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Synthesis and properties of some new *N*,*N*′-disubstituted 2,5-dihydro-1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrroles

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Abstract

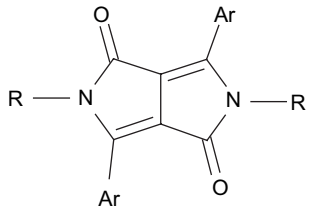
A variety of substituents have been introduced on the nitrogen atoms of the parent 2,5-dihydro-1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole upon treatment with alkylating agents in a basic medium. Crystal structure as well as absorption and fluorescence properties of the new DPP pigments so obtained is discussed.

Keywords: Organic pigments; *N*-Alkylation; Crystal structure; Spectroscopic studies; Fluorescence

1. Introduction

3,6-Diaryl-2,5-dihydro-1,4-dioxopyrrolo[3,4-*c*]pyrroles (**1**), commonly referred to as DPPs, constitute the most recent addition to the class of the high-performance pigments [1–7]. They are endowed with brilliant shades (ranging from yellow-orange to red-violet) and exhibit outstanding chemical, heat, light, and weather fastness. Furthermore, some of their physical properties such as the high melting points and the insolubility in most common solvents are exceptional in view of the low molecular weight relative to pigment standards. In view of their actual importance as pigments, of their promising applications as charge generating materials for laser printers and information storage systems [8–12], and of their potential utility as the core unit in luminescent polymers [13,14], these heterocyclic compounds have been the object of crystallographic studies [4,15–18], photophysical investigations [9,10], and theoretical calculations [19,20]. However, a limited number of new 3,6-diaryl-2,5-dihydro-1,4-dioxopyrrolo[3,4-*c*]pyrroles have been added [9,10,13,17,21] to the first ones discovered in the pioneering 80 years and a surprising paucity of substrates of general formula **1** is so far known in the literature. Interestingly, structurally related 3-alkyl-6-aryl [17] and 3,6-di(heteroaryl) [17,18] derivatives have been recently described.

In the above context, we thought it would be advisable to have in hand a more variegate array of representatives of this chemical class and tried to synthesize some *N*,*N*′-disubstituted 2,5-dihydro-1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrroles in order to compare their properties to those of the parent *N*,*N*′-unsubstituted term. To our knowledge, the following groups have been hitherto reported on the nitrogen atoms of the 2,5-dihydro-1,4-dioxopyrrolo[3,4-*c*]pyrrole skeleton: methyl [3,10,17], Boc [17], hexyl [13,14], 6-hydroxyhexyl [13], and allyl [9].



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2. Results and discussion

2.1. Synthesis

The parent 2,5-dihydro-1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*] pyrrole (**2**) was prepared in 55% yield following the literature procedure [3], namely upon reaction of benzonitrile with 0.5 equivalents of dimethyl succinate and an excess of potassium *t*-butoxide in 2-methyl-2-butanol as solvent. The subsequent functionalization of the nitrogen atoms of **2** was accomplished in DMF in the presence of potassium carbonate as a base: the alkylating agents were methyl 4-toluenesulphonate, benzyl bromide, 4-(*t*-butyl)benzyl bromide, allyl bromide, propargyl bromide, ethyl 2-bromoacetate, and α,4-dibromoacetophenone. Reaction temperature and times as well as isolation yields are indicated in Scheme 1. All products of **3** were characterized by spectral data (IR, mass, ^{1}H and ^{13}C NMR) which are reported in Section 3.

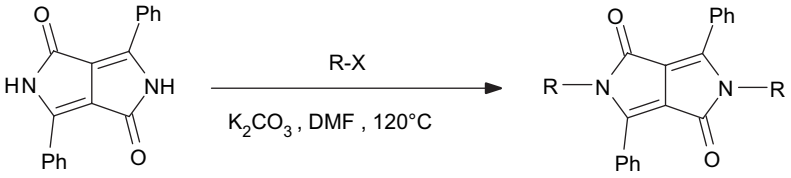
2.2. Crystal structure

The single-crystal X-ray analysis was performed on two terms of the above series of new compounds, namely **3d** and **3f**. Their molecular diagrams are shown in Fig. 1.

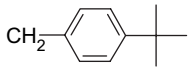
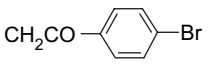
In the first case, the molecule lies on a crystallographic centre of symmetry and presents the following features: (i) the heterocyclic nucleus is strictly planar, with bond lengths of 1.222, 1.423, 1.389, 1.380, 1.419, and 1.446 Å for the conjugated system O5–C1–N2–C3–C4–C4′–C1; (ii) the plane of each phenyl ring is rotated by 35.8° with respect to the heterocycle; (iii) the allylic chains are nearly perpendicular to the heterocycle (torsion angle −87.5°), their conformation being stabilized by a weak hydrogen bond between N2 and H8 (distance 2.57 Å).

In the case of **3f**, although the isolated molecule would have C_i symmetry, it happens to lose any symmetry in the crystal. In fact, the two planar pyrrole rings are twisted each other of 6.0° and the planes of the phenyl rings are differently rotated with respect to the heterocycle, the torsion angles being 36.5° for *A*/*C* and 68.8° for *B*/*D*. Also the two *N*-pendants are not equivalent because one of them assumes a roughly linear disposition due to an about all-*trans* conformation, while the other one presents a more twisted disposition due to a torsion angle of −84.6° at C24, O26, C27, C28.

It seems interesting to mention that the parent molecule **2** was shown [4] to be almost planar with the phenyl rings tilted out of the plane of the heterocyclic chromophore by about 7° and its intermolecular interaction energy was calculated [19]



2 **3**

Entry	R	t (min)	Yield (%)
3a	Me	70	71
3b	CH_2Ph	70	74
3c		120	63
3d	$CH_2—CH=CH_2$	100	79
3e	$CH_2—C\equiv CH$	100	74
3f	CH_2COOEt	70	76
3g		70	60

Scheme 1.

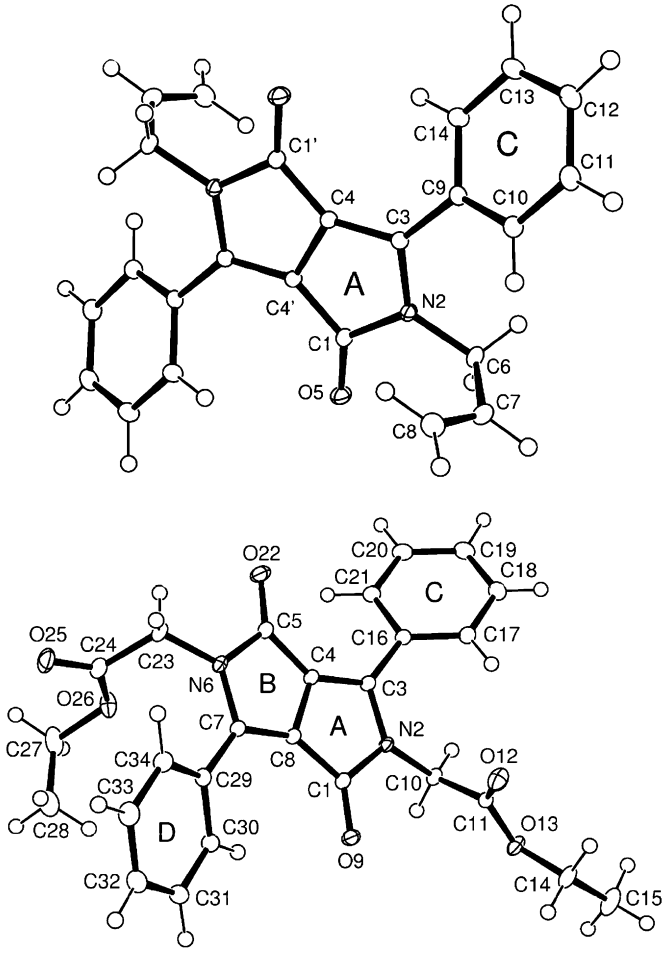


Fig. 1. Molecular diagrams of compounds **3d** (top) and **3f** (bottom): thermal ellipsoids at 50% of probability level; hydrogen atoms not to scale. In the case of **3d**, the numbering is limited to one half of the molecule because it lies on a crystallographic centre of symmetry.

deriving from π–π stacking forces (42%), hydrogen bonds (21%), electrostatic attractions (19%), and an array of other minor contributors. The results presented here confirm that the *N*,*N*′-disubstitution of the DDP skeleton not only precludes any strong intermolecular hydrogen bonding, but also interferes with the intermolecular π–π stacking of the (hetero)aryl rings. On these grounds, one can explain the increased solubility of *N*,*N*′-disubstituted DDPs in comparison with the *N*,*N*′-unsubstituted ones.

2.3. Absorption and fluorescence properties

At this point of our investigation, we measured the absorption and fluorescence maxima of compounds **3**, which are listed in Table 1 along with the corresponding Stokes shifts. The absorption wavelengths are in the reported range [3,9,10,13] for *N*,*N*-dialkylsubstituted DDPs. They are lower than those of the parent species **2** (496 nm) and of other *N*,*N*-unsubstituted DPPs, unless the latter are endowed with an *ortho*-substituent on the phenyl groups so interfering with the molecular planarity [3]. The observed Stokes shifts are about 50 nm (the typical value required, for instance, in the case of laser dyes [9]) and a good mirror-type shape of the absorption and luminescence bands has been detected (see Fig. 2 as an example). Table 1 also reports for each substrate the fluorescence quantum yield (Φ), determined according to the comparative method of Williams et al. [22].

Table 1
Absorption and fluorescence properties of compounds **3a–g**

Compound	Absorption (λ_{max}, nm)	Fluorescence (λ_{max}, nm)	Stokes shift ($\Delta\lambda$, nm)	Φ
3a	477	529	52	0.55
3b	468	523	55	0.43
3c	469	522	53	0.50
3d	469	521	52	0.45
3e	463	515	52	0.56
3f	456	510	54	0.43
3g	457	514	57	0.50

2.4. Conclusions

The *N*,*N*′-disubstitution of the DDP skeleton is not convenient if one considers strictly the requisites of the so-called high-performance pigments for paint industries. However, a number of peculiar features of *N*,*N*′-disubstituted DDPs, such as large Stokes shifts and solubility in organic solvents, may be attractive and potentially valuable in other fields of application of colourants.

3. Experimental

3.1. General

Melting points were determined on a Büchi B-450 apparatus and are uncorrected. IR spectra were recorded on a Jasco FT-IR 5300 spectrophotometer. NMR spectra were taken on an Avance Bruker 400 instrument and chemical shifts are expressed in ppm downfield from $SiMe_4$. Mass spectra were measured on a WG-70EQ spectrometer.

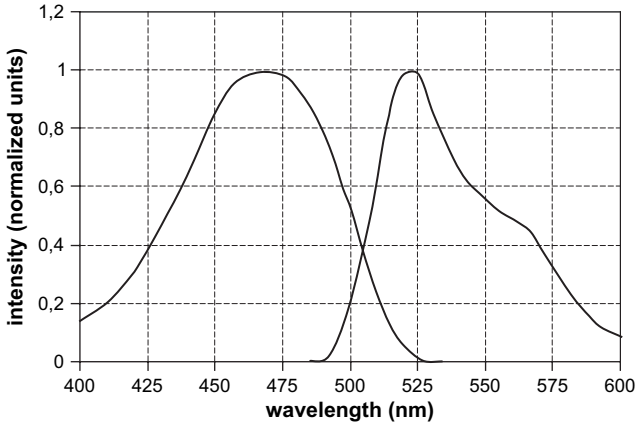


Fig. 2. Absorption and fluorescence spectra of compound **3b** (excitation wavelength: 450 nm).

3.2. Preparation of 2,5-dihydro-1,4-dioxo-3, 6-diphenylpyrrolo[3,4-c]pyrrole (**2**)

A mixture of *t*-BuOK (84.2 g, 0.75 mol) and benzonitrile (25.8 g, 0.25 mol) in 2-methyl-2-butanol (0.16 l) was heated at 110 °C. At this temperature and under vigorous stirring, dimethyl succinate (19.0 g, 0.13 mol) was dropped during 2 h. After further stirring for 2 h at 110 °C, the mixture was cooled at 50 °C and treated with methanol (0.35 l) and AcOH (44 ml). After cooling at room temperature, the precipitate was collected by filtration and washed repeatedly with methanol to give **2** (19.9 g, 55%) as orange-red crystals [3].

3.3. General procedure for the preparation of N,N′-disubstituted 2,5-dihydro-1,4-dioxo-3, 6-diphenylpyrrolo[3,4-c]pyrroles (**3**)

A suspension of **2** (0.29 g, 1 mmol) and potassium carbonate (1.50 g, 11 mmol) in DMF (18 ml) was heated at 120 °C. At this temperature and under vigorous stirring, a solution of the alkylating agent (10 mmol) in DMF (8 ml) was dropped during 40 min. Stirring and heating at 120 °C were continued to reach the overall time as indicated in Scheme 1. After cooling at room temperature, water (50 ml) was added under stirring. The precipitate was collected by filtration and washed repeatedly with water. Recrystallization of the crude product from ethanol–toluene gave pure **3** (see yields in Scheme 1). Physical and spectral properties of compound **3a** were identical to those reported in the literature [3].

Compound **3b**: Mp 278–280 °C; IR (KBr): 1661 cm^{-1}; ^1H NMR ($CDCl_3$): 5.01 (4H, s), 7.19–7.23 (4H, m), 7.26–7.35 (6H, m), 7.44–7.50 (6H, m), 7.75–7.79 (4H, m); ^{13}C NMR ($CDCl_3$): 46.0 (t), 110.1 (s), 127.1 (d), 127.8 (d), 128.3 (s), 129.2 (d), 129.3 (d), 129.5 (d), 131.8 (d), 137.9 (s), 149.4 (s), 163.2 (s); MS: *m/z* 468 (M^+). Found: C, 81.69; H, 5.25; N, 5.90; $C_{32}H_{24}N_2O_2$ requires C, 81.89; H, 5.17; N, 5.98%.

Compound **3c**: Mp 219–220 °C; IR (KBr): 1664 cm^{-1}; ^1H NMR ($CDCl_3$): 1.30 (18H, s), 4.98 (4H, s), 7.14 (4H, d, $J = 8.3$ Hz), 7.33 (4H, d, $J = 8.3$ Hz), 7.46–7.50 (6H, m), 7.78–7.82 (4H, m); ^{13}C NMR ($CDCl_3$): 31.7 (q), 34.9 (s), 45.7 (t), 110.1 (s), 126.1 (d), 126.9 (d), 128.4 (s), 129.3 (d), 129.5 (d), 131.7 (d), 134.8 (s), 149.4 (s), 150.6 (s), 163.2 (s); MS: *m/z* 581 (M^+). Found: C, 82.64; H, 6.89; N, 4.88; $C_{40}H_{40}N_2O_2$ requires C, 82.71; H, 6.96; N, 4.82%.

Compound **3d**: Mp 218–219 °C; IR (KBr): 1674 cm^{-1}; ^1H NMR ($CDCl_3$): 4.40 (4H, d, $J = 4.6$ Hz), 5.23 (2H, d, $J = 15.9$ Hz), 5.27 (2H, d, $J = 8.1$ Hz), 5.98 (2H, tdd, $J = 4.6$, 15.9, 8.1 Hz), 7.51–7.55 (6H, m), 7.91–7.95 (4H, m); ^{13}C NMR ($CDCl_3$): 44.8 (t), 109.9 (s), 117.3 (t), 128.3 (s), 129.3 (d), 129.4 (d), 131.8 (d), 133.8 (d), 149.2 (s), 162.8 (s); MS: *m/z* 368 (M^+). Found: C, 78.33; H, 5.41; N, 7.65; $C_{24}H_{20}N_2O_2$ requires C, 78.23; H, 5.48; N, 7.60%.

Compound **3e**: Mp 272–273 °C; IR (KBr): 1671 cm^{-1}; ^1H NMR ($CDCl_3$): 2.36 (2H, t, $J = 2.4$ Hz), 4.51 (4H, d, $J = 2.4$ Hz), 7.57–7.61 (6H, m), 8.06–8.10 (4H, m); ^{13}C NMR ($CDCl_3$): 32.4 (t), 72.9 (d), 79.2 (s), 109.7 (s), 127.9 (s), 129.5 (d), 132.1 (d), 148.4 (s), 162.2 (s); MS: *m/z* 364 (M^+). Found: C, 78.97; H, 4.49; N, 7.73; $C_{24}H_{16}N_2O_2$ requires C, 79.10; H, 4.43; N, 7.69%.

Compound **3f**: Mp 207–208 °C; IR (KBr): 1734, 1683 cm^{-1}; ^1H NMR ($CDCl_3$): 1.25 (6H, t, $J = 7.0$ Hz), 4.21 (4H, q, $J = 7.0$ Hz), 4.51 (4H, s), 7.50–7.55 (6H, m), 7.76–7.81 (4H, m); ^{13}C NMR ($CDCl_3$) 14.5 (q), 44.0 (t), 110.1 (s), 128.0 (s), 129.1 (d), 129.5 (d), 131.9 (d), 148.7 (s), 162.7 (s), 168.8 (s); MS: *m/z* 460 (M^+). Found: C, 67.90; H, 5.18; N, 6.13; $C_{26}H_{24}N_2O_6$ requires C, 67.81; H, 5.26; N, 6.08%.

Compound **3g**: Mp 204–205 °C; IR (KBr): 1694, 1675 cm^{-1}; ^1H NMR ($CDCl_3$): 5.16 (4H, s), 7.45–7.49 (6H, m), 7.65 (4H, d, $J = 8.5$ Hz), 7.71–7.75 (4H, m), 7.83 (4H, d, $J = 8.5$ Hz); ^{13}C NMR ($CDCl_3$): 48.5 (t), 110.1 (s), 128.0 (s), 128.8 (d), 129.4 (d), 129.6 (s), 129.9 (d), 131.8 (d), 132.5 (d), 133.6 (s), 148.9 (s), 162.5 (s), 192.8 (s); MS: *m/z* 685 [$(M+4)^+$], 683 [$(M+2)^+$], 681 (M^+). Found: C, 59.69; H, 3.38; N, 4.23; $C_{34}H_{22}N_2O_4Br_2$ requires C, 59.84; H, 3.26; N, 4.11%.

3.4. X-ray crystallographic analysis of compounds **3d** and **3f**

Crystallographic data of both structures were collected on a Bruker SMART APEX diffractometer using Mo Kα radiation, $\lambda = 0.71073$ Å. The temperature of the experiments was fixed at 90 K, using an OXFORD low temperature device. The structures were solved by *SIR*2002 [23] and refined by *SHELX*97 [24]. All crystallographic data, excluding structure factors, were deposited at the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 286655 and CCDC 286656 for **3f** and **3d**, respectively.

3.4.1. Cystallographic data of **3f**

$C_{26}H_{24}N_2O_6$, $M_r = 460.47$, monoclinic, space group $P2_1/c$, $a = 9.7567(14)$, $b = 16.093(2)$, $c = 13.961(2)$ Å, $\beta = 93.88(2)°$, $V = 2187.1(5)$ $Å^3$, $T = 90$ K, $Z = 4$, $\rho = 1.399$ g cm^{-3}, μ(Mo Kα) = 0.100 mm^{-1}, 41 093 reflection collected, 8352 independent, $R_{ave} = 0.0333$, 6816 with $I_o > 2\sigma(I_o)$, $2\theta_{max}$ 67.54°; final discrepancy values on all reflections: $R = 0.0482$, $wR(F_o^2) = 0.1006$, goodness-of-fit 1.030, $-0.21 < \Delta\rho < 0.44$ e$Å^{-3}$.

3.4.2. Cystallographic data of **3d**

$C_{24}H_{20}N_2O_2$, $M_r = 368.42$, monoclinic, space group $P2_1/n$, $a = 8.8869(10)$, $b = 8.9526(10)$, $c = 11.3973(12)$ Å, $\beta = 96.745(8)°$, $V = 900.5(2)$ $Å^3$, $T = 90$ K, $Z = 2$, $\rho = 1.359$ g cm^{-3}, μ(Mo Kα) = 0.087 mm^{-1}, 17 107 reflection collected, 3476 independent, $R_{ave} = 0.0255$, 3165 with $I_o > 2\sigma(I_o)$, $2\theta_{max}$ 67.70°; final discrepancy values on all reflections: $R = 0.0371$, $wR(F_o^2) = 0.1000$, goodness-of-fit 1.086, $-0.19 < \Delta\rho < 0.50$ e$Å^{-3}$.

3.5. Determination of absorption and fluorescence properties

UV–vis absorption and fluorescence spectra were recorded in chloroform solutions on Perkin–Elmer Lambda 15 and SPEX Fluorolog (FL111 model) instruments, respectively. Fluorescence quantum yields were determined according to

the comparative method of Williams et al. [22], by using a fluorescein solution in 0.1 M aqueous NaOH as standard and taking $\Phi_{ST} = 0.79$ [25]. In order to minimize re-absorption effects [26], concentrations of the analyzed samples were properly chosen to ensure absorbance values never exceeding 0.1 at the excitation wavelength. Plots of integrated fluorescence intensity vs. absorbance were linear with correlation coefficients in the range 0.989–0.999 and their slopes $Grad_X$ and $Grad_{ST}$ were used to calculate the absolute Φ_X values by the equation

$$\Phi_X = \Phi_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right)\left(\frac{\eta^2}{\eta_{ST}^2}\right)$$

where η is the refractive index of chloroform (1.442) and η_{ST} is the refractive index of a 0.1 M aqueous solution of NaOH (1.334).

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