Synthesis and Some Properties of A New Class of Six Membered Heteroaromatic Betaines, 3*H*-Pyrido[3,2,1-*ij*][1,2,4]benzotriazin-4-ylium-3-ides

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A series of 3*H*-pyrido[3,2,1-*ij*][1,2,4]benzotriazin-4-ylium-3-ides has been synthesised by reaction of 8-acylaminoquinolines with *O*-mesitylenesulphonylhydroxylamine followed by treatment with aqueous alkali. The spectral (u.v., ^{1}H n.m.r., and ^{13}C n.m.r. spectra) and chemical properties (bromination and 1,3-dipolar cycloaddition) of the new mesomeric betaines have been investigated.

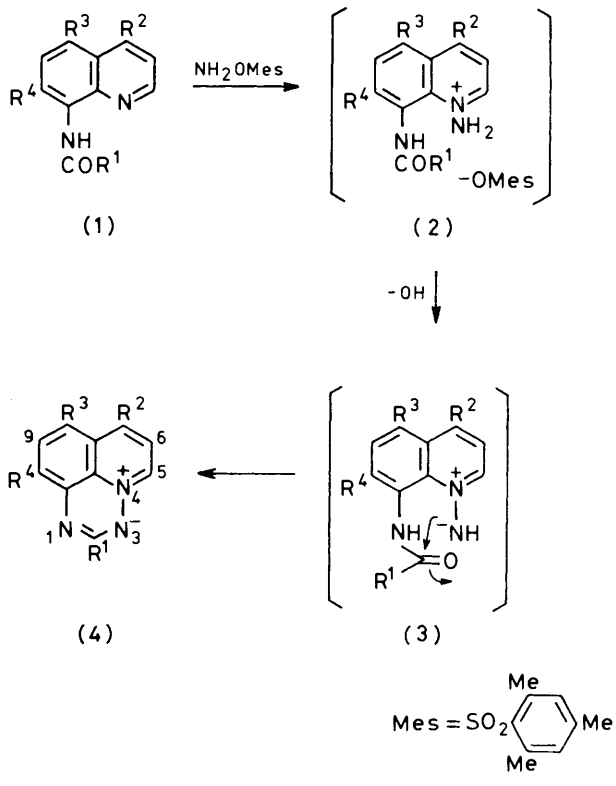
The chemistry of six-membered heteroaromatic betaines has attracted increasing attention in recent years.[1] In connection with our interest in this field,[2] we wish to describe the synthesis and some properties of a new class of tricyclic six-membered heteroaromatic betaines, 3*H*-pyrido[3,2,1-*ij*][1,2,4]-benzotriazin-4-ylium-3-ides (4).[3] Recently a synthesis of a closely related system, 3*H*-pyrido[1,2,3-*de*]quinoxalin-4-ylium-3-ides, has been reported, but they are unstable and unisolable.[4]

Synthesis.—Reaction of 8-formylaminoquinoline (1a) with an equimolar quantity of *O*-mesitylenesulphonylhydroxylamine (MSH) [5] in methylene dichloride at room temperature for 1—2 days, followed by treatment of the crude *N*-aminated product (2a) with 10% potassium hydroxide, gave the pyrido-benzotriazin-4-ylium-3-ide (4a) as deep red crystals in 44% overall yield. Similarly compounds (1b—g) gave the corresponding betaines (4b—g) in variable yields.

This transformation can be formulated as proceeding *via* the *N*-imides (3) which undergo cyclodehydration to give the products (4).

Physical Properties.—The u.v. spectrum (in ethanol) of the unsubstituted betaine (4a) exhibited the most intense band at 262 nm and several weaker absorption bands between 310 and 542 nm. The positions of its absorption maxima were fairly dependent on the solvent used. The absorption maxima above 300 nm in particular were shifted to longer wavelengths (10—20 nm) by changing the solvent from the protic solvent ethanol to aprotic solvents such as chloroform or dioxan. In an acidic solution (4a) formed a conjugated acid and the long-wavelength absorptions were shifted to shorter wavelengths and their intensity was greatly decreased (Table 1). These observations suggest that the negative charge on the imido-nitrogen atom is delocalised over the quinoline ring (see resonance structures A—F).

The complete analysis of the ^{1}H n.m.r. spectrum (90 MHz) of compound (4a) was made by comparison with those of the methyl-substituted derivatives (4b—e). In general the signals were resolved better in [^{2}H$_6$]dimethyl sulphoxide than in [^{2}H]chloroform. The chemical shifts and spin-coupling constants are recorded in Table 2. The signals of 8-H and 10-H of compound (4a) appear at relatively high magnetic fields, reflecting the high electron density at these positions (*i.e.*, a contribution from resonance forms C and D). In addition, the signal of 5-H (δ 7.42 in $CDCl_3$) of (4a) occurs at much higher field than the signal of 2-H of quinoline (δ 8.84), even though the possible decrease of the electron density at 5-H, due to the proximity to a quaternary nitrogen atom (*i.e.*, a contribution from form G), might be expected to induce a downfield shift.* This upfield shift of the signal of 5-H suggests that resonance forms E and F contribute significantly to the total structure of (4a).



a ; $R^1 = R^2 = R^3 = R^4 = H$
b ; R^1 = Me, $R^2 = R^3 = R^4 = H$
c ; R^2 = Me, $R^1 = R^3 = R^4 = H$
d ; R^3 = Me, $R^1 = R^2 = R^4 = H$
e ; R^4 = Me, $R^1 = R^2 = R^3 = H$
f ; R^4 = Br, $R^1 = R^2 = R^3 = H$
g ; R^1 = Ph, $R^2 = R^3 = R^4 = H$

Scheme 1.

The ^{13}C n.m.r. spectrum of (4a) was assigned on the basis of the following considerations: (i) the signal multiplicity in the off-resonance decoupled spectrum and the intensity of

* The signal of 5-H of (4a) appeared at δ 8.39 in CF_3CO_2H.

Table 1. U.v. spectra of compound (4a) in various solvents

Solvent	$\lambda_{max.}$ (log ε)									
EtOH	262 (4.32)	266sh (4.30)	310sh (3.41)	325 (3.76)	338 (3.94)	396 (3.46)	415 (3.52)	470 (3.42)	502 (3.40)	542 (3.09)
$CHCl_3$	266 (4.29)	271sh (4.28)	318sh (3.39)	333 (3.76)	346.5 (4.00)	409 (3.47)	425 (3.55)	483 (3.45)	514 (3.47)	552 (3.17)
Dioxan	265sh (4.29)	270 (4.30)	320sh (3.40)	335 (3.83)	350 (4.12)	414 (3.52)	430 (3.57)	486 (3.44)	516 (3.44)	557 (3.12)
EtOH + 1 drop of 1M-HCl	259 (4.34)	265 (4.30)	285 (3.36)	300 (3.54)	313 (3.64)	350 (3.20)	366 (3.27)		429 (3.33)	

Table 2. ^{1}H N.m.r. spectral data for the 3*H*-pyrido[3,2,1-*ij*][1,2,4]benzotriazin-4-ylium-3-ides (4) [a]

Compd.	2-H	5-H	6-H	7-H	8-H	9-H	10-H	Me	$J_{5,6}$	$J_{5,7}$	$J_{6,7}$	$J_{8,9}$	$J_{8,10}$	$J_{9,10}$
(4a)	7.14 (s)	7.65 (dd)	7.00 (dd)	7.46 (dd)	6.73 (dd)	7.11 (t)	6.38 (dd)		6	1	9	8	1	8
(4a) [b]	7.26 (s)	7.42 (dd)	6.81 (dd)	7.26 (dd)	6.70 (dd)	7.16 (t)	6.62 (dd)		6	1	9	8	1	8
(4b)		7.68 (dd)	7.00 (dd)	7.46 (bd)	6.75 (bd)	7.12 (t)	6.39 (dd)	1.82 (s)	6	1	9	8	1	8
(4c)	7.19 (s)	7.71 (d)	7.00 (bd)		6.68 (dd)	7.21 (t)	6.47 (dd)	2.23 (s)	6			8	1	8
(4d)	7.16 (s)	7.71 (dd)	6.9—7.2 [c]	7.40 (dd)		7.04 (d)	6.38 (d)	2.13 (s)	6	1	9			8
(4d) [b]	7.25 (s)	7.46 (dd)	6.83 (dd)	7.24 (dd)		7.02 (d)	6.57 (d)	2.16 (s)	6	1	9			8
(4e)	7.22 (s)	7.62 (dd)	6.90 (dd)	7.44 (dd)	6.71 (d)	7.09 (d)		2.01 (s)	6	1	9	8		
(4f)	7.36 (s)	7.89 (dd)	7.14 (dd)	7.64 (dd)	6.78 (d)	7.43 (d)			6	1	9	9		
(6)	7.33 (s)	7.86 (dd)	7.25 (dd)	7.55 (dd)		7.48 (d)	6.43 (d)		6	1	9			8
(7) [b]	7.62 (s)	7.73 (dd)	7.10 (dd)	7.68 (dd)		7.79 (s)			6	1	9			

[a] Chemical shifts in p.p.m. from internal Me_4Si; unless otherwise indicated, solvent is $(CD_3)_2SO$; coupling constants are given in Hz. [b] Solvent $CDCl_3$. [c] Overlapped with other proton signals.

Table 3. ^{13}C N.m.r. spectral data for the 3*H*-pyrido[3,2,1-*ij*][1,2,4]benzotriazin-4-ylium-3-ides (4) [a]

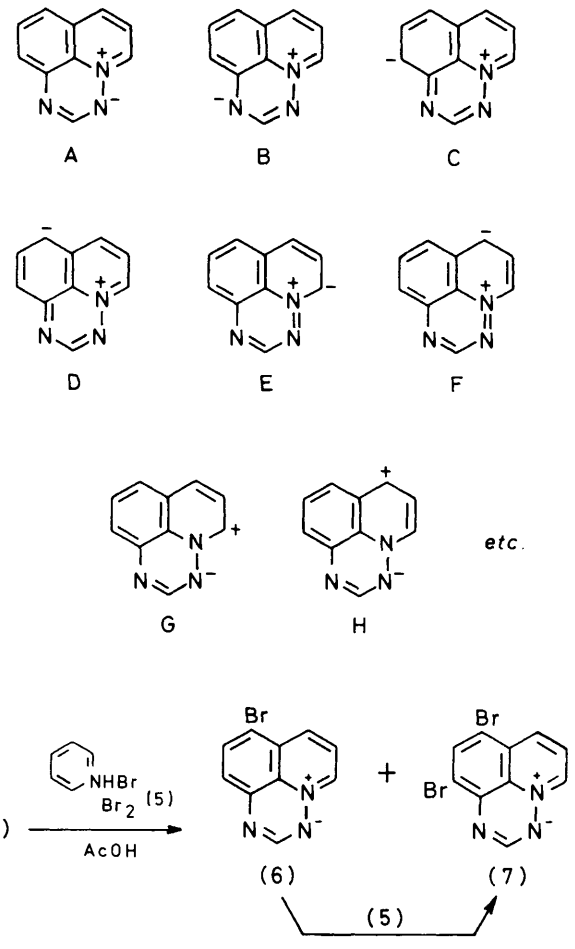
Compd.	C-2	C-5	C-6	C-7	C-7a	C-8	C-9	C-10	C-10a	C-10b	Me
(4a)	158.27(d)	125.70(d)	132.08(d)	130.61(d)	132.88(s)	114.97(d)	122.10(d)	115.39(d)	145.92(s)	135.10(s)	
(4b)	166.36(s)	125.13(d)	132.17(d)	130.04(d)	132.68(s)	114.28(d)	122.04(d)	114.76(d)	146.55(s)	132.68(s)	23.07(q)
(4c)	157.70(d)	125.31(d)	131.93(d)	139.93(s)	131.69(s)	111.82(d)	121.89(d)	115.51(d)	146.13(s)	133.42(s)	18.96(q)
(4d)	157.58(d)	125.70(d)	132.47(d)	127.58(d)	131.12(s)	121.80(s)	122.01(d)	114.76(d)	143.53(s)	135.10(s)	18.15(q)
(4e)	158.03(d)	125.60(d)	133.69(d)	130.85(d)	131.06(s)	114.04(d)	120.99(d)	123.75(s)	142.96(s)	134.50(s)	16.83(q)

[a] Chemical shifts in p.p.m. from internal Me_4Si; solvent $CDCl_3$; multiplicity in the off-resonance decoupled spectrum indicated in parentheses.

the decoupled spectrum which allow the tertiary and quaternary carbons to be easily distinguished, and (ii) the shifts caused by the introduction of a methyl group at the appropriate position. The results are summarised in Table 3. Among the three quaternary carbons, C-10b is the lowest in intensity as might be expected for a carbon remote from protons. In the ^{13}C n.m.r. spectra of the methyl derivatives (4b—e) the *ipso*-position is shifted to lower field (6.3—9.3 p.p.m.) and both the *ortho*- and *para*-positions are shifted to higher field (0.1—3.0 p.p.m. for the *ortho* and 1.8—2.4 p.p.m. for the *para*) relative to the corresponding signals of (4a), while the *meta*-position is not much different with the exception of C-10b in the 7-methyl derivative (4c) (downfield shift of 1.68 p.p.m.). The *peri*-position [C-8 in (4c) and C-7 in (4d)] is shifted *ca.* 3.0 p.p.m. to higher field because of steric effects.[6] It is noteworthy that the signals of C-5, C-7, C-8, C-10, and C-10b of compound (4a) occur at higher field than those of quinoline itself,[7] reflecting high electron density at these positions (see resonance structures A—F). Among them the structures C and D appear to be particularly important contributors to the resonance of (4a) because the signals of C-8 and C-10 occur at higher field than the others.

Chemical Properties.—We were interested to see how the structural features are reflected by the chemical properties of the betaines (4), and we consequently examined the reactivity of compound (4a) toward nucleophiles, electrophiles, and 1,3-dipolarophiles. We found that it is inert to nucleophiles such as hydroxide ion or cyanide ion under various conditions (*e.g.*, refluxing in alcoholic potassium hydroxide or methanolic potassium cyanide for 10 h). However, it reacted with a brominating reagent and dimethyl acetylenedicarboxylate (DMAD).

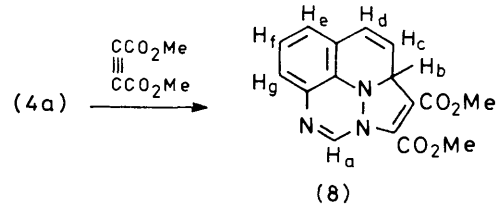
Treatment of the betaine (4a) with pyridinium hydrobromide perbromide (5) in acetic acid at room temperature



Scheme 2.

gave the monobromo-derivative (6) and the dibromo-derivative (7), the relative yields of which depended upon the amounts of (5) used. Thus, when 1 mol equiv. of (5) was used, the betaine (4a) gave the bromo-compounds (6) and (7) in 54 and 17% yields, respectively, in addition to unchanged (4a) (25%), while use of 2 mol equiv. of (5) afforded (6) and (7) in 6 and 89% yields, respectively. Both the compounds are deep red crystals; their structures are supported by satisfactory elemental analyses and by spectral data. The u.v. spectra (in ethanol) of the bromo-compounds (6) and (7) were similar to that of the starting betaine (4a). In the ^{1}H n.m.r. spectrum [$(CD_3)_2SO$] of (6) the signal assignable to 8-H disappeared and the 9-H and 10-H signals appeared as an AB quartet (J 8 Hz) at δ 7.48 and 6.43, respectively. The final confirmation of structure (6) was given by a synthesis of the isomeric 10-bromo-derivative (4f) from 7-bromo-8-formylaminoquinoline (1f); ^{1}H n.m.r. spectrum of compound (4f) is different to that of (6). The ^{1}H n.m.r. spectrum ($CDCl_3$) of (7) revealed the disappearance of both the 8-H and 10-H signals and the appearance of a singlet due to 9-H at δ 7.79. Further evidence for structure (7) was obtained when it was produced by bromination of the monobromo-compound (6).

Although the betaine (4a) did not react with olefinic dipolarophiles (*e.g.* *N*-phenylmaleimide and dimethyl fumarate), it reacted with an excess of DMAD in refluxing methanol to give a 1 : 1 adduct (8) in 47% yield. The structure of (8) was demonstrated by its ^{1}H n.m.r. spectrum ($CDCl_3$) which revealed the presence of two methoxy-singlets at δ 3.55



Scheme 3.

and 4.05, a doublet (1 H, J 10 Hz, H_d) at δ 6.93, a doublet (1 H, J 4 Hz, H_b) at δ 6.38, a doublet of doublets (1 H, J 10 and 4 Hz, H_c) at δ 6.05, and a singlet (1 H, H_a) at δ 6.85. However, the signals due to H_e, H_f, and H_g gave complex multiplets probably because the chemical shifts of H_e and H_f are very close to each other. In fact, measurement of the ^{1}H n.m.r. spectrum in $(CD_3)_2SO$ removed the complexity to give an expected doublet with small splitting (1 H, J 7 and 2 Hz, H_e) at δ 7.62, a doublet with small splitting (1 H, J 7 and 2 Hz, H_g) at δ 7.35, and a triplet (1 H, J 7 Hz, H_f) at δ 7.18. The behaviour of (4a) toward DMAD parallels that of phenanthridinio-*N*-benzoylamidate.[8]

Finally, in view of the high electron density at C-5, it was of interest to see if compound (4a) would undergo hydrogen–deuterium exchange. A solution of (4a) in [$^2H_6$]dimethyl sulphoxide in the presence of deuterium oxide was stirred at 34 °C * for 2 days, but the starting material was recovered without deuterium exchange.

Experimental

^{1}H N.m.r. spectra were determined with a Hitachi R-22 spectrometer (tetramethylsilane as internal standard) and ^{13}C n.m.r. spectra were obtained by Fourier transformation carried out on a Hitachi R-900 spectrometer at 22.6 MHz. I.r. spectra were recorded with a Hitachi EPI-G2 spectrophotometer, and u.v. spectra with a Hitachi 124 spectrophotometer. Mass spectra were obtained with a JMS-D-300 instrument with a direct inlet system operating at 70 eV. 8-Formylamino-(1a),[10] 8-acetylamino-(1b),[10] and 8-benzoylamino-quinolines (1g),[10] and 8-nitrolepidine [11] were prepared according to the reported procedure.

5- *and* 7-*Methyl*-8-*nitroquinolines*.—Essentially the procedure of Long and Schofield [12] was employed for nitration. To an ice-cooled solution of a mixture of 5- and 7-methylquinolines (9.0 g) (available from Tokyo Kasei as a mixture in a ratio of 27.5 : 72.5) in concentrated sulphuric acid (23 ml) was added dropwise fuming nitric acid (3.6 ml). After being stirred for 5 min at room temperature, the reaction mixture was poured into water and the white precipitate was collected, washed with water, and dried to give 7-methyl-8-nitroquinoline (6.5 g, 74%), m.p. 188—189 °C (from acetone) (lit.,[12] m.p. 183—184 °C). The mother liquor was made alkaline with concentrated ammonia and the precipitate was collected, washed with water and dried. The crystals were purified on a short silica-gel column, eluting with benzene–ethyl acetate (1 : 1), followed by recrystallization from ethanol to give *5-methyl-8-nitroquinoline* (2.2 g, 69%), m.p. 138—139 °C (Found: C, 63.9; H, 4.1; N, 14.9. $C_{10}H_8N_2O_2$ requires C, 63.8; H, 4.3; N, 14.9%).

* Under these conditions pyridinio-*N*-arylimides and 1-alkylbenzimidazolio-3-acylamidates undergo deuterium exchange.[9]

General Procedure for the 8-Formylaminoquinolines (1c—f).—A solution of an 8-nitroquinoline (30 mmol) in ethanol (200 ml) was hydrogenated over 5% palladium–charcoal (500 mg) at 2 atm and room temperature for 3 h. The mixture was filtered and the filtrate was concentrated to give a crude crystalline 8-aminoquinoline, which was dissolved in 99% formic acid (13 ml). The mixture was refluxed for 5—24 h and neutralised with dilute ammonia. The precipitated crystals were collected, washed with water, dried, and recrystallised. *8-Formylaminolepidine* (1c) (74%) had m.p. 198—198.5 °C (from benzene) (Found: C, 71.2; H, 5.3; N, 15.2. $C_{11}H_{10}N_2O$ requires C, 70.95; H, 5.4; N, 15.05%); *8-formylamino-5-methylquinoline* (1d) (72%) had m.p. 180—181 °C (from benzene) (Found: C, 71.2; H, 5.3; N, 15.0. $C_{11}H_{10}N_2O$ requires C, 70.95; H, 5.4; N, 15.05%); *8-formylamino-7-methylquinoline* (1e) (64%) had m.p. 191—191.5 °C (from benzene) (Found: C; 70.9; H, 5.2; N, 15.0. $C_{11}H_{10}N_2O$ requires C, 70.95; H, 5.4; N, 15.05%); *7-bromo-8-formylaminoquinoline* (1f) (69%) was prepared by formylation of 8-amino-7-bromoquinoline [13] in a similar manner to that described above, m.p. 178—179 °C (from benzene) (Found: C, 48.0; H, 2.7; N, 11.3. $C_{10}H_7BrN_2O$ requires C, 47.8; H, 2.8; N, 11.2%).

General Procedure for 3H-Pyrido[3,2,1-ij][1,2,4]*benzotriazin-4-ylium-3-ides* (4a—g).—A solution of the 8-acylaminoquinoline (1a—g) (2 mmol) and MSH (2 mmol) in methylene dichloride (10 ml) was stirred at room temperature for 1—2 days. The reaction mixture was concentrated and washed with ether. The insoluble residue was treated with cold 10% aqueous potassium hydroxide (5 ml) for 5 min to give a deep red solution. The mixture was extracted with chloroform and the extract was washed with water, dried (Na_2SO_4), and concentrated. The residual solid was recrystallised. *3H-Pyrido*[3,2,1-ij][1,2,4]*benzotriazin-4-ylium-3-ide* (4a) (44%) formed red crystals, m.p. 155—158 °C [from CH_2Cl_2–light petroleum (b.p. 30–60 °C)] (Found: C, 69.4; H, 4.2; N, 24.8%; M^+ 169. $C_{10}H_7N_3 \cdot 1/5H_2O$ requires C, 69.5; H, 4.3; N, 24.3%; *M* 169). It formed the picrate, m.p. 238—240 °C (from ethanol) (Found: C, 48.2; H, 2.7; N, 20.7. $C_{16}H_{10}N_6O_7$ requires C, 48.25; H, 2.5; N, 21.1%); the *2-methyl derivative* (4b) (58%) formed red crystals, m.p. 173—174 °C (decomp.) (from acetone) (Found: C, 72.2; H, 4.8; N, 22.6%; M^+ 183. $C_{11}H_9N_3$ requires C, 72.1; H, 4.95; N, 22.9%; *M* 183); $\lambda_{max.}$ (EtOH) 262, 265, 310sh, 324, 337, 369, 414, 468, 502, and 534 nm (log ε 4.17, 4.20, 3.19, 3.56, 3.77, 3.26, 3.35, 3.29, 3.27, and 3.00); the *7-methyl derivative* (4c) (41%) formed dark yellow crystals, m.p. 162—163 °C (decomp.) (from acetone) (Found: C, 71.5; H, 4.8; N, 22.5%; M^+ 183. $C_{11}H_9N_3$ requires C, 72.1; H, 4.95; N, 22.9%; *M* 183); $\lambda_{max.}$ (EtOH) 261, 314sh, 330, 343, 422, 460, 484, and 520 nm (log ε 4.49, 3.53, 3.92, 4.11, 3.79, 3.76, 3.74, and 3.45); the *8-methyl derivative* (4d) (37%) formed deep red crystals, m.p. 166—167 °C (decomp.) (from acetone) (Found: C, 70.6; H, 4.75; N, 22.0%; M^+ 183. $C_{11}H_9N_3 \cdot 1/5H_2O$ requires C, 70.7; H, 5.1; N, 22.5%; *M* 183); $\lambda_{max.}$ (EtOH) 265, 271, 314sh, 330, 344, 406, 422, 487, 520, and 560 nm (log ε 4.45, 4.45, 3.58, 3.91, 4.11, 3.56, 3.61, 3.54, 3.52, and 3.20). It formed the picrate, m.p. 245—246 °C (decomp.) (from acetone) (Found: C, 49.4; H, 2.9; N, 20.5. $C_{17}H_{12}N_6O_7$ requires C, 49.5; H, 2.9; N, 20.4%); the *10-methyl derivative* (4e) (59%) formed deep red crystals, m.p. 131—133 °C (from acetone) (Found: C, 72.1; H, 4.8; N, 22.9%; M^+ 183. $C_{11}H_9N_3$ requires C, 72.1; H, 4.95; N, 22.9%; *M* 183); $\lambda_{max.}$ (EtOH) 268, 273, 314sh, 328, 342, 405, 421, 487, 518, and 560 nm (log ε 4.49, 4.49, 3.52, 3.87, 4.09, 3.56, 3.61, 3.52, 3.46, and 3.11); the *10-bromo-derivative* (4f) (28%) formed red crystals, m.p. 190—191 °C (decomp.) (from acetone) (Found: C, 47.8; H, 2.35; N, 16.4%; M^+ 247/249. $C_{10}H_6BrN_3$ requires C, 48.4; H, 2.4; N, 16.9%; *M* 247/249); $\lambda_{max.}$ (EtOH) 273, 278, 317sh, 332, 345, 406, 426, 475, 506, and 546 nm (log ε 4.36, 4.37, 3.38, 3.79, 4.03, 3.44, 3.52, 3.35, 3.31, and 2.92); the *2-phenyl derivative* (4g) (64%) formed red crystals, m.p. 148—149 °C (from acetone) (Found: C, 78.2; H, 4.5; N, 17.2%; M^+ 245. $C_{16}H_{11}N_3$ requires C, 78.35; H, 4.5; N, 17.1%; *M* 245); $\lambda_{max.}$ (EtOH) 246, 264, 284sh, 342sh, 355, 406, 425, 480, and 515 nm (log ε 4.29, 4.34, 4.13, 3.71, 3.46, 3.56, 3.63, 3.38, and 3.34); δ($CDCl_3$) 6.55—7.6 (9 H, m, aromatic protons) and 8.0—8.2 (2 H, m, aromatic protons).

Bromination of the Betaine (4a).—(a) A mixture of (4a) (84.5 mg, 0.5 mmol) and pyridinium hydrobromide perbromide (5) (160 mg, 0.5 mmol) in acetic acid (10 ml) was stirred at room temperature for 1 h. The reaction mixture was neutralised with saturated aqueous sodium hydrogen carbonate and extracted with chloroform. The extract was washed with water, dried (Na_2SO_4), and concentrated. The residue was chromatographed on silica gel. Elution with ethyl acetate gave *8,10-dibromo-3H-pyrido*[3,2,1-ij][1,2,4]*benzotriazin-4-ylium-3-ide* (7) (27 mg, 17%), *8-bromo-3H-pyrido*[3,2,1-ij][1,2,4]*benzotriazin-4-ylium-3-ide* (6) (67 mg, 54%), and unchanged starting material (1a) (21 mg, 25%) in that order. The dibromide (7) formed red crystals, m.p. 244—245 °C (decomp.) (from chloroform) (Found: C, 36.65; H, 1.4; N, 13.1%; M^+ 325/327/329. $C_{10}H_5Br_2N_3$ requires C, 36.7; H, 1.5; N, 12.85%; *M* 325/327/329); $\lambda_{max.}$ (EtOH) 266, 273, 320sh, 337, 351, 420, 438, 480, 513, and 551 nm (exact intensities were not determined because of extremely low solubility in ethanol. The monobromide (6) formed red crystals, m.p. 189—190 °C (decomp.) (from acetone) (Found: C, 48.2; H, 2.3; N, 16.6%; M^+ 247/249. $C_{10}H_6BrN_3$ requires C, 48.4; H, 2.4; N, 16.9%; *M* 247/249); $\lambda_{max.}$ (EtOH) 260, 265, 318sh, 332, 347, 414, 429, 480, 510, and 552 nm (log ε 4.30, 4.27, 3.64, 3.81, 4.08, 3.51, 3.56, 3.42, 3.40, and 3.04).

(b) The betaine (4a) (84.5 mg, 0.5 mmol) was brominated by compound (5) (320 mg, 1.0 mmol) in acetic acid (10 ml) and work-up gave products (7) (145 mg, 89%) and (6) (7 mg, 6%).

Bromination of the Monobromo-derivative (6).—A mixture of (6) (50 mg, 0.2 mmol) and compound (5) (96 mg, 0.3 mmol) in acetic acid (5 ml) was stirred at room temperature for 1 h. Work-up gave the dibromo-product (7) (60 mg, 91%).

Dimethyl 9aH-2a,4,9b-Triazacyclopenta[cd]*phenalene-1,2-dicarboxylate* (8).—A solution of compound (4a) (84.5 mg, 0.5 mmol) and DMAD (156 mg, 1.1 mmol) in anhydrous methanol (10 ml) was refluxed for 1 h under nitrogen. The reaction mixture was concentrated and the residue was chromatographed on alumina using chloroform as solvent to give the *triazacyclopentaphenalene* (8) (73 mg, 47%), m.p. >290 °C (from acetone) (Found: C, 61.5; H, 4.2; N, 13.5%; M^+ 311. $C_{16}H_{13}N_3O_4$ requires C, 61.7; H, 4.2; N, 13.5%; *M* 311); $\nu_{max.}$ ($CDCl_3$) 1 740 and 1 620 cm^{-1}; $\lambda_{max.}$ (EtOH) 223, 245, 249, 271, 279sh, and 335 nm (log ε 4.47, 4.41, 4.42, 4.20, 4.15, and 4.03); δ($CDCl_3$) 3.55, 4.05 (3 H, each, s each, 2 × OCH_3), 6.05 (1 H, dd, *J* 10 and 4 Hz, H_c), 6.38 (1 H, d, *J* 4 Hz, H_b), 6.85 (1 H, s, H_a), 6.93 (1 H, d, *J* 10 Hz, H_d), 7.05—7.25 (2 H, m, $H_{e,f}$), and 7.65 (1 H, m, H_g).

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