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The synthesis, absorption and fluorescence of polar diketo-pyrrolo-pyrroles

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ABSTRACT

The effect of electron-donor (piperidino) and electron-acceptor (cyano) groups on the absorption maxima of some diketo-pyrrolo-pyrroles in DMSO solution was investigated both experimentally and theoretically. The syntheses of push–pull substituted 3-(4-piperidinophenyl)-6-(4-cyanophenyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrol-1,4-dione are reported for the first time; 3,6-diphenyl-2,5-dihydropyrrolo[3,4-*c*]pyrrol-1,4-diones substituted with either one or two piperidino or cyano groups in the *para*-positions of the phenyl rings were also synthesized. Whilst both types of substituent produce a bathochromic and hyperchromic shifts with respect to the parent unsubstituted compound, the influence of the piperidino group is strongest. Symmetrically substituted derivatives show well-resolved vibronic structures, while the spectra of polar, unsymmetrical compounds were poorly resolved because of strong dipole–dipole interaction with the polar solvent. The fluorescence of all compounds was intense and a significant increase in the Stokes shift of polar derivatives was another consequence of dipole–dipole interactions with the solvent in the excited state.

1. Introduction

Introduction of polar substituents into organic chromophores causes a redistribution of electronic density in both the ground state and the excited state, which can strongly modify their absorption and fluorescence properties [1]. At present, the push–pull substituted organic π compounds are at the centre of interest of physicists, because they can produce strong second-order nonlinear optical effects [2]. On the other hand, quadrupolar chromophores are suitable for producing third-order NLO behaviour. As organic pigments generally represent photostable systems, their modification by introduction of polar substituents to get dipolar or quadrupolar molecules is very promising in this respect. Phthalocyanine is perhaps the most frequently investigated typical pigment chromophore in this field [3].

Common organic pigments often consist of centrosymmetric molecules, having thus a zero dipole moment. Usually, the last reaction step giving the final chromophore can be used for a synthesis of quadrupolar systems, but it is not appropriate for syntheses of unsymmetrical dipolar derivatives. Hence, it is necessary to find straightforward highly selective synthetic routes leading from push–pull pigments, since these can usually be easily purified by low-molecular starting materials; on the other hand, if a reaction produces a mixture of pigments, the purification is difficult or impossible due to their extremely low solubility. An illustrative example comes from the area of perylenes. Reaction of perylene dianhydride with various primary amines gives unambiguous rise to symmetrical perylene diimides, a successful family of commercial high performance pigments [4]. Its reaction with *ortho*-phenylenediamine produces a mixture of *syn*/*anti*-amidine isomers, among which the *syn*-isomer is the compound with one of the highest two-photon absorption cross-sections ever found [5,6]. Some of its derivatives are reported only as an isomeric mixture, because the way to their separation was not found [7].

The whole family of commercial diketo-pyrrolo-pyrrole pigments (DPPs) is symmetrical, produced by a base catalyzed condensation of 2 mol of (substituted) benzonitrile and 1 mol of succinic diester [4]. Substituent in benzonitrile can be neutral (H (P.R.255), *p*-phenyl, *p*-*tert*-butyl), electron-donating (*p*-methoxy) or electron-withdrawing (*m*-cyano). The most widely used pigment is P.R.254 (*p*-Cl).

The synthesis of unsymmetrical DPPs is also possible by base catalyzed condensation of 1 molecule of an aromatic nitrile (the reaction does not take place with aliphatic nitriles), e.g. benzonitrile and 1 molecule of pyrrolinone ester, i.e. ethyl 4,5-dihydro-5-oxo-2-aryl(1*H*)pyrrole-3-carboxylate (Fig. 1). Unfortunately, only a few

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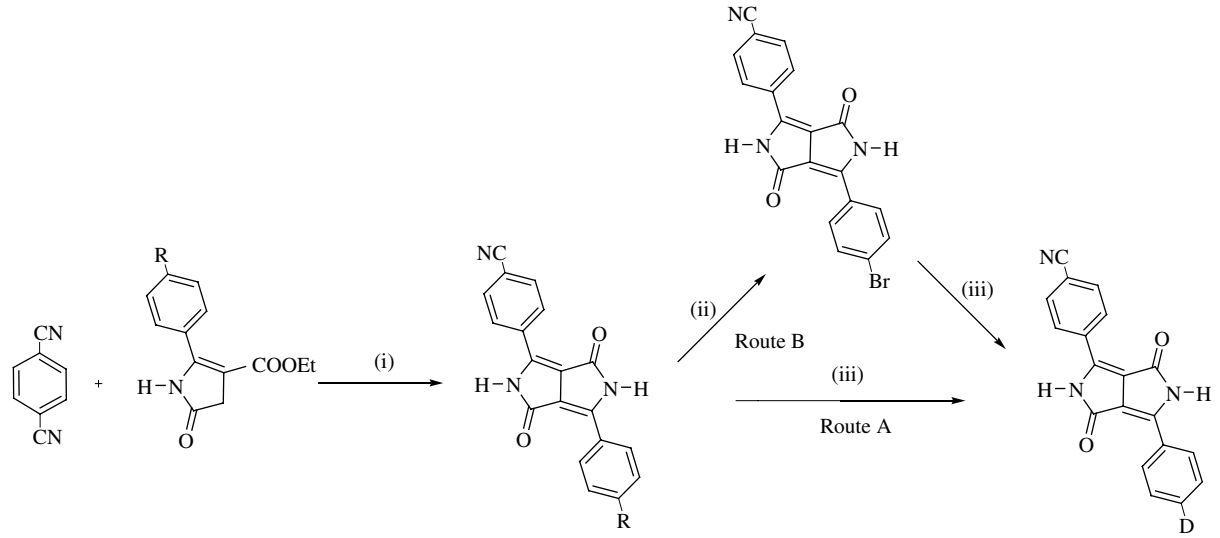


Fig. 1. Synthesis of push–pull DPP.

such pyrrolinone esters with different aryls were reported (aryl = e.g. phenyl, biphenyl-4-yl [8–11], 4-chlorophenyl [9–11]) and none of them with a strong electron-withdrawing or electron-donating substituent. Hence, this reaction cannot be used as a final synthetic step to form push–pull substituted DPP derivatives either.

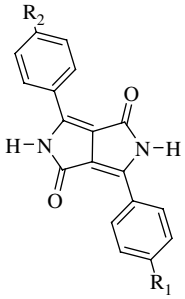
The only report on a synthesis of a push–pull substituted diphenyl DPP chromophore comes from Ciba patent [11]. It is based on a nucleophilic substitution of chlorine atom in 3-(4-chlorophenyl)-6-(4-cyanophenyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1, 4-dione (synthesized according to Fig. 1 (Route A) from 1,4-dicyano-benzene and ethyl 4,5-dihydro-5-oxo-2-(4-chlorophenyl) (1*H*)pyrrole-3-carboxylate) by an amine-type group (dimethylamine, pyrrolidine) in *N*-methylpyrrolidone under pressure.

There exists another synthetic way leading to a halogen substituted DPP chromophore: direct halogenation. In general, chlorine preferably attacks the pyrrolinone rings, but for bromine attack conditions can be selected so that only aryl hydrogen atoms are substituted, and a mixture of derivatives brominated in the pendant aryl groups results [12]. The only report on highly selective and efficient bromination on *para*-phenyl positions of P.R.255 comes also from patent literature and is based on a vapour/solid phase reaction taking about two weeks at room temperature [13].

Three symmetrical compounds (**I**, **III**, **V**, see Fig. 2) were prepared according to classical procedures whilst two unsymmetrical compounds (**II**, **IV**) were prepared according to Fig. 1 (i). Bromination of **II** to form **VIII** (ii) was carried out according to Ref. [13] and the substitution of bromine by piperidine (iii) according to Ref. [11] to form **VI**. Compound **V** was also synthesized by bromination of **I** to form **VII**, followed by the above-mentioned pressure amination.

To the best of our knowledge, compounds **VI** and **VIII** have so far been mentioned neither in an article nor in patent. Piperidine-substituted DPPs are very rare; we have found only two patent references for compound **V**, one of them [14] also mentioning application of compound **IV** as a part of a photoconducting device. Compound **II** is mentioned exclusively in patents (5 references were found by SciFinder); 17 references were found for compound **III** (16 patents and one article describing its use as a ligand in transition-metal complexes [15]). Twenty-four references were found for compound **VII** (mainly patents, but also its interesting application as a monomer in copolymerisation [16,17]).

The pigments synthesized show very limited solubilities in common organic solvents (especially **III**, **V** and **VI**); hence, only dimethyl sulphoxide (DMSO) was found to be a suitable solvent for spectral studies. Quantum chemical calculations of the spectral properties were carried out in order to evaluate the effect of polar substituents. Density functional theory (DFT) was used for geometry calculations and time dependent (TD) DFT to calculate the vertical excitation energies, with the same B3LYP exchange-correlation functional. The solvent effect was involved through polarized continuum model (PCM).



I: $R_1 = R_2 = H$

II: $R_1 = H$, $R_2 = CN$

III: $R_1 = R_2 = CN$

IV: $R_1 =$, $R_2 = H$

V: $R_1 = R_2 =$

VI: $R_1 =$, $R_2 = CN$

VII: $R_1 = R_2 = Br$

VIII: $R_1 = Br$, $R_2 = CN$

Fig. 2. Synthesized DPP derivatives.

2. Results

2.1. Syntheses

The syntheses of both symmetrical derivatives (**III**, **V**) by a classical procedure and the unsymmetrical ones (**II**, **IV**) according to Fig. 1 provided better reaction yields if starting from the cyano-substituted nitrile than if starting from the piperidino-substituted nitrile. The vapour/solid phase bromination of both **I** and **II** gave compounds **VII** and **VIII** with excellent yields and in surprising purity. The final pressure amination proceeded quantitatively: no residual bromine was found by elemental analysis and mass spectroscopy. For details of the syntheses, see Experimental.

2.2. DFT ground state geometry

The B3LYP calculations resulted in a strictly planar geometry for all the compounds except the piperidine moiety, which shows its N atom lying in the plane of DPP chromophore, but with pyramidal arrangement (pyramidal angle is about 30°), and piperidine ring rotated out of plane (rotation angle is about 24°) for compounds **IV**, **V** and **VI**. The conformation of piperidine ring is twist chair.

Four almost isoenergetic minima corresponding to two C_2 and C_i symmetrical and two unsymmetrical rotamers of compound **V** are obtained (both pyramids on N atoms are on the same side, or on opposite sides, of DPP plane, and there are two possible mutual senses of rotation for each), depending on the starting geometry. Thus, the geometry was computed only for the constrained C_i centrosymmetry, which is usual for DPPs.

2.3. PCM TD DFT vertical excitation energies

The lowest vertical excitation energies in DMSO correspond to the allowed HOMO–LUMO $\pi\pi^*$ transition for all the compounds. Both these frontier MOs are shown in Figs. 3 and 4. The energies expressed as wavelengths are summarized in Table 1 together with the experimental energies.

2.4. UV/VIS absorption spectra

The absorption spectra of compounds **I**–**VI** were measured in DMSO at room temperature. The spectra of compounds **I**, **II**, **III** and **V** show two vibronic maxima, the 0–0 vibronic transition being more intensive than 0–1 (e.g., see Fig. 5 for **V**). For compounds **IV** and **VI**, the 0–1 vibronic transition is only detectable as a shoulder (Figs. 6 and 7). The absolute absorption maxima corresponding to 0–0 vibronic transition are summarized in Table 1. The molar absorptivity of compound **III** was not measured due to its low solubility.

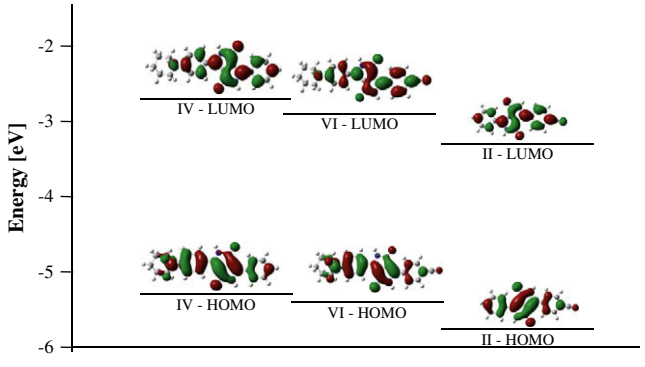


Fig. 3. PCM TD DFT computed energies and shapes of HOMO and LUMO for dipolar derivatives.

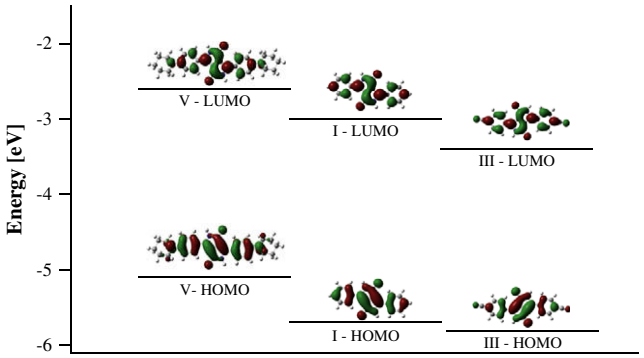


Fig. 4. PCM TD DFT computed energies and shapes of HOMO and LUMO for centrosymmetrical derivatives.

2.5. Fluorescence excitation and emission spectra

Fluorescence excitation and emission spectra were also measured in DMSO. In general, the fluorescence excitation spectra correspond to the absorption spectra, thus confirming the purity of the pigments. Compound **I** was the only one for which two vibronic emission maxima were observed. The other compounds lost their mirror symmetry between emission and excitation. For derivatives **II**, **III** and **V**, the longer wavelength shoulders corresponding to 0–1 vibronic transition were observed (Figs. 5 and 6). Compound **VI** completely lost its vibronic structure (Fig. 7). The absolute fluorescence emission maxima corresponding to 0–0 vibronic transition are summarized in Table 1 together with the absorption maxima.

3. Discussion

The vapour/solid phase bromination procedure is very promising on small scale, because it provides high selectivity and almost quantitative reaction yields. Unfortunately, it cannot be considered as a general bromination procedure for organic pigments. We also applied the vapour/solid phase bromination to a variety of perylene pigments, but without success.

Furthermore, contrary to the published information on substitution of chlorine [11], no contamination of di-donor (**V**) and D-A (**VI**) pigments with residual bromo derivatives was observed after the amination. Such purity can be very important in optical and electronic applications. While substitution of halogen is the only known way leading to push–pull derivatives, in the case of di-donor substitution (**V**) it is possible to choose between the classical

Table 1
Theoretical and experimental excitation energies of the first $\pi\pi^*$ transition (converted to λ_{max}) in DMSO.

Compound	Theor. λ_{00} [nm] (f_{osc})	Exp. Abs. λ_{max} [nm] (ε [l mol^{-1} cm^{-1}])	Exp. Fluor. λ_{max} [nm]	Stokes [nm]
I	494 (0.641)	505.5 (34 200)	517.0	11.5
II	525 (0.714)	524.5 (35 600)	550.0	25.5
III	544 (0.781)	539.0 (–)	565.0	26.0
IV	535 (1.018)	540.0 (38 600)	586.5	46.5
V	554 (1.332)	560.0 (129 200)	588.0	28.0
VI	582 (1.147)	575.5 (57 090)	653.0	77.5

λ_{max} – measured absorption or fluorescence maximum of 0–0 vibronic band.
ε – measured molar absorptivity of 0–0 vibronic band.
λ_{00} – computed absorption maximum of 0–0 vibronic band.
f_{osc} – computed oscillator strength of 0–0 vibronic band.

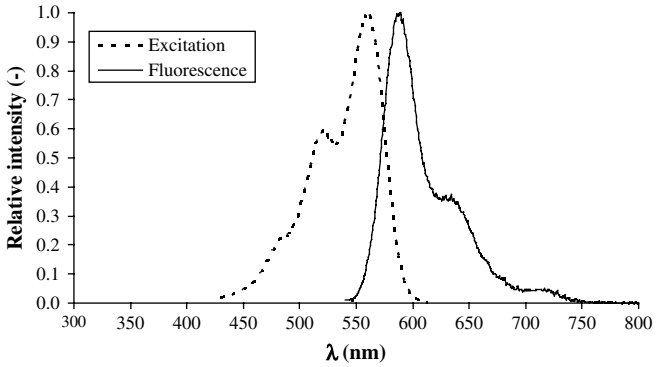


Fig. 5. Absorption and fluorescence emission and excitation spectra of compound **V** in DMSO.

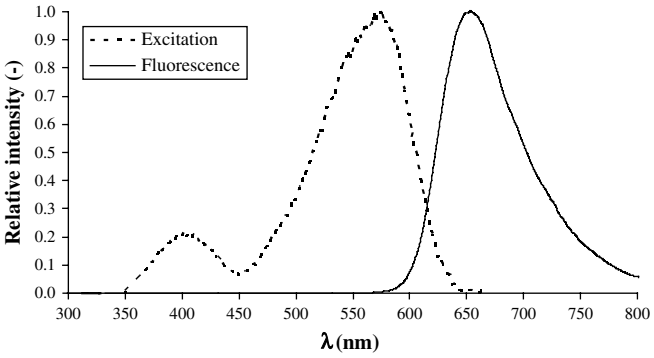


Fig. 7. Absorption and fluorescence emission and excitation spectra of compound **VI** in DMSO.

procedure starting from *p*-piperidino-substituted nitrile and substitution of bromine by piperidine.

In general, the direct synthesis of the symmetrical electron-donating compound **V** from benzonitrile derivative gave a small yield, but the purity of the product was good. The nucleophilic substitution of bromine in compound **VIII** by one electron-donating group gave the push–pull derivative **VI** in a high yield, and also its purity was good. On the other hand, the nucleophilic substitution of bromine atoms in compound **VII** by two electron-donating groups was not so selective. The mass spectrometry analysis of the reaction product revealed two substances: one of them was the required product (i.e. bromine was successfully substituted by the electron-donating group) and the other was a by-product in which bromine was replaced by hydrogen, i.e. compound **IV**.

We failed to find conditions for selective synthesis of compound **V** by this procedure. The yield of crude product was ca 70% (which was estimated from the calculated intensity ratio of the two peaks in MS spectrum). The by-product was more soluble due to its lost symmetry and higher polarity; hence, it was quite successfully removed by washing with NMP. In all the experiments, bromine was completely substituted, which was confirmed by MS as a very selective method for detection of bromine due to the presence of two bromine isotopes.

With respect to phenyl–pyrrolinone rotation, the predicted geometry of the synthesized compounds is planar. The X-ray structure of compound **I** shows slightly rotated phenyl rings (7°) [18]. We ascribe this type of perturbed planarity to packing effects in crystal phase, as e.g. C.I. Pigment Red 254 (compound **I** with two chlorine substituents in *para*-positions of both phenyl groups) shows the corresponding dihedral angle only 2° [19]. So we suppose that DPP derivatives can adopt a planar geometry in solution. The non-planar arrangement of piperidine moiety is enforced by steric reasons, since it is almost independent of the other substituents.

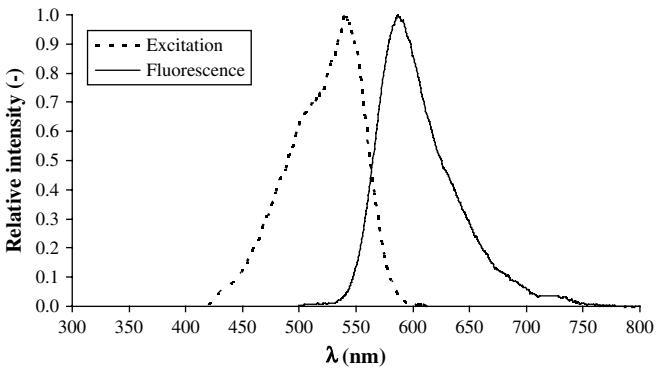


Fig. 6. Absorption and fluorescence emission and excitation spectra of compound **IV** in DMSO.

The absorption maxima show clear (and well known [20]) dependence on substitution. Any substitution of the parent nucleus causes a bathochromic shift. The extent of this shift is significantly higher for an electron-donating substituent. If we take compound **I** as a parent compound, the shift induced by substituent is 35 nm for **IV** and only 19 nm for **II**. The substitution by a second substituent of the same character brings further 20 nm in the electron-donor series (**V**) and only 14 nm in the electron-acceptor series (**III**). The highest bathochromic shift of 70 nm, as compared with compound **I**, is observed for the push–pull substituted derivative **VI**.

We had some doubts if the PCM TD DFT methodology based on the findings described by Jacquemin et al. [21] would be able to correctly describe compounds with strongly polar substituents. A large discrepancy between computed and experimental absorption maxima of isoindigo was recently ascribed [21] to the inability of this theoretical access to handle compounds (transitions) having a significant charge-transfer (CT) character. Theoretical reasons for such behaviour were also given: they are based on the inability of the TD DFT method (based on usual exchange-correlation functionals like B3LYP) to describe the correct asymptotic behaviour with respect to the distance between charges in CT transitions [22].

Thus, a good agreement between the computed and measured absorption maxima was rather surprising. The highest difference was found for the unsubstituted compound **I** (11 nm) and the differences of others are ca 6 nm. The correlation between oscillator strength and molar absorptivity is also good; only its extremely increased ε value for compound **V** was not predicted quantitatively. In general, cyano group stabilizes both FMOs, while piperidino group destabilizes them (and even to a greater extent), as shown in Figs. 3 and 4. An electron-donor substituent increases the electron density on the phenyl group to which it is attached, and on acceptor C═O group of the second pyrrolinone ring in HOMO, while in LUMO further CT is observed to the opposite phenyl group (more to the CN-substituted phenyl group in compound **VI** than to the unsubstituted phenyl group in compound **IV**) and to the closer C═O group. Although the situation is not so simple, a similarity in can be seen to the behaviour of the first $\pi\pi^*$ transition of *para*-(di)substituted aromatic azobenzenes with respect to both types of substituents [1,23], which indicates the electron-acceptor character of the whole central dipyrrolinone moiety resembling that of an azo group. The accepting capability is mainly localized on keto groups, in accordance with the coupled merocyanine concept [24].

The absorption spectra of the symmetrical compounds **I**, **III**, **V** and unsymmetrical compound **II** show resolved vibronic structure even in strongly polar DMSO. We ascribe the poor resolution of this

structure in the case of compounds **IV** and **VI** to significantly higher dipole moment interacting with the polar solvent by dipole–dipole interaction. From this point of view, compound **II**, though unsymmetrical and substituted by polar substituent, should not be considered as strongly polar.

The fluorescence spectra of DPPs usually show small Stokes shifts [25], which are significantly increased by *N*-substitution (e.g. alkylation) inducing higher degree of nonplanarity [26]. Thus the *N*-substituted derivatives are promising with respect to OLED application [27]. The Stokes shift between 0-0 vibronic bands in absorption and fluorescence spectra is higher for all five derivatives than that for parent compound **I** (12 nm). It is quantitatively similar for symmetrical derivatives **III**, **V** and unsymmetrical compound **II** (26–28 nm). Its significant increase is observed for compounds **IV** (47 nm) and **VI** (78 nm) as a result of much stronger excited state solvent relaxation of these polar compounds. In our opinion, the effect of potential geometrical relaxation is of minor importance.

The spectral data strongly confirm the dipolar character of compound **IV** and especially **VI**, giving them some chance to produce second-order nonlinear optical phenomena. Compound V is of D–π–A–π–D character, which is considered as a paradigmatic quadrupolar pattern, promising in the field of the third-order nonlinear optics [2]. Especially, the outstanding increase in its molar absorptivity is promising.

4. Conclusions

Highly selective and efficient vapour/solid phase bromination of DPP pigments gives brominated precursors that can be effectively substituted by strong nucleophils of the secondary amine type. In this way, the push–pull substituted DPPs can be easily obtained without contamination by residual bromine. Such a push–pull derivative shows strongly dipolar character manifesting itself by unusual Stokes shift and, hence, a negligible reabsorption of fluorescence.

The low solubility of the synthesized pigments prevented the measurement of solvatochromism, which is usually connected with NLO effects, e.g. two-photon absorption [28]. Therefore, at present we are preparing the *N*-alkylated derivatives of **IV**, **V** and **VI**, which can be expected to possess much better solubility because of the perturbed planarity and the absence of intermolecular hydrogen bonding.

5. Experimental

5.1. 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 [8] whilst that of **I** was described in the previous paper [29]. Benzene-1,4-dicarbonitrile, DMSO and *tert*-amyl alcohol were purchased from Aldrich; 4-fluorobenzonitrile was obtained from Research Institute of Organic Synthesis.

5.1.1. 3-(Phenyl)-6-(4-cyanophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (*II*)

tert-Amyl alcohol (330 ml) and 6 g (0.260 mol) sodium metal (in three portions) were charged into an 1.5 dm^3 Keller flask equipped with a stirrer, reflux condenser, thermometer and a nitrogen inlet. The sodium metal was dissolved under the reflux in the presence of catalytic amount of $FeCl_3$ (approximately 2 h), whereupon 16.6 g (0.129 mol) benzene-1,4-dicarbonitrile (which forms a suspension) was added. After that, 30 g (0.129 mol) pyrrolinone ester dissolved in 100 ml *tert*-amyl alcohol was continuously introduced within 15 min. A blue suspension of sodium salt of compound **II** was formed during the reaction. Subsequently, this mixture was stirred under the reflux for 2 h. The reaction mixture was cooled to 60 °C, whereupon 20 ml acetic acid was added during 10 min to protolyse the salt. The dark violet product was collected by suction, and the filter cake was washed with hot water until neutral washings. The filter cake was dried and suspended in 1.5 dm^3 ethanol/water mixture (1:1). The suspension was heated to boiling and refluxed for 1 h. The hot suspension was filtered, the filter cake was washed with ethanol and finally with hot water. Yield: 30 g (74%) compound **II**.

Calculated: C (72.84), H (3.54), N (13.41). Found: C (72.00), H (3.42), N (12.94).

MW = 313 Da; positive-ion APCI-MS: *m*/*z* 314 $[M+H]^+$ (100%).

^{1}H chemical shifts: 11.57 and 11.54 (2 × NH, br s), 8.63 (Ar*H*, 2H, m), 8.56 (Ar*H*, 2H, m), 8.11 (Ar*H*, 2H, m), 7.67 (Ar*H*, 3H, m).

5.1.2. 3,6-Di-(4-cyanophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (*III*)

tert-Amyl alcohol (150 ml) and 6 g (0.154 mol) potassium metal were charged into an 0.5 dm^3 flask equipped with a stirrer, reflux condenser, thermometer and a nitrogen inlet. The potassium metal was dissolved under the reflux within ca 1 h, whereupon 25.6 g (0.2 mol) of benzene-1,4-dicarbonitrile (it forms a suspension) was added. After that, 8.3 ml (0.05 mol) diethyl succinate dissolved in 100 ml *tert*-amyl alcohol was continuously introduced within 2 h. A blue suspension of potassium salt of compound **III** was formed during the reaction. Subsequently, this mixture was stirred and refluxed for 2 h. The reaction mixture was cooled to 60 °C, and then 10 ml acetic acid dissolved in 100 ml methanol was added during 10 min to protolyse the salt. The dark violet product was collected by suction, and the filter cake was washed with hot water until neutral washings. The filter cake was dried and suspended in 0.5 l acetonitrile. The suspension was heated to boiling and refluxed for 1 h. The hot suspension was filtered, the filter cake was washed with acetonitrile and finally with hot water. Yield: 13 g (77%) compound **III**.

Calculated: C (71.00), H (2.98), N (16.56). Found: C (69.76), H (2.86), N (16.49).

MW = 338 Da; Negative-ion APCI-MS: *m*/*z* 337 $[M-H]^-$ (100%).

^{1}H chemical shifts: 8.67 (Ar*H*, 4H, m), 8.10 (Ar*H*,4H, m).

5.2. Synthesis of 4-piperidine-1-yl-benzonitrile (starting nitrile)

Dry and pure *N*,*N*-dimethylacetamide (400 ml), 47.8 g (0.4 mol) *p*-fluorobenzonitrile and 84 g (0.99 mol) piperidine were charged into an 1 dm^3 Erlenmeyer flask equipped with a stirrer and condenser. The reaction was carried out at 100–110 °C for 8 h. The reaction gases from the reaction were let out to fume-chamber. Subsequently, the reaction mixture was poured onto 1 kg ice. The crude product was collected by filtration and recrystallized from 80% ethanol. Yield: 43.5 g (60%) 4-piperidine-1-yl-benzonitrile (m.p. exp. 53–55 °C, lit. 54–55 °C [30]).

5.2.1. 3-(Phenyl)-6-(4-piperidinophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (*IV*)

tert-Amyl alcohol (80 ml) and 2.8 g (0.12 mol) sodium metal were charged into a 250 cm^3 flask equipped with a stirrer, reflux condenser, thermometer and a nitrogen inlet. The sodium metal was dissolved under the reflux in the presence of catalytic amount of $FeCl_3$ (which approximately took 2 h), whereupon 7.4 g (0.04 mol) 4-piperidin-1-yl-benzonitrile was added. After that, 9.2 g (0.04 mol) pyrrolinone ester (in small portions) was continuously added within 0.5 h. Finally, this mixture was stirred and refluxed for 2 h. The hot suspension of sodium salt of compound **IV** was collected by suction. The filter cake was charged into 200 ml

propan-2-ol/water mixture (3/2 by vol.), and the suspension was heated to boiling and refluxed for 2 h. The product was collected by filtration, and the filter cake was charged into 100 ml methanol and refluxed for a short time. The hot suspension was filtered, the filter cake was washed with methanol and finally with hot water. Yield: 5.5 g (37%) compound **IV**.

Calculated: C (74.37), H (5.70), N (11.31). Found: C (74.05), H (5.68), N (11.30).

MW = 371 Da; Positive-ion APCI-MS: *m*/*z* 372 $[M+H]^+$ (100%).

^{1}H chemical shifts: 10.85 (2H, br s, N*H*), 8.45 (4H, m, Ar*H*), 7.55 (3H, m, Ar*H*), 7.07 (2H, d, $J = 8.5$ Hz, Ar*H*), 3.46 (4H, m, $-CH_2CH_2CH_2N$), 1.67 (6H, m, $-CH_2CH_2CH_2N$ and $-CH_2CH_2CH_2N$).

5.2.2. 3,6-Di-(4-piperidinophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (*V*)

Procedure A: 390 ml *tert*-amyl alcohol and 24.4 g (1 mol) sodium metal (in three portions) were charged into an 1.5 dm^3 Keller flask equipped with a stirrer, reflux condenser, thermometer and nitrogen inlet. The sodium metal was dissolved under reflux in the presence of catalytic amount of $FeCl_3$ (which approximately took 2 h), and 67 g (0.36 mol) 4-piperidine-1-yl-benzonitrile was added. After that, diisopropyl succinate (36.3 g; 0.18 mol) dissolved in 36.3 g *tert*-amyl alcohol was continuously introduced within 3 h. Subsequently, this mixture was stirred under reflux for 1 h. The reaction mixture was cooled to 60 °C, and then 0.7 l 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 was washed with hot water to neutral washings. The filter cake was dried and suspended in 0.8 l 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%) compound **V**.

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%).

^{1}H chemical shifts: 10.93 (2H, br s, N*H*), 8.36 (4H, m, Ar*H*), 7.07 (4H, m, Ar*H*), 3.43 (8H, m, $-CH_2CH_2CH_2N$), 1.65 (12H, m, $-CH_2CH_2CH_2N$ and $-CH_2CH_2CH_2N$).

Procedure B: 10 g (0.02 mol) compound **VII** was dispersed in 300 ml *N*-methylpyrrolidone using ultrasonic bath for a short time. Subsequently, this mixture was charged into 1 dm^3 glass autoclave (Büchiglasuster) together with 18.6 ml (0.19 mol) piperidine. This mixture was stirred at 190 °C ($p = 1$ bar) for 10 h. After cooling, the product was collected by suction, and the filter cake was washed with *N*-methylpyrrolidone, methanol, and hot water. The filter cake was dried and dispersed in 300 ml methanol. The suspension was heated to boiling and refluxed for 1 h. The hot suspension was filtered; the filter cake was washed with methanol and hot water.

MW = 454 Da; Positive-ion APCI-MS: *m*/*z* 455 $[M+H]^+$ (100%).

MW = 371 Da; Positive-ion APCI-MS: *m*/*z* 372 $[M+H]^+$ (100%).

The crude product was heated in 100 ml NMP at the temperature of 150 °C for a short time. Yield: 3.5 g (35%) compound **V** was obtained after filtration.

MW = 454 Da; Positive-ion APCI-MS: *m*/*z* 455 $[M+H]^+$ (100%).

5.2.3. 3-(4-Cyanophenyl)-6-(4-piperidinophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (*VI*)

Compound **VIII** (10 g; 0.02 mol) was dispersed in 300 ml *N*-methylpyrrolidone using ultrasonic bath for a short time. Subsequently, this mixture was charged into 0.5 dm^3 glass autoclave (Büchiglasuster) together with 16 g (0.19 mol) piperidine. This mixture was stirred at 190 °C ($p = 1$ bar) for 10 h. After cooling, the product was collected by suction, and the filter cake was washed with *N*-methylpyrrolidone, methanol, and hot water. The filter cake was dried and charged into 400 ml of methanol. The suspension was heated to boiling and refluxed for 1 h. The hot suspension was filtered, washed with methanol and hot water. Yield: 6.4 g (73%) compound **VI**.

Calculated: C (72.71), H (5.08), N (14.03). Found: C (72.69), H (5.07), N (14.13).

MW = 396 Da; Negative-ion APCI-MS: *m*/*z* 395 $[M-H]^-$ (100%).

^{1}H chemical shifts: 11.28 and 11.25 (2H, br s, N*H*), 8.53 (2H, m, Ar*H*), 8.46 (2H, m, Ar*H*), 8.03 (2H, m, Ar*H*), 7.11 (2H, m, Ar*H*), 3.54 (4H, m, $-CH_2CH_2CH_2N$), 1.66 (6H, m, $-CH_2CH_2CH_2N$ and $-CH_2CH_2CH_2N$).

5.2.4. 3,6-Di-(4-bromophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (*VII*)

Compound **I** (15 g; 0.05 mol) was placed on a Petri dish and placed in a desiccator. Bromine (80 g) was added at the bottom of the desiccator and bromination was carried out at room temperature for 13 days, while the desiccator valve was partially vented (via safe extraction) during reaction. Subsequently, the Petri dish with the product and free absorbed bromine was carefully placed in another empty desiccator and evacuated for 5 h; in this way, free bromine was removed (via safe extraction). The product was introduced into a cold mixture of 125 ml cyclohexene and 60 ml carbon tetrachloride and the ensuing mixture was slowly heated to boiling and was refluxed for 30 min. The hot suspension was filtered, and the filter cake was charged into 800 ml methanol and refluxed for a short time. The hot suspension was filtered; the filter cake was washed with methanol and hot water. Yield: 21.98 g (95%) compound **VII**.

Calculated: C (48.46), H (2.26), Br (35.82), N (6.28). Found: C (48.32), H (2.29), Br (36.00) N (6.06).

MW = 444 Da; Negative-ion APCI-MS: *m*/*z* 443 (50%), *m*/*z* 445 (100%), *m*/*z* 447 (50%).

^{1}H chemical shifts: 11.43 (2H, br s, N*H*), 8.44 (4H, m, Ar*H*), 7.86 (4H, m, Ar*H*).

5.2.5. 3-(4-Cyanophenyl)-6-(4-bromophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (*VIII*)

Compound **II** (30 g; 0.1 mol) was placed on Petri dish and put into the desiccator. Bromine (160 g) was added at the bottom of the desiccator and bromination was carried out at room temperature for 13 days while the desiccator valve was partially vented (via safe extraction) during reaction. Subsequently, the Petri dish with the product and free absorbed bromine was carefully put into another empty desiccator and evacuated for 5 h (via safe extraction); in this way, free bromine was removed. The product was introduced into a cold mixture of 200 ml cyclohexene and 300 ml carbon tetrachloride. This mixture was slowly heated to boiling and refluxed for 1 h. The hot suspension was filtered, and the filter cake was charged into 800 ml methanol and refluxed for short time. The hot suspension was filtered, washed with methanol and hot water. Yield: 32.6 g (87%) compound **VIII**.

Calculated: C (58.18), H (2.57), Br (20.37), N (10.71). Found: C (56.89), H (2.72), Br (20.08), N (10.09).

MW = 391 Da; Positive-ion APCI-MS: *m*/*z* 392 (100%), *m*/*z* 394 (100%).

^{1}H chemical shifts: 11.54 and 11.47 (2H, br s, N*H*), 8.57 (2H, m, Ar*H*), 8.46 (2H, m, Ar*H*), 8.10 (2H, m, Ar*H*), 7.86 (2H, m, Ar*H*).

5.3. Instrumental equipment

5.3.1. Absorption and fluorescence spectra

Perkin Elmer Lambda 35 was used for the measurements of absorption spectra and Perkin Elmer LS 35 for fluorescence emission and excitation spectra at room temperature in DMSO solutions.

5.3.2. 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 are drying gas flow rate 7 L 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.

5.3.3. Elemental analysis

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

5.3.4. Nuclear magnetic resonance

Bruker AVANCE 500 NMR spectrometer operating at 500.13 MHz for ^{1}H was used for measurements of the ^{1}H NMR spectra. The samples were dissolved in hexadeuteriodimethyl sulphoxide. The ^{1}H chemical shifts were referenced to the central signal of the solvent ($\delta = 2.55$ (^{1}H)). Positive values of chemical shifts denote shifts to higher frequencies. The ^{13}C chemical shifts were not determined due to the very low solubility of the samples.

5.3.5. Computational procedures

The geometry of all the six compounds was optimised using quantum chemical calculations based on DFT. The hybrid three-parameter B3LYP functional in combination with 6-311G(d,p) basis was adopted. No constraints were employed, except for compound **V**. No imaginary frequencies were found after diagonalization of Hessian matrix, confirming that the computed geometries were the real minima on the ground state hypersurfaces.

TD DFT method was used for the computation of vertical excitation energies on the above-mentioned geometries. The B3LYP/6-311 + G(2d,p) combination was employed. The solvent effect was involved by means of the non-equilibrium PCM.

All the methods came from the Gaussian03W program suite [31], and the default values of computational parameters were used. The results were analyzed using GaussViewW from Gaussian Inc, too.

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