Heterocyclic Mesomeric Betaines. Part 5.[1] Synthesis and Cycloaddition Reactions of Hetero Derivatives of the 2-Methylene-1,2-dihydro-1,3-phenalenylene Dianion

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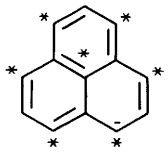
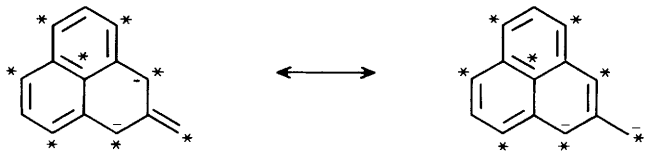
Conjugated heterocyclic mesomeric betaines (**5**; R = H, Me, Ph) which are isoconjugate with the 2-methylene-1,2-dihydro-1,3-phenalenylene dianion (**2**) have been synthesized. These heterocyclic mesomeric betaines could not be isolated, but they have been characterized by 1,3-dipolar cycloaddition with olefinic dipolarophiles. Cycloadducts (**7a**) and (**8a**) underwent an acid-catalysed retro-Michael reaction.

One of the useful features of our recently proposed classification of heterocyclic mesomeric betaines[2] is that new types of heterocyclic mesomeric betaines can be devised which are isoconjugate with novel alternant and non-alternant hydrocarbon anions and dianions. In Part 1,[3] we discussed the chemistry of conjugated heterocyclic mesomeric betaines isoconjugate with the alternant phenalen-1-ide anion (**1**). We now report upon the synthesis and cycloaddition reactions of novel conjugated heterocyclic mesomeric betaines which are isoconjugate with the even alternant 2-methylene-1,2-dihydro-1,3-phenalenylene dianion (**2**).

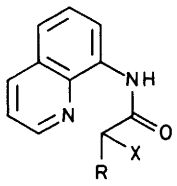


(1)



(2a) (2b)

8-Aminoquinoline and chloroacetyl chloride yielded 8-chloroacetamidoquinoline (**3a**) which was transformed into the salt (**4a**) by heating at 140 °C. Similarly, reaction of 8-aminoquinoline with the corresponding α-halogeno acid chlorides yielded the salts (**4b**) and (**4c**) directly. The salts (**4a**—**c**) were yellow ($\lambda_{max.}$ 324—330 nm) and showed amide carbonyl absorption (ν_{CO} 1 690—1 695 cm^{-1}). Treatment of the salts (**4a**—**c**) with triethylamine in aqueous chloroform at room temperature produced an immediate red colouration [bathochromic shift: (**4a**) ($\lambda_{max.}$ 330 nm; ε 340) ⟶ (**5a**) ($\lambda_{max.}$ 508 nm; ε 80)]. This bathochromic shift induced by triethylamine was attributed to deprotonation yielding a heterocyclic mesomeric betaine. Two possible structures (**5**) or (**6**) could have been produced by deprotonation of the cation of the salts (**4**). One possible structure was that of a conjugated heterocyclic mesomeric betaine represented as the *N*-ylide (**5**). Conjugation in this *N*-ylide (**5**) extends over the tricyclic system and this *N*-ylide is isoconjugate with the even alternant 2-methylene-1,2-dihydro-1,3-phenalenylene dianion (**2**). Alternatively, the deprotonation products might have been the conjugated mesomeric betaines (**6**) in which the conjugation is essentially restricted to the bicyclic quinolinium-8-aminide system.



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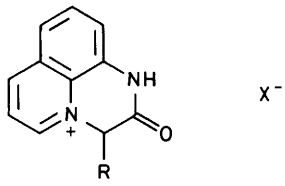

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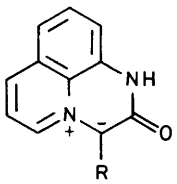

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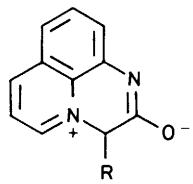


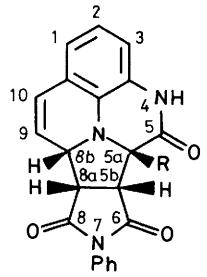
(6)

In formulae (**3**)—(**6**): **a**, R = H, X = Cl; **b**, R = Me, X = Br; **c**, R = Ph, X = Br

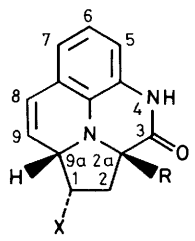
The deprotonation products (**5**) or (**6**) could not be isolated and characterized. However, our preference for the *N*-ylide structure (**5**) rather than the alternative mesomeric betaine structure (**6**) was obviously supported by the trapping of the deprotonation products by 1,3-dipolarophiles.

Cycloadditions of the N-*Ylides* (**5**).—The novel conjugated heterocyclic *N*-ylides (**5a**—**c**) have been trapped by their generation in the presence of either *N*-phenylmaleimide, ethyl acrylate, or acrylonitrile.

The 1,3-dipolar cycloaddition between the heterocyclic *N*-ylides (**5a**—**c**) and *N*-phenylmaleimide was demonstrably stereospecific because the cycloadducts, which were formed exclusively, were shown to have the *endo* configuration (**7**). The *endo* configuration was established by determining the coupling constant ($J_{8a,8b}$) for the protons 8a-H and 8b-H. The coupling constants ($J_{8a,8b}$) were calculated using a version ($J = 10\cos\theta$)[4] of the Karplus equation and estimates of the torsion angle θ. This procedure gave the indicated coupling



(7)



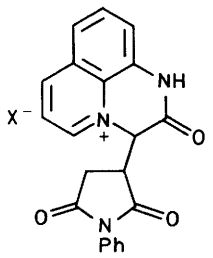
(8) X = CO_2Et
(9) X = CN

In formulae (7)—(9): **a**, R = H; **b**, R = Me; **c**, R = Ph

constants for the *endo* configuration (**7**) ($J_{8a,8b}$ 8—9 Hz) and the corresponding *exo* configuration ($J_{8a,8b}$ 3 Hz). The observed coupling constants for (**7a**) ($J_{8a,8b}$ 9 Hz), (**7b**) ($J_{8a,8b}$ 8.5 Hz), and (**7c**) ($J_{8a,8b}$ 8 Hz) established that these three cycloadducts with *N*-phenylmaleimide all have the *endo* configuration (**7**).

The 1,3-dipolar cycloaddition between the heterocyclic *N*-ylides (**5a**—**c**) and either ethyl acrylate or acrylonitrile are demonstrably regiospecific and stereospecific. Ethyl acrylate yields the *endo*-1,3-dipolar cycloadducts (**8a**—**c**) and acrylonitrile similarly yields the 1,3-dipolar cycloadducts (**9a**—**c**). The regiochemistry of these cycloadditions is firmly established by the observation that 9a-H is *coupled to two protons only* at 9-H and at 1-H. The *endo* configuration of the ethyl acrylate cycloadduct was supported by the chemical shift of the methyl groups of the ethoxycarbonyl groups of the cycloadducts: (**8a**) [$\delta(OCH_2CH_3)$ = 0.98], (**8b**) [$\delta(OCH_2CH_3)$ = 0.93], and (**8c**) (δ = 0.93). This shift to high field is attributed to positive shielding of these methyl groups by the appositely placed benzene ring.

Acid-catalysed Transformation of the Cycloadducts (**7a**) *and* (**8a**).—The cycloadduct (**7a**) gave a normal ^{1}H n.m.r. spectrum when its ^{1}H n.m.r. spectrum was determined in [$^2H_6$]dimethyl sulphoxide solution. However, when the spectrum of the cycloadduct (**7a**) was determined in trifluoroacetic acid solution, it was clear that the transformation (**7a**) ⟶ (**10**) (X = CF_3CO_2) had occurred. Addition of perchloric acid gave the salt (**10**; X = ClO_4). Similarly, the ethyl acrylate cycloadduct (**8a**) was smoothly transformed by trifluoracetic acid to the trifluoroacetate salt (**11**; X = CF_3CO_2) and this salt yielded the perchlorate salt (**11**; X = ClO_4).



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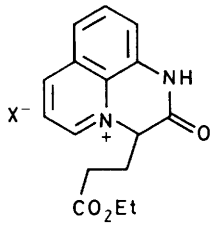
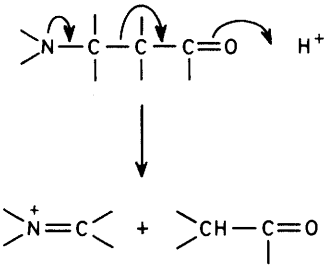


(11)

These reactions are examples of the well-known acid-catalysed retro-Michael reaction of β-amino ketones.

These transformations (**7a**) ⟶ (**10**) and (**8a**) ⟶ (**11**) are obviously mechanistic analogues of the acid-catalysed cleavage of the 1,3-dipolar cycloadducts of pyridinium methylides recently reported by Tsuge.[5,6]



Experimental

General experimental directions are given in Part 1.[3]

2,3-*Dihydro*-2-*oxo*-1H-1,3aλ^5-*diazaphenalen*-3a-*ium Chloride* (**4a**).—8-Chloroacetamidoquinoline[7] (**3a**) (1.0 g) was heated (1 h) at 140 °C. The melt rapidly solidified to give the *title compound* (**4a**) (0.95 g, 95%) as a yellow, amorphous solid, m.p. > 300 °C (lit.,[7] m.p. not reported) (Found: C, 60.0; H, 4.2; N, 12.6. $C_{11}H_9ClN_2O$ requires C, 59.9; H, 4.1; N, 12.7%); $\lambda_{max.}$(EtOH) 330 nm (ε 340); $\nu_{max.}$(KBr) 1 690 cm^{-1}; δ(TFA) 9.10 (2 H, m, ArH), 8.17 (1 H, dd, *J* 8 and 6 Hz, ArH), 8.10—7.95 (2 H, m, ArH), 7.82 (1 H, dd, *J* 8 and 1 Hz, ArH), and 6.02 (2 H, s, CH_2). In the cooler regions of the reaction vessel, a small quantity of white material sublimed and was identified as starting material (**3a**).

2,3-*Dihydro*-3-*methyl*-2-*oxo*-1H-1,3aλ^5-*diazaphenalen*-3a-*ium Bromide* (**4b**).—To an ice-cooled, stirred solution of 8-aminoquinoline (2.8 g) in ether (100 ml) was added 2-bromopropionyl bromide (3.0 ml) over 5 min. The mixture was stirred (0.5 h) and filtered to give a tan solid (5.02 g). A portion (4.0 g) of this solid was partitioned between a mixture of chloroform (40 ml), triethylamine (4.0 ml), and water (40 ml). After shaking, the organic layer was separated and the aqueous layer was extracted with chloroform (2 × 30 ml). The combined organic layers were washed with water (2 × 20 ml), dried (Na_2SO_4), and evaporated. The resulting brown residue was fractionated by column chromatography (silica gel; hexane–ether, 5:1) to give a yellow oil (1.24 g). This oil was kept at room temperature (4 days) and then heated on a steam-bath overnight to give the *title compound* (**4b**) (0.98 g, 18%) as a yellow solid, m.p. 296—300 °C (from methanol) (Found: C, 51.9; H, 4.0; Br, 28.2; N, 9.9. $C_{12}H_{11}BrN_2O$ requires C, 51.6; H, 4.0; Br, 28.6; N, 10.0%); $\lambda_{max.}$(EtOH) 268 and 324 nm (ε 980 and 640); $\nu_{max.}$(KBr) 1 695 cm^{-1}; δ(TFA) 9.36 (1 H, d, $J_{4,5}$ 6 Hz, 4-H), 9.16 (1 H, d, $J_{5,6}$ 8 Hz, 6-H), 8.26 (1 H, dd, $J_{4,5}$ 6 and $J_{5,6}$ 8 Hz, 5-H), 8.20—8.00 (2 H, m, ArH), 7.91 (1 H, dd, *J* 8 and 1 Hz, ArH), 6.18 (1 H, q, $J_{3,methyl}$ 8 Hz, 3-H), and 2.14 (3 H, d, $J_{3,methyl}$ 8 Hz, CH_3).

2,3-*Dihydro*-2-*oxo*-3-*phenyl*-1H-1,3aλ^5-*diazaphenalen*-3a-*ium Bromide* (**4c**).—To an ice-cooled, stirred solution of 8-aminoquinoline (2.5 g) and triethylamine (5.0 ml) in tetrahydrofuran (50 ml) was added 1-bromophenylacetyl chloride [freshly prepared from 1-bromophenylacetic acid (5.0 g) and thionyl chloride (10 ml)] over 1 min. The mixture was stirred (0.5 h), filtered, and evaporated to give a red oil. This oil was fractionated by column chromatography (silica gel; hexane–ethyl acetate, 5:1) to give a yellow oil (4.0 g) which was kept (2 days) at room temperature. Ether (*ca.* 10 ml) was added and the resulting solid was collected to give the title compound (**4c**) (1.55 g, 26%) as a yellow solid.

Evaporation of the filtrate and storage of the residue (1 week) gave additional (**4c**) (0.40 g, 7%). Recrystallization from ethanol gave irregular yellow crystals, m.p. 255—258 °C (decomp.) (with softening at 170 °C). Alternatively, precipitation from

methanol solution by slow addition of a large volume of ether afforded yellow, irregular plates, m.p. 172—175 °C. The ^1H n.m.r. spectra of the isomorphs, m.p. 225—228 °C and m.p. 172—175 °C were identical (Found: C, 60.0; H, 4.0; Br, 23.2; N, 8.0. $C_{17}H_{13}BrN_2O$ requires C, 59.8; H, 3.9; Br, 23.4; N, 8.2%); $\lambda_{max.}$(EtOH) 322 nm (ε 570); $\nu_{max.}$(KBr) 1 690 cm^{-1}; δ(TFA) 9.11 (2 H, m, ArH), 8.10 (3 H, m, ArH), 7.96 (1 H, dd, *J* 1.5 and 7 Hz, ArH), 7.60—7.30 (5 H, m, ArH), and 7.11 (1 H, s, 3-H).

Cycloadduct Formation: General Method.—Unless otherwise stated, cycloadducts were prepared as follows. To a rapidly stirred mixture of the appropriate salt (**4a**—**c**) and the 1,3-dipolarophile in a mixture of chloroform (10 ml) and water (10 ml) at room temperature was added triethylamine. Stirring was continued (0.25—1 h) and the organic layer was then separated. The aqueous layer was extracted with chloroform and the combined organic fractions were washed with water, dried (Na_2SO_4), and evaporated to give the cycloadduct.

(5aα,5bα,8aα,8bα)-5a,5b,8a,8b-*Tetrahydro*-7-*phenyl*-4,7,10c-*triazapentaleno*[1,2,3-cd]*phenalene*-5,6,8(4H)-*trione* (**7a**).—The salt (**4a**) (0.32 g), *N*-phenylmaleimide (0.30 g), and triethylamine (0.2 ml) afforded the *cycloadduct* (**7a**) (0.20 g, 39%) as white needles, m.p. 220 °C (from methanol–acetone) (Found: C, 70.7; H, 4.4; N, 11.5. $C_{21}H_{15}N_3O_3$ requires C, 70.6; H, 4.2; N, 11.7%); $\nu_{max.}$(KBr) 1 700 cm^{-1}; δ([$^2H_6$]DMSO) 10.69 (1 H, s, NH), 7.30 (3 H, m, ArH), 6.68 (3 H, s, ArH), 6.55 (1 H, d, $J_{9,10}$ 10 Hz, 10-H), 6.38 (2 H, m, ArH), 6.04 (1 H, dd, $J_{9,10}$ 10 Hz and $J_{8b,9}$ 5 Hz, 9-H), 4.54 (1 H, dd, $J_{8a,8b}$ 9 Hz and $J_{8b,9}$ 5 Hz, 8b-H), 4.24 (1 H, d, $J_{5a,5b}$ 9 Hz, 5a-H), 3.88 (1 H, t, $J_{5a,5b}$ 9 Hz and $J_{5b,8a}$ 9 Hz, 5b-H), and 3.58 (1 H, t, $J_{8a,8b}$ 9 Hz and $J_{5b,8a}$ 9 Hz, 8a-H).

(5aα,5bα,8aα,8bα)-5a,5b,8a,8b-*Tetrahydro*-5a-*methyl*-7-*phenyl*-4,7,10c-*triazapentaleno*[1,2,3-cd]*phenalene*-5,6,8(4H)-*trione* (**7b**).—The salt (**4b**) (0.16 g), *N*-phenylmaleimide (0.16 g), and triethylamine (0.10 ml) afforded the *cycloadduct* (**7b**) (0.15 g, 66%) as cream needles, m.p. 144—148 °C (decomp.) from ethanol) (Found: C, 70.6; H, 4.5; N, 11.6; $C_{22}H_{17}N_3O_3$ requires C, 70.6; H, 4.2; N, 11.8%); $\nu_{max.}$ (KBr) 1 715, 1 680, 1 480, and 1 395 cm^{-1}; δ([$^2H_6$]DMSO) 10.66 (1 H, s, NH), 7.32—7.25 (3 H, m, ArH), 6.66—6.60 (3 H, m, ArH), 6.50 (1 H, dd, $J_{9,10}$ 10 Hz and $J_{8b,10}$ 1 Hz, 10-H), 6.40—6.34 (2 H, m), 5.97 (1 H, dd, $J_{9,10}$ 10 Hz and $J_{8b,9}$ 5 Hz, 9-H), 4.90 (1 H, ddd, $J_{8b,10}$ 1 Hz, $J_{8b,9}$ 5 Hz, and $J_{8a,8b}$ 7.5 Hz, 8b-H), 3.70 (1 H, t, $J_{8a,8b}$ 7.5 Hz and $J_{5b,8a}$ 7.5 Hz, 8a-H), 3.63 (1 H, d, $J_{5b,8a}$ 7.5 Hz, 5b-H), and 1.60 (3 H, s, CH_3).

(5aα,5bα,8aα,8bα)-5a,5b,8a,8b-*Tetrahydro*-5a,7-*diphenyl*-4,7,10c-*triazapentaleno*[1,2,3-cd]*phenalene*-5,6,8(4H)-*trione* (**7c**).—The salt (**4c**) (0.25 g), *N*-phenylmaleimide (0.30 g), and triethylamine (0.20 ml) afforded the *cycloadduct* (**7c**) as a solid in the reaction mixture and this was filtered off (0.11 g, 32%). It was obtained as cream needles, m.p. 267—270 °C (from ethanol–acetone) (Found: C, 74.3; H, 4.8; N, 9.5%; $M^{+\bullet}$, 443. $C_{27}H_{19}N_3O_3$ requires C, 74.8; H, 4.4; N, 9.7%; *M*, 443); $\nu_{max.}$(KBr) 1 705 and 1 480 cm^{-1}; δ([$^2H_6$]DMSO) 8.33 (1 H, s, NH), 7.71 (2 H, m, ArH), 7.50—7.30 (6 H, m, ArH), 6.80—6.65 (3 H, m, ArH), 6.56 (1 H, d, $J_{9,10}$ 10 Hz, 10-H), 6.50—6.42 (2 H, m, ArH), 5.88 (1 H, dd, $J_{9,10}$ 10 Hz and $J_{9,8b}$ 5 Hz, 9-H), 4.64 (1 H, d, $J_{5b,8a}$ 8 Hz, 5b-H), 4.23 (1 H, dd, $J_{8a,8b}$ 8 Hz and $J_{8b,9}$ 5 Hz, 8b-H), and 3.49 (1 H, t, $J_{8a,8b}$ 8 Hz and $J_{5b,8a}$ 8 Hz, 8a-H).

(1β,2aα,9aα)-*Ethyl* 1,2,2a,3,4,9a-*Hexahydro*-3-*oxo*-4,9b-*diazacyclopenta*[cd]*phenalene*-1-*carboxylate* (**8a**).—The salt (**4a**) (0.38 g), ethyl acrylate (0.30 ml), and triethylamine (0.30 ml) afforded the *cycloadduct* (**8a**) (0.20 g, 41%) as orange needles, m.p. 170—173 °C (from ethanol) (Found: C, 67.4; H, 5.5; N, 9.8%; $M^{+\bullet}$, 284. $C_{16}H_{16}N_2O_3$ requires C, 67.6; H, 5.7; N, 9.9%; *M*, 284); $\nu_{max.}$(KBr) 1 725 and 1 675 cm^{-1}; δ([$^2H_6$]DMSO) 10.48 (1 H, s, NH), 6.70—6.45 (4 H, m, ArH + 8-H), 5.81 (1 H, dd, $J_{8,9}$ 10 Hz and $J_{9,9a}$ 5 Hz, 9-H), 4.41 (1 H, dd, $J_{9,9a}$ 5 Hz and $J_{1,9a}$ 8 Hz, 9a-H), 3.85 (3 H, m, OCH_2CH_3 and 2a-H), 3.08 (1 H, m, 1-H), 2.33 (1 H, m, 2-H), 1.91 (1 H, m, 2-H), and 0.98 (3 H, t, *J* 8 Hz, CH_2CH_3).

(1β,2aα,9aα)-*Ethyl* 1,2,2a,3,4,9a-*Hexahydro*-2a-*methyl*-3-*oxo*-4,9b-*diazacyclopenta*[cd]*phenalene*-1-*carboxylate* (**8b**).—The salt (**4b**) (0.18 g), ethyl acrylate (0.10 ml), and triethylamine (0.10 ml) afforded a semisolid (0.17 g). Trituration with ether afforded the crude cycloadduct (**8b**) (0.08 g, 42%). Preparative thick layer chromatography (silica gel; ether) gave the *cycloadduct* (**8b**) as pale orange prisms, m.p. 167—170 °C [Found: *m/z* 296.1136. $C_{17}H_{16}N_2O_3$ (*M* − 2H) requires *m/z* 296.1161]; $\nu_{max.}$(KBr) 1 725 and 1 675 cm^{-1}; δ 9.11 (1 H, s, NH), 6.53 (3 H, m, ArH), 6.42 (1 H, d, $J_{8,9}$ 10 Hz, 8-H), 5.76 (1 H, dd, $J_{8,9}$ 10 Hz and $J_{9,9a}$ 5 Hz, 9-H), 4.73 (1 H, dd, $J_{9,9a}$ 5 Hz and $J_{1,9a}$ 6 Hz, 9a-H), 3.89 (2 H, m, OCH_2CH_3), 3.09 (1 H, m, 1-H), 2.51 (1 H, dd, $J_{1,2}$ 5 Hz and $J_{2,2'}$ 13 Hz, 2-H), 2.12 (1 H, dd, $J_{1,2}$ 9 Hz and $J_{2,2'}$ 13 Hz, 2′-H), 1.58 (3 H, s, CH_3), and 0.93 (3 H, t, *J* 6 Hz, CH_2CH_3).

(1β,2aα,9aα)-*Ethyl* 1,2,2a,3,4,9a-*Hexahydro*-3-*oxo*-2a-*phenyl*-4,9b-*diazacyclopenta*[cd]*phenalene*-1-*carboxylate* (**8c**).—The salt (**4c**) (0.14 g), ethyl acrylate (0.10 ml), and triethylamine (0.10 ml) afforded a yellow oil (0.14 g) which was triturated with ethanol to give the *cycloadduct* (**8c**) (0.07 g, 47%) as pale orange rhombs, m.p. 183—186 °C (from ethanol) [Found: C, 73.5; H, 5.6; N, 7.8; *m/z* 260 (*M* − ethyl acrylate). $C_{22}H_{20}N_2O_3$ requires C, 73.3; H, 5.6; N, 7.8%; *M*, 360]; $\nu_{max.}$(KBr) 1 720 and 1 680 cm^{-1}; δ 9.16 (1 H, s, NH), 7.69 (2 H, d, *J* 8 Hz, ArH), 7.4—7.1 (4 H, m, ArH), 6.7—6.5 (2 H, m, ArH), 6.46 (1 H, d, $J_{8,9}$ 11 Hz, 8-H), 5.66 (1 H, dd, $J_{8,9}$ 11 Hz and $J_{9,9a}$ 5 Hz, 9-H), 4.37 (1 H, m, 9a-H), 3.92 (2 H, m, OCH_2CH_3), 2.95 (1 H, m, 1-H), 2.81 (1 H, m, 2-H), 1.27 (1 H, m, 2′-H), and 0.93 (3 H, t, *J* 8 Hz, CH_2CH_3).

1,2,2a,3,4,9a-*Hexahydro*-3-*oxo*-4,9b-*diazacyclopenta*[cd]-*phenalene*-1-*carbonitrile* (**9a**).—The salt (**4a**) (0.33 g), acrylonitrile (0.20 ml), and triethylamine (0.20 ml) afforded the *cycloadduct* (**9a**) (0.27 g, 75%) as cream needles, m.p. 203—205 °C (decomp.) (from ethanol) (Found: C, 71.1; H, 4.6; N, 17.6%; $M^{+\bullet}$, 237. $C_{14}H_{11}N_3O$ requires C, 70.8; H, 4.7; N, 17.1%; *M*, 237); $\nu_{max.}$(KBr) 2 230 and 1 675 cm^{-1}; δ([$^2H_6$]DMSO) 10.62 (1 H, s, NH), 6.80—6.60 (4 H, m, ArH + 8-H), 5.94 (1 H, dd, $J_{8,9}$ 10 Hz and $J_{9,9a}$ 5 Hz, 9-H), 4.27 (1 H, ddd, $J_{1,9a}$ 8 Hz, $J_{2,9a}$ 1 Hz, and $J_{9,9a}$ 5 Hz, 9a-H), 3.84 (1 H, dd, *J* 7 Hz and 10 Hz, 2a-H), 3.43 (1 H, m, 1-H), 2.63 (1 H, m, 2-H), and 1.67 (1 H, m, 2′-H).

1,2,2a,3,4,9a-*Hexahydro*-2a-*methyl*-3-*oxo*-4,9b-*diazacyclopenta*[cd]*phenalene*-1-*carbonitrile* (**9b**).—The salt (**4b**) (0.20 g), acrylonitrile (0.10 ml), and triethylamine (0.10 ml) afforded the *cycloadduct* (**9b**) (0.15 g, 83%) as pale orange plates, m.p. 175—176 °C (decomp.) (from ethanol–ether) [Found: C, 71.5; H, 5.1; N, 16.6%; *m/z* 250 (*M* − 1) and 197 (*M* − acrylonitrile). $C_{15}H_{13}N_3O$ requires C, 71.7; H, 5.2; N, 16.7%; *M*, 251]; $\nu_{max.}$(KBr) 2 130 and 1 675 cm^{-1}; δ 9.86 (1 H, s, NH), 6.76—6.66 (3 H, m, ArH + 8-H), 6.55 (1 H, dd, *J* 8 and 2 Hz, ArH), 5.87 (1 H, dd, $J_{8,9}$ 10 Hz and $J_{9,9a}$ 5 Hz, 9-H), 4.69 (1 H, ddd, $J_{1,9a}$ 7 Hz, $J_{2,9a}$ 1 Hz, and $J_{9,9a}$ 5 Hz, 9a-H), 3.22 (1 H, m, 1-H), 2.48 (1 H, dd, $J_{2,2'}$ 13 Hz and $J_{1,2}$ 9 Hz, 2-H), 2.25 (1 H, dd, $J_{2,2'}$ 13 Hz and $J_{1,2'}$ 5 Hz, 2′-H), and 1.58 (3 H, s, CH_3).

1,2,2a,3,4,9a-*Hexahydro*-3-*oxo*-2a-*phenyl*-4,9b-*diazacyclopenta*[cd]*phenalene*-1-*carbonitrile* (**9c**).—The salt (**9c**) (0.16 g), acrylonitrile (0.10 ml), and triethylamine (0.10 ml) afforded the crude *cycloadduct* (**9c**) (0.14 g, 92%). Preparative thick layer chromatography (silica gel; ether) afforded the *cycloadduct* (**9c**) as a light tan solid, m.p. 120—123 °C [Found: *m/z* 260.0951. $C_{17}H_{12}N_2O$ (*M* − acrylonitrile) requires *M*, 260.0949]; $\nu_{max.}$ 3 390, 2 220, and 1 685 cm^{-1}; δ($CDCl_3$) 3.37 (1 H, s, NH), 7.63 (2 H, m, ArH), 7.33 (3 H, m, ArH), 6.80—6.50 (4 H, m, ArH and 8-H), 5.71 (1 H, dd, *J* 9 and 5 Hz, 9-H), 4.27 (1 H, dd, *J* 6 and 5 Hz, 9a-H), 3.21 (1 H, dd, *J* 13 and 9 Hz, 2-H), 2.97 (1 H, m, 1-H), and 2.42 (1 H, dd, *J* 13 and 6 Hz, 2′-H).

Acid-catalysed Transformation of the Cycloadducts (**7a**) *and* (**8a**).—(3α,3′α)-3-(2,5-*Dioxo*-1-*phenylpyrrolidin*-3-*yl*)-2,3-*dihydro*-2-*oxo*-1H-1,3aλ^5-*diazaphenalen*-3a-*ium Perchlorate* (**10**; X = ClO_4).—The cycloadduct (**7a**) (0.10 g) was added to trifluoroacetic acid (1.0 ml). The ^{1}H n.m.r. spectrum of the solution revealed the formation of the salt (**10**; X = CF_3CO_2); δ(TFA) 9.53 (1 H, d, $J_{4,5}$ 6 Hz, 4-H), 9.21 (1 H, d, $J_{5,6}$ 9 Hz, 6-H), 8.27 (1 H, dd, $J_{4,5}$ 6 Hz and $J_{5,6}$ 9 Hz, 5-H), 8.20—7.88 (3 H, m, ArH), 7.56 (3 H, m, ArH), 7.50 (2 H, m, ArH), 6.78 (1 H, d, ABM*X* system, J_{MX} 5 Hz, 3-H), 4.31 (1 H, m, AB*M*X system, 3′-H), and 3.25 (2 H, *AB*MX system, δ_A 3.33 and δ_B 3.12, J_{AB} 20 Hz, J_{AM} 9 Hz, and J_{BM} 5 Hz, 4′-H). Perchloric acid (70%; 10 drops) was added to the solution followed by ether (40 ml). The resulting precipitate was collected to give the *perchlorate* (**10**; X = ClO_4) (0.10 g, 77%) as a yellow solid, m.p. 260—262 °C [Found: *m/z* 357.1138. $C_{21}H_{15}N_3O_3$ (*M* − $HClO_4$) requires *m/z* 357.1113]; $\nu_{max.}$(KBr) 1 705, 1 545, 1 430, 1 390, 1 195, 1 140, 1 110, and 1 080 cm^{-1}; δ([$^2H_6$]DMSO) 12.13 (1 H, s, NH), 9.59 (1 H, d, $J_{4,5}$ 6 Hz, 4-H), 9.31 (1 H, d, $J_{5,6}$ 8 Hz, 6-H), 8.30 (1 H, dd, $J_{4,5}$ 6 Hz and $J_{5,6}$ 8 Hz, 5-H), 8.10 (1 H, d, *J* 8 Hz, ArH), 7.9 (1 H, t, $J_{8,9}$ 8 Hz and $J_{7,8}$ 8 Hz, 8-H), 7.64 (1 H, d, *J* 8 Hz, ArH), 7.60—7.40 (3 H, m, ArH), 7.75 (2 H, m, ArH), 6.38 (1 H, d, $J_{3,3'}$ 5 Hz, 3-H), 3.98 (1 H, m, 3′-H), and 2.88 (2 H, AB system, δ_A 3.07 and δ_B 2.75, J_{AB} 18 Hz, 4′-H); δ(TFA) 9.46 (1 H, d, $J_{4,5}$ 6 Hz, 4-H), 9.07 (1 H, d, $J_{5,6}$ 8 Hz, 6-H), 8.19 (1 H, dd, $J_{5,6}$ 8 Hz and $J_{4,5}$ 6 Hz, 5-H), 8.10—7.90 (2 H, m, ArH), 7.83 (1 H, d, *J* 7 Hz, ArH), 7.50 (3 H, m, ArH), 7.27 (2 H, m, ArH), 6.72 (1 H, d, $J_{3,3'}$ 5 Hz, 3-H), 4.31 (1 H, dt, $J_{3,3'}$ 5 Hz and $J_{3',4'}$ 9 Hz, 3′-H), and 3.24 (2 H, AB system, δ_A 3.33 and δ_B 3.14, J_{AB} 18 Hz, 4′-H).

3-(2-*Ethoxycarbonylethyl*)-2,3-*dihydro*-2-*oxo*-1H-1,3aλ^5-*diazaphenalen*-3a-*ium Perchlorate* (**11**; X = ClO_4).—The cycloadduct (**8a**) (0.08 g) was added to trifluoroacetic acid (1.0 ml). The ^{1}H n.m.r. spectrum of the solution revealed formation of the salt (**11**; X = CF_3CO_2); δ(TFA) 9.36 (1 H, d, $J_{4,5}$ 6 Hz, 4-H), 9.18 (1 H, d, $J_{5,6}$ 9 Hz, 6-H), 8.25 (1 H, dd, $J_{4,5}$ 6 Hz and $J_{5,6}$ 9 Hz, 5-H), 8.10 (2 H, m, ArH), 7.88 (1 H, d, *J* 8 Hz, ArH), 6.08 (1 H, t, $J_{1',3}$ 6 Hz, 3-H), 4.27 (2 H, q, *J* 8 Hz, OCH_2CH_3), 3.0—2.6 (4 H, m, 2 × CH_2), and 1.32 (3 H, t, *J* 8 Hz, CH_2CH_3). Perchloric acid (70%; 10 drops) was added to the solution followed by ether (30 ml) to give a yellow gum. The supernatant liquid was decanted and the gum was dissolved in acetonitrile (2 ml) and the solution was filtered. Ether was then added to the filtrate to precipitate the *perchlorate* (**11**; X = ClO_4) (0.07 g, 64%) as a yellow solid, m.p. 135—138 °C (Found: C, 50.0; H, 4.6; Cl, 9.1; N, 7.5. $C_{16}H_{17}ClN_2O_7$ requires C, 49.9; H, 4.5; Cl, 9.2; N, 7.3%); $\nu_{max.}$(KBr) 3 000, 1 740, and 1 695 cm^{-1}; δ([$^2H_6$]DMSO) 10.30 (1 H, s, NH), 9.49 (1 H, d, $J_{4,5}$ 6 Hz, 4-H), 9.28 (1 H, d, $J_{5,6}$ 9 Hz, 6-H), 8.32 (1 H, dd, $J_{5,6}$ 9 Hz and $J_{4,5}$ 6 Hz, 5-H), 8.1—7.9 (2 H, m, ArH), 7.63 (1 H, d, *J* 8 Hz, ArH), 5.89 (1 H, m, 3-H), 3.88 (2 H, m, OCH_2CH_3), 2.50 (4 H, m, 2 × CH_2), and 1.07 (3 H, t, *J* 8 Hz, CH_2CH_3).

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