Dibenzo[2,3:5,6]pyrrolizino[1,7-*bc*]indolo[1,2,3-*lm*]carbazole: a new electron donor†

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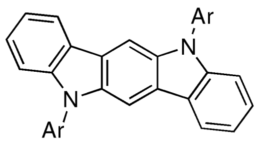
The new heterocyclic system, dibenzo[2,3:5,6]pyrrolizino-[1,7-*bc*]indolo[1,2,3-*lm*]carbazole 3, which can be considered as a planar hybrid of carbazole and *p*-phenylenediamine, can readily be prepared from commercial precursors and possesses high thermal stability and strong electron donor properties comparable to tetra- and pentacene.

Organic π-conjugated compounds are the focus of much current research owing to their potential as components of charge transporting, nonlinear optical and other advanced materials. In particular, derivatives of triaryl amines and carbazole are considered to be the most promising classes of organic electron donors and are the subjects of intensive investigations. Applications related to photoconductivity require high stability of both electron donors and their oxidized forms and, therefore, several structural modification patterns have been exploited.[1] For instance, the known instability of the triaryl amine cation radicals, which undergo dimerization to form tetraarylbenzidines[2] has led to the design of fully reversible redox systems[3] involving the *p*-phenylenediamine moiety.[4] Carbazoles, involving a larger planar aromatic system, exhibit also strong fluorescence[5] and enhanced thermal stability. These derivatives can also serve as the efficient electron donating moieties in two-photon absorbing (TPA) chromophores.[6] However, their oxidation gives rise to oligomerization.[7] Further structural variations of carbazoles have demonstrated the potential of indolocarbazoles **1**[8] and, very recently, bisindoloquinolines **2**[9] for applications involving charge transfer.

Here we report on the preparation and properties of hitherto unknown parent heterocyclic system, dibenzo [2,3:5,6]pyrrolizino-[1,7-*bc*]indolo[1,2,3-*lm*]carbazole **3**, which can be considered as a planar hybrid of carbazole and *p*-phenylenediamine. This compound can be prepared both *via* C–C (Scheme 1, route A) and C–N (route B) cyclization. Route A employs arylation of 5,11-dihydroindolo[3,2-*b*]carbazole with *o*-iodonitrobenzene (59% yield), reduction of the resulting *o*-nitrophenyl derivative by $SnCl_2$ to the *o*-diaminophenyl derivative (61% yield). Diazotization of the latter in sulfuric acid provides bis-diazonium



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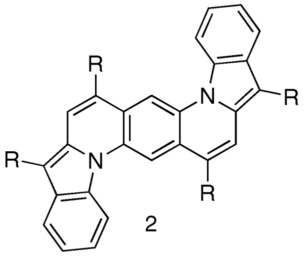

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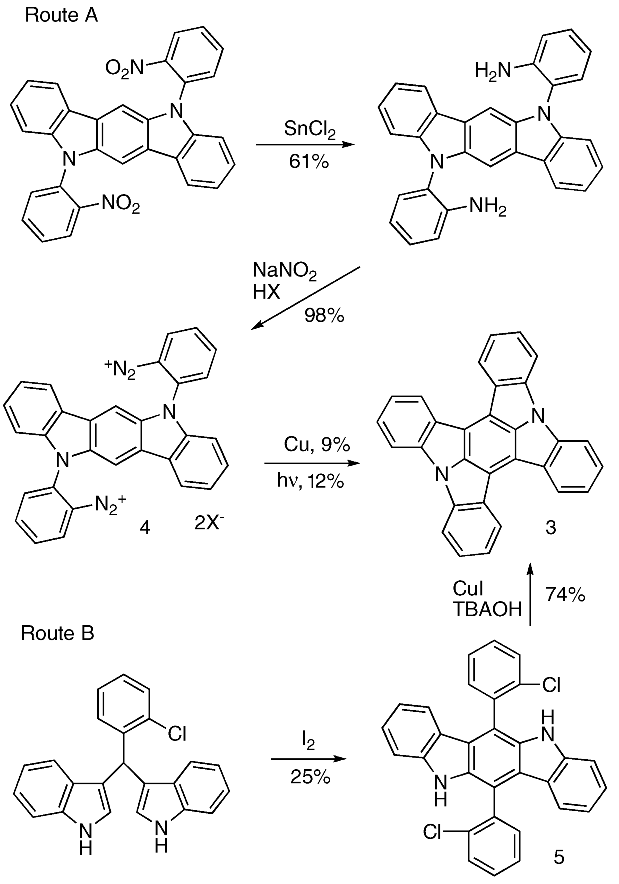

Scheme 1

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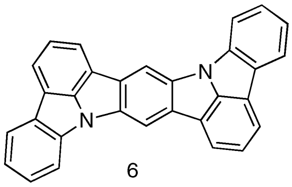
† Electronic supplementary information (ESI) available: Experimental part, spectra fitting details, TD B3LYP calculation results, CV of **3** and EPR spectrum of the cation radical. CCDC 706871. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00100g

salt **4**, which can be isolated quantitatively as the purple perchlorate.

Refluxing the perchlorate in acetic acid with or without copper powder afforded a mixture of **3** along with the symmetrical and asymmetrical isomers **6** and **7**, from which pure **3** can be isolated in 5–9% yield. The same reaction occurs when solid **4** or its DMSO solution are exposed to light. It is noteworthy that upon light exposure solid **4** forms **3** in 10–12% yield without admixture of the isomers, probably owing to the fixed favorable conformation within the solid. Route B is more suitable for the large-scale preparation of **3**. Derivative **5** can be prepared in two steps from indole and *o*-chlorobenzaldehyde.[10] It undergoes cyclization to **3** upon heating in DMF in the presence of tetrabutylammonium hydroxide and catalytic amount of CuI in 74% yield. The second approach is more flexible and allows substituent variations. Thus, starting from 2-chloro-4,5-dimethoxybenzaldehyde, 2,3,11,12-tetramethoxy derivative of **3** was obtained in 75% yield on the cyclization step.



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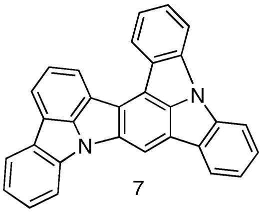

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The new heterocycle **3** possesses high thermal stability: it does not melt and sublimes above 300 °C. The X-ray structure determination showed that the molecule is almost planar (the terminal benzenic rings are twisted by 5° from the molecular plane). The molecules in crystal form slipped π-stacks with the distance between each molecular plane of 3.380 Å (Fig. 1).

In solution **3** exhibits a number of unique features. It shows strong fluorescence (the quantum yield is close to 100% in toluene) and features unprecedentedly small Stokes shift of 3 nm (Fig. 2). However, both visible absorption and fluorescence maxima are only parts of the broader vibronically split bands. Surprisingly, the same is true for TPA. Whereas the TPA cross section expectedly is not large (about 20 GM at 850 nm), the narrow peaks that cover all the investigated range are apparently vibronically split as well. Indeed, both the one-photon and TPA spectra can easily be fitted using the Pekarian functions[11] with the high precision (see ESI† for the details).

Deconvolution showed that minimum two Pekarian functions are needed to reproduce the shape of the fluorescence and TPA spectra, whereas four such functions were needed for the one-photon absorption (OPA) spectra. The determined from fitting absorption maxima are given in Table S1 (ESI†). These are in good agreement with the electronic absorption spectra calculated using the TD B3LYP/6-31G(d,p) method (Table S1, ESI†).[12] The individual deconvoluted band shapes of OPA, TPA and fluorescence are strikingly similar. In particular, the fluorescence band shape indicates that fluorescence occurs from two almost degenerate excited states.

The electron donating properties of **3** could be evaluated using cyclic voltammetry; however, the solubility of this compound in most of the suitable solvents does not exceed 10^{-4} M. Only poorly discernible oxidation peaks were observed in warm DMSO at about 1 V (*vs.* Ag/AgCl), which is very close to the peak oxidation potential of *N*,*N*′-diethyl-5,11-dihydroindolo[3,2-*b*]carbazole prepared by alkylation of the *N*-unsubstituted derivative. The immediate deposition of a black shining product on the working electrode at this potential confirmed that oxidation indeed occurs, but prevented verification of its reversibility. However, the green cation radical of **3** can easily be prepared by chemical[13] oxidation. It is also poorly soluble and features a broad vibronically split absorption band centered at about 730 nm and the EPR signal can be seen in benzonitrile and propylene carbonate. In the presence of trace amounts of water, a part of the radical cation species undergo reduction to **3** and the neutral species interact with the radical cations producing π-stacked aggregates, which can exist in the solution as dimers and/or oligomers. This process can be monitored by the UV-Vis-NIR spectral

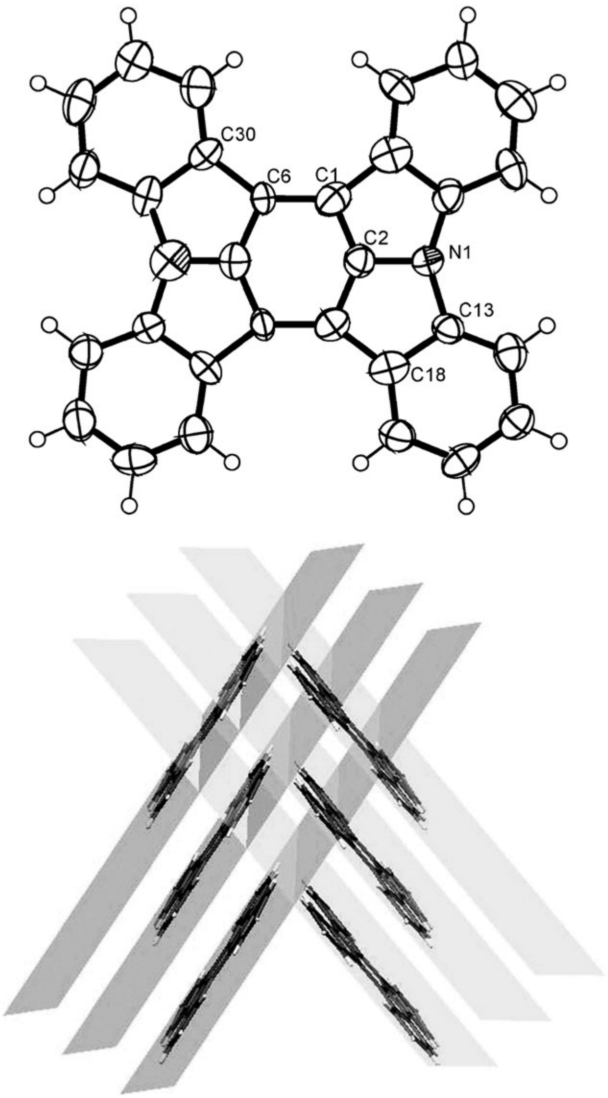

Fig. 1 Molecular and crystal structure of **3** (thermal ellipsoids are presented at 50% of probability). Selected bond lengths in Å: C1–C2 1.366(14); C1–C6 1.411(12); C2–N1 1.384(12); C13–N1 1.437(10); C13–C18 1.438(14); C6–C30 1.476(13).

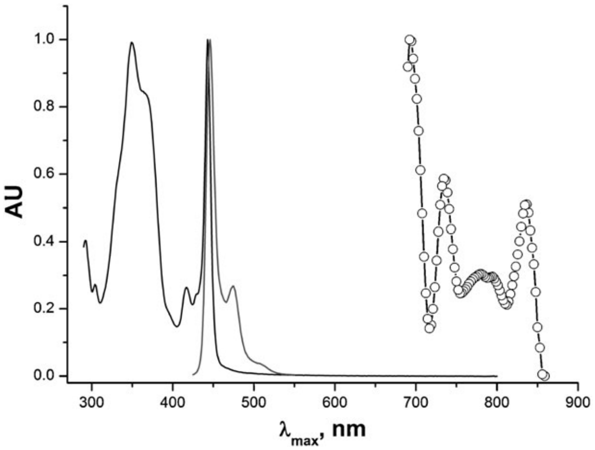

Fig. 2 One-photon absorption (black trace), two-photon excitation (blue trace) and fluorescence (red trace) spectra of **3** in toluene.

changes: the band at 730 nm loses the fine structure and a broad band characteristic of π-stacked aggregates appears above 1500 nm. No further changes occur even in the presence of excess of water, but warming the solution at 80 °C leads to the quantitative recovery of **3**. The dication of **3** prepared by chemical oxidation absorbs at 500 nm.

We conclude that the new heterocyclic system **3** is a thermally stable compound possessing strong electron donor ability close to those of tetra- and pentacene. This compound or its properly substituted derivatives can serve as a promising component for applications involving charge transporting and as the efficient electron donating moiety for fluorescent chromophores including those with strong TPA absorption.

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Experimental

Unless otherwise noted, starting materials, reagents and solvents were obtained from commercial suppliers and were used without further purification. UV-VIS and fluorescence measurements were, respectively, carried out on a Varian Cary 50 Scan UV-Visible and Fluorescence spectrophotometers. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 250 MHz spectrometer. Two photon excitation spectra were obtained using broad band (690–1020 nm) femtosecond laser (Mai Tai, Spectra Physics). The laser beam was focalised by fast optical objective (f = 15 mm, NA = 0.7). Constant mean power excitation (1 W) at 80 MHz repetition rate was used. Pulse duration was 100 fs. Photoluminescence spectra were monitored at 90° detection geometry on the Acton 500 monochromator coupled with gated ICCD camera (π-Star, Prinston Instrument). The quantum yield of fluorescence was determined using 9,10-diphenylanthracene as a reference in toluene at 20 °C.

Crystals of **3** have been grown by slow cooling of a toluene solution down from 200 °C in a sealed ampoule. Data sets were collected on Bruker-Nonius KappaCCD diffractometer with MoK$_\alpha$ radiation, λ = 0.71073 Å. $C_{30}H_{16}N_2$, M = 404.44, monoclinic, space group $P21$, a 5.795(5), b 15.097(5), c 10.982(5) Å, α 90°, β 99.368(5)°, γ 90°, U = 948.0(10) Å^3, T = 293(2) K, Z = 2, 7689 reflections measured, 1298 unique, 1018 with $I > 2\sigma(I)$ were used in all calculations. The final $R(F^2)$ was 0.0850 (observed data). CCDC 706871.

Dibenzo[2,3:5,6]pyrrolizino[1,7-*bc*]indolo[1,2,3-*lm*]carbazole (3)

(a) Route A: 2-[11-(2-aminophenyl)indolo[3,2-*b*]carbazol-5(11*H*)-yl]aniline (0.25 g, 0.57 mmol) was dissolved in 6 ml of acetic acid. A solution of 7.2 ml of concentrated sulfuric acid and 18 ml of water was added dropwise to the mixture. The mixture was cooled to 10 °C and a solution of sodium nitrite (0.10 g, 1.49 mmol) was added in one portion. After 2 min of stirring the mixture was diluted with 30 ml of water. Activated copper (0.20 g, 3.15 mmol) was added and the mixture was refluxed for 1 h. A green precipitate was filtered and dried. The crude product was dissolved in hot toluene, filtered and the concentrated filtrate was filtered through a 20 cm silica gel column. The first yellow fraction was collected and evaporated. The resulting orange solid was dissolved in carbon disulfide filtered through a 10 cm silica gel column. The first yellow fraction afforded 0.023 g of the crude product. Crystallization from benzonitrile gave 0.02 g of **3** (9%) as yellow micro-needles, which sublimed above 300 °C without melting. ^{1}H NMR (in CS_2, referenced to acetone d_6) δ, ppm: 6.78 (t, J = 7.4 Hz, 4H), 6.93 (t, J = 7.4 Hz, 4H), 7.33 (d, J = 8.1 Hz, 4H), 7.80 J = 8.1 Hz, 4H). HRMS calcd. for $C_{30}H_{16}N_2$: 404.1313; found: 404.1320.

(b) Route A—*hν*: compound **4** (0.15 g, 0.22 mmol) was exposed to sunlight under glass cover for 2 h with frequent scratching of the top layer. The dark green solid obtained was extracted with boiling toluene. The workup analogous to (a) gave 0.011 g (12%) of **3**.

(c) Route B: a suspension of compound **5** in freshly distilled DMF (~3 ml) was purged with argon for 15 min. A solution of 40% of tetrabutylammonium hydroxide in methanol (0.15 g, 0.23 mmol), previously degassed with argon, was added at room temperature to the reaction mixture. After all **5** went into solution, CuI (0.01 g, 0.05 mmol) was added and the mixture was then warmed to 120 °C and stirred at this temperature for 20 h. The reaction mixture was then cooled down to room temperature. The precipitate was isolated by filtration, washed with acetonitrile and dried. It was purified by recrystallization in benzonitrile to afford pure **3** (0.03 g) as fine yellow needles in 74% yield.

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