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A simple and convenient method for synthesizing dipyrido[1,2-*a*:1′,2′-*a*′]benzo[1,2-*d*:5,4-*d*]diimidazole-6,13-dione

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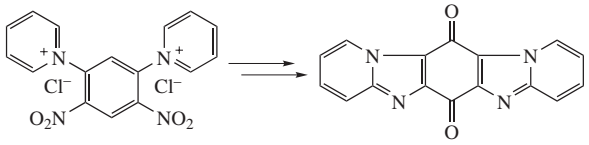
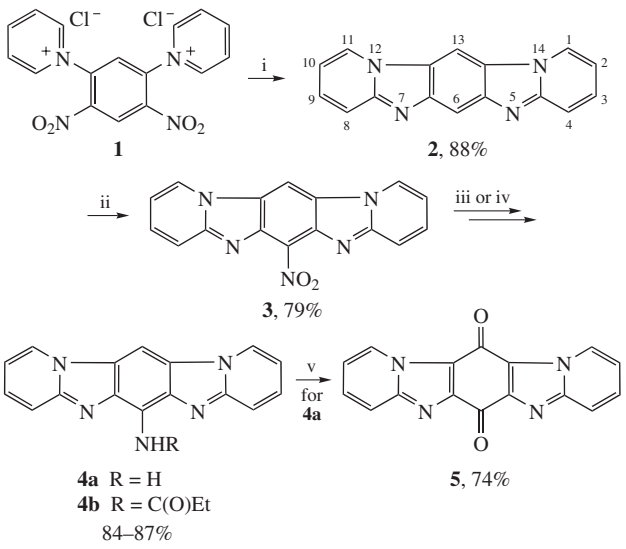
Reduction of 1,1′-(4,6-dinitro-1,3-phenylene)dipyridinium dichloride with $SnCl_2$ afforded dipyrido[1,2-*a*:1′,2′-*a*′]benzo-[1,2-*d*:5,4-*d*]diimidazole which was converted into the corresponding quinone-type 6,13-dione in three simple steps.



Carbonyl-containing derivatives of dipyrido[1,2-*a*:1′,2′-*a*′]benzo-[1,2-*d*:4,5-*d*]diimidazole are promising in development of new polyfunctional materials.[1–5] The electron-deficient nature of these compounds and large π-bond conjugation make them good n-type semiconductors,[2] which can be employed for creating organic field-effect transistors (OFET) useful in electronic devices with flexible displays or radio-frequency identifiers and sensors. Owing to the conjugated π-system, such compounds are excellent pH-dependent chromophores with intense fluorescence that can be used as pigments or dyes.[3] Carbonyl derivatives of dipyrido-[1,2-*a*:1′,2′-*a*′]benzo[1,2-*d*:4,5-*d*]diimidazole can undergo reversible lithiation–delithiation reactions in the course of charging and discharging,[4] which makes them prospective organic cathode materials in lithium-ion batteries. Dipyrido[1,2-*a*:1′,2′-*a*′]benzo-[1,2-*d*:4,5-*d*]diimidazole-6,13-diones find application as efficient ligands for synthesizing coordination polymers[5] possessing properties of semiconductors,[6,7] nonlinear optics[8,9] and luminophores.[10–12]

It may be expected that the 6,13-dioxo derivative of dipyrido-[1,2-*a*:1′,2′-*a*′]benzo[1,2-*d*:5,4-*d*]diimidazole can also be a promising compound for the creation of efficient polyfunctional materials. Only one example of the synthesis of this compound was published[13] based on the boiling of 2-aminopyridine and chloranil in ethanol for 72 h to afford a mixture of dipyrido[1,2-*a*:1′,2′-*a*′]benzo[1,2-*d*:4,5-*d*]- and dipyrido[1,2-*a*:1′,2′-*a*′]benzo-[1,2-*d*:5,4-*d*]diimidazole-6,13-diones, with the total yield and the isomer ratio having not been reported.

This study was aimed at development of a simple and convenient synthesis of dipyrido[1,2-*a*:1′,2′-*a*′]benzo[1,2-*d*:5,4-*d*]diimidazole-6,13-dione from available 1,1′-(4,6-dinitro-1,3-phenylene)dipyridinium dichloride **1** which can be readily obtained from pyridine and 1,3-dichloro-4,6-dinitrobenzene.[14] The fused pentacyclic system **2** was created by reductive cyclization of reactant **1** (Scheme 1).† This type of cascade reactions initiated by transfer of several electrons to a pyridinium salt is efficient in the preparation of fused imidazole derivatives with a bridgehead nitrogen atom.[15–18] However, it was not used previously to form two imidazole rings simultaneously. Reductive heterocyclization of compound **1** was caused by $SnCl_2$ as the electron donor in acidic water–alcohol medium at 40 °C for 15 min. To optimize the yield of product **2**, we studied the effect of **1**/$SnCl_2$ ratio and HCl concentration. The maximum (88%) yield of compound **2** was achieved with application of 4.5 equiv. of $SnCl_2$, which indicated that the cyclization occurred at the stage of reduction of nitro group to a hydroxylamino one. The optimal concentration of HCl was 0.5 mol dm^{-3}, while at higher concentrations the reaction was non-selective. It is worthwhile to note that previously[19] compound **2** was prepared by ten hour-long photocyclization of 4,6-dichloro-*N*,*N*′-di(pyridin-2-yl)benzene-1,3-diamine in 80% aqueous *tert*-butyl alcohol in the yield of 38%.



Scheme 1 *Reagents and conditions:* i, $SnCl_2 \cdot 2H_2O$, 4% HCl, 80% Pr^iOH, 40 °C, 15 min; ii, KNO_3, conc. H_2SO_4, 30 °C, 4 h, iii (for **4a**), $SnCl_2$, 36% HCl, 60 °C, 0.5 h; iv (for **4b**), $SnCl_2$, 36% HCl, 60 °C, 0.5 h, then $(EtCO)_2O$, DMF, 90 °C, 2 h; v, KNO_3, conc. H_2SO_4, 20 °C, 10 h.

† For the detailed synthetic procedures, see Online Supplementary Materials.

Substrate **2** readily underwent nitration at the 6-position with 1.2 equiv. of the electrophile at 30 °C for 4 h. The yield of 6-nitro derivative **3** was 79%. This compound was easily reduced to amine **4a** with $SnCl_2$ in concentrated HCl. The subsequent oxidation of compound **4a** should be carried out in an acidic medium since the pyridine ring included into pyrido[1,2-*a*]benzimidazole system is base-unstable and can easily undergo destruction.[20] At first, the $K_2Cr_2O_7$–H_2SO_4–H_2O system was tested as it is widely employed to convert aromatic amines to quinones.[21–24] The reaction was carried out at 5 °C since in acidic aqueous solutions $K_2Cr_2O_7$ initiates oxidative polymerization of aniline and its derivatives[25–27] containing both electron-donating[28] and electron-withdrawing groups.[29] In 20 h, quinone **5** was obtained in 43% yield. The KNO_3–conc. H_2SO_4 system, which is usually used as a nitrating mixture, was suggested as another oxidant.[30] Luckily, its application at 20 °C for 10 h did not cause formation of nitro derivative of **4a** but promoted formation of quinone system to afford target compound **5** in 74% yield. No nitro group was incorporated into the substrate or the product if the reaction temperature was raised to 100 °C or when starting from N-acylated derivative **4b** under similar conditions (20–50 °C, 2–8 h). In the latter case, quinone was not formed.

The structures of compounds **2**, **3** and **5** were studied by single-crystal X-ray diffraction analysis. The single crystals were grown by gradual cooling of solutions of the compounds in DMF or in the Pr^iOH–DMF mixture (1 : 1). The bond lengths and bond angles in compound **2**‡ (Figure 1) were quite close to the average values in pyrido[1,2-*a*]benzimidazoles.[31]

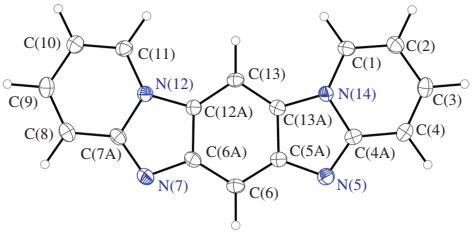


Figure 1 General view of dipyrido[1,2-*a*:1′,2′-*a*′]benzo[1,2-*d*:5,4-*d*]diimidazole **2** in a crystal. Anisotropic displacement parameters for non-hydrogen atoms are drawn at 50% probability.

‡ The single-crystal X-ray diffraction data were collected on Bruker SMART APEX II (for sample **2**) and Bruker APEX DUO (for samples **3** and **5**) diffractometers (both instruments were equipped with a CCD detector, graphite-monochromated MoKα radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2_{hkl} in anisotropic approximation with SHELX software package. Hydrogen atoms were placed in calculated positions and refined in riding model with $U_{iso}(H) = 1.2U_{eq}(C)$ of the connected carbon atom. Detailed crystallographic information is available in Online Supplementary Materials.

Crystal data for **2**. $C_{16}H_{10}N_4$ (M = 258.28), orthorhombic, space group *Pbca*, at 120 K: a = 8.3797(13), b = 13.613(2) and c = 20.377(3) Å, V = = 2324.5(6) Å^3, Z =8, d_{calc} = 1.476 g cm^{-3}, μ = 0.92 cm^{-1}. Total of 13570 reflections were measured and 2319 independent reflections were used in a further refinement. The refinement converged to wR_2 = 0.1073 and GOF = 1.014 for all independent reflections [R_1 = 0.0469 was calculated against F for 1522 observed reflections with $I > 2\sigma(I)$].

Crystal data for **3**. $C_{16}H_{11}N_5O_3$ (M = 321.30), monoclinic, space group $P2_1/n$, at 120 K: a = 7.9238(3), b = 11.6203(5) and c = 15.1992(7) Å, V = 1363.93(10) Å^3, Z = 4, d_{calc} = 1.565 g cm^{-3}, μ = 1.13 cm^{-1}. Total of 20142 reflections were measured and 3981 independent reflections were used in a further refinement. The refinement converged to wR_2 = 0.1235 and GOF = 1.025 for all independent reflections [R_1 = 0.0452 was calculated against F for 3096 observed reflections with $I > 2\sigma(I)$]. Hydrogen atoms of the solvating water molecule in **3** was found from difference Fourier synthesis and refined in isotropic approximation.

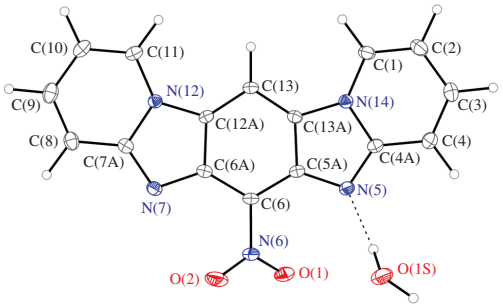


Figure 2 General view of 6-nitrodipyrido[1,2-*a*:1′,2′-*a*′]benzo[1,2-*d*:5,4-*d*]-diimidazole **3** in a crystal. Anisotropic displacement parameters for non-hydrogen atoms are drawn at 50% probability.

Incorporation of a nitro group into the molecule in case of compound **3** did not influence considerably on the molecule geometry. Compound **3** crystallized with one water molecule in the solvation shell to form an intermolecular hydrogen bond involving nitrogen atoms of the heterocycle [the average O···N(10) and O···N(12) distances are 2.8715(16) and 2.9003(16) Å, respectively] (Figure 2).‡

The bond lengths and bond angles in quinone **5** (Figure 3)‡ are very close to those observed in the structure of the centrosymmetric quinone reported by Yong *et al.*[5] The bonds with the C(6) and C(13) central atoms are elongated considerably with respect to those of unsaturated analogue **2**, namely, C(11)–C(10A) is 1.480(3) Å, C(11)–C(11A) is 1.484(3) Å [*cf.* 1.394(3) and 1.395(3) Å in **2**]; C(4B)–C(5) is 1.452(3) Å, C(5)–C(5A) is 1.449(3) Å [*cf.* 1.382(3) and 1.386(3) Å in **2**]. The bonds with the C(4B) and C(5A) carbon atoms bound with the nitrogen atom of the pyridine moiety are *ca.* 0.03 Å shorter; the same was also observed in the structure of the centrosymmetric quinone.[5] Note that the following bonds are shortened in the conjugated system in comparison with **2**, namely, N(10)–C(10A) is 1.352(2) Å, C(10A)–C(5A) is 1.377(3), N(12)–C(11A) is 1.353(2) Å and C(11A)–C(4B) is 1.380(3) Å. The molecule of **5** is nearly planar and very close to C_{2v} symmetry, but it is slightly twisted around the C(5)···C(11) line [the C(11A)–C(11)–C(5)–C(5A) dihedral angle is 177.8°]. The molecules in a crystal are arranged parallel to each other and bound by strong stacking interactions (C···C 3.2–3.5 Å) into a complex three-dimensional structure.

In summary, a simple and convenient synthesis of dipyrido-[1,2-*a*:1′,2′-*a*′]benzo[1,2-*d*:5,4-*d*]diimidazole and its conversion

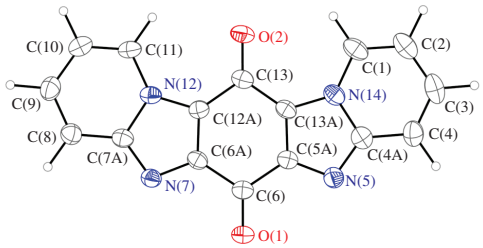


Figure 3 General view of dipyrido[1,2-*a*:1′,2′-*a*′]benzo[1,2-*d*:5,4-*d*]diimidazole-6,13-dione **5** in a crystal. Anisotropic displacement parameters for non-hydrogen atoms are drawn at 50% probability.

Crystal data for **5**. $C_{16}H_8N_4O_2$ (M = 288.26), monoclinic, space group $P2_1/c$, at 120 K: a = 11.549(3), b = 13.735(3) and c = 7.7401(19) Å, V = = 1227.5(7) Å^3, Z = 4, d_{calc} = 1.560 g cm^{-3}, μ = 1.08 cm^{-1}. Total of 13975 reflections were measured and 2971 independent reflections were used in a further refinement. The refinement converged to wR_2 = 0.1195 and GOF = 1.032 for all independent reflections [R_1 = 0.0522 was calculated against F for 1838 observed reflections with $I > 2\sigma(I)$].

CCDC 1490353–1490355 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

to the 6,13-oxo quinone were developed. The use of the oxidizing system KNO_3–conc. H_2SO_4 allowed us to perform the oxidation of the strongly electron-deficient heterocyclic amine into quinone under mild conditions without formation of side products.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.03.023.

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