A new C-C bond forming annulation reaction leading to pH switchable organic materials

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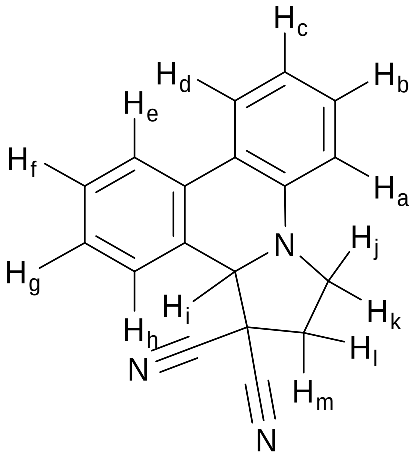
Synthetic and Spectroscopic Data

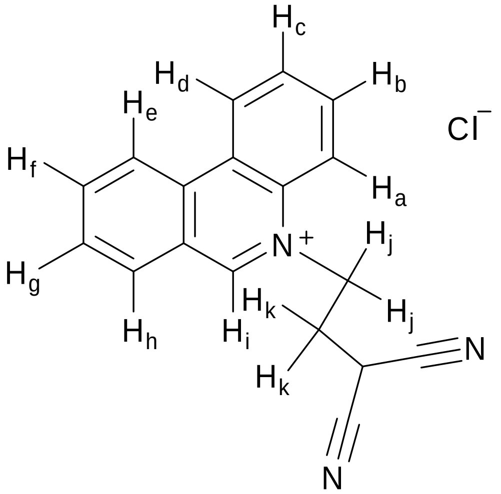
2,3-Dihydro-12H-pyrrolo[1,2-f]phenanthridine-1,1-dicarbonitrile. (2)



To a stirred solution of malononitrile **45** (1.00 g, 15.1 mmol) in MeOH (30 ml) was added 5-(2-bromo-ethyl)-phenanthridinium bromide **3** (5.56 g, 15.1 mmol). To the reaction mixture was then added triethylamine (7.659 g, 7.57 mmol). The reaction mixture was then stirred under a N_2 atmosphere for 1 hour, during which time a white precipitate had formed. The precipitate was isolated by filtration and washed with cold MeOH (5ml) to yield 2,3-Dihydro-12H-pyrrolo[1,2-f]phenanthridine-1,1-dicarbonitrile **47** as a white microcrystalline powder (3.57 g, 13.6 mmol). Single crystals suitable for X-Ray crystal analysis were obtained by recrystallising the product from hot MeOH.

Yield: 87%; mp: 45.3-46.1 ˚C ; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89(H_a, d, 1H, J=8.0 Hz), δ 7.78 (H_d, dd, 1H, J_1=1.28 Hz, J_2=8.0 Hz), δ 7.65 (H_h, d, 1H, J=7.6 Hz), δ 7.50 (H_b, t, 1H, J=7.38 Hz), δ 7.43 (H_c, dt, 1H, J_1=1.24 Hz, J_2=7.52 Hz), δ 7.27 (H_g, t, 1H, *J*=7.7 Hz), δ 6.96 (H_f, t, 1H, *J*=7.58 Hz), δ 6.65 (H_e, d, 1H, *J*=8.1 Hz), δ 5.14 (H_i, s, 1H,), δ 3.85 ($H_{j\text{ or }k}$, ddd, 1H, J_1=6.6 Hz, J_2=8.8 Hz, J_3=9.6 Hz), δ 3.51 ($H_{j\text{ or }k}$, ddd, 1H, J_1=4.3 Hz, J_2=J_3=10.0 Hz), δ 3.06 ($H_{l\text{ or }m}$, ddd, 1H, J_1=4.2 Hz, J_2=8.6 Hz, J_3=13.4 Hz), δ 2.82 ($H_{l\text{ or }m}$, ddd, 1H, J_1=6.5 Hz, J_2=10.2 Hz, J_3=13.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 35.85 (CH_2), δ 38.38 (C_q), δ 44.26 (CH_2), δ 68.59 (CH), δ 112.73 (CH), δ 113.67 (C_q), δ 115.06 (C_q), δ 119.98 (CH), δ 121.05 (C_q), δ 123.19 (CH), δ 123.55 (CH), δ 124.75 (CH), δ 127.94 (C_q), δ 128.22 (CH), δ 129.67 (CH), δ 129.75 (CH), δ 131.62 (C_q), δ 141.95 (C_q); IR (KBr, cm^{-1}): 2930.31 (m), 2874.34 (m), 2788.56 (m), 2248.59 (w), 1602.56 (m), 1493.6 (s), 1451.17 (s), 1377.89 (m), 1294.00 (m), 1218.79 (m), 778.14 (m), 741.50 (s), 613.25 (w); MS (FAB^+): 271.13 (33) (M^+), 219.22 (12), 179.10 (100); Anal. Calcd for $C_{18}H_{13}N_3$: C, 79.68; H, 4.83; N, 15.49; Found: C, 79.72; H, 4.91; N, 15.62.

5-(3,3-Dicyano-propyl)-phenanthridinium chloride. (2')

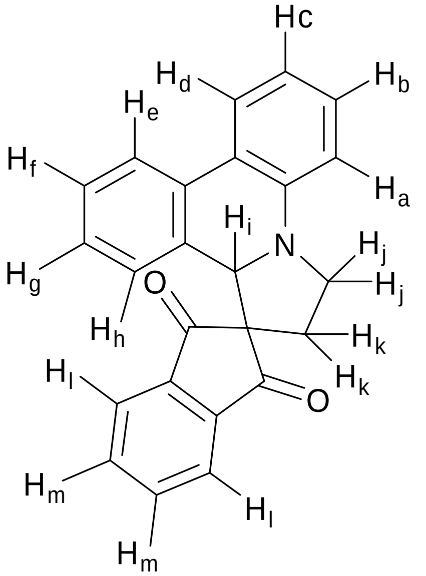


2,3-Dihydro-12H-pyrrolo[1,2-f]phenanthridine-1,1-dicarbonitrile **47** (100 mg, 0.37 mmol) was suspended in MeOH (10 ml). To this concentrated hydrochloric acid was added dropwise until all the starting material had dissolved. The reaction mixture was then stirred for one hour. The product was then precipitated by addition of diethyl ether and isolated by filtration to yield (**49**) as a white powder (111 mg, 0.36 mmol).

Yield: 99 %; ^1H NMR (MeOD, 400 MHz): δ 10.30 (H_i, s, 1H), δ 9.22 (H_a, dd, 1H, J_1=1.4 Hz, J_2=9.6 Hz), δ 9.15 (H_d, d, 1H, *J*=8.5 Hz), δ 8.65 (H_h, d, 1H, *J*=8.1 Hz), δ

8.60 (H_e, d, 1H, J=8.6 Hz), δ 8.47 (H_b, ddd, 1H, J_1=1.28 Hz J_2=7.2 Hz, J_3=8.44 Hz), δ 8.25 (H_c, ddd, 1H, J_1=1.4 Hz, J_2=7.1 Hz, J_3=8.6 Hz), δ 8.18 ($H_{g \text{ and } f}$, m, 2H), δ 5.45 (H_j, m, 2H), δ 3.01 (H_k, m, 2H) ; ^{13}C NMR (MeOD, 100 MHz): δ 30.60 (CH_2), δ 56.01 (CH_2), δ 113.95 (C_q), δ 120.47 (CH), δ 124.37 (CH), δ 125.37 (C_q), δ 126.52 (CH), δ 128.06 (C_q), δ 131.76 (CH), δ 132.01 (CH), δ 133.84 (CH), δ 134.46 (CH), δ 134.68 (C_q), δ 137.06 (CH), δ 140.13 (CH), δ 157.56 (CH); IR (KBr, cm^{-1}): 3419.17 (b, m), 3010.34 (w), 2798.21 (w), 2256.31 (w), 1626.66 (s), 1534.10 (m), 1451.17 (m), 1423.21 (w), 1262.18 (w), 760.78 (s), 720.28 (m); MS (CI$^+$): 272.13 (16) (M$^+$), 207.25 (8), 193.25 (28), 179.26 (100), 75.23 (82); Anal. $C_{18}H_{14}ClN_3$: C, 70.24; H, 4.58; N, 13.65; Found: C, 69.03; H, 4.62; N, 13.44.

2,3-Dihydro-12H-pyrrolo[1,2-f]phenanthridine-1-indan-1,3-dione. (3)

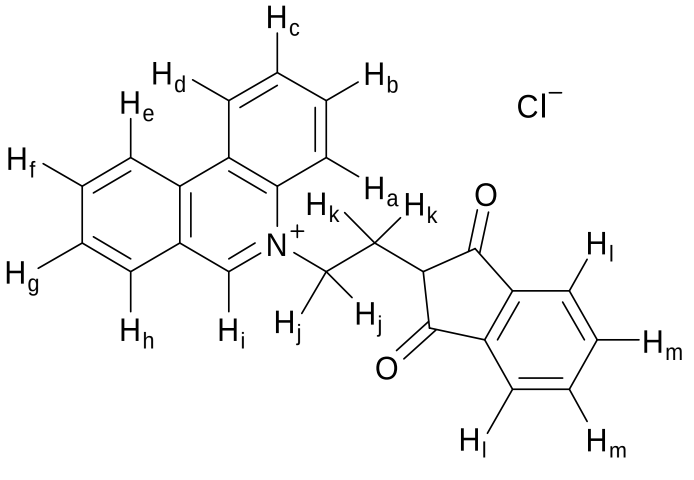


To a stirred solution of indan-1,3-dione (1.00 g, 6.8 mmol) in EtOAc (40 ml), was added 5% aqueous Na_2CO_3 (40 ml) followed by 5-(2-Bromo-ethyl)-phenanthridinium bromide **3** (2.51 g, 6.8 mmol). The Reaction mixture was then stirred for 3 hours under N_2 during which time the mixture turned a deep orange colour. The EtOAc layer was then separated, washed three time with water and dried over $MgSO_4$. The EtOAc was then removed under vacuum and the crude product recrystallised from warm MeOH to yield 2,3-Dihydro-12H-pyrrolo[1,2-f]phenanthridine-1-indan-1,3-

dione **48** as an orange microcrystalline powder (1.76 g, 5.0 mmol). Single crystals suitable for X-Ray chrystallography were grown by recrystallising the product from MeOH.

Yield: 73%; mp: 86.4-87.4 ˚C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (H_l, m, 2H), δ 7.75 (H_m, m, 2H), δ 7.641 (H_a, d, 1H, *J*=8.0 Hz), δ 7.58 (H_d, dd, 1H, J_1=1.12 Hz, J_2=7.8 Hz), δ 7.14 (H_h, t, 1H, *J*=7.7 Hz), δ 7.0437 (H_b, t, 1H, *J*=7.7 Hz), δ 6.72 (H_c, t, 1H, *J*=7.5 Hz), δ 6.66 (H_g, t, 1H, *J*=7.5 Hz), δ 6.62 (H_f, d, 1H, *J*=8.1 Hz), δ 6.30 (H_e, d, 1H, *J*=7.6 Hz), δ 5.36 (H_i, s, 1H), δ 3.74 (H_j, t, 2H, *J*=7.2 Hz), δ 2.30 (H_k, t, 2H, *J*=7.18 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 201.15 (C_q), δ 142.44 (C_q), δ 135.74 (CH), δ 131.62 (C_q), δ 129.63 (CH), δ 129.32 (C_q), δ 128.15 (CH), δ 126.56 (CH), δ 124.93 (CH), δ 123.34 (C_q), δ 123.37 (CH), δ 122.91 (CH), δ 122.55 (CH), δ 119.83 (C_q), δ 117.99 (CH), δ 112.54 (CH), δ 68.14 (CH), δ 63.98 (C_q), δ 47.95 (CH_2), δ 32.40 (CH_2); IR (KBr, cm^{-1}): 3424.96 (b, m), 2844.49 (w), 1737.55 (m), 1703.80 (s), 1602.56 (m), 1494.56 (m), 1242.90 (s), 736.67 (s); MS (FAB$^+$): 351.13 (21) (M$^+$), 275.10 (15), 247.11 (23), 219.11 (58), 179.13 (100); Anal. Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99; Found: C, 81.88; H, 4.76; N, 4.11.

5-(3,-(indan-1,3-dione)-propyl)-phenanthridinium chloride. (3')



2,3-Dihydro-12H-pyrrolo[1,2-f]phenanthridine-1-indan-1,3-dione **48** (100 mg, 0.28 mmol) was suspended in MeOH (10 ml). To this concentrated hydrochloric acid was added dropwise until all the starting material had dissolved. The reaction mixture was then stirred for one hour. The product was then precipitated by addition of diethyl ether and isolated by filtration to yield 5-(3,-(indan-1,3-dione)-propyl)-phenanthridinium chloride **50** as a bright yellow powder (101 mg, 0.26 mmol).

Yield: 91%; ^{1}H NMR (MeOD, 400 MHz): δ 8.55 (H_i, s, 1H), δ 7.48 (H_a, d, 1H, *J*=8.2 Hz), δ 7.42 (H_d, d, 1H, *J*=8.4 Hz), δ 6.99 (H_h, d, 1H, *J*=8.6 Hz), δ 6.89 (H_e, d, 1, *J*=8.2 Hz), δ 6.73 (H_b, t, 1H, *J*=8.0 Hz), δ 6.46 ($H_{c\text{ and }l}$, m, 3H), δ 6.25 ($H_{g,\text{ f and m}}$, m, 4H), δ 3.83 (H_j, t, 2H, *J*=7.6 Hz), δ 1.03 (H_k, t, 2H, *J*=7.5 Hz); ^{13}C NMR (MeOD, 100 MHz): δ 27.16 (CH_2), δ 57.71 (CH_2), δ 120.79 (CH), δ 120.81 (CH), δ 124.26 (CH), δ 124.31 (CH), δ 125.51 (C_q), δ 126.36 (CH), δ 128.08 (C_q), δ 131.61 (CH), δ 131.83 (CH), δ 132.58 (C_q), δ 133.57 (CH), δ 134.16 (CH), δ 134.89 (C_q), δ 137.80 (CH), δ 139.68 (CH), δ 143.34 (C_q), δ 156.97 (CH), δ 200.70 (C_q); IR (KBr, cm^{-1}): 3425.96 (m), 2486.76 (w), 1683.55 (m), 1624.73 (s), 1586.16 (s), 1455.99 (w), 1310.39 (w), 1260.25 (s), 1157.08 (w), 956.52 (w), 767.53 (m), 733.78 (m); MS (CI$^+$): 352.13 (26) (M$^+$), 207.16 (67), 179.08 (89), 145.06 (100); Anal. Calcd for $C_{24}H_{18}ClNO_2$: C, 74.32; H, 4.68; N, 3.61; Found: C, 73.56; H, 4.52; N, 3.70.

^{1}H NMR Spectroscopy Experiment on the Switching of (2/2')

A ^{1}H NMR spectrum was recorded of a suspension of **47** in *d*$_4$-methanol, to this suspension was added one drop of conc. DCL (36% in D_2O). Upon addition the material became fully dissolved and a second ^{1}H NMR was recorded. To this same NMR sample was then added two drops of TEA. Upon addition a suspension of white crystalline product was formed and a third ^{1}H NMR spectrum was recorded. All NMR spectra were collected at 400 MHz over 16 scans.

UV and Emission Spectra of Compounds 4, 5, 6 and 7 conditions.

Stock solutions of each compound to be studied were prepared at 5×10^{-5} M concentrations and UV spectra were recorded for each sample. Conditions for the emission spectra of each compound are given below:

(**47**): 5x10^{-5} M, excitation wavelength: 347 nm, scan range: 350-520 nm, slit (ex) 3 nm, slit (em) 1.5 nm.

(**49**): 5x10^{-5} M, excitation wavelength: 347 nm, scan range: 350-520 nm, slit (ex) 3 nm, slit (em) 1.5 nm.

(**48**): 5x10^{-5} M, excitation wavelength: 315 nm, scan range: 350-520 nm, slit (ex) 5 nm, slit (em) 5 nm.

(**50**): 5x10^{-5} M, excitation wavelength: 322 nm, scan range: 350-520 nm, slit (ex) 5 nm, slit (em) 3 nm.

Crystallographic Data

Single crystals of **2** and **3** suitable for X-Ray diffraction studies were grown by dissolving a small amount of material in MeOH and allowing the solvent to evaporate over the course of 1 week. Structures were solved using Patterson or Direct methods with SHELXS-97[1] using WinGX[2] routines. Refinement was accomplished by full matrix least-squares on F^2 *via* SHELXL-97. All non-hydrogen atoms were refined anisotropically

	Compound 2 (CCDC: 724252)	**Compound 3 (CCDC: 724253)**
Formula	$C_{18}H_{13}N_3$	$C_{24}H_{17}NO_2$
Mr g mol^{-1}	271.31	351.39
crystal system	Monoclinic	Triclinic
space group	*P*2(1)/*c*	*P*-1
a [Å]	17.8112(8)	6.2544(4)
b [Å]	6.4552(3)	11.5568(8)
c [Å]	11.8419(5)	11.9526(6)
α°	90	98.758(4)
β°	99.737(4)	97.634(4)
γ°	90	97.453(3)
V [$Å^3$]	1341.91(10)	836.33(9)
Z	4	2
ρ [g cm^{-3}]	1.343	1.395
$\mu(Mo_{K\alpha})$ mm^{-1}	0.082	0.089
T [K]	150(2)	150(2)
no.rflns (measd)	7323	10103
no. rflns (unique)	2111 (Rint = 0.0614)	3106 (R(int)= 0.0427)
no. params.	190	244
R1 ($I>2\sigma(I)$)	0.0389	0.0481
*w*R2 (all data)	0.0694	0.1075

Table S1: Structure refinement details for the X-Ray crystal structures of 2 and 3.

References

1, G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112

2, L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837