Reactions of (Vinylimino)-λ⁵-phosphanes and Related Compounds. Part 29.[1,2] Synthesis and Chemical and Structural Properties of 11*H*-Cyclohepta[*b*]indeno[2,1-*d*]pyrrole and Acenaphtho[1,2-*b*]cyclohepta[*d*]pyrrole

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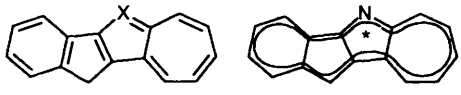
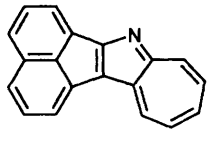
The reaction [(inden-3-yl)imino]- and [(acenaphthylen-1-yl)imino]-tributyl-λ⁵-phosphanes with 2-chlorotropone gave novel 11*H*-cyclohepta[*b*]indeno[2,1-*d*]pyrrole **2** and acenaphtho[1,2-*b*]cyclohepta[*d*]pyrrole **5**, respectively. A deuterium exchange reaction of **2** suggested the intermediacy of 18π electronic anion **3**. Compound **2** was converted into 11*H*-cyclohepta[*b*]indeno[2,1-*d*]pyrrol-11-one **14** and -11-ol **13**. These compounds are stable in acidic media and no 16π electronic system **4** was observed. Compound **5** is composed of naphthalene and 1-azaazulene moieties. The reduction potentials and the basicities of **2**, **13**, **14** and **5** were measured to clarify their electronic properties and are discussed on the basis of AM1 calculations.

Recently, the preparation of nitrogen heterocycles by means of an aza-Wittig reaction has been widely utilized because of the ready availability of functionalized imino-λ⁵-phosphanes.[3] We have also demonstrated that (vinylimino)-λ⁵-phosphanes are convenient synthons for nitrogen heterocycles[4] including 1-azaazulenes.[5-8] Since azulenes and azaazulenes[9] have played a major role in advancing our understanding of cyclic conjugation,[10] and as methodology for the construction of azulenes condensed with several ring systems has appeared,[11-13] we have explored methodology for the synthesis of annulated 1-azaazulenes.[6,8] Although the synthesis of 11*H*-indeno[2,1-*a*]azulene **1** has been accomplished previously,[14,15] no attempt to generate anion or cationic species similar to **3** and **4** has appeared. In this paper, we describe a simple preparation and



1 X = CH
2 X = N

3 * = −
4 * = +



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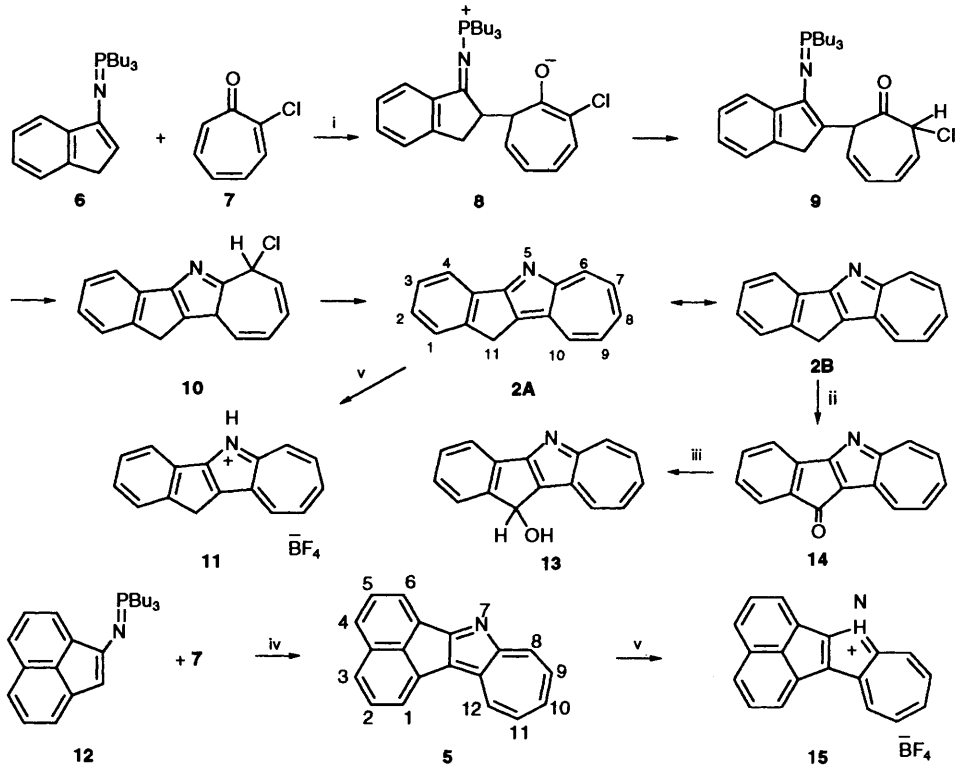
chemical and structural properties of 11*H*-cyclohepta[*b*]-indeno[2,1-*d*]pyrrole **2** and its derivatives **13** and **14**. Furthermore, since the synthesis of azulenes fused with acenaphthylene such as azuleno[4,5-*a*]acenaphthylene[16] and azuleno[1,2-*a*]-acenaphthylene[17,18] has appeared, an aza-analogue of the latter, acenaphtho[1,2-*b*]cyclohepta[*d*]pyrrole **5**, which is annulated at the C-1 and C-11 positions of **2** with benzene, is also prepared. The reduction potentials and the basicities [that is, the acidities (pK_a) of the conjugate acids] of **2**, **13**, **14** and **5** are also studied, and discussed on the basis of AM1 calculations.

Results and Discussion

The tributyl[(inden-3-yl)imino]-λ⁵-phosphane **6** was easily prepared *in situ* by the Staudinger reaction[19] of 3-azidoindene[20] with PBu_3 in anhydrous benzene at room temperature for 1 h.[21,22] To this mixture was added 2-chlorotropone (2-chlorocyclohepta-2,4,6-trienone) **7** and triethylamine in benzene, and the mixture was heated under reflux for 3 h. The product **2** was purified through treatment of a mixture of **2** and tributylphosphane oxide with tetrafluoroboric acid giving **11**, which was treated with aqueous $NaHCO_3$ to give 65% of **2**. The proposed reaction pathways are outlined in Scheme 1.[4,5] The β-carbon atom of imino-λ⁵-phosphane **6** undergoes an enamine-type alkylation onto C-7 of 2-chlorotropone **7** to give **8**.[4,5] Hydrogen migration and ketonization give the intermediate **9** and subsequent intramolecular aza-Wittig reaction in **9** gives **10**. The intermediate **10** undergoes aromatizing dehydrochlorination in the presence of NEt_3 to give compound **2**. In a similar fashion, the reaction of [(acenaphthylen-1-yl)imino]-tributyl-λ⁵-phosphorane **12**, prepared *in situ* from 1-azidoacenaphthylene and PBu_3,[22] with 2-chlorotropone **7** and NEt_3 in toluene afforded acenaphtho[1,2-*b*]cyclohepta[*d*]pyrrole **5** in good yield (Scheme 1). The methylene group of **2** was then successfully modified. On oxidation of **2** with Bu^{t}OOH and a catalytic amount of CrO_3,[23] 11*H*-cyclohepta[*b*]indeno[2,1-*d*]pyrrol-11-one **14** was obtained as orange needles in good yield. Compound **14** was easily reduced with $NaBH_4$ in MeOH to give 11-hydroxy-11*H*-cyclohepta[*b*]indeno[2,1-*d*]pyrrole **13** as red needles.

The structures of **2**, **13**, **14** and **5** were deduced from ^1H NMR, ^{13}C NMR, IR and electronic spectral data (Table 1), as well as high resolution mass and elemental analyses. The ^1H NMR spectrum (400 MHz) of **2** was assigned completely. In contrast to the parent 1-azaazulene, the difference between the coupling constants $J_{6,7}$ and $J_{9,10}$ for compound **2** (1.5 Hz) is slightly larger than that for some coupling constants in 2-phenyl-1-azaazulene (*J* 1.0 Hz).[24] Thus, there is a slight bond-length alternation and the canonical structure **2A** would be favoured over **2B** (Scheme 1). The spectroscopic characteristics of alcohol **13** and ketone **14** are similar to those of compound **2**. The ^1H NMR signals for the ring protons of **5** were observed in the aromatic region, and all the signals were assigned. The difference in coupling constant between $J_{8,9}$ and $J_{11,12}$ is small (0.9 Hz) as compared with the corresponding values for **2** and 2-phenyl-1-azaazulene (*vide supra*). These observations indicate that bond-length alternation in **5** is small and that **5** is composed of 1-azaazulene and naphthalene moieties rather than 8-azaheptafulvene and acenaphthylene moieties. This feature resembles that of a hydrocarbon analogue, azuleno[1,2-*a*]-



Scheme 1 *Reagents and conditions:* i, reflux in PhH–NEt_3; ii, CrO_3–Bu'OOH in CH_2Cl_2; iii, $NaBH_4$–MeOH at room temp.; iv, reflux in PhMe–NEt_3; v, HBF_4–Ac_2O

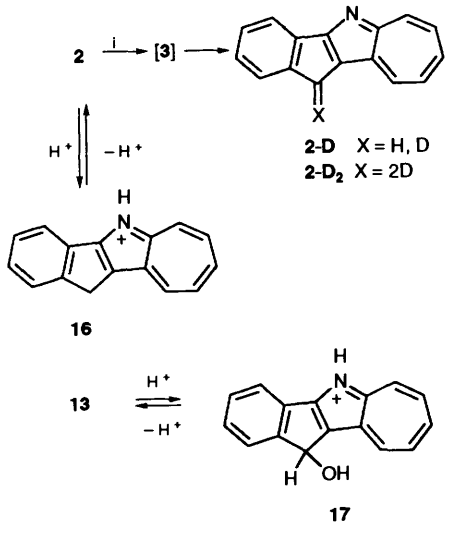
Table 1 Electronic spectra of 1-azaazulene derivatives, **2**, **13**, **14** and **5**

Compd.	Solvent	λ_{max}/nm (log ε)
2	EtOH	292 (4.46), 312 (4.32), 324 (4.40), 351 (3.84), 369 (3.81), 490 (3.44), 514 (3.41), 553 (3.03 sh)
	EtOH–TFA	264 (4.05), 308 (4.41), 456 (3.96), 504 (3.64 sh)
	10% H_2SO_4	285 (4.42 sh), 308 (4.62), 458 (4.15), 502 (3.79 sh)
	conc. H_2SO_4	305 (4.70), 440 (4.08 sh), 459 (4.15), 485 (3.92 sh)
13	EtOH	291 (4.53), 307 (4.48), 321 (4.55), 351 (3.89), 367 (3.86), 485 (3.58), 506 (3.56), 543 (3.23 sh)
	10% H_2SO_4	284 (4.27), 307 (4.46), 459 (4.11), 502 (3.64 sh)
	conc. H_2SO_4	309 (4.48), 448 (4.09 sh), 464 (4.12), 496 (3.83 sh)
14	EtOH	260 (4.05), 310 (4.71), 353 (3.98), 427 (3.37 sh), 455 (3.45), 477 (3.42), 505 (3.14 sh)
	10% H_2SO_4	259 (4.29), 302 (4.79), 431 (3.99), 452 (3.99), 482 (3.67 sh)
	conc. H_2SO_4	262 (4.57), 303 (4.30), 366 (3.97), 410 (3.61 sh), 435 (3.46)
11	MeCN	289 (4.25 sh), 307 (4.39), 465 (3.86, 502 (3.53 sh)
5	EtOH	288 (4.63), 334 (4.63), 350 (4.67), 541 (2.89), 572 (2.87), 620 (2.52 sh)
	EtOH–TFA	338 (4.31), 371 (4.58), 399 (4.28), 506 (3.48), 525 (3.46), 578 (3.05 sh)

acenaphthylene.[18] As in the case of **2**, on treatment with tetrafluoroboric acid in Ac_2O, compound **5** was converted into **15**, which regenerates **5** by treatment with aqueous $NaHCO_3$ (Scheme 1).

The electronic spectra of **2**, **13**, **14** and **5** were recorded in acidic media (Table 1, Schemes 2 and 3). The protonation process is reversible, and the compounds were regenerated by neutralization with aqueous $NaHCO_3$. The spectra of **2** exhibited hypsochromic shifts[8] in 10% and conc. H_2SO_4, showing an absorption in these solvents similar to that of **11** in MeCN (Table 1). This finding and the ^1H NMR spectrum of **2** in CF_3CO_2, showing a downfield shift of all the proton signals, indicates that **2** exists as the protonated azaazulenium ion **16** in acidic media. On treatment of **2** with Bu'OK in MeOD at 0 °C and quenching with H_2O, the methylene hydrogens of **2** were exchanged with deuterium to give mono-**2-D** and di-deuteriated **2-D_2** derivatives in a ratio of *ca.* 4:6 in 60% yield. Thus, the intermediacy of a formal 18π electronic anion **3** was suggested.

The spectral properties of alcohol **13**, are similar to those of **2** (Table 1), implying the existence of **17** in acidic media. The protonation occurs at the nitrogen atom, and no dehydroxylation leading to dication, which is isoelectronic with **4** (16π electronic system), took place even in conc. H_2SO_4. The electronic spectrum of ketone **14** in 10% H_2SO_4 is very similar to that of **2**. This finding indicates that **14** is also protonated at the nitrogen atom rather than on the carbonyl oxygen, giving a cation analogous to **16** (*i.e.* cation **18**). However, the electronic spectrum of **14** in conc. H_2SO_4 is markedly different from those in EtOH and 10% H_2SO_4, and is similar to that of 2-phenylinden-1-one [λ_{max}(MeOH)/nm (log ε) 261 (4.51), 275 (4.32 sh), 300 (3.24 sh), 430 (3.23)].[25] This fact suggests that **14** is doubly protonated at the nitrogen atom, rather than singly protonated at the nitrogen and carbonyl oxygen, and it seems to exist as **19**, rather than **20**, in conc. H_2SO_4. Similarly, compound **5** exists as **21** in acidic media as shown in Table 1 and Scheme 3.



Scheme 2 *Reagents and conditions:* i, Bu^{t}OK–MeOD

Table 2 Reduction potential, pK_a, calculated energy level of LUMO and HOMO and electron density on the nitrogen atom of compounds **2**, **13**, **14** and **5**

Compd.	$E_{\frac{1}{2}}$/V	LUMO/eV	HOMO/eV	pK_a	Electron density[a]
2	−1.43	−1.14	−8.27	6.2	−0.125
13	−1.36	−1.27	−8.44	5.6	−0.124
14	−1.09	−1.47	−8.66	3.1	−0.122
5	−1.30	−1.19	−8.05	5.6	−0.119

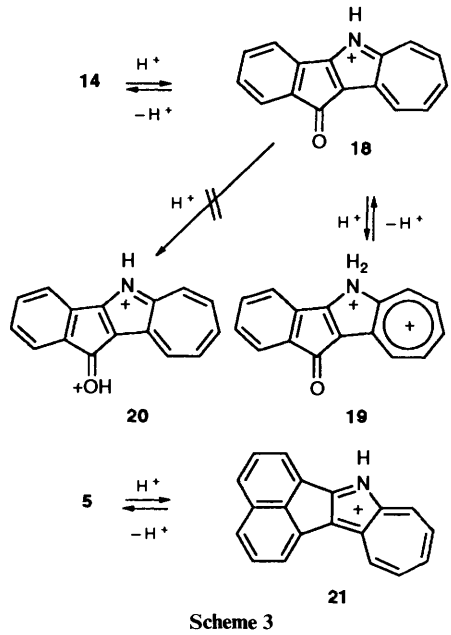
[a] Electron density on the nitrogen atom.

Cyclic voltammetry of the 1-azaazulenes **2**, **13**, **14** and **5** in MeCN gave reversible reduction waves, and the half-height potentials of the reduction waves ($E_{\frac{1}{2}}$) have been measured. Furthermore, the basicities of **2**, **13**, **14** and **5** [that is, the acidities (pK_a) of their conjugate acids] have also been measured, and the results, along with the calculated energy levels of LUMO, HOMO, and electron densities of the nitrogen atom, predicted by using AM1 calculations,[26] are listed in Table 2. In the series of **2**, **13** and **14**, the $E_{\frac{1}{2}}$ of compound **2** moves in a positive direction when the methylene group is transformed into alcohol **13** and ketone **14**. This feature is clearly reflected in the lowering of the calculated energy levels of LUMO for **13** and **14**. The difference in pK_a values of compounds **2**, **13** and **14** shows a similar trend to that of $E_{\frac{1}{2}}$. The basicity of the amines is determined by the availability of the lone pair on the nitrogen (Scheme 3). The pK_a values of compound **2** become lower when the methylene protons are changed into alcohol and carbonyl functions. This can be attributed to the electron-withdrawing properties of hydroxy and carbonyl functions. Thus, the series of pK_a values are in agreement with the electron density on the nitrogen atom predicted by AM1 calculations. The $E_{\frac{1}{2}}$ and pK_a values of **5** are similar to those of **2** and **13**, suggesting that **5** is composed of naphthalene and azaazulene moieties, and not of acenaphthylene and 8-azaheptafulvene moieties (*vide supra*).

We believe that the foregoing methodology has considerable potential for the preparation of annulated 1-azaazulene ring systems, which have theoretical interest and demonstrated utility.

Experimental

IR spectra were recorded on a Shimadzu IR-400 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi R-90 spectrometer and a JEOL GSX400 spectrometer. Chemical shifts are given in ppm (δ) relative to internal $SiMe_4$ standard. *J* Values are given in Hz. Mass spectra and high-resolution mass spectra were measured by Shimadzu GCMS QP-1000 and JEOL DX-300 spectrometers. All the reactions were carried out in anhydrous solvent under a dry nitrogen atmosphere. M.p.s were measured on a Yamato mp-21 apparatus and are uncorrected. Tributyl[(inden-3-yl)imino]-λ^5-phosphane **6**[21] and [(acenaphthylen-1-yl)imino]tributyl-λ^5-phosphane **12**[22] were prepared as reported previously, and used subsequently for the preparative reactions.



Scheme 3

Preparation of 11H-*Cyclohepta*[b]*indeno*[2,1-d]*pyrrole* **2**.—A solution of imino-λ^5-phosphane **6**, which was prepared from 3-azidoindene (826 mg, 3.56 mmol) and PBu_3 (719 mg, 3.56 mmol) in benzene (40 cm^3), 2-chlorotropone **7** (498 mg, 3.56 mmol) and NEt_3 (350 mg, 3.56 mmol) was heated under reflux for 3 h. The reaction mixture was filtered through Celite and then the filtrate was dissolved in acetic anhydride (5 cm^3) and 42% aqueous HBF_4 (1.1 g, 5.34 mmol) and stirred for 30 min. To this reaction mixture was added diethyl ether (20 cm^3) and the mixture was stirred for a further 1.5 h. The precipitate was then collected by filtration to give compound **11** as orange prisms, m.p. 220 °C (from MeCN–AcOEt) (Found: C, 63.2; H, 4.2; N, 4.7. $C_{16}H_{12}BF_4N$ requires C, 62.99; H, 3.96; N, 4.59%).

Compound **11** was then dissolved in MeCN (3 cm^3) and treated with aqueous $NaHCO_3$, extracted with $CHCl_3$ and the extract was dried over Na_2SO_4. After evaporation of the $CHCl_3$, the residue was purified by column chromatography on alumina. The fractions eluted with $CHCl_3$–AcOEt (4:1) gave the title compound **2** (507 mg, 64%) as reddish violet needles, m.p. 184–185 °C (from EtOH); δ_H($CDCl_3$; 400 MHz) 3.88 (2 H, s, 11-H), 7.41 (1 H, dt, *J* 7.3, 1.5, 2-H), 7.45 (1 H, ddd, *J* 7.7, 7.3, 1.5, 3-H), 7.49 (1 H, ddd, *J* 10.3, 8.8, 0.5, 9-H), 7.57 (1 H, dd, *J* 7.3, 1.5, 1-H), 7.63 (1 H, dd, *J* 10.3, 8.8, 7-H), 7.68 (1 H, dddd, *J* 10.3, 8.8, 1.8, 1.1, 8-H), 8.16 (1 H, dd, *J* 7.7, 1.5, 4-H), 8.61 (1 H, ddd, *J* 8.8, 1.5, 1.1, 6-H) and 8.33 (1 H, dd, *J* 10.3, 1.1, 10-H); δ_H(CF_3CO_2H; 90 MHz) 4.08 (2 H, s, 11-H), 7.30–7.81 (3 H, m, 1-, 2-, 3-H), 7.81–8.36 (4 H, m, 4-, 7-, 8-, 9-H) and 8.58–8.98 (2 H, m, 6-, 10-H); δ_C($CDCl_3$; 23 MHz) 29.2 (t, C-11), 122.1 (d), 125.8 (d), 127.2 (d), 127.6 (d), 128.8 (d), 129.0 (d), 130.7 (s), 131.8 (d), 134.4 (d), 135.4 (d), 136.6 (s), 138.6 (s), 150.7 (s), 163.7 (s) and 175.9 (s); ν_{max}/cm^{-1} 2940, 1610 and 1498; *m*/*z* (rel.

intensity) (M^+, 100%) (Found: M^+, 217.0892. $C_{16}H_{11}N$ requires *M*, 217.0892).

A solution of isolated **2** (100 mg, 0.46 mmol) and 42% aqueous HBF_4 (81 mg, 0.92 mmol) in acetic anhydride (1 cm^3) was stirred at room temperature for 10 min and then diethyl ether (10 cm^3) was added to the solution and stirred for a further 10 min. The resulting precipitate was collected by filtration to give compound **11** (132 mg, 94%), which is identical with an authentic specimen.

Preparation of Acenaphtho[1,2-b]*cyclohepta*[d]*pyrrole* **5**.—A solution of imino-λ^5-phosphane **12** was prepared from 1-azidoacenaphthylene (1.18 g, 6.0 mmol) and PBu_3 (1.11 g, 5.5 mmol) in dry toluene (20 cm^3) by stirring at room temperature for 15 min. To this solution was added 2-chlorotropone **7** (702 mg, 5 mmol) and NEt_3 (1.01 g, 10 mmol), and the mixture was heated under reflux for 20 h. The reaction mixture was filtered through Celite and then the filtrate was concentrated and the residue was chromatographed on silica gel (AcOEt) to give the title compound **5** (1.13 g, 89%) as dark violet needles, m.p. 196–197 °C (from EtOH); $\delta_H(CDCl_3$; 400 MHz) 7.57 (1 H, ddd, *J* 10.1, 9.1, 1.1, 11-H), 7.62 (1 H, dd, *J* 8.2, 6.8, 2-H), 7.64 (1 H, ddd, *J* 9.9, 9.3, 1.1, 9-H), 7.70 (1 H, dd, *J* 8.2, 7.0, 5-H), 7.72 (1 H, ddt, *J* 9.9, 9.1, 1.1, 10-H), 7.77 (1 H, d, *J* 8.2, 3-H), 7.92 (1 H, d, *J* 6.8, 1-H), 7.94 (1 H, d, *J* 8.2, 4-H), 8.30 (1 H, d, *J* 7.0, 6-H), 8.61 (1 H, dd, *J* 9.3, 1.1, 8-H) and 8.68 (1 H, dd, *J* 10.1, 1.1, 12-H); $\delta_C(CDCl_3$; 100 MHz) 119.8 (C-1), 122.8 (C-6), 125.2 (C-3), 127.9 (C-5), 128.1 (C-2), 128.5 (C-11), 129.2 (C-9), 129.4 (C-4), 132.7 (C-12), 135.3 (C-8), 136.3 (C-10), 129.3, 130.2, 131.3, 131.5, 136.5, 138.8, 164.6 and 175.1 (quaternary-C); $\nu_{max}(CHCl_3)/cm^{-1}$ 2950, 1607, 1550 and 1522; *m*/*z* (rel. intensity) 253 (M^+, 100%) (Found: C, 89.9; H, 4.3; N, 5.4%; M^+, 253.0889. $C_{19}H_{11}N$ requires C, 90.09; H, 4.38; N, 5.53%; *M*, 253.0892).

A solution of **5** (101 mg, 0.4 mmol) and 42% aqueous HBF_4 (168 mg, 0.8 mmol) in CH_2Cl_2 (1 cm^3) and acetic anhydride (3 cm^3) was stirred at room temperature for 12 h. To this mixture was added diethyl ether (20 cm^3), and the resulting precipitate was collected by filtration to give 7*H*-acenaphtho-[1,2-*b*]cyclohepta[*d*]pyrrol-7-ium tetrafluoroborate **15** (132 mg, 97%) as red prisms, m.p. 250 °C (decomp.) from AcOEt–MeCN); $\delta_H([^2H_6]$DMSO, 400 MHz) 7.59 (1 H, dd, *J* 8.1, 7.0, 2-H), 7.70 (1 H, dd, *J* 8.1, 7.0, 5-H), 7.82 (1 H, d, *J* 8.1, 3-H), 7.99 (1 H, dd, *J* 7.0, 6-H), 8.05 (1 H, d, *J* 8.1, 4-H), 8.08 (1 H, d, *J* 7.0, 1-H), 8.13 (1 H, dd, *J* 9.9, 9.4, 11-H), 8.22 (1 H, dd, *J* 10.5, 9.2, 9-H), 8.39 (1 H, dd, *J* 10.5, 9.4, 10-H), 8.69 (1 H, d, *J* 9.2, 8-H) and 9.07 (1 H, d, *J* 9.9, 12-H); $\delta_C(CDCl_3$; 100 MHz) 123.4 (C-1), 125.8 (C-6), 127.3 (C-3), 128.4 (C-5), 128.5 (C-2), 132.3 (C-4), 134.3 (C-8), 135.6 (C-9), 136.0 (C-11), 138.8 (C-12), 143.9 (C-10), 123.9, 126.8, 127.8, 129.1, 133.4, 151.1 and 157.7 (quaternary-C) (Found: C, 65.8; H, 3.4; N, 4.0. $C_{19}H_{12}BF_4N$ requires C, 66.90; H, 3.55; N, 4.11%).

Oxidation of Compound **2**.—A solution of compound **2** (65 mg, 0.3 mmol), CrO_3 (1.5 mg, 0.015 mmol) and Bu^{t}OOH (2.1 mmol) in CH_2Cl_2 (2 cm^3) was heated under reflux. The reaction mixture was then filtered through Celite, and the filtrate was washed with water and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by TLC on silica gel (AcOEt) to give 11*H*-cyclohepta[*b*]indeno[2,1-*d*]pyrrol-11-one **14** (55 mg, 79%) as yellow needles, m.p. 203–204 °C (from EtOH); $\delta_H(CDCl_3$; 90 MHz) 7.26–7.48 (2 H, m, 2-, 3-H), 7.50–7.78 (5 H, m, 1-, 4-, 7-, 8-, 9-H) and 8.42–8.66 (2 H, m, 6-, 10-H); $\delta_H(CF_3CO_2H$; 90 MHz) 7.48–7.96 (4 H, m, 1-, 2-, 3-, 4-H), 8.16–8.50 (3 H, m, 7-, 8-, 9-H) and 8.96–9.22 (2 H, m, 6-, 10-H); $\delta_C(CDCl_3$; 23 MHz) 121.9 (d), 123.6 (d), 123.7 (s), 131.6 (d), 133.0 (d), 133.4 (d), 133.6 (d), 134.3 (d), 137.2 (d), 138.2 (d), 138.2 (s), 141.0 (s), 144.1 (s), 167.2 (s), 181.1 (s) and 185.6 (s); $\nu_{max}(CHCl_3)/cm^{-1}$ 2974, 1694, 1605, 1558 and 1528; *m*/*z* (rel. intensity) 231 (M^+, 100%) (Found: C, 83.3; H, 3.6; N, 6.2%; M^+, 231.0706. $C_{16}H_9NO$ requires C, 83.10; H, 3.92; N, 6.06%; *M*, 231.0684).

Reduction of Pyrrolone **14** *with* $NaBH_4$.—A solution of pyrrolone **14** (231 mg, 1 mmol) and $NaBH_4$ (19 mg, 0.5 mmol) in MeOH (50 cm^3) was stirred at room temperature for 4 h. The reaction mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on alumina (AcOEt–MeOH, 20:1) to give 11*H*-cyclohept[*b*]indeno[2,1-*d*]pyrrol-11-ol **13** as red needles, m.p. 178–179 °C (from EtOH); $\delta_H([^2H_6]$DMSO; 90 MHz) 5.60–6.18 (2 H, s, 11-H and OH), 7.33–7.52 (2 H, m, 2-, 3-H), 7.55–7.93 (5 H, m, 1-, 4-, 7-, 8-, 9-H), 8.38–8.63 (2 H, m, 6-, 10-H); $\delta_H(CF_3CO_2H$; 90 MHz) 5.96 (1 H, s, 11-H), 7.54–8.04 (4 H, m, 1-, 2-, 3-, 4-H), 8.26–8.55 (3 H, m, 7-, 8-, 9-H) and 8.92–9.18 (2 H, m, 6-, 10-H); ν_{max}(KBr)/cm^{-1} 3200, 2900, 1608, 1544 and 1525; *m*/*z* (rel. intensity) 233 (M^+, 71%) and 232 (100) (Found: C, 82.6; H, 4.5; N, 6.2%; M^+, 233.0824. $C_{16}H_{11}NO$ requires C, 82.38; H, 4.75; N, 6.00; *M*, 233.0841).

Deuterium Exchange of Compound **2**.—A solution of compound **2** (22 mg, 0.1 mmol) and Bu^{t}OK (23 mg, 0.2 mmol) in CH_3OD (0.5 cm^3) and tetrahydrofuran (THF) (5 cm^3) was stirred at 0 °C for 2 h. The reaction mixture was then poured into water, and the mixture was extracted with CH_2Cl_2 and the extract was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by TLC on silica gel (AcOEt) to give a mixture of mono **2-D** and di-deuteriated **2-D_2** in a ratio of *ca.* 4:6 (13 mg, 60%) (Found: M^+, 218.0932. $C_{16}H_{10}DN$ requires *M*, 218.0955. Found: M^+, 219.0999. $C_{16}H_9D_2N$ requires *M*, 219.1018).

Cyclic Voltammetry of Compounds **2**, **13**, **14** *and* **5**.—Reduction potentials of compounds **2**, **13**, **14** and **5** were determined by means of a CV-27 voltammetry controller (BAS Co.). A three-electrode cell was used, consisting of Ag working and Pt counter electrodes and a reference standard calomel electrode (SCE). An acetonitrile solution (10 cm^3) of the compounds (1 mmol dm^{-3}) and Bu_4NClO_4 (0.1 mol dm^{-3}) was deaerated by bubbling nitrogen through the solution. The measurements were made at a scan rate of 0.1 V s^{-1}, and the voltammograms recorded on a WX-1000-UM0101 (Graphtec Co.) X-Y recorder. Immediately after the measurements, ferrocene (0.2 mmol dm^{-3}) ($E_{\frac{1}{2}}$ +0.083) was added as an internal standard, and the observed cathodic peak potential was corrected with reference to this standard. All the compounds exhibited common reversible reduction waves. The cathodic peak potentials $E_{\frac{1}{2}}$ are summarized in Table 2.

Determination of pK_a*s of Compounds* **2**, **13**, **14** *and* **5**.—Buffer solutions of slightly different acidities (pH 3.8–6.7) were prepared by mixing a citric acid solution (0.1 mol dm^{-3}) in 20% aqueous MeCN (1:4 by volume) and a solution of Na_2HPO_4 (0.2 mol dm^{-3}) in 20% aqueous MeCN, in various proportions. For the preparation of sample solutions, 1 cm^3 portions of the stock solution, prepared by dissolving 1 mg of the compound in MeCN (10 cm^3), were diluted to 10 cm^3 with the buffer solution. The UV–VIS spectrum was recorded for each compound in different solutions of buffers. Immediately after recording the spectrum, the pH of each sample solution was determined on a pH meter calibrated with standard buffers. The observed absorbance at a specific absorption wavelength (460 nm for **2**, 430 nm for **13**, 460 nm for **14** and 500 nm for **5**) of each compound was plotted against the pH to give a classical titration curve, whose midpoint was taken as the pK_a and summarized in Table 2.

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