Unexpected condensation of 4,5-dimethyl-1,2-phenylenediamine with phthalaldehyde to 4,5-dimethyldiisoindolo[2,1-*a*:1,2-*c*]quinoxaline-1,8-dione initiated by Ni^{II} complexes

Igor L. Eremenko,* Aleksei E. Malkov, Aleksei A. Sidorov, Grygory G. Aleksandrov and Ilya I. Moiseev

N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 954 1279; e-mail: ilerem@igic.ras.ru

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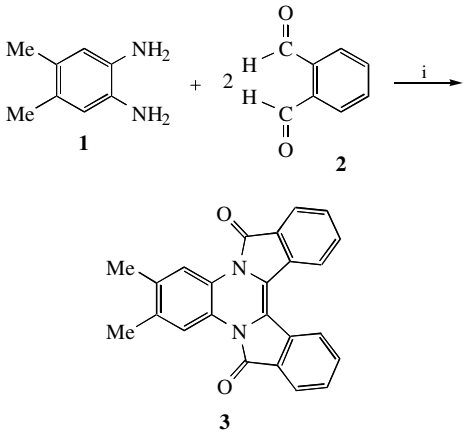
The title condensation initiated by $Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(OOCCMe_3)_{12}$ in toluene or $NiCl_2{\cdot}6H_2O$ in ethanol was studied, and the molecular structure of the product was found using X-ray diffraction.

The addition of amines to aldehydes is a general pathway towards imines.[1] The presence of aryl groups at nitrogen or carbon atoms is responsible for the stability of the compounds. The reaction is the best way to prepare Schiff bases and is often used to perform ring closure like in the Fridländer quinoline synthesis.[2]

In an attempt to synthesise a macrocyclic ligand from 4,5-dimethyl-1,2-phenylendiamine **1** and phthalaldehyde **2** in the presence of a Ni^{II} compound, we obtained unexpectedly 4,5-dimethyldiisoindolo[2,1-*a*:1,2-*c*]quinoxaline-1,8-dione **3**† (Scheme 1).

Reactants **1** and **2** and Ni^{II} nine-nuclear hydroxo pivalate cluster $Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(OOCCMe_3)_{12}$ **4**[3] (the reactant ratio **1**:**2**:[Ni_9] = 1:1:0.058) in toluene were allowed to react in air at 110 °C. Product **3** was isolated from the reaction solution as red crystals. The same result was found when $NiCl_2{\cdot}6H_2O$ in ethanol at 20 °C was used instead of cluster **4** in a toluene solution. The reaction does not take place in the absence of Ni^{II} complexes under the same conditions.

Compound **3** was characterised by X-ray diffraction data‡ (Figure 1). The planar molecule of **3** consists of four six-membered and two five-membered rings. Three peripheral six-membered rings are aryl systems exhibiting typical C–C bonding [1.370(5)–1.397(5) Å].[4] The central six-membered fragment contains two nitrogen atoms [N–C of 1.416(4)–1.427(4) Å] involved in the C–N bonding of neighbouring condensed five-membered rings. The last two contain two carbonyl C=O fragments [both are 1.225(4)Å].



Scheme 1 *Reagents and conditions*: i, $Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(OOCCMe_3)_{12}$, toluene, 110 °C or $NiCl_2{\cdot}6H_2O$, EtOH, 20 °C.

Formally, compound **3** is a condensation product of two dialdehyde molecules and a diamine molecule in spite of the initial 1:1 ratio between reactants. This unusual reaction is

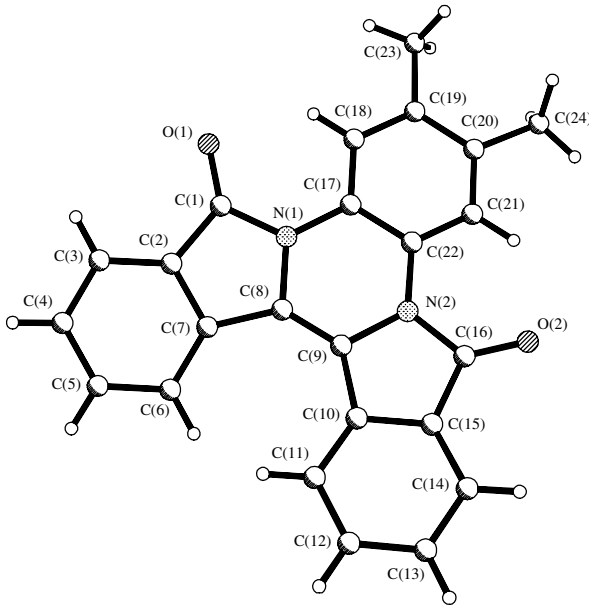


Figure 1 Molecular structure of 4,5-dimethyldiisoindolo[2,1-*a*:1,2-*c*]-quinoxaline-1,8-dione **3**.

† The reaction mixture consisting of the cluster $Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(OOCCMe_3)_{12}$ (0.6 g, 0.26 mmol), 4,5-dimethyl-1,2-phenylenediamine (0.62 g, 4.5 mmol) and phthalaldehyde (0.6 g, 4.6 mmol) in 20 ml of toluene was stirred for 0.5 h in air at 110 °C until a dark-red colour. The resulting solution was concentrated to 10 ml and applied to a column (5×20 cm) with Kieselgel 60. The red zone was eluted with ethanol (50 ml, R_f 0.90). The solution thus obtained was concentrated to 10 ml at 80 °C (0.1 Torr) and kept at 20 °C for 7 days. The precipitated red crystals of 4,5-dimethyldiisoindolo[2,1-*a*:1,2-*c*]quinoxaline-1,8-dione **3** were separated from the solution by decantation, washed with cold ethanol and dried in air. Yield 0.17 g (20%) (40% based on compound **2**). IR (ν/cm^{-1}): 3375 (w), 2972 (w), 2912 (w), 1696 (w), 1616 (vs), 1572 (s), 1484 (s), 1448 (s), 1364 (m), 1340 (m), 1292 (m), 1256 (w), 1192 (w), 1144 (s), 1084 (m), 1024 (w), 996 (w), 956 (s), 904 (m), 888 (m), 836 (m), 796 (m), 748 (w), 740 (w), 688 (vs), 620 (w), 588 (w), 516 (w), 492 (w), 408 (w). Found (%): C, 79.2; H, 4.47; N, 7.52. Calc. for $C_{24}H_{16}N_2O_2$ (%): C, 79.12; H, 4.39; N, 7.69.

The reaction was performed analogously in ethanol at room temperature with the use of $NiCl_2{\cdot}6H_2O$ as a catalyst and afforded **3** in 25% yield (50% based on compound **2**).

‡ *Crystal data for* **3**: $C_{24}H_{16}N_2O_2$, 0.22×0.19×0.15 mm, M = 364.39; red prismatic crystal, orthorombic, space group *Pbcn*, a = 20.066(18), b = = 11.980(12), c = 14.075(16) Å, V = 3383(6) Å^3; Z = 8, d_{calc} = 1.431 g cm^{-3}, μ(MoKα) = 0.092 mm^{-1}, F(000) = 1520. 3024 reflections collected at –160 °C on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector [graphite monochromator, MoKα radiation (λ = 0.71073 Å), ω scanning technique, scan step was 0.3°, frames were exposed for 30 s] using a standard procedure.[7] The structure was solved by direct methods and Fourier techniques, refined by full-matrix least-squares on F^2 data using SHELXS-97[8] and converted at R_1 = 0.0529, wR_2 = 0.0778.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 196699. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2003.

initiated by Ni^{II} atoms. However, the reaction of pyrrole-2,5-dialdehyde with the same diamine gives rise to a macrocyclic ligand.[5,6] Thus, the reaction seems to be effective only if the dialdehyde groups are in the 1,2- rather than 1,3-positions. The formation of compound **3** probably includes the stages of coordination and dissociation of initial organic molecules and formation of reactive intermediates and the final product. The reaction seems to involve an oxidation step. The Ni^{II} atoms as a catalyst and atmospheric oxygen or aldehyde groups as oxidants could be involved into the step.

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