

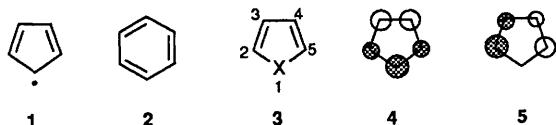
## Electron Spin Resonance Spectroscopy of Pyrrole Radical Cations

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The ESR spectra are reported for the radical cations of the following pyrrole derivatives in fluid solution: 2,5-di-*t*-butyl- and 2,5-diphenyl-pyrrole; *N*-amino-, *N*-phthalimido- and *N*-(4-amino-phenyl)-2,5-dimethylpyrrole; 1,4-bis-(2,5-dimethylpyrrol-1-yl)-, 1,4-bis-(2,5-diethylpyrrol-1-yl)-, and 1-(2,5-diethylpyrrol-1-yl)-4-(2,5-dimethylpyrrol-1-yl)-benzene; 1,4-bis-(2,5-dimethylpyrrol-1-yl)-2,3,5,6-tetramethylbenzene; 1,4-bis-(2,5-dimethylpyrrol-1-yl)butane, bis-(2,5-dimethylpyrrol-1-yl)methane, and bi-(2,5-dimethylpyrrol-1-yl); and 8b,8c-diazapyracyclene. The spectra are discussed in terms of the nuclear and electronic structures of the compounds.

A great deal of work has been published in recent years on the ESR spectroscopy of the homoannulene radicals,<sup>1a</sup> radical anions,<sup>1b</sup> and radical cations,<sup>1c</sup>  $(\text{CH})_n^{\bullet/+}$ . When  $n$  is an odd number these radicals are electrically neutral, but when  $n$  is even the neutral annulenes have a closed shell, and only the cations or anions formed by removal or addition of a  $\pi$ -electron are paramagnetic.



Within this family of annulene radicals, the cyclopentadienyl radicals **1** have been prepared mainly by the photolysis of the carbon-metal bond in organometallic derivatives of cyclopentadiene,  $\text{R}_n\text{C}_5\text{H}_{5-n}\text{M}$ , when  $n = 0, 1$  or  $2$ , and  $\text{M}$  is an organometallic group,<sup>2-5</sup> or of a carbon-hydrogen bond in the cyclopentadienes  $\text{R}_n\text{C}_5\text{H}_{6-n}$  when  $n = 3, 4$  or  $5$ .<sup>6,7</sup> The ESR spectra have been investigated when  $\text{R}_n = \text{Me}, \text{Et}, \text{Pr}^i, \text{Bu}^t, \text{Me}_2\text{-Me}_3, \text{Me}_4\text{Et}, \text{Me}_4\text{Pr}, \text{Me}_4\text{Bu}, \text{Me}_3\text{Et}_2, \text{R}'_3\text{Si}, \text{R}'_3\text{Ge}$  or  $\text{R}'_3\text{Sn}$ ,<sup>5</sup> and have been interpreted to provide a quantitative measure of the electronic effect of the substituents in breaking the orbital degeneracy of the  $\pi$ -electron system.<sup>5</sup>

The benzene radical anion **2**<sup>-</sup> can be prepared by reaction of benzene with sodium or potassium, and is long lived,<sup>1b</sup> but the radical cation **2**<sup>+</sup>,<sup>1c</sup> which is formed for example by oxidation with mercury(II) trifluoroacetate in trifluoroacetic acid (TFAH), rapidly reacts with its parent to form the dimer radical cation  $(\text{C}_6\text{H}_6)_2^{\bullet+}$  and then the biphenyl radical cation.<sup>8</sup> A lot of alkylbenzene radical cations  $(\text{R}_n\text{C}_6\text{H}_{6-n})^{\bullet+}$  ( $n = 3-6$ )<sup>1c</sup> and radical anions  $(\text{R}_n\text{C}_6\text{H}_{6-n})^{\bullet-}$  ( $n = 1$  or  $2$ ),<sup>1b</sup> have been observed in fluid solution, and again the ESR spectra have been interpreted in terms of the interaction between the substituents and the  $\pi$ -electron system.

Extensive studies have been reported on the ESR spectroscopy of the radical cations and anions of both condensed and non-condensed polycyclic aromatic hydrocarbons,<sup>1b,c</sup> and indeed many of the principles relating to matters such as the dependence of <sup>1</sup>H and <sup>13</sup>C hyperfine coupling (hfc) constants on spin densities, the restriction of rotation about Ar-Ar bonds, the interaction between parallel arene rings (in cyclophanes), and the aromatic substitution reactions undergone by arene radical cations, were developed with this family of compounds.

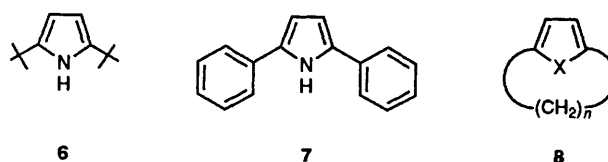
It was against this background that we set out to observe the ESR spectra of the radical cations of the hetero-5-annulenes **3**.<sup>9,10</sup> We found that, by a variety of methods, the ESR spectra of the radical cations of furans, thiophenes and pyrroles **3**;  $\text{X} = \text{O}, \text{S}$  or  $\text{NR}$  could readily be observed in fluid solution as long as

substituents were present in the 2- and 5-position to prevent polymerization. In all three families of compounds, the spectra show that the electronegative atom  $\text{X}$  lowers the energy of the  $\psi_B$  orbital **4** below that of the  $\psi_A$  orbital **5**, which are degenerate in the isoelectronic cyclopentadienyl radical **1**. The unpaired electron is therefore located principally in the  $\psi_A$  orbital, and shows a large hfc constant to substituents at the 2- and 5-position, and a small one to substituents at the 3- and 4-position. As the two molecular orbitals are no longer degenerate, the spectra are relatively insensitive to substituent effects. In the pyrrole radical cations, the nitrogen atoms lie in the nodal plane of  $\psi_A$  and hence show only a small hfc constant of 3-5 G.

We have chosen the pyrroles rather than the furans or thiophenes for a more thorough investigation of those factors which are familiar in the chemistry of the hydrocarbon radical cations,<sup>10</sup> because the pyrrole ring is present in many natural products, and because the 3-valent nitrogen makes it possible to vary the group  $\text{NR}$  in the same way that the group  $\text{CR}$  can be varied in hydrocarbon annulenes.

### Results and Discussion

*2,5-Dialkyl- and 2,5-Diaryl-pyrroles.*—In our previous paper<sup>9</sup> we reported the ESR spectra of 2,5-di-*t*-butylfuran [ $a(18\text{H})$  0.6,  $a(2\text{H})$  3.8 G,  $g$  2.0023] and of 2,5-di-*t*-butylthiophene [ $a(18\text{H})$  0.85,  $s(2\text{H})$  3.75 G,  $g$  2.0019]. Fig. 1 shows the spectrum of 2,5-di-*t*-butylpyrrole **6**, which can be simulated with the hfc constants  $a(18\text{H})$  0.62,  $a(2\text{H})$  3.58,  $a(\text{N})$  4.05 and  $a(1\text{H})$  0.91 G,  $g$  2.0025. The spectrum is best obtained by dissolution of the pyrrole in TFAH containing thallium(III) trifluoroacetate [ $\text{Tl}(\text{TFA})_3$ ], and under these conditions the spectrum can be observed for more than one week. In contrast, under the same conditions, the spectrum of 2,5-dimethylpyrrole can be observed for only 1 h, when the decay is presumably by loss of a proton from the methyl group. The similarity in the hfc constants of the corresponding furan, thiophene and pyrrole emphasizes the common occupancy by the unpaired electron of the  $\psi_A$  MO.



The spectrum which was obtained from 2,5-diphenylpyrrole **7** in TFAH- $\text{Tl}(\text{TFA})_3$  was too weak to be useful, but in TFAH- $\text{Hg}(\text{TFA})_2$  the spectrum shown in Fig. 2 was obtained. This shows satellites due to mercury hfc with  $a(^{199}\text{Hg})$  64.5 G; no satellites which should be observable if two  $^{199}\text{Hg}$  atoms

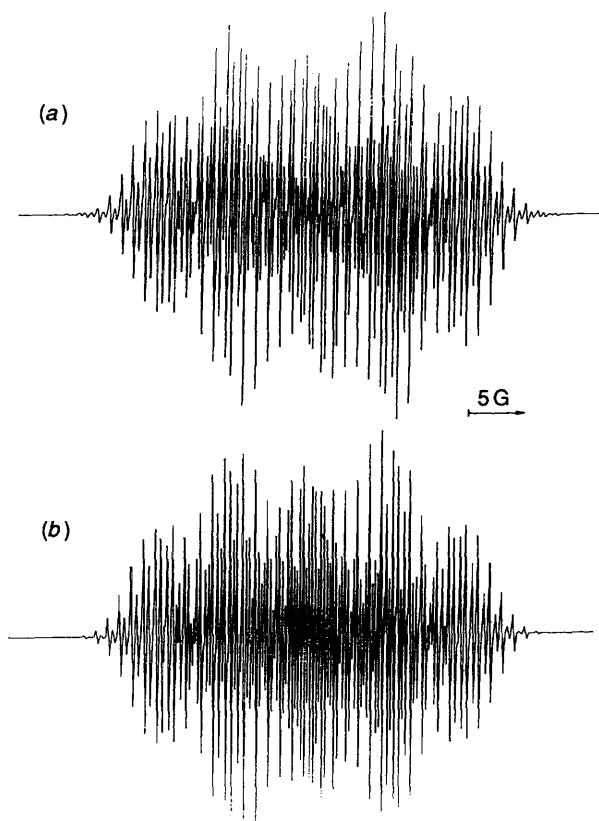


Fig. 1 (a) ESR spectrum of the 2,5-di-*t*-butylpyrrole radical cation  $6^{+\bullet}$  in TFAH at 260 K. (b) Computer simulation.

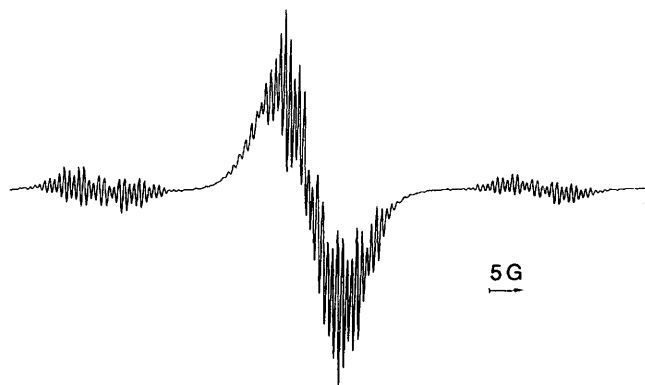


Fig. 2 ESR spectrum of the radical cation obtained from 2,5-diphenylpyrrole **7** in TFAH- $\text{Hg}(\text{TFA})_2$  at 260 K, showing  $^{199}\text{Hg}$  satellites

entered into coupling could be detected at increased gain. It appears therefore that a single mercurideprotonation has taken place, similar to that which we have observed for many aromatic hydrocarbons.<sup>11</sup>

In that work we showed that mercuriation always occurred at the position where  $a(\text{H})$  was largest, and that the ratio between the hfc constant of the incoming  $^{199}\text{Hg}$  and the outgoing  $^1\text{H}$  was always *ca.* 20.6; hence we calculate the value of  $a(\text{H})$  for the displaced proton in  $7^{+\bullet}$  to be *ca.* 3.13 G.

The radical cation of 2,5-diphenylfuran  $7^{+\bullet}$ ,  $\text{X} = \text{O}$  shows  $a(2\text{H})$  2.78 (3-, 4-H),  $a(2\text{H})$  2.41 and 2.42 (2-, 2'-H),  $a(2\text{H})$  0.69 and 0.77, (3-, 3'-H),  $a(2\text{H})$  3.38 G (4-, 4'-H) (implying restriction of rotation about the furan-phenyl bonds),<sup>12,13</sup> and that of 2,5-diphenylthiophene  $7^{+\bullet}$ ;  $\text{X} = \text{S}$  shows  $a(2\text{H})$  2.48 (3-, 4-H),  $a(4\text{H})$  2.42 (2-, 2'-H),  $a(4\text{H})$  0.73 (3-, 3'-H),  $a(2\text{H})$  3.48 G (4'-H) (implying free rotation about the thiophene-phenyl bonds).<sup>12</sup> The assignments to 3-H, 2-H and 2'-H may be interchanged; the

assignment of the largest hfc constant to the 4'-position is based on PM3/INDO calculations<sup>12</sup> and on studies of methyl- and chloro-substituted<sup>13</sup> diphenylfuran. Rather similar hfc constants are also obtained for 2,5-diphenylselenophene (in which there is free rotation about the selenophene-phenyl bonds), and in 2,5-diphenyltellurophene (in which rotation is restricted).<sup>12</sup>

We therefore assign the value of  $a(\text{H})$  3.31 G in 2,5-diphenylpyrrole to the *para* (4'-H) protons of the phenyl groups, and identify this as the site of mercuriation. This assignment is supported by the fact that we have observed no mercuriation in the radical cations of the 2,5-dialkylpyrroles. However, the presence of  $^{14}\text{N}$  hfc, and the fact that the monomermercuriation renders the molecule unsymmetrical, made the spectrum of the diphenylpyrrole radical cation too complicated for us to analyse it in detail.

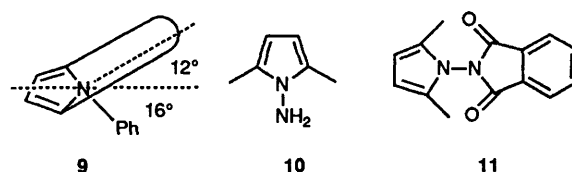
The radicals of the pyrrolophanes containing an oligomethylene loop between the 2- and 5-position are potentially interesting because the protons at the  $\alpha$ -methylene groups might be magnetically non-equivalent, and in principle it might be possible to determine the activation energy for the transit of the NR group through the loop in the radical cation from a variable-temperature ESR study.

The [8](2,5)pyrrolophanes **8** ( $\text{X} = \text{NH}$  and  $\text{X} = \text{NPh}$ )\* and the [8](2,5)furanophane **8** ( $\text{X} = \text{O}$ ) were therefore prepared, but unfortunately we were unable to observe any ESR spectrum when these compounds were subjected to the following oxidizing agents, all without and with the assistance of various degrees of photolysis: TFAH, TFAH- $\text{Hg}(\text{TFA})_2$ , TFAH-Tl(TFA)<sub>3</sub>, TFAH- $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_2$ - $\text{H}_2\text{SO}_4$ ,  $\text{SO}_2$ - $\text{FSO}_3\text{H}$ ,  $\text{SbCl}_5$ - $\text{CH}_2\text{Cl}_2$  and  $\text{AlCl}_3$ - $\text{CH}_2\text{Cl}_2$ .

All the other 2,5-dialkyl-pyrroles and -furans which we had handled previously<sup>9</sup> had readily shown spectra of the radical cations (though we report some further failures below), which might be taken to imply that there may be some structural feature about these heterocyclophanes which renders them atypical.

Dreiding models show that there must be a considerable amount of strain in these compounds, and further evidence for this revealed by a bathochromic shift of the  $\pi \rightarrow \pi^*$  UV absorption in compounds **8** ( $\text{X} = \text{NH}$ , O or S) and by anomalous  $^1\text{H}$  NMR signals for the methylene groups.<sup>14</sup>

A partial determination of the structure of compound **8** ( $\text{X} = \text{NPh}$ ) has been carried out by Povey and Smith,<sup>15</sup> and they find that the N-phenyl bond is bent by  $16.5^\circ$  out of the plane of the pyrrole ring, and that the bonds to the  $\alpha$ -methylene groups are bent away from the ring by  $12^\circ$  in the opposite direction, as shown in structure **9**. The  $\pi$ -electron system may therefore resemble that of an isolated 1,4-dialkylbuta-1,3-diene rather than a heteroarene, and we find that we need at least terminal tetraalkylation of butadiene before we can observe the spectra of radical cations under the conditions we have used for the compounds **8**.<sup>16</sup>



*N*-Amino- and *N*-Phthalimido-2,5-dimethylpyrrole.—*N*-Amino- and *N*-phthalimido-2,5-dimethylpyrrole, **10** and **11** respectively, are common intermediates in the preparation of

\* In ref. 10 these compounds were referred to in error as [10]pyrrolophanes.

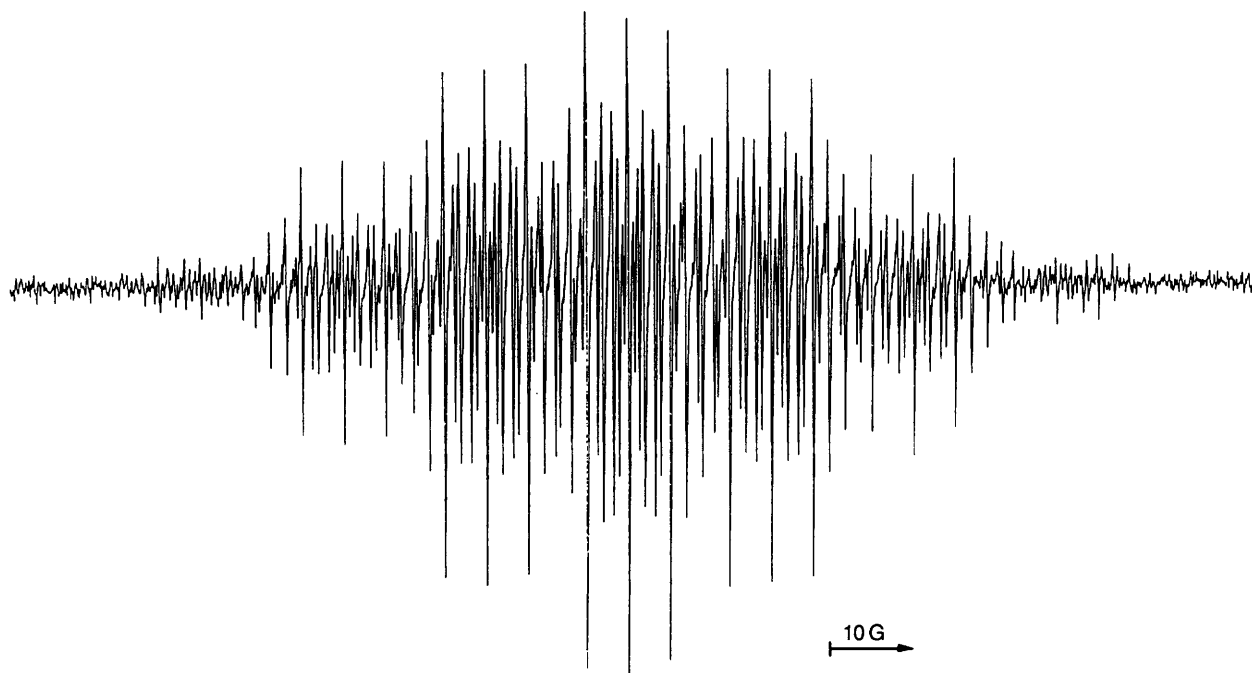


Fig. 3 ESR spectrum of *N*-amino-2,5-dimethylpyrrole radical cation  $10^{\bullet+}$  in TFAH at 260 K

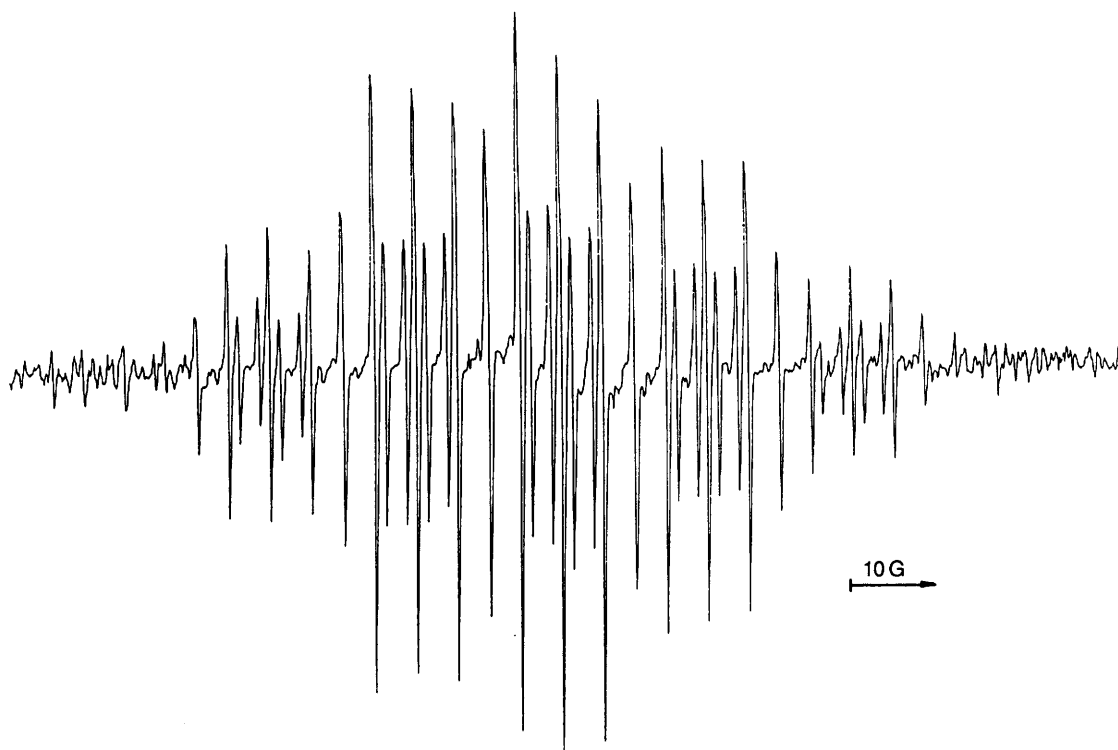


Fig. 4 ESR spectrum of the 2,5-dimethyl-*N*-phthalimidopyrrole radical cation  $11^{\bullet+}$  in TFAH-Tl(TFA)<sub>3</sub> at 260 K

*N,N'*-bipyrrolyl compounds, and it was interesting to determine whether the presence of the hydrazine moiety had any effect on the electron distribution in the corresponding radical cations.

The spectrum of radical cation  $10^{\bullet+}$ , which is formed when compound **10** is dissolved in TFAH-Tl(TFA)<sub>3</sub>, is shown in Fig. 3, and can be simulated with the hfc constants  $a(6H)$  16.10 (2Me),  $a(2H)$  3.60 (3-, 4-H),  $a(N)$  4.75 (N-1),  $a(N)$  1.75 (NH<sub>2</sub>),  $a(2H)$  1.75 (NH<sub>2</sub>) G,  $g$  2.0025. The coupling constants associated with the methyl groups, the ring protons, and the ring nitrogen atom, and the  $g$ -value, are close to the corresponding values in *N*,2,5-trimethylpyrrole (16.0, 3.3 and

4.2 G, and 2.0026 respectively). Clearly the hydrazine moiety exerts no significant perturbation on the electron distribution.

The spectrum of radical cation  $11^{\bullet+}$  is shown in Fig. 4, and shows a very similar spectrum to that of  $10^{\bullet+}$ , with  $a(6H)$  16.44 (2Me),  $a(2H)$  3.52 (3-, 4-H),  $a(N)$  4.70 (N-1) G,  $g$  2.0024, with no resolvable coupling to the phthalimido nitrogen. The phthalimido ring is probably orthogonal to the pyrrole ring, and this may account for the absence of hfc by the second nitrogen atom.

*N-Arylpyrroles*.—The radical cation of 2,5-dimethyl-*N*-

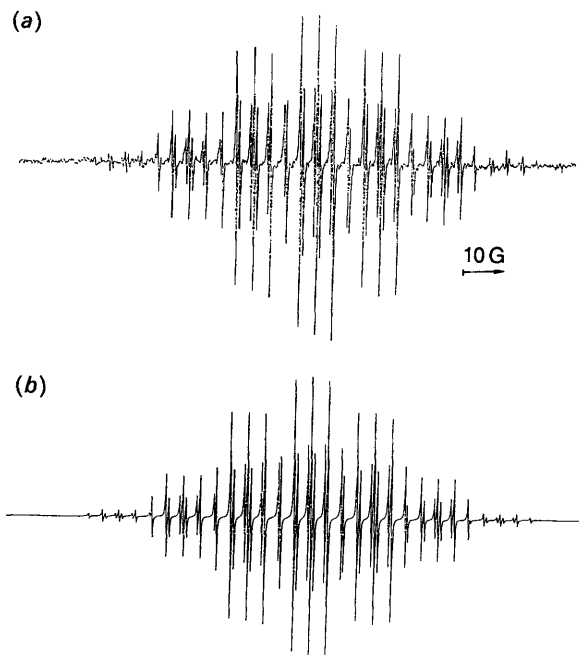
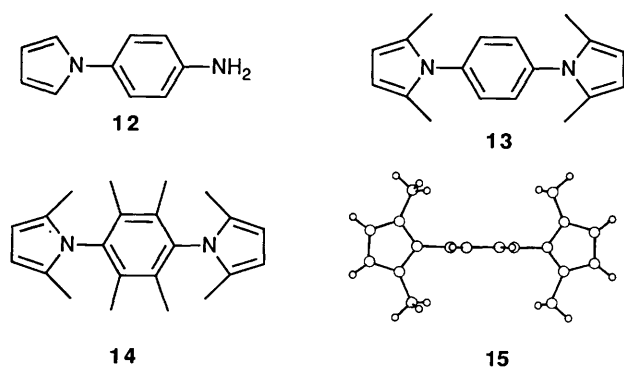


Fig. 5 (a) ESR spectrum of the 1,4-bis-(2,5-dimethylpyrrol-1-yl)benzene radical cation  $13^{+\cdot}$  in TFAH at 260 K. (b) Computer simulation.

phenylpyrrole shows the familiar spectrum of the 2,5-dimethylpyrrole moiety [ $a(6H)$  16.00 (2Me),  $a(2H)$  3.68 (3-, 4-H),  $a(N)$  4.32 G], with no detectable coupling to the protons of the phenyl group.<sup>9</sup> It seemed possible that an aminyl substituent might lower the ionization energy of the phenyl group below that of the pyrrole ring ( $E_i$  pyrrole 7.69 eV,  $PhNH_2$  7.7 eV) but *N*-(4-aminophenyl)-2,5-dimethylpyrrole **12** gave a radical cation with  $a(6H)$  16.40,  $a(2H)$  3.40,  $a(N)$  4.36 G,  $g$  2.0026.

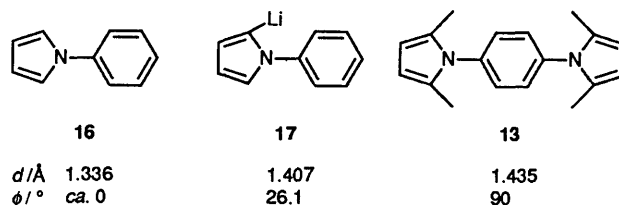
1,4-Bis-(2,5-dimethylpyrrol-1-yl)benzene **13** in TFAH-Tl(TFA)<sub>3</sub> shows a very similar spectrum (Fig. 5), with  $a(6H)$  16.20 (2Me),  $a(2H)$  3.50 (3-, 4-H),  $a(N)$  4.32 G,  $g$  2.0025, showing that the unpaired electron is confined to one pyrrolyl unit.



The ionization energies of 2,5-dimethylpyrrole and of 1,4-diaminobenzene are 7.69 and 7.15 eV respectively,<sup>17</sup> and if compound **13** is regarded as being composed of these units, it may seem surprising that electron loss to give the radical cation is confined to a pyrrole moiety with the higher ionization energy. The electron pair on the pyrrolic nitrogen atoms are less free than those on aminyl nitrogen atoms to conjugate with the central benzene ring, but even if this is tetramethylated to reduce its ionization energy further (1,4-diamino-2,3,5,6-tetramethylbenzene,  $E_i$  6.43 eV<sup>17</sup>), as in structure **14**, the electron loss is still restricted to one of the pyrrole rings, and species  $14^{+\cdot}$  shows  $a(6H)$  16.40,  $a(2H)$  3.52,  $a(N)$  4.28 G,  $g$  2.0025 (Fig. 6).

The reason for this behaviour becomes clear from an inspection of the crystal structure of compound **13**<sup>18</sup> which is

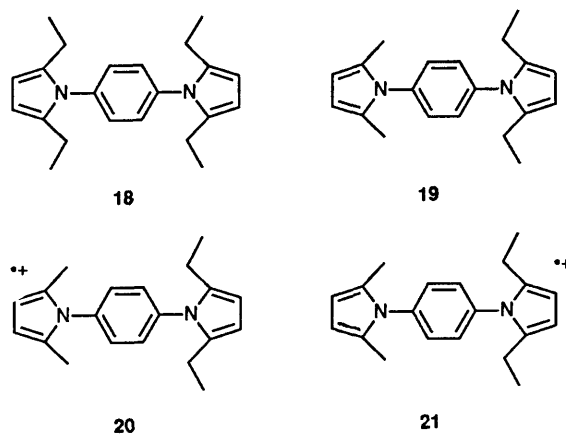
shown in structure **15**. The central benzene ring is orthogonal to the terminal pyrrole rings, and as the  $\pi$ -systems are similarly orthogonal, conjugative electron release from the nitrogen atoms into the benzene ring does not occur. Support for this is given by the structures of the compounds **16**,<sup>19</sup> **17**<sup>20</sup> and **13**<sup>18</sup> in which the N-Ar bond lengths ( $d$ ) increase as the dihedral angles ( $\phi$ ) between the rings increase.



The pyrrolic nitrogen atoms can therefore affect the arene ring only by inductive electron attraction so that it has a higher ionization energy than does the pyrrole ring. This is borne out by the photoelectron spectrum of 2,5-dimethyl-*N*-phenylpyrrole which shows ionization energies of 7.44, 8.39, 9.45 and 9.7 eV, which are assigned principally to the pyrrole  $\psi_A$ , pyrrole  $\psi_B$ , benzene  $\psi_S$  and benzene  $\psi_A$  MOs respectively.<sup>21</sup>

1,4-Bis-(2,5-diethylpyrrol-1-yl)benzene **18** in TFAH-Tl(TFA)<sub>3</sub> gave a radical cation with hfc constants  $a(4H)$  17.24,  $a(2H)$  3.60,  $a(N)$  4.22 G and  $g$  2.0025; in 2,5-diethyl-*N*-alkylpyrroles we observed values of  $a(4H)$  16.60–16.72,  $a(2H)$  3.44–3.66,  $a(N)$  4.00–4.32 G.<sup>9</sup>

1-(2,5-Diethylpyrrol-1-yl)-4-(2,5-dimethylpyrrol-1-yl)benzene **19** in TFAH-Tl(TFA)<sub>3</sub> at 260 K shows an ESR spectrum which resembles a superposition of the spectra of the 2,5-dimethylpyrrole and the 2,5-diethylpyrrole radical cations. Simulation of the spectrum shows that the dimethylpyrrole (**20**) and the diethylpyrrole (**21**) radical cations are present in the ratio 1:4, implying that electron release by the methyl groups destabilizes the SOMO 5 in species **20** more than do the ethyl groups in species **21**.



Using a different argument, we reached the same conclusion (that electron release by methyl is greater than by ethyl groups), by a comparison of the ESR spectra of the pentamethyl-, tetramethylethyl- and 1,3,5-trimethyl-2,4-diethyl-cyclopentadienyl radicals, which are isoelectronic with the pyrrole radical cations.<sup>5</sup> Again, on a rather different basis, Sakurai reached the same conclusion from a comparison of the spectra of the methyl- and ethyl-cyclopentadienyl radicals.<sup>22</sup> This effect is discussed in more detail in refs. 3 and 4.

*Bis(pyrrol-1-yl) compounds.*—Radical ions of compounds in which two  $\pi$ -electron systems are connected through alkyl chains are interesting because they provide evidence regarding the interaction of the two  $\pi$ -systems. Thus the radical cations

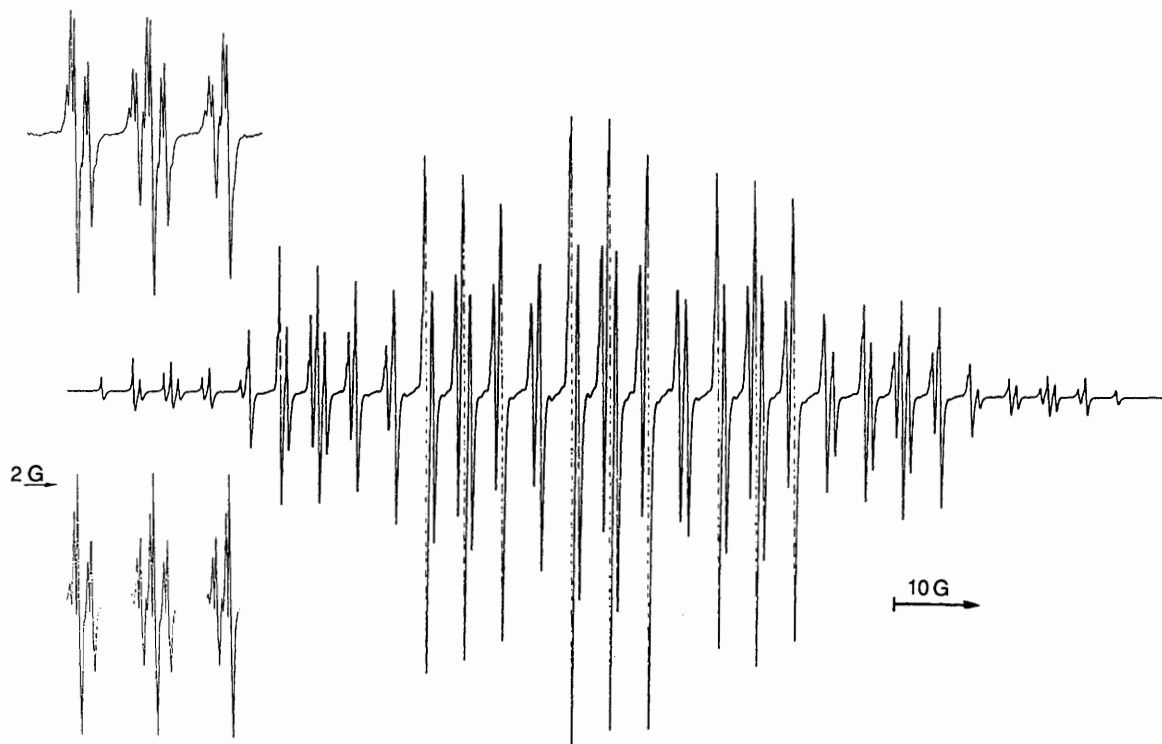
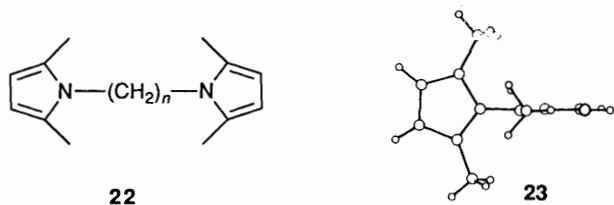


Fig. 6 ESR spectrum of the 1,4-bis-(2,5-dimethylpyrrol-1-yl)-2,3,5,6-tetramethylbenzene radical cation  $14^{+\bullet}$  in TFAH-Tl(TFA)<sub>3</sub> at 260 K. The inset shows second-order detail, and simulation, of the central multiplet.

of the bis-(9-anthryl)alkanes, Ar[CH<sub>2</sub>]<sub>n</sub>Ar, show that the electron vacancy is located in one anthracene unit when  $n = 1, 2$  or  $4$ , but is delocalized over both units when  $n = 3$ . In the corresponding radical anions,  $n = 2-4$ , the electron can be localized or delocalized depending on the polarity of the solvent.<sup>23</sup> We have previously described the ESR spectra of the radical cations of the  $\alpha,\omega$ -bis(pyrrol-1-yl)alkanes **22** where  $n = 2$  or  $3$ , and have found no delocalization of the unpaired electron between the two rings. When  $n = 3$ , the radical cation could be obtained using TFAH-Hg(TFA)<sub>2</sub>, but, rather surprisingly, when  $n = 2$  this method was unsuccessful, and oxidation had to be carried out with TFAH-Tl(TFA)<sub>3</sub>.



We have now extended the range of the compounds **22**. When  $n = 4$ , a rather poor spectrum of the radical cation was obtained in TFAH-Hg(TFA)<sub>2</sub> with photolysis; with TFAH-Tl(TFA)<sub>3</sub> in the dark a strong spectrum was obtained with  $a(6H) 15.92$ ,  $a(2H) 3.40$ ,  $a(N) 3.40$ ,  $a(2H) 0.90$  G: clearly the electron vacancy is still localized in one ring. Unfortunately, bis(pyrrol-1-yl)methane **22** ( $n = 1$ ) showed no spectrum when it was treated under a variety of oxidizing conditions [TFAH-Hg(TFA)<sub>2</sub>, TFAH-Tl(TFA)<sub>3</sub>, TFAH-H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, AlCl<sub>3</sub>-CH<sub>2</sub>Cl<sub>2</sub>, all with or without varying degrees of photolysis]. The reason for this dependence of the ease of oxidation on the value of  $n$  is by no means clear.

The bi(pyrrol-1-yl) radical cation  $22^{+\bullet}$  ( $n = 0$ ) is isoelectronic with the fulvalene radical anion for which the ESR spectrum shows that the SOMO can be regarded as a combination of two  $\psi_A$  cyclopentadienyl orbitals **5**.<sup>24</sup> In pyrrole, however, the  $\psi_A$  MO is lower in energy than the  $\psi_S$  MO, and *ab initio*

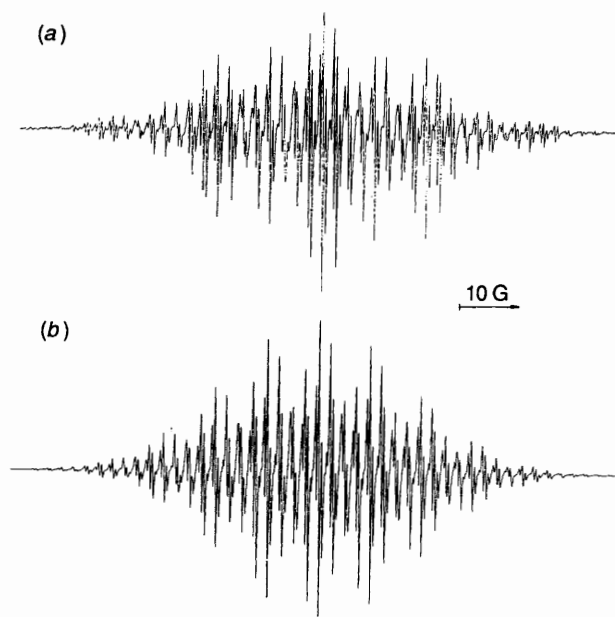


Fig. 7 (a) ESR spectrum of the bi(pyrrol-1-yl) radical cation  $23^{+\bullet}$  in TFAH at 260 K. (b) Computer simulation.

calculations suggests that the HOMO of bi(pyrrol-1-yl) can be represented as a combination of two  $\psi_S$  MOs.<sup>25</sup> The situation is complicated, however, by the fact that whereas fulvalene is planar, the presence of the methyl groups which we need in bi(pyrrol-1-yl) to render the radical cation persistent, also preclude the planarity of the molecule. Chang and Adams showed in 1931 that 2,2',5,5'-tetramethylbi(pyrrol-1-yl)-3,3'-dicarboxylic acid could be resolved into optical isomers,<sup>26</sup> and we have found that in the crystal the two rings in bi(pyrrol-1-yl) are mutually perpendicular to within experimental error, as shown in structure **23**.<sup>18</sup>

In TFAH-Hg(TFA)<sub>2</sub> from 200–270 K, bi(pyrrol-1-yl) gave

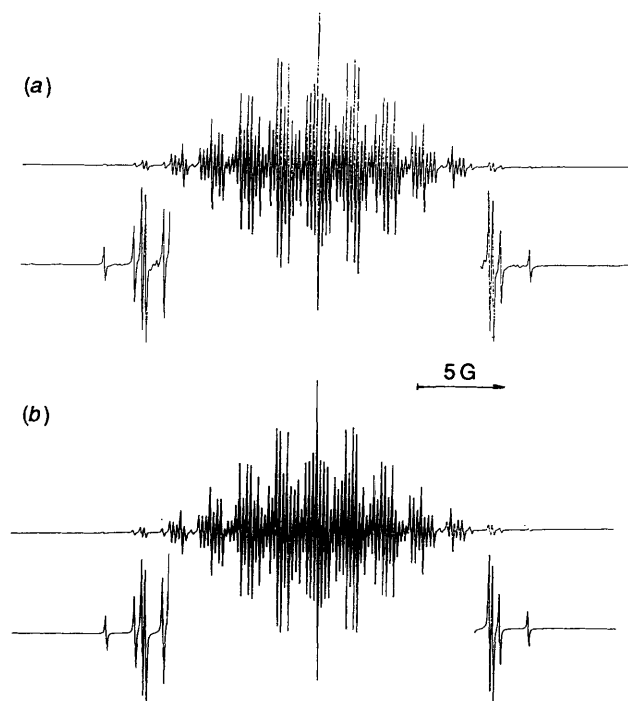
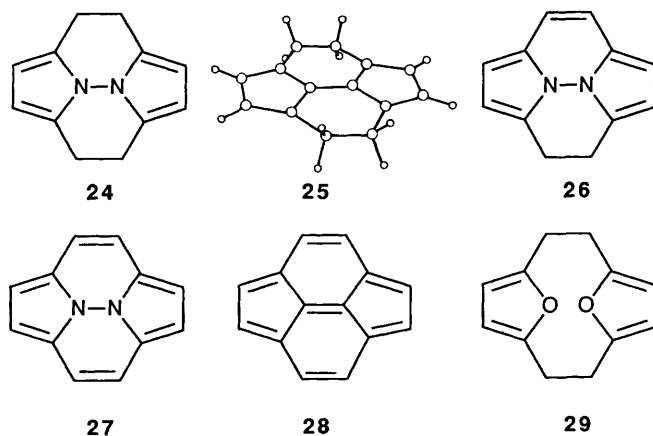


Fig. 8 (a) ESR spectrum of the 8*b*,8*c*-diazapyracyclene radical cation  $27^{+}$  in TFAH at 260 K. (b) Computer simulation.

the strong spectrum of the radical cation shown in Fig. 7, which can be simulated using the hfc constants  $a(12\text{H})$  8.32,  $a(4\text{H})$  1.79,  $a(2\text{N})$  3.40 G,  $g$  2.0026. MO calculations suggest that the unpaired electron should be located in the  $\psi_A$  orbital of one ring, and our spectrum would be compatible with this model, with the electron in rapid exchange between the two rings.

**Diazapyracyclenes.**—As the tetramethylbi(pyrrol-1-yl) **22** ( $n = 0$ ) had the orthogonal structure **23** we were interested in investigating a polycyclic bipyrrolyl in which the pyrrole rings might be held coplanar. 3,4,7,8-Tetrahydro-8*b*,8*c*-diazapyracyclene **24** appeared to offer this possibility, and indeed a single-crystal X-ray study showed that the two rings are coplanar within 0.004 Å as shown in structure **25**.<sup>18</sup> Unfortunately we were not able to observe the spectrum of a radical cation when compound **24** was treated with a variety of oxidizing agents [ $\text{H}_2\text{SO}_4$  with or without  $\text{SO}_2$ ; TFAH with or without  $\text{Hg}(\text{TFA})_2$ ,  $\text{Ti}(\text{TFA})_3$ , or  $\text{H}_2\text{SO}_4$ ;  $\text{AlCl}_3\text{-CH}_2\text{Cl}_2$ ;  $\text{SbCl}_5\text{-CH}_2\text{Cl}_2$ ; all with and without photolysis]. It may be that the radical cation  $24^{+}$  rapidly undergoes deprotonation because the C–H bonds are nearly coparallel with the axis of the  $\pi$ -system. Indeed, work-up of a solution of compound **24** in



TFAH– $\text{Hg}(\text{TFA})_2$  yielded substrate **24** and the corresponding 3,4-dihydro compound **26** in approximately equal amounts, but it is surprising that we could not then observe, starting from compound **24**, the spectrum of the species  $26^{+}$  or perhaps that of the parent diazapyracyclene **27**.

8*b*,8*c*-Diazapyracyclene itself **27** readily afforded a good spectrum of its radical cation  $27^{+}$  (Fig. 8), which was much stronger with TFAH– $\text{Hg}(\text{TFA})_2$  than with TFAH– $\text{Ti}(\text{TFA})_3$ . The spectrum can be simulated using the hfc constants  $a(4\text{H})$  2.22 (3-, 4-, 7-, 8-H),  $a(4\text{H})$  2.44 (1-, 2-, 5-, 6-H),  $a(2\text{N})$  1.77 G,  $g$  2.0027. The assignment of the proton hfc constants is tentative and is based on an INDO calculation which gives  $a(4\text{H})$  1.63 (3-, 4-, 10-, 11-H),  $a(4\text{H})$  1.86 (6-, 7-, 13-, 14-H),  $a(2\text{N})$  1.22 G. The radical anion of pyracyclene **28**, which is isoelectronic with the radical cation of compound **27**, shows a similar electron distribution, with the corresponding values of the hfc constants being  $a(4\text{H})$  2.52 and 1.88 G.<sup>27</sup> It is interesting that attempts to generate the radical anion of pyracyclene have been unsuccessful.<sup>28</sup>

When the radical cation of the diazapyracyclene **27** was generated in TFAH– $\text{Hg}(\text{TFA})_2$ , mercurideprotonation occurred, and satellites due to mercury coupling could be observed, with  $^{199}\text{Hg}$  48 G (Fig. 9), but we were not able to analyse the spectrum completely. The mercuriated species had a characteristically low  $g$ -value of 2.0004. Our rules<sup>11</sup> that mercuriation should occur at the position of highest spin density, and that  $a(\text{Hg})/a(\text{H})$  should be  $\sim 20.6$ , imply that  $a$  for the displaced proton should be  $\sim 2.33$  G. This could refer to either type of peripheral proton, and as the spin density is fairly evenly distributed around the ring, it may be that mercurideprotonation occurs at both types of position.

[2.2](2,5)*Furanophane* **29**.—The tetrahydrodiazapyracyclene **24** was prepared through [2.2](2,5)furanophane **29**. The crystal structure of compound **29** is in the literature:<sup>29</sup> the oxygen atoms are displaced out of the plane containing the furan carbon atoms by 0.085 Å, and the methylene groups are displaced in the opposite direction by 0.4 Å. The ionization energy is only 7.50 eV,<sup>30</sup> and as 2,5-dialkylfurans usually readily show the ESR spectra of their radical cations, we expected to be able to observe the spectrum of the species  $29^{+}$ . However, treatment of compound **29** with all of the reagents used above for the tetrahydrodiazapyracyclene failed to yield any spectrum. The reason for this failure again is not obvious.

**Conclusions.**—The ESR spectra which we have observed are unexceptional, and can readily be correlated with the nuclear and electronic structures of the radical cations on the basis of the principles which have been developed for homoarene radical ions. The surprising aspect of this work is the number of compounds for which we have not been able to observe ESR spectra, although we have tried all the usual chemical methods for one-electron oxidation including those which are successful for closely related pyrrole derivatives. Molecular distortion may be invoked to excuse the failure with the pyrrolophanes **8** ( $\text{X} = \text{NH}$  or  $\text{NPh}$ ) and the furanophane **8**;  $\text{X} = \text{O}$ , but it is not easy to understand why we could observe no spectrum from the bis(pyrrol-1-yl)methane **22** ( $n = 1$ ) whereas the bis(pyrrol-1-yl)alkanes **22** ( $n = 0$  or 2–4) provided strong spectra, and why we were similarly unsuccessful with the tetrahydropyracyclene **24**, the dihydropyracyclene **26**, and the furanophane **29**.

## Experimental

**Spectroscopy.**—NMR spectra were recorded in  $\text{CDCl}_3$  on a Varian XL-200 or VXR-400 instrument with  $\text{SiMe}_4$  as internal standard. Mass spectra were recorded on a VG7070H instrument. ESR spectra were recorded using a Varian E109 or

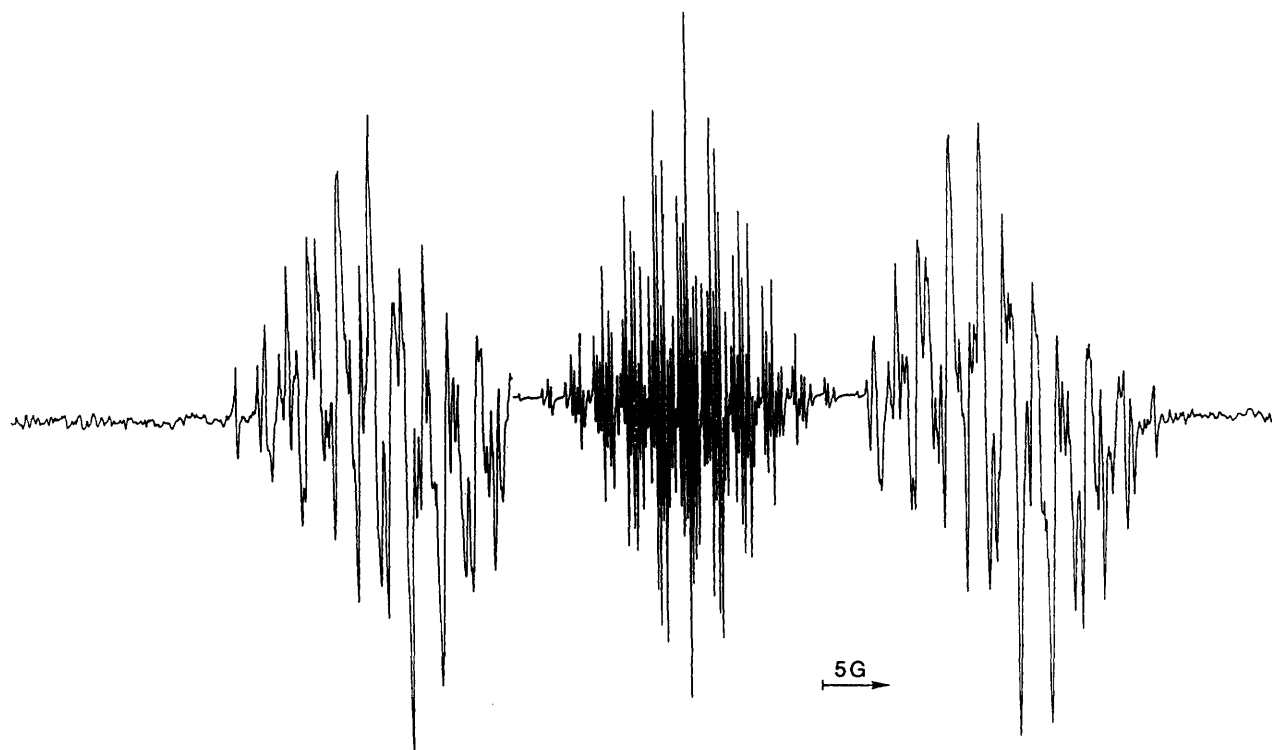


Fig. 9 ESR spectrum obtained from 8b,8c-diazapyracyclene **27** in TFAH-Hg(TFA)<sub>2</sub> at 260 K showing (at increased gain) the <sup>199</sup>Hg satellites

Bruker ESR300 instrument operating at *ca.* 9.1 GHz, fitted with a 500 W high-pressure mercury lamp, focused on the cavity by using a fused silica condensing lens. The intensity of the light was attenuated with neutral (metal gauze 3, 10 and 30% transmittance) and glass filters (soda and Pyrex glass).

Samples were prepared in Suprasil silica tubes; the following procedures are typical.

(1) A mixture of TFAH (1 cm<sup>3</sup>) and either Hg(TFA)<sub>2</sub> or Tl(TFA)<sub>3</sub> (~10 mg) at ~260 K was purged of oxygen by bubbling nitrogen through the solution (*ca.* 2 min). The substrate (0.05–10 mg) was added in TFAH or CH<sub>2</sub>Cl<sub>2</sub> and the mixture was degassed with nitrogen for a further minute.

(2) A mixture of CH<sub>2</sub>Cl<sub>2</sub> (1 cm<sup>3</sup>) and either AlCl<sub>3</sub> or SbCl<sub>5</sub> (~10 mg) at ~190 K was purged of oxygen by bubbling nitrogen through the mixture (*ca.* 2 min). The substrate (0.05–10 mg) was added in CH<sub>2</sub>Cl<sub>2</sub> and the solution was degassed for a further minute.

(3) SO<sub>2</sub> (0.5 cm<sup>3</sup>) and HFSO<sub>4</sub> (0.5 cm<sup>3</sup>) ~190 K were purged of oxygen by bubbling nitrogen through the mixture (*ca.* 2 min). The substrate (0.05–10 mg) was added in CH<sub>2</sub>Cl<sub>2</sub> and the solution was degassed for a further minute.

*MO Calculations.*—Calculations were carried out on a Vax 6310 computer using the MOPAC 5 programs.

*Substrates.*—The following intermediates and products were prepared by literature methods and showed the reported m.p. or b.p. and satisfactory NMR spectra: 2,2,7,7-tetramethyloctane-3,6-dione,<sup>31</sup> 2,5-di-*t*-butylpyrrole **6**,<sup>32</sup> 2,5-diphenylpyrrole **7**,<sup>33</sup> cyclodecane-1,4-dione,<sup>34</sup> [8](2,5)pyrrolophane **8** (X = NH, *n* = 8),<sup>14b</sup> 10-phenyl[8](2,5)pyrrolophane, **8** (X = NPh, *n* = 8),<sup>14b</sup> [8](2,5)furanophane **8** (X = O; *n* = 8),<sup>14b</sup> octane-3,6-dione,<sup>9</sup> *N*-amino-2,5-dimethylpyrrole **10**,<sup>35</sup> *N*-phthalimido-2,5-dimethylpyrrole **11**,<sup>35</sup> 1,4-bis-(2,5-dimethylpyrrol-1-yl)benzene **13**,<sup>36</sup> 2,2',5,5'-tetramethylbi(pyrrol-1-yl) **22** (*n* = 0),<sup>35</sup> 3,4,7,8-tetrahydro-8b,8c-diazapyracyclene **24**,<sup>37</sup> 3,4-dihydro-8b,8c-diazapyracyclene **26**,<sup>37</sup> bicyclo[8.2.0]dodecan-1-ol<sup>34</sup> and diazapyracyclene **27**.<sup>37</sup>

New compounds were prepared as follows.

**1-Amino-4-(2,5-dimethylpyrrol-1-yl)benzene 12.**—A mixture of 1,4-diaminobenzene (1.89 g, 17.54 mmol), hexane-2,5-dione (1.00 g, 8.77 mmol) and conc. hydrochloric acid (0.2 cm<sup>3</sup>) in ethanol (50 cm<sup>3</sup>) was heated to reflux for 1 h. After cooling, the mixture was neutralized with a slight excess of sodium carbonate, water was added, and the mixture was extracted with diethyl ether. The crude solid which was obtained on work-up of the extract was sublimed at 120 °C and 0.1 mmHg, to yield *compound 12* (0.74 g, 22%), m.p. 98 °C (from aq. EtOH) (Found: C, 77.4; H, 7.5; N, 14.8. C<sub>12</sub>H<sub>14</sub>N<sub>2</sub> requires C, 77.38; H, 7.58; N, 14.83%; δ<sub>H</sub>(200 MHz; CDCl<sub>3</sub>) 1.98 (6 H, s, Me), 3.69–3.79 (2 H, s, NH<sub>2</sub>), 5.85 (2 H, s, -CH=), 6.65–6.74 (2 H, m, ArH) and 6.90–7.00 (2 H, m, ArH).

**1,4-Bis-(2,5-dimethylpyrrol-1-yl)-2,3,5,6-tetramethylbenzene 14.**—A mixture of 1,4-diamino-2,3,5,6-tetramethylbenzene (1.64 g, 10 mmol), hexane-2,5-dione (2.28 g, 20 mmol) and conc. hydrochloric acid (0.2 cm<sup>3</sup>) in ethanol (50 cm<sup>3</sup>) was heated to reflux for 1 h. The product was isolated as above, to yield *compound 14* (1.98 g, 62%), m.p. 189 °C (from EtOH) (Found: C, 82.1; H, 8.9; N, 8.8%; M<sup>+</sup>, 320.222. C<sub>22</sub>H<sub>28</sub>N<sub>2</sub> requires C, 82.45; H, 8.81; N, 8.74%; M, 320.2252; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 1.83 (12 H, s, Me), 1.88 (12 H, s, Me) and 5.96 (4 H, s, CH=).

**1,4-Bis-(2,5-diethylpyrrol-1-yl)benzene 18.**—A mixture of 1,4-diaminobenzene (0.80 g, 7.02 mmol), octane-3,6-dione (1.00 g, 7.02 mmol) and conc. hydrochloric acid (0.1 cm<sup>3</sup>) in ethanol (25 cm<sup>3</sup>) was heated to reflux for 1 h. The crude product, dissolved in dichloromethane, was filtered through silica to yield *compound 18* (1.1 g, 49%), m.p. 278 °C (from EtOH) (Found: C, 82.2; H, 8.75; N, 8.7. C<sub>22</sub>N<sub>2</sub>H<sub>28</sub> requires C, 82.45; H, 8.81; N, 8.74%; δ<sub>H</sub>(200 MHz; CDCl<sub>3</sub>) 1.13 (12 H, t, <sup>3</sup>J 7.6, Me), 2.40 (8 H, q, CH<sub>2</sub>), 5.99 (4 H, s, -CH=) and 7.31 (4 H, s, ArH).

**1-(2,5-Diethylpyrrol-1-yl)-4-(2,5-dimethylpyrrol-1-yl)benzene 19.**—A mixture of 1-amino-(2,5-dimethylpyrrol-1-yl)benzene (10.1 g, 0.53 mmol), octane-3,6-dione (0.076 g, 0.53 mmol) and

conc. hydrochloric acid (0.1 cm<sup>3</sup>) in ethanol (5 cm<sup>3</sup>) was heated to reflux for 1 h. The product was isolated as above to yield **compound 19** (0.077 g, 52%), m.p. 192 °C (from EtOH) (Found: C, 81.8; H, 8.25; N, 9.5. C<sub>20</sub>H<sub>24</sub>N<sub>2</sub> requires C, 82.13; H, 8.27; N, 9.58%);  $\delta_{\text{H}}$ (200 MHz; CDCl<sub>3</sub>) 1.10 (6 H, t, <sup>3</sup>J 7.4, Me), 2.08 (6 H, s, Me), 2.36 (4 H, q, MeCH<sub>2</sub>), 5.94 [2 H, s, -CH= (MePy)], 5.99 [2 H, s, -CH= (EtPy)] and 7.29 (4 H, s, ArH).

**1,4-Bis-(2,5-dimethylpyrrol-1-yl)butane 22** (*n* = 4).—1,4-Diaminobutane (0.882 g, 10 mmol) in diethyl ether (5 cm<sup>3</sup>) was mixed thoroughly with Montmorillonite clay K10 (4 g) and the solvent was then removed under reduced pressure. Hexane-2,5-dione (2.28 g, 20 mmol) was then added dropwise to the stirred mixture at ~0 °C. After 24 h at ~20 °C, the product was extracted into dichloromethane and the extract was quickly filtered through silica to yield **compound 22**; *n* = 4 (2.39 g, 96%), m.p. 140 °C (from EtOH) (Found: C, 78.7; H, 10.1; N, 11.4. C<sub>16</sub>H<sub>24</sub>N<sub>2</sub> requires C, 78.64; H, 9.90; N, 11.43%);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 1.62–1.67 (4 H, m, CH<sub>2</sub>), 2.20 (12 H, s, Me), 3.69–3.74 (4 H, m, NCH<sub>2</sub>) and 5.75 (4 H, s, -CH=).

**Bis-(2,5-dimethylpyrrol-1-yl)methane 22** (*n* = 1).—*n*-Butyllithium (20 cm<sup>3</sup>; 2.5 mol dm<sup>-3</sup> in cyclohexane) was added under nitrogen to a stirred solution of 2,5-dimethylpyrrole (4.76 g, 50 mmol) in diethyl ether (30 cm<sup>3</sup>)–hexamethylphosphoric triamide (HMPA) (30 cm<sup>3</sup>). The ether and cyclohexane were distilled off, and the resulting lithium pyrrolate solution was added slowly at 25 °C to a stirred mixture of HMPA (30 cm<sup>3</sup>) and dichloromethane (30 cm<sup>3</sup>). After 15 h the mixture was extracted with a mixture of diethyl ether and saturated aq. sodium carbonate (1 : 1; 200 cm<sup>3</sup>). The ethereal phase yielded the crude product, which was taken up in dichloromethane and the solution was quickly filtered through silica to yield the **title product 22**; *n* = 1 (1.92 g, 38%), m.p. 123.5 °C (from EtOH) (Found: C, 77.0; H, 8.7; N, 13.9. C<sub>13</sub>H<sub>18</sub>N<sub>2</sub> requires C, 77.18; H, 8.97; N, 13.85%);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 2.06 (12 H, s, Me), 5.73 (2 H, s, CH<sub>2</sub>) and 5.78 (4 H, s, =CH-).

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