New phenanthrene systems: spiro-fused tricyclic phenanthro-1,2,4-triazolo-[4,3-*d*]-1,2,4-triazines and -[3,4-*d*]-1,2,5-oxadiazines: ring expansions of *N*-methylphenanthroazoliums

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New routes to substituted phenanthro[9,10-*e*]-1,2,4-triazines and phenanthro[9,10-*c*]-1,2,5-oxadiazines are described. Cycloadditions of these with *C*-phenyl-*N*-*p*-nitrophenylnitrile imide [IUPAC name: 2-benzylidene-1-(*p*-nitrophenyl)hydrazin-2-ium-1-ide] gave new substituted spiro-tricyclic phenanthro-1,2,4-triazolo[4,3-*d*][1,2,4]triazines and phenanthro-1,2,4-triazolo[3,4-*d*][1,2,5]oxadiazines. An X-ray crystal structure is reported on 7,10-diphenyl-5-(4′-nitrophenyl)-9,10-dihydro-5*H*-phenanthro[9,10-*e*][1,2,4]-triazolo[4,3-*d*][1,2,4]triazine 5a.

The fusion of azole rings at the 9,10-bond of phenanthrene has aroused recent interest[1–4] and in particular phenanthro[9,10-*d*]-1,2,3-triazole derivatives[3,4] have been used to develop synthetic scope in the phenanthrene series. Recently we have described[5] an easy synthesis of the phenanthrotriazole series **1A**. Herein we use these substrates **1A** and the oxygen analogue the phenanthro-1,2,5-oxadiazole system **1B** to provide a new route to the phenanthro-triazine and -oxadiazine systems **4A** and **4B** *via* a ring expansion of *N*-methyl quaternised salts **2**. The products **4A** and **4B** are used in turn to generate the new tricyclic fused phenanthro-1,2,4-triazoloazine systems **5** and **6**.

Results and discussion

The compounds **1A** (**a**–**e**) and **1B** were readily quaternised to *N*-methylazolium salts on being heated in dimethyl sulfate. Anion exchange with sodium perchlorate gave high yields of the phenanthroazolium perchlorate salts **2A** and **2B** (Table 1). Treatment of suspensions of the salts **2** in toluene, dichloromethane or dimethylformamide with ethanolic NaOEt gave an apparently instantaneous ring-expansion to the bright red phenanthro-[9,10-*e*]-1,2,4-triazines **4A** and yellow phenanthro[9,10-*c*]-1,2,5-oxadiazine **4B**. This ring expansion reaction is likely to involve a deprotonation of the quaternary methyl group giving the fused hetero-1,3,5-triene intermediate **3** which undergoes a 1,6-electrocyclisation to the products **4** (Table 1). The presence of the more electronegative oxygen atom in **2B** rendered the reaction less efficacious (43% ring expansion) and demethylation to **1B** competed strongly (31%) in this case with the ethoxide base removing the methyl group from the ring nitrogen as well as attacking the methyl C–H. However, the use of a more sterically restricted base, potassium *tert*-butoxide, oriented the reaction back towards ring expansion and reduced the extent of demethylation (Table 1, entry 12).

The compounds **4** contain two potentially reactive C=N bonds conjugated to the phenanthrene system. It was of interest to examine which, if any of these would be the reactive site in a cycloaddition. When solutions of compounds **4** in dry benzene were treated with 1.2 mol equiv. of the nitrile imide 1,3-dipole, benzonitrile-*N*-*p*-nitrophenylimide [IUPAC name: 2-benzylidyne-1-(*p*-nitrophenyl)hydrazin-2-ium-1-ide], cycloadditions occurred on the N–4–C–4a bond in a regioselective manner and gave high yields of the new spiro fused systems **5** and **6**. The alternative orientation of the cycloaddition which would involve new C–C and N–N bond formation was not observed. This could have arisen since the N-atom is not necessarily the nucleophilic terminus of the nitrile imide 1,3-dipole particularly in the bent form which is necessary for the cycloaddition transition state.[6,7]

The structures of the products were established from microanalyses (Table 1), IR, proton and carbon-13 NMR spectra which showed all of the expected signals (Scheme 1 and Experimental section). In the series **5** the coupling constant between the diastereotopic hydrogens at C-9 was 11.7–12.4 Hz indicating no strain at C-9 in these systems. An X-ray crystal structure of compound **5A** (Fig. 1) confirmed the structure and showed a small out-of-plane tilt (8.4°) between the benzene rings of the phenanthrene unit.† The two H atoms at C-9 showed significantly different shielding with one appearing at δ 4.06–4.15 and the other at δ 5.19–5.32. The more shielded of the two is probably endo to the face of the phenanthrene moiety and experiencing shielding from it.[1] Similar effects are observed for the methylene hydrogens of compound **6**.

Experimental

Mps were measured on an Electrothermal apparatus. IR spectra were measured with a Perkin-Elmer 983G spectrophotometer. NMR spectra were measured on a JEOL JNM-GX-270 instrument with tetramethylsilane as internal reference and deuteriochloroform or hexadeuteriodimethyl sulfoxide as solvent; *J* values are given in Hz. NMR assignments were supported by decoupled and off-resonance decoupled spectra. Microanalyses were measured on a Perkin-Elmer model 240 CHN analyser.

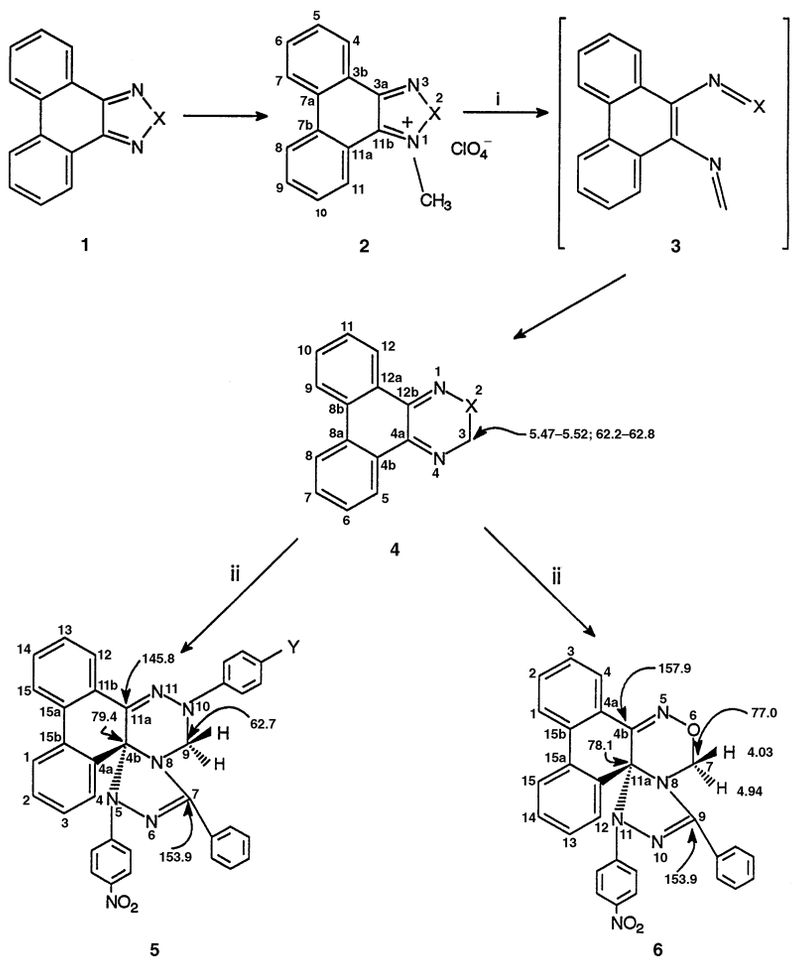
The substrate **1Ac** (mp 244–246 °C, EtOH) was prepared by the synthetic route which we have recently described[5] and compounds **1Aa** and **1Ab** were similarly prepared from the reaction of 2,2′-diphenyldialdehyde with the appropriate arylhydrazine. For the substrates **1Ad** (mp 199–200 °C, THF) and **1Ae** (mp 232–233 °C, EtOH), a modification was necessary. In the

† Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/79.

Table 1 Characterisation of products

Entry	Comp.	Mp/ °C	Yield (%)	Microanalysis found % (required %) C	H	N
1	**2Aa**	259–260 [a]	76	61.3 (61.5)	3.6 (3.9)	10.4 (10.25)
2	**2Ab**	230–231 [a]	79	51.8 (51.6)	3.2 (3.1)	8.4 (8.6)
3	**2Ac**	243–245 [a]	93	56.5 (56.8)	3.6 (3.4)	9.7 (9.5)
4	**2Ad**	250–252 [a]	82	60.5 (60.05)	3.8 (4.1)	9.7 (9.55)
5	**2Ae**	251–253 [a]	95	62.6 (62.35)	4.9 (4.65)	10.0 (9.9)
6	**2B**	212–214 [a]	90	54.05 (53.8)	3.5 (3.3)	8.6 (8.4)
7	**4Aa**	140–141 [b]	92	81.7 (81.55)	4.9 (4.85)	13.4 (13.6)
8	**4Ab**	180–181 [c]	93	64.8 (64.95)	3.6 (3.6)	10.6 (10.8)
9	**4Ac**	156–158 [b]	72	73.7 (73.4)	3.9 (4.05)	12.4 (12.2)
10	**4Ad**	126–128 [d]	88	78.0 (77.9)	4.75 (5.05)	12.6 (12.4)
11	**4Ae**	182–184 [d]	87	82.0 (81.7)	5.0 (5.3)	12.8 (13.0)
12	**4B**	250–252 [e]	53	76.75 (76.9)	4.4 (4.25)	11.8 (11.95)
13	**5a**	213–215 [f]	78	74.2 (74.4)	4.2 (4.4)	15.0 (15.3)
14	**5b**	192–193 [f]	72	65.2 (65.4)	3.0 (3.35)	13.2 (13.5)
15	**5c**	185–187 [f]	77	69.8 (70.0)	3.9 (3.95)	14.0 (14.4)
16	**5d**	205–206 [f]	75	72.8 (72.85)	4.3 (4.5)	14.4 (14.5)
17	**5e**	212–214 [f]	82	74.0 (74.2)	4.5 (4.75)	15.4 (15.25)
18	**6**	328–330 [g]	85	70.8 (71.0)	3.9 (4.0)	14.65 (14.8)

[a] From acetone–diethyl ether. [b] From EtOH. [c] From toluene. [d] From MeOH. [e] With dimethylformamide as solvent and KOBu^t, demethylation to **1B** (19%) competed with ring expansion. [f] From dichloromethane–light petroleum (bp 40–60 °C). [g] From CH_2Cl_2.



Scheme 1 *Reagents:* i, NaOEt; ii, *p*-$NO_2C_6H_4$–$\bar{N}$–$\overset{+}{N}$≡C–Ph. Some key ^{1}H and ^{13}C NMR shifts shown for Y = H and for the **4A** series.

reaction of 2,2′-diphenyldialdehyde‡ with the *para*-electron-donating arylhydrazines the hydrazine was added to the aldehyde solution and the bishydrazone generated underwent *in situ* air oxidation to the 9,10-bis(arylazo)-9,10-dihydrophenanthrene thus removing one step from the synthetic sequence.[5] The substrate **1B** (mp 183–184 °C, EtOH, 65%) was obtained by deoxygenation of its *N*-oxide (mp 230 °C, lit.,[8] 233 °C, $CHCl_3$) by heating it under reflux in triethyl phosphite (3.9 mmol in 19 cm^3) for 24 h under an atmosphere of nitrogen followed by

‡ IUPAC name: biphenyl-2,2′-dicarbaldehyde.

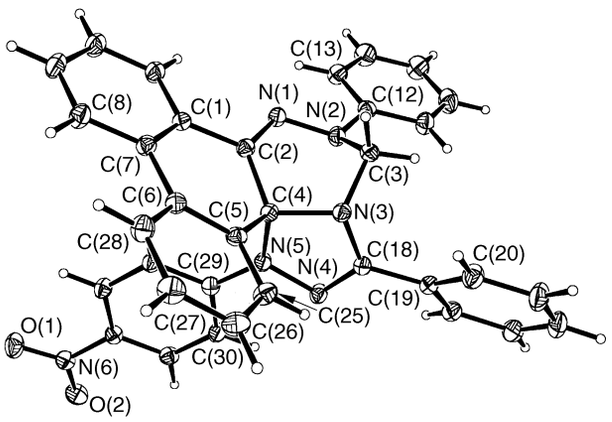


Fig. 1 X-Ray crystal structure of **5a**

addition of the hot solution to a mixture of conc. HCl (5 cm^3) in water (150 cm^3). The following are typical examples of the reactions in Table 1.

1-Methyl-2-phenyl-2*H*-phenanthro[9,10-*d*]-1,2,3-triazolium perchlorate 2Aa

A solution of the triazole **1Aa** (0.5 g, 1.69 mmol) in dimethyl sulfate (5 cm^3) was stirred at 120 °C for 10 h. The mixture was then cooled and treated with an aqueous solution (2 cm^3) of sodium perchlorate (2.07 g, 16.9 mmol) with rapid stirring. Addition of diethyl ether caused precipitation of compound **2Aa** (0.52 g, 76%), mp 259–260 °C (from acetone–diethyl ether); ν_{max}(Nujol)/cm^{-1} 1094 (ClO_4^-); δ_H([$^2H_6$]DMSO, 80 °C) 4.83 (3 H, s, N–Me), 8.01–8.22 (9 H, m, Ph, H-2′, H-3′, H-4′, H-5, H-6, H-9, H-10), 8.74 (1 H, d, H-8), 8.92 (1 H, d, H-7), 9.07 (1 H, d, H-11), 9.19 (1 H, d, H-4); δ_C(80 °C) 40.7 (N–Me), 117.1 and 120.6 (C-7a and C-7b), 122.8 (C-11a), 127.3 (C-2′), 129.5 (C-4′), 130.0 (C-3b), 130.3 (C-3′), 132.5 (C-11b), 140.0 (C-1′), 141.4 (C-3a), remaining aromatic: 124.5, 125.3, 129.0, 130.5, 132.0 and 133.1 (two signals overlapped).

2-Phenyl-2,3-dihydrophenanthro[9,10-*e*]-1,2,4-triazine 4Aa

A suspension of salt **2Aa** (0.5 g, 1.22 mmol) in toluene (10 cm^3) was treated with an excess of sodium ethoxide (0.09 g, 1.34 mmol). The resulting red solution was stirred at room temperature for 2 h. Evaporation of solvent under reduced pressure yielded the red product **4Aa** (0.35 g, 92%), mp 140–141 °C (from ethanol); δ_H($CDCl_3$, 60 °C) 7.15 (1 H, t, N–Ph, H-4′), 5.52 (2 H, s, 3-CH_2), 7.40–7.59 (8 H, m, N–Ph, H-2′, H-3′, H-6, H-7, H-10, H-11), 8.08–8.15 (3 H, m, H-5, H-8, H-9), 8.46 (1 H, d, H-12); δ_C(60 °C) 62.7 (3-CH_2), 117.7, 123.6, 128.7 and 144.3 (N–Ph, C-2′, C-4′, C-3′ and C-1′), 123.7 (C-9), 123.9 (C-8), 124.2 (C-10), 125.7 (C-7), 128.3 (C-6), 129.6 (C-12), 130.0 and 130.5 (C-8a and C-8b), 131.2 (C-12a), 131.7 (C-5), 134.1 (C-4b), 137.3 (C-12b), 152.2 (C-4a) (one signal overlapped).

7,10-Diphenyl-5-(4′-nitrophenyl)-9,10-dihydro-5*H*-phenanthro-[9,10-*e*][1,2,4]triazolo[4,3-*d*][1,2,4]triazine 5a

A solution of **4Aa** (0.12 g, 0.39 mmol) and *N*-(*p*-nitrophenyl)benzohydrazonoyl bromide[9] (0.15 g, 0.47 mmol) in dry benzene (15 cm^3) was treated dropwise with Et_3N (0.11 cm^3, 0.78 mmol) in dry benzene (5 cm^3) and the mixture stirred at ambient temperature for 24 h, filtered, the solvent removed under reduced pressure and the residue in dichloromethane placed on a silica gel column (70–230 mesh ASTM) and eluted with gradient mixtures of light petroleum (bp 40–60 °C)–dichloromethane (30:70 v/v) to pure dichloromethane yielding **5a**, mp 213–215 °C (dichloromethane–light petroleum bp 40–60 °C), in the later fractions (0.17 g, 78%); δ_H($CDCl_3$) 4.17, 5.35 (2 H, AB doublets, *J* 12.5, 9-CH_2), 7.06 (2 H, m, Ar), 7.2–8.0 (18 H, m, Ar), 8.12 (2 H, d, 5-$C_6H_4NO_2$-*p*, H_{meta}); δ_C 62.7 (C-9), 79.4 (C-4b), 150.25, 116.8, 142.8 (5-$C_6H_4NO_2$-*p*, C-1′, C-2′, C-4′), 143.5 (10-Ph, C-1′), 145.8 (C-11a), 153.9 (C-7), 135.5 (7-Ph, C-1′), 121.1, 123.3, 123.5, 123.7, 124.6, 126.9, 127.2, 127.9, 129.0, 129.3, 129.5, 130.05, 130.6, 131.1, 132.5 (remaining Ar); four Ar signals overlapped; for the X-ray structure, see Fig. 1.

1-Methylphenanthro[9,10-*c*][1,2,5]oxadiazolium perchlorate 2B

A solution of **1B** (2 g, 9.09 mmol) in dimethyl sulfate (10 cm^3) was stirred at 130 °C for 48 h, cooled and treated with aqueous sodium perchlorate (1.34 g, 2 cm^3) with vigorous stirring. Addition of diethyl ether caused precipitation of compound **2B** (2.74 g, 90%), mp 212–214 °C (acetone–Et_2O); ν_{max}(Nujol)/cm^{-1} 1089.8 (ClO_4^-); δ_H([$^2H_6$]DMSO) 5.28 (3 H, s, N–Me), 8.06–8.93 (8 H, m, Ar); insolubility prevented measurement of a carbon-13 spectrum.

3*H*-Phenanthro[9,10-*c*][1,2,5]oxadiazine 4B

A solution of compound **2B** (1 g, 2.98 mmol) in dry dimethylformamide (25 cm^3) was treated with KOBu^t (0.4 g, 3.58 mmol), stirred at ambient temperature for 24 h, filtered to remove salts and evaporated under reduced pressure. The residue in CH_2Cl_2 (4 cm^3) was placed on a silica gel column (70–230 mesh ASTM) and eluted with gradient mixtures of light petroleum (bp 40–60 °C)–dichloromethane (30:70 v/v to 0:1). Compound **1B** (19%) was eluted first from the column followed by **4B**, mp 250–252 °C (CH_2Cl_2–light petroleum bp 40–60 °C) (0.37 g, 53%); δ_H($CDCl_3$) 5.5 (2 H, s, 3-CH_2), 7.39–7.61 (4 H, m, H-6, H-7, H-10, H-11), 8.02–8.8 (3 H, m, H-8, H-9, H-5), 8.36 (1 H, d, *J* 7.3, H-12); δ_C 78.9 (C-3), 150.5 (C-4a), 149.9 (C-12b), 132.7, 131.5 (C-12, C-5), 133.6, 132.4 (C-12a, C-4b), 129.6, 128.7 (C-8a, C-8b), 123.7, 124.8, 125.8, 128.8 (Ar, CH), two signals overlapped.

11-(4′-Nitrophenyl)-9-phenyl-7*H*,11*H*-phenanthro[9,10-*c*]-[1,2,4]triazolo[4,3-*d*][1,2,5]oxadiazine 6

A solution of **4B** (0.07 g, 0.3 mmol) and *N*-(*p*-nitrophenyl)-benzohydrazonoyl bromide[9] (0.12 g, 0.36 mmol) in dry benzene (15 cm^3) was treated dropwise with a solution of Et_3N (0.084 cm^3, 0.6 mmol) in dry benzene (5 cm^3) and the mixture stirred at ambient temperature for 24 h, filtered to remove salts and evaporated under reduced pressure. The residue in dichloromethane (4 cm^3) was placed on a silica gel column (70–230 mesh ASTM) and eluted with gradient mixtures of light petroleum (bp 40–60 °C)–dichloromethane (30:70 v/v to 0:1) yielding bright yellow **6**, mp 328–330 °C (CH_2Cl_2) in the later fractions (0.12 g, 85%); δ_H(C_6D_6) 4.03, 4.94 (2 H, an AB pair of doublets, *J* 11, 7-CH_2), 6.65 (2 H, d, *J* 8.8, 1-*p*-$NO_2C_6H_4$, H_o), 6.85–7.6 (13 H, m, Ar), 7.7 (1 H, d) and 7.90 (1 H, d) (H-4, H-12); δ_C(C_6D_6) 77.0 (C-7), 78.1 (C-11a), 150.4, 122.1, 143.6 (11-$C_6H_4NO_2$-*p*, C-1′, C-2′, C-4′), 157.9 (C-4b), 153.9 (C-9), 135.2 (9-Ph, C-1′) 133.6, 133.0 (C-4a, C-11b), 132.3, 131.5, 131.1, 129.8, 128.7, 128.3, 127.8, 127.5, 127.1, 125.5, 125.4, 124.3, 123.9 (remaining Ar), one Ar signal overlapped.

X-Ray crystal structure determination of compound 5a

The structure was solved by direct methods, SHELX-86[10] and refined by full matrix least squares using SHELXL-93.[11] SHELX operations were rendered paperless using ORTEX which was also used to obtain the drawings.[12] Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated position with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. There was one water of crystallisation disordered over two positions 1 Å apart. This water did not make H-bond contacts to any other atoms. The relatively high residual peak in the final difference map of 1.5 e $Å^{-3}$ was close to this water molecule. This residual peak and the unexpectedly high *R* index are both associated with problems involved in modelling the disordered solvent. All calculations were performed on a Silicon Graphics R4000 computer.

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