

Enhancing the helical distortion in pyrrolo[1,2-*a*][1,10]phenanthrolines

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Abstract

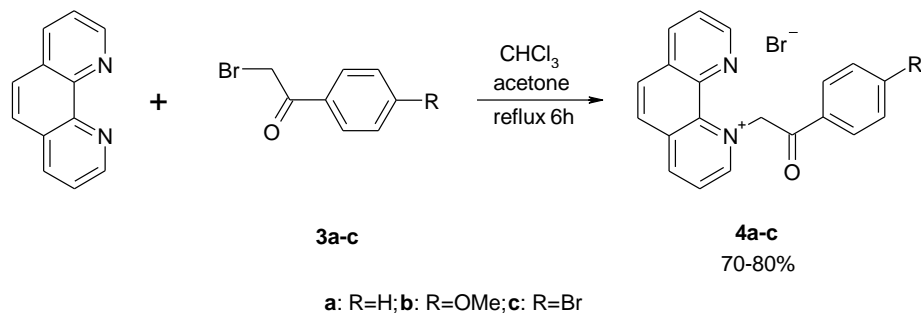
Nine new helical compounds were synthesized using a one-pot reaction between phenanthrolium *N*-ylides and quinones as cyclic olefinic dipolarophiles. 1,4-naphthoquinone, 1,4-benzoquinone and 1,2-naphthoquinone were used as dipolarophiles, resulting in excellent to moderate yields. The structure of the compounds was deduced using NMR spectroscopy and the helical distortion was ascertained using X-ray analysis.

Keywords: Azahelicene, *N*-ylide, helical chirality, 1,2-naphthoquinone

Introduction

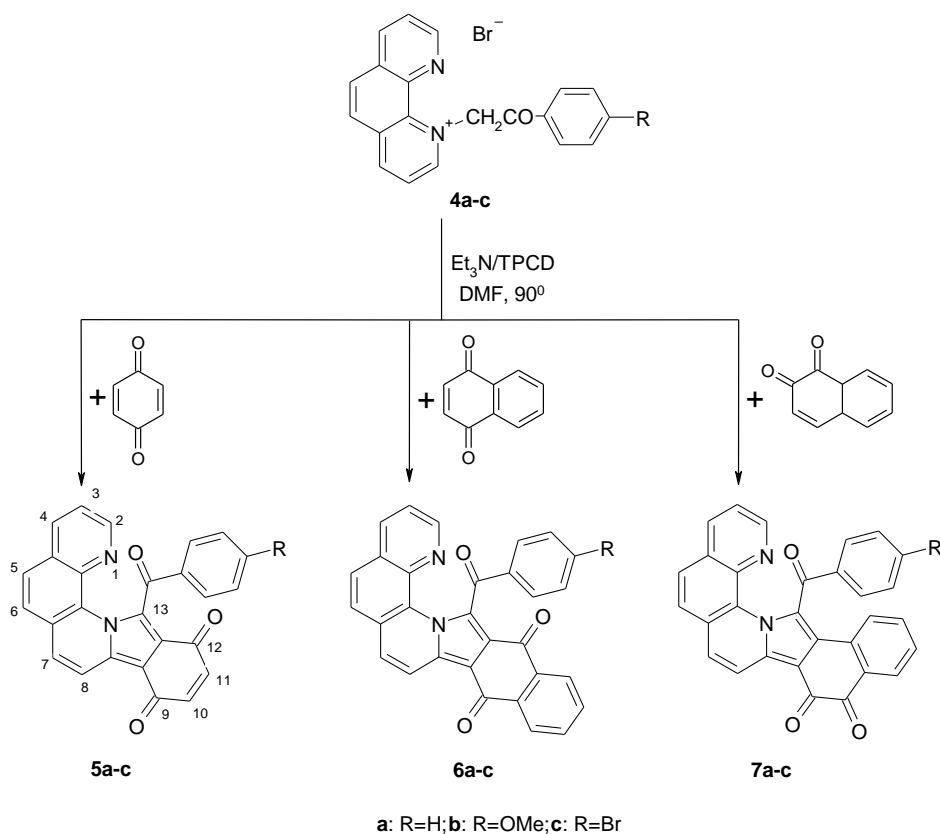
The interest in helical molecules, although initially only academic, steadily increased due to their attractive properties. As a result, numerous papers and reviews exist on carbohelicenes.¹ These properties can be altered and diversified by including one or more heteroatoms in the helical ring system.² A special class of heterohelicenes are aza and polyazahelicenes^{3,4} which exhibit interesting optical properties and have many other applications. Normally, for helicity to occur, the presence of five or more *ortho*-condensed aromatic rings is required. In the past two decades however, the synthetic strategies for aza and polyazahelicenes increased in number, as more papers describe the preparation of helical molecules of four or three *ortho* condensed rings.⁵ In the latter case, helicity is conferred by inserting bulky substituents in key regions of the molecules.

One of the most versatile synthetic tools for obtaining pyrroloazines is 1,3-dipolar *N*-ylide cycloaddition reaction. This method has been used successfully to obtain many compounds otherwise difficult to obtain.⁶ Using *N*-ylide 1,3-dipolar cycloadditions, our group obtained pyrrolo[1,2-*b*][1,10]phenanthrolines⁷ and pyrrolo[1,2-*a*][4,5]diazafuorenones,⁸ both classes of compounds showing a significant helical distortion both in the solid state and in solution.



Scheme 2

Compounds **5** and **6** were obtained in excellent yields by reacting the corresponding phenanthroline salt **4** with 1,4-benzoquinone and 1,4-naphthoquinone, respectively, using triethylamine and TPCD as oxidant in DMF in a one-pot procedure (Scheme 3). When applying the same synthetic protocol using 1,2-naphthoquinone as dipolarophile, the yields obtained for compounds **7** were good, but lower than those for compounds **5** or **6**. The purification of cycloadducts **5-7** was performed using Soxhlet extraction with chloroform and their NMR spectra were recorded in CDCl_3 + TFA (trifluoroacetic acid) mixture. For comparison purposes, the $^1\text{H-NMR}$ spectra of **6b** and **7b** were also recorded in CDCl_3 at high dilution.

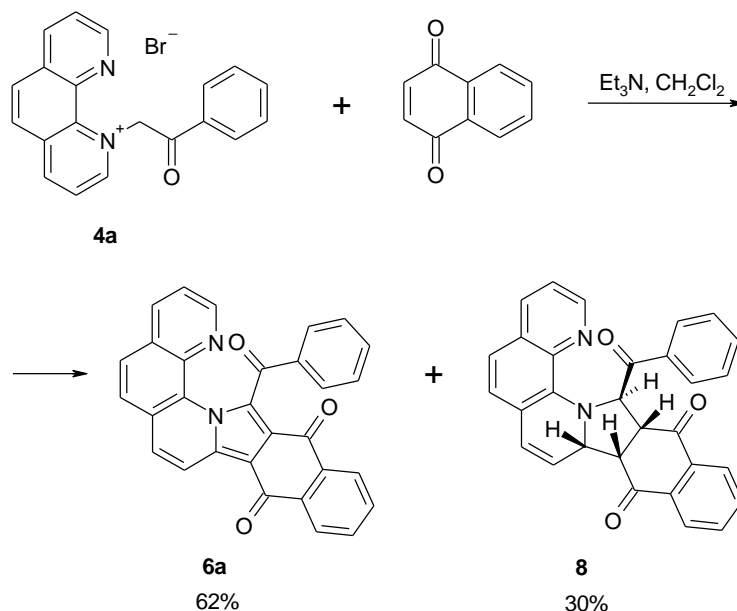


Scheme 3

In the $^1\text{H-NMR}$ spectra, proton H-8, having the chemical shift of $\delta = 8.66$ ppm is more deshielded than H-7, $\delta = 8.13$ ppm, due to the spatial proximity of the oxygen atom from the quinone moiety. Protons H-5 and H-6 appear as an A_2 system at $\delta = 8.41$ ppm. As the terminal pyridine ring is protonated by the presence of TFA, protons H-2, H-3 and H-4 are strongly deshielded and appear at $\delta = 9.64$ ppm, 8.31 ppm and 9.21 ppm, respectively. A very distinct feature of cycloadducts **5** are protons H-10 and H-11 which appear at $\delta = 7.06$ ppm and 6.87 ppm with $J = 10.2$ Hz.

The most distinctive characteristics of the $^{13}\text{C-NMR}$ spectra are the signals for the two CO groups at $\delta \sim 183.0$ ppm for the 1,4-benzoquinone derivatives and $\delta \sim 181.0$ ppm for the 1,4-naphthoquinone cycloadducts.

When a different experimental procedure was used, consisting of reacting at room temperature the phenanthroline salt and 1,4-naphthoquinone in the presence of triethylamine in methylene chloride, the formation of the tetrahydro derivative **8** was observed together with that of **6a**, in a 1:2 molar ratio (Scheme 4). Compound **8** was isolated and characterized using $^1\text{H-NMR}$ spectroscopy. The tendency of **8** to undergo an *in situ* oxidative aromatization to **6a** was observed.



Scheme 4

In order to measure the helical distortion in the series **5-7**, X-ray single crystal analysis was performed on the representative compound **6a**. Crystals were grown by slow evaporation from chloroform.

Figure 1 shows the molecular structure of **6a**¹¹ with the seven rings labeled for reference. The compound was isolated in the form of its 1:1 solvate with chloroform.

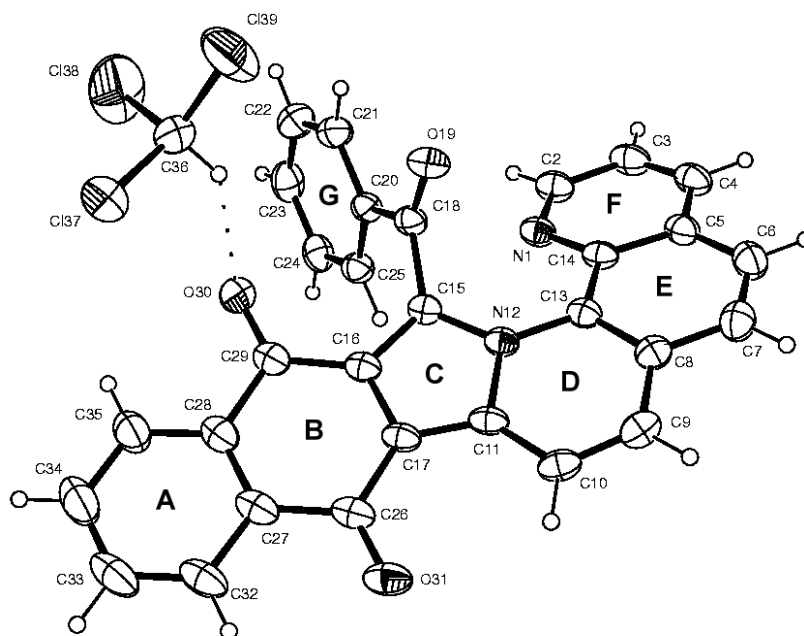


Figure 1. ORTEP diagram of the asymmetric unit in the crystal of **6a**·CHCl₃. Non-H atoms are drawn at the 50% probability level.

Several abnormally short intramolecular contacts in the molecule of **6a** contribute to the ring system A-F adopting helical chirality, namely N1...C18 2.437 Å, N1...C15 2.808 Å, N1...C20 2.875 Å, C20...O30 2.968 Å (all e.s.d.s 0.003 Å). As a result of these steric influences, rings A-F present an undulating, helical surface (Figure 2) with the following angles of intersection between their successive mean planes: A[^]B 0.5°, B[^]C 3.9°, C[^]D 6.1°, D[^]E 11.5°, E[^]F 7.3° (all e.s.d.s 0.1°). The cumulative effect of these progressive ring twists is that the acute angle between terminal rings A and F is 27.0(1)°. Accompanying this distortion, ring D adopts a slightly twisted conformation, with the endocyclic torsion angles ranging from 0.2(3)° (C9-C10-C11-N12) to -13.5(3)° (C8-C13-N12-C11), such that atoms C9 and C10 lie above the plane of ring C. Proceeding from ring D to E to F there is progressive bending of the ring system downward. In addition, the severe steric constraints result in atom C18 lying 0.366(2) Å above the plane of ring C and they direct the carbonyl bond C18-O19 and the plane of the phenyl ring G roughly perpendicular to ring C (Figure 1, torsion angles C16-C15-C18-O19 105.4(3)°, N12-C15-C18-C20 133.0(2)°).

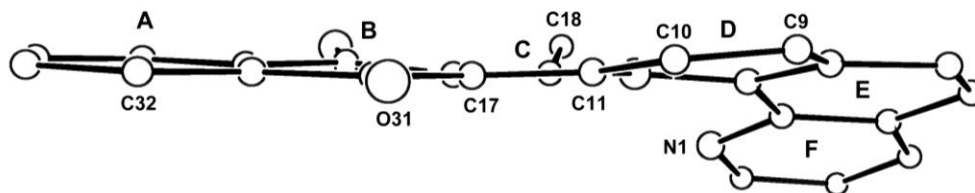


Figure 2. Perspective view of the non-hydrogen atoms of rings A-F viewed parallel to the plane of ring C. Key atoms are labeled.

A hydrogen bond, C36-H...O30, linking the chloroform molecule to the parent **6a** is indicated in Figure 1. This has C...O 3.057(3) Å and angle C-H...O 144(1)°. The crystal of **6a**·CHCl₃ is a channel-inclusion compound, the solvent molecules being in close contact (Cl36...Cl38' 3.662(1) Å) and forming a linear array parallel to the crystal *c*-axis.

Conclusions

Three new heterocyclic ring systems were obtained using a one-pot reaction between phenanthrolium N-ylides and quinones as dipolarophiles. The use of 1,4-benzoquinone and 1,4-naphthoquinone resulted in high yields, while the novel use of 1,2-naphthoquinone as dipolarophile gave moderate yields.

Structural assignment was established on the basis of elemental analysis and NMR spectroscopy. The helical nature of the new compounds was determined using X-ray analysis. As compared to similar cycloadducts, the new compounds possess a higher degree of helical distortion, warranting a possible enantiomeric separation either by using a chiral complexing agent or by using chromatographic methods.

Acknowledgements

MRC thanks the University of Cape Town and the NRF for research support.

Experimental Section

General. Melting points were determined on a Boëtius hot plate. The NMR spectra were recorded on a Varian Gemini 300 BB instrument, operating at 300 MHz for ¹H and 75 MHz for ¹³C. Supplementary evidence was given by HETCOR and COSY experiments.

General procedure for compounds 5, 6 and 7

To a solution of the corresponding salt (5 mmol) and quinone (5 mmol) in 35 ml DMF, a solution of triethylamine (0.7 mL, 5 mmol) dissolved in 5 mL of DMF was added dropwise. After 20 minutes of stirring at room temperature, 5 mmol TPCD (tetrakis pyridino cobalt(II) dichromate) were added and the reaction mixture was stirred at 80-90 °C for 6 h on a water bath. After cooling to room temperature, 50 ml of a 5% aqueous HCl solution was added. The resulting precipitate was filtered and washed with ethanol. The crude product was purified by Soxhlet extraction with chloroform.

General procedure for compound 8

5 Mmol of the corresponding salt were suspended in dichloromethane (50 mL) and the 1,4-benzoquinone (5 mmol) was then added. Under vigorous stirring, triethylamine (0.7 mL, 5 mmol, dissolved in 5 mL of methylene chloride) was added dropwise. After 20 min the reaction mixture was washed with water. The precipitated fully aromatic compound was filtered off. The tetrahydro derivative was precipitated from the remaining solution by the addition of ethanol.

13-Benzoylisoindolo[2,1-a][1,10]phenanthroline-9,12-dione (5a). Red powder with mp 304-306 °C, yield 90%. Anal. Calcd. for C₂₆H₁₄N₂O₃: C, 77.60; H, 3.51; N, 6.96. Found: C, 77.61; H, 3.51; N 6.97. ¹H-NMR (300 MHz, CDCl₃+TFA) δ: 9.64 (d, 1H, *J* = 6 Hz, H-2); 9.21 (d, 1H, *J* = 8 Hz, H-4); 8.66 (d, 1H, *J* = 9.4 Hz, H-8); 8.41 (m, 2H, H-5, H-6); 8.31 (dd, 1H, *J* = 8, 6 Hz, H-3); 8.13 (d, 1H, *J* = 9.4 Hz, H-7); 7.42-7.31 (m, 5H, H-2', H-3', H-4', H-5', H-6'); 7.06, 6.87 (2d, 2H, *J* = 10.2 Hz, H-10, H-11). ¹³C-NMR (75 MHz, CDCl₃+TFA) δ: 183.7 (COAr); 183.0 (2CO); 148.0 (C-4); 145.2 (C-2); 141.4 (C-10); 139.4 (C-11); 131.9 (C-4'); 130.6, 127.3 (C-5, C-6); 129.8 (C-2', C-6'); 127.9 (C-7); 125.6 (C-3); 124.8 (C-8); 124.2 (C-3', C-5'); 130.4, 129.1, 126.9; 126.4, 122.8, 121.6, 118.4, 114.0 (C-4a, C-6a, C-8a, C-9a, C-12a, C-13, C-14a, C-14b); 95.1 (C-9a).

13-(4-Methoxybenzoyl)isoindolo[2,1-a][1,10]phenanthroline-9,12-dione (5b). Red powder with mp 327-329 °C, yield 89%. Anal. Calcd. for C₂₇H₁₆N₂O₄: C, 74.99; H, 3.73; N, 6.48. Found: C, 75.01; H, 3.72; N, 6.49. ¹H-NMR (300 MHz, CDCl₃+TFA) δ: 9.64 (d, 1H, *J* = 6 Hz, H-2); 9.19 (d, 1H, *J* = 8.2 Hz, H-4); 8.65 (d, 1H, *J* = 9.3 Hz, H-8); 8.40 (m, 2H, H-5, H-6); 8.33-8.28 (m, 1H, H-3); 8.12 (d, 1H, *J* = 9.4 Hz, H-7); 7.33 (d, 2H, *J* = 8.8 Hz, H-2', H-6'); 7.05 (d, 1H, *J* = 10.4 Hz, H-11); 6.90-6.83 (m, 3H, H-10, H-3', H-5'). ¹³C-NMR (75 MHz, CDCl₃+TFA) δ: 183.5 (COAr); 183.1 (2CO); 161.6; 147.7 (C-4); 145.0 (C-2); 141.2 (C-10); 139.3 (C-11); 133.9 ; 130.4 (C-5); 127.9 (C-7); 127.2 (C-6); 126.1 (C-2', C-6'); 125.4 (C-3); 124.6 (C-8); 114.9 (C-3', C-5'); 102.4 (C-4'); 130.3, 128.9, 126.9, 126.2, 123.1, 121.3, 118.2, 113.8 (C-4a, C-6a, C-8a, C-9a, C-12a, C-13, C-14a, C-14b); 95.2 (C-9a); 55.5 (CH₃).

13-(4-Bromobenzoyl)isoindolo[2,1-a][1,10]phenanthroline-9,12-dione (5c). Red powder with mp 348-349 °C, yield 85%. Anal. Calcd. for C₂₆H₁₃BrN₂O₃: C, 64.88; H, 2.72; Br, 16.60; N, 5.82. Found: C, 64.91; H, 2.71; Br, 16.58; N, 5.83. ¹H-NMR (300 MHz, CDCl₃+TFA) δ: 9.54 (d, 1H, *J* = 4.8 Hz, H-2); 9.21 (d, 1H, *J* = 7.1 Hz, H-4); 8.64 (d, 1H, *J* = 9.2 Hz, H-8); 8.39 (m, 2H, H-5, H-6); 8.29 (m, 1H, 6 Hz, H-3); 8.13 (d, 1H, *J* = 9.1 Hz, H-7); 7.47 (d, 2H, *J* = 8 Hz, H-2',

H-6'); 7.33 (d, 2H, $J = 8$ Hz, H-3', H-5'); 7.02, 6.84 (2d, 2H, $J = 10.2$ Hz, H-10, H-11). ^{13}C -NMR (75 MHz, CDCl_3 +TFA) δ : 183.3 (COAr); 182.8 (2CO); 148.2 (C-4); 145.3 (C-2); 141.3 (C-10); 140.5 (C-4'); 139.5 (C-11); 133.0 (C-2', C-6'); 130.8, 127.4 (C-5, C-6); 127.8 (C-7); 130.5, 129.2, 126.7, 126.5, 122.9, 121.9, 118.4, 113.5 (C-4a, C-6a, C-8a, C-9a, C-12a, C-13, C-14a, C-14b); 126.6 (C-3', C-5'); 125.7 (C-3); 125.0 (C-8); 95.4(C-9a).

15-Benzoylbenzo[f]isoindolo[2,1-a][1,10]phenanthrolin-9,14-dione (6a). Pale orange powder with mp 348-349 °C, yield 94%. Anal. Calcd. for $\text{C}_{30}\text{H}_{16}\text{N}_2\text{O}_3$: C, 79.64; H, 3.56; N, 6.19. Found: C, 79.60; H, 3.60; N, 6.19. ^1H -NMR (300 MHz, CDCl_3 +TFA) δ : 9.68 (m, 1H, H-2); 9.22 (m, 1H, H-4); 8.78 (d, 1H, $J = 9.3$ Hz, H-8); 8.41-8.31 (m, 3H, H-3, H-5, H-6); 8.23, 8.19 (2dd, 2H, $J = 7.6, 1.5$ Hz, H-10, H-13); 7.99 (d, 1H, $J = 9.3$ Hz, H-7); 7.79, 7.73 (2td, 2H, $J = 7.6, 1.5$ Hz, H-11, H-12); 7.44-7.32 (m, 5H, H-2', H-3', H-4', H-5', H-6'). ^{13}C -NMR (75 MHz, CDCl_3 +TFA) δ : 182.4 (COAr); 181.5, 181.4 (2CO); 148.2 (C-4); 144.9 (C-2); 142.1 (Cq); 135.6 (CH); 135.3 (Cq); 134.5 (CH); 133.9 (Cq); 131.8 (C-4'); 130.6 (CH); 130.3 (Cq); 129.9 (C-2', C-6'); 129.1 (Cq); 128.2 (CH); 127.6 (C-10, C-13); 127.1 (C-7); 126.2 (Cq); 125.7 (C-3); 125.2 (C-8); 123.8 (C-3', C-5'); 123.0 (Cq); 122.3 (Cq); 118.3 (Cq); 115.6 (Cq); 94.7(C-9a).

15-(4-Methoxybenzoyl)benzo[f]isoindolo[2,1-a][1,10]phenanthrolin-9,14-dione (6b). Pale orange powder with mp 340-342 °C, yield 92%. Anal. Calcd. for $\text{C}_{31}\text{H}_{18}\text{N}_2\text{O}_4$: C, 77.17; H, 3.76; N, 5.81. Found: C, 77.17; H, 3.76; N, 5.81. ^1H -NMR (300 MHz, CDCl_3 +TFA) δ : 9.78 (d, 1H, $J = 6.1$ Hz, H-2); 9.23 (d, 1H, $J = 8.2$ Hz, H-4); 8.78 (d, 1H, $J = 9.3$ Hz, H-8); 8.43-8.33 (m, 3H, H-3, H-5, H-6); 8.25, 8.21 (2d, 2H, $J = 7.3$ Hz, H-10, H-13); 8.10 (d, 1H, $J = 9.3$ Hz, H-7); 7.87-7.75 (m, 2H, H-11, H-12); 7.27 (d, 2H, $J = 9.0$ Hz, H-2', H-6'); 6.80 (d, 2H, $J = 9.0$ Hz, H-3', H-5'); 3.72 (s, 3H, CH_3). ^{13}C -NMR (75 MHz, CDCl_3 +TFA) δ : 182.8 (COAr); 181.1, 181.0 (2CO); 147.8 (C-4); 144.6 (C-2); 135.8 (C-11); 135.2 (Cq); 134.7 (CH); 134.6 (Cq); 133.8 (Cq); 130.5 (C-5); 130.4 (Cq); 129.1 (Cq); 128.3 (CH); 128.1 (Cq); 127.9 (CH); 127.4 (C-6); 127.1 (C-7); 126.0 (Cq); 125.6 (C-3); 125.3 (C-8); 122.8 (Cq); 118.2 (Cq); 115.1 (CH); 94.5 (C-9a); 55.5 (CH_3). ^1H -NMR (300 MHz, CDCl_3) δ : 8.91 (d, 1H, $J = 9.1$ Hz, H-8); 8.33 (dd, 1H, $J = 7.7, 1.4$ Hz, H-2); 8.29-8.21 (m, 2H, H-5, H-6); 8.12 (dd, 1H, $J = 7.7, 1.4$ Hz, H-4); 7.92 (dd, 2H, $J = 7.4, 1.6$ Hz, H-10, H-13); 7.85 (d, 1H, $J = 9.1$ Hz, H-7); 7.81 (t, 1H, $J = 7.7$ Hz, H-3); 7.73, 7.65 (2td, 2H, H-11, H-12); 7.09 (d, 2H, $J = 9.1$ Hz, H-2', H-6'); 6.80 (d, 2H, $J = 9.1$ Hz, H-3', H-5'); 3.72 (s, 3H, CH_3).

15-(4-Bromobenzoyl)benzo[f]isoindolo[2,1-a][1,10]phenanthrolin-9,14-dione (6c). Pale orange powder with mp 366-368 °C, yield 91%. Anal. Calcd. for $\text{C}_{30}\text{H}_{15}\text{BrN}_2\text{O}_3$: C, 67.81; H 2.85; Br 15.04; N 5.27. Found: C, 67.81; H, 2.86; Br, 15.01; N, 5.28. ^1H -NMR (300 MHz, CDCl_3 +TFA) δ : 9.70 (d, 1H, $J = 5.7$ Hz, H-2); 9.22 (d, 1H, $J = 8.5$ Hz, H-4); 8.75 (d, 1H, $J = 9.2$ Hz, H-8); 8.45-8.33 (m, 3H, H-3, H-5, H-6); 8.23-8.13 (m, 2H, H-10, H-13); 8.19 (2dd, 2H, $J = 7.6, 1.5$ Hz, H-10, H-13); 8.08 (d, 1H, $J = 9.2$ Hz, H-7); 7.82-7.71 (m, 2H, H-11, H-12); 7.44 (d, 2H, $J = 8.6$ Hz, H-2', H-6'); 7.27 (d, 2H, $J = 8$ Hz, H-3', H-5'). ^{13}C -NMR (75 MHz, CDCl_3 +TFA) δ : 182.4 (COAr); 180.7 (2CO); 148.2 (C-4); 144.7 (C-2); 140.8 (Cq); 135.7 (CH); 135.1 (Cq); 134.7 (C-11, C-12); 133.8 (Cq); 133.0 (CH); 130.6 (CH); 130.4 (Cq); 129.0 (Cq); 128.2 (Cq);

127.7 (C-10, C-13); 127.4 (C-5, C-6); 127.1 (C-7); 126.4 (Cq); 126.1 (Cq); 125.6 (CH); 125.5 (C-3); 125.3 (C-8); 120.6 (Cq); 116.8 (Cq); 94.3 (C-9a).

15-Benzoylbenzo[e]isoindolo[2,1-a][1,10]phenanthrolin-9,10-dione (7a). Orange powder with mp 313-317 °C, yield 50%. Anal. Calcd. for C₃₀H₁₆N₂O₃: C, 79.64; H, 3.56; N, 6.19. Found: C, 79.60; H, 3.60; N, 6.19. ¹H-NMR (300 MHz, CDCl₃+TFA) δ: 9.81 (d, 1H, *J* = 4.9 Hz, H-2); 9.17 (d, 1H, *J* = 7.4 Hz, H-4); 8.61-7.95 (m, 7H, H-5, H-6, H-7, H-8, H-3, H-11, H-13); 7.84-7.16 (m, 6H, H-14, H-2', H-3', H-4', H-5', H-6'); 7.37(bs, 1H, H-12).

15-(4'-Methoxybenzoyl)benzo[e]isoindolo[2,1-a][1,10]phenanthrolin-9,10-dione (7b). Orange powder with mp 324-326 °C, yield 51%. Anal. Calcd. for C₃₁H₁₈N₂O₄: C, 77.17; H, 3.76; N, 5.81. Found: C, 77.17; H, 3.76; N, 5.81. ¹H-NMR (300 MHz, CDCl₃+TFA) δ: 9.84 (d, 1H, *J* = 4.9 Hz, H-2); 9.15 (d, 1H, *J* = 7.4 Hz, H-4); 8.46-8.28 (m, 4H, H-5, H-6, H-8, H-3); 8.21 (d, 1H, *J* = 8.0 Hz, H-11); 8.12 (bs, 1H, H-13); 7.73-7.46 (m, 4H, H-7, H-14, H-2', H-6'); 7.37(bs, 1H, H-12); 6.88 (d, 2H, *J* = 7.1 Hz, H-3', H-5'); 3.74 (s, 3H, CH₃). ¹H-NMR (300 MHz, CDCl₃) δ: 8.90 (d, 1H, *J* = 9.1 Hz, H-2); 8.21 (dd, 1H, *J* = 8.2, 1.8 Hz, H-4); 8.18-8.15 (m, 1H, H-8); 8.09 (dd, 1H, *J* = 4.4, 1.7 Hz, H-11); 7.94 (d, 2H, *J* = 9.1 Hz, H-2', H-6'); 7.92-7.81 (m, 3H, H-5, H-6, H-13); 7.45 (dd, 1H, 1H, *J* = 8.2, 4.4 Hz, H-12); 7.31-7.22 (m, 2H, H-3, H-14); 6.88(d, 2H, 1H, *J* = 9.1 Hz, H-3', H-5'); 3.74 (s, 3H, CH₃).

15-(4'-Bromobenzoyl)benzo[e]isoindolo[2,1-a][1,10]phenanthrolin-9,10-dione (7c). Orange powder with mp 340-344 °C, yield 57%. Anal. Calcd. for C₃₀H₁₅BrN₂O₃: C, 67.81; H, 2.85; Br, 15.04; N, 5.27. Found: C, 67.81; H, 2.86; Br, 15.01; N, 5.28. ¹H-NMR (300 MHz, CDCl₃+TFA) δ: 9.86 (d, 1H, *J* = 4.9 Hz, H-2); 9.09 (d, 1H, *J* = 7.4 Hz, H-4); 8.45-7.88 (m, 7H, H-5, H-6, H-7, H-8, H-3, H-11, H-13); 7.76-7.2 (m, 6H, H-14, H-2', H-3', H-5', H-6', H-12).

8a,9a,14a,15-Tetrahydro-15-benzoylbenzo[f]isoindolo[2,1-a][1,10]phenanthrolin-9,14-dione (8). Orange powder, yield 30%. Anal. Calcd. for C₃₀H₂₀N₂O₃: C, 78.93; H, 4.42; N, 6.14. Found: C, 78.91; H, 4.43; N, 6.15. ¹H-NMR (300 MHz, CDCl₃) δ: 8.23 (d, 2H, *J* = 7.2 Hz, H-2', H-6'); 8.20 (d, 1H, *J* = 7.4 Hz, H-2); 8.06 (d, 1H, *J* = 7.4 Hz, H-4); 7.88 (m, 2H, H-5, H-6); 7.84-7.71 (m, 2H, H-10, H-13); 7.66-7.51 (m, 3H, H-11, H-12, H-4'); 7.12-6.96 (m, 4H, H-3', H-5', H-3, H-15); 6.29 (dd, 1H, *J* = 9.5, 2.4 Hz, H-14a); 5.72 (d, 1H, *J* = 10.1 Hz, H-7); 5.15 (dd, 1H, *J* = 9.5, 1.0 Hz, H-9a); 4.41 (dd, 1H, *J* = 10.1, 8.0 Hz, H-8); 3.59 (dd, 1H, *J* = 8.0, 1.0 Hz, H-8a).

References and Notes

- (a) Martin, R. H. *Angew. Chem. Int. Ed.* **1974**, *13*, 649. (b) Laarhoven, W. H.; Prinsen, W. J. C., *Topp. Curr. Chem.* **1984**, *125*, 65. (c) Meurer, K. P.; Voegtle, F. *Topp. Curr. Chem.* **1985**, *127*, 1. (d) Grimme, S.; Harren, J.; Sobanski, A.; Voegtle, F. *Eur. J. Org. Chem.* **1998**, 1491. (e) Urbano, A.; *Angew. Chem. Int. Ed.* **2003**, *42*, 3986.
- (a) Wynberg, H. *Acc. Chem. Res.* **1971**, *4*, 65. (b) Groen, M. B.; Schandenbergh, H.; Wynberg, H. *J. Org. Chem.* **1971**, *19*, 27. (c) Groen, M. B.; Wynberg, H. *J. Am. Chem. Soc.* **1971**, *93*, 2968.

3. Sato, K.; Arai, S. Heterohelicenes Containing Nitrogen Aromatics: Azahelicenes and Azoniahelicenes In *Cyclophane Chemistry for the 21st Century* Takemura, H., Ed., Research Signpost: Kerena, India, 2002; pp 173-197.
4. Dumitrascu, F.; Dumitrescu, D. G.; Aron, I. *Arkivoc* **2010**, (i), 1.
5. (a) Benin, V.; Kaszynski, P.; Pink, M.; Young, V. G. Jr. *J. Org. Chem.* **2000**, *65*, 6388. (b) Rozen, S.; Dayan, S. *Angew. Chem. Int. Ed.* **1999**, *38*, 3472. (c) Granzhan, A.; Ihmels, H.; Mikhlina, K.; Deiseroth, H. J.; Mikus, H. *Eur. J. Org. Chem.* **2005**, 4098. (d) Watanabe, M.; Sukuki, H.; Tanaka, Y.; Ishida, T.; Oshikawa, T.; Tori-I, A. *J. Org. Chem.* **2004**, *69*, 7794. (e) Field, J. E.; Hill, T.; Venkataraman, D. *J. Org. Chem.* **2003**, *68*, 6071. (f) Laursen, W. B.; Krebs, F. C. *Angew. Chem. Int. Ed.* **2000**, *39*, 3432.
6. (a) Georgescu, E.; Georgescu, F.; Caira, M. R.; Nicolescu, A.; Deleanu, C.; Danilă, M.; Petru, F.; Dumitrascu, F. *Arkivoc* **2009**, (xii), 232. (b) Caira, M. R.; Georgescu, E.; Georgescu, F.; Popa, M. M.; Dumitrascu, F. *Arkivoc* **2009**, (xii), 242. (c) Georgescu, E.; Caira, M. R.; Georgescu, F.; Draghici, B.; Popa, M. M.; Dumitrascu, F. *Synlett* **2009**, 1795. (d) Dumitrascu, F.; Caira, M. R.; Drăghici, C.; Caproiu, M. T.; Miu, B.; Barbu, L. *Arkivoc* **2008**, (xii), 51. (e) Dumitrascu, F.; Dumitrescu, D. G. *Arkivoc* **2008**, (i), 232. (f) Najera, C.; Sansano, J. M. *Curr. Org. Chem.* **2003**, *7*, 1105. (g) Willy, B.; Müller, T. J. J. *Arkivoc* **2008**, (i), 195. (h) Georgescu, E.; Georgescu, F.; Roibu, C.; Iuhas, C. P.; Drăghici, C.; Filip, I. P. *Arkivoc* **2008**, (xii), 60.
7. (a) Dumitrașcu, F.; Mitan, C. I.; Drăghici, C.; Căproiu, M. T.; Răileanu, D. *Tetrahedron Lett.* **2001**, *42*, 8379. (b) Dumitrascu, F.; Drăghici, C.; Caira, M. R.; Bădoiu, A.; Barbu, L.; Cristea, M. *Arkivoc* **2005**, (x), 165. (c) Dumitrascu, F.; Caira, M. R.; Drăghici, C.; Căproiu, M. T.; Barbu, L.; Bădoiu, A. *J. Chem. Crystallogr.* **2005**, *35*, 361. (d) Dumitrascu, F.; Caira, M. R.; Draghici, C.; Caproiu, M. T. *Anal. Sci. X* **2007**, *23*, x13. (e) Dumitrascu, F.; Caira, M. R.; Drăghici, C.; Căproiu, M. T.; Barbu, L.; Miu, B. *Rev. Roum. Chim.* **2008**, *53*, 183.
8. (a) Dumitrascu, F.; Caira, M. R.; Draghici, C.; Dumitrescu, D. G. *Anal. Sci. X* **2006**, *22*, x259. (b) Caira, M. R.; Dumitrascu, F.; Dumitrescu, D. G.; Barbu, M.; Draghici, B. *Anal. Sci. X* **2007**, *23*, x173. (c) Dumitrascu, F.; Caira, M. R.; Vasilescu, M.; Barbu, L.; Drăghici, C.; Dumitrescu, D. G. *Arkivoc* **2007**, (xvi), 101.
9. (a) Mitsumori, T.; Bendikov, M.; Sedó, J.; Wudl, F. *Chem. Mater.* **2003**, *15*, 3759. (b) Biniang, W.; Ting, H.; Hongen, H. *Acta Chim. Sinica*, **2003**, *61*, 889. (c) Butler, R. N.; Coyne, A. G.; Cunningham, W. J.; Burke, L. A. *J. Chem. Soc. Perkin Trans. 2* **2002**, 1807.
10. Gelman, D. M.; Mayes, P. A.; Mulder, R.; Perlmutter, P. *Tetrahedron-Asymmetr.*, **2006**, *17*, 3341.
11. Crystal data for **6a**: C₃₀H₁₆N₂O₃·CHCl₃, *M* = 571.82, 0.25 x 0.16 x 0.07 mm³, monoclinic, space group *P2*₁/*c* (No. 14), *a* = 7.3356(2), *b* = 27.5813(9), *c* = 12.3848(4) Å, β = 93.478(2)°, *V* = 2501.14(13) Å³, *Z* = 4, *D*_c = 1.519 g/cm³, *F*₀₀₀ = 1168, MoK α radiation, λ = 0.71073 Å, *T* = 173(2)K, 2 θ _{max} = 51.4°, 34129 reflections collected, 4732 unique (*R*_{int} = 0.0425). Final *GooF* = 1.028, *RI* = 0.0488, *wR2* = 0.1126, *R* indices based on 3538 reflections with *I* > 2 σ (*I*) (refinement on *F*²), 352 parameters, 0 restraints. Lorentz-

polarization and absorption corrections applied, $\mu = 0.406 \text{ mm}^{-1}$.
The CIF File has been deposited at the Cambridge Crystallographic Data Centre (deposition no. CCDC 760049).