15. Syntheses and X-Ray Structures for Model Compounds of a Pyrimidinediyl-Based Rigid-Rod Aromatic Polyamide

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(17.X.91)

A variety of model compounds for the pyrimidinediyl-based rigid-rod polyamide poly[imino-(pyrimidine-2,5-diyl)-imino-tetraphthaloyl] (PPYMT) was prepared, in order to compare their conformations to several model compounds of the related, fully aromatic polymer poly(p-phenyleneterephthalamide) (PPTA). In particular, the structures of N-(2-pyrimidyl)benzamide (PYMB) and its complexed form bis[N-(pyrimidin-2-yl)benzamide]nickel(II) dichloride (NiPYMB) were determined by X-ray diffraction. The molecular packing in these crystals provides us with a model for the possible 'cross-linking' of PPYMT fibers. The structures of the trimer model compounds N,N'-bis(2-pyrimidyl)terephthalamide (PYTA) and N,N'-bis(benzoyl)-2,5-diaminopyrimidine (BDAP) yield information about the conformation of PPYMT chains and are compared to analogous model compounds of PPTA.

Introduction. – Fully aromatic, fiber-forming rigid-rod polyamides with their outstanding mechanical properties (*i.e.* high tensile modulus and tensile strength) and their excellent thermal and chemical resistance were widely investigated [1–5]. Poly-(p-phenyleneterephthalamide) (= poly[iminocarbonyl(phen-1,4-ylene)carbonylimino-(phen-1,4-ylene)]; PPTA; 1), in particular, found wide-spread use in various applications. We synthesized [6] the analogous poly[imino(pyrimidine-2,5-diyl)iminoterephthaloyl] (= poly[(pyrimidin-2,5-diyl)iminocarbonyl(phen-1,4-ylene)carbonylimino] PPYMT; 2) in order to investigate the influence of intermolecular interactions on the properties of polymers of type **1**. The difference in molecular constitution between **1** and **2** does not significantly change the geometry of the polymer chains, and a preliminary investigation of fiber packing indicates that similarities between the two do exist [7]. The pyrimidine rings in the polymer may be seen as functional groups for complexation of the polymer with transition-metal cations such as Fe^{2+}, Co^{2+}, Cu^{2+}, or Ni^{2+}. Complexation of the polymer can thus be used to 'cross-link' polymer chains aligned in a parallel fashion and might lead to fibers with changed mechanical properties.

　　Information about the conformation of the polymer in the solid state is not easy to obtain [7]. Thus, we synthesized small model compounds which correspond to dimer and trimer segments of **2**. The N-(pyrimidin-2-yl)benzamide (**3**) and its complexed form bis[N-(pyrimidin-2-yl)benzamide]nickel(II) dichloride (**4**) were prepared and crystallized for X-ray diffraction. The trimer model compounds N,N'-bis(pyrimidin-2-yl)benzene-1,4-dicarboxamide (**5**) and its nonsymmetric analogue N,N'-(pyrimidine-2,5-diyl)bis-[benzamide] (**6**) were also prepared and crystallized, but the metallated forms could not

1 (PPTA)

2 (PPYMT)

3

4

5   6
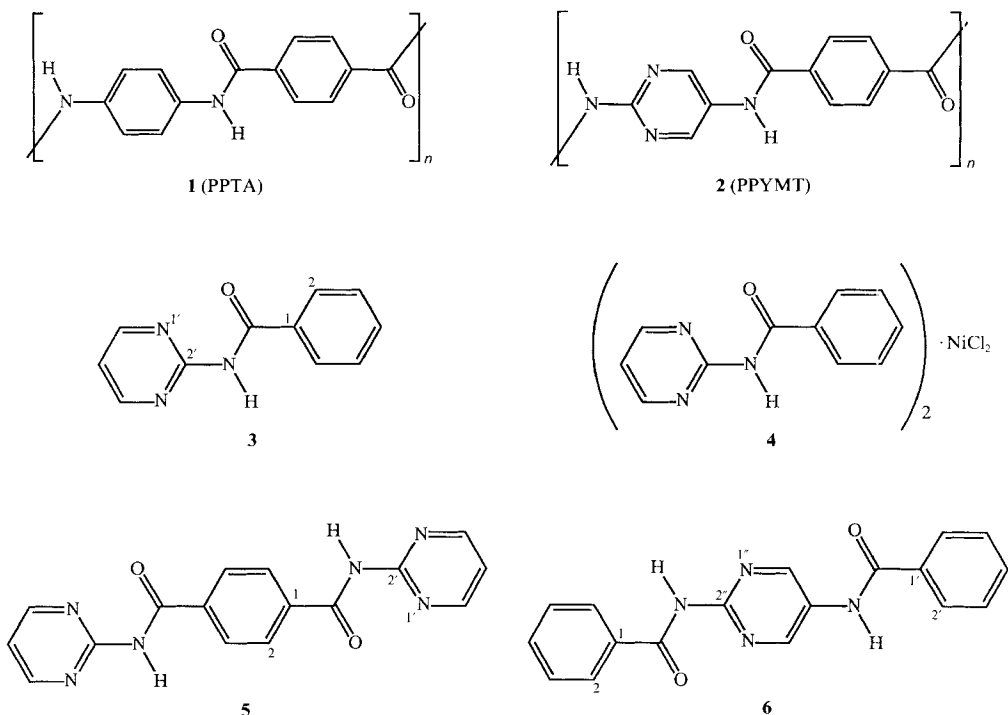
be obtained as single crystals suitable for X-ray analysis, probably due to the formation of insoluble networks of complexed trimers.

The unmetallated forms **3**, **5**, and **6** yield information about the conformation and packing of polymer chains **2**, *i.e.* dihedral and torsion angles; the metallated form of **3** serves as a model of complexation and presumably cross-linking of molecular chains in polymer fibers.

Results and Discussion. – The model compounds **3**, **5**, and **6** for the new, fully aromatic, 'cross-linkable' polyamide **2** were readily prepared and crystals suitable for X-ray diffraction obtained. Metallation of these compounds was also possible, but only **3** formed a well-defined 2:1 complex, while **5** and **6** yielded crude products of varying
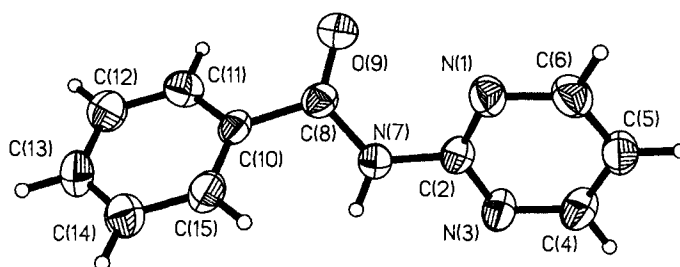

Fig. 1. *Molecular structure of* **3**. Arbitrary numbering scheme; thermal ellipsoids at the 50% level.
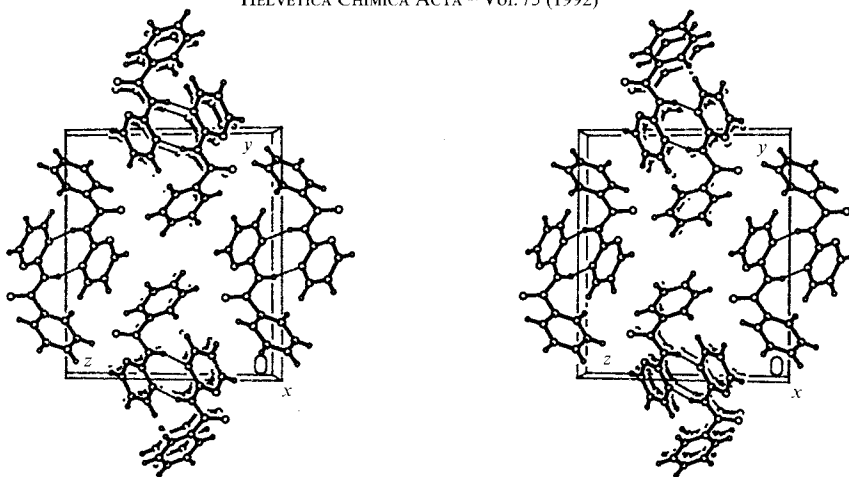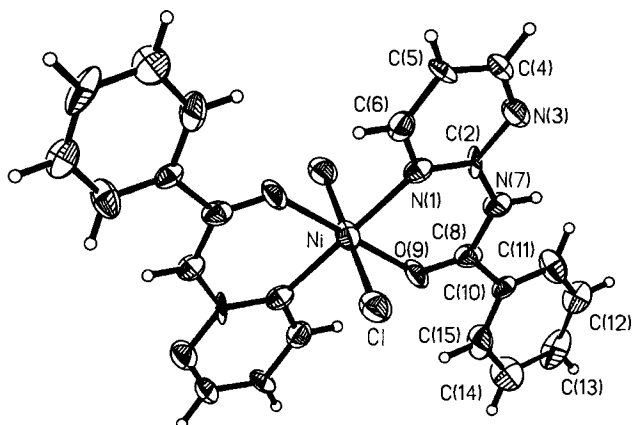
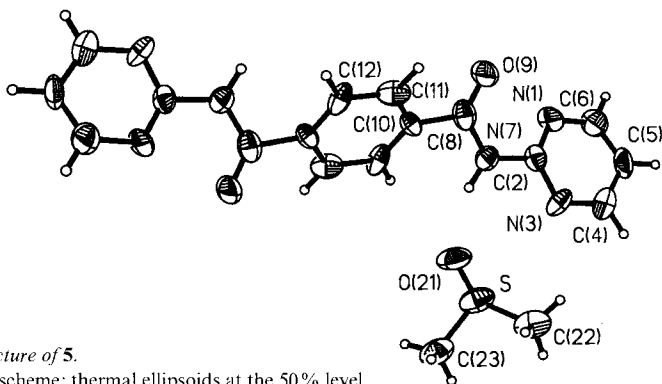Fig. 2. *Stereoview of the packing diagram of* **3**

Fig. 3. *Molecular structure of* **4**. Arbitrary numbering scheme; thermal ellipsoids at the 50% level.

Fig. 4. *Molecular structure of* **5**.
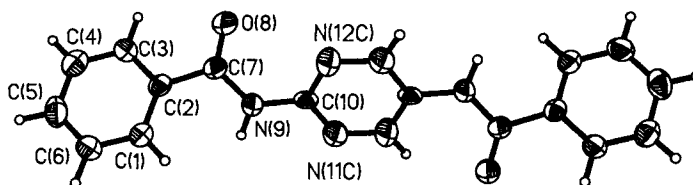Arbitrary numbering scheme; thermal ellipsoids at the 50% level.

Fig. 5. *Molecular structure of* **6**. Arbitrary numbering scheme; thermal ellipsoids at the 50% level. The letter C at N(11C) and N(12C) indicates a disordered arrangement of the molecule with respect to the center of inversion in the middle of the pyrimidine ring.

composition. Products were characterized by melting points, IR and UV spectra, elemental analysis, and ^{1}H-NMR and ^{13}C-NMR spectroscopy. All resonances could be assigned. Due to the paramagnetic character of the Ni^{II} complex **4**, its ^{1}H-NMR spectra show dramatic broadening of the signals.

Figs. 1, 4, and *5* display molecular conformations in the crystal of **3**, **5**, and **6**, *Fig. 3* depicts the Ni^{II} complex **4**, and *Fig. 2* shows a packing diagram for **3**. Some results of the X-ray diffraction analysis are collected in *Table 1*. Interplanar angles between the amide groups and the pyrimidinyl and phenylene rings are given in *Table 2*.

Table 1. *X-Ray Experimental Parameters for* **3–6**

	3	**4**	**5**	**6**
Formula	$C_{11}H_9N_3O$	$C_{22}H_{18}Cl_2N_6NiO_2$	$C_{16}H_{12}N_6O_2 \cdot (CH_3)_2SO$	$C_{18}H_{14}N_4O_2$
a [Å]	5.325(4)	7.265(2)	10.356(9)	22.57(2)
b [Å]	14.666(9)	8.273(2)	8.676(7)	5.303(3)
c [Å]	12.735(11)	9.844(2)	13.037(9)	12.613(9)
α [°]	90	81.09(2)	90	90
β [°]	101.15(7)	78.67(2)	95.28(7)	102.50(5)
γ [°]	90	75.36(2)	90	90
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$C2/c$
Molecules/cell	4	1	2	4
Unique refl.	910	1027	1088	685
Obs. $(F > 4\sigma(F))$	697	605	614	522
Final R	0.043	0.045	0.056	0.043

Table 2. *Angles* [°] *between the Amide-Group Plane* (I), *Pyrimidyl Moiety* (II), *and the Plane of the Phenylene Ring* (III) *in the Model Compounds* **3–6**

	3	**4**	**5**	**6**
$\not\subset$ (I–II)	38.3	4.6	34.2	23.8
$\not\subset$ (I–III)	40.4	12.6	30.9	33.0
$\not\subset$ (II–III)	75.5	11.2	64.9	56.2[a])

[a])   Disordered, see *Exper. Part*.

The dihedral angles for **3** (see *Table 2*) are comparable with those for benzanilide [8] (29.4, 37.3, and 62.6°, resp.). However, the intermolecular interactions are different in these two crystal structures: the benzanilide molecules are linked by NH $\cdots$ O H-bonds to form 'chains', whereas in crystals of **3**, dimers are observed; the length of the NH $\cdots$ N

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bridge indicated in *Fig. 2* is 3.11(1) Å. The dihedral angles for the trimer compounds are similar to the corresponding values of *N,N'*-diphenylterephthalamide [9] (30.4, 30.6, and 60.7°, resp.; values of the other trimer model compound for **1**, *N,N'*-(phenyl-1,4-ene)bis[benzamide] [10], 29.1, 25.9, and 64.5°, resp.). These values are also very similar to those measured and estimated for polymer **1** [11] [12].

The metallated form **4** has very much smaller dihedral angles than the unmetallated **3**. It can be seen from *Fig. 3* that the small dihedral angle between the amide group and the pyrimidinyl ring is mainly caused by the Ni–O(9) and Ni–N(1) bonds. It is not possible, however, to determine whether special packing features of the crystal structure of **4** or more general resonance effects (as discussed in [8]) are responsible for this flat, board-like molecular arrangement.

We postulate the possibility of complexing and, therefore, 'cross-linking' for the polymer PPYMT (**2**) similar to that in model compound **4**. Recent results indicate a significant uptake (11 wt-%) of Ni^{2+} cations into freshly spun PPYMT fibres by diffusion from a $NiCl_2$/1-methylpyrrolidin-2-one rinsing bath. We think that the postulated 'cross-linking' occurs between the chains of a single sheet in the 'pleated-sheet' structure of the PPYMT fibres, a structure that was reported for PPTA [13] [14]. Considering the H-bond between Cl-atoms and amide protons, there is also a possibility of 'cross-linking' in a second dimension, *i.e.* between the pleated sheets. However, more experimental work needs to be done for further confirmation.

Experimental Part

General. UV spectra: λ_{max} (ε) in nm. IR spectra: $\tilde{v}$ in cm^{-1}. NMR spectra: δ in ppm rel. to TMS (= 0 ppm), *J* in Hz.

N-(Pyrimidin-2'-yl)benzamide (**3**). To a soln. of 13.933 g (146.5 mmol) of 2-aminopyrimidine in 200 ml of dry pyridine, 20.595 g (146.5 mmol) of benzoyl chloride were added with a syringe. The soln. warmed up slightly and was stirred for 18 h at r.t. The dark orange soln. was evaporated to a small volume, then cooled to 5°, and the precipitate was filtered off with suction and dried: 21.2 g (72%) of crude product. Crystallization from EtOH yielded pure white needles. M.p. 142–143°. UV (EtOH): 250.2 (24275). IR (KBr, 1 wt.-%): 3233, 1702, 1586, 1433, 1276, 1246. ¹H-NMR (300 MHz, (D₆)DMSO): 11.02 (*s*, NH); 8.74 (*d*, *J* = 4.9, H–C(4'), H–C(6')); 7.97 (*m*, H–C(2), H–C(6)); 7.61 (*tt*, H–C(4)); 7.51 (*m*, H–C(3), H–C(5)); 7.26 (*t*, *J* = 4.8, H–C(5')). ¹³C-NMR (50 MHz, (D₆)DMSO): 165.4 (CON); 158.3 (C(4'), C(6')); 158.1 (C(2')); 134.1 (C(1)); 132 (C(4)); 128.3 (C(3), C(5)); 128.1 (C(2), C(6)), 117.2 (C(5')). CP-MAS-NMR (75.5 MHz, TOSS): 168.0, 158.0, 135.6, 130.4, 128.5, 117.2. Anal. calc. for $C_{11}H_9N_3O$ (199.1): C 66.32, H 4.55, N 21.09; found: C 66.74, H 4.43, N 21.04.

Bis[N-(pyrimidin-2-yl)benzamide]nickel(II)Dichloride (**4**). A soln. of 1.793 g (9 mmol) of **3** in 100 ml of EtOH was quickly poured to a vigorously stirred soln. of 1.072 g (4.5 mmol) of $NiCl_2 \cdot 6 H_2O$ in 50 ml of EtOH (green→aquamarine). After a few min, a green solid precipitated. After cooling to 5° for a few h, the precipitate was collected with suction and washed with cooled EtOH to yield 2.11 g (89%) of **4**. The substance was crystallized from dry EtOH. M.p. 353–355°. UV (EtOH): 247.7 (29725), 296 (sh), 284 (sh). IR (KBr, 1 wt.-%): 3405, 3218, 1646, 1603, 1519, 1425, 1341, 1292, 793, 705. ¹H-NMR (200 MHz, CD₃OD; all signals broad): 11.76, 10.77, 9.53, 8.71, 8.30, 6.89. Anal. calc. for $C_{22}H_{18}Cl_2N_6NiO_2$ (527.6): C 50.00, H 3.41, Cl 13.43, N 15.91; found: C 49.35, H 3.44, Cl 13.28, N 15.43.

N,N'-Bis(pyrimidin-2'-yl)benzene-1,4-dicarboxamide (**5**). A soln. of 10.25 g (107.8 mmol) of dry 2-aminopyrimidine in 80 ml of 1-methylpyrrolidin-2-one containing 10.5 g of LiCl was cooled to 0°, and 10.943 g (53.9 mmol) of freshly sublimed benzene-1,4-dicarbonyl dichloride were added at once. The orange soln. was stirred for 48 h at r.t. The product was then precipitated by pouring the mixture into 400 ml of H_2O. The white precipitate was filtered off and washed with H_2O to remove all remaining traces of LiCl (AgNO₃ test). The anal. sample was crystallized from DMSO/EtOH; 5·DMSO. M.p. 272–274°. IR (KBr, 0.6 wt.-%): 3406, 3211, 3162, 1672, 1591, 1441, 1420, 1299, 1283, 1257. ¹H-NMR (300 MHz, (D₆)DMSO): 10.74 (*s*, 2 H, NH); 8.71 (*d*, *J* = 4.8, 4 H, H–C(4'), H–C(6'));

8.05 (s, 4H, H–C(2), H–C(3), H–C(5), H–C(6)); 7.23 (t, $J = 4.8$, 2H, H–C(5′)). ^{13}C-NMR (75 MHz, (D$_6$)DMSO): 165.0 (CON); 158.2 (C(4′), C(6′)); 158.2 (C(2′)); 137.4 (C(1), C(4)); 128.0 (C(2), C(3), C(5), C(6)); 117.4 (C(5′)). Anal. calc. for C$_{16}$H$_{12}$N$_6$O (320.3): C 60.00, H 3.78, N 26.24; found: C 59.67, H 3.76, N 26.07.

N,N′-(Pyrimidine-2″,5″-diyl)bis[benzamide] (**6**) was synthesized using a procedure analogous to that described for **5**. M.p. 282–284°. IR (KBr, 1 wt.-%): 3329, 3050, 1674, 1663, 1527, 1441, 1378, 1286. ^{1}H-NMR (300 MHz, (D$_6$)DMSO): 11.06 (s, 1H, NH–C(2″)); 10.64 (s, 1H, NH–C(5″)); 9.11 (s, 2H, H–C(4″), H–C(6″)); 8.01 (td, $J = 8.5$, 1.4, 4H, H–C(3), H–C(5), H–C(3′), H–C(5′)); 7.68–7.50 (m, 6H, H–C(2), H–C(4), H–C(6), H–C(2′), H–C(4′), H–C(6′)). ^{13}C-NMR (75 MHz, (D$_6$)DMSO): 165.7 (CONH–C(2″)); 165.3 (CONH–C(5″)); 153.6 (C(2″)); 149.7 (C(4″), C(6″)); 134.1 (C(1)); 133.6 (C(1′)); 132.0 (C(4)); 131.9 (C(4′)); 130.5 (C(5″)); 128.5, 128.3, 128.0, 127.7 (C(2), C(3), C(5), C(6), C(2′), C(3′), C(5′), C(6′)). Anal. calc. for C$_{18}$H$_{14}$N$_4$O$_2$ (318.3): C 67.92, H 4.43, N 17.60; found: C 67.38, H 4.39, N 17.47.

X-Ray Diffraction. Crystals obtained as described above were used for the X-ray structure analysis with Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å). Diffraction data up to $\sin\theta/\lambda = 0.48$ were collected on *Picker* (upgraded by *Stoe*) [15] and *Syntex P21* [16] diffractometers. Since only small crystals were available (average edge length < 0.1 mm), no absorption corrections were applicable. No significant decay or instability was detectable during the measurements. Individual experimental and structural information is compiled in *Table 1*. The structure of **6** could not be refined in the appropriate non-centrosymmetric space group: residual electron density corresponding to 1/2 H-atoms remained invariably near atoms N(11) and N(12) (*Fig. 5*). These atoms and their vicinal C–H groups are superimposed by the pseudo twofold rotation due to a disorder effect in the centrosymmetric space group $C2/c$. Atomic parameters, bond lengths, and angles of all structures were deposited with the *Cambridge Crystallographic Data Centre.* The calculations were performed with the SHELXTL program system [16].

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