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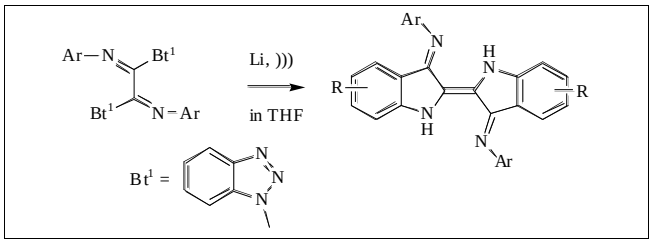

Bis-imidoylchlorides derived from oxalic acid can easily be transformed into the corresponding *bis*-imino benzotriazoles. The fact that benzotriazole is a well-established leaving group has been exploited for an improved synthesis of indigodianiles. Employing metallic lithium, the benzotriazoles can be converted in a cascade reaction into indigo *bis*-arylimines in yields up to 45%. Formation of the reduced form of dimeric isocyanides is suggested as a key step.

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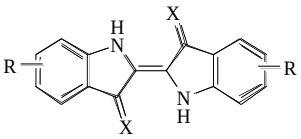
Introduction.

Indigoid systems show increasing importance as functional dyes due to their effective chromophoric systems connected with their chemical and thermal stability. A variation of the conjugated system can be achieved, *e.g.*, by transformation of both the carbonyl groups of **1** into the corresponding imines **2**. Indigo and its derivatives are in the center of interest as textile dyes and functional materials, however insufficient data is available pertaining to imines of type **2**.

Scheme 1

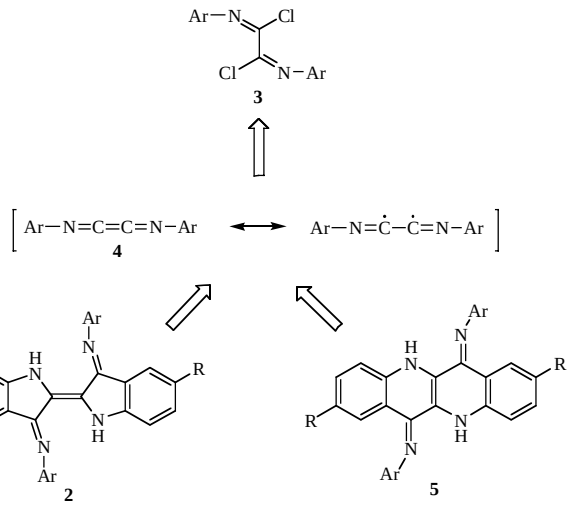


1 X = O
2 X = NAr

Already during the distillation of phenylisocyanide an intense blue-green color was observed and at first ascribed to the phenylisocyanide [1]. Publications in the following period [2] regarding the productive synthesis by heating indigo and aniline together with boric acid are in doubt. Detailed investigations of this crystalline substance which precipitated from pure phenylisocyanide, finally allowed the identification of the product resulting from the condensation of indigo and aniline as indigodianile [3].

In 1999 we reported a formation reaction of indigodianiles starting from *bis*-imidoylchlorides of oxalic acid **3** [4]. Such acylderivatives are valuable building blocks for numerous heterocyclic compounds which were often formed *via* cascade reactions [5]. We could demonstrate that by employing metallic magnesium as a reducing agent, the *bis*-imidoylchlorides **3** can serve as precursor molecules for dimeric isocyanides **4** [4]. In a smooth reaction, diarylimines of indigo **2** as well as their isomers, the diimines of epindolidione **5**, were isolated in low yields. Heterocumulenes of type **4** have already been postulated as intermediates [6], however, have never been isolated. Comparable to the corresponding oxa-analogue, ethenedione, they should possess a triplett structure in their ground state [7] and should therefore display the

Scheme 2

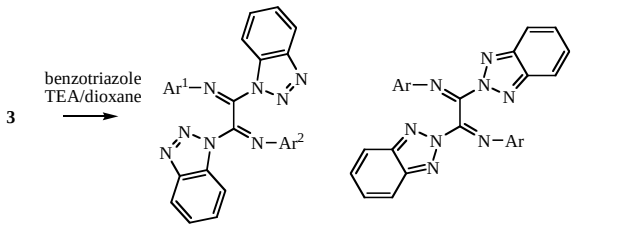


reactivity of a biradical. Recently, indigodianiles **2** (R = F, Ar = 4-FC_6H_4) have been isolated and structurally characterized as by-products in the course of a thermic induced oligomerization reaction of isocyanides [8].

Results and Discussion.

Not only the low yields which were obtained for **2** and **5**, but also their interesting spectral properties offered us incentives to search for better suitable starting materials for these compounds. A promising reaction was the replacement of both of the chlorides in bielectrophiles **3** by better leaving-groups which should minimize the amounts of by-products due to a lower nucleophilicity.

Scheme 3



6 a: $Ar^1/Ar^2 = C_6H_5$
6 b: Ar^1/Ar^2 = 4-MeC_6H_4
6 c: Ar^1/Ar^2 = 4-*tert*BuC_6H_4
6 d: Ar^1/Ar^2 = 4-BrC_6H_4
6 e: Ar^1/Ar^2 = 3-$CF_3C_6H_4$
6 f: Ar^1/Ar^2 = 1-naphthyl
6 g: Ar^1 = 4-MeC_6H_4 Ar^2 = 2-BrC_6H_4
6 h: Ar = 2,4,6-$Me_3C_6H_2$

Benzotriazole, which is extensively applied in organic synthesis, seemed to be the most promising candidate [9]. A series of imidoyl derivatives of benzotriazole has already been shown to be a valuable precursor molecule for the construction of new heterocyclic systems. By means of these acyl-equivalents a great variety of imidates and thioimidates [10], guanidines [10] as well as ketones [11] and several heteroaromatics [12] could be synthesized. *Bis*-phenylimidoyl benzotriazole **6a**, for example, is easily accessible *via* the reaction of oxalic acid anilide with *in-situ* generated sulfinyl *bis*-benzotriazole in the presence of trimethylchlorosilane with 86% yield [10,11,13]. Due to the fact that imidoylchlorides **3** are well-established in our group [14], we alternatively employed their substitution reaction with benzotriazole. Upon heating derivatives **3** with a small excess of benzotriazole together with triethylamine under reflux in dioxane, the *bis*-imidoylbenzotriazoles of type **6** are prepared in high yield.

The procedure results in the formation of 1-benzotriazoles with a high regioselectivity (Bt^1 as the exclusive regioisomer in nearly all cases) as could be determined *via* NMR spectroscopy. The 2-regioisomer (Bt^2) could be detected only for the sterically demanding mesityl group in derivative **6h**, in addition to a mixed (1- and 2-regioisomer) product. Furthermore, the non-symmetric *bis*-benzotriazole **6g** (Ar^1=4-$CH_3C_6H_4$, Ar^2=2-BrC_6H_4) was prepared in this manner.

In contrast to the starting material **3** the new bifunctional benzotriazoles of type **6** are crystalline pale-yellow compounds which are stable against hydrolysis. The synthesis starting from *bis*-imidoylchlorides **3** has been optimized and now tolerates a great variety of substituents. In contrast to the earlier described protocol [10], a smaller amount of benzotriazole (2 equivalents instead of 6) was employed.

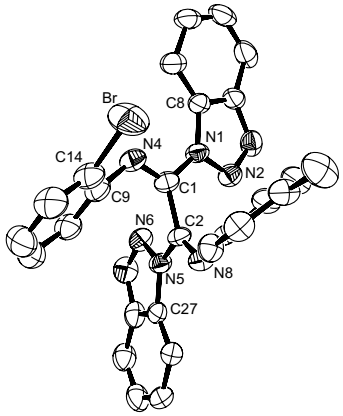


Figure 1. ORTEP drawing of the molecule **6g** [16]: Selected bond lengths C1-C2 (1.512(8) Å), C1-N1 (1.410(8) Å), C1-N4 (1.255(7) Å), C2-N5 (1.403(7) Å), C2-N8 (1.261(7) Å)

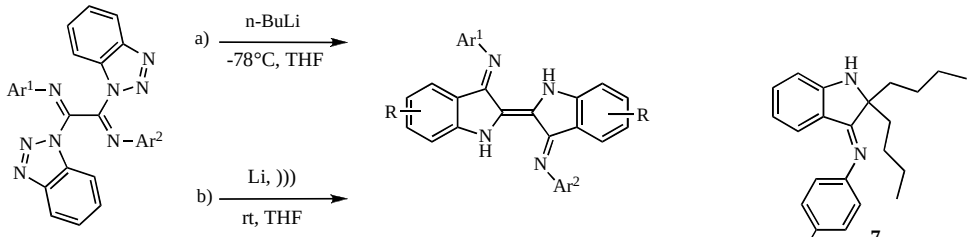
Furthermore, an X-ray structural analysis could be obtained from single crystals (from DMSO) of **6g**, the result of which is depicted in Figure 1. In comparison to the starting material of type **3**, this crystal structure revealed two essential distinctions. The planes of the amidine units N4-C1-N1 and N8-C2-N5 are considerably twisted with approximately 80° (*bis*-(2,5-diisopropyl-phenylimidoylchloride: 6° [15]). As a consequence, the central C-C bond in **6g** is slightly extended (1.512(8) Å, **3**: 1.495 Å). The bond lengths between the central carbon and the new introduced leaving groups are fundamentally shorter (1.410(8)Å) than the carbon-chlorine bonds in derivatives **3** (1.752 Å).

These crystal data make them promising candidates for experiments for the generation of dimeric isocyanides. Firstly, solutions of benzotriazoles **6a-c** and **6f** were treated with *n*-BuLi in order to test the quality of the leaving groups. Even at -78°C, the reaction resulted in a deep red/brown mixture which became light brown-yellowish for a short time during the warm-up period. On contact with air, the color immediately changed to deep blue and the indigodianiles of type **2** could be detected by TLC. The isolated yields for compounds **2** were in the range of approx. 10% and therefore somewhat higher than

reported starting from **3** [4]. The halogen substituted derivatives **6d, e** were reacted similarly. In this case, only tarry-like materials were isolated which most likely resulted from the competition of the halogen-lithium exchange followed by oligomerization reactions. However, for the benzotriazole **6g** a bromine-lithium exchange in the desired position seems to be the key-step for an *ortho*-cyclization to give a small amount of indolone derivative **7** *via* a cascade-reaction.

Monitoring of both formation reactions by ESR-spectroscopy displayed different radical species. Despite well-resolved spectra with a hyperfine-structure, the structural assignment is difficult. Spectra of different derivatives of type **6** are nearly identical. Most likely the radicals formed in both reaction pathways derive from benzotriazole derivatives [18]. Taking these findings into account, the following mechanism is proposed for the reaction with metallic lithium. Upon step-wise cleavage

Scheme 4



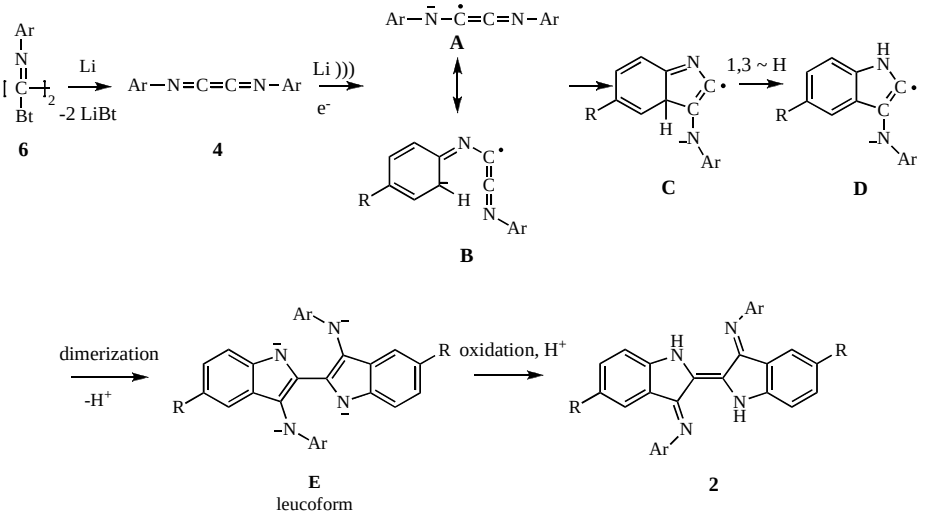
6 a: $Ar^1/Ar^2 = C_6H_5$
6 b: $Ar^1/Ar^2 = 4\text{-}MeC_6H_4$
6 c: $Ar^1/Ar^2 = 4\text{-}tertBuC_6H_4$
6 f: Ar^1/Ar^2 = 1-naphthyl
6 g: $Ar^1 = 4\text{-}MeC_6H_4$ $Ar^2 = 2\text{-}BrC_6H_4$

2 a: $Ar^1/Ar^2 = C_6H_5$ R = H
2 b: $Ar^1/Ar^2 = 4\text{-}MeC_6H_4$ R = Me
2 c: $Ar^1/Ar^2 = 4\text{-}tertBuC_6H_4$ R = *tert*Bu
2 d: Ar^1/Ar^2 = 1-naphthyl R = benz[*g*]

According to earlier experiments [4,17], the benzotriazoles **6** reacted with metallic lithium under ultrasonic irradiation. Already at the start of the reaction, a rapid change in color of the solution from reddish brown to finally deep green could be observed. Usually, the reaction reached completion after 30 minutes and no starting material could be detected by TLC. Treatment of the mixture with methanol yielded indigodianiles **2** up to 45% as well as polymeric material. Elemental analyses and NMR data of the deep blue-green compounds were in agreement with the structure of dianiles of type **2**.

of both benzotriazole units the dimeric isocyanides **4** were generated. These predicted and *in situ* generated intermediates are not stable enough to be detected. Immediately, the reduction with lithium forms the radical anion **A** *via* single-electron transfer step and is stabilized by its non-aromatic mesomeric form **B**. Thereafter, common cyclization reaction (**C**) followed by a 1,3-hydride shift which gives **D** takes place. The dimerization reaction of this radical may furnish **E** which can also be regarded as the leuco-form of the dianiles **2**. Finally, on contact with air and methanol, an oxidation/protonation-

Scheme 5



step produces **2**. It is not obvious at which stage (**A** or **D**) dimerization takes places to form the final products.

Other well-established one-electron transfer reagents showed different results. Whereas sodium naphthalenide showed no reaction with **6**, lithium di-*tert*.-butyl-biphenylide gave the dianiles **2**, however in poorer yields.

EXPERIMENTAL

Reactions were monitored by tlc, carried out on 0.2 mm Merck silica gel plates (60 F_{254}) or Merck Aluminium sheets Aluminium oxide (150 F_{254}) using uv light. Column chromatography was carried out on Merck silica gel 60 (0.040 – 0.063 mm) or Merck neutral alumina 90 (0.063 – 0.0209 mm; activity V). ^{1}H- and ^{13}C-nmr spectra were obtained on a Bruker DRX 400 or AVANCE 400, Bruker AC 250 or AVANCE 200 spectrometer. The remaining protons of the deuterated solvents were used as internal standard. The esr spectra were recorded with a Bruker ESP 300 E spectrometer. Melting points are measured with a Galen III apparatus (Boëtius system) and are uncorrected. uv/vis spectra were recorded on a UNICAM UV 500 spectrophotometer. ir: Digital Division FTS 25 from BioRad. Ms spectra were taken from measurements on a Finnigan MAT SAQ 710 mass spectrometer or TRIO 2000 from FISONS. Elemental analyses were carried out in-house with an automatic analyzer LECO CHNS 932. Crystal Structure Determination: The intensity data for the compound was collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption [19,20]. The structure was solved by direct methods (SHELXS [21]) and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97 [22]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically [22]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

The bis-imidoylchlorides **3a-h** and **3f** were synthesized according to literature [23]. Other reagents were commercially available and were used without further purification. All solvents were of reagent grade and were dried and distilled before use using standard techniques.

General Procedure for *Bis*-(imidoylbenzotriazoles) of Oxalic acid.

Bis-(arylimidoylchlorides) **3a-h**, 10 mmol, triethylamine, 30 mmol and 1*H*-benzotriazole, 25 mmol, were heated under reflux in 80 ml of dioxane for several hours (maximum 72 hours) and the progress of the reaction was monitored by tlc (silicagel, toluene). The precipitate was filtered off. The solvent was removed *in vacuo* and the residue was recrystallised from ethanol/methylenchloride to give pure derivatives **6a-h** (yields 75-95%).

Bis-(phenylimidoyl-1-benzotriazole) (**6a**).

This compound was obtained as pale yellow solid, 3.9 g, (88%), mp 187°C (87°C [13]); ir (ATR): 3060, 3033 (w) (arC-H), 1650 (m) (C=N) cm^{-1}; ^{1}H nmr (200 MHz, $CDCl_3$): δ 8.46 (d, J = 8.2 Hz, 2H), 8.15 (d, J = 8.4 Hz, 2H), 7.68 (t, J = 7.5 Hz, 2H), 7.55 (t, J = 7.5 Hz, 2H), 7.17-7.11 (m, 6H), 6.62-6.55 ppm (m, 4H); ^{13}C nmr (50 MHz, $CDCl_3$): δ 146.1 (N=C-C=N), 144.9, 142.5, 130.6, 129.6, 128.6, 125.9, 125.6, 119.9, 119.8, 114.6 (aryl) ppm; ms: m/z (DCI with H_2O) 443 (100) (M^++H^+), 415 (10), 388 (35), 385 (45), 324 (100), 312 (28), 296 (23), 284 (10), 241 (58), 221 (80), 193 (35), 166 (10), 120 (10), 96 (35), 90 (20), 78 (30).

Anal. Calcd. for $C_{26}H_{18}N_8$: C, 70.58; H, 4.10; N, 25.32. Found: C, 70.21; H, 4.05; N, 24.95.

Bis-(4-tolylimidoyl-1-benzotriazole) (**6b**).

This compound was obtained as pale yellow solid, 4.5 g, (95%), mp 215°C; ir (ATR): 3029, 2918 (w) (arC-H), 1645 (m) (C=N) cm^{-1}; ^{1}H nmr (250 MHz, $CDCl_3$): δ 8.38 (d, J = 8.3 Hz, 2H), 8.05 (d, J = 8.2 Hz, 2H), 7.59 (t, J = 7.7 Hz, 2H), 7.46 (t, J = 7.4 Hz, 2H), 6.87 (d, J = 8.3 Hz, 4H), 6.43 (d, J = 8.3 Hz, 4H), 2.21 ppm (s, 6H); ^{13}C nmr (63 MHz, $CDCl_3$): δ 146.3 (N=C-C=N), 142.7, 135.7, 130.9, 129.9, 129.5, 126.2, 120.3, 120.1, 119.8, 115.1 (aryl), 21.0 (CH_3) ppm; ms: m/z (DEI) 470 (7) (M^+), 413 (100), 399 (7), 324 (70), 308 (10), 268 (80), 235 (20), 207 (95), 192 (65), 180 (30), 134 (10), 117 (25), 107 (35), 91 (100), 65 (30).

Anal. Calcd. for $C_{28}H_{22}N_8$: C, 71.47, H, 4.71, N, 23.81. Found: C, 71.27, H, 5.00, N, 23.75.

Bis-(4-*tert*butylphenylimidoyl-1-benzotriazole) (**6c**).

This compound was obtained as pale yellow solid, 5 g (90%), mp 209°C; ir (ATR): 3034 (w) (arC-H), 1654 (m) (C=N) cm^{-1}; ^{1}H nmr (250 MHz, $CDCl_3$): δ 8.45 (d, J = 8.3 Hz, 2H), 8.13 (d, J = 8.2 Hz, 2H), 7.67 (t, J = 7.5 Hz, 2H), 7.54 (t, J = 7.2 Hz, 2H), 7.13 (d, J = 8.5 Hz, 4H), 6.51 (d, J = 8.5 Hz, 4H), 1.29 ppm (s, 18H); ^{13}C nmr (63 MHz, $CDCl_3$): δ 149.2 (N=C-C=N), 146.2, 142.5, 142.3, 131.0, 129.7, 126.1, 125.7, 120.1, 119.9, 115.0 (aryl), 34.4 (C_{quat}), 31.3 (CH_3) ppm; ms: m/z (DEI) 554 (1) (M^+), 525 (0.5), 497 (60), 193 (70), 144 (80), 116 (90), 57 (100).

Anal. Calcd. for $C_{34}H_{34}N_8$: C, 73.62; H, 6.18; N, 20.20. Found: C, 73.97; H, 6.47; N, 20.05.

Bis-(1-naphthylimidoyl-1-benzotriazole) (**6f**).

This compound was obtained as pale yellow solid, 4.6 g, (86%), mp 276°C; ir (ATR): 3053 (w) (arC-H), 1666 (m) (C=N) cm^{-1}; ^{1}H nmr (250 MHz, $CDCl_3$): δ 8.57 (d, J = 8.2 Hz, 2H), 8.21 (d, J = 8.3 Hz, 2H), 7.77-7.56 (m, 4H), 7.37-7.25 (m, 4H), 7.08-7.02 (m, 4H), 6.85-6.81 ppm (m, 6H); ^{13}C nmr (50 MHz, $CDCl_3$): δ 146.1 (N=C-C=N), 142.5, 141.6, 133.0, 130.8, 129.8, 128.6, 126.7, 126.2, 126.0, 125.5, 124.8, 124.6, 121.7, 119.8, 114.7, 112.6 (aryl) ppm; ms: m/z (DEI) 542 (0.3) (M^+), 519 (0.2), 485 (20), 396 (10), 344 (10), 243 (60), 216 (75), 153 (100), 127 (60).

Anal. Calcd. for $C_{34}H_{22}N_8$: C, 75.26; H, 4.09; N, 20.65. Found: C, 75.39; H, 4.14; N, 19.10.

Bis-(3-trifluoromethylphenylimidoyl-1-benzotriazole) (**6e**).

This compound was obtained as pale yellow crystals, 4.7g (81%), mp 145°C; ir (ATR): 1661 (m) (C=N) cm^{-1}; ^{1}H nmr (250 MHz, $CDCl_3$): δ 8.40 (d, J = 8.2 Hz, 2H), 8.18 (d, J = 8.2 Hz, 2H), 7.71 (t, J = 7.7 Hz, 2H), 7.59 (t, J = 7.7 Hz, 2H), 7.41 (d, J = 7.9 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 6.83 (d, J = 7.9 Hz, 2H), 6.74 ppm (s, 2H); ^{13}C nmr (63 MHz, $CDCl_3$): 146.5 (N=C-C=N), 145.4, 143.8, 131.8 (q, J_{CF} = 33 Hz) (C-CF_3), 130.7, 130.5, 129.9, 126.8, 123.4 (q, J_{CF} = 273 Hz) (CF_3), 122.9, 120.5, 117.9,

114.8 (aryl) ppm; ms: m/z (DEI) 578 (0.3), 521 (25), 261 (50), 145 (70), 90 (100).

Anal. Calcd. for $C_{28}H_{16}F_6N_8$: C, 58.14; H, 2.79; N, 19.37. Found: C, 57.90; H, 2.75; N, 19.08.

Bis-(4-bromophenylimidoyl-1-benzotriazole) (**6d**).

This compound was obtained as pale yellow solid, 4.6 g, (77%), mp 230°C; ir (ATR): 3067 (w) (arC-H), 1650 (m) (C=N) cm^{-1}; ^1H nmr (250 MHz, $CDCl_3$): δ 8.33 (d, J = 8.3 Hz, 2H), 8.07 (d, J = 8.2 Hz, 2H), 7.62 (t, J = 7.7 Hz, 2H), 7.49 (t, J = 7.7 Hz, 2H), 7.22 (d, J = 8.7 Hz, 4H), 6.41 ppm (d, J = 8.7 Hz, 4H); ^{13}C nmr (63 MHz, $CDCl_3$): δ 146.3 (N=C-C=N), 144.1, 143.1, 132.1, 130.7, 130.3, 126.6, 122.0, 120.3, 119.6, 114.9 (aryl) ppm; ms: m/z (DEI) 600 (1) (M^+), 543 (10), 454 (3), 389 (10), 273 (35), 192 (100), 157 (40), 90 (80).

Anal. Calcd. for $C_{26}H_{16}Br_2N_8$: C, 52.02; H, 2.69; N, 18.67; Br, 26.62. Found: C, 52.25; H, 2.81; N, 18.39; Br, 26.18.

N^1-(2-Bromophenyl)-N^2-4-tolyl-oxalo diimidoyl dibenzotriazol (**6g**).

3g was prepared starting from ethyl(2-bromophenyl-amino)oxoacetate [24] that was heated at reflux with 4-toluidine in xylene for several days to give the N^1-(2-bromophenyl)-N^2-4-tolyloxalamide [25]. The latter was chlorinated following the general protocol [23] for imidoylchlorides (in toluene with phosphorus pentachloride) to give the N^1-(2-Bromo-phenyl)-N^2-4-tolyl-oxalodiimidoyl dichloride [26].

This compound (**6g**) was obtained as pale yellow crystals, 4.4 g (82%), mp 232°C; ir (ATR): 3058 (w) (arC-H), 1650 (m) (C=N) cm^{-1}; ^1H nmr (250 MHz, DMSO-d_6): δ 8.55 (d, J = 8.3 Hz, 1H), 8.41 (d, J = 8.3 Hz, 1H), 8.32 (d, J = 8.3 Hz, 2H), 7.86 (q, J = 7.5 Hz, 2H), 7.70 (t, J = 7.5 Hz, 2H), 7.59 (d, J = 7.8 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 8.1 Hz, 2H), 6.80 (d, J = 7.5 Hz, 1H), 6.33 (d, J = 8.2 Hz, 2H), 2.22 ppm (s, 3H); ^{13}C nmr (63 MHz, DMSO-d_6): δ 145.63 (C=N), 145.59 (C=N), 142.8, 142.5, 142.1, 141.8, 141.7, 141.5, 136.1, 135.9, 133.0, 131.2, 131.1, 131.0, 130.0, 129.6, 128.6, 128.4, 127.2, 127.0, 120.4, 120.0, 119.2, 118.5, 114.3, 114.2 (aryl), 20.5 (CH_3) ppm; ms: m/z (DEI) 535 (0.1) (M^+), 479 (5), 413 (20), 399 (80), 308 (45), 207 (60), 192 (100).

Anal. Calcd. for $C_{27}H_{19}BrN_8$: C, 60.57; H, 3.58; N, 20.93. Found: C, 61.12; H, 3.83; N, 20.98.

Crystal Data for **6g** [16].

Compound **6g** has $C_{27}H_{19}BrN_8$, Mr = 535.41 $gmol^{-1}$, colorless prism, size 0.04 x 0.04 x 0.03 mm^3, orthorhombic, space group Pbca, a = 15.3324(5), b = 15.5069(5), c = 20.4728(7) Å, V = 4867.6(3) $Å^3$, T= -90 °C, Z = 8, $\rho_{calcd.}$ = 1.461 gcm^{-3}, μ (Mo-K_α) = 17.22 cm^{-1}, F(000) = 2176, 31297 reflections in h(-19/17), k(-20/19), l(-26/26), measured in the range 2.12° ≤ Θ ≤ 27.48°, completeness Θ max = 99.9 %, 5572 independent reflections, R_{int} = 0.088, 3307 reflections with $F_o > 4\sigma(F_o)$, 326 parameters, 0 restraints, $R1_{obs}$ = 0.096, wR^2_{obs} = 0.264, $R1_{all}$ = 0.153, wR^2_{all} = 0.295, GOOF = 1.093, largest difference peak and hole: 1.233 / -1.442 e $Å^{-3}$.

Bis-(2,4,6-trimethylphenylimidoyl-2-benzotriazole) (**6h**).

This compound was obtained as yellow crystals, 2.4 g (46%) after column chromatography (silica gel, $CHCl_3$), mp 228°C; ir (ATR): 2960, 2920, 2855 (w) (arC-H), 1669 (m) (C=N) cm^{-1}; ^1H nmr (250 MHz, $CDCl_3$): δ 8.08 (d, J = 7.5 Hz, 4H), 7.54-7.44 (m, 4H), 6.67 (s, 4H), 2.27 (s, 6H), 1.72 ppm (s, br, 12H); ^{13}C nmr (63 MHz, $CDCl_3$): δ 145.9 (N=C-C=N), 140.2, 134.6, 131.3, 129.6, 129.0, 128.7, 125,8, 120.1, 114.5 (aryl), 20.6 (2-CH_3), 18.0 (4-CH_3) ppm; ms: m/z (DEI) 526 (0.1) (M^+), 455 (10), 380 (20), 235 (40), 220 (100), 130 (35).

Anal. Calcd. for $C_{32}H_{30}N_8$: C, 72.98; H, 5.74; N, 21.28. Found: C, 72.30; H, 5.70; N, 21.00.

General Procedure for the Synthesis of Indigodianiles.

a) With *n*-BuLi.

To a degassed solution of benzotriazole **6** (0.5 mmol) in dried THF was added dropwise *n*-butyllithium (2.5 *M* in hexane) (1 mmol) at -78°C. The solution instantly became deeply red. After stirring for 30min at -78°C the solution was allowed to warm up. The color turned into brownish-green. Finally the solution was filtered, whereby in the presence of oxygen the color turned to deep blue-green. Evaporation of the solvent gave crude product which was immediately purified by column chromatography on alumina (toluene). The yields were all in the range of 10-20%.

b) With Li granulate.

To a degassed solution of benzotriazole **6** (0.5 mmol) in dried THF was added lithium granulate (5 mmol) and the mixture was irradiated with ultra sound for about 30min. The progress of the reaction was monitored by tlc unless no benzotriazole **6** was there. After adding dropwise methanol, filtration on air followed. The solution was evaporated and the residue was purified by column chromatography (alumina, toluene).

3,3'-Bis-[phenylimino]-1,3,1',3'-tetrahydro-[2,2']biindolylidene (**2a**).

This compound was obtained as dark blue solid, 93 mg (45%), mp 284°C; ir (ATR): 3303 (w) (N-H), 3060 (w) (arC-H), 1665 (m) (C=N) cm^{-1}; uv/vis ($CHCl_3$) λ (logε) 285 (4.4), 342 (4.0), 361 (4.0), 596 (4.1), 657 (3.9), 730 (2.4); ^1H nmr (250 MHz, THF-d_8): δ 10.2 (s, br), 7.43-6.61 (m, 18H); ^{13}C nmr (63 MHz, THF-d_8): δ 148.2 (C=N), 146.0 (C=C), 128.5, 127.1, 122.6, 121.6, 118.5, 117.2, 116.8, 113.2, 112.5 (aryl) ppm; ms: m/z (DEI) 412 (M^+) (100), 335 (40), 320 (70), 218 (20), 206 (30), 178 (30), 77 (70).

Anal. Calcd. for $C_{28}H_{20}N_4$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.16; H, 4.45; N, 13.23.

5,5'-Dimethyl-3,3'-bis-[4-tolylimino]-1,3,1',3'-tetrahydro[2,2']bi-indolylidene (**2b**).

This compound was obtained as dark blue solid, 94 mg (40%), mp 298°C; ir (ATR): 3374 (m) (N-H), 3052, 3021 (m) (arC-H), 1615 (m) (C=N) cm^{-1}; uv/vis ($CHCl_3$) λ (logε) 289 (4.4), 353 (4.0), 624 (4.0), 673 (4.0), 745 (3.8); ^1H nmr (250 MHz, CD_2Cl_2): δ 9.73 (br, s, 2H), 7.15 (d, J = 8.0 Hz, 4H), 7.09 (d, J = 8.0 Hz, 2H), 7.02-6.98 (m, 6H), 6.75 (s, 2H), 2.32 (s, 6H), 2.10 ppm (s, 6H); ^{13}C nmr (63 MHz, CD_2Cl_2): δ 146.7 (C=N), 142.6 (C=C), 132.3, 130.0, 129.2, 128.3, 123.1, 118.1, 117.7, 113.8 (aryl), 19.6, 19.3 (CH_3) ppm; ms: m/z (DEI) 468 (M^+) (100), 377 (40), 362 (80), 348 (15), 234 (20), 91 (30), 65 (20).

Anal. Calcd. for $C_{32}H_{28}N_4$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.81; H, 5.84; N, 11.71.

5,5'-Di-*tert*-butyl-3,3'-bis-[4-*tert*-butyl-phenylimino]-1,3,1',3'-tetrahydro-[2,2']biindolylidene (**2c**).

This compound was obtained as dark blue solid, 110 mg (35%), mp 305°C; ir (ATR): 3367 (w) (N-H); 3038 (w) (arC-H), 1615 (m) (C=N) cm^{-1}; uv/vis ($CHCl_3$) λ (logε) 292 (4.3), 353 (3.9), 604 (4.0), 670 (3.9), 740 (2.8); ^1H nmr (200 MHz, $CDCl_3$): δ 7.46 (d, J = 8 Hz, 4H), 7.33-7.13 (m, 10H), 6.83 (s, 2H), 1.40 (s, 18H), 1.13 ppm (s, 18H); ^{13}C nmr (50 MHz, $CDCl_3$): δ 147.6 (C=N), 146.8 (C=C), 144.8, 143.1, 128.7, 127.9, 125.6, 121.3, 119.4, 118.3, 113.9 (aryl), 34.1, 34.05 (C_{quat}), 31.2, 30.9 (CH_3) ppm; ms: m/z (DEI) 636 (M^+) (25), 318 ($M^+/2$) (100), 303 (50), 134 (25), 57 (25).

Anal. Calcd. for $C_{44}H_{52}N_4$: C, 82.97; H, 8.23; N, 8.80. Found: C, 82.59; H, 8.11; N, 8.45.

3,3'-Bis-[naphthalen-1-ylimino]-1,3,1',3'-tetrahydro[2,2']bi[benz-[*g*]indolylidene] (**2d**).

This compound was obtained as dark purple solid, 92 mg (31%), mp 258°C (decomp.); ir (ATR): 3347 (w) (N-H), 3049 (w) (arC-H), 1658 (w) (C=N) cm^{-1}; uv/vis (DMF) λ (logε) 285 (4.6), 336 (4.1), 514 (3.8); ^1H nmr (250 MHz, DMSO-d_6): δ 10.5 (s, 2H), 7.61-7.43 (m, 14H), 7.26-7.14 ppm (m, 12H); ms: m/z (DEI) 612 (100) (M^+), 485 (10), 470 (20), 396 (15), 306 (10), 143 (20), 28 (100).

Anal. Calcd. for $C_{44}H_{28}N_4$: C, 86.25; H, 4.61; N, 9.14. Found: C, 85.95; H, 4.25; N, 8.90.

[2,2-Di-*n*-butyl-1,2-dihydro-indol-(3)-ylidene]-4-tolyl-amine (**7**).

This compound was obtained (following procedure **a**) as yellow solid, 140mg (42%), mp 145°C (decomp.); ir (ATR): 3253 (w) (N-H), 3022 (w) (arC-H), 1638 (m) (C=N) cm^{-1}; uv/vis ($CHCl_3$) λ (logε) 263 (3.9), 379 (3.7); ^1H nmr (400 MHz, $CDCl_3$): δ 7.13 (m, 3H), 6.76 (d, 7.6 Hz, 2H), 6.71-6.69 (m, 1H), 6.40-6.31 (m, 2H), 4.2 (br, s, 1H), 2.40 (s, 3H), 1.84 (m, 2H), 1.65 (m, 2H), 1.24 (m, 8H), 0.86 ppm (m, 6H); ^{13}C nmr (63 MHz, $CDCl_3$): δ 172.1 (C=N), 156.2 (N=C-C), 148.9 (C_{indol}-NH), 132.4 (C_{quat}), 131.4 (C_{quat}), 128.9 (indol-CH), 128.0 (C_{quat}), 118.8 (tolyl-CH), 117.8 (indol-CH), 116.1 (indol-CH), 109.9 (tolyl-CH), 67.8 (C_{spiro}), 39.3, 24.4, 22.1 (butyl-CH_2), 20.4 (tolyl-CH_3), 13.1 (butyl-CH_3) ppm; ms: m/z (DEI) 334 (M^+) (5), 291, 278 (100), 235 (50), 219 (25), 186 (15), 91 (30), 41 (40).

Anal. Calcd. for $C_{23}H_{30}N_2$: C, 82.59; H, 9.04; N, 8.37. Found: C, 82.22; H, 8.72; N, 8.09.

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[24] Ethyl (2-bromophenylamino)oxoacetate (This compound was obtained as colorless oil; ^1H nmr (250 MHz, DMSO-d_6): δ 10.23 (s, 1H), 7.77-7.68 (m, 2H), 7.45-7.39 (m, 1H), 7.23-7.19 (m, 1H), 4.30 (q, J = 7.1Hz, 2H), 1.31 ppm (t, J = 7.1Hz, 3H); ^{13}C nmr (63 MHz, DMSO-d6): δ 160.2, 155.3, 134.7, 132.7, 129.1, 128.3, 125.7, 117.7, 62.6, 13.7 ppm. *Anal.* Calcd. for $C_{10}H_{10}BrNO_3$: C, 44.14; H, 3.70; Br, 29.37; N, 5.15; O, 17.64; Found: C, 44.23; H, 3.49; Br, 29.47; N, 5.08.)

[25] N^1-(2-Bromophenyl)-N^2-4-tolyloxalamide (This compound was obtained as white solid, mp: 177°C; ir (ATR): 3282 (m) (N-H), 3033 (w) (arC-H), 1664 (s) (C=O); ^1H nmr (250 MHz, DMSO-d6): δ 10.71 (br, s, 1H), 10.31 (br, s, 1H), 7.99 (d, J = 10 Hz, 1H), 7.76-7.70 (m, 3H), 7.46 (t, J = 7.5Hz, 1H), 7.22-7.15 (m, 3H), 2.27 ppm (s, 3H); ^{13}C nmr (63 MHz, DMSO-d6): δ 158.4, 158.1, 157.8, 135.1, 133.9, 132.7, 129.1, 128.5, 127.3, 124.0, 120.5, 120.3, 116.4, 20.5 ppm. *Anal.* Calcd. for $C_{15}H_{13}BrN_2O_2$: C, 54.07; H, 3.93; Br, 23.98; N, 8.41; O, 9.60; Found: C, 54.65; H, 4.05; Br, 23.48; N, 8.30.).

[26] N^1-(2-Bromo-phenyl)-N^2-4-tolyl-oxalodiimidoyl dichloride (This compound was obtained after recrystallisation from *n*-heptane as yellow needles, mp: 63°C; ^1H nmr (250 MHz, $CDCl_3$): δ 7.56-6.91 (m, 8H), 2.31 ppm (s, 3H); ^{13}C nmr (63 MHz, DMSO-d6): δ 145.4, 142.7, 137.5, 133.1, 129.6, 128.7, 127.9, 127.2, 122.4, 120.1, 114.1, 21.2 ppm. *Anal.* Calcd. for $C_{15}H_{11}BrCl_2N_2$: C, 48.68; H, 3.00; Br, 21.59; Cl, 19.16; N, 7.57; Found: C, 48.94; H, 3.45; N, 7.16.).