Lanthanide triiodide-catalyzed amination of phthalonitrile. The structure of 1-isopropylamino-3-(isopropylimino)isoindole*

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The reactions of phthalonitrile with $MeNH_2$, Pr^nNH_2, and Pr^iNH_2 in the presence of catalytic amounts of LnI_3 (Ln = Nd or Dy) or $LnI_3(THF)_3$ (Ln = Gd or Nd) afford 1,3-bis(alkylimino)isoindolines (Alk = Me (**1**), Pr^n (**2**), or Pr^i (**3**), respectively). Under analogous conditions, 2-aminopyridine gives 1,3-bis(2-pyridylimino)isoindoline (**4**). The X-ray diffraction study of compound **3** showed that, in the crystalline state, this compound exists as the isomer, 1-isopropylamino-3-(isopropylimino)isoindole.

Key words: alkyliminoisoindolines, amines, lanthanide triiodides, primary amines, pyridyliminoisoindoline, catalysis.

1,3-Bis(alkylimino)isoindolines have attracted attention as specific tridentate ligands, whose rigid planar structure hinders the formation of a tetrahedral core with the result that complexes with another structure can be synthesized.[1,2] In addition, these compounds serve as components for the template synthesis of phthalocyanines and their metal complexes[3] used in many fields of medicine and engineering. Recently, isoindole derivatives have found new use. Thus, it was found that phenyl-substituted ethylcarbazolylisoindole has good charge-transport properties,[4] whereas indolizino[3,4,5-*ab*]isoindole derivatives show high electroluminescence activity.[5] Hence, these heterocyclic compounds can be considered as promising materials for organic light-emitting diodes. Nevertheless, in spite of considerable interest in isoindolines and their derivatives, the structures and physical properties of these compounds are poorly known. There are several methods for the synthesis of diiminoisoindolines.[6—10] The simplest method is based on the reaction of primary amines with phthalonitrile in the presence of catalytic amounts of alkaline-earth metal salts[9] or sulfur.[10] Recently, it has been found that lanthanide triiodides efficiently catalyze the amination of acetonitrile and benzonitrile giving rise to mono- and *N,N*′-disubstituted amidines.[11] As a continuation of this research, we found that lanthanide triiodides catalyze also the addition of amines to phthalonitrile; however, these reactions afford 1,3-bis(alkylimino)isoindolines. In the present study, we report the amination of phthalonitrile, discuss the possible reaction pathway, and describe the structure of one of the isoindolines.

Results and Discussion

The reactions of phthalonitrile with excess RNH_2 (R = Me, Pr^nNH_2, or Pr^iNH_2) in the presence of the NdI_3, DyI_3, $NdI_3(THF)_3$, or $GdI_3(THF)_3$ salts (1—1.5 mol) afford the corresponding 1,3-bis(alkylimino)isoindolines **1—3**. The reactions performed at room temperature for 6—8 h give products in 55—85% yields. However, the GLC monitoring showed that the 100% conversion of phthalonitrile in the reactions with $Pr^iNH_2/C_6H_4(CN)_2/NdI_3$ is achieved within 1 h at 40 °C. The addition of 2-aminopyridine at the C≡N bond of phthalonitrile proceeds with difficulty. After heating of the reaction mixture (a solution of the reagents in benzene) at 80 °C for 20 h, more than 30% of 2-aminopyridine remained unconsumed, and the yield of 1,3-bis(2-pyridylimino)isoindoline (**4**) was at most 20%. After removal of the excess amine and the resulting isoindoline, a wax-like emerald-green compound was always obtained as a residue in 5—10% yield based on the starting amount of $C_6H_4(CN)_2$. The UV spectra of this compound show a set of bands characteristic of phthalocyanine. It should be noted that the formation of phthalocyanine as a by-product is observed also in reactions catalyzed by alkaline earth metal salts.[9]

Lanthanide salts used as catalysts are isolated (after completion of the reactions) as complexes with amine and isoindoline that is formed in the reaction. These salts have the formulas $LnI_3(Pr^iNH_2)_4$ (Ln = Nd, Gd, or Dy),

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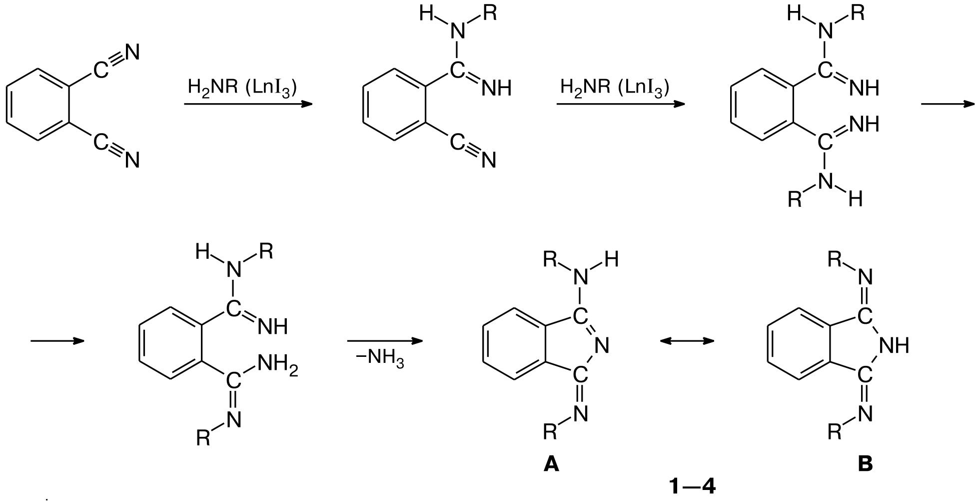
Scheme 1



R = Me (**1**), Pr^n (**2**), Pr^i (**3**), 2-C_5H_5N (**4**)

$NdI_3(Pr^nNH_2)_5$, and $NdI_3(MeNH_2)(L)$ (L is 1,3-bis(methylimino)isoindoline (**1**)). We suggested that these complexes serve as catalysts in the processes under consideration. To confirm this hypothesis, we performed the reaction of phthalonitrile with Pr^iNH_2 in the presence of $NdI_3(Pr^iNH_2)_4$ at room temperature. After 6 h, this reaction afforded 1,3-bis(isopropylimino)isoindoline (**3**) in 73% yield. The intermediates in these reactions were not identified. However, taking into account the similarity of the reactions of amines with acetonitrile[11] and phthalonitrile, the general reaction pathway for the formation of isoindoline can be represented by Scheme 1.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in two crystallographically independent molecules (I and II) of 1-isopropylamino-3-(isopropylimino)isoindole (**3**)

Parameter	Value	
	I	II
Bond	*d*/Å	
N(1)—C(1)	1.324(2)	1.323(2)
N(1)—C(8)	1.401(1)	1.403(1)
N(2)—C(1)	1.330(1)	1.333(1)
N(2)—C(9)	1.474(2)	1.473(2)
N(3)—C(8)	1.285(2)	1.286(2)
N(3)—C(12)	1.477(2)	1.474(2)
C(1)—C(2)	1.487(2)	1.482(2)
C(7)—C(8)	1.491(2)	1.484(2)
Angle	ω/deg	
C(1)—N(2)—C(9)	121.2(1)	122.1(1)
N(1)—C(1)—C(2)	112.8(1)	112.8(1)
C(1)—N(1)—C(8)	106.5(1)	106.6(1)
N(1)—C(8)—C(7)	109.3(1)	109.3(1)
C(8)—N(3)—C(12)	116.7(1)	117.0(1)

Ammonia that is eliminated in the last step of the reaction can be detected as ammonium chloride, which is formed upon the treatment of volatile products with HCl. Apparently, ammonia partially (5—10%) reacts with phthalonitrile to give phthalocyanine.

Isoindolines **2** and **3** can easily be isolated from the reaction mixture as colorless crystals by sublimation *in vacuo*. Products **1** and **4** can also be isolated by sublimation *in vacuo*; however, the reaction mixture should be pretreated with methanol (after the removal of the catalyst and excess amine).

Isoindoline **3** was studied by X-ray diffraction. Information on the structures of free 1,3-bis(imino)isoindolines[12—14] and transition metal and main-group metal complexes with isoindoline ligands[1,2,15—17] from the Cambridge Structural Database can be used for comparison with the structure of **3**. The X-ray diffraction study of compound **3** showed that there are two independent molecules with similar geometry per asymmetric unit (Table 1). The geometric characteristics of only one of these molecules are discussed below. The structure of the molecular core clearly indicates that, in the crystalline state, compound **3** exists as the isomer **A** with the hydrogen atom at the side nitrogen atom (Fig. 1).

Although the N(1)—C(1) and C(1)—N(2) bonds (1.324(2) and 1.330(1) Å, respectively) are shorter than the other C—N bonds, they are substantially longer than the true C=N double bond (C(8)—N(3), 1.285(2) Å), which is indicative of the substantial electron density delocalization in the N(1)—C(1)—N(2) fragment. In the N(1)—C(8)—N(3) group, the electron density delocalization is less pronounced. Thus, the N(1)—C(8) bond is 1.401(1) Å (1.403(1) Å), but the C(8)—N(3) bond is 1.285(2) Å (1.286(2) Å). The molecular structure of **3**

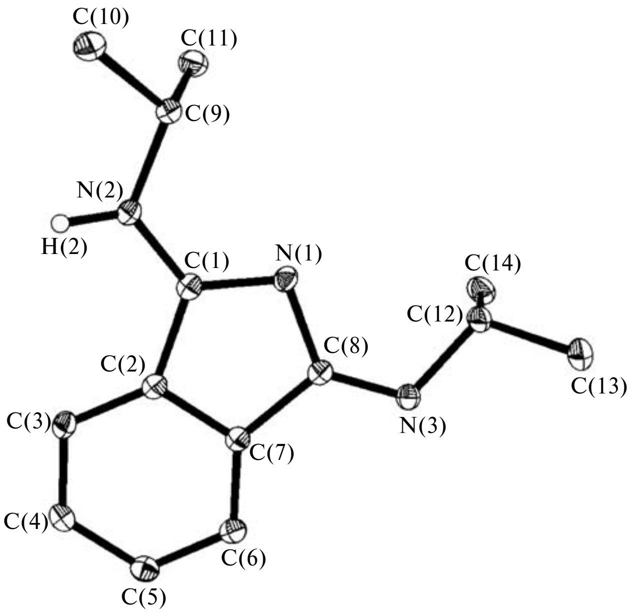


Fig. 1. Molecular structure of 1,3-bis(isopropylimino)isoindole (**3**).

is similar (except for the geometry of the substituents) to the structures of free 1,3-bis(imino)isoindoline,[12] 5-(1-aminoisoindol-3-ylideneamino)-1,3,4-thiadiazole-2(3*H*)-thione,[13] and *anti*-1-amino-3-(phenylimino)isoindoline,[14] although the electron density delocalization in the N(2)—C(1)—N(1)—C(8)—N(3) fragment in these compounds is somewhat different (judging from the bond lengths). It is interesting that isoindolines containing aromatic substituents, such as 1,3-bis(phenylimino)isoindoline[14] and 1,3-bis(2-pyridylimino)isoindoline, crystallize as the isomer **B**.[18] In the zinc and copper complexes with 1,3-bis[(5-methyl-2-pyridyl)imino]isoindoline ligands,[1] the differences in the C(1)—N(1) and N(1)—C(8) bond lengths (0.01 and 0.008 Å, respectively), as well as the differences in the C(1)—N(2) (0.017 Å) and C(8)—N(3) bond lengths (0.004 Å), are substantially smaller than the corresponding differences in isoindoline **3**, which is indicative of the substantial electron density delocalization in the ligands coordinated to the metal center.

In the crystal structure, molecules **3** form double chains through intermolecular N...H hydrogen bonds (Fig. 2).

Along the chains, these bonds are formed between the imino N atoms and the amino N atoms (N(3AA)...H(2BA) and N(3AC)...H(2BB), 2.120(15) Å; N(3BA)...H(2AB) and N(3BC)...H(2AC), 2.119(8) Å). These bonds are shorter than 2.3 Å and correspond to typical N—H hydrogen bonds.[19] The lateral bonds in the double chains (N(1AA)...H(11B), N(1AC)......H(11A), and N(1AB)... H(11C), 2.553(17) Å) are formed between the N atoms of the isoindole fragment from one chain and one of the H atoms of the methyl groups of the amino fragment from another chain. The length of these contacts (2.553(17) Å) is close to the length of the van der Waals intermolecular interaction (2.64 Å).[19]

The signals for the protons of the N—H groups in the ^{1}H NMR spectra of compounds **1**, **2**, and **3** (δ 5.2, 7.38, and 2.4, respectively) are substantially broadened, which confirms the well-known equilibrium between the isomers **A** and **B** of isoindolines in solution.

Unlike the above-mentioned indolizinoisoindole derivatives, the isoindolines synthesized in the present study do not show photo- and electroluminescence properties,

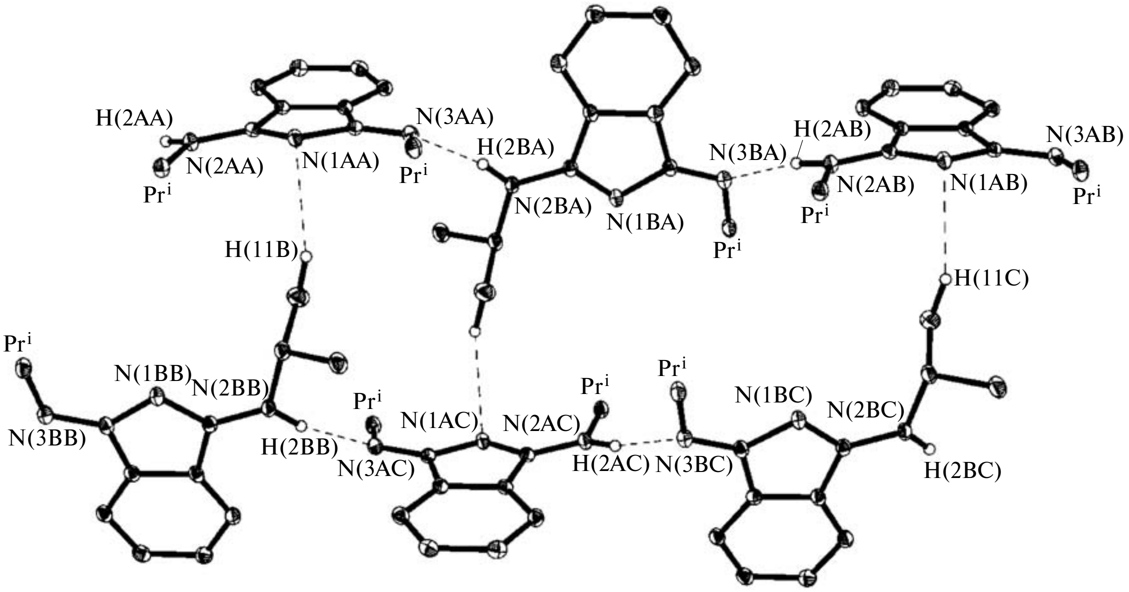


Fig. 2. Association of isoindoline molecules **3** in the crystal structure.

but exhibit noticeable p-type conductivity. The reactions of these compounds with lanthanide silylamides $Ln[N(SiMe_3)_2]_3$ afforded new complexes of composition $Ln(L)_3$ (L is 1,3-bis(imino)isoindoline). Investigations of the properties and structures of the latter compounds are presently underway.

Hence, we found that lanthanide triiodides LnI_3 efficiently catalyze the amination of phthalonitrile giving rise to 1,3-bis(alkylimino)isoindolines. Iodides containing coordinated THF have the same catalytic activity. The X-ray diffraction study of isoindoline **3** showed that, in the crystalline state, this compound exists as the isomer with the hydrogen atom at the terminal nitrogen atom, *viz*., as 1-isopropylamino-3-(isopropylimino)isoindole.

Experimental

Materials and methods. All reactions and operations were carried out *in vacuo* using the standard Schlenk technique. Commercial phthalonitrile and amines (Aldrich) were used. Methylamine was prepared from $MeNH_2 \cdot HCl$ by distillation over NaOH followed by condensation into a cold trap. The amine was treated with 5 mol.% NdI_2 before use. Other amines were dried with NdI_2 (3—5 mol.%, 10 min) immediately before use and then condensed into a reaction vessel *in vacuo*. Unsolvated lanthanide iodides LnI_3 were prepared by burning a Ln/I_2 mixture;[20] $GdI_3(THF)_3$ and $NdI_3(THF)_3$ were prepared by crystallization of GdI_3 and NdI_3, respectively, from THF. The ^1H NMR spectra were recorded in CD_3CN or $CDCl_3$ at 298 K on a Bruker DPX 200 spectrometer; the chemical shifts are expressed in ppm with respect to the chemical shifts of the residual protons of deuterated solvents. The IR spectra were recorded on a FSM 1201 Fourier-transform IR spectrometer as Nujol mulls. The UV-Vis spectra were measured on a Perkin Elmer Lambda 25 spectrometer. The GLC analysis of volatile products was carried out on a Tsvet-530 chromatograph. The melting points (uncorrected) were determined in sealed tubes.

1,3-Bis(methylimino)isoindoline (1). A NdI_3 powder (0.439 g, 0.84 mmol) was added to a solution of phthalonitrile (0.516 g, 4.03 mmol) in $MeNH_2$ (2.5 g, 80.5 mmol). The reaction mixture was stirred at 10 °C for 6 h, during which the solution turned emerald-green. The crystalline precipitate was filtered off and dried *in vacuo*. The product $NdI_3(MeNH_2)(L)$ (L is 1,3-bis(methylimino)isoindoline) was obtained in a yield of 0.48 g (79%). Found (%): I, 52.93; Nd, 19.87. $C_{11}H_{16}N_4I_3Nd$ (729.128). Calculated (%): I, 52.21; Nd, 19.78. IR, ν/cm^{-1}: 3147 (N—H); 1630 (C=N); 1588 (N—H); 1527 (C—C); 1115, 1020, 853, 711 (C—H). Volatile products and $MeNH_2$ were separated from the green filtrate by vacuum condensation. The non-crystalline yellow precipitate was treated with MeOH. The solution was separated from the precipitate by decantation. Then volatile products were removed from the solution by vacuum condensation. The yellow precipitate was sublimed at 100—120 °C (0.2 Torr). Isoindoline **1** was obtained in a yield of 0.361 g (52%) as colorless crystals, m.p. 175—177 °C (decomp.) (*cf.* lit. data[6]: m.p. 172 °C (decomp.)). Found (%): C, 69.30; H, 6.33. $C_{10}H_{11}N_3$ (173.118). Calculated (%): C, 69.38; H, 6.40. ^1H NMR ($CDCl_3$, 200 MHz), δ: 3.46 (s, 6 H, CH_3); 5.2 (br.s, 1 H, NH); 7.41—7.66 (m, AA´BB´, 4 H, C_6H_4). IR, ν/cm^{-1}: 3197, 3139 (N—H); 3050 (C—H); 1665 (C=N); 1584, 1531 (C=C, N—H); 1405, 1120, 1026, 860, 772 (C—H). UV (MeCN, 10^{-4} mol L^{-1}), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$): 258.8 (10.2), 305 (4.9).

1,3-Bis(propylimino)isoindoline (2). A mixture of phthalonitrile (1.39 g, 10.85 mmol), Pr^nNH_2 (4,59 g, 77.65 mmol), and a NdI_3 powder (0.72 g, 1.37 mmol) was stirred at room temperature for 8 h, after which a green solution and a precipitate of $NdI_3(Pr^nNH_2)_5$ were obtained. The precipitate was filtered off, washed with amine, and dried *in vacuo*; the yield was 1.077 g (96%). Found (%): I, 46.76; Nd, 17.79. $C_{15}H_{45}N_5I_3Nd$ (820.5). Calculated (%): I, 46.40; Nd, 17.58. IR, ν/cm^{-1}: 3462, 3293, 3235 (N—H); 1631 (C=N); 1565 (C—C); 1042, 938, 807, 700 (C—H). Propylamine and volatile products were removed from the filtrate by vacuum condensation. The residue was sublimed at 140 °C (0.2 Torr). 1,3-Bis(propylimino)isoindoline **2** was obtained in a yield of 0.671 g (27%) as colorless crystals, m.p. 110 °C. Found (%): C, 73.30; H, 8.52; N, 18.18. $C_{14}H_{19}N_3$ (229.32). Calculated (%): C, 73.32; H, 8.35; N, 18.32. ^1H NMR (CD_3CN, 200 MHz), δ: 1.01 (t, 6 H, CH_3; J = 7.4 Hz); 1.83 (m, 4 H, β-CH_2); 3.79 (t, 4 H, α-CH_2, J = 7.1 Hz); 7.38 (s, NH); 7.68—8.21 (m, AA´BB´, 4 H, C_6H_4). IR, ν/cm^{-1}: 3293, 3181 (N—H); 3031 (C—H); 1619 (C=N); 1311, 1234, 1157, 1096, 1011, 973, 769, 711, 669, 642. UV (MeCN, 10^{-4} mol L^{-1}), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$): 261 (26.5), 312 (14.4).

1,3-Bis(isopropylimino)isoindoline (3). A NdI_3 powder (0.36 g, 0.9 mmol) was added with stirring to a solution of phthalonitrile (0.774 g, 6.04 mmol) in Pr^iNH_2 (5.842 g, 98.8 mmol). The reaction mixture was magnetically stirred at room temperature for 8 h. The white crystalline precipitate of $NdI_3(Pr^iNH_2)_4$ was filtered off, washed with Pr^iNH_2 (2S5 mL), and dried *in vacuo*. The yield was 0.457 g (75.2%). Found (%): I, 50.33; Nd, 19.25. $C_{12}H_{36}N_4I_3Nd$ (761.39). Calculated (%): I, 50.00; Nd, 18.94. IR, ν/cm^{-1}: 3451, 3317 (N—H); 3038 (C—H); 1657 (C=C); 1603 (C=N); 1193, 720, 489. Unconsumed Pr^iNH_2 and volatile products were removed from the filtrate by vacuum condensation. The residue was sublimed at 140 °C (0.2 Torr). Isoindoline **3** was obtained in a yield of 0.713 g (52%) as colorless crystals, m.p. 159 °C. One crystal was used for X-ray diffraction study. Found (%): C, 73.33; H, 8.43. $C_{14}H_{19}N_3$ (229.32). Calculated (%): C, 73.32; H, 8.35. ^1H NMR (CD_3CN, 200 MHz), δ: 1.26 (d, 12 H, $CH(CH_3)_2$, J = 6.4 Hz); 2.4 (br.s, NH); 4.46 (sept, 2 H, $C\underline{H}(CH_3)_2$, J = 6.4 Hz); 7.45—7.68 (m, AA´BB´, 4 H, C_6H_4). IR, ν/cm^{-1}: 3223 (N—H); 3022 (C—H); 1649 (C=N); 1568, 1525 (C—H, N—H); 1342, 1324, 1283, 1225, 1154, 1140, 1129, 1098, 1017, 983, 947, 886, 843, 775, 715, 662, 646, 557, 555, 472. UV (MeCN, 10^{-4} mol L^{-1}), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$): 261 (9.4), 312 (5.1).

Isoindoline **3** was synthesized analogously from phthalonitrile (0.716 g, 5.6 mmol), Pr^iNH_2 (5.09 g, 86.1 mmol), and DyI_3 (0.137 g, 0.25 mmol) in a yield of 0.93 g (73%). 1,3-Bis(isopropylimino)isoindoline **3** was synthesized analogously from phthalonitrile (1.5 g, 1.2 mmol), Pr^iNH_2 (6.94 g, 117.4 mmol), and $GdI_3(THF)_3$ (0.9 g, 1.2 mmol) in a yield of 2.08 g (78%). Compound **3** was synthesized also from phthalonitrile (1.076 g, 8.4 mmol), Pr^iNH_2 (6.94 g, 117.4 mmol), and $NdI_3(THF)_3$ (1.058 g, 1.4 mmol) in a yield of 1.632 g (85%).

1,3-Bis(2-pyridylimino)isoindoline (4). A NdI_3 powder (0.84 g, 1.6 mmol) was added to a solution of phthalonitrile (0.526 g, 4.11 mmol) and 2-aminopyridine (0.773 g, 8.21 mmol) in ben-

Table 2. Crystallographic parameters and the X-ray diffraction data collection and refinement statistics for compound **3**

Parameter	Characteristics
Molecular formula	$C_{14}H_{19}N_3$
Molecular weight	229.32
T/K	100(2)
Crystal system	Triclinic
Space group	P-1
Unit cell parameters	
a/Å	8.5909(3)
b/Å	12.9617(5)
c/Å	13.4752(5)
α/deg	104.7590(10)
β/deg	108.4750(10)
γ/deg	101.3230(10)
V/Å^3	1311.91(8)
Z	4
d_{calc} /g cm^{-3}	1.161
μ/mm^{-1}	0.071
F(000)	496
Crystal dimensions/mm^3	0.20×0.13×0.07
θ-Scan range/deg	1.69—26.00
Number of observed reflections	11431
Number of independent reflections	5136
R_{int}	0.0334
Completeness of X-ray data (%)	99.7
Number of refined parameters	5136/1/459
Goodness-of-fit on F^2	1.001
R_1/wR_2 ($I > 2\sigma(I)$)	0.0470/0.1036
R_1/wR_2 (based on all parameters)	0.0759/0.1140
Residual electron density (e Å^{-3}), ρ_{max}/ρ_{min}	0.243/–0.174

zene (10 mL). The reaction mixture was magnetically stirred at 80 °C for 20 h, after which a green solution and a precipitate were obtained. The solution was removed by decantation, The precipitate was washed with benzene and dried *in vacuo*. Benzene and unconsumed 2-aminopyridine (0.274 g, 35%) were separated by condensation and sublimation *in vacuo*. The yellow precipitate was treated with MeOH (5 mL) and H_2O (5 mL). The yellow powder insoluble in water was dried and sublimed at 140—160 °C (0.2 Torr). Isoindoline **4** was obtained in a yield of 0.2 g (16%) as yellow crystals, m.p. 178—180 °C (*cf.* lit data[9]: m.p. 181—183 °C). Found (%): C, 72.66; H, 4.69; N, 22.65. $C_{18}H_{13}N_5$ (299.33). Calculated (%): C, 72.23; H, 4.38; N, 23.40. ^{1}H NMR ($CDCl_3$, 200 MHz), δ: pyridine protons 8.62 (dd, 1 H, J = 4.8 Hz, J = 1.3 Hz); 7.76 (td, 1 H, J = 7.5 Hz, J = 1.8 Hz); 7.46 (d, 1 H, J = 8.0 Hz); 7.12 (m, 1 H); 8.08 (m, AA´, 2 H, C_6H_4); 7.65 (m, BB´, 2 H, C_6H_4). IR, ν/cm^{-1}: 3254, 3200 (N—H); 3062, 3050, 3037 (C—H); 1630 (C=N); 1606 (N—H); 1583, 1553 (C—C, N—H); 1430, 1110, 1035, 853, 786 (C—H).

X-ray diffraction study. Single crystals of compound **3** were grown by sublimation. The X-ray diffraction data were collected on a SMART APEX diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, 100 K, ω—φ scanning technique). The crystallographic parameters and the X-ray diffraction data collection and refinement statistics for compound **3** are given in Table 2. The intensities were integrated using the SAINT program.[21] Absorption corrections were applied with the use of the SADABS program.[22] All calculations for the structure of **3** were performed with the use of the SHELXTL program package.[23] The positional and thermal parameters of nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located in Fourier maps and refined isotropically. Two crystallographically independent molecules **3** occupy general positions.

The atomic coordinates and complete data on the bond lengths and bond angles were deposited with the Cambridge Structural Database (CCDC 668002).

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