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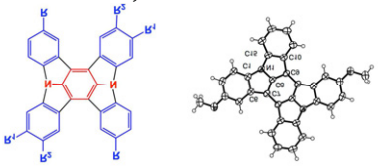

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ABSTRACT

The synthesis and spectroscopic properties of a series of new organic electron donors derived from dibenzo[2,3:5,6]pyrrolizino-[1,7-*bc*]indolo[1,2,3-*lm*]carbazole are described. These compounds can be considered as planar hybrids of carbazole and *p*-phenylenediamine and possess high thermal stability. The electron donating properties and one- and two-photon spectroscopic features of methoxy derivatives are very sensitive to the number and positions of the methoxy groups. The X-ray structure of the 2,11-dimethoxy derivatives features slipped π-stacks and short interplanar distance between the molecules in the stacks similar to those found in the unsubstituted derivative.

1. Introduction

Currently, small organic π-conjugated molecules constitute one of the most extensively studied field of research owing to their potential as components of charge transporting, nonlinear optical and other advanced materials,[1] in particular, organic field-effect transistors.[2,3] Derivatives of triaryl amines and carbazole, especially indolo[3,2-b]carbazoles, are considered to be the most promising classes of organic electron donors and are the subjects of intensive investigations. Research efforts in this field cover a broad spectrum of topics for biological targets[4] and numerous investigations of potential applications of such materials as components for organic light-emitting diodes,[5,6] organic thin-film transistors[7] and photovoltaic cells.[8] The charge transfer within aromatic amines occurs in a chain of redox processes between the neutral molecule and its cation radical in their ground state,[9] which requires high stability of both electron donors and their oxidized forms. Thus, the known instability of the triaryl amine cation radicals, which undergo dimerization to form tetraarylbenzidines[10] was the driving force to design fully reversible redox systems involving the *p*-phenylenediamine moiety.[11-13]

Carbazoles, as a larger planar aromatic system, possess also strong fluorescence in both solution and solid state[14,15] and enhanced thermal stability. These derivatives can also serve as the efficient electron donating moieties in second harmonic generating[16] and two-photon absorbing (TPA) chromophores.[17,18] However, their oxidation gives rise to oligomerization.[19] Further structural variations of carbazoles have demonstrated the potential of indolocarbazoles[5,8,20] and bisindoloquinolines[21] for applications involving charge transfer. Recently, we showed that a new heterocyclic system, dibenzo[2,3:5,6]pyrrolizino-[1,7-*bc*]indolo[1,2,3-*lm*] carbazole, which can be considered as a planar hybrid of carbazole and *p*-phenylenediamine, can readily be prepared from commercial precursors and possesses high thermal stability and strong electron donor properties comparable to tetra- and pentacene.[22] However, the only known derivative of the parent compound with four methoxy groups at 2,3,11,12 positions was highly insoluble[22] that prevented the spectroscopic and electrochemical characterization of this compound, which was supposed to be a stronger electron donor. Here we report on the preparation and properties of a number of other substituted derivatives which solubility is sufficient for, at least, spectroscopic characterization.

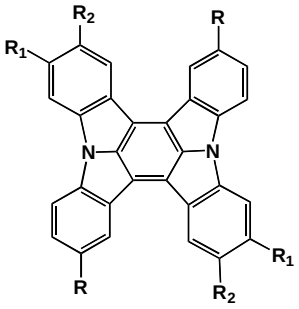
2. Results and discussion

2.1. Synthesis

Of two possible synthetic routes employed previously for the synthesis of the parent unsubstituted derivative **1** (R = R_1 = H),[22] the cyclization of the dichloro substituted derivatives **2** in the presence of CuI and a base is certainly the most suitable for the preparative purpose.

Thus, the substituted 6,12-diaryl-5,11-dihydroindolo[3,2-b]carbazoles **2** can serve as convenient precursors of derivatives

of **1**. The known synthetic routes toward derivatives **2** are based on the condensation of aryl aldehydes and indoles. One of the approaches involves iodine catalyzed self-condensation of 3,3'-bis(indolyl)methanes,[23] whereas the direct condensation of an indole and an aromatic aldehyde in the presence of iodine was supposed to afford isomeric 6,12-diaryl-5,7-dihydroindolo[2,3-b]carbazoles.[24] It was demonstrated later[25] that the purported isomeric 6,12-diphenyl [2,3-b] derivative is actually 6,12-diphenyl-5,6,11,12-tetrahydroindolo[3,2-b]carbazole. Moreover, the reported high yields of the products were not reproducible. An alternative catalyst, hydroiodic acid, was proposed[25] as an efficient catalyst of the reaction of indoles with aromatic aldehydes.



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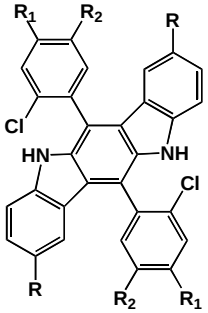
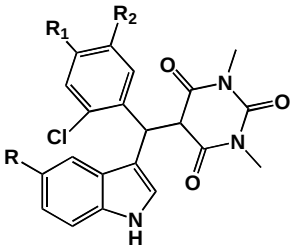


2

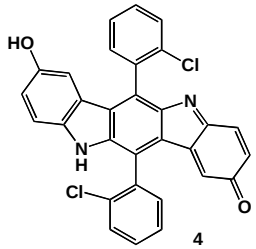
Another approach involves a thermal reaction of 3-alkylated indole derivatives, which form in a three-component solvent-free reaction of indole, aromatic aldehydes and *N*,*N*-dimethylbarbituric acid.[26]



2

3 a) R = R_1 = R_2 = H; b) R = OMe, R_1 = R_2 = H
c) R = R_1 = OMe, R_2 = H; d) R = R_2 = OMe, R_1 = H;
e) R = COOH, R_1 = R_2 = H; f) R = NO_2, R_1 = R_2 = H;
g) R = OCH_2Ph, R_1 = R_2 = H; h) R = OH, R_1 = R_2 = H

We tested both the above approaches using 2-chlorobenzaldehydes and found that the route involving 3-alkylated indole derivatives **3**[26] is the most general and convenient in the cases when 2-chlorobenzaldehyde itself is used. Derivatives **3a, b, e-h** were prepared in fair to excellent yields according to the procedure[27] as colorless crystals and their structures were confirmed by the X-ray analysis. However, we were unable to prepare derivatives **3c** and **3d** from the corresponding methoxy 2-chlorobenzaldehydes. The conversion of **3** into indolocarbazoles **2** required much more time than reported.[26] Thus, **2a** was obtained in 40 % yield after 20 h of reflux in acetic acid (instead of 45% during 40 min of reflux reported in[26]). In some cases, using formic acid considerably increased the yields and shortened the reaction time, however, the purification of the compounds from the side products becomes more complicated.



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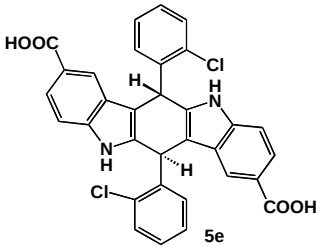


5e

Derivatives **3g** and **3h** afforded the same deeply colored insoluble product. This compound may correspond to the oxidized quinoid form of **2h** (**4**) and was not further investigated. Derivatives **2c** and **2d** were prepared from 5-methoxyindole, the corresponding methoxy 2-chlorobenzaldehyde and catalytic amount of hydroiodic acid according to the published procedure.[25]

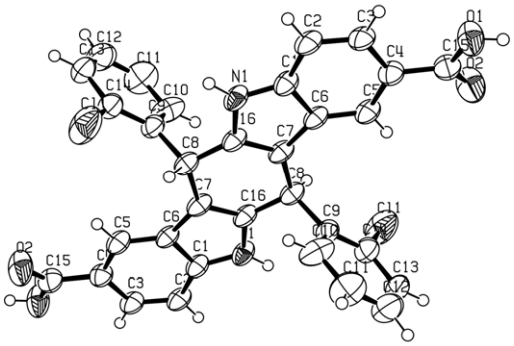
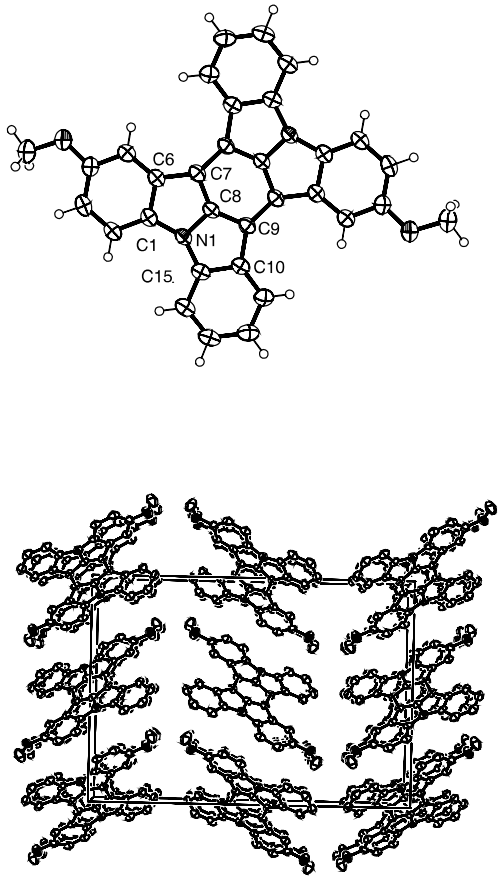


Fig. 1: Molecular and crystal structure of **5e** (thermal ellipsoids are presented at 50% of probability).

The formation of dihydroindolocarbazoles **2** was always accompanied by the formation of some amount of the tetrahydro derivatives **5**. These derivatives seem indeed to be the primary reaction products, which undergo relatively rapid oxidation in solution, but owing to the low solubility they precipitate out of the reaction mixture avoiding thus further oxidation. In particular, we isolated the tetrahydro derivative **5e**, which is less soluble than **2e**. Interestingly, this compound forms the same 6,12-*trans* isomer (Fig. 1) isolated in the case of the 6,12-diphenyl analog.[25] The tetrahydro derivatives **5** can be oxidized to **2** by refluxing their solutions in the presence of iodine.[25] However, we found that in the presence of a base (TBAOH) during the cyclization step, the oxidation of derivatives **5** occurs easily by residual oxygen and may additionally be catalized by CuI so that the separation of **2** and **5** from their mixtures is not necessary.

The mixtures of derivatives **2a-e**/**5a-e** underwent cyclization under the conditions described earlier for **1a** and the synthesis can be scaled up without the loss in the yields. The mixture of **2f**/**5f** did not cyclize even under drastic conditions. New derivatives **1b** and **c** form yellow needle-like crystals limitedly soluble in non-polar solvents (about 10^{-4} M in toluene) similarly to **1a**, and **1d** forms dark yellow microcrystals with metallic luster, soluble in benzonitrile (about 10^{-5} M). These compounds possess high thermal stability: they do not melt and sublime above 300°C. Derivative **1e** is insoluble in most common organic solvents, but forms soluble salts upon addition of TBAOH or KOH. Yellow prisms of **1b** suitable for the X-ray analysis were grown from benzonitrile.



a)

b)

Fig.2. Molecular (a) and crystal (b) structures of **1b**. Selected bond lengths in Å: C1–C6 1.431(3); C6-C7 1.460(3); C7-C8 1.399(3); C8 C9 1.393(3); C9 C10 1.462(3); C10 C15 1.431(3); C15 N1 1.400(3); C1 N1 1.406(3); C8 N1 1.372(3)

The X-ray structure determination showed that the molecules of **1b** are almost planar, the terminal benzenic rings are twisted from the molecular plane less than observed for **1a** (1.5° vs. 5°, respectively). The methoxy groups are twisted by 11.3° from the molecular plane. The molecules in crystal form slipped π-stacks with the distance between each mean square molecular planes of 3.29 Å (that is even shorter than found for **1a**: 3.380 Å) (Fig. 2).

2.2. UV-Vis absorption and fluorescence spectra

The basic features of UV-Vis absorption and fluorescence spectra of **1a** have already been discussed in ref.[22]. The positions of the longest wavelength absorption maxima of **1b** - **d** undergo strong shifts upon increasing the number of the methoxy groups (Fig. 3).

The direction of the shifts strongly depends on the substitution position and two methoxy groups at 2,11 positions (**1b**) give rise to *ca*. 20 nm red shift. Further substitution by the two methoxy groups at 8,17 positions (**1d**) moves the longest wavelength absorption band toward red by 20 nm, while the substitution by the two methoxy groups at 7, 16 position (**1c**) brings about a blue shift *ca.* 15 nm compared to **1b**. Only weak positive solvatochromism of about 4 – 6 nm roughly correlating with the refractive indices of solvents was observed. The Stokes shifts increase with the increasing number of the methoxy groups: from 4 nm (**1a**) up to 19 nm (**1d**). The *p*-methoxy substituents diminish the intensity of the longest wavelength absorption band: the molar absorption coefficient of **1b** is 9 000 $M^{-1}cm^{-1}$, more than twice smaller compared to 20 200 $M^{-1}cm^{-1}$ measured for **1a**. The fluorescence quantum yields in toluene for **1b** and **1c** were found to amount 41 and 53%, respectively.

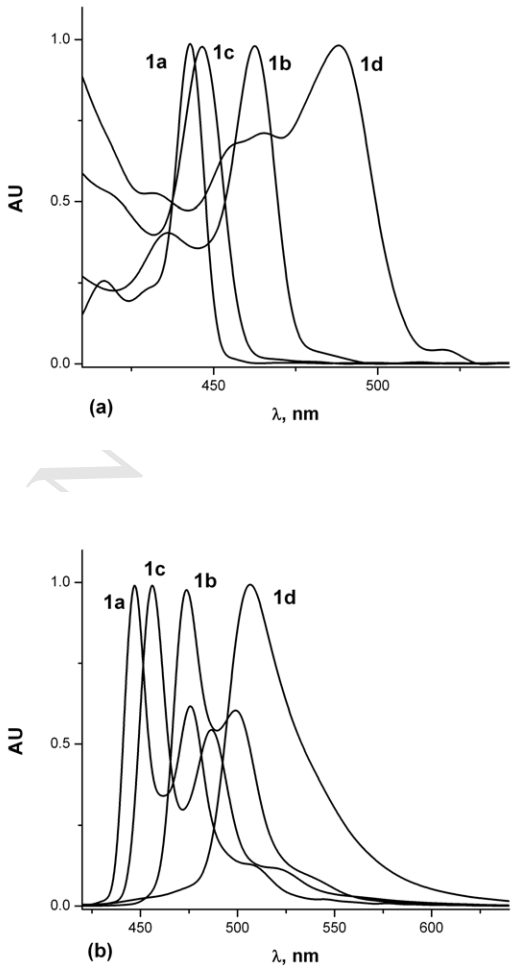


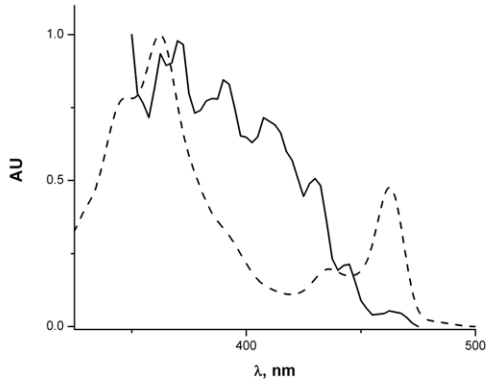
Fig. 3. Normalized absorption (a) and fluorescence (b) spectra: **1a** – **1c** in toluene, **1d** in benzonitrile.

The two-photon fluorescence excitation spectra of **1b** and **1c** (Fig. 4) resemble that of **1a** and exhibit broad vibronically split bands stretching from 900 nm down to 700 nm and, probably, below. Indeed, solutions of **1b** and **1c** fluoresce upon irradiation by 532 and 640 nm lasers. The two-photon absorption cross sections were found to amount 30 and 60 GM for **1b** and **1c**, respectively, at 740 nm, larger than found for **1a** (20 GM at 730 nm).

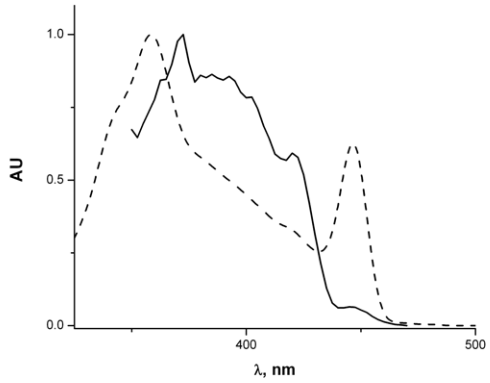
The absorption and fluorescence spectra of the dipotassium and TBA salts of **1e** are similar to those of **1a**.

2.3. Electron donating properties

The low solubility of derivatives **1** prevented the detailed electrochemical studies. The propensity of the oxidized form of **1a** to deposit on the electrode as a black shining film during the CV experiments[22] is even stronger for the substituted derivatives. We were able to observe the oxidation peak only for **1b** in warm DMSO at about 0.5 V (Pt electrode, $TBAPF_6$, *vs*. SCE). It is a considerable shift compared to the unsubstituted derivative (about 1 V *vs*. SCE under the same conditions). Addition of strong acceptors (tetracyanoethylene or tetracyanoquinodimethane) to solutions of **1b** in toluene led to immediate development of dark green color and eventual formation of a black precipitate.



a)



b)

Fig. 4. Two-photon (solid curves) and one-photon (dashed curves) fluorescence excitation spectra of **1b** (a) and **1c** (b) in toluene. For the two-photon spectra the X-axis values are λ/2.

In order to reveal the effect of the substitution on the electron donating properties of the new heterocyclic system, we performed quantum mechanical calculations at the semiempirical (AM1//AM1) and DFT (TD B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p)) levels.[28] The ionization potentials (IP) and electron affinities (EA) were calculated as the energy difference between the neutral molecule and the corresponding radical cation (IP) and between the radical anion and neutral molecule (EA). The major results are collated in Table 1. The effect of the methoxy groups at 8,17 positions on the electron donating properties should be considerably stronger than at 7,16 positions. Thus, the symmetrically substituted derivative **1d** is calculated to be the strongest donor of the series with the IP by 0.67 eV lower than that of **1a**. The AM1 calculation results showed a similar trend judging by the HOMO/LUMO energy changes. The discussed above shifts in the position of the longest wavelength absorption maxima within the series **1a** – **1d** are well reproduced by the calculations. The calculated oscillator strengths f are also in agreement with the experimental molar absorption coefficients found for **1a** and **1b**.

3. Conclusion

The new derivatives of dibenzo[2,3:5,6]pyrrolizino-[1,7-*bc*]indolo[1,2,3-*lm*]carbazole possess many of the properties required by applications involving charge transporting and optical phenomena. The remarkable sensitivity of the parent heterocycle to the number and position of substituents suggests the possibility of further tuning the electron donating ability and the electronic transition energies.

Table 1. Quantum mechanical calculations summary

Compd	$E_{HOMO/LUMO}$ (AM1)(eV)	IP (eV)	EA (eV)	E_{ET}[1](f)
1a	-8.05/-1.25	6.53	0.64	2.98 (0.14)
1b	-7.91/-1.33	6.26	0.66	2.78 (0.08)
1c	-7.79/-1.18	5.95	0.42	2.85 (0.16)
1d	-7.67/-1.24	5.86	0.55	2.57 (0.08)

[1] The energy of the 1st electronic transition calculated by the TD DFT method.

4. Experimental section

4.1. General

All chemicals including the solvents were used without prior drying except DMF, which was freshly distilled over P_2O_5. All reagents and solvents were of reagent grade. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AC-250 (^{1}H spectra: 250 MHz; ^{13}C spectra: 62.5 MHz) using TMS as an internal standard. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. Elemental analyses were performed on a Thermo Finnigan Flash EA1112 series. Melting points (uncorrected) were determined using a Buchi-510 apparatus. X-Ray crystallography data were collected on a Bruker-Nonius KappaCCD diffractometer with CCD detector using MoK_α radiation (λ=0.71073 Å). UV-Vis absorption spectra were recorded on an Ocean Optics USB 4000 spectrophotometer combined with UV-Vis-IR Light Source Micropack DH-2000. Fluorescence spectra were recorded on a Fluorolog-3 (Jobin Yvon) fluorimeter. The quantum yields of fluorescence were determined in toluene at 20 °C using quinine sulfate in a solution of H_2SO_4 (0.1 M) as a reference.

Commercially available reagents were used as received.

Two-photon absorption cross sections were determined by photoluminescence excitation spectroscopy. A tunable Ti:Sapphire femtosecond laser (MaiTai HP, Spectra-Physics, 150 fs pulses at 80 MHz) in the 690-1050 nm range was used for excitation of toluene solutions in a 1 cm quartz cell. The laser beam was focused in the cell using a NA 0.4 objective. The generated photoluminescence was collected in a 90° geometry and filtered with a short-pass interference filter. It was then sent into a monochromator (Spectra Pro 500i, Acton) before being detected by a ICCD camera (Roper Scientific). Photoluminescence spectra were recorded for excitation wavelength ranging typically from 700 to 950 nm, with a 5 nm

span. Integration time ranged from 10 ms to 2 s. The average laser power was typically kept around 500 mW. Two-photon absorption spectra were then calculated by integration of the photoluminescence spectrum for each excitation wavelength. They were normalized by the integration time and the square of the average laser power.

The two-photon cross sections were determined by comparing the two-photon absorption spectra with rhodamine B in methanol and normalizing by their quantum yields. The known literature values have been determined with the same typical pulse duration of ~150 fs.[29]

4.2. Synthesis

*4.2.1. A general procedure for 5-[(2-chlorophenyl)(1H-indol-3-yl)methyl]-1,3 dimethylpyrimidine-2,4,6(1H,3H,5H)-triones (**3**).* Equimolar amounts of an indole derivative, 2-chloro benzaldehyde and *N,N*-dimethylbarbituric acid were heated for 15 min. The reaction mixture was cooled down and a mixture of petroleum ether:ethanol (4:1) was added. The precipitate was filtered off and washed with ethanol. Crystals of **3** were obtained by crystallization from ethanol. The identities of derivatives **3** were confirmed by the X-ray structure determination and the crystal structures have been deposited at the Cambridge Crystallographic Data Centre.

*4.2.1.1. 5-[(2-chlorophenyl)(1H-indol-3-yl)methyl]-1,3 dimethylpyrimidine-2,4,6(1H,3H,5H)-trione **3a**.* From indole, at 85°C, 80% yield, m.p. 197-199°C. ^{1}H NMR (DMSO-d6): δ = 2.88 (s, 3H, CH_3), 3.04 (s, 3H, CH_3), 4.40 (d, ^3J = 3.63, 1H, CH), 5.53 (d, ^3J = 3.48, 1H, CH), 7.06 (m, 9H, CH), 11.04 (s, 1H, NH).^{13}C NMR (DMSO-d6): δ = 167.84 (C), 167.63 (C), 151.18(C), 137.59 (C), 135.86 (C), 132.35 (C), 131.39 (CH), 129.00 (CH), 128.62 (CH), 126.61 (CH), 126.26 (C), 123.94 (CH), 121.35 (CH), 118.73 (CH), 117.63 (CH), 112.19 (C), 111.57 (CH), 53.13 (CH), 41.28 (CH), 28.09 (CH_3), 27.87 (CH_3). $C_{21}H_{18}Cl_1N_3O_3$. Unit cell parameters: *a* = 8.3515(2), *b* = 29.0327(8), *c* = 7.7279(2), □ = 94.731(2), space group P 21/c. Deposition number CCDC 905654.

*4.2.1.2. 5-[(2-chlorophenyl)(5-methoxy-1H-indol-3-yl)methyl]-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione **3b**.* From 5-methoxyindole, at 85°, 75% yield, m.p. 147-149°C. ^{1}H NMR ($CDCl_3$): δ = 3.00 (s, 3H, CH_3), 3.21 (s, 3H, CH_3), 3.72 (s, 3H, CH_3), 4.40 (d, ^3J = 3.16, 1H, CH), 5.68 (d, ^3J = 3.16, 1H, CH), 7.10 (m, 8H, CH), 8.04 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ = 168.07 (C), 167.68 (C), 164.65 (C), 154.18 (C), 136.69 (C), 133.41 (C), 131.02 (C), 130.90 (CH), 129.51 (CH), 128.88 (CH), 127.05 (C), 126.70 (CH), 123.84 (CH), 114.34 (C), 112.69 (CH), 111.84 (CH), 100.65 (CH), 55.69 (OCH_3), 53.87 (CH), 42.80, 28.74 (CH_3), 28.45 (CH_3). $C_{22}H_{20}Cl_1N_3O_4$. Unit cell parameters: *a* = 9.4793(2), *b* = 9.6922(2), *c* = 11.7006(3), □ = 74.031(1), □ = 86.420(1), □ = 77.097(2), space group P -1. Deposition number CCDC 906218.

*4.2.1.3. 3-[(2-chlorophenyl)(1,3-dimethyl-2,4,6-trioxohexahydropyrimidin-5-yl)methyl]-1H-indole-5-carboxylic acid **3e**.* From indole-5-carboxylic acid at 95°C, 80% yield, m.p. 226-228°C. ^{1}H NMR (DMSO-d6): δ = 2.91 (s, 3H, CH_3), 3.03 (s, 3H, CH_3), 4.45 (d, ^3J = 3.63, 1H, CH), 5.58 (d, ^3J = 3.63, 1H, CH), 7.48 (m, 8H, CH), 11.41 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d6): δ = 168.07 (C), 167.77 (C), 167.69 (C), 151.18 (C), 138.39 (C), 137.49 (C), 132.36 (C), 131.36 (CH), 129.16 (C), 128.81 (CH), 126.80 (CH), 125.93 (CH), 125.85 (CH), 122.74 (CH), 121.42 (CH), 120.38 (CH), 113.56 (C), 111.43 (CH), 53.08 (CH), 40.96 (CH), 28.13 (CH_3), 27.97 (CH_3). $C_{22}H_{18}Cl_1N_3O_5$. Unit cell parameters: *a* = 15.2196(3), *b* = 9.2427(2), *c* = 15.2568(4), □ = 112.403(1), space group P21/n. Deposition number CCDC 905656.

*4.2.1.4. 5-[(2-chlorophenyl)(5-nitro-1H-indol-3-yl)methyl]1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione **3f**.* From 5-nitroindole, at 90°C, 46% yield, yellow crystals from acetone, m.p. 141-143°C. ^{1}H NMR (DMSO-d6): δ = 2.93 (s, 3H, CH_3), 3.03 (s, 3H, CH_3), 4.53 (d, ^3J = 3.95 Hz, 1H, CH), 5.60 (d, ^3J = 3.79 Hz, 1H, CH), 7.60 (m, 8H, CH), 11.81 (s, 1H, NH). ^{13}C NMR (DMSO-d6): δ = 167.64 (C), 167.53 (C), 151.18 (C), 140.44 (C), 139.12 (C), 137.04 (C), 132.42 (C), 131.27 (CH), 129.27 (CH), 129.00 (CH), 128.39 (CH), 126.92 (CH), 125.65 (C), 116.88 (CH), 114.98 (C), 114.67 (CH), 112.28 (CH), 52.92 (CH), 40.57 (CH), 28.17 (CH_3), 28.02 (CH_3). $C_{21}H_{17}Cl_1N_4O_5$. Unit cell parameters: *a* = 9.3874(2), *b* = 25.5888(6), *c* = 8.8179(2), □ = 101.582(1), space group P21/c. Deposition number CCDC 905659.

*4.2.1.5. 5-[[5-(benzyloxy)-1H-indol-3-yl](2-chlorophenyl) methyl]-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione **3g**.* From 5-benzyloxyindole, at 90°C, 66% yield, m.p. 150-152°C. ^{1}H NMR (DMSO-d6): δ = 2.89 (s, 3H, CH_3), 3.05 (s, 3H, CH_3), 4.39 (d, ^3J = 3.63, 1H, CH), 4.95 (s, 2H, CH_2), 5.43 (d, ^3J = 3.32, 1H, CH), 6.60 (s, 14H, CH), 10.91 (s, 1H, NH). ^{13}C NMR (DMSO-d6): δ = 167.87 (C), 167.65 (C), 152.03 (C), 151.21 (C), 137.43 (C), 132.39 (C), 131.30 (C), 131.18 (C), 129.02 (C), 128.62 (CH), 128.26 (CH), 127.52 (CH), 126.62 (CH), 124.71 (CH), 112.25 (CH), 111.98 (C), 111.79 (CH), 101.57 (CH), 69.77 (CH_2), 53.19 (CH), 41.35 (CH), 28.11 (CH), 27.90 (CH). $C_{28}H_{24}Cl_1N_3O_4$ x H_2O. Unit cell parameters: *a* = 7.8046(2), *b* = 8.2404(2), *c* = 20.6471(6), □ = 87.541(1), □ = 86.842(1), □ = 85.098(1), space group P -1. Deposition number CCDC 905658.

*4.2.1.6. 5-[(2-chlorophenyl)(5-hydroxy-1H-indol-3-yl)methyl]1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione **3h**.* From 5-hydroxyindole, at 90°C, 46%, m.p. 154-156°C. ^{1}H NMR (DMSO-d6): δ = 2.89 (s, 3H, CH_3), 3.06 (s, 3H, CH_3), 4.36 (d, ^3J = 3.48, 1H, CH), 5.42 (d, ^3J = 3.48, 1H, CH), 6.44 (d, ^4J = 2.05, 1H, CH), 6.57 (dd, ^3J = 8.61, ^4J = 2.29, 1H, CH), 7.31 (m, 6H, CH), 10.74 (s, 1H, NH). ^{13}C NMR (DMSO-d6): δ = 167.91 (C), 167.69 (C), 151.23 (C), 150.48 (C), 137.73 (C), 132.37 (C), 131.48 (CH), 130.34 (CH), 128.99 (CH), 128.58 (CH), 127.06 (C), 126.61 (CH), 124.15 (CH), 111.93 (CH), 111.80 (CH), 101.74 (CH), 53.08 (CH), 41.41 (CH), 28.12 (CH_3), 27.92 (CH_3). $C_{21}H_{18}Cl_1N_3O_4$ x C_2H_5OH. Unit cell parameters: *a* = 7.7795(2), *b* = 8.2998(3), *c* = 17.6713(6), □ = 102.884(1), □ = 91.024(1), □ = 95.201(3), space group P -1. Deposition number CCDC 905657.

*4.2.2. Mixtures of 6,12-bis(2-chlorophenyl)-5,11-dihydroindolo[3,2-b]carbazoles (**2**) and 6,12-bis(2-chlorophenyl)-5,6,11,12-tetrahydroindolo[3,2-b]carbazoles (**5**).* a) A solution of **3** (16.1 mmol) in 40 ml of glacial acetic acid was refluxed during 20h. The reaction mixture was cooled down, a yellowish mixture of **2** and **5** was filtered off and washed thoroughly with hot ethanol. The yields of **2a**, **b**, **e** and **f** containing 15 to 20% of the respective **5** (evidenced by the presence of the ^{1}H NMR signal about 5.7 ppm) varied between 5% (**2e**/**5e**), 40% (**2a**/**5a**), 74% (**2f**/**5f**) and 80% (**2b**/**5b**). The mixtures were used in the next step without further purification. b) A solution of 5-methoxyindole (3 mmol), 2-chloro-4(5)-methoxybenzaldehyde (3 mmol) and hydroiodic acid (1.4 mmol)(57% water solution) in 20 ml of acetonitrile was refluxed under Ar for 15 h. After evaporation of the solvent, the residue was washed by methanol, filtered and washed with acetonitrile. The resulting mixtures of **2c**/**5c** (10% yield) and **2d**/**5d** (4% yield) were used in the next step without further purification. Derivative **5e** was isolated by crystallization of the mixture of **2e** and **5e** from DMSO as colorless crystals involving one molecule

of DMSO. $C_{32}H_{26}Cl_2N_2O_5S_1$. Unit cell parameters: *a* = 13.4133(4), *b* = 8.6773(2), *c* = 15.3735(4), □ = 101.709(1), space group P 21/c. Deposition number CCDC 905653.

*4.2.3. Dibenzo[2,3:5,6]pyrrolizino[1,7-bc]indolo[1,2,3-lm]carbazoles (**1**).* The mixture of **2** and **5** (2.3 mmol), CuI (2.3 mmol) and tetrabutylammonium hydroxide (5.13 mmol) (40% methanol solution) were suspended in 30 ml of freshly distilled DMF under Ar and heated at 120°C during 24h. The mixture was cooled down to room temperature, and the yellow precipitate was filtered off and washed with MeCN. Pure products can be obtained by crystallization from benzonitrile.

*4.2.3.1. Dibenzo[2,3:5,6]pyrrolizino[1,7-bc]indolo[1,2,3-lm]carbazole (**1a**).* Yellow needles from benzonitrile identical to described in[22] yield 73%.

*4.2.3.2. 2,11-dimethoxydibenzo[2,3:5,6]pyrrolizino[1,7–bc]indolo [1,2,3-lm]carbazole (**1b**).* Yellow needles from benzonitrile, 39% yield. Sublime above 300°C. $C_{32}H_{20}N_2O_2$. Unit cell parameters: *a* = 5.7821(2), *b* = 16.3748(5), *c* = 23.1997(8), space group P bca. Deposition number CCDC 905655.

*4.2.3.3. 2,7,11,16-tetramethoxydibenzo[2,3;5,6]pyrrolizino[1,7-bc]indolo[1,2,3-lm]carbazole (**1c**).* Yellow microcrystals from benzonitrile, 10% yield, sublime above 300°C. Calcd $C_{34}H_{24}N_2O_4$: C (77.85 %), H (4.61 %), N (5.34 %). Found: C (77.89 %), H (4.50 %), N (5.37 %).

*4.2.3.4. 2,8,11,17-tetramethoxydibenzo[2,3;5,6]pyrrolizino[1,7-bc]indolo[1,2,3-lm]carbazole (**1d**).* Dark yellow microcrystals with metallic luster from benzonitrile, 38% yield, sublime above 300°C. Calcd $C_{34}H_{24}N_2O_4$: C (77.85 %), H (4.61 %), N (5.34 %). Found: C (77.99 %), H (4.55 %), N (5.38 %).

*4.2.3.5. Dibenzo[2,3:5,6]pyrrolizino[1,7-bc]indolo[1,2,3-lm]carbazole-2,11-dicarboxylic acid (**1e**).* Brownish microcrystals, 88% yield. Decompose above 300°C. Calcd for $C_{32}H_{16}N_2O_4$: C (78.04 %), H (3.27 %), N (5.69 %). Found: C (78.15 %), H (3.22 %), N (5.61 %). ^{1}H NMR (DMSO-d6 + TBAOH): δ = 0.94 (t, 12H, CH_3), 1.31 (m, 8H, CH_2), 1.57 (m, 8H, CH_2), 3.16 (m, 8H, CH_2), 6.93 (d, ^3J = 8.29, 1H, CH), 7.02 (td, ^3J = 8.28, ^4J = 1.25 Hz, 2H, CH), 7.08 (d, ^3J = 8.28, 1H, CH), 7.35 (dd, ^3J = 8.37, ^4J = 1.25 Hz, 1H, CH), 7.62 (dd, ^3J = 8.35, ^4J = 1.22, 1H, CH), 7.69 (dd, ^3J = 8.39, ^4J = 1.21, 1H, CH), 7.78 (td, ^3J = 8.28, ^4J = 1.25 Hz, 2H, CH), 8.38 (d, ^4J = 1.25, 1H, CH), 8.55 (d, ^3J = 7.90, 1H, CH), 8.75 (d, ^3J = 7.90, 2H, CH), 9.18(d, ^4J = 1.25, 1H, CH).

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