2,3-Dihydro-1*H*-benzo[*c*]pyrazolo[1,2-*a*]cinnolines and Derived Radical Cations

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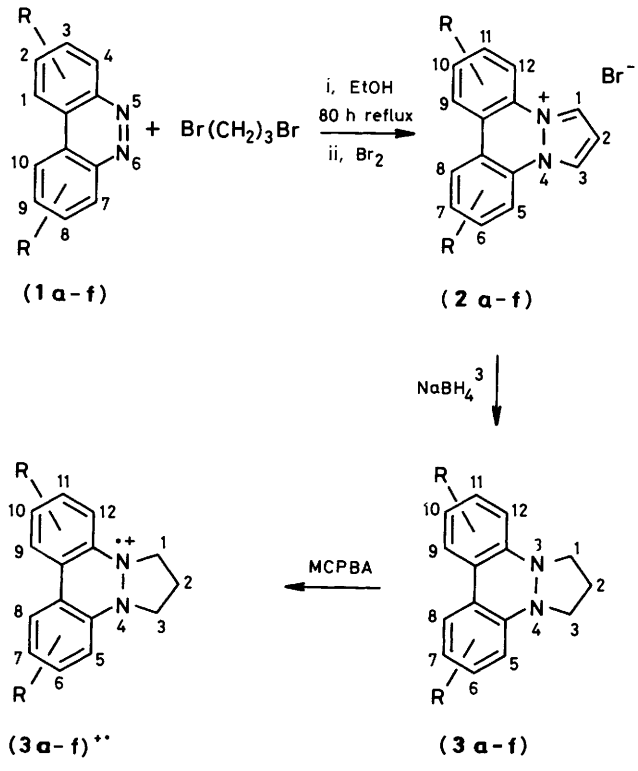
A series of 2,3-dihydro-1*H*-benzo[*c*]pyrazolo[1,2-*a*]cinnolines (**3a–f**) has been prepared *via* alkylation of the benzo[*c*]cinnolines (**1a–f**) with 1,3-dibromopropane and subsequent reduction of the formed benzo[*c*]pyrazolo[1,2-*a*]cinnolinium bromides (**2a–f**) with sodium borohydride. The dark-red intermediate in the synthesis, reported to have a 2,3-dihydrobenzo[*c*]pyrazolo[1,2-*a*]cinnolinium structure (**6a**), is shown to be (**2a**) contaminated with some radical cation (**3a**)$^{+\bullet}$. The radical cations (**3a–f**)$^{+\bullet}$, readily generated in the oxidation of (**3a–f**), have been studied using e.s.r. and ENDOR spectroscopy. Relative signs of the ^{1}H-coupling constants have been obtained by general triple resonance. This has led to full assignments in all cases.

5,6-Diphenyl-5,6-dihydrobenzo[*c*]cinnoline shows an unexpected two-electron transfer in the cyclovoltammetric oxidation.[1] This unusual electrochemical behaviour seems to be related to the conformation of the cyclic hydrazine in which the diaxial (*aa*) conformer is sterically favoured. It was of interest to extend these studies to 2,3-dihydro-1*H*-benzo[*c*]pyrazolo-[1,2-*a*]cinnolines (**3a–f**) in which both nitrogens are linked by a 1,3-trimethylene bridge to give an additional five-membered ring. Like similar bicyclic hydrazines, such as hexahydro-1*H*-pyrazolo[1,2-*a*]pyridazine,[2] (**3a–f**) can exist in a diequatorial (*ee*) conformation. We comment here upon the synthesis of (**3a–f**) and report on the generation of the corresponding radical cations which were studied using e.s.r., ENDOR, and triple resonance spectroscopic techniques.

Results and Discussion

2,3-Dihydro-1*H*-benzo[*c*]pyrazolo[1,2-*a*]cinnoline (**3a**) has already been synthesized by Farnum *et al.*[3] The reaction of benzo[*c*]cinnoline (**1a**) with 1,3-dibromopropane in boiling ethanol was reported to yield the immonium bromide (**6a**) (*ca.* 70% yield) as dark-red crystals. The structural assignment was based on the ionic structure of the red product and on the absence of NH absorption from 4 000–2 500 cm^{-1}. Oxidation of the red product with chloranil or *N*-bromosuccinimide (NBS) afforded the colourless benzo[*c*]pyrazolo[1,2-*a*]cinnolinium bromide (**2a**) and hydrogenation in the presence of Raney nickel gave (**3a**). N.m.r. spectroscopic data for the red product as well as for (**3a**) were not reported, although (**2a**) was characterised by ^{1}H n.m.r. spectroscopy. The ^{1}H n.m.r. spectrum of the red product in $(CD_3)_2SO$ shows broad signals with shifts similar to those for (**2a**). The observed line broadening might be caused by the presence of a paramagnetic impurity or by the main component of the red product. We therefore investigated the red crystals by e.s.r. spectroscopy. As expected they exhibited a very strong one-line e.s.r. signal, linewidth 8.2 G, g = 2.004. In ethanolic solution a highly resolved complex e.s.r. spectrum was observed: a(N) = 9.06 (2 N), a(H) = 10.05 (4 H), a(H) = 2.65 (2 H), a(H) = 2.05 (2 H), a(H) = 0.55 (4 H), and a(H) = 0.20 G (2 H), g = 2.0031; the assignment is given in the e.s.r. discussion below and in Table 1. This e.s.r. spectrum identifies the paramagnetic species as the radical cation (**3a**)$^{+\bullet}$. Additional information on the composition of the red product was obtained by the comparison of the u.v.–vis. spectra of the red product with compounds (**2a**), (**3a**), and (**3a**)$^{+\bullet}$ (see Table 2). All short-wave absorption bands, from 200–340 nm, of the red



(1) **a**; R = H
b; R = 1,3,8,10-$^2H_4$
c; R = 3,8-$(CH_3)_2$
d; R = 2,9-$(CH_3)_2$
e; R = 1,10-$(CH_3)_2$
f; R = 3,8-$(OCH_3)_2$

(2), (3) **a**; R = H
b; R = 6,8,9,11-$^2H_4$
c; R = 6,11-$(CH_3)_2$
d; R = 7,10-$(CH_3)_2$
e; R = 8,9-$(CH_3)_2$
f; R = 6,11-$(OCH_3)_2$

Scheme 1.

product agree well with those of (**2a**), whereas the weak long-wave absorption bands, 370, 482, 528, and 635 nm, correspond to those of (**3a**)$^{+\bullet}$. These results suggest that the red product consists mainly of (**2a**) (*ca.* 90%) and a small amount of (**3a**)$^{+\bullet}$. Additional impurities, such as (**6a**), may by present but were not identified. Our analysis is confirmed by the *X*-ray structure determination of the red crystals which clearly shows a benzo[*c*]pyrazolo[1,2-*a*]cinnolinium bromide structure (**2a**)

Table 1. Isotropic hyperfine coupling constants and *g* values of the radical cations (**3a–f**)$^{+\bullet}$ in toluene–trifluoroacetic acid (9:1); e.s.r. at 298, ENDOR at 260 K.

		$a(N^{4,13})$/G	$a(H^{1,1,3,3})$/G	$a(H^{2,2})$/G	$a(H^{5,12})$/G	$a(H^{6,11})$/G	$a(H^{7,10})$/G	$a(H^{8,9})$/G	*g* Value
(**3a**)$^{+\bullet}$	e.s.r.	8.94	10.05	0.56	2.01		2.64	0.56	2.0031
	ENDOR		+10.09	−0.55	−2.02	+0.16	−2.64	+0.55	
a	e.s.r.	9.06	10.05	0.55	2.05	0.20	2.65	0.55	2.0031
(**3b**)$^{+\bullet}$	e.s.r.	8.97	10.04	0.57	2.00		2.61		
	ENDOR		+10.11	−0.58	−2.01		−2.65		
(**3c**)$^{+\bullet}$	e.s.r.	8.76	9.79	0.52	1.77		2.76	0.52	2.0031
	ENDOR	8.71	+9.83	−0.53	−1.78	−0.08[b]	−2.76	+0.53	
(**3d**)$^{+\bullet}$	e.s.r.	8.93	9.85	0.59	1.98		2.91[b]	0.59	2.0031
	ENDOR		+9.92	−0.58	−1.98		+2.92[b]	+0.58	
(**3e**)$^{+\bullet}$	e.s.r.	8.60	10.00[c] 9.16[c]	*d*	2.21	0.43	2.80	0.76[b]	2.0030
	ENDOR	8.56	+10.00[c] +9.16[c]	*d*	−2.21	+0.43	−2.80	−0.76[b]	
(**3f**)$^{+\bullet}$	e.s.r.	8.2	9.3		1.2		3.0		2.0031
	ENDOR		9.27	0.40	1.22		3.01	0.40	

[a] Red product in EtOH. [b] $a(H^{CH_3})$, 6 H. [c] $a(H^{1,3})$, 2 H. [d] These protons may have *a*(H) *ca.* 0.76 G; simulation of the e.s.r. spectrum gave no clear evidence.

Table 2. U.v.–vis. spectra: $\lambda_{max.}$ of (**2a**), (**3a**), the red product and (**6a**)[3] in EtOH, and of (**3a**)$^{+\bullet}$ in toluene–trifluoroacetic acid (9:1).

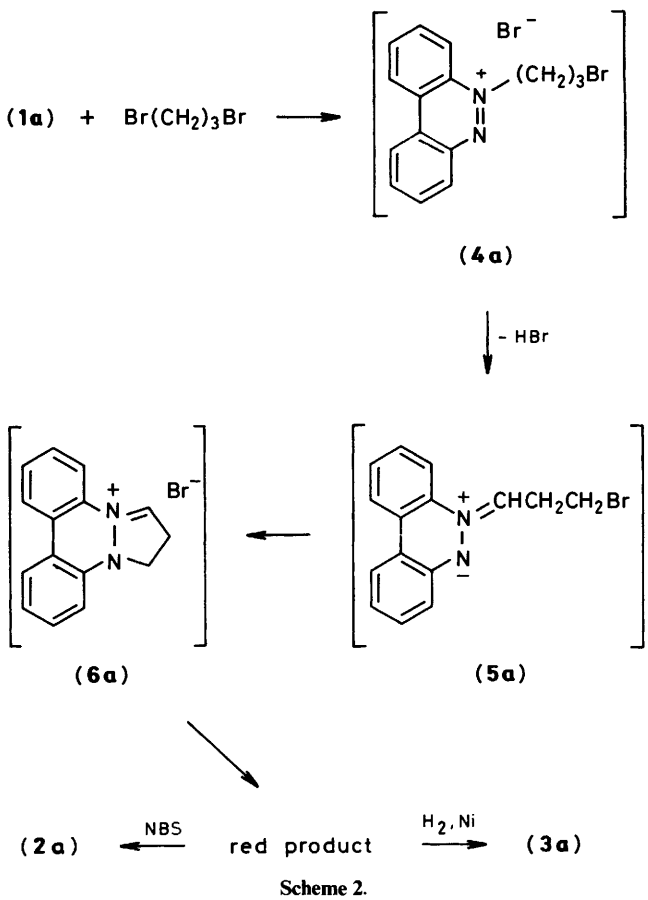
(**2a**)		(**3a**)		(**3a**)$^{+\bullet}$[a]		Red product		(**6a**)[3]	
λ/nm	log ε	λ/nm	log ε	λ/nm	log *E*	λ/nm	log ε	λ/nm	log ε
217	4.15					217	4.15	222	4.08
258	4.72	250	4.60			258	4.67	259	4.69
293	3.84					293	3.77	295	3.76
318	3.72	318	3.28			318	3.68	320	3.70
333	3.71					332	3.69	333	3.72
				364	1.61	370	3.27	373	2.87
		383	3.24	(382)[b]	(1.90)[b]	389	3.55	391	3.11
						455	3.03		
				488	1.28	482	3.05	487	2.53
				533	1.34	528	2.92	528	2.53
				630	0.20	635	1.76		

[a] (**3a**)$^{+\bullet}$ generated as in e.s.r. sample, qualitative data. [b] This band seemingly belongs to (**3a**).

with a refinement of $R = 0.064$.* Several recrystallisations of the red product did not significantly affect its composition.

The formation of the red product proceeds, apparently, *via* the cinnolinium bromide (**4a**) from which the ylide (**5a**) is formed by HBr elimination.[4] Subsequent intramolecular alkylation leads to the immonium bromide (**6a**) which is oxidised to (**2a**) under the experimental conditions. The accompanying (**3a**)$^{+\bullet}$ in the red product results apparently from disproportionation of (**6a**).

In the preparation of (**2a–f**) the oxidation was completed by the addition of bromine to the red product dissolved in methanol until the colour faded. Reduction of (**2a–f**) with sodium borohydride[3] afforded the bicyclic hydrazines (**3a–f**) which are sensitive to oxidation and readily generate the corresponding radical cations. Since traces of radical cations cause severe line broadening, the n.m.r. spectra of (**3a–f**) were usually measured in the presence of potassium t-butoxide to prevent oxidation of the hydrazines. In the case of (**3a**) the $AA'X_2X'_2$ signal pattern of the five-membered ring protons was analysed by simulation. Variable temperature ^1H and ^{13}C



Scheme 2.

studies of (**3a**) and (**3f**) revealed no unusual changes between 345 and 235 K. The n.m.r. spectra indicate a twofold symmetry axis for (**3a–f**) in agreement with an *ee* conformation, but there is the possibility that even at 235 K a rapidly equilibrating mixture of *ae* and *ee* conformers is observed.

For the e.s.r. and ENDOR measurements, the radical cations (**3a–f**)$^{+\bullet}$ were generated in toluene–trifluoroacetic acid (9:1) by oxidation of (**3a–f**) with 3-chloroperbenzoic acid (MCPBA). Results are collected in Table 1. Figures 1 and 2 show e.s.r. spectra of (**3b**)$^{+\bullet}$ and (**3c**)$^{+\bullet}$, respectively. Most of the e.s.r. spectra are well resolved and well simulated with the values

* C. Krieger: Monoclinic, $C2/c$, $Z = 4$, $D_x = 1.567$ g cm^{-3}; $a = 9.813(2)$, $b = 17.956(3)$, $c = 7.218(2)$ Å; $\beta = 94.27(2)°$. 1 606 unique reflections measured ($\sin\theta/\lambda \leq 0.62$ Å^{-1}); final conventional $R = 0.064$ for 919 observed reflections.

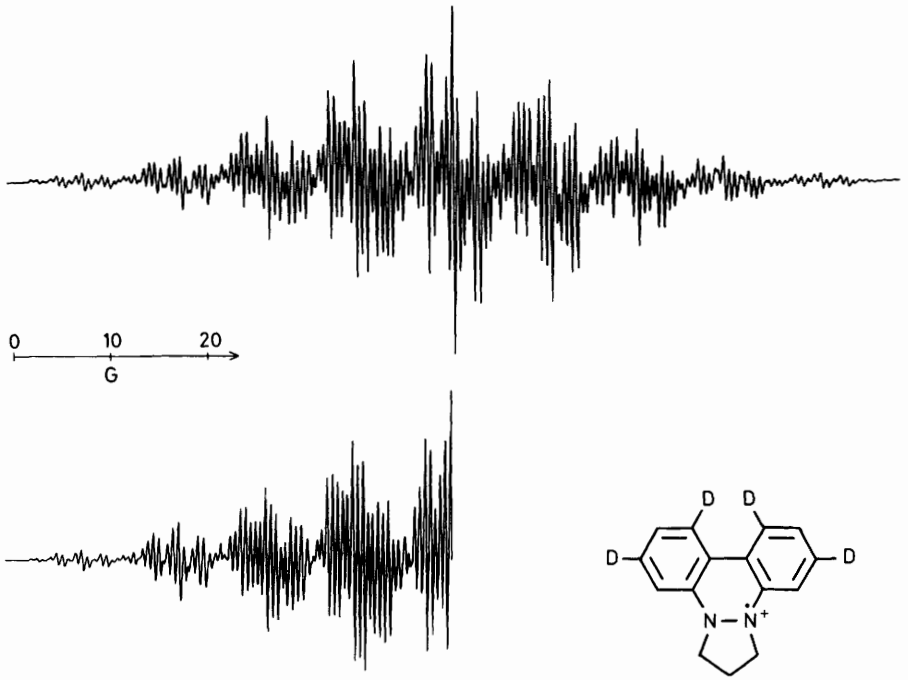


Figure 1. E.s.r. spectrum of $(\mathbf{3b})^{+\bullet}$ in toluene–trifluoroacetic acid (9:1) at 298 K together with a simulation using the data in Table 1.

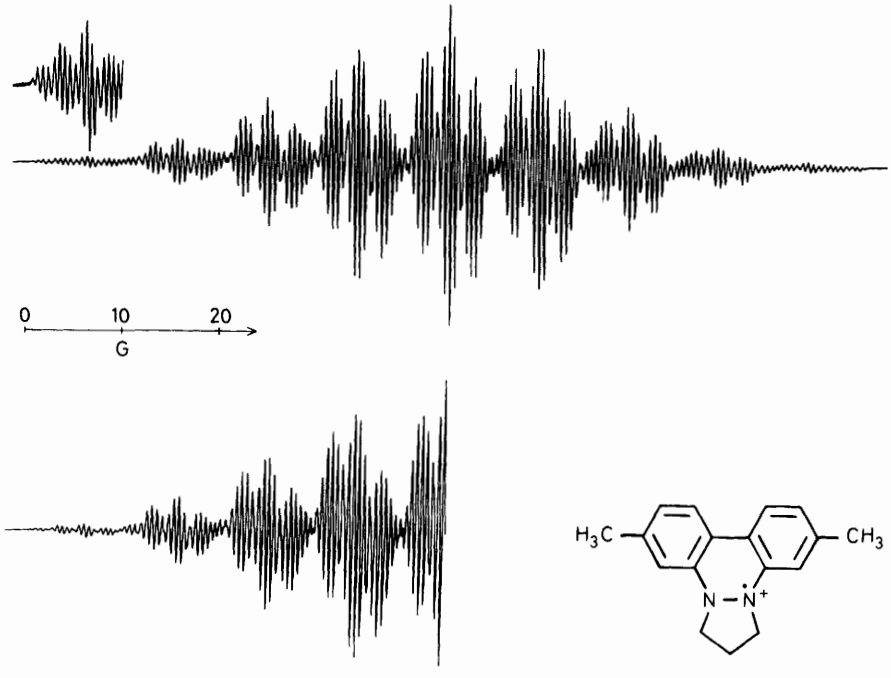


Figure 2. E.s.r. spectrum of $(\mathbf{3c})^{+\bullet}$ in toluene–trifluoroacetic acid (9:1) at 298 K together with a simulation using the data in Table 1.

given in Table 1. Their analysis is substantially facilitated by the ENDOR studies. In the ENDOR spectra [see, for example, Figure 3(*a*)] all ^{1}H coupling constants were clearly detected and, in addition, by performing general triple experiments[5] [Figure 3(*b*)] relative signs were determined. ^{14}N ENDOR lines of low intensity were only observed for $(\mathbf{3c})^{+\bullet}$ and $(\mathbf{3e})^{+\bullet}$. In the ENDOR spectra of the other radical cations the weak ^{14}N lines lie in the range of proton signals; *e.g.* in the case of $(\mathbf{3a})^{+\bullet}$, near 11.5 and 13.6 MHz [see Figure 3(*a*)]. The nitrogen and β-proton (1-H_2, 3-H_2) coupling constants are considered to be positive. The latter are taken as the reference protons for all further assignments of sign derived from general triple resonance. Methyl substitution replaces the α-proton coupling constant by a methyl-proton splitting of similar magnitude, but opposite sign. Using these relations the results of $(\mathbf{3b–f})^{+\bullet}$ yield a complete, unambiguous assignment of all ^{1}H coupling constants of $(\mathbf{3a})^{+\bullet}$. As in the related 5,6-dihydro-5,6-dimethylbenzo[*c*]cinnoline radical cation[6,*] the most negative *ca.* 2 G

* In the course of the present work we also studied the 5,6-dihydro-1,5,6,10-tetramethylbenzo[*c*]cinnoline radical cation generated in toluene–trifluoroacetic acid (9:1) by oxdiation of the parent hydrazine[7] with MCPBA at room temperature: $a(N^{5,6}) = +8.58$, $a(H^{5\text{-}CH_3,\ 6\text{-}CH_3}) = +8.46$, $a(H^{2,9}) = -2.42$, $a(H^{4,7}) = -1.96$, $a(H^{3,8}) = +0.49$, and $a(H^{1\text{-}CH_3,\ 10\text{-}CH_3}) = -0.66$ G; $g = 2.0031$.

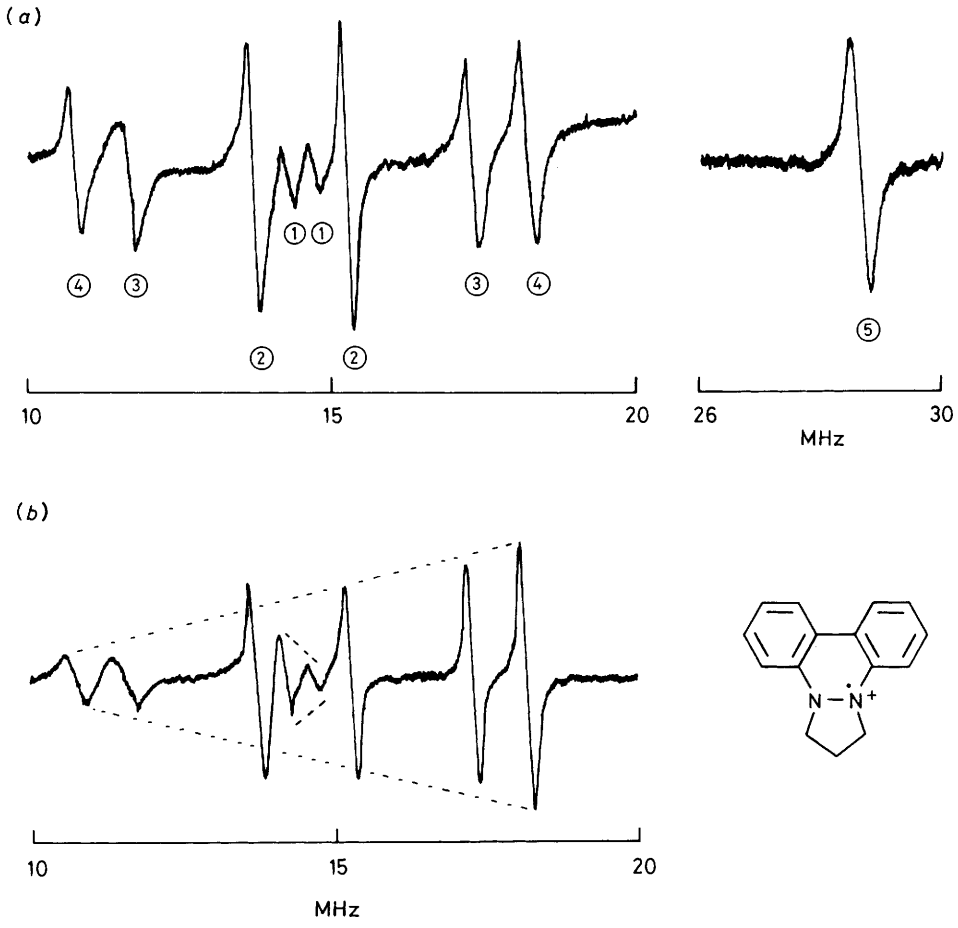


Figure 3. ENDOR (*a*) and general triple resonance (*b*) spectra of $(\mathbf{3a})^{+\bullet}$ in toluene–trifluoroacetic acid (9:1) at 260 K.

proton splitting [a(H) = −2.64 G] is assigned to 7-H and 10-H, the smaller [a(H) = −2.02 G] to 5-H and 12-H. As shown by $(\mathbf{3b})^{+\bullet}$ the small negative splitting, a(H) = −0.55 G, represents the CH_2 protons in position 2. For the positive ^{1}H coupling constants, the assignment $a(H^{8,9})$ = +0.55 and $a(H^{3,11})$ = +0.16 G is obtained. The equivalent β-proton (1-H_2, 3-H_2) splittings (within the e.s.r. time scale) of $(\mathbf{3a–d})^{+\bullet}$ and $(\mathbf{3f})^{+\bullet}$ indicate a coplanar arrangement of the attached five-membered ring, *i.e.* a planar $>N\text{–}\overset{+\bullet}{N}<$ moiety. But a rapidly equilibrating mixture of non-planar ring conformations is also a possibility. For the case of $(\mathbf{3e})^{+\bullet}$ the steric interaction of the methyl groups in positions 8 and 9 leads to a considerable distortion about the C-8a–C-8b bond. Therefore in this radical cation the β-protons are apparently non-equivalent $a(H^{1,3})$ = +10.00 and $a(H^{1',3'})$ = +9.16 G.

All attempts to isolate a 2,3-dihydro-1*H*-benzo[*c*]pyrazolo-[1,2-*a*]cinnoline radical cation salt in a pure state failed.

Experimental

U.v.–vis. spectra were obtained on a Cary 17 spectrophotometer. N.m.r. spectra were recorded on a Bruker AM 500 spectrometer, ^{1}H (500 MHz), ^{13}C (125.77 MHz). Chemical shifts are reported as δ values with Me_4Si as an internal reference. Mass spectra were taken on Dupont CEC 21-492. E.s.r., ENDOR, and triple resonance spectra were recorded on a Bruker ESP 300 spectrometer equipped with the ER 252 (ENMR) ENDOR system; g values were determined by using a n.m.r. gaussmeter and the Hewlett–Packard frequency converter 5246 L. This was calibrated with the perylene radical cation.

[1,3,8,10-$^2H_4$]*Benzo*[c]*cinnoline* (**1b**).—This was prepared according to literature methods from [4,6-$^2H_2$]-2-nitroaniline, obtained by refluxing 2-nitroaniline in 20% DCl in D_2O, *via* [4,6-$^2H_2$]-1-chloro-2-nitrobenzene[8] and [4,4′,6,6′-$^2H_4$]-2,2′-dinitro-1,1′-biphenyl,[9] which was reduced to give (**1b**).[10]

Benzo[c]*pyrazolo*[1,2-a]*cinnolinium Bromides* (**12a–f**).—These were prepared from the corresponding benzo[*c*]cinnolines (**1a**), (**1b**), (**1c**),[11] (**1d**),[12], (**1e**),[7] and (**1f**)[13] following the literature procedure for preparation of (**6a**).[3] The dark products obtained were dissolved in hot methanol. To complete the oxidation small amounts of bromine were added until the solution was decolourised. Addition of ethyl acetate precipitated pure, colourless products.

Benzo[c]*pyrazolo*[1,2-a]*cinnolinium Bromide* (**2a**).[3] Yield 63%; δ_H[$(CD_3)_2SO$; 303 K] 7.76 (1 H, t, $^3J_{1,2}$ 3.1 Hz, 2-H), 7.83 (2 H, t, ^3J *ca.* 7.3 Hz, 7-H, 10-H), 7.90 (2 H, t, ^3J *ca.* 7.7 Hz, 6-H, 11-H), 8.58 (2 H, d, $^3J_{5,6}$ 8.5 Hz, 5-H, 12-H), 8.73 (2 H, d, $^3J_{7,8}$ 7.4 Hz, 8-H, 9-H), and 9.97 (2 H, d, 1-H, 3-H).

[6,8,9,11-$^2H_4$]*Benzo*[c]*pyrazolo*[1,2-a]*cinnolinium Bromide* (**2b**). Yield 52%; no melt below 315 °C; δ_H[$(CD_3)_2SO$; 303 K] 7.76 (1 H, t, $^3J_{1,2}$ 3.1 Hz, 2-H), 7.83 (2 H, s, 7-H, 10-H), 8.57 (2 H, s, 5-H, 12-H), and 9.97 (2 H, d, 1-H, 3-H).

6,11-*Dimethylbenzo*[c]*pyrazolo*[1,2-a]*cinnolinium Bromide* (**2c**). Yield 43%; no melt below 315 °C; δ_H[$(CD_3)_2SO$; 303 K] 2.55 (6 H, s, 6-CH_3, 11-CH_3), 7.58 (2 H, d, $^3J_{7,8}$ 8.2 Hz, 7-H, 10-H), 7.60 (1 H, t, $^3J_{1,2}$ 3.0 Hz, 2-H), 8.40 (2 H, s, 5-H, 12-H),

8.45 (2 H, d, 8-H, 9-H), and 9.90 (2 H, d, 1-H, 3-H) (Found: C, 61.85; H, 4.55; Br, 24.6; N, 8.3. $C_{17}H_{15}BrN_2$ [327.2] requires C, 62.40; H, 4.62; Br, 24.42; N, 8.56%).

7,10-*Dimethylbenzo*[c]*pyrazolo*[1,2-a]*cinnolinium Bromide* (**2d**). Yield 28%; no melt below 315 °C; δ_H[$(CD_3)_2SO$; 303 K] 2.55 (6 H, s, 7-CH_3, 10-CH_3), 7.67 (2 H, d, $^3J_{5,6}$ 8.5 Hz, 6-H, 11-H), 7.69 (1 H, t, $^3J_{1,2}$ 2.9 Hz, 2-H), 8.41 (2 H, d, 5-H, 12-H), 8.49 (2 H, s, 8-H, 9-H), and 9.85 (2 H, d, 1-H, 3-H) (Found: C, 61.65; H, 4.8; Br, 24.5; N, 8.35%).

8,9-*Dimethylbenzo*[c]*pyrazolo*[1,2-a]*cinnolinium Bromide* (**2e**). Yield 16%; m.p. 164–165 °C; δ_H[$(CD_3)_2SO$; 303 K] 2.48 (6 H, s, 8-CH_3, 9-CH_3), 7.66 (2 H, d, $^3J_{6,7}$ 7.6 Hz, 7-H, 10-H), 7.70 (1 H, t, $^3J_{1,2}$ 3.1 Hz, 2-H), 7.78 (2 H, t, 6-H, 11-H), 8.34 (2 H, d, $^3J_{5,6}$ 8.2 Hz, 5-H, 12-H), and 9.93 (2 H, d, 1-H, 3-H) (Found: C, 61.7; H, 5.0; Br, 24.05; N, 8.4%).

6,11-*Dimethoxybenzo*[c]*pyrazolo*[1,2-a]*cinnolinium Bromide* (**2f**). Yield 67%; m.p. 308–310 °C (decomp.); δ_H[$(CD_3)_2SO$; 303 K] 4.00 (6 H, s, 6-OCH_3, 11-OCH_3), 7.38 (2 H, dd, 7-H, 10-H), 7.78 (1 H, t, $^3J_{1,2}$ 3.2 Hz, 2-H), 8.02 (2 H, d, $^4J_{5,7}$ 2.3 Hz, 5-H, 12-H), 8.51 (2 H, d, $^3J_{7,8}$ 9.0 Hz, 8-H, 9-H), and 10.01 (2 H, d, 1-H, 3-H) (Found: C, 56.75; H, 4.45; N, 7.95. $C_{17}H_{15}BrN_2O_2$ [359.2] requires C, 56.84; H, 4.21; N, 7.80%).

2,3-*Dihydro*-1H-*benzo*[c]*pyrazolo*[1,2-a]*cinnolines* (**3a–f**).—These were obtained by reduction of (**2a–f**) with sodium borohydride (procedure C).[3]

2,3-*Dihydro*-1H-*benzo*[c]*pyrazolo*[1,2-a]*cinnoline* (**2a**)[3] δ_H[$(CD_3)_2SO$; 303 K] 2.22 (2 H, 'quintet,' 2-H_2, AA'), 3.14 (4 H, 't,' 1-H_2, 3-H_2, $X_2X'_2$), 6.57 (2 H, d, $^3J_{5,6}$ 7.9 Hz, 5-H, 12-H), 6.85 (2 H, t, ^3J *ca.* 7.7 Hz, 7-H, 10-H), 7.10 (2 H, t, ^3J *ca* 8 Hz, 6-H, 11-H), and 7.44 (2 H, d, $^3J_{7,8}$ 7.6 8-H, 9-H); δ_H[$DCON(CD_3)_2$; 303 K] 2.27 (2 H, m, 'quintet,' 2-H_2, AA'), 3.20 (4 H, m, 't,' 1-H_2, 3-H_2, $X_2X'_2$), 6.61 (2 H, d, $^3J_{5,6}$ 7.9 Hz, 5-H, 12-H), 6.87 (2 H, t, ^3J *ca.* 7.5 Hz, 7-H, 10-H), 7.12 (2 H, t, ^3J *ca.* 7.9 Hz, 6-H, 11-H), and 7.49 (2 H, d, $^3J_{7,8}$ 7.6 Hz, 8-H, 9-H). Simulation of the $AA'X_2X'_2$ system (303 K) was carried out using PANIC82 (Aspect 2000 Bruker) and PANIC84.3004 (Aspect 3000) programs: $\delta_A = \delta_{A'} =$ 1 132.5 Hz (2-H_2); $\delta_X = \delta_{X'} =$ 1 599.0 Hz (1-H_2, 3-H_2), $^2J_{A,A'}$ −10.5 Hz, $^2J_{X,X'}$ −13.5 Hz, $^3J_{A,X} = {}^3J_{A',X'}$ 10.5 Hz, $^3J_{A,X'} = {}^3J_{A',X}$ 5.0 Hz.

δ_H[CD_3CN + trace of $KOC(CH_3)_3$; 345 K] 2.26 (2 H, 'quintet,' 2-H_2, AA'), 3.18 (4 H, 't,' 1-H_2, 3-H_2, $X_2X'_2$), 6.56 (2 H, dd, $^3J_{5,6}$ 8.0 Hz, $^4J_{5,7}$ 1.1 Hz, 5-H, 12-H), 6.86 (2 H, td, ^3J *ca.* 7.6 Hz, 7-H, 10-H), 7.10 (2 H, td, ^3J *ca.* 7.7 Hz, $^4J_{6,8}$ 1.4 Hz, 6-H, 11-H), and 7.41 (2 H, dd, $^3J_{7,8}$ 7.6 Hz, 8-H, 9-H); (235 K) 2.27 (2 H, 'quintet,' 2-H_2, AA'), 3.18 (4 H, 't,' 1-H_2, 3-H_2, $X_2X'_2$), 6.60 (2 H, dd, $^3J_{5,6}$ 8.0 Hz, $^4J_{5,7}$ = 1.0 Hz, 5-H, 12-H), 6.91 (2 H, td, ^3J *ca.* 7.6 Hz, 7-H, 10-H), 7.15 (2 H, td, ^3J *ca.* 7.8 Hz, $^4J_{6,8}$ 1.4 Hz, 6-H, 11-H), and 7.45 (2 H, dd, $^3J_{7,8}$ 7.5 Hz, 8-H, 9-H); δ_C [^{1}H, ^{13}C-COSY; CD_3CN + trace of $KOC(CH_3)_3$; 345 K] 23.58 (C-2), 48.52 (1-H_2, C-3), 114.42 (C-5, C-12), 122.81 (C-7, C-10), 123.33 (C-8, C-9), 125.42 (C-8a, C-8b), 130.7 (C-6, C-11), and 150.59 (C-4a, C-12a); (235 K) 23.25 (C-2), 48.55 (C-1, C-3), 114.70 (C-5, C-12), 122.99 (C-7, C-10), 123.48 (C-8, C-9), 125.16 (C-8a, C-8b), 130.31 (C-6, C-11), and 150.43 (C-4a, C-12a).

[6,8,9,11-$^2H_4$]-2,3-*Dihydro*-1H-*benzo*[c]*pyrazolo*[1,2-a]*cinnoline* (**3b**).—From EtOH orange needles (63%), m.p. 194–195 °C; δ_H[$(CD_3)_2SO$; 303 K] 2.22 (2 H, 'quintet,' 2-H_2, AA'), 3.14 (4 H, 't,' 1-H_2, 3-H_2, $X_2X'_2$), 6.57 (2 H, s, 5-H, 12-H), and 6.85 (2 H, s, 7-H, 10-H); Deuteriation ≥ 90%; *m/z* 226 (M^+, 100%).

2,3-*Dihydro*-6,11-*dimethyl*-1H-*benzo*[c]*pyrazolo*[1,2-a]*cinnoline* (**3c**).—From hexane yellow needles (52%), m.p. 141–142 °C; δ_H[$(CD_3)_2SO$ + trace of $KOC(CH_3)_3$; 303 K] 2.19 (4 H, 'quintet,' 2-H_2, AA'), 2.21 (6 H, s, 6-CH_3, 11-CH_3), 3.13 (4 H, 't,' 1-H_2, 3-H_2, $X_2X'_2$), 6.39 (2 H, s, 5-H, 12-H), 6.65 (2 H, d, $^3J_{7,8}$ 7.7 Hz, 7-H, 10-H), and 7.28 (2 H, d, 8-H, 9-H); *m/z* 250 (M^+, 100%) (Found: C, 81.7; H, 7.3; N, 11.0. $C_{17}H_{18}N_2$ [250.4] requires C, 81.56; H, 7.25; N, 11.19%).

2,3-*Dihydro*-7,10-*dimethyl*-1H-*benzo*[c]*pyrazolo*[1,2-a]*cinnoline* (**3d**).—From methanol yellow needles (44%), m.p. 180–181 °C; δ_H[$(CD_3)_2SO$ + trace of $KOC(CH_3)_3$; 303 K] 2.18 (2 H, 'quintet,' 2-H_2, AA'), 2.22 (6 H, s, 7-CH_3, 10-CH_3), 3.10 (4 H, 't,' 1-H_2, 3-H_2, $X_2X'_2$), 6.47 (2 H, d, $^3J_{5,6}$ 8.0 Hz, 5-H, 12-H), 6.91 (2 H, d, 6-H, 11-H), and 7.28 (2 H, s, 8-H, 9-H); *m/z* 250 (M^+, 90%) (Found: C, 81.4; H, 7.35; N, 11.2%).

2,3-*Dihydro*-8,9-*dimethyl*-1H-*benzo*[c]*pyrazolo*[1,2-a]*cinnoline* (**3e**).—From methanol yellow needles (25%), m.p. 130–131 °C; δ_H[$(CD_3)_2SO$ + trace of $KOC(CH_3)_3$; 303 K] 2.12 (6 H, s, 8-CH_3, 9-CH_3), 2.26 (2 H, m, 2-H, 2-H'), 2.75 (2 H, m, 1-H, 3-H), 3.45 (2 H, m, 1-H', 3-H'), 6.56 (2 H, d, $^3J_{5,6}$ 7.2 Hz, 5-H, 12-H), 6.87 (2 H, d, $^3J_{6,7}$ 7.0 Hz, 7-H, 10-H), and 7.09 (2 H, dd, 6-H, 11-H); *m/z* 250 (M^+, 100%) (Found: C, 81.5; H, 7.3; N, 10.95%).

δ_H[CD_3CN + trace of $KOC(CH_3)_3$; 345 K] 2.17 (6 H, s, 8-CH_3, 9-CH_3), 2.30 (2 H, m, 2-H, 2-H'), 2.85 (2 H, m, 1-H, 3-H), 3.45 (2 H, m, 1-H', 3-H'), 6.45 (2 H, d, $^3J_{5,6}$ 7.8 Hz, 5-H, 12-H), 6.87 (2 H, d, $^3J_{6,7}$ 7.7 Hz, 7-H, 10-H), and 7.09 (2 H, dd, 6-H, 11-H); (235 K) 2.15 (6 H, s, 8-CH_3, 9-CH_3), 2.31 (2 H, m, 2-H, 2-H'), 2.80 (2 H, m, 1-H, 3-H), 3.48 (2 H, m, 1-H', 3-H'), 6.59 (2 H, d, $^3J_{5,6}$ 7.8 Hz, 5-H, 12-H), 6.91 (2 H, d, $^3J_{6,7}$ 7.7 Hz, 7-H, 10-H), and 7.14 (2 H, dd, 6-H, 11-H); δ_C[^{1}H, ^{13}C-COSY; CD_3CN + trace of $KOC(CH_3)_3$; 345 K] 20.94 (8-CH_3, 9-CH_3), 24.56 (C-2), 49.00 (C-1, C-3), 111.16 (C-5, C-12), 125.65 (C-8a, C-7, C-10), 128.57 (C-6, C-11), 135.69 (C-8, C-9), and 155.84 (C-4a, C-12a); (235 K) 21.03 (8-CH_3, 9-CH_3), 24.18 (C-2), 49.13 (C-1, C-3), 111.45 (C-5, C-12), 125.20 (C-8a, C-8b), 125.72 (C-7, C-10), 128.84 (C-6, C-11), 135.85 (C-8, C-9), and 155.08 (C-4a, C-12a).

2,3-*Dihydro*-6,11-*dimethoxy*-1H-*benzo*[c]*pyrazolo*[1,2-a]*cinnoline* (**3f**).—From ethyl acetate yellow needles (33%), m.p. 190–191 °C; δ_H[$(CD_3)_2SO$ + trace of $KOC(CH_3)_3$; 303 K] 2.19 (2 H, 'quintet,' 2-H_2, AA'), 3.16 (4 H, 't,' 1-H_2, 3-H_2, $X_2X'_2$), 3.73 (6 H, s, 6-OCH_3, 11-OCH_3), 6.14 (2 H, d, $^4J_{5,7}$ 2.5 Hz, 5-H, 12-H), 6.40 (2 H, dd, $^3J_{7,8}$ 8.4 Hz, 7-H, 10-H), and 7.29 (2 H, d, 8-H, 9-H); *m/z* (M^+, 100%) (Found: C, 72.55; H, 6.3; N, 9.75. $C_{17}H_{18}N_2O_2$ [282.4] requires C, 72.32; H, 6.43; N, 9.92%).

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