

## 6-(2-pyridyl)-3,5-hexadiyn-1-ol의 용매 非依存 分子構造

徐日煥, 李珍昊, 朴晶欄, 徐政徹, 金順男, 李興宰, 沈相哲\*

忠南大學校 物理學科

\*韓國科學技術院, 化學科

## The Solvent-Independent Structure of 6-(2-pyridyl)-3,5-hexadiyn-1-ol

Il-Hwan Suh, Jin-Ho Lee Jeong-Ran Park, Min Chul Suh, Sun Nam Kim,  
Heung Jae Lee and Sang Chul Shim\*

Department of Physics, Chungnam National University

\*Department of Chemistry, Korea Advanced Institute of Science and Technology

### 요 약

上記題目的 化合物의 두가지 單結晶이 n-hexane/CH<sub>2</sub>Cl<sub>2</sub> 과 n-hexane/Et<sub>2</sub>O 의 溶媒에 依하여 얻어졌으며, 그들의 서로 다른 空間群에도 不拘하고 그들의 分子構造는 同一함이 밝혀졌다:

C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> (I), Mr=343.70, Monoclinic, Pa, a=14.595(2), b=5.413(2), c=12.218(2)Å, β=96.86(1)°, V=958.3 Å<sup>3</sup>, Z=2, Dx=1.19 Mgm<sup>-3</sup>, λ(MoK α)=0.71069 Å, μ=0.072 mm<sup>-1</sup>, F(000)=360.0, T=292K, 756 唯一한 反射強度에 對하여 R=0.104이다. 한 非對稱單位는 分子間的 二個의 N-H...O 水素結合으로 連結된 dimer이다.

C<sub>11</sub>H<sub>9</sub>NO (II), Mr=171.85, Monoclinic, P2<sub>1</sub>/a, a=14.611(2), b=5.423(6), c=12.191(2)Å, β=96.89(1)°, V=959.0 Å<sup>3</sup>, Z=4, Dx=1.19 Mgm<sup>-3</sup>, λ(MoK α)=0.71069 Å, μ=0.072 mm<sup>-1</sup>, F(000)=360.0, T=293K, 824 個의 唯一한 反射強度에 對하여 R=0.066이다. 한 分子가 非對稱單位를 이루고 있으며 對稱中心關係에 있는 二個의 N-H...O 水素結合이 dimer를 形成한다.

兩쪽 構造에서 共히 線形인 diyne chain 에 依하여 連結된 pyridyl 고리와 C(10)-C(11)-O가 만드는 平面間的 二面角은 垂直에 가까우며, 그 分子들은 b-軸을 反復週期로하여 b-軸을 따라 쌓여있다.

### Abstract

Two types of single crystals of the title compound [6-(2-pyridyl)-3, 5-hexadiyn-1-ol, PyHxD)] were obtained by solution of n-hexane/CH<sub>2</sub>Cl<sub>2</sub> and n-hexane/Et<sub>2</sub>O, and their molecular conformations are proved identical in spite of different space groups:

$C_{22}H_{18}N_2O_2$  (I),  $M_r=343.70$ , Monoclinic, Pa,  $a=14.595(2)$ ,  $b=5.413(2)$ ,  $c=12.218(2)$  Å,  $\beta=96.86(1)^\circ$ ,  $V=958.3$  Å<sup>3</sup>,  $Z=2$ ,  $D_x=1.19$  Mg m<sup>-3</sup>,  $\lambda$  (MoK  $\alpha$ )=0.71069 Å,  $\mu=0.072$  mm<sup>-1</sup>,  $F(000)=360.0$ ,  $T=292$  K,  $R=0.104$  for 756 unique observed reflections. An asymmetric unit contains a dimer connected by two N-H...O intermolecular hydrogen bonds.

$C_{11}H_9NO$  (II),  $M_r=171.85$ , Monoclinic,  $P2_1/a$ ,  $a=14.611(2)$ ,  $b=5.423(6)$ ,  $c=12.191(2)$  Å,  $\beta=96.89(1)^\circ$ ,  $V=959.0$  Å<sup>3</sup>,  $Z=4$ ,  $D_x=1.19$  Mg m<sup>-3</sup>,  $\lambda$  (MoK  $\alpha$ )=0.71069 Å,  $\mu=0.072$  mm<sup>-1</sup>,  $F(000)=360.0$ ,  $T=293$  K,  $R=0.066$  for 824 unique observed reflection. The structural asymmetric unit contains a molecule, but two N-H...O hydrogen bonds related by centrosymmetry make the molecules form a dimer.

In both structures, the dihedral angle between the planar pyridyl ring and the plane defined by C(10)-C(11)-O connected by linear diyne chain is approximately normal, and the molecules are stacked along b-axis with the unit repeat of b-axis.

## 1. Introduction

There is growing interest in polydiacetylenes (PDAs) from basic and applicational view points. These polymers are of particular interest because of their conducting and nonlinear optical properties.

Some diacetylenes (R-C≡C-C≡C-R') undergo solid-state polymerization reaction by heating, irradiation or mechanical stimulation. Not all diacetylenes, however, are reactive, only those diacetylenes polymerize which have suitable molecular packing condition.<sup>1,2,3</sup>

In order to investigate the reactivity of the diacetylene crystals in the polymerization reaction and to specify the conformation of molecules, the structures of two single crystals obtained from two different solvents, n-hexane/CH<sub>2</sub>Cl<sub>2</sub> and n-hexane/diethyl ether, have been elucidated by X-ray diffraction method.

## 2. Experimental

The crystallographic data of the two compounds (I) and (II) are listed in Table 1. Cell refinement, data collection and data reduction were done using SDP program<sup>4</sup>. The intensity variation during data collection

for the compound(I) was quite high because of the weak intensities of the three standard reflections.

The structures of both compounds were solved using SHELX86<sup>5</sup> and refined by full-matrix least squares with SHELX76<sup>6</sup>. The high final R value for the compound (I) is attributed to the poor quality of the crystal specimen. For the compound (I), x and z coordinates of oxygen atom were fixed because of the space group Pa of second setting and all H atom positions except for hydroxy group were calculated geometrically (C-H:1.08 Å), while all H atoms in the compound (II) were found from difference Fourier synthesis. All H-atoms were refined isotropically.

## 3. Discussion

Final atomic coordinates and equivalent isotropic temperature factors for (I) and (II) are given in Table 2. ORTEP<sup>7</sup> drawings of the molecular conformation with atomic labelling scheme are presented in Fig. 1(a) and Fig. 1(b), and Fig. 2(a) and Fig. 2(b) are the unit-cell packing diagrams, viewed down the c axis. Two independent molecules in the asymmetric unit of compound (I) are connected by two oxygen...nitrogen

Table 1. The comparison of crystallographic data of the two compounds (I) and (II).

	Compound (I)	Compound (II)
Crystal data	C <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>11</sub> H <sub>9</sub> NO
formula	n-hexane/CH <sub>2</sub> Cl <sub>2</sub>	n-hexane/Et <sub>2</sub> O
solvent	343.794	171.847
Mr	Monoclinic	Monoclinic
crystal system	Pa	P2 <sub>1</sub> /a
space group	14.595(2)	14.611(2)
a, Å	5.413(2)	5.423(2)
b, Å	12.218(2)	12.191(2)
c, Å	96.86(1)	96.89(1)
β, deg	2	4
Z	958.3	959.0
V, Å <sup>3</sup>	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
radiation		
cell parameter determination from	24 reflections	24 reflections
θ, °	8 → 13	11.38 → 14.11
μ, mm <sup>-1</sup>	0.072	0.072
dcalc, Mg m <sup>-3</sup>	1.19	1.19
temperature, K	288	293
crystal shape	needle	needle
colour	colourless	colourless
crystal size, mm	0.36×0.32×0.48	0.50×0.17×0.20
Data collection		
diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
data collection method	ω/2θ	ω/2θ
scan width	(0.8+0.34 tan θ)	(0.8+0.34 tan θ)
θ max, deg	23	23
h	0 → 16	0 → 16
k	0 → 6	0 → 6
l	-13 → 12	-13 → 13
No. of reflection measured	1702	1716
No. of ind. reflections	1681	1683
No. of observed reflections	756	733
criterion for observed reflections	Fo ≥ σ(Fo), n =	4
standard reflections	3	3
interval, minutes	180	120
intensity variation, %	7	1
L-P correction	applied	applied
decay correction	applied	none
absorption correction	none	none
Rint	none	none
Refinement		
Refinement on	F	F
ω	1/[σ <sup>2</sup> (Fo)+0.066017Fo <sup>2</sup> ]	1/[σ <sup>2</sup> (Fo)+0.000101Fo <sup>2</sup> ]
R	0.104	0.066
ωR	0.110	0.063
S	0.4608	2.7142
no. of parameter	249	154
(Δ/σ)max	0.72	0.03
Δρ max, e Å <sup>-3</sup>	0.30	0.287
Δρ min, e Å <sup>-3</sup>	-0.35	-0.23
Atomic scattering factor from	SHELX76(Sheldrix, 1975)	SHELX76(Sheldrix, 1975)

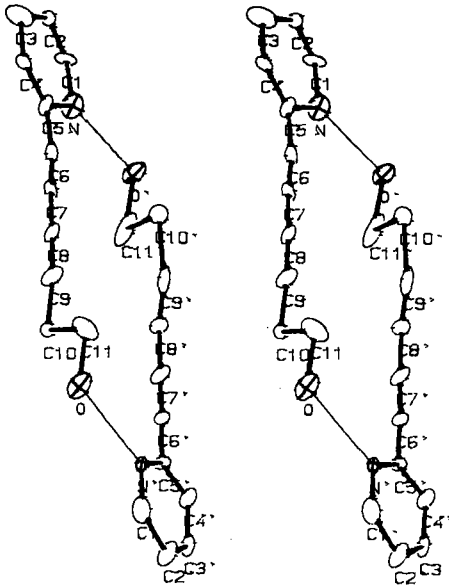


Fig. 1(a). A stereoview of a dimer with labelling scheme for the compound (I). The dimer is an asymmetric unit. Thin lines denote hydrogen bonds.

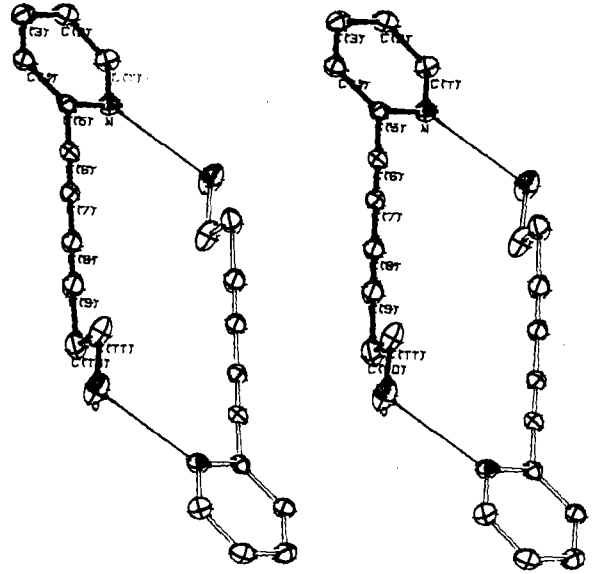


Fig. 1(b). A stereoview of a dimer with labelling scheme for the compound (II). The distances among the atoms in an asymmetric unit are shown in black. Thin lines denote hydrogen bonds.

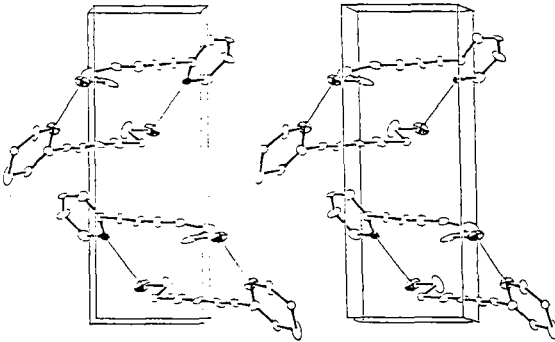


Fig. 2(a). A stereoview of the unit-cell packing for compound (I): origin, lower left; b-axis, horizontal; a-axis, vertical. H-atoms are omitted for clarity. Thin lines denote hydrogen bonds.

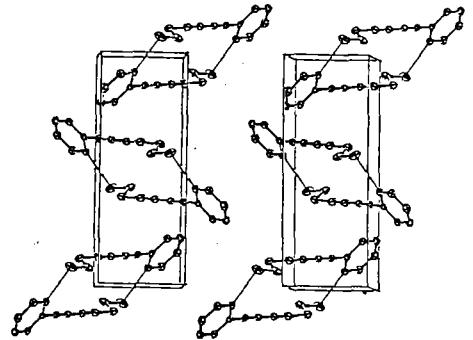


Fig. 2(b). A stereoview of the unit-cell packing for compound (II): origin, lower left; b-axis, horizontal; a-axis, vertical. H-atoms are omitted for clarity. Thin lines denote hydrogen bonds.

hydrogen bonds. Their intermolecular hydrogen-bond lengths are  $O\dots N'=2.91(2)$  and  $O'-N=2.63(3)$  Å. In compound (II), the molecules are observed as

hydrogen-bonded dimer with  $O\dots N$  (related by  $1-x, -1-y, 1-z$ ) [ $2.807(6)$  Å] with  $O-H$  [ $0.90(8)$  Å],  $H\dots N$  [ $1.952(8)$  Å] and  $\angle O-N\dots H$  angle [ $157(7)^\circ$ ]. As shown in Figs.

Table 2. Final atomic fractional coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors with e.s.d.'s in parentheses for (I) and (II).

$$U_{eq} = \frac{1}{3} \left[ U_{22} + \frac{1}{\sin^2 \beta} (U_{11} + U_{33} + 2U_{13} \cos \beta) \right]$$

Compound (I)	x	y	z	$U_{eq}(\text{\AA}^2)$
N	1102(18)	3602(42)	1663(20)	0.100(9)
C(1)	919(20)	5217(36)	732(20)	0.080(8)
C(2)	387(18)	6992(29)	594(19)	0.059(6)
C(3)	-348(27)	7484(44)	1371(23)	0.154(15)
C(4)	-269(19)	5803(36)	2195(18)	0.064(7)
C(5)	370(19)	3899(32)	2405(24)	0.082(8)
C(6)	508(18)	2389(45)	3309(19)	0.068(7)
C(7)	541(17)	1040(33)	4009(19)	0.054(6)
C(8)	609(16)	-625(51)	4682(23)	0.078(9)
C(9)	664(20)	-2276(50)	5493(23)	0.098(10)
C(10)	712(17)	-4532(34)	6248(18)	0.059(6)
C(11)	1125(22)	-3456(49)	7372(23)	0.103(12)
O	1192(0)	-5422(45)	8186(0)	0.117(9)
N'	2755(14)	-8795(30)	8448(19)	0.068(6)
C(1')	2830(20)	-10433(59)	9268(23)	0.101(11)
C(2')	3545(21)	-12280(50)	9458(29)	0.118(11)
C(3')	4074(15)	-12443(45)	8674(25)	0.082(9)
C(4')	3998(28)	-10804(60)	7764(25)	0.115(13)
C(5')	3333(18)	-9186(44)	7681(19)	0.066(7)
C(6')	3277(21)	-7459(41)	6807(33)	0.111(11)
C(7')	3213(19)	-5861(63)	6163(40)	0.130(15)
C(8')	3136(20)	-4060(40)	5148(23)	0.083(9)
C(9')	3107(22)	-2193(45)	4573(26)	0.104(11)
C(10')	2922(26)	-26(83)	3814(47)	0.247(34)
C(11')	2571(20)	-1147(94)	2706(26)	0.221(23)
O'	2630(13)	997(44)	1932(15)	0.124(10)

Compound (II)	x	y	z	$U_{eq}(\text{\AA}^2)$
N	4157(3)	1207(7)	1614(3)	0.071(2)
C(1)	4083(5)	2737(12)	758(5)	0.083(3)
C(2)	3437(5)	4575(13)	592(6)	0.090(3)
C(3)	2829(5)	4870(12)	1341(5)	0.088(3)
C(4)	2883(4)	3320(11)	2226(5)	0.074(2)
C(5)	3549(3)	1529(9)	2347(4)	0.064(2)
C(6)	3629(3)	-157(9)	3262(4)	0.067(2)
C(7)	3678(3)	-1591(10)	3991(4)	0.070(2)
C(8)	3744(3)	-3337(11)	4796(4)	0.082(2)
C(9)	3793(3)	-4890(13)	5448(5)	0.099(3)
C(10)	3873(6)	-7073(16)	6253(6)	0.109(4)
C(11)	4294(6)	-6120(17)	7308(6)	0.116(4)
O	4275(3)	-8174(10)	8124(3)	0.127(2)

Table 3. Bond length and angles with e.s.d.'s in parentheses for the compounds.

	1) Bond lengths (Å)		
	unprimed molecule(I)	primed molecule(I)	molecule(II)
N-C(1)	1.434(24)	1.332(31)	1.327(6)
N-C(5)	1.490(29)	1.351(24)	1.345(5)
C(1)-C(2)	1.234(26)	1.443(32)	1.371(7)
C(2)-C(3)	1.538(35)	1.303(34)	1.357(7)
C(3)-C(4)	1.352(28)	1.417(36)	1.363(7)
C(4)-C(5)	1.393(24)	1.303(35)	1.370(6)
C(5)-C(6)	1.369(29)	1.414(33)	1.436(6)
C(6)-C(7)	1.121(25)	1.165(48)	1.177(6)
C(7)-C(8)	1.216(29)	1.571(49)	1.359(8)
C(8)-C(9)	1.330(29)	1.229(31)	1.154(7)
C(9)-C(10)	1.527(24)	1.500(1)	1.533(9)
C(10)-C(11)	1.547(27)	1.516(62)	1.454(8)
O-C(11)	1.451(31)	1.506(47)	1.495(10)
	2) Bond angles (°)		
	unprimed molecule(I)	primed molecule(I)	molecule(II)
C(1)-N-C(5)	109.8(18)	114.5(16)	116.3(5)
N-C(1)-C(2)	129.6(19)	125.2(20)	124.1(6)
C(1)-C(2)-C(3)	121.6(16)	114.2(26)	118.7(6)
C(2)-C(3)-C(4)	109.9(20)	122.4(23)	118.7(7)
C(3)-C(4)-C(5)	129.1(22)	118.0(27)	119.7(6)
N-C(5)-C(4)	118.7(20)	125.0(19)	122.6(5)
N-C(5)-C(6)	112.3(17)	115.9(20)	115.7(5)
C(4)-C(5)-C(6)	128.4(23)	118.6(23)	121.7(5)
C(5)-C(6)-C(7)	173.1(18)	173.2(33)	177.9(5)
C(6)-C(7)-C(8)	172.4(21)	170.4(28)	177.1(5)
C(7)-C(8)-C(9)	174.2(24)	163.0(23)	177.3(6)
C(8)-C(9)-C(10)	169.1(25)	171.3(25)	176.1(7)
C(9)-C(10)-C(11)	102.7(17)	104.8(37)	106.5(7)
O-C(11)-C(10)	108.7(18)	102.3(35)	106.5(7)
	3) Torsion angles		
	unprimed molecule(I)	primed molecule(I)	molecule(II)
C(1)-N-C(1)-C(2)	14.8(26)	9.1(27)	0.1(6)
C(1)-N-C(5)-C(4)	-8.5(22)	-8.4(29)	0.3(5)
C(1)-N-C(5)-C(6)	179.8(30)	-179.3(34)	179.3(7)
N-C(1)-C(2)-C(3)	-12.5(25)	-7.8(27)	-0.1(6)
C(1)-C(2)-C(3)-C(4)	2.9(25)	5.0(28)	-0.3(6)
C(2)-C(3)-C(4)-C(5)	1.9(24)	-4.6(30)	0.7(6)
C(3)-C(4)-C(5)-N	1.5(26)	6.2(25)	-0.7(5)
C(3)-C(4)-C(5)-C(6)	171.8(46)	176.9(44)	-179.6(8)
N-C(5)-C(6)-C(7)	-116(10)	35(10)	-84(10)
C(4)-C(5)-C(6)-C(7)	73(10)	-137(10)	95(10)
C(5)-C(6)-C(7)-C(8)	76(10)	-172(10)	45(10)
C(6)-C(7)-C(8)-C(9)	175(10)	-170(10)	-22(10)
C(7)-C(8)-C(9)-C(10)	164(10)	-116(10)	23(10)
C(8)-C(9)-C(10)-C(11)	162(10)	-54(10)	143(10)
C(9)-C(10)-C(11)-O	178.8(25)	-166.1(38)	173.7(6)

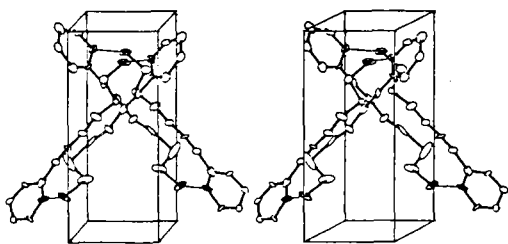


Fig. 3(a). A stereoview of a unit cell packing for (I). Origin, lower left ; b-axis, horizontal; c-axis, vertical. Thin lines denote hydrogen bonds.

1(a) and 1(b), the molecular conformations of (I) and (II) are identical from a statistical viewpoint, and the lower R factor of 0.066 in the compound (II) may indicate a high reliability in its geometric parameters. Therefore the further discussion was conducted only on the compound (II).

The bond lengths, angles and torsion angles of (II) are listed in Table 3. The bond distances in the linear diacetylene chain  $C(7)-C(8) = 1.359(8)$ ,  $C(6)=C(7) = 1.177(6)$  and  $C(8)=C(9) = 1.154(7)$  Å are compared with the respective values 1.39(3) and 1.18(3) Å reported for 1,4-diphenyl-1,3-butadiyne<sup>8</sup>) and 1.369(4) and 1.192(7) Å for 1,4-Bis(3-quinolyl)-1,3-butadiyne<sup>9</sup>). The  $C(6)=C(7)-C(8)$  bond is almost linear [ $C(6)-C(7)-C(8) = 177.1(5)^\circ$ ]. The angle of  $C(8)-C(9)-C(10)$  is  $176.1(7)^\circ$  and the torsion angle of  $C(9)-C(10)-C(11)-O$  is  $173.7(6)^\circ$ , so that the diacetylene chain linking pyridyl ring and C(10), C(11), O group has also nearly linear form. The pyridyl ring is planar, with a maximum deviation of  $-0.004(4)$  Å, and observed bond distances, from  $N-C(1) = 1.327(6)$  to  $C(1)-C(2) = 1.371(7)$  Å, are in agreement with those of 1,4-Bis(3-pyridyl)-1,3-butadiyne<sup>10</sup>). The atoms C(10) and C(11) deviate by  $-0.56(2)$  and  $0.69(2)$  Å, respectively, from the best plane of pyridyl. The pyridyl ring is

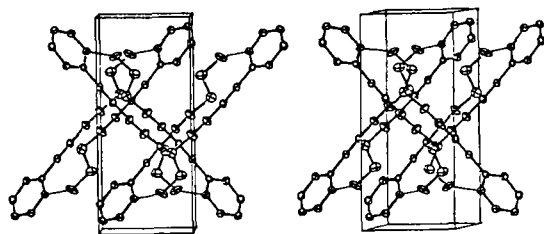


Fig. 3(b). A stereoview of a unit cell packing for (II). Origin, lower left ; b-axis, horizontal; c-axis, vertical. Thin lines denote hydrogen bonds.

approximately perpendicular to the plane defined by  $C(10)-C(11)-O$ , forming dihedral angle of  $77.0(7)^\circ$ . The angles of  $C(9)-C(10)-C(11) = 106.5(7)^\circ$  and  $O-C(11)-C(10) = 106.5(7)^\circ$  are very close to the tetrahedral angle.

Fig. 3 represents the stereopacking of the molecules, viewed down the a-axis. In the packing, hydrogen bonds hinder specific rotation which is necessary for polymerization. As shown in Fig. 3, the dimers are stacked along b-axis with a repeat distances 5.423 Å. The diacetylene chains of a dimer are aligned making an angle ca.  $45^\circ$  with (010) and the ones of the neighbouring dimer the same angle with (001). Therefore in the projection along a-axis, the diyne chains of the hydrogen-bonded dimers are perpendicular to each other. The nearest interdimer distance of  $3.294(7)$  Å between O and C(1) [ $x, 1+y, -1+z$ ] confirms that only van der Waals interactions are present between the hydrogen-bonded dimers.

In conclusion, the monomer structure of the (II), although the space group was different, was identical with the one of (I) suggesting that both of crystals cannot be polymerized in the solid state and the crystal structure might be the most stable structure of PyHxD.

But, because of its packing condition as shown in Fig. 2, it is possible to polymerize if the hydrogen bond between pyridyl N atom and hydroxyl H atom is broken during polymerization.

10. K. Swaminathan, U. C. Sinha, M. B. Kamath, S. S. Talwar & R. Bohra, (1989). *Acta Cryst.* C45, 504-506.

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### References

1. R. H. Baughman, (1974). *J. Polym. Sci.* 12, 1511-1535.
2. G. Wegner, (1977). *Chemistry and Physics of One Dimensional Metals*, edited by H. J. Keller, pp. 297-314. New York: Plenum.
3. D. Bloor. (1982). *Developments in Crystalline Polymers*, Vol. 1, edited by D. C. Bassett, p. 151. London: Applied Science Publishers.
4. Enraf-Nonius, Structure Determination Package, Enraf-Nonius, delft, The Netherlands (1985).
5. Sheldrick G. M. SHELX86, Program for Crystal Structure Determination. Univ. of Cambridge, England. (1986).
6. Sheldrick G. M. SHELX76, Program for Crystal Structure Determination. Univ. of Cambridge, England. (1976).
7. Johnson, C. K. ORTEP. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA. (1965).
8. E. H. Wiebenga, (1940). *Z. Kristallogr.* 102, 193-206.
9. K. Das, U. C. Sinha, S. S. Talwar, M. B. Kamath & R. Bohra, (1990). *Acta Cryst.* C46, 2126-2128.