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New Indigoid Compounds by Reduction of *Bis*-Imidoylchlorides of Oxalic Acid – A Further Evidence for Dimeric Isocyanides?

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Summary. *Bis*-imidoylchlorides of oxalic acid react rapidly with magnesium shreds in dry *THF* under ultrasonic conditions to give 1,5-naphthyridine derivatives and the isomeric indigodianiles. Using a cross-over experiment the existence of key intermediates corresponding to dimeric isocyanides could be verified.

Keywords. Dimeric isocyanides; Indigodianil; 1,5-Naphthyridine; Spectroscopic properties.

Neue indigoide Verbindungen durch Reduktion von *Bis*-imidoylchloriden der Oxalsäure – ein weiterer Beweis für dimere Isocyanide?

Zusammenfassung. *Bis*-imidoylchloride der Oxalsäure reagieren mit Magnesiumspänen in trockenem *THF* und unter Ultraschallbedingungen zu den 1,5-Naphthyridinderivaten und den isomeren Indigodianilen. Durch Untersuchungen des Reaktionsmechanismus konnten Hinweise auf radikalische C_2-Schlüsselintermediate vom Typ dimerer Isocyanide erbracht werden.

Introduction

The well investigated isocyanides have an electronic configuration which resembles that of carbon monoxide. Unlike the latter, its imino derivatives have been known to undergo oligomerization processes. For instance, the blue-greenish color in neat phenyl isocyanide has been proved to be due to the presence of the tetramer, indigodianil [1]. The long-known trimer of benzoyl isocyanide, whose originally proposed four membered ring structure was doubted later, has now been established as an oxazolo[5,4-*d*]oxazine [2]. Probably, dimeric imidoyl isocyanides constitute intermediates in the ring closure reaction leading to 4,4′-*bis*-(quinazolines) [3].

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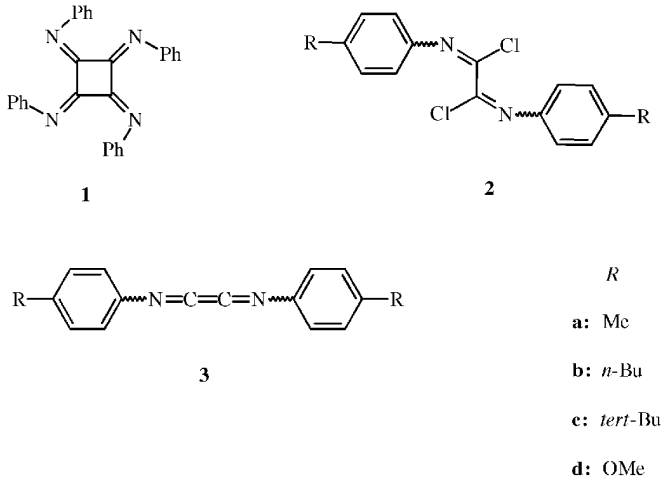


Scheme 1

Oligomeric as well as polymeric isocyanides have been reported in Ref. [4]. Among previous attempts to synthesize dimeric isocyanides we would like to mention especially those by *Bestmann* and coworkers using a heterometathesis reaction [5, 6]. However, the isolation of a dimer failed; furthermore, a corresponding tetramer, the tetraanile of cyclobutanetetrone (**1**), could be isolated as a stable red colored compound. Corresponding iminoethenethiones (RN=C=C=S) have been found to be stable on the microsecond time scale of neutralization-reionization mass spectroscopy experiments [7].

Bis-imidoylchlorides of oxalic acid (**2**), bearing an electron deficient 1,4-diaza-1,3-diene substructure, are easily accessible [8] and constitute a bielectrophilic building block with a well defined selectivity [9–11]. Recently, we have described the reduction of their aminolysis products, substituted oxalic amidines, by metallic lithium [12]. This reaction proceeds nearly quantitatively leading to starting compounds for tetraaminoethenes [13, 14]. This circumstance encouraged an attempt to explore the reduction of the above described imidoylchlorides to the to date unknown ethenediimines **3**.

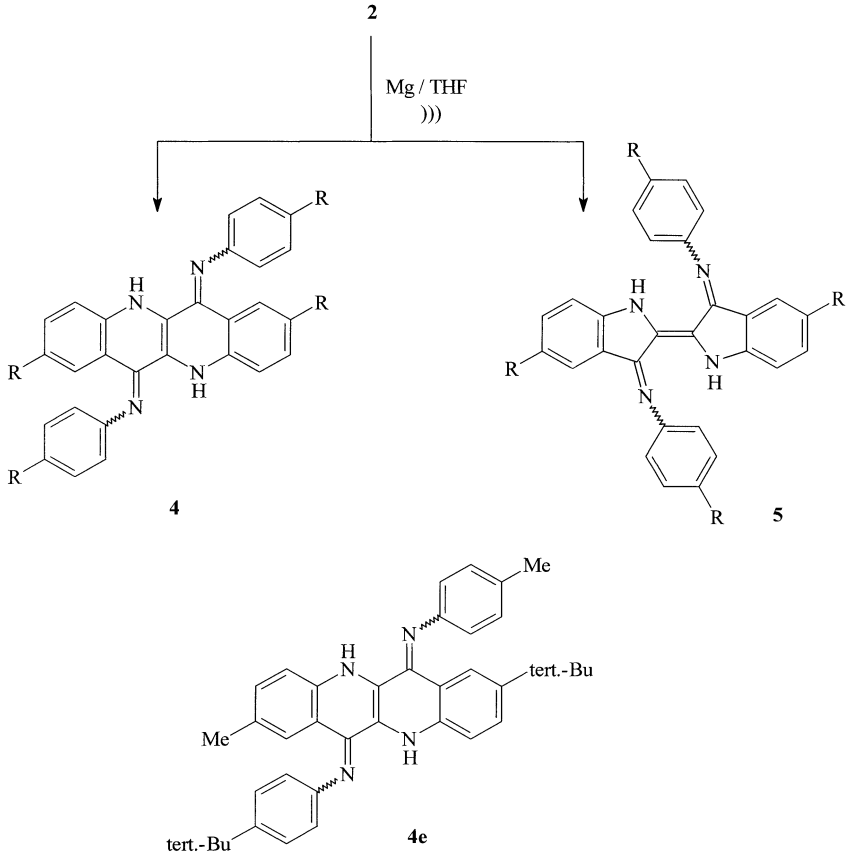
Results and Discussion

We made use of the concept of *Staudinger* [15] who attempted to reduce oxalyl bromide with metallic mercury to ethylenedione [16]. Instead of mercury, metallic magnesium under ultrasonic conditions led to the best results.

The *bis*-imidoylchlorides of type **2** react rapidly with magnesium shreds in dry *THF* under ultrasonic conditions to give in all cases deeply red colored solutions. After work-up by adding ethanol and filtration, the products could be purified by subsequent flash chromatography. When **2a–c** were treated under the conditions described above, in each case two products **4** and **5** could be isolated. Due to their better solubility, the compounds derived from **2b** and **2c** bearing the 4-*n*-butyl/4-*tert*-butyl groups allowed detailed spectroscopic investigations. Differentiation

between structures **1** and **4** was easily performed by comparison of IR and NMR data. Thus, the ^{1}H NMR spectrum of **4c** revealed two singlets for two different tert.-butyl groups at 1.1 and 1.35 ppm. The presence of two 1,4-disubstituted aryl residues and two 1,2,4-trisubstituted aromatic systems indicated by further signals as well as by 2D NMR experiments. Consequently, it was most likely that a twofold *ortho* ring closure had taken place which led to the 1,5-naphthyridine derivatives of type **4**. This annelation process was evidenced also by comparison of UV/Vis spectra with those of the known (5*H*,11*H*)-dibenzo[*b*,*g*][1,5]naphthyridine-6,12-diones [17]. Recently, the so called epindolidiones have been isolated as products of the thermal isomerization of indigo [18]. In contrast to these oxo compounds, the absorption band of the new arylimino derivatives **4** was bathochromically shifted by about 100 nm. It is worth mentioning that **4c**, a red microcrystalline compound, shows an intensive yellow fluorescence with a fluorescence quantum of yield of $\Phi_{FL} = 37\%$ in solution.

The solvent has a negligible influence on the absorption and fluorescence maxima of compounds **4a–d**. This behaviour is caused by their rigid structure which prevents changes in geometry of the molecules as a response to solvent polarity both in ground and excited states. The form of the absorption and fluorescence bands is similar to the spectra of the naphthyridinedione described by *Haucke* [18] but are shifted approximately 120 nm to the red due to the larger π-



Scheme 2

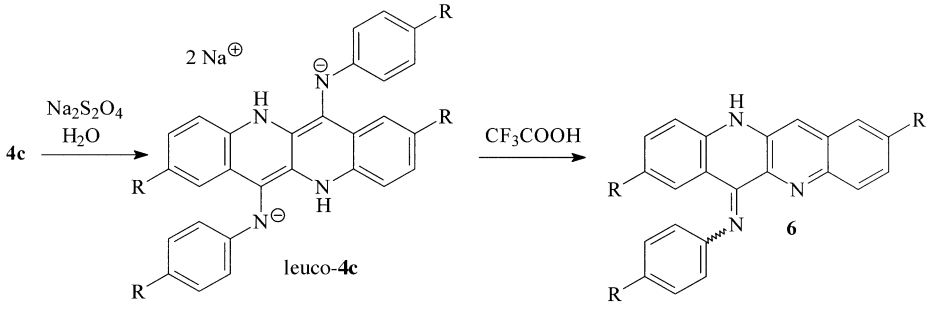
systems. The distance of 30 to 40 nm between the maxima of absorption and fluorescence can also be explained by the rigidity of the molecules and the resulting similarity of the geometries in ground and first excited state. **4d** exhibits the largest *Stokes* shift in all solvents where fluorescence occurs. In this compound, the free electron pairs of the oxygen atoms in the methoxy groups can interact with the π-systems of the aromatic rings. Thus, after excitation of the molecule a rotation around the C_{arom}–O-bond may stabilize the S_1 state, leading to a different geometry compared with the ground state. The result ist the observed slightly larger *Stokes* shift.

The photochemical behaviour of the compounds was also investigated **4a** and **4c** were irradiated with monochromatic light at a wavelength of 546 nm. A shrinking of the long wavelength absorption was observed together with an isosbestic point in the set of recorded absorption spectra. A graphical ranking analysis [19] resulted in a rank of ‚1' for this photoreaction. The conclusion can be drawn that a single product is obtained. The characterization of this photoproduct will be part of a forthcoming paper.

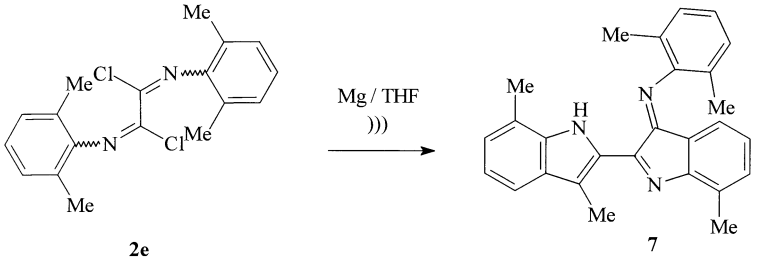
In regard to the well known redox properties of indigoid systems, it is possible to reduce the tetracyclic compounds **4** to their leuco derivatives by use of sodium dithionite. This reversible reaction is accompanied by a distinct color change from dark red to yellow. Exposure to air immediately reconstitutes the oxidized indigoid form. Treatment of leuco-**4c** with trifluoroacetic acid at room temperature led to a partial aromatization under formation of **6**.

In contrast to compounds **4** (yields 10–25%), the derivatives **5** could be isolated only in yields below 10%. Elemental analysis and MS data likewise revealed a tetrameric arrangement of the corresponding isocyanide residues as shown for the naphthyridines **4**. However, the deeply blue colored compounds which absorb between 665 and 669 nm pointed to another type of chromophore. The highly symmetrical nature became evident from the NMR spectra of compounds **5b,c** which revealed their structure to be consistent with that of the structural isomer of indigodianiles. Attempts to isolate further oligomeric isocyanides by varying the conditions of the reduction reaction were unsuccessful. In each case, beside changing amounts of **4** and **5** only polymeric material could be obtained.

Starting from *bis*-(2,6-dimethyl-phenyl)-oxalimidoylchloride (**2e**), the influence of methyl substituents at positions 2 and 6 of the *bis*-imidoylchloride was investigated. The reaction proceeded readily under the same conditions to give



Scheme 3



Scheme 4

small amounts of a new compound. After chromatographic purification, the deeply blue derivative **7** was isolated. The mass spectrum of **7** was in agreement with a trimeric structure with respect to 2,6-dimethylphenyl isocyanide. In its ^{1}H NMR spectrum only five peaks in the range of chemical shifts of methyl protons could be detected. However, final and unambiguous structural confirmation was achieved from an X-ray analysis obtained from a single crystal of **7** (Fig. 1). The result confirms the assumption that an aromatic methyl group was transformed into a quaternary carbon atom as well as that a methyl migration had taken place.

The suggested mechanistic pathway of the reduction of *bis*-imidoylchlorides **2** is given in Scheme 5. In the first step, a metal-induced dehalogenation reaction takes place. Comparable to its parent carbonyl compound ethylenedione [16], the unstable 'dimeric isocyanide' **3** should be present in its triplet state. Therefore, a subsequent dimerization of **3** forms the diradical **8**. Inferring the reaction of *bis*-imidoylchlorides **2a–c**, the reaction was accomplished by a 1,3-H-shift which finally yields aromatic derivatives. Consequently, an intramolecular *ortho* cyclization reaction is proposed. There are a few examples in the literature [20, 21] where the insertion reaction of isocyanides into heterocumulenes is described. In most cases, the authors have postulated an initiating 1,4-cycloaddition reaction leading to indolenines. However, our investigation allowed to detect persistent radicals by means of ESR spectroscopy as intermediates in each case which varied in the course of the reduction. Because of the poorly resolved spectra which did not show any hyperfine splitting a structure determination was not possible. All attempts to stabilize these radical species by spin-trapping or by cycloaddition reactions failed.

Preferably, this ring closure forms the naphthyridines **4a–d** in which both central carbon atoms are members of both fused six-ring systems. The indigodianiles **5a–c** were formed in a similiar manner where both carbon atoms combine two different five-membered rings. Using a cross-over experiment, the existence of key intermediates corresponding to **3** and **8** could be verified. Thus, an equimolar mixture of the imidoyl chlorides **2a** and **2c** was reduced under the conditions described above. Work-up of the reaction by flash chromatography yielded a mixture of the naphthyridines **4a**, **4c**, and only one mixed tetramer **4e** (detection by mass spectroscopy) which was formed by dimerization of **3a** with **3c**. As expected, the cyclization also proceeds in an *ipso* position occupied by the methyl group as in **2e**, affording **7** [20, 21]. Due to the radical character of the intermediates, a methyl group migration might be involved in the formation of **7**.

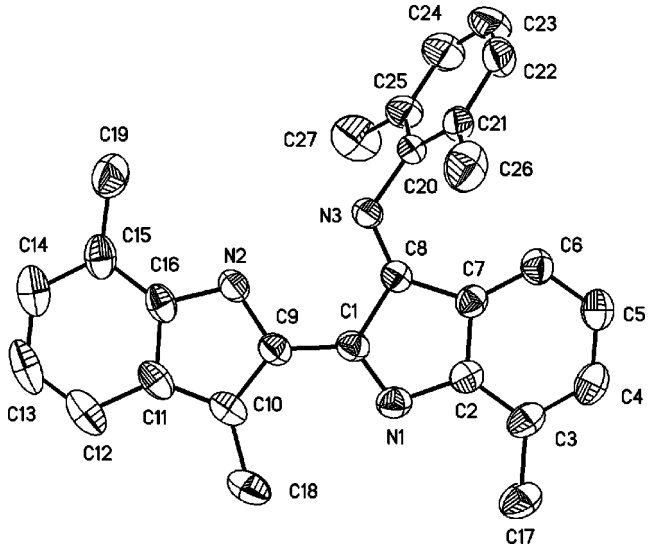
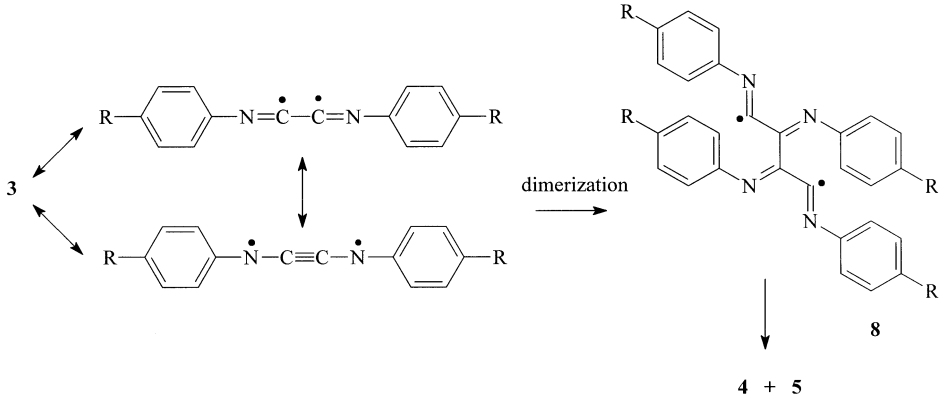


Fig. 1. X-Ray structure of compound **7**



Scheme 5

Experimental

CHN Analyses: Leco CHN automat CHNS-932; the results were in good agreement with the calculated values. Mass spectra: TRIO 2000 FISONS. UV/Vis spectra: Perkin-Elmer UV/Vis/NIR spectrophotometer. IR spectra: Nicolet Impact 400. Melting points (uncorrected): Cambridge Instruments micro hot stage Galen III according to Boetius. Chemical yields are not optimized. All reactions were monitored by TLC carried out on 0.25mm Merck Al_2O_3 plates ($60F_{254}$) using UV light for detection. ^1H and ^{13}C NMR spectra: Bruker AC 250 and DRX 400, 5 mm multinuclear probe head, ^1H NMR shifts relative to ^1H signals of the solvent.

X-Ray diffraction data for **7**: CAD4 diffractometer using graphite-monochromated MoK_α radiation. The crystal was mounted in a cold nitrogen stream ($-90°C$). Data were corrected for *Lorentz* and polarization effects, but not for absorption [22]. The structures were solved by direct methods (SHELXS [23]) and refined by full-matrix least squares techniques against F^2 (SHELXL-93 [24]). The hydrogen atoms were located from the difference *Fourier* map and refined isotropically; all non-hydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-ray Instruments,

Inc.) was used for structure representations. Crystal Data: $C_{27}H_{25}N_3$, $M_r = 391.5\ g \cdot mol^{-1}$, dark red cuboid, size $0.40 \times 0.33 \times 0.20\ mm^3$, triclinic, space group P^{-1}, $a = 9.390(1)$, $b = 11.567(1)$, $c = 11.892(1)$ Å, $\alpha = 109.77(1)$, $\beta = 101.32(1)$, $\gamma = 109.39(1)°$, $V = 1075.1$ (2) Å^3, $Z = 2$, $\rho_{calcd.} = 1.209\ g \cdot cm^{-3}$, $\mu(MoK_\alpha) = 0.72\ cm^{-1}$, F(000) = 416, 5122 reflections in $\pm h$, $\pm k$, $+l$ measured in the range $2.30° \leq \Theta \leq 27.41°$, 4887 independent reflections, $R_{int} = 0.021$, 3609 reflections with $F_o > 4\sigma(F_o)$, 371 parameters, $R = 0.051$, $wR^2 = 0.117$, $GOOF = 0.98$, largest difference peak: $0.20\ e \cdot Å^{-3}$. The results were deposited at the Cambridge Structural Data Center,12 Union Road, GB-Cambridge CB2 1EZ under the depository number CSD-406 872.

General procedure for the synthesis of compounds **4**, **5**, *and* **7**

In a 250 cm^3 Schlenk vessel 4.9 mmol of the corresponding *bis*-imidoylchloride **2** were dissolved under argon in *ca*. 30 cm^3 of *THF*, and 1.5 g Mg (62.5 mmol) was added. The mixture was brought to reaction in an ultrasonic bath (Bandelin SONOREX RK 156, 240 W). After 3–4 h, a dark red solution was obtained. To the solution, 30 cm^3 ethanol were added at room temperature. $MgCl_2$ was separated, and the filtrate was evaporated to dryness under vaccum. The residue was purified by column chromatography (compounds **4** and **5**: Merck Al_2O_3 90 (particle size 0.063–0.2 mm, 70-230 mesh ASTM, activity V), toluene/heptan = 7:3; compound **5c**: Fluka silica gel 60 (particle size 0.063–0.2 mm, 70-230 mesh ASTM), toluene).

N6,N12-Di-(4-methylphenyl)-2,8-dimethyl-5,6,11,12-tetrahydrodibenzo[b,g][1,5]-naphthyridine-6,12-diimine (**4a**; $C_{32}H_{28}N_4$)

Yield: 16% (0.19 g); m.p.: 340°C; ^{1}H NMR (250 MHz, δ, CF_3COOD): 2.82 (s, 6H), 2.89 (s, 6H), 7.65 (d, 2H, $J = 8.8$ Hz), 7.79 (d, 4H $J = 8.35$ Hz), 7.88 (d, 4H, $J = 8.3$ Hz), 8.23 (d, 2H, $J = 8.9$ Hz), 8.35 (s, 2H) ppm; ^{13}C NMR (63 MHz, δ CF_3COOD): 22.34, 22.84, 117.99, 121.86, 124.12, 125.18, 127.67, 134.39, 136.23, 139.68, 142.96, 143.32, 145.56, 159.20 ppm; MS (CI with H_2O): *m/z* (%) = 469 (45) [M^++1], 468 (20) [M^+], 364 (2), 340 (2), 223 (2), 134 (3), 108 (37), 93 (100); UV/Vis (dioxane): λ_{max} (lgε) = 542.4 (4.3), 508.0 (4.21) nm; IR (KBr): $\nu = 3290$, 3024, 2914, 1558, 1513, 1484, 1259 cm^{-1}.

N6,N12-Di-(4-n-butylphenyl)-2,8-di-n-butyl-5,6,11,12-tetrahydrodibenzo[b,g][1,5]-naphthyridine-6,12-diimine (**4b**; $C_{44}H_{52}N_4$)

Yield: 21% (0.33 g); m.p.: 307°C; ^{1}H NMR (400 MHz, δ, CD_2Cl_2): 0.87 (t, 6H, $J = 7.4$ Hz), 0.96 (t, 6H, $J = 7.4$ Hz), 1.27 (m, 4H), 1.40 (m, 4H), 1.48 (m, 4H), 1.62 (m, 4H), 2.53 (t, 4H, $J = 7.6$ Hz), 2.65 (t, 4H, $J = 7.7$ Hz), 7.20 (m, 7H), 7.42 (m, 4H), 7.56 (m, 1H), 7.91 (d, 2H, $J = 8.82$ Hz), 9.42 (s, 2H) ppm; ^{13}C NMR (100 MHz, δ, CD_2 Cl_2): 13.68, 13.72, 22.12, 22.26, 33.65, 33.83, 35.06, 35.50, 114.80, 119.67, 122.64, 123.42, 129.01, 129.48, 129.62, 131.82, 132.26, 135.99, 139.25, 140.53, 144.3, 147.53 ppm; MS (EI): *m/z* (%) = 637 (17) [M^++1], 636 (48) [M^+], 593 (6), 352 (100), 309 (14), 149 (12), 106 (18); UV/Vis (toluene): λ_{max} (lgε) = 542.4 (4.24), 508.0 (4.15) nm; IR (KBr): $\nu = 3289$, 2953, 2929, 1561, 1514, 1491, 1426, 1260 cm^{-1}.

N6,N12-Di-(4-tert-butyl-phenyl)-2,8-di-tert-butyl-5,6,11,12-tetrahydrodibenzo[b,g][1,5]-naphthyridine-6,12-diimine (**4c**; $C_{44}H_{52}N_4$)

Yield: 24% (0.38 g); m.p.: 337°C; ^{1}H NMR (250 MHz, δ *THF*-d_8): 1.13 (s, 18H), 1.37 (s, 18H), 7.27 (d, 4H, $J = 13.5$ Hz), 7.45 (d, 4H $J = 13.2$ Hz), 7.64 (m, 4H), 7.90 (d, 2H, $J = 14.2$ Hz) ppm; ^{13}C NMR (63 MHz, δ, *THF*-d_8): 31.00, 31.76, 35.14, 35.39, 114.97, 121.49, 124.43, 126.79, 129.22, 141.85, 144.20, 146.07, 148.37 ppm; MS (CI with H_2O): *m/z* (%) = 637 (24) [M^++1], 636 (10)

[M^+], 475 (2), 359 (2), 303 (1), 205 (2), 162 (7), 150 (39), 134 (15), 93 (100); UV/Vis (toluene): λ_{max} (lgε) = 468.8 (3.87), 501.6 (4.20), 536 (4.27) nm; IR (KBr): ν = 3440, 2959, 2904, 2869, 1552, 1516, 1481, 1260 cm^{-1}.

N6,N12-Di-(4-methoxyphenyl)-2,8-dimethoxy-5,6,11,12-tetrahydrodibenzo[b,g][1,5]-naphthyridin-6,12-diimine (**4d**; $C_{32}H_{28}N_4O_4$)

Yield: 18% (0.21 g); m.p.: 251°C; ^{1}H NMR (250 MHz, δ, CF_3COOD): 4.08 (s, 6H, OCH_3), 4.38 (s, 6H, OCH_3), 7.48–7.76 (m, 7H), 7.86–8.24 (m, 7H) ppm; ^{13}C NMR (62 MHz, δ, CF_3COOD): 57.91 (OCH_3), 52.32 (OCH_3), 104.42, 119.21, 119.52, 123.59, 129.56, 130.83, 131.62, 133.09, 135.05, 138.25, 148.87, 161.78, 163.19 ppm; MS (CI with H_2O): *m/z* (%) = 533 [M^++1] (100), 388 (20) 301 (10), 266 (46), 134 (27), 124 (47).

N3-(4-Methylphenyl)-5-methyl-2-(5-methyl-3-(4-methylphenylimino)-2,3-dihydro-1H-2-indolylidene)-3-indolinimine (**5a**; $C_{32}H_{28}N_4$)

Yield: 6% (70 mg); m.p.: 301°C; ^{1}H NMR (250 MHz, δ, $CDCl_3$): 2.17 (s, 6H), 2.40 (s, 6H), 6.81 (s, 2H), 7.13 (m, 12H), 9.8 (br s, 2H) ppm; ^{13}C NMR (63 MHz, δ, $CDCl_3$): 20.98, 21.27, 115.20, 119.19, 119.68, 122.43, 124.01, 124.63, 129.04, 129.60, 129.72, 131.46, 133.49, 144.13 ppm; MS (CI with H_2O) *m/z* (%) = 469 (44) [M^++1], 468 (11) [M^+], 391 (24), 340 (10), 279 (5), 223 (7), 162 (9), 134 (13), 108 (28), 93 (100); UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 622.4 (3.86), 668.8 (3.84) nm.

N3-(4-n-Butyl-phenyl)-5-methyl-2-(5-n-butyl-3-(4-n-butyl-phenylimino)-2,3-dihydro-1H-2-indolylidene)-3-indolinimine (**5b**; $C_{44}H_{52}N_4$)

Yield: 7% (95 mg); m.p.: 237°C; ^{1}H NMR (250 MHz, δ, $CDCl_3$): 0.85 (t, 6H, J = 11.5 Hz), 0.95 (t, 6H, J = 11.6 Hz), 1.69 (m, 12 H), 1.64 (m, 4H), 2.4 (t, 4H, J = 12.2 Hz), 2.66 (t, 4H, J = 11.9 Hz), 6.71 (s, 2H), 7.14 (m, 12H), 9.2 (br s, 1H) ppm; ^{13}C NMR (63 MHz, δ, $CDCl_3$): 13.88, 13.96, 22.02, 22.25, 33.49, 33.90, 35.13, 35.16, 115.00, 119.07, 119.67, 123.87, 124.21, 129.08, 130.96, 135.31, 138.64, 144.65, 148.29, 151.98 ppm; MS (CI with H_2O): *m/z* (%) = 637 (100) [M^++1], 593 (2), 466 (2), 391 (5), 335 (15), 319 (9), 279 (4), 204 (6), 150 (4); UV/Vis ($CHCl_3$): λ_{max} (lgε) = 616.0 (4.06), 668.8 (4.01), 738.4 (3.85) nm.

N3-(4-tert-Butyl-phenyl)-5-methyl-2-(5-tert-butyl-3-(4-tert-butyl-phenylimino)-2,3-dihydro-1H-2-indolylidene)-3-indolinimine (**5c**; $C_{44}H_{52}N_4$)

Yield: 9% (143 mg); m.p.: 310°C; ^{1}H NMR (400 MHz, δ, CD_2Cl_2): 1.11 (s, 18H), 1.38 (s, 18H), 6.82 (d, 2H, J = 1.9 Hz), 7.12 (d, 4H, J = 8.7 Hz), 7.14 (dd, 2H, J = 9.0 Hz), 7.31 (dd, 2H, J = 8.5 Hz), 7.47 (m, 4H) ppm; ^{13}C NMR (100 MHz, δ, CD_2Cl_2): 30.98, 31.21, 34.28, 114.21, 118.53, 119.49, 121.56, 125.96, 128.18, 134.28, 143.61, 144.93, 147.21, 147.80, 153.39 ppm; MS (CI with H_2O): *m/z* (%) = 637 (100) [M^++1], 636 (46) [M^+], 473 (3), 318 (50), 303 (15), 279 (6), 205 (10), 167 (8), 154 (20), 150 (10), 93 (32); UV/Vis ($CHCl_3$): λ_{max} (lgε) = 603.2 (4.16), 665.6 (4.02), 728.8 (3.90) nm.

N-(4-tert-Butyl-phenyl)-N-(2,8-di-tert-butyl-6,11-dihydrodibenzo[b,g][1,5]-naphthyridin-6-ylidene)-amine (**6**; $C_{34}H_{40}N_3$)

To a stirred solution of 1 g **4c** (1.5 mmol in 30 cm^3 *THF*) at room temperature a saturated aqueous solution of sodium dithionite was added. The colour of the reaction solution turned from red to yellow. Then 1 cm^3 of conc. CF_3COOH was added dropwise. The solution was extracted three times

with 30 cm^3 of toluene. After drying (Na_2SO_4), the solvent was evaporated and the residue was purified by column chromatography (Fluka silica gel 60 (particle size 0.063–0.2 mm, 70–230 mesh ASTM) toluene).

Yield: 79% (0.6 g); m.p.: 338°C; ^{1}H NMR (400 MHz, δ, CD_2Cl_2): 1.12 (s, 9H), 1.36 (s, 9H), 1.47 (s, 9H), 7.28 (d, 2H, $J = 8.5$ Hz), 7.45 (d, 2H, $J = 8.7$ Hz), 7.58 (d, 1H, $J = 1.8$ Hz), 7.69 (dd, 1H, $J = 11.3$ Hz), 7.85 (dd, 1H, $J = 11.3$ Hz), 7.91 (d, 1H, $J = 10.8$ Hz), 8.12 (d, 1H, $J = 9.2$ Hz), 8.91 (s, 1H) ppm; ^{13}C NMR (100 MHz, δ, CD_2Cl_2): 30.20, 30.45, 31.07, 34.40, 34.56, 35.00, 113.10, 120.67, 122.16, 123.73, 126.19, 128.69, 129.24, 129.57, 129.84, 130.05, 133.88, 134.78, 139.95, 140.48, 143.59, 145.50, 145.94, 148.36, 148.82, 150.63 ppm; MS (CI with H_2O): *m/z* (%) = 490 (100) [M^++1], 489 (28) [M^+], 432 (4), 313 (5), 257 (23), 246 (28), 230 (13), 190 (34), 150 (51), 134 (22), 93 (61); UV/Vis (toluene): λ_{max} (lgε) = 392.8 (3.88), 506.6 (3.94) nm.

N3-(2,6-Dimethylphenyl)-2-(3,7-dimethyl-1H-2-indolyl)-7-methyl-3H-3-indolimine (**7**; $C_{27}H_{25}N_3$)

Yield: 14% (179 mg); m.p.: 190°C; ^{1}H NMR (400 MHz, δ, CD_2Cl_2): 2.10 (s, 6H), 2.48 (s, 3H), 2.53 (s, 3H), 2.92 (s, 3H), 6.17 (d, 1H, $J = 7.3$ Hz), 6.75 (t, 1H, $J = 7.6$ Hz), 7.15 (m, 6H), 7.56 (d, 1H, $J = 7.5$ Hz) ppm; ^{13}C NMR (100 MHz, δ, CD_2Cl_2): 11.32, 15.55, 16.32, 17.82, 29.69, 117.78, 119.99, 121.00, 121.28, 122.49, 124.85, 125.00, 125.08, 126.27, 127.65, 128.10, 128.41, 130.75, 135.61, 137.31, 147.45, 157.34, 158.08, 168.73 ppm; MS (CI with H_2O): *m/z* (%) = 392 (100) [M^++1], 391 (16) [M^+], 390 (21), 286 (2), 261 (3), 220 (3), 196 (6), 93 (49); UV/Vis (heptane): λ_{max} (lgε) = 529.6 (3.82) nm.

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