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Mendeleev Commun., 2015, **25**, 140–141
Mendeleev Communications

Synthesis of new AB-type monomers for polybenzimidazoles from *N*-(4,5-dichloro-2-nitrophenyl)acetamide

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DOI: 10.1016/j.mencom.2015.03.022

S_NAr reaction between *N*-(4,5-dichloro-2-nitrophenyl)acetamide and 4-hydroxybenzoic acid gives 4-(5-acetylamino-2-chloro-4-nitrophenoxy)benzoic acid and 4-{5-[(5-acetylamino-2-chloro-4-nitrophenyl)amino]-2-chloro-4-nitrophenoxy}benzoic acid which were used for the synthesis of new AB-type monomers for polybenzimidazoles.

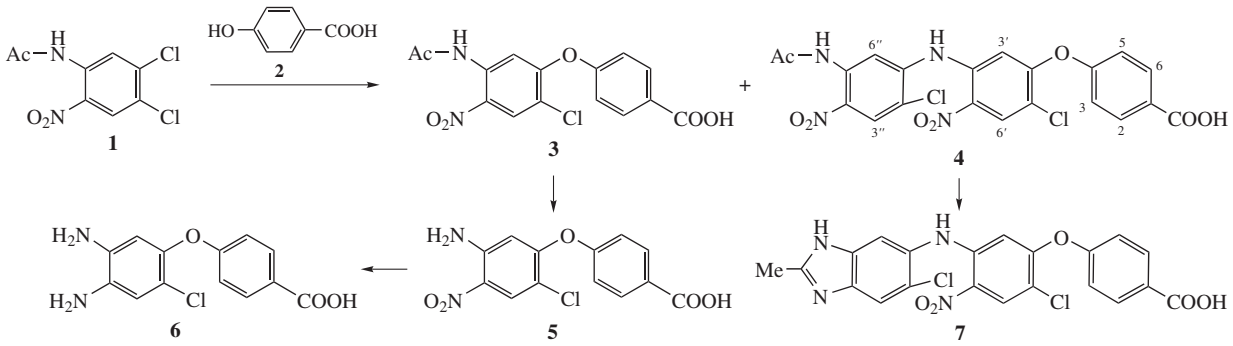
Chemistry of aromatic condensation polymers, containing heterocyclic fragments in the main chain, is currently actively developed.[1] Therefore, the synthesis of new monomers for their preparation is an actual problem. The AB-type monomers are promising for the synthesis of polybenzimidazoles because such polymers have a well-ordered structure and possess good physicochemical characteristics.[2] Recently,[3] we obtained 4-(3,4-diaminophenoxy)-benzoic acid and prepared poly-2-(4′-hydroxyphenylene)-5-benzimidazole on its basis, which exhibited good thermomechanical properties.[4] In this development, we intended to carry out the synthesis of a new AB-type monomer containing a chlorine atom. According to published data, the presence of halogens bound to the benzene fragments of a main polymer chain in polybenzimidazoles improves polymer properties such as solubility, film formation, incombustibility and capability for binding larger dopant amounts[5] without impairing other physicochemical characteristics.[6]

The use of *N*-(4,5-dichloro-2-nitrophenyl)acetamide **1** instead of *N*-(5-chloro-2-nitrophenyl)acetamide in the S_NAr reaction with 4-hydroxybenzoic acid **2** unexpectedly gave two products **3** and **4** at the first stage (Scheme 1), which were separated and whose structures were established.†

Compound **3** was an expected one. The structure of compound **4** was confirmed by ^1H, ^{13}C NMR and {^1H-^1H} NOESY spectroscopy as well as mass spectrometry and elemental analysis.

Apparently, the formation of product **4** occurs due to aromatic nucleophilic substitution involving N-nucleophile from *N*-acetylaniline moiety (N-deprotonation–substitution–N-deacetylation, or N-deacetylation–substitution). Special experiment in the absence of substrate **2**, regarding N-nucleophilic properties of compound **1** (Scheme 2) brought about 17% of diarylamino product **8**.‡ Its ^1H NMR spectrum exhibited four signals due to aromatic protons as intense singlets and two signals of protons bound to nitrogen atoms. In this case, the signal of a secondary amine proton observed at δ 9.35 appeared as a broadened singlet.[7] Mass-spectrometric data showed a molecular ion of *m*/*z* 418.

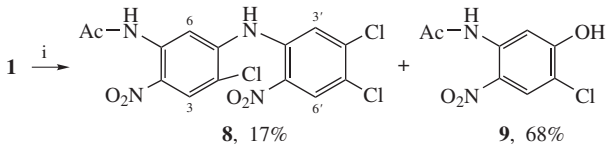
According to the ^1H NMR and mass spectra, compound **9** was a product of the replacement of a chlorine atom by the hydroxy group. In its ^1H NMR spectrum, the signal of a 6-positioned proton of the benzene ring was upfield shifted (δ 7.75) in comparison with the signal of this proton in initial compound **1** at δ 8.06; this can be explained by the presence of an electron-donor substituent, the hydroxy group, in the *ortho*-position, whose proton signal appears at δ 11.88.



Scheme 1

† The NMR spectra were recorded on a Bruker DRX500 instrument (500 MHz for ^1H and 125 MHz for ^{13}C) using DMSO-d_6 as a solvent and TMS as an internal standard. The mass spectra were recorded on FINNIGAN MAT INCOS 50 at an electron energy of 70 eV. Elemental analysis was performed on a Carlo Erba 1106 CHN analyzer.

4-(5-Acetylamino-2-chloro-4-nitrophenoxy)benzoic acid **3**. Compound **1** (2.5 g, 0.01 mol) in 50 ml of DMSO was added to 5.8 g (0.042 mol) of K_2CO_3 and 1.9 g (0.014 mol) of **2** in 100 ml of DMSO at 100 °C for 1.5 h. The reaction mass was stirred at 100 °C for 1 h. After cooling, the mixture was poured into water and filtered. The filtrate was treated with acetic acid to pH 6; the precipitate formed was filtered off, dried and recrystallized from a mixture of Pr^{i}OH and DMF. Yield 87%, mp 270–276 °C. ^1H NMR, δ: 2.05 (s, 3H, Me), 7.25 (d, 2H, H$^{3',5'}$, *J* 8.72 Hz), 7.42 (s, 1H, H^6), 8.04 (d, 2H, H$^{2',6'}$, *J* 8.77 Hz), 8.29 (s, 1H, H^3), 10.31 (s, 1H, NH), 13.05 (s, 1H, COOH). MS, *m*/*z* (%): 350 [M]$^+$ (7), 308 (22), 304 (16), 227 (3), 183 (15), 76 (5), 65 (12), 43 (100). Found (%): C, 51.34; H, 3.05; N, 8.05. Calc. for $C_{15}H_{11}ClN_2O_6$ (%): C, 51.36; H, 3.14; N, 7.99.



Scheme 2 *Reagents and conditions*: i, K_2CO_3, DMSO, 100 °C.

Thus, more than 60% compound **1** was converted into hydrolysis product **9**, which was not observed as a by-product in the main reaction. Furthermore, the formation of binuclear product **8** in only 17% suggests that initial compound **1** cannot serve as an active nucleophilic agent. Most probably, trinuclear product **4** is formed during the reaction of compound **3** with parent substance **1**. This is facilitated by an increase in the basicity of the nitrogen atom in the NHAc group of compound **3** as a result of the replacement of the electron-acceptor chlorine atom by the aryloxy group as an electron-donor substituent. This assumption was confirmed by the preparation of compound **4** from substrate **1** and product **3** under the reaction conditions of (K_2CO_3, DMSO, 100 °C, 2 h) in 82% yield.

To obtain individual compounds **3** and **4**, we studied the influence of a reactant ratio on the course of the main and side reactions. Only one product **3** was detected in the reaction mass after the synthesis performed with a 2.4-fold excess of nucleophile **2**. Meantime, when the molar ratio **1** : **2** was 2 : 1, only compound **4** was formed. With the gradual introduction of electrophile **1** into the reaction mass for 1.5 h, only a 1.4-fold molar excess of the nucleophile was required for obtaining **3** in 87% yield.

Finally, compound **3** was converted into required monomer **6** in accordance with a procedure[2] developed for the synthesis of 4-(3,4-diaminophenoxy)benzoic acid.[§] Compound **4** was reduced with $SnCl_2$ in acetic acid in the presence of catalytic amounts of HCl to give benzimidazole derivative **7**.[¶]

In summary, we obtained two new AB-type monomers for the synthesis of polybenzimidazoles.

This work was supported by the Ministry of Education and Science of the Russian Federation (project no. 178).

References

1 (*a*) V. A. Kostyanovsky, D. K. Susarova, G. Adam, R. N. Lyubovskaya and P. A. Troshin, *Mendeleev Commun.*, 2013, **23**, 26; (*b*) A. Parhamia, S. S. Nasaba, M. Abbasia and R. Jafarazada, *Designed Monomers and Polymers*, 2014, **17**, 736; (*c*) I. A. Ronova, M. Bruma, A. A. Kuznetsov and A. Y. Nikolaev, *Polym. Adv. Technol*., 2013, **24**, 615.
2 J. A. Asensio and P. Gómez-Romero, *Fuel Cells*, 2005, **5**, 336.
3 R. S. Begunov and A. L. Zubishina, *RF Patent 2409554*, C07C 217/90, C07C 213/06, C07C 213/02, 2009 (*J. Am. Chem. Soc*., 2011, **154**, 132938).
4 A. Yu. Leikin, A. L. Rusanov, R. S. Begunov and A. I. Fomenkov, *Polymer Sci., Ser. C*, 2009, **51**, 12 (*Vysokomol. Soedin., Ser. C*, 2009, **51**, 1264).
5 (*a*) S. C. Kumbharkar, M. N. Islam, R. A. Potrekar and U. K. Kharul, *Polymer*, 2009, **50**, 1403; (*b*) V. I. Kodolov, *Goryuchest i ognestoikost polimernykh materialov (Flammability and Fire Resistance of Polymeric Materials)*, Khimiya, Moscow, 1976 (in Russian).
6 J. Varga, A. A. Izyneev, V. P. Mazurevskij, J. P. Mazurevskaya and I. S. Novak, *Periodica Polytechnica*, 1985, **29**, 51.
7 (*a*) A. V. Gulevskaya, I. N. Tyaglivaya, S. Verbeeck, B. U. W. Maes and A. V. Tkachuk, *Arkivoc*, 2011, **ix**, 238; (*b*) M. A. Carroll and R. A. Wood, *Tetrahedron*, 2007, **63**, 11349.

Received: 5th June 2014; Com. 14/4390

4-{5-[(5-Acetylamino-2-chloro-4-nitrophenyl)amino]-2-chloro-4-nitrophenoxy}benzoic acid **4**. Compound **1** (12.5 g, 0.05 mol) was added to 10.4 g (0.075 mol) of K_2CO_3 and 3.5 g (0.025 mol) of compound **2** in 200 ml of DMSO. The reaction mass was stirred at 100 °C for 3 h. After cooling, the reaction mixture was poured into water. The precipitate formed was filtered off, washed with water several times, dried and recrystallized from a mixture of Pr^iOH and DMF. Yield 88%, mp 292–306 °C. ^{1}H NMR, δ: 2.11 (s, 3H, Me), 7.13 (s, 1H, H$^{6'}$), 7.22 (d, 2H, H^{3,5}, *J* 8.76 Hz), 7.80 (s, 1H, H$^{6''}$), 7.97 (d, 2H, H^{2,6}, *J* 8.74 Hz), 8.25 (s, 1H, H$^{3''}$), 8.48 (s, 1H, H$^{3'}$), 9.39 (s, 1H, NH), 10.26 (s, 1H, N*H*COMe), 13.00 (s, 1H, COOH). ^{13}C NMR, δ: 23.98 (MeCO), 111.28 (C$^{6''}$), 112.04 (C$^{6'}$), 117.58 (C$^{2'}$), 117.78 (C$^{2''}$), 118.31 (C^{3,5}), 126.83 (C$^{3''}$), 127.81 (C^{1}), 128.49 (C$^{3'}$), 131.68 (C^{2,6}), 132.99 (C$^{1''}$), 133.83 (C$^{5''}$), 134.76 (C$^{5'}$), 137.28 (C$^{4'}$), 143.11 (C$^{4''}$), 156.18 (C$^{1'}$), 157.88 (C$^{4'}$), 166.66 (COOH), 168.77 (COMe). MS, *m*/*z* (%): 521 [M]$^+$ (79), 480 (3), 474 (12) [M – NO_2]$^+$, 461 (4), 460 (21), 458 (42), 456 (100), 443 (6), 427 (18), 413 (6), 399 (4), 397 (9), 365 (3), 353 (4), 351 (7), 306 (4), 244 (4), 140 (3), 44 (12), 43 (30). Found (%): C, 48.28; H, 2.82; N, 10.59. Calc. for $C_{21}H_{14}Cl_2N_4O_8$ (%): C, 48.37; H, 2.69; N, 10.75.

4-(5-Amino-2-chloro-4-nitrophenoxy)benzoic acid **5**. Compound **3** (14.0 g, 0.04 mol) in 200 ml of a 20% aqueous solution of KOH was stirred at 60 °C for 1 h. The precipitate formed was filtered off and treated with acetic acid to pH 6. Yield 98%, mp 226–228 °C. ^{1}H NMR, δ: 6.57 (s, 1H, H$^{6'}$), 7.20 (d, 2H, H^{3,5}, *J* 9.5 Hz), 7.46 (s, 2H, NH_2), 8.04 (d, 2H, H^{2,6}, *J* 10.0 Hz), 8.12 (s, 1H, H$^{3'}$), 13.00 (s, 1H, COOH). MS, *m*/*z* (%): 308 [M]$^+$ (7), 292 (4), 256 (11), 188 (26), 136 (100), 90 (7). Found (%): C, 51.54; H, 2.95; N, 9.06. Calc. for $C_{13}H_9ClN_2O_5$ (%): C, 51.57; H, 2.92; N, 9.08.

‡ *Compounds* **8** *and* **9**. Potassium carbonate (3.1 g, 0.023 mol) and compound **1** (3.7 g, 0.015 mol) were stirred in 150 ml of DMSO at 100 °C for 2 h. After cooling, the mixture was poured into water. The resulting precipitate was filtered off, repeatedly washed with water and dried. The yield of compound **8** was 17%. The filtrate was treated with acetic acid to pH 5–6 and the resulting precipitate was filtered off, washed with water and dried. The yield of compound **9** was 68%.

N-*{4-Chloro-5-[(4,5-dichloro-2-nitrophenyl)amino]-2-nitrophenyl}acetamide* **8**: mp 208–210 °C. ^{1}H NMR, δ: 2.10 (s, 3H, Me), 7.78 (s, 1H, H^6), 7.80 (s, 1H, H$^{6'}$), 8.24 (s, 1H, H^3), 8.44 (s, 1H, H$^{3'}$), 9.35 (br. s, 1H, NH), 10.32 (s, 1H, N*H*COMe). MS, *m*/*z* (%): 418 [M]$^+$ (7), 372 (22), 325 (5), 295 (6), 262 (3), 25 (7), 97 (19), 73 (37), 30 (76). Found (%): C, 40.15; H, 2.07; N, 13.33. Calc. for $C_{14}H_9Cl_3N_4O_5$ (%): C, 40.05; H, 2.15; N, 13.35.

N-*(4-Chloro-5-hydroxy-2-nitrophenyl)acetamide* **9**: mp > 300 °C. ^{1}H NMR, δ: 2.13 (s, 1H, Me), 7.75 (s, 1H, H^6), 8.10 (s, 1H, H^3), 10.28 (s, 1H, NH), 11.88 (s, 1H, OH). MS, *m*/*z* (%): 230 [M]$^+$ (6), 183 (26), 182 (10), 158 (9), 142 (9), 43 (100). Found (%): C, 41.45; H, 3.12; N, 12.17. Calc. for $C_8H_7ClN_2O_4$ (%): C, 41.65; H, 3.04; N, 12.15.

§ *4-(4,5-Diamino-2-chlorophenoxy)benzoic acid* **6**. Compound **5** (9.3 g, 0.03 mol) and $SnCl_2 \cdot 2H_2O$ (22.6 g, 0.10 mol) were stirred in 100 ml of 36% HCl at 90 °C for 1 h. After cooling, the reaction mixture was treated with a 25% aqueous ammonia solution to pH 7–8. The precipitate was filtered off and dried at 60 °C. Then, the precipitate was added to 400 ml of anhydrous isopropanol, and the mixture was heated to boiling with stirring for 0.5 h. The hot alcohol was separated by filtration. The precipitate formed was filtered off after cooling the alcohol. Yield 90%, mp 231–232 °C. ^{1}H NMR, δ: 6.38 (s, 1H, H$^{6'}$), 6.64 (s, 1H, H$^{3'}$), 6.86 (d, 2H, H^{3,5}, *J* 9.5 Hz), 7.88 (d, 2H, H^{2,6}, *J* 10.0 Hz). Signals due to the protons of NH_2 and COOH groups were absent from the ^{1}H NMR spectrum because of rapid deuterium exchange. MS, *m*/*z* (%): 279 [M]$^+$ (73), 242 (17), 226 (27), 198 (15), 166 (100), 110 (68), 92 (9), 74 (28). Found (%): C, 55.58; H, 3.95; N, 10.07. Calc. for $C_{13}H_{11}ClN_2O_3$ (%): C, 56.01; H, 3.95; N, 10.05.

¶ *4-{4-Amino-2-chloro-5-[(5-chloro-2-methyl-1*H*-benz[*d*]imidazol-6-yl)amino]phenoxy}benzoic acid* **7**. Compound **4** (15.6 g, 0.030 mol), $SnCl_2 \cdot 2H_2O$ (44.1 g, 0.195 mol) and 36% HCl (2 ml) were stirred in 200 ml of glacial acetic acid at 100 °C for 1 h. Then, 190 ml of acetic acid was distilled off and the residue was treated with a 25% aqueous ammonia solution to pH 7–8. The precipitate was filtered off and dried at 60 °C. Thereafter, the precipitate was added to 400 ml of anhydrous isopropanol and the mixture was heated to boiling with stirring for 0.5 h. The hot alcohol was separated by filtration. After cooling the alcohol, the resulting precipitate was filtered off. Yield 86%, mp > 300 °C. ^{1}H NMR, δ: 2.43 (s, 3H, Me), 6.42 (s, 1H, H$^{6'}$), 6.67 (s, 1H, H$^{3'}$), 6.86 (d, 2H, H^{3,5}, *J* 9.03 Hz), 6.91 (s, 1H, H$^{7''}$), 6.98 (s, 1H, H$^{4''}$), 7.89 (d, 2H, H^{2,6}, *J* 8.77 Hz), 8.34 [s, 1H, N*H*(Ph)$_2$], 12.11 (s, 1H, NH). Signals due to the protons of NH_2 and COOH groups were absent from the ^{1}H NMR spectrum because of rapid deuterium exchange. MS, *m*/*z* (%): 443 [M]$^+$ (69), 407 (45), 371 (32), 276 (74), 230 (63), 166 (19), 136 (23), 130 (47), 74 (39), 41 (32). Found (%): C, 56.73; H, 3.58; N, 12.67. Calc. for $C_{21}H_{16}Cl_2N_4O_3$ (%): C, 56.88; H, 3.61; N, 12.64.