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Novel, soluble diphenyl-diketo-pyrrolopyrroles: Experimental and theoretical study

M. Vala^{a,*}, J. Vyňuchal^b, P. Toman^c, M. Weiter^a, S. Luňák Jr.^d

^a Faculty of Chemistry, Brno University of Technology, Purkyňova 464/118, CZ-612 00 Brno, Czech Republic

^b Research Institute of Organic Syntheses, Rybitví 296, CZ-533 54 Rybitví, Czech Republic

^c Institute of Macromolecular Chemistry v. v. i., Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, CZ-162 00 Prague, Czech Republic

^d Faculty of Chemical Technology, University of Pardubice, Studentská 95, CZ-530 09 Pardubice, Czech Republic

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ABSTRACT

Derivatives of diphenyl-diketo-pyrrolopyrrole, possessing electron-donating or withdrawing groups in the *p*-position of the phenyl, were synthesized and studied using optical characterization (absorption, fluorescence, time-resolved fluorescence) and quantum chemical calculation. An increase in absorption coefficient $\geq 10^5$ dm³ mol⁻¹ cm⁻¹ was observed using electron-donor groups; a bathochromic shift in both absorption and luminescence peaks was observed as a result of increased conjugation. Soluble derivatives were obtained by the introduction of alkyl groups (by N-alkylation) in the central pyrrolopyrrole unit. Calculated phenyl torsion angles using HF and B3LYP methods showed that the loss of molecule planarity reduced the extent of overlap between the π -orbitals of the central pyrrolopyrrole unit and phenyls after N-alkylation. This treatment thus reduced both the bathochromic shift and increased absorption coefficient. The presence of the donor or acceptor groups in itself does not influence molecule planarity.

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1. Introduction

Derivatives of 3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione, commonly referred to as DPPs, constitute an important class of high-performance pigments [1-13] (parent molecule I in Fig. 1). The compounds are endowed with brilliant shades (ranging from yellow-orange to red-violet) and exhibit exceptional resistance to chemical, heat, light, and weather. Furthermore, some of their physical properties such as high melting points are exceptional in view of their very low $M_{\rm r}$, in conventional pigment molecule terms. It has been shown that DPP units introduced into various materials, such as polymers [14-23] dendrimers [24], polymer-surfactant complexes [25], and oligomers [26] results in deeply coloured, highly photoluminescent [15-26] and electroluminescent [19,20] materials. Owing to their interesting properties, there is wide range of possible applications which have been already investigated covering for example latent pigment [27], charge generating materials for laser printers and information storage systems [28-33], solid-state dye lasers [30] or gas detectors [34,35].

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The key issue for the construction of any device either in the form of thin film composed of DPP or incorporation of the DPP unit into supporting matrix, is solubility. DPPs are insoluble in the majority of common solvents. Whilst this is favourable for many applications, the ability to solubilize the compounds would offer the possibility of using solution-based techniques (spin-coating, drop-casting, inject printing, etc.) to prepare devices from DPPs. One reason for their insolubility is the existence of H-bonds between the –NH group and oxygen. Since the basic DPP core is perfectly planar, π - π electron overlap occurs in the solid state and also contributes to their insolubility. These interactions can be so strong as to impart colour change between the solid and dissolved forms and influence other properties, such as fluorescence and Stokes shift [36]. It is therefore clear, that modified solubility can be achieved either through N-substitution and/or disruption of molecular planarity [8].

A previous contribution by the present workers [37] discussed the influence of *N*-alkylation on optical properties and employed quantum chemical calculations to correlate the results with molecule geometry. In this paper, electron-donating (**IV–VIII**) or accepting (**IX**, **X**) groups were introduced at the *p*-position on the phenyl so as to influence the electronic spectra of the compounds. Further, some of these derivatives were *N*-alkylated in order to modify their solubility (**VII–X**). These derivatives were compared





^{*} Corresponding author. Tel.: +420 541 149 411; fax: +420 541 149 398. *E-mail address:* vala@fch.vutbr.cz (M. Vala).



Fig. 1. The basic structure of 3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (I), also known as DPP and the respective derivatives used in this study. The definition of calculated torsion angles α and β .

with the parent (I) and *N*-alkylated (II, III) 3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (Fig. 1). The observed optical properties of both, the donor or acceptor substituted only and substituted and *N*-alkylated derivatives are explained according to the results obtained by quantum chemical calculations.

2. Experimental

The UV–VIS absorption and photoluminescence spectra were recorded in dimethylsufoxide (DMSO) purchased from Aldrich. The molar absorption coefficients were calculated from the linear part of the concentration dependence of absorption A = f(c) measured in 5 cm quartz cuvette. The photoluminescence spectra and quantum yields (*PLQYs*) were obtained according to the comparative method [38], where for each test sample gradient of integrated fluorescence intensity *vs.* absorbance PL = f(A) is used to calculate the *PLQY* using two known standards. The standards were previously cross-calibrated to verify the method. This calibration revealed accuracy better than ~3%. The photoluminescence lifetime τ_{PL} was measured using spectrograph and fast ICCD camera. The samples were excited by second or third harmonic of Nd:YAG laser (532 or 355 nm) with light pulse time duration of ~30 ps. The temporal resolution of the system is approximately 25 ps.

3. Results and discussion

3.1. Absorption

The spectral properties of the prepared derivatives are compared in Figs. 2 and 3 and summarised in Table 1. The Influence of *N*-substitution on the parent derivative **I** on absorption is depicted in Fig. 2a. It can be seen, that insertion of an alkyl group decreases molar absorption coefficient (hypochromic shift) and simultaneously the longer wavelength maximum is shifted towards higher energy region (hypsochromic shift). Furthermore, the vibration structure is less pronounced. As was pointed out in our previous paper [37], this is caused by torsion between pyrrolinone central part and phenyl adjacent to the alkyl group and consequently, is caused by loss of molecule planarity which is in turn responsible for loss of effective conjugation. Since the addition of second alkyl rotates also the second phenyl group, this effect is even

more pronounced. The loss of vibration structure can be attributed to the increased dipole moment interacting with polar DMSO solvent [39]. The dipole–dipole interaction of bi-substituted derivatives with the completely non-planar structure is the most pronounced. No dependency on the length of the alkyl used was found in our previous work [37].

Introduction of electron-donating groups has significant effect on the DPP absorption [40]. Increase of the absorption coefficient from $\varepsilon = 3.4 \times 10^4$ dm³ mol⁻¹ cm⁻¹ of the parent compound I to $\varepsilon = 1.3 \times 10^5$ dm³ mol⁻¹ cm⁻¹ for compound V bi-substituted by N,N-dimethylamin in *p*-position on phenyls, accompanied with strong bathochromic shift (up to 55 nm), was observed (Fig. 2b). This behaviour implies that charge separation occurs via electron delocalization leading to creation of permanent dipole moment. Therefore, the central part composed of H-chromophores behaves as an electron-accepting group. Blurring of vibration structure in case of the mono-substituted derivative (IV) was observed, whereas for the bi-substituted (V) was not. We explain this finding by the fact that due to symmetry of the bi-substituted derivative is its resulting dipole moment smaller than for the mono-substituted asymmetric derivative.

Similar increase of the absorption coefficient ε value and change of the peak position was achieved using piperidine group (**VI**) (Fig. 2c). For this derivative, we studied also the impact of *N*-alkylation. Introduction of one alkyl (**VII**) decreased the ε only slightly. After addition of second alkyl (**VIII**) we observed almost the same value as for the parent molecule (**I**). This was accompanied by the hypsochromic shift and blurring of the vibration structure. We propose the same mechanism as for the *N*-alkylated only derivatives: the *N*-alkylation causes rotation of the phenyls and consequently breaks the molecule symmetry and hence the effective conjugation and increases the polarity.

To describe the influence of groups with the electron-withdrawing character, derivatives with the halogen element (chloride) were prepared. Since the aim was to prepare soluble derivatives we will discuss the alkylated only derivatives. Fig. 2d compares the observed absorption coefficients ε . The introduction of the chloride did not caused increase of ε . This is further evidence for the electron-accepting character of the central part. For the alkylated derivatives we observed hypso- and hypochromic shift with the loss of vibration structure again.



Fig. 2. The influence of N-alkyl substitution (a), and various donor (b, c) and acceptor (d) groups on the DPP central part on molar absorption coefficient.



Fig. 3. Comparison of photoluminescence spectra scaled using the PL quantum yields (PLQY-PL/PL_{max}) of N-alkylated (a), donor (b, c) and acceptor (d) substituted DPP derivatives.

Table 1

Experimental values for molar absorption coefficient ε , position of absorption λ_{Abs} and luminescence λ_{PL} peak maximums, Stokes shift $\Delta \lambda_{Stokes}$, and photoluminescence quantum yield *PLQY* and lifetime τ_{PL} of the prepared DPPs in dimethylsulfoxide.

	$(dm^3 mol^{-1} cm^{-1})$	λ _{Abs} (nm)	λ _{PL} (nm)	$\Delta \lambda_{\mathrm{Stokes}}$ (nm)	PLQY (-)	τ _{PL} (ns)
I	34 300	507	519	12	0.74	6.21
II	21 300	493	525	32	0.69	6.67
Ш	18 500	467	530	63	0.69	6.57
IV	86 500	544	580	36	0.49	2.88
V	126 000	562	580	18	0.57	3.46
VI	108 000	562	582	20	0.58	3.66
VII	100 600	553	592	39	0.42	3.38
VIII	42 400	536	599	63	0.41	3.37
IX	36 000	501	534	33	0.60	6.79
х	24 500	473	538	65	0.51	6.63

3.2. Photoluminescence

The photoluminescence (PL) spectra are compared in Fig. 3. The PL intensity is recalculated using PL quantum yield (*PLQY*): the measured spectra were normalised to its maximum and multiplied by PL quantum yield ($PL = PLQY \cdot PL_{\lambda}/PL_{Max}$). After this transformation, the heights of the curves give direct evidence of the efficiency of the light emission similarly to the ε in the case of light absorption.

For the *N*-alkylated derivatives, we found practically the same *PLQY* in the accuracy range of the method. The Stokes shift was increased from 12 nm for the parent derivative to 32 nm and 63 nm for the monoalkylated and dialkylated derivatives, respectively. The observed spectra (Fig. 3a) were characteristic by graduate loss of mirror symmetry of absorption-fluorescence and vibronic structure. As was pointed out, the phenyl torsion due to the *N*-alkylation is the main mechanism for this behaviour in polar DMSO.

Fig. 3b and c show the influence of electron-donating groups. The mono-substituted derivative shows a smaller *PLQY* compared to the di-substituted one. This is in accordance with the values of the absorption coefficient ε : the polarity of the mono-substituted molecule (**IV**) is higher compared to the symmetric **V** and **VI**. The observed Stokes shifts confirm this hypothesis: for the mono-substituted **V** and **VI** is only 18 nm and 20 nm, respectively. The *N*-alkylation causes further decrease of *PLQY* accompanied with increasing Stokes shift similarly to the *N*-alkylated only derivatives. The electron-withdrawing group (**IX** and **X**) causes analogous behaviour (Fig. 3d).

We also determined fluorescence lifetime τ_{PL} of the prepared derivatives. Table 1 summarises the obtained results. All of the observed fluorescence decays followed first order kinetics, i.e. showed monoexponencial decay, see Fig. 4. The *N*-alkylation only



Fig. 4. Typical photoluminescence decay of DPP (here V) after 30 ps excitation at 532 nm (on top) with weighted residuals to monoexponential fit (on bottom).

caused slight increase of the lifetime. As for the *PLQY*, the lifetime of the donor-substituted derivatives decreased relative to the parent **I**. Subsequent alkylation caused further reduction of the observed lifetime. The longest lifetime was observed for chlorine substituted derivative with broken symmetry (**IX**). The shortest lifetime was observed for the compound **IV** mono-substituted by N,N-dimethylamin in *p*-position on phenyl. The lifetime of its bi-substituted counterpart **V** was found to be higher.

3.3. Quantum chemical study

3.3.1. Methods

The molecular conformations and absorption and luminescence spectra of the synthesized derivatives were characterized by means of the quantum chemical methods in order to better understand the observed behaviour.

The molecular conformations were optimized by means of both the Hartree-Fock (HF) and the hybrid HF/density functional theory method B3LYP [41,42] at the 6-31G* level. The HF method usually provides a fairly good description of the ground state molecular conformations and is used for a major part of the present-day calculations of the electronic properties. The latter method was successfully used for the conformation study of many different π -conjugated systems [43–45]. Although the B3LYP method requires more computational time than the HF method, its computational requirements are much lower than demands of other "correlated" methods. The main difference of the HF and B3LYP methods is that usually the former underestimates and the latter slightly overestimates the electron delocalization and the degree of conjugation in the conjugated molecules. The B3LYP conformations are usually close to the conformations either calculated by the Møller–Plesset method or obtained experimentally, see e.g. [46–48].

First excited states S_1 of the studied derivatives were calculated using time-dependent B3LYP (TD–B3LYP) method at the optimized HF geometry. Time-dependent density functional methods recently became an effective and rather accurate tool for single point calculations of electronic excitations in various, namely conjugated, molecular systems [49–51]. However, this method is not suitable for the excited state conformation optimization necessary for luminescence spectra calculations. For this reason, relaxed (exciton) conformations of the S_1 state were optimized by means of ab initio configuration interaction method with single-excitation (CIS) method. The exciton conformations were subsequently used for the luminescence spectra calculations using TD–B3LYP method. Keeping the same level of the calculations enabled determination of the Stokes shift ΔE_{Stokes} and deformation energy E_{def} of the relaxed exciton state.

3.3.2. Results

The calculated molecular parameters of the studied derivatives are presented in Table 2. Comparison of the phenyl torsion angles calculated by means of HF and B3LYP methods, respectively, shows the same trends determined by both methods. The differences in absolute values can be explained by the different electron delocalization predicted by these methods. The results show that the Nalkylated derivatives possess significantly rotated phenyl groups of the central DPP unit in the position adjacent to the alkyl, while the basic I molecule is completely planar. Phenyl group rotation significantly decreases the overlap between π -orbitals of the central DPP unit and the respective phenyl. As a result, the frontier orbital (HOMO and LUMO) energetic levels are shifted and consequently, absorption and luminescence spectra are modified. The absorption peak energies $E_{S0 \rightarrow S1}$ of the N-alkylated derivatives show a hypsochromic shift strongly correlated with the phenyl torsion angles α and β (for the definition of the angles see Fig. 1).

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Phenyl torsion angles calculated by the HF and B3LYP methods. Lowest absorption energy $E_{S0 \rightarrow S1}$, oscillator strength $f_{S0 \rightarrow S1}$ of this transition, 1st luminescence peak E_{lum} . Stokes shift ΔE_{Stokes} , and deformation energy E_{def} of the relaxed excited state calculated by the ab initio CIS method.

	B3LYP metho	d	HF metho	od	$E_{S0 \rightarrow S1}$ (eV)	$f_{\rm SO \rightarrow S1}$	E _{lum} (eV)	ΔE_{Stokes} (eV)	E _{def} (eV)
	α (°)	β(°)	α (°)	β(°)					
I	0.0	0.0	0.0	0.0	2.837	0.49	2.427	0.410	0.339
П	36.0	6.7	46.9	16.9	2.935	0.40	2.424	0.511	0.437
Ш	36.5	36.5	46.1	46.1	3.012	0.37	2.441	0.571	0.482
IV	0.0	0.0	0.0	0.0	2.691	0.79	2.365	0.327	0.309
v	0.0	0.0	0.0	0.0	2.640	1.03	2.325	0.315	0.294
VI	3.1	3.1	10.5	10.5	2.624	1.13	2.293	0.331	0.326
VII	27.5	6.3	42.6	12.5	2.714	0.95	2.296	0.417	0.394
VIII	29.7	29.7	41.6	41.6	2.786	0.78	2.262	0.482	0.459
IX	34.1	6.7	45.7	16.2	2.875	0.49	2.366	0.508	0.439
х	34.4	34.4	44.9	44.9	2.949	0.43	2.382	0.567	0.483

Simultaneously, the oscillator strengths of the absorption peaks of the molecules **IV–VIII** are notably higher than that of the basic **I** molecule. On the other hand, the absorption peaks of the molecules **II**, **III**, and **X** are reduced. These findings are in a good agreement with the experimentally measured molar absorption coefficients shown in Fig. 2. The calculated results further show, that Stokes shifts ΔE_{Stokes} and deformation energies E_{def} of the excited state of the *N*-alkylated derivatives are considerably increased. The calculated luminescence peak E_{lum} depends only slightly on the phenyl torsion angles α and β .

The substitution of phenyls by donor or acceptor groups has almost no influence on the phenyl torsion angles and the molecular conformation of the central DPP unit. However, it leads to the bathochromic shift of the absorption and luminescence peaks due to the increased effective extent of the conjugation.

3.4. Syntheses and analyses

The synthesis of the starting ethyl 4,5-dihydro-5-oxo-2-phenyl(1-H)pyrrole-3-carboxylate (pyrrolinone ester) was described previously [52], as was the syntheses of 3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**I**), 3,6-Diphenyl-2-butyl-2,5-dihydro-pyrrolo [3,4-*c*]pyrrole-1,4-dione (**II**) and 3,6-Diphenyl-2,5-dibutyl-2,5-dihydro-pyrrolo [3,4-*c*]pyrrole-1,4-dione (**III**) [37]. The 4-fluorobenzoni-trile, diisopropyl succinate, natrium, tert-amyl alcohol and the remaining common solvents were obtained from the Research Institute of Organic Syntheses.

3.4.1. Synthesis of 3-(phenyl)-6-(4-dimethylamino-phenyl)-2, 5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (IV)

80 ml of tert-amyl alcohol and 2.8 g (0.12 mol) of sodium metal (caution: extremely dangerous and corrosive; highly unstable; reacts violently with water; can form flammable hydrogen in contact with air.; incompatible with water, oxygen, carbon dioxide, carbon tetrachloride, halogens, acetylene, metal halides, ammonium salts, oxides, oxidizing agents, acids, alcohols, chlorinated organic compounds, many other substances) (in three portions) were charged into the 250 ml three-necked flask equipped with a magnetic stirrer, a reflux condenser, a thermometer and a nitrogen inlet. The sodium metal was dissolved under reflux in the presence of a catalytic amount of FeCl₃ (approximately 2 h) and 5.8 g (0.04 mol) of 4-dimethylamino-benzonitrile was added. After that, pyrrolinone ester [44] (9.2 g, 0.04 mol) was continuously introduced in small portions within 0.5 h. Subsequently, this mixture was stirred under reflux for 2 h and the ensuing hot salt was filtered. The protolysis was made separately in 120 ml of 2propanol and 80 ml of distilled water under reflux for 2 h. The product was filtered and the filter cake washed with hot water to neutral washings. The filter cake was dried and suspended in 100 ml of methanol. The suspension was heated to boiling and refluxed for 1 h; the ensuing hot suspension was filtered, washed with methanol and hot water. Yield: 2 g (30%) of **IV** compound.

Calculated: C (72.49), H (5.17), N (12.68). Found: C (71.96), H (5.18), N (12.43). MW = 331 Da; Negative-ion APCI-MS: m/z 330 [M - H]⁻ (100%). ¹H chemical shifts: chemical shifts were not determined due to a very low solubility of the sample.

3.4.2. Synthesis of 3,6-bis-(4-dimethylamino-phenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (V)

182 ml of tert-amyl alcohol and 11.4 g (0.50 mol) of sodium metal (in three portions) were charged into the 0.5 dm³ Keller flask equipped with a stirrer, a reflux condenser, a thermometer and a nitrogen inlet. The sodium metal was dissolved under the reflux in the presence of catalytic amount of FeCl₃ (approximately 2 h), and 25 g (0.7 mol) of 4-dimethylamino-benzonitrile was added. Diisopropyl succinate (16.9 g, 0.08 mol) dissolved in 16.9 g of tertamyl alcohol was introduced over 3 h and the mixture stirred at reflux for 1 h. The reaction mixture was cooled to 60 °C and then 500 ml of distilled water was added to protolyse the salt. The protolysis was carried out at 80 °C for 2 h. The resulting hot suspension was filtered and the filter cake washed with hot water to neutral washings. The filter cake was dried and suspended in 500 ml of acetone. The suspension was heated to boiling and refluxed for 1 h: the hot suspension was filtered, washed with acetone and hot water. Yield: 3.1 g (10%) of V compound.

Calculated: C (70.57), H (5.92), N (14.96). Found: C (69.14), H (5.95), N (14.40). MW = 374 Da; Negative-ion APCI-MS: m/z 373 [M - H]⁻ (100%). ¹H chemical shifts: chemical shifts were not determined due to a very low solubility of the sample.

3.4.3. Synthesis of 3,6-di-(4-piperidinophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (VI)

Synthesis of 4-piperidine-1-yl-benzonitrile (starting nitrile): Dry, pure *N*,*N*-dimethylacetamide (400 ml), 47.8 g (0.4 mol) *p*-fluorobenzonitrile (caution: incompatible with strong oxidizing agents, strong acids, strong bases) and 84 g (0.99 mol) of piperidine were charged into a 1 dm³ Erlenmeyer flask equipped with stirrer and condenser. Reaction was carried out at 100 \div 110 °C for 8 h, the gases from the reaction being exhausted via the fume-chamber. Subsequently, the reaction mixture was poured onto 1 kg ice and the crude product was collected by filtration and recrystallized from 80% ethanol. Yield: 43.5 g (60%) of 4-piperidine-1-yl-benzonitrile (m.p. 53 \div 55 °C).

Synthesis of VI: 390 ml of tert-amyl alcohol and 24.4 g (1 mol) of sodium metal (in three portions) were charged to a 1.5 dm³ Keller flask equipped with stirrer, reflux condenser, thermometer and a nitrogen inlet. The sodium metal was dissolved under reflux in the presence of a catalytic amount of FeCl₃ (which took approximately 2 h), and 67 g (0.36 mol) of 4-piperidine-1-yl-benzonitrile was added. After that, diisopropyl succinate (36.3 g, 0.18 mol) dissolved in 36.3 g of tert-amyl alcohol was added over 3 h. Subsequently, the mixture was stirred at reflux for 1 h and the ensuing mixture was cooled to 60 °C, and then 700 ml distilled water was added to protolyse the salt. Protolysis was carried out at 80 °C for 2 h. The resulting hot suspension was filtered and the filter cake was washed with hot water to neutral washings. The filter cake was dried and suspended in 800 ml acetone. The suspension was heated to boiling and refluxed for 1 h. The hot suspension was filtered, washed with acetone and hot water. Yield: 12 g (15%) of VI compound.

Calculated: C (73.98), H (6.65), N (12.33). Found: C (73.23), H (6.55), N (12.11). MW = 454 Da; Negative-ion APCI-MS: *m*/*z* 453

[M – H][–] (100%). ¹H chemical shifts: 10.93 (2H, br s, NH), 8.36 (4H, m, ArH); 7.07 (4H, m, ArH); 3.43 (8H, m, –CH₂ CH₂CH₂N); 1.65 (12H, m, –CH₂CH₂ CH₂ CH₂N and –CH₂CH₂CH₂N)

3.4.4. Synthesis of 3,6-di-(4-piperidinophenyl)-2-butyl-2, 5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (VII) and 3,6-di-(4-piperidinophenyl)-2,5-butyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (VIII)

13.7 g (0.03 mol) of the intermediate VI and 90 g of dry DMF were charged into an evaporating flask and stirred. 12.2 g of 30% methanolic solution of sodium methylate was added. The fine slurry of sodium salt of VI was stirred for 20 min, methanol was distilled under vacuum ($t < 40 \circ C$, p = 40 mbar) and then 12.6 g (0.093 mol) of *n*-butyl bromide was added. The mixture was heated to 80 °C and stirred for 20 h after which time, the temperature was increased to 80–100 °C and this was maintained with stirring for a further 2 h. The reaction mixture was added to 1000 ml of distilled water and the ensuing solution boiled. The final mixture was cooled to 10 °C and the product filtered. The filter cake was reslurried in 200 ml of methanol, the suspension boiled and then filtered. In this step all byproducts from alkylation were removed by TLC (mobile phase: acetone:n-hexane (2:3), thin layer: Alugram Sil G/UV). The filter cake from the previous step (a mixture of mono-, di-substituted product and starting material) was reslurried in 300 ml of acetone. The suspension was boiled and filtered. After cooling, the di-substituted product was obtained. This extraction procedure was repeated twice after which, the raw, di-substituted product was recrystallized from acetone. In this way 1.7 g of dark blue VIII was obtained. The filter cake from the previous step (a mixture of mono-alkylate product and starting material) was reslurried in 300 ml of acetone together with 10 g silica gel for column chromatography (0.06–0.2 mm, pore diameter 6 nm). The suspension was boiled and filtered; acetone from the filtrate was evaporated and 0.22 g of dark blue VII was obtained after the filtration.

VII: Calculated: C (75.26), H (7.50), N (10.97). Found: C (74.21), H (7.23), N (10.83). MW = 510 Da; Negative-ion APCI-MS: m/z 511 $[M - H]^-$ (100%). ¹H chemical shifts: 10.90 (1H, br. s, NH); 8.38 (2H, m, H-ortho); 7.81 (2H, m, H-ortho); 7.08 (4H, m, H-meta); 3.86 (4H, *t*, NCH₂); 3.43 (8H, m, -CH₂ CH₂CH₂N); 1.65 (12H, m, -CH₂CH₂CH₂N); 1.65 (2H, m, CH₂); 0.87 (3H, *t*, CH₃).

VIII: Calculated: C (76.29), H (8.18), N (9.89). Found: C (76.08), H (8.09), N (9.84). MW = 566 Da; Pozitive-ion APCI-MS: m/z 567 [M + H]⁺ (100%). ¹H chemical shifts: 7.84 (4H, m); 7.1 (4H, m); 3.81 (4H, *t*, NCH₂); 3.40 (8H, m, -CH₂ CH₂CH₂N); 1.65 (12H, m, -CH₂CH₂CH₂N) (2H₂N and -CH₂CH₂CH₂N) 1.50 (4H, m, CH₂); 1.25 (4H, m, CH₂); 0.86 (6H, *t*, CH₃).

3.4.5. Syntheses of 3,6-bis-(4-chloro-phenyl))-2-butyl-2,5dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (IX) and 3,6-bis-(4-chlorophenyl))-2,5-butyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (X)

The starting 3,6-Bis-(4-chloro-phenyl)-2,5-dihydro-pyrrolo-[3,4-c]pyrrole-1,4-dione was purchased from Synthesia as the commercial pigment *Versal Red DP3G*. The sample was refluxed in 2-propanol before for 1 h and the ensuing hot suspension was filtered, washed with 2-propanol and hot water. 46.6 g (0.13 mol) of this intermediate and 500 ml of dry DMF were charged into an evaporating flask and stirred. Subsequently, a methanolic solution of sodium methylate prepared from 6 g (0.26 mol) of sodium metal and 50 ml of methanol was added. The fine slurry of the sodium salt of I was stirred for 20 min, methanol was distilled under vacuum ($t < 40 \,^{\circ}$ C, p = 40 mbar) and then 100 g (0.735 mol) of n-butyl bromide was added. The mixture was heated to 60 $\,^{\circ}$ C and stirred for 20 h, after which time the temperature was increased to 100 $\,^{\circ}$ C and maintained at this temperature for a further 2 h with stirring. The reaction mixture was added to 4500 ml of distilled water and boiled; the final mixture was cooled to 10 $^\circ C$ and the product was filtered

The filter cake was reslurried in the mixture of methanol (300 ml) and acetone (300 ml) and the ensuing suspension was boiled and filtered. The filter cake (10.8 g) was identified as a starting material. After cooling of the filtrates, a reddish substance (a mixture of **IX** and **X**) was obtained which was recrystallized from ethanol. The more soluble **X** was separated from the filtrate by evaporation of ethanol and the less-soluble derivative **IX** was obtained from the filter cake. Derivatives **IX** a **X** were three times recrystallized from ethanol.

IX: Calculated: C (63.93), H (4.39), N (6.78), Cl (17.16). Found: C (63.51), H (4.5), N (6.70), Cl (N/N). MW = 412 Da; Negative-ion APCI-MS: m/z 411 [M – H][–] (100%). ¹H chemical shifts: 11.30 (1H, br. s, NH); 8.53 (2H, m, H-ortho); 7.91 (2H, m, H-ortho); 7.73 (4H, m, H-meta); 3.83 (2H, *t*, NCH₂); 1.45 (2H, m, CH₂); 1.20 (2H, m, CH₂); 0.80 (3H, *t*, CH₃).

X: Calculated: C (66.53), H (5.58), N (5.97), Cl (15.11). Found: C (66.42), H (5.73), N (5.92), Cl (15.81). MW = 468 Da; Positive-ion APCI-MS: m/z 469 [M – H][–] (100%). ¹H chemical shifts: 7.83 (4H, m); 7.65 (4H, m); 3.67 (4H, *t*, NCH₂); 1.35 (4H, m, CH₂); 1.11 (4H, m, CH₂); 0.73 (6H, *t*, CH₃).

3.5. Experimental equipment

3.5.1. Mass spectrometry

The ion trap mass spectrometer MSD TRAP XCT Plus system (Agilent Technologies, USA) equipped with APCI probe was used. Positive-ion and negative-ion APCI mass spectra were measured in the mass range of 50–1000 Da in all the experiments. The ion trap analyzer was tuned to obtain the optimum response in the range of the expected m/z values (the target mass was set from m/z 289 to m/z 454). The other APCI ion source parameters: drying gas flow rate 7 dm³ min⁻¹, nebulizer gas pressure 60 psi, drying gas temperature 350 °C, nebulizer gas temperature 350 °C.

The samples were dissolved in a mixture of DMSO/acetonitrile and methanol in various ratios. All the samples were analyzed by means of direct infusion into LC/MS.

3.5.2. Elemental analysis

Perkin Elmer PE 2400 SERIES II CHNS/O and EA 1108 FISONS instruments were used for elemental analyses.

3.5.3. Nuclear magnetic resonance

Bruker AVANCE 500 NMR spectrometer operating at 500.13 MHz for 1H was used for measurements of the 1H NMR spectra and A Bruker AMX 360 NMR spectrometer, operating at 360.13 MHz for 1H and 90,56 MHz for 13C, was used for measurements of 1H and 13C NMR spectra. The compounds were dissolved in hexadeuteriodimethyl sulfoxide. The 1H and 13C chemical shifts were referred to the central signal of the solvent (δ = 2.55 (1H) and 39.60 (13C)). Positive values of chemical shifts denote shifts to higher frequencies.

3.5.4. IR spectrometry

IR spectra were determined by FT-IR spectrometer Nicolet Magna-IR 760. Samples were measured by KBr pellet technique. KBr pellet (diameter 13 mm) was prepared from 1 mg sample and 300 mg KBr.

4. Conclusions

Novel diphenyl-diketo-pyrrolopyrroles with electron-donating or withdrawing groups were prepared. To increase their solubility, we introduced N-alkylation on the central DPP part. The prepared materials were studied experimentally and by the quantum chemical calculations. One of the key-parameter governing absorption and luminescence is the effective extent of the conjugation. This is maximised when the molecule is perfectly planar. Substitution of electron-donating or withdrawing groups affected the molecule planarity only slightly. However, hyperchromic and bathochromic shift in absorption was observed using electron-donating groups suggesting electron-accepting character of the central part. On the other hand, *N*-alkylation introduced to increase the solubility of the DPP derivatives broke the planarity and thus reduced this effect.

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