shown an exciton band in UV spectra. These results may be interpreted that high regularity in the structure of polymers can not be maintained during thermal polymerization.[11]

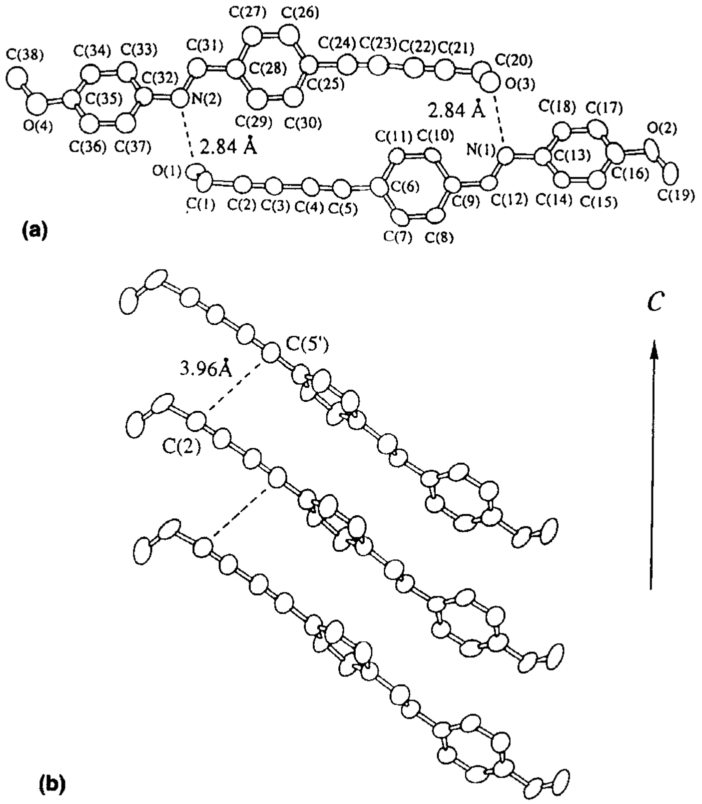


FIGURE 1 *ORTEP* drawing of diacetylene **1**: monoclinic, Space group is $P2_1$, $Z = 4$, (a) two independent molecules in the unit cell, and (b) projection along the *c* axis.

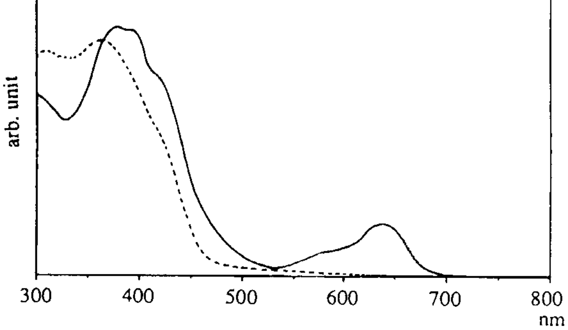


FIGURE 2 UV/Vis spectra of monomer **1** (dashed line) and the obtained polymer (solid line).

CONCLUSION

We prepared unsymmetrically aryl-substituted diacetylene **1**. The crystal structure of **1** was found to be favorable for polymerization and it showed photoreactivity to afford unsymmetrically aryl-substituted polydiacetylenes with a blue phase. Since the benzylideneaniline group could be removed by hydrolysis after the polymerization, a various substituents may be introduced to expand a variety of polydiacetylene derivatives.

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