

## SYNTHESIS OF 4-AMINO-7-HYDROXYBENZIMIDAZOLE

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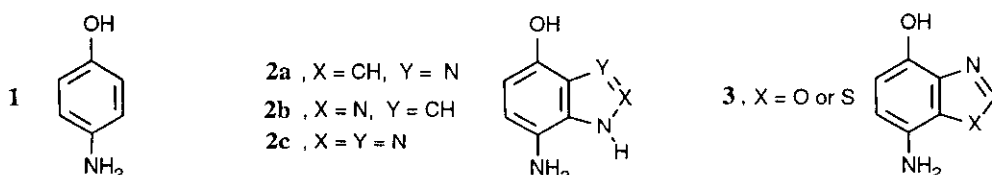
**Abstract** - A simple and efficient synthesis of 4-amino-7-hydroxybenzimidazole (**2a**) was developed involving condensation of 2,3-diaminophenol with triethyl orthoformate, coupling the 4-hydroxybenzimidazole (**6**) thus obtained with 4-ethylbenzodiazonium chloride to give 4-(4-ethylphenylazo)-7-hydroxybenzimidazole (**7**) and hydrogenolysis of **7** to give **2a**. Acetylation of **2a** with acetic anhydride gave triacetyl derivative (**8**), the structure of which was proved by X-ray crystallographic analysis.

4-Aminophenol (**1**) is a frequently used starting material in organic synthesis. Recent applications of **1** involve preparation of hair coloring formulations,<sup>1</sup> various azo compounds,<sup>2</sup> electrophotographic toners<sup>3</sup>, photothermography materials,<sup>4</sup> photochromic substances,<sup>5</sup> photography developers,<sup>6</sup> various pharmaceuticals,<sup>7</sup> liquid crystals<sup>8</sup> and heat resistant polymers.<sup>9</sup> To our surprise, benzazole analogues (**2**) and (**3**) of 4-aminophenol, which could have significant potential applications, appeared to be unknown. We now report an efficient synthesis of 4-amino-7-hydroxybenzimidazole (**2a**, X = CH, Y = N).

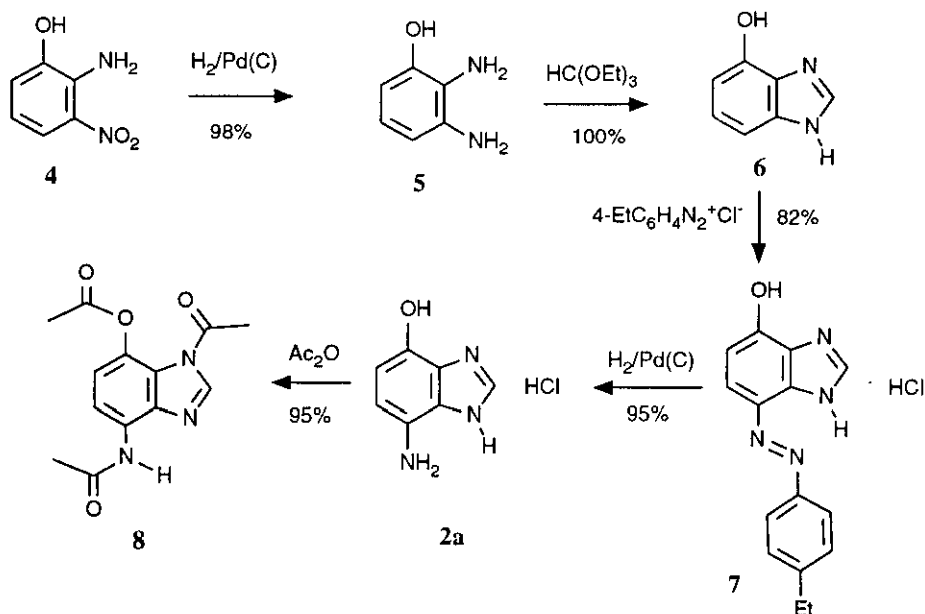
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<sup>†</sup> This paper is dedicated to **Professor Fritz Sauter**, holder of the Chair of Organic Chemistry of the Technical University of Vienna, in honor of his 65th birthday, and in admiration of his success in promoting east-west understanding.

The literature procedure<sup>10</sup> for the preparation of 4-hydroxybenzimidazole (**3**) is laborious involving successively: (i) hydrogenation of 3-nitro-2-aminophenol (**4**); (ii) refluxing the 2,3-diaminophenol (**5**) obtained with a mixture of formic acid and acetic anhydride; (iii) sublimation of the crude product to give a formyl derivative of **6** (in 42% yield) and (iv) hydrolysis with concentrated hydrochloric acid to give **6** as its hydrochloride. In our hands, this procedure gave a complex mixture containing 4-hydroxy-2-methylbenzimidazole<sup>11</sup> in addition to **6**, indicating that acetic acid can compete with formic acid in the cyclocondensation process.



We now report that triethyl orthoformate converts diamine (**5**) quantitatively into benzimidazole (**6**). Problems associated with the high solubility of **6** in water were avoided because the aqueous work-up was no longer needed. Attempted nitration of hydroxybenzimidazole (**6**) produced a difficult to separate equimolar mixture of the 5- and 7-nitro derivatives. Coupling reactions with aryldiazonium salts are more selective. Thus, condensation of **6** with 4-ethylbenzenediazonium chloride gave a mixture from which the pure azo compound hydrochloride (**7**), was obtained in 82% yield upon recrystallization from 10% HCl/EtOH (1:1).



Hydrogenolysis of **7** produced a mixture of the desired 4-amino-7-hydroxybenzimidazole (**2a**) and 4-ethylaniline which was easily separated by removing liquid 4-ethylaniline from solid **2a** using ether. Coupling with unsubstituted benzenediazonium chloride was less useful in this process due to the difficulty of separating aniline from **2a**. Compound (**2a**) is extremely sensitive to contact with air, changing from a white solid into a black mass within minutes. To obtain a stable derivative which could be analyzed, amine (**2a**) was treated with acetic anhydride. The nmr spectra and CHN analysis indicated three acetyl groups had been incorporated into the molecule. Because of five potential acetylation sites (including the possibility of two acetyl groups on the amino nitrogen atom), several possible structures had to be considered and the problem could not be solved on the basis of the nmr spectra. X-Ray crystallographic analysis allowed us to assign structure (**8**) for the triacetyl derivative.

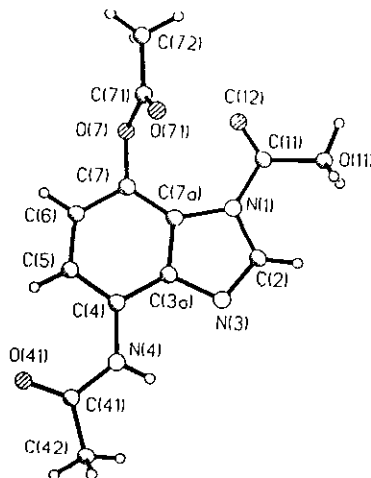


Figure 1. Perspective view and atom labelling of one of the two independent molecules of **8**.

Figure 1 shows a perspective view and atom labelling of one of the two independent molecules of **8**. Table 1 lists the bond lengths and angles. The geometry and conformations of the two crystallographically independent molecules are the same within experimental error. The benzimidazole ring system is planar to within 0.020 Å. The C- and N- acetyl groups are approximately coplanar with the benzimidazole plane (angles between the meanplanes 11.1 and 11.3° for the C-acetyl and 8.6 and 5.9° for the N-acetyl) while the O-acetyl group is inclined at angles of 66.4 and 65.9° for the two independent molecules. Intermolecular hydrogen bonds link the molecules with N(4)H bonded to O(71) of an adjacent molecule with the following parameters: N(4)...O(71) = 2.99 Å, H(4)...O(71) = 2.2 Å, N(4) - H(4)...O(71) = 145°.

Table 1. Bond lengths (Å) and angles (°) for the two independent molecules of **8**.

|                   |          |          |                  |          |          |
|-------------------|----------|----------|------------------|----------|----------|
| N(1)-C(2)         | 1.382(7) | 1.385(7) | N(1)-C(7A)       | 1.390(7) | 1.388(8) |
| N(1)-C(11)        | 1.441(7) | 1.432(7) | C(2)-N(3)        | 1.298(8) | 1.293(8) |
| N(3)-C(3A)        | 1.390(8) | 1.384(7) | C(3A)-C(7A)      | 1.396(9) | 1.414(8) |
| C(3A)-C(4)        | 1.393(8) | 1.384(8) | C(4)-C(5)        | 1.381(8) | 1.368(8) |
| C(4)-N(4)         | 1.399(7) | 1.411(7) | C(5)-C(6)        | 1.388(9) | 1.388(8) |
| C(6)-C(7)         | 1.372(8) | 1.382(8) | C(7)-C(7)        | 1.382(7) | 1.378(8) |
| C(7)-C(7A)        | 1.383(8) | 1.393(7) | C(11)-O(11)      | 1.186(8) | 1.178(8) |
| C(11)-C(12)       | 1.476(9) | 1.488(8) | N(4)-C(41)       | 1.365(8) | 1.364(7) |
| C(41)-O(41)       | 1.217(8) | 1.214(8) | C(41)-C(42)      | 1.496(9) | 1.493(8) |
| O(7)-C(71)        | 1.367(7) | 1.368(8) | C(71)-O(71)      | 1.186(7) | 1.189(7) |
| C(71)-C(72)       | 1.485(8) | 1.483(8) |                  |          |          |
| C(2)-N(1)-C(7A)   | 106.8(5) | 106.0(4) | C(2)-N(1)-C(11)  | 123.7(5) | 124.4(5) |
| C(7A)-N(1)-C(11)  | 128.6(5) | 129.0(5) | N(3)-C(2)-N(1)   | 113.2(5) | 114.5(5) |
| C(2)-N(3)-C(3A)   | 104.7(5) | 104.2(6) | C(7A)-C(3A)-N(3) | 111.3(5) | 111.2(5) |
| C(7A)-C(3A)-C(4)  | 122.9(6) | 122.0(5) | N(3)-C(3A)-C(4)  | 125.8(6) | 126.7(6) |
| C(5)-C(4)-N(4)    | 125.4(6) | 125.4(6) | C(5)-C(4)-C(3A)  | 116.7(6) | 118.0(6) |
| N(4)-C(4)-C(3A)   | 117.8(6) | 116.5(6) | C(4)-C(5)-C(6)   | 120.3(6) | 120.0(6) |
| C(7)-C(6)-C(5)    | 122.8(6) | 122.7(6) | C(6)-C(7)-O(7)   | 117.0(5) | 117.9(5) |
| C(6)-C(7)-C(7A)   | 118.0(6) | 117.2(5) | O(7)-C(7)-C(7A)  | 125.0(6) | 124.8(6) |
| C(7)-C(7A)-C(3A)  | 119.2(6) | 119.1(6) | C(7)-C(7A)-N(1)  | 136.7(6) | 136.8(6) |
| C(3A)-C(7A)-N(1)  | 104.0(5) | 104.0(5) | O(11)-C(11)-N(1) | 119.9(6) | 120.0(6) |
| O(11)-C(11)-C(12) | 124.9(6) | 124.8(6) | N(1)-C(11)-C(12) | 115.0(6) | 115.1(6) |
| C(41)-N(4)-C(4)   | 127.2(6) | 126.6(5) | O(41)-C(41)-N(4) | 122.7(7) | 123.1(6) |
| O(41)-C(41)-C(42) | 122.4(7) | 121.8(6) | N(4)-C(41)-C(42) | 114.8(6) | 115.1(5) |
| C(71)-O(7)-C(7)   | 116.7(5) | 115.9(5) | O(71)-C(71)-O(7) | 122.0(6) | 122.5(6) |
| O(71)-C(71)-C(72) | 127.0(6) | 127.5(6) | O(7)-C(71)-C(72) | 110.9(5) | 110.0(5) |

## EXPERIMENTAL

Melting points were determined with a Thomas Hoover capillary melting point apparatus and are uncorrected.

$^1\text{H}$  and  $^{13}\text{C}$  nmr spectra were recorded on a Varian VXR 300 spectrometer in  $\text{DMSO}-d_6$  with TMS as the reference. 2,3-Diaminophenol (**5**, mp 166 °C; lit.,<sup>12</sup> mp 164-165 °C) was obtained in 98% yield by catalytic reduction of 2-amino-3-nitrophenol (**4**), purchased from Aldrich.

**4-Hydroxybenzimidazole (6):** A mixture of 2,3-diaminophenol (1.24 g, 10 mmol) and triethyl orthoformate (1.48 g, 10 mmol) and a catalytic amount of *p*-toluenesulfonic acid was heated at 120 °C till no more ethanol distilled off. Toluene was then added to completely remove the ethanol. The solid residue was recrystallized from EtOH to give pure **6** (1.20g, 90%), mp 182-183 °C.  $^1\text{H}$  Nmr  $\delta$  6.67 (d,  $J = 7.2$  Hz, 1 H), 7.06 (m, 2 H), 8.08 (s, 1 H), 9.6-10.9 (bs, 2 H, OH and NH).  $^{13}\text{C}$  Nmr  $\delta$  105.6, 107.2, 123.3, 129.0, 138.8, 140.2, 147.3. Anal. Calcd for  $\text{C}_7\text{H}_6\text{N}_2\text{O}$ : C, 62.68; H, 4.51; N, 20.88. Found: C, 62.29; H, 4.54; N, 20.64.

**7-(4-Ethylphenylazo)-4-hydroxybenzimidazole hydrochloride (7):** 36% Hydrochloric acid (24 ml) was added dropwise to *p*-ethylaniline (9.5 ml, 77 mmol) kept in an ice/salt bath. After 10 min, a solution of  $\text{NaNO}_2$  (6.8 g, 99 mmol) in water (40 ml) was added portionwise to maintain a temperature of  $0^\circ\text{C}$ . The reaction mixture was stirred for 15 min. In the meantime, a solution of 4-hydroxybenzimidazole **6** (9.4 g, 70 mmol) in a mixture of EtOH and  $\text{H}_2\text{O}$  (60 ml + 60 ml) was added in one portion to a sodium acetate solution (54 g) in water (200 ml) while stirring at  $0$ - $5^\circ\text{C}$ . To this solution, the above the diazonium salt was added portionwise at such a rate that the temperature of the reaction mixture was never higher than  $5^\circ\text{C}$ . Formation of a heavy red precipitate was observed. After the addition the reaction mixture was left at room temperature for 1 h. The precipitate was filtered off and washed with water to give the crude product which was purified by recrystallization from a mixture of 10% HCl and EtOH (1:1) to give brown-red needles (15.3 g, 82%), mp  $268$ - $270^\circ\text{C}$ .  $^1\text{H}$  Nmr:  $\delta$  1.23 (t,  $J = 7.6$  Hz, 3 H), 2.68 (q,  $J = 7.6$  Hz, 2 H), 6.86 (d,  $J = 8.5$  Hz, 1 H), 7.38 (d,  $J = 8.3$  Hz, 2 H), 7.80 (d,  $J = 8.5$  Hz, 1 H), 7.96 (d,  $J = 8.3$  Hz, 2 H), 8.28 (s, 1 H).  $^{13}\text{C}$  Nmr:  $\delta$  15.3, 28.0, 109.8, 121.2 (2 C), 127.7, 128.5 (2 C), 129.3, 132.3, 132.8, 141.4, 145.3, 149.7, 156.1. Anal. Calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_4\text{OCl}$ : C, 59.51; H, 4.99; N, 18.51. Found C, 59.32; H, 4.61; N, 18.59.

**4-Amino-7-hydroxybenzimidazole hydrochloride (2a):** The suspension of compound (7) (2.66 g, 10 mmol) in MeOH (50 ml) was placed in a reactor for hydrogenation and palladium catalyst (Pd/C - 10%, 0.50 g) was added. After it was closed, 20 kG/cm<sup>2</sup> pressure of hydrogen was applied and the reaction left at room temperature for 2 h. After opening, the crude reaction mixture was filtered (to remove catalyst), washed very quickly with methanol and the solvent was evaporated under vacuum. Trituration of the dark solid residue with ether gave **2a** (1.35 g, 72%), mp  $320$ - $325^\circ\text{C}$  which decomposed quickly on exposure to air.  $^1\text{H}$  Nmr:  $\delta$  1.83 (br s, 2 H), 2.51 (br s, 2 H), 6.18 (d,  $J = 8.0$  Hz, 1 H), 6.34 (d,  $J = 8.0$  Hz, 1 H), 7.93 (s, 1 H).  $^{13}\text{C}$  Nmr:  $\delta$  104.6, 106.9, 107.9, 130.0, 136.3, 136.5, 138.7.

**1-Acetyl-4-acetamino-7-acetoxymethylimidazole (8):** A solution of 7-amino-4-hydroxybenzimidazole hydrochloride (0.30 g, 2 mmol) in acetic anhydride (1 ml, 10 mmol) was heated under reflux for 1 h. Toluene (10 ml) was added and the excess of acetic anhydride was distilled off to give 0.85 g of solid **8**. Recrystallization of crude **8** from EtOH gave fine white needles (0.42 g, 94%), mp  $201^\circ\text{C}$ .  $^1\text{H}$  Nmr:  $\delta$  2.20 (s, 3 H), 2.28 (s, 3 H), 2.77 (s, 3 H), 7.06 (d,  $J = 8.6$  Hz, 1 H), 8.09 (d,  $J = 8.6$  Hz, 1 H), 8.88 (s, 1 H), 10.02 (br s, 1 H, NH).  $^{13}\text{C}$  Nmr:  $\delta$  20.7, 23.9, 24.3, 115.6, 119.6, 123.8, 125.8, 128.4, 132.5, 137.0, 144.0, 167.6 (carbonyl), 169.2 (2 carbonyl). Anal. Calcd for  $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_4$ : C, 56.72; H, 4.76; N, 15.27. Found C, 56.83; H, 4.75;

N, 15.40.

**Crystal data for 8 at -143°C:**  $C_{13}H_{13}N_3O_4$ , MW = 275.3, orthorhombic, space group  $Pna2_1$ ,  $a = 14.531(2)$ ,  $b = 12.487(3)$ ,  $c = 13.561(2)$  Å,  $U = 2460.6(8)$  Å<sup>3</sup>,  $F(000) = 1152$ ,  $Z = 8$ ,  $D_c = 1.486$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 1.13$  cm<sup>-1</sup>,  $0.42 \times 0.34 \times 0.25$  mm,  $\omega$  scans,  $2\Theta_{\text{max}} = 52^\circ$ ,  $N = 2519$ , 367 parameters,  $S = 1.07$ ,  $wR(F^2) = 0.127$ ,  $R = 0.059$  for 1590 reflections with  $I > 2\sigma(I)$ .

Intensity data were collected at -143°C with a Nicolet R3m four-circle diffractometer by using monochromatized Mo K $\alpha$  ( $\lambda = 0.7107$ Å) radiation. Cell parameters were determined by least squares refinements, the setting angles of 28 accurately centred reflections ( $2\Theta > 27^\circ$ ) being used. Throughout data collections the intensities of three standard reflections were monitored at regular intervals and this indicated no significant crystal decomposition. The intensities were corrected for Lorenz and polarization effects but not for absorption.

Table 2. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters (Å<sup>2</sup> $\times 10^3$ ) for 8.

|       | x       | y        | z        | U <sub>eq</sub> <sup>a</sup> |        | x       | y        | z       | U <sub>eq</sub> <sup>a</sup> |
|-------|---------|----------|----------|------------------------------|--------|---------|----------|---------|------------------------------|
| N(1)  | 5925(3) | 4494(4)  | 10424(4) | 19(1)                        | N(1')  | 6632(3) | -489(4)  | 8117(4) | 18(1)                        |
| C(2)  | 5199(4) | 3810(5)  | 10234(5) | 20(2)                        | C(2')  | 7360(4) | -1183(5) | 8277(5) | 22(2)                        |
| N(3)  | 5431(4) | 2807(5)  | 10254(4) | 20(1)                        | N(3')  | 7142(3) | -2186(5) | 8250(5) | 20(1)                        |
| C(3A) | 6367(4) | 2813(5)  | 10467(6) | 18(2)                        | C(3A') | 6205(4) | -2166(5) | 8072(5) | 18(1)                        |
| C(4)  | 6925(4) | 1913(5)  | 10569(5) | 17(1)                        | C(4')  | 5647(4) | -3074(5) | 7945(6) | 22(2)                        |
| C(5)  | 7848(4) | 2094(6)  | 10745(5) | 19(2)                        | C(5')  | 4739(4) | -2908(5) | 7731(5) | 17(2)                        |
| C(6)  | 8183(4) | 3133(5)  | 10806(5) | 20(2)                        | C(6')  | 4390(4) | -1874(5) | 7699(5) | 16(2)                        |
| C(7)  | 7627(4) | 4017(5)  | 10728(5) | 17(1)                        | C(7')  | 4934(4) | -978(4)  | 7831(5) | 18(1)                        |
| C(7A) | 6698(4) | 3857(5)  | 10568(5) | 17(2)                        | C(7A') | 5863(4) | -1130(5) | 7975(6) | 16(2)                        |
| C(11) | 5819(4) | 5625(5)  | 10604(6) | 22(2)                        | C(11') | 6725(5) | 645(5)   | 7991(5) | 23(2)                        |
| C(12) | 4922(5) | 6076(6)  | 10308(6) | 32(2)                        | C(12') | 7667(4) | 1074(5)  | 8158(6) | 31(2)                        |
| O(11) | 6448(3) | 6131(4)  | 10911(4) | 32(1)                        | O(11') | 6089(3) | 1159(4)  | 7733(5) | 30(1)                        |
| N(4)  | 6509(4) | 906(4)   | 10495(5) | 17(1)                        | N(4')  | 6081(4) | -4063(4) | 8007(5) | 18(1)                        |
| C(41) | 6922(5) | -70(5)   | 10593(5) | 27(2)                        | C(41') | 5679(4) | -5057(5) | 7861(5) | 19(1)                        |
| C(42) | 6276(5) | -1002(6) | 10611(7) | 28(2)                        | C(42') | 6321(5) | -5990(6) | 7889(6) | 23(2)                        |
| O(41) | 7751(3) | -174(5)  | 10678(5) | 37(2)                        | O(41') | 4862(3) | -5166(4) | 7699(5) | 36(1)                        |
| O(7)  | 8045(3) | 5006(4)  | 10825(3) | 18(1)                        | O(7')  | 4508(3) | 18(4)    | 7747(4) | 21(1)                        |
| C(71) | 8028(4) | 5659(5)  | 10017(5) | 17(1)                        | C(71') | 4515(4) | 641(5)   | 8576(5) | 20(2)                        |
| C(72) | 8487(5) | 6696(5)  | 10230(6) | 28(2)                        | C(72') | 4059(5) | 1685(5)  | 8371(5) | 25(2)                        |
| O(71) | 7714(3) | 5377(3)  | 9253(3)  | 22(1)                        | O(71') | 4829(3) | 339(3)   | 9337(3) | 23(1)                        |

<sup>a</sup>Equivalent isotropic U defined as one third of the trace of the orthogonalised  $U_{ij}$  tensor

The structure was solved by direct methods, and refined on  $F^2$  using SHELXL93.<sup>13</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.3 times the isotropic equivalent of their carrier carbons. The rotational

orientations of the methyl groups were deduced from Fourier syntheses. The function minimized was  $\Sigma w(F_o^2 - F_c^2)$ , with  $w = [\sigma^2(F_o^2) + 0.078P^2]^{-1}$  where  $P = [\max(F_o^2 + 2F_c^2)]/3$ . Attempts to refine the structure in a higher symmetry space group were unsuccessful. Final atom coordinates are listed in Table 2. Tabulations of hydrogen atom coordinates, anisotropic thermal parameters, structure factors and equations of meanplanes are available from the author P.J.S.

## REFERENCES

1. a) A. Junino, J. J. Vandenbossche, H. Borowiak, and G. Lang, *Eur. Pat.* 370,880 (1990) (*Chem. Abstr.*, 1990, **113**, 151993d). b) C. Vayssie, D. Bauer, F. Richard, and A. Junino, *Fr. Pat.* 2,649,887 (1991) (*Chem. Abstr.*, 1991, **115**, 56951w). c) J. Zimnicki, Z. Zaremba, J. Kulawinek, and W. Szlubowska, *Pol. Pat.* 152,511 (1991) (*Chem. Abstr.*, 1991, **115**, 119826g). d) G. Wenke, *U.S. Pat.* 5,034,014 (1991) (*Chem. Abstr.*, 1991, **115**, 141999n). e) T. Tamura, A. Kiyomine, Y. Nishizawa, H. Tagami, T. Yoshihara, and J. Kawase, *Eur. Pat.* 410,471 (1991) (*Chem. Abstr.*, 1991, **115**, 258295w).
2. a) M. S. Masoud and Z. M. Zaki, *Transition Met. Chem.* (London), 1988, **13**, 321. b) R. Jain, A. Dixit, and P. Pandey, *J. Indian. Chem. Soc.* 1989, **66**, 486. c) M. A. Shaban, N. A. Abdou, S. El-Meligie, and A. Taher, *A. Alexandria J. Pharm. Sci.*, 1990, **4**, 93 (*Chem. Abstr.*, 1991, **114**, 42636q). d) O. M. O. Habib, E. B. Moawad, E. B., D. S. Badawy, and F. A. M. Mansour, *J. Prakt. Chem.*, 1990, **332**, 791. e) S. S. Kandil, Y. L. Ali, and A. A. El-Barbary, *Synth. React. Inorg. Met.-Org. Chem.*, 1992, **22**, 83.
3. a) M. Kato, Y. Nishioka, Y. To, and A. Yabe, *Jpn. Pat.* 62,265,666, (1987) (*Chem. Abstr.*, 1988, **109**, 46126t). b) I. Yoshida and S. Tamura, *Jpn. Pat.* 62,265,667 (1987) (*Chem. Abstr.*, 1988, **109**, 30063j). c) B. S. Ong, W. Mychajlowskij, and L. Alexandru, *U.S. Pat.* 4,778,742 (1988) (*Chem. Abstr.*, 1989, **111**, 48042c).
4. a) Y. Yamamoto, T. Takehara, H. Fujii, K. Uhara, and H. Tanaka, *Ger. Pat.* 3,636,222 (1987) (*Chem. Abstr.*, 1987, **107**, 208941t). b) T. Takeda and Y. Hayakawa, *Jpn. Pat.* 61,228,441 (1986) (*Chem. Abstr.*, 1987, **106**, 205281w). c) K. Takeda, *Eur. Pat.* 202,490 (1986) (*Chem. Abstr.*, 1987, **106**, 224542y). d) P. K. Gupta, V. Raman, and R. Kumar, *Indian Pat.* 164,415 (1989) (*Chem. Abstr.*, 1990, **113**, 68434b). e) K. Nakamura, T. Nakamura, A. Suzuki, H. Yanagi, and H. Yamazaki, *Jpn. Pat.* 01,141,786 (1989) (*Chem. Abstr.*, 1990, **112**, 45825v).
5. a) O. Iwamoto, H. Sugiyama, and T. Hara, *Eur. Pat.* 420,397 (1991) (*Chem. Abstr.*, 1991, **115**, 92062r).

- b) S. Yamamoto and T. Taniguchi, *Jpn. Pat.* 03 11,081 (1991) (*Chem. Abstr.*, 1991, **115**, 82311g).
6. a) S. Aoki, S. Koboshi, and M. Kurematsu, *Jpn. Pat.* 62,178, 959 (1987) (*Chem. Abstr.*, 1988, **109**, 46011b). b) M. Yagihara, T. Ishikawa, Y. Fujita, and H. Fujimoto, *Jpn. Pat.* 62,200,348 (1987) (*Chem. Abstr.*, 1988, **108**, 177019n). c) M. J. M. Noppe and L. A. M. Van Nuffel, *Eur. Pat.* 446,993 (1991) (*Chem. Abstr.*, 1992, **117**, 44090t).
7. a) H. Boeshagen, B. Junge, A. Paessens, and M. Schueller, *Eur. Pat.* 313,974 (1989) (*Chem. Abstr.*, 1990, **112**, 56576r). b) I. Lalezari and P. Lalezari, *PCT Int. Appl. WO* 89 12,622 (1989) (*Chem. Abstr.*, 1990, **113**, 23397a). c) W. Von der Saal, A. Mertens, H. Zilch, and E. Boehm, *Ger. Pat.* 3,830,054 (1990) (*Chem. Abstr.*, 1990, **113**, 152047k). d) R. J. Iffe, T. H. Brown, and C. A. Leach, *PCT Int. Appl. WO* 89 08,105 (1989) (*Chem. Abstr.*, 1990, **113**, 211861w). e) R. C. Allen, J. T. Klein, and R. C. Effland, *U.S. Pat.* 4,959,378 (1990) (*Chem. Abstr.*, 1991, **114**, 101747b). f) M. Klaus and P. Mohr, *Eur. Pat.* 410,358 (1991) (*Chem. Abstr.*, 1991, **115**, 28910p). g) E. B. Sjogren and M. A. Rider, *U.S. Pat.* 5,034,410 (1991) (*Chem. Abstr.*, 1991, **115**, 182859k). h) B. C. Pearce, *Eur. Pat.* 476,493 (1992) (*Chem. Abstr.*, 1992, **117**, 26849t).
8. a) F. Casagrande, M. Foa, and L. L. Chapoy, *Eur. Pat.* 433,708 (1991) (*Chem. Abstr.*, 1991, **115**, 184193n). b) S. Abdul-Jawad and M. H. Alhaj-Mohammad, *Appl. Phys. Commun.*, 1992, **11**, 245 (*Chem. Abstr.*, 1992, **117**, 131886a). c) A. Kaito and K. Nakayama, *Macromolecules* 1992, **25**, 4882. d) S. A. Jawad and M. H. Alhaj-Mohammad, *Mater. Lett.*, 1992, **13**, 312 (*Chem. Abstr.*, 1992, **117**, 49603x). e) K. Itoyama, *J. Polym. Sci., Part C: Polym. Lett.*, 1989, **27**, 369.
9. a) I. Matsuda, H. Maezawa, and K. Tokumaru, *Jpn. Pat.* 03 09,974 (1991) (*Chem. Abstr.*, 1992, **116**, 22416f). b) C. Hedtmann-Rein and G. Heinz, *Ger. Pat.* 3,900,674 (1990) (*Chem. Abstr.*, 1991, **114**, 63023c). c) H. R. Lubowitz and C. H. Sheppard, *PCT Int. Appl. WO*, 90 14,374 (1990) (*Chem. Abstr.*, 1991, **114**, 248488b). d) B. J. Jensen, P. M. Hergenrother, and R. G. Bass, *High Perform. Polym.*, 1991, **3**, 3 (*Chem. Abstr.*, 1992, **116**, 129763u). e) I. Matsuda, T. Miki, and H. Maezawa, *Jpn. Pat.* 04,122,716 (1992) (*Chem. Abstr.*, 1992, **117**, 214126d).
10. E. Sorkin, W. Roth, and H. Erlenmeyer, *Helv. Chim. Acta*, 1952, **35**, 1736.
11. E. S. Lane and C. Williams, *J. Chem. Soc.*, 1956, 569.
12. E. Sorkin and W. Roth, *Helv. Chim. Acta*, 1951, **34**, 427.
13. G. M. Sheldrick, SHELXL93. University of Gottingen, 1993.