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Synthesis and redox properties of ferrocenylquinoxalines

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Abstract—The ferrocenyl 1,2-diketone [$(C_5H_5)Fe(C_5H_4)COCOPh$] when condensed with aromatic 1,2-diamines forms a range of ferrocenyl-substituted quinoxalines: when the diamine is unsymmetrically substituted the quinoxaline is formed as a mixture of two regio-isomers, which can in some cases be separated by careful chromatography. Electrochemical studies show that these present ferrocenylquinoxalines undergo the expected reversible one-electron oxidation centred on the ferrocenyl moiety and a two-electron reduction process centred on the quinoxalyl fragment, which is accompanied by chemical complications. The oxidation of the ferrocenyl group occurs at potentials slightly higher than that of unsubstituted ferrocene (by about 100–150 mV, depending on the substituents) indicating that the quinoxalyl substituent is slightly electron-withdrawing with respect to ferrocene.

Keywords: cyclic voltammetry; electrochemistry; ferrocene; quinoxaline.

INTRODUCTION

The reaction between 1,2-diketones and 1,2-diamines to form quinoxalines, well-known as a characteristic reaction for both components, has been successfully exploited as a polymer-forming process when applied to combinations of bis(1,2-diketones) and bis(1,2-diamines) [1–3]. For polymer synthesis, the reaction can generally be performed under solvent-free (melt-phase) conditions, when the sole by-product is water which distills from the reaction mixture at the melting temperature of the components. It is the removal of the water by-product, along with the *in situ* formation of new heteroaromatic rings, which drives the process to completion. The effectiveness of this reaction [1–3] makes it an attractive route for the synthesis of organometallic polymers, for example by reaction of 1,1′-ferrocenediylbis(1,2-diketones) with bis(1,2-diamines). We have recently described effective routes to a range of ferrocenyl 1,2-diketones [4, 5] and here we present the results of a study of reactions of a representative ferrocenyl diketone, FcCOCOPh [4, 6] [$Fc = (C_5H_5)Fe(C_5H_4)$] with a range of 1,2-diamines, to form the corresponding ferrocenylquinoxalines, along with an electrochemical study of their redox properties. Monomeric ferrocenylquinoxalines are themselves potentially of interest and importance: a number of quinoxalines are powerful antibiotics and some examples show potential as anti-cancer drugs [7] and their action in this respect is dependent on their binding to DNA by intercalation [8]. At the same time, some rather simple ferricinium salts have been shown to exhibit powerful anti-tumour activity against a range of human tumour types [9]: the introduction of ferrocenyl substituents onto the quinoxaline framework could perhaps provide, in a single molecular species, a powerful combination of these two actions.

RESULTS AND DISCUSSION

Syntheses of ferrocenylquinoxalines

Reaction of 1-ferrocenyl-2-phenylethanedione, FcCOCOPh, **1**, with 1,2-diaminobenzene, **2**, yields the corresponding 2-ferrocenyl-3-phenylquinoxaline, **3**. When the reaction is conducted in the absence of solvent by melting together the two components under

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an inert atmosphere, the yield of the deep-purple product is generally somewhat less than 50%, after chromatographic purification. However, if the two reactants are first mixed in dioxan solution and then slowly heated first in solution and, subsequently, after all the solvent has evaporated, as a melt, the yield of purified product is consistently around 65%.

The product **3** is readily characterised by its analytical data and its ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum contains, as well as characteristic signals from the monosubstituted ferrocenyl fragment, well-separated resonances arising from the phenyl and quinoxalyl fragments: the ^{13}C spectrum again shows the characteristic resonances from the ferrocenyl fragment, together with seven CH and five quaternary resonances in the aromatic region. A single-crystal X-ray diffraction analysis of **3**, prepared in this manner, has been published [10]. Because of the significantly enhanced yield obtained when the reactants were first heated in dioxan (b.p. 101°C) prior to the melt-phase condensation, the reactions of **1** with other aromatic 1,2-diamines were all conducted under similar conditions; in all these reactions, the choice of solvent was influenced by a combination of reactant solubility and solvent volatility. As with compound **3**, nearly all the resulting quinoxalines were isolated after chromatography on silica or alumina as hydrates, either monohydrates or hemihydrates.

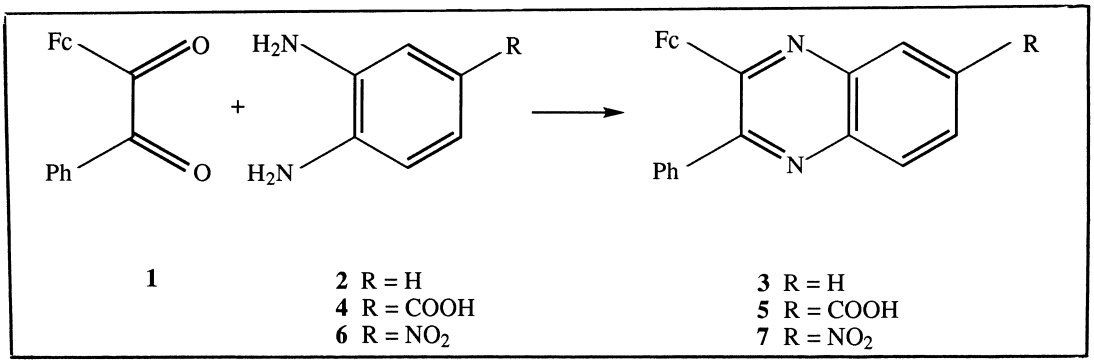
Thus, when the ferrocenyl diketone **1** was reacted with 3,4-diaminobenzoic acid **4**, initially in chlorobenzene (b.p. 132°C), the quinoxaline **5** was obtained in *ca.* 80% yield after chromatographic purification. However, both the ^{1}H and ^{13}C NMR spectra indicated the presence of the two regio-isomers **5a** and **5b**, arising from the alternative orientations of the reactants in the condensation process: integration of the ^{1}H spectrum in the ferrocenyl region indicated a major:minor isomer ratio of 2:1.

No chromatographic conditions could be found under which the isomers were separable and consequently the assignment of the major and minor isomers as either **5a** or **5b** was not possible. However, it was possible, despite some peak overlap, to analyse completely for each isomer the quinoxalyl region of the ^{1}H NMR spectrum in terms of an ABX pattern having a J_{AX} ($= {}^5J_{HH}$) of zero. Similarly, with the 4-nitrodiamine **6**, the two regio-isomers **7a** and **7b** of the corresponding nitroquinoxaline are formed, with in this case a major:minor isomer ratio of 3:1; again, the quinoxalyl region of the ^{1}H NMR spectrum was analysed in terms of two ABX patterns each with a J_{AX} of zero.

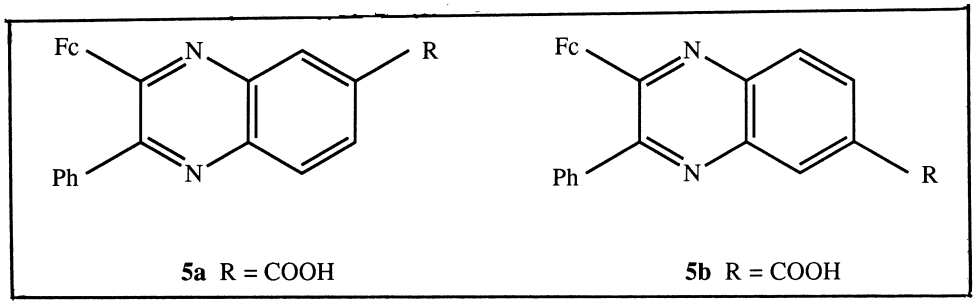
From the condensation of the diketone **1** with 2,3-diaminotoluene, again a mixture of two regio-isomers **8a** and **8b** was formed, with a major:minor ratio of 3:2 as judged from the ^{1}H NMR spectrum, but on this occasion the two isomers were separable by careful chromatography on silica. On the other hand, the two regio-isomers **9a** and **9b** obtained using 2,3-diaminopyridine were not separable on silica, but were found to be separable on alumina provided that pure dichloromethane was employed as eluent: even the slightest increase in the polarity of the mobile phase caused the isomers to elute together.

In the quinoxaline-forming condensations involving substituted diamines, the modest regio-selectivity is determined by the relative nucleophilicities of the two amino groups in the diamine component, and the relative electrophilicities of the two carbonyl carbon atoms in the diketone **1**. It is assumed that the more nucleophilic amino group reacts faster with the more electrophilic carbonyl. In diamines **4** and **6**, in which the substituent R is electron-withdrawing, the amino group *meta* to R will be the more nucleophilic, while the carbonyl adjacent to the phenyl ring in **1** will be the more electrophilic, because of the strong electron-donating character of the ferrocenyl fragment. Hence, it is to be expected that **5b** is the more abundant isomer of **5**; similarly for **7**, the ferrocenyl fragment is preferentially *para* to the deactivating substituent. In 2,3-diaminotoluene, the amino group *ortho* to methyl is the more nucleophilic, so that **8b** is expected to predominate, while the strong deactivation of the 2-amino group in 2,3-diaminopyridine leads to the expectation of **9a** as the major isomer.

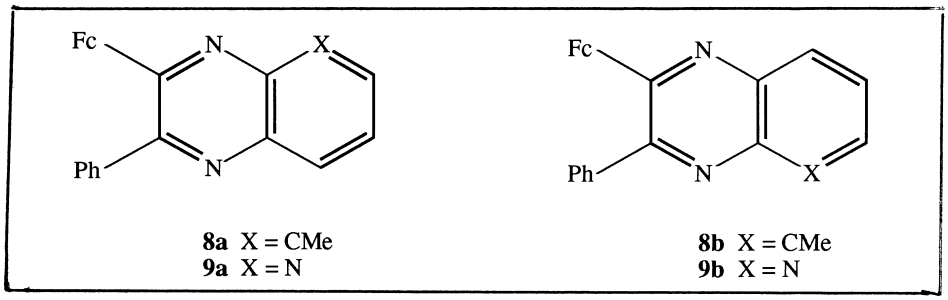
Use of the bis-1,2-diamine, **10**, under the reaction conditions employed for the formation of quinoxalines **3**, **5**, **7**, **8** and **9** and using dioxan as solvent



1 **2** R = H; **4** R = COOH; **6** R = NO_2 **3** R = H; **5** R = COOH; **7** R = NO_2



5a R = COOH **5b** R = COOH



8a X = CMe
9a X = N

8b X = CMe
9b X = N

gave, as a mixture of regio-isomers, the expected bis-product **11**. However, when the ferrocenyl diketone **1** and the bis-diamine **10** were reacted together in alkaline aqueous solution [11], the predominant product was the monoquinoxaline **12**, accompanied by only a trace of **11**.

Electrochemistry

Figure 1, which refers to compound **3**, shows the typical cyclic voltammogram exhibited by the present compounds in dichloromethane solution. Both an oxidation process possessing features of chemical reversibility and an apparently irreversible reduction process, which is about twice greater in height than the oxidation step, are apparent.

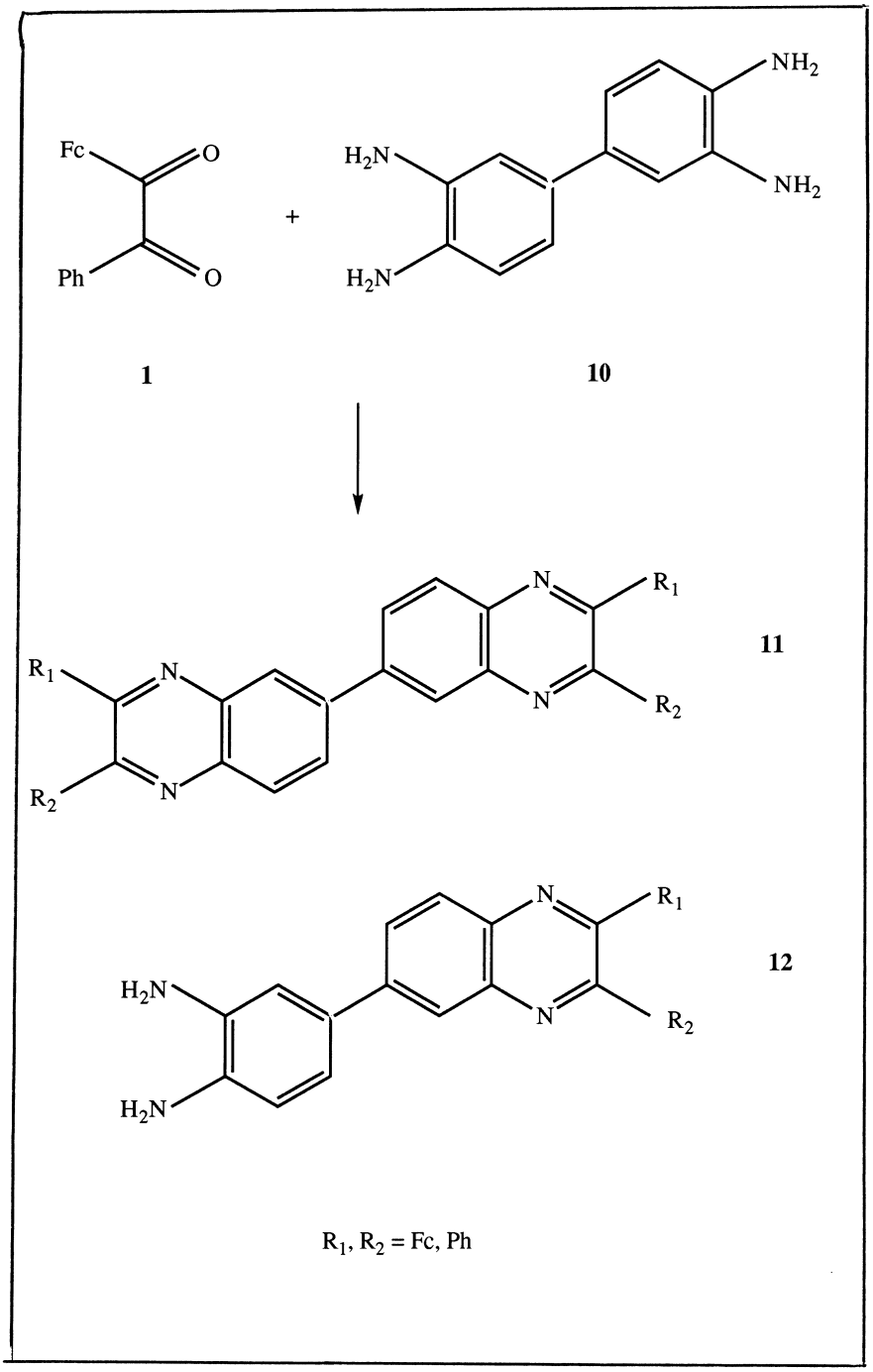
Controlled-potential coulometric investigation of the anodic process ($E_w = +0.7$ V) show the consumption of one electron/molecule. Upon exhaustive one-electron oxidation the original ruby-red solution of **3** turns jade-green and displays an absorption in the visible region at $\lambda_{max} = 692$ nm. In confirmation of the chemical reversibility of the ferrocene/ferricenium oxidation, cyclic-voltammetric tests performed on the oxidised green solution display voltammetric profiles entirely complementary to that shown in Fig. 1.

Analysis [12] of the cyclic-voltammetric anodic responses with scan rates varying from 0.02 to 1.00 V s^{-1} show parameters which are diagnostic of a one-electron removal which is essentially reversible from the electrochemical viewpoint. As a matter of fact, the i_{pc}/i_{pa} ratio is constantly equal to unity, the current function $i_{pa}/v^{1/2}$ remains constant and the peak-to-peak separation progressively increases from 70 to 170 mV. Such a slight departure from the constant value of 59 mV expected for an electrochemically-reversible one-electron process neatly parallels that observed for the one-electron oxidation of unsubstituted ferrocene, so that it may be attributed to uncompensated solution resistances.

So far as the reduction process is concerned, it was not possible to perform macroelectrolysis investigations because of the closeness of the solvent reduction. Based on the relative heights, we assign it to a single two-reduction process, which is however complicated by subsequent reactions, as yet uncharacterised. As the inset of Fig. 1 shows, when the scan rate was increased beyond 2.00 V s^{-1}, a reoxidation appears directly associated to the reduction process. This means that the rate of the chemical complication falls within the cyclic voltammetry time window, allowing estimation of *ca.* 0.05 s as the half-life of the electrogenerable $[\mathbf{3}]^{2-}$ anion [13].

Table 1 presents for all the compounds studied the formal electrode potentials of the redox changes discussed above and, for comparison, the corresponding data for the unsubstituted 2-ferrocenylquinoxaline (**13**) are also reported. The electrogenerated ferricenium species $[\mathbf{5}]^+$, $[\mathbf{9}]^+$ and $[\mathbf{13}]^+$ proved to be not fully stable and to undergo slow decomposition.

In comparison with unsubstituted ferrocene itself, the ferrocenylquinoxalines oxidise at potential values some 100–150 mV higher, thus indicating that the quinoxaline exerts a significant electron-withdrawing



effect. However, the effects of the substituents on the quinoxaline ring are always readily interpreted. Comparison between **13** and **3**, indicates that the 3-phenyl substituent, which might have been expected to make the oxidation more difficult, in fact makes the oxidation slightly easier, suggesting that resonance effects predominate over inductive effects. This could also explain the absence of inductive effects exerted by the methyl group in **8**, or the carboxyl group in **5**, compared with **3**. On the other hand, the strongly electron-withdrawing NO_2 group in **7** generates its expected effect.

The redox behaviour of the biferrocene complex **11** merits comment. It exhibits a single oxidation process, but unfortunately, because of its very low solubility satisfactory controlled-potential coulometry was not possible. However, in view of the absence of further oxidation processes up to $+1.2$ V, it may be specu-

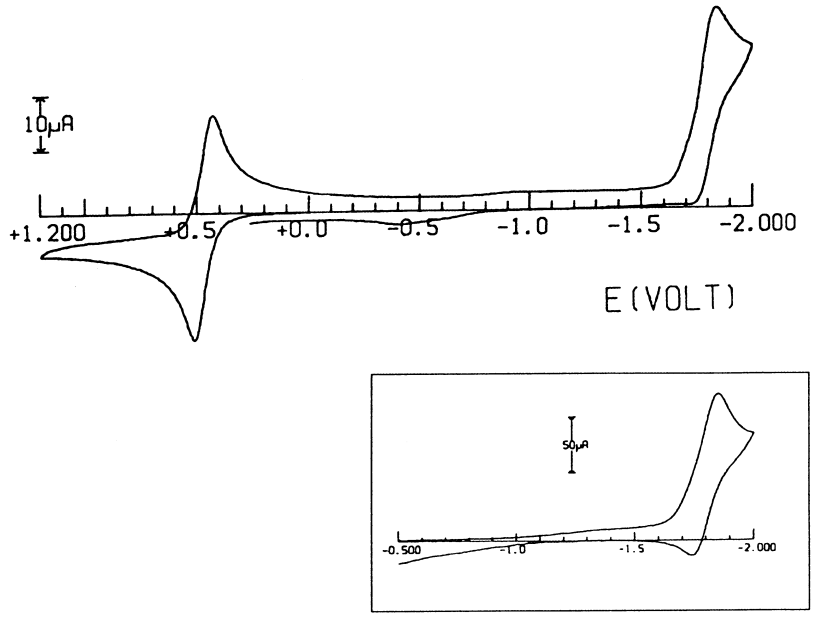


Fig. 1. Cyclic voltammogram recorded at a platinum electrode on a CH_2Cl_2 solution containing **3** (1.3×10^{-3} mol dm^{-3}) and $[NBu_4][PF_6]$ (0.2 mol dm^{-3}). Scan rates: main figure, 0.20 V s^{-1}; inset, 2.00 V s^{-1}.

Table 1. Formal electrode potentials (in V, vs S.C.E.), peak-to-peak separations (in mV) and spectroscopic data (in nm) for the redox changes exhibited by the present ferrocenylquinoxalines in dichloromethane solution.

Complex	$E^0_{0/1+}{}'$	ΔE_p[a]	λ_{max}[b]	$E^0_{0/2-}{}'$
3	+0.47	80	692	−1.80[c]
5	+0.49	97	680	—
7	+0.55	75	660	−1.55[d,e]
8	+0.49	79	705	−1.80[d]
9	+0.55	75	681	−1.51[c]
11	+0.46[f]	70	—	—
13	+0.53	95	675	−1.79[d]
FcH	+0.39	84	620	—

[a] Measured at 0.1 V s^{-1}.
[b] Absorption band of the oxidized species.
[c] Measured at 2.0 V s^{-1}.
[d] Peak potential value.
[e] A preceding reduction centred on the NO_2 group is present at $E^{0\prime} = -0.95$ V.
[f] Two-electron step.

lated that this is due to a single two-electron step. Were this to be so, it would imply that no electronic communication occurs between the two quinoxalyl units.

Finally, as far as the presence of isomeric species is concerned, as noted above for compounds **5**, **7**, **8**, **9** and **11**, it may be pointed out that only in the case of compound **5** was the presence of two almost overlapping oxidation processes observed, which could account for the somewhat greater peak-to-peak separation in **5** compared with the other species.

EXPERIMENTAL

The diketone FcCOCOPh was prepared as previously described [4]. Aromatic diamines were obtained from commercial sources and were purified using published methods [14]. NMR spectra were recorded at ambient temperatures, in $CDCl_3$ solution unless stated otherwise, on a Bruker AM-300 spectrometer operating at 300.135 MHz for ^{1}H and 75.469 MHz for ^{13}C. Diethyl ether and light petroleum (b.p. 40–60°C) were dried over sodium wire. Elemental analyses were by the Microanalytical Laboratory of this School.

Synthesis of 2-ferrocenyl-3-phenylquinoxaline

Melt-phase reaction Ferrocenylphenylethanedione **1** (0.2 g, 0.63 mmol) and 1,2-diaminobenzene **2** (0.1 g, 0.93 mmol) were taken in a Pyrex glass test tube with a side arm and fitted with a bubbler. The mixture was heated to melting in an oil bath at 140°C under nitrogen for 30 min, water vapours were observed condensing on the walls of tube. After cooling the crude material was dissolved in dichloromethane and checked by TLC; this showed one purplish-red spot almost at the same R_f value as ferrocenylphenylethanedione. This crude product was chromatographed on silica gel using dichloromethane as the eluting solvent, concentrated and crystallised to

give dark purple crystals of 2-ferrocenyl-3-phenylquinoxaline **3** (0.11 g, 45%).

Reaction in dioxan solution Ferrocenylphenylethanedione **1** (0.2 g, 0.63 mmol), 1,2-diaminobenzene **2** (0.1 g, 0.93 mmol) were dissolved in 1,4-dioxan (3 cm^3) in a Pyrex glass test tube with a side arm and fitted with a bubbler. This mixture was heated in an oil bath at 110°C under a gentle stream of nitrogen until dryness. The temperature of the bath was raised to 140°C and held at this temperature for 20 min. The crude product was purified as for the melt-phase reaction. Weight of chromatographed product 0.16 g (65%).

The products from these two processes were found to be identical by TLC and by ^1H and ^{13}C NMR. Anal. found C 72.2, H 4.4, N 6.9; $C_{24}H_{18}FeN_2$ requires C 73.9, H 4.7, N 7.2%; $C_{24}H_{18}FeN_2.0.5H_2O$ requires C 72.2, H 4.8, N 7.0%. M.p. 208–210°C (lit. 208–209°C [4]). NMR δ(H) 4.00. (5H, s, C_5H_5); 4.35 (2H, m) and 4.55 (2H, m) (C_5H_4); 7.50–7.55 (5H, m, Ph); 7.72 (2H, m) and 8.08 (2H, m) (quinoxalyl); δ(C) 69.9 (d, C_5H_5); 70.1 (d), 70.8 (d) and 82.3 (s) (C_5H_4); 128.4 (d), 128.8 (d), 128.9 (d), 129.0 (d), 129.2 (d), 129.3 (d), 129.9 (d), 139.8 (s), 140.3 (s), 141.9 (s), 154.1 (s) and 154.1 (s) (phenyl and quinoxalyl).

Synthesis of ferrocenylphenylquinoxalylcarboxylic acid

In a similar manner, ferrocenylphenylethanedione **1** (0.5 g, 1.57 mmol), 3,4-diaminobenzoic acid **4** (0.26 g, 1.7 mmol) and chlorobenzene (5 cm^3) were heated in a silicone oil bath at 140°C under a gentle stream of nitrogen; after 1 h. TLC showed that no unreacted diketone remained. During the reaction time the colour of the mixture also changed from dark red to dark purple. The mixture was then heated to dryness. After cooling, the solid residue was dissolved in dichloromethane, filtered, washed with water, dried (Na_2SO_4), concentrated and chromatographed over silica gel using diethyl ether as the mobile phase to yield ferrocenylphenylquinoxalylcarboxylic acid **5** (0.55 g, 81%) as a dark purple solid. The ^1H NMR spectrum showed the presence of two regio-isomers. The relative yield of the regio-isomers as calculated from the ^1H NMR integration is 2:1. Anal. found C 66.9, H 4.7, N 5.7; $C_{25}H_{18}FeN_2O_2$ requires C 69.1, H 4.2, N 6.5; $C_{25}H_{18}FeN_2O_2.H_2O$ requires C 66.4, H 4.5, N 6.2%. NMR δ(H) (major isomer) 4.01 (5H, s, C_5H_5); 4.38 (2H, m) and 4.58 (2H, m) (C_5H_4); 7.4–7.7 (5H, m, Ph); 8.15 (1H, d; *J*, 8.8), 8.35 (1H, dd; *J*, 8.8 and 1.6) and 8.92 (1H, d; *J*, 1.6) (quinoxalyl);. (minor isomer) 4.03 (5H, s, C_5H_5); 4.40 (2H, m) and 4.60 (2H, m) (C_5H_4); 7.4–7.7 (5H, m, Ph); 8.15 (1H, d; *J*, 8.8), 8.38 (1H, dd; *J*, 8.8 and 1.6) and 8.91 (1H, d; *J*, 1.6) (quinoxalyl); δ(C) (major isomer) 68.4_7 (d, C_5H_5); 69.0 (d), 69.5 (d) and 80.1 (s) (C_5H_4); (minor isomer) 68.5_3 (d, C_5H_5); 69.3 (d), 69.6 (d) and 80.4 (s) (C_5H_4); (both isomers) 126.9_3 (d), 126.9_6 (d), 127.0_5 (d), 127.1_6 (d), 127.6_3 (d), 127.7_2 (d), 127.7_8 (d), 128.3 (d), 129.6 (d), 129.8 (d), 130.1 (d), 131.1 (d), 137.3 (s), 138.1_7 (s), 138.2_4 (s), 139.4 (s), 140.0 (s), 142.0 (s), 152.4 (s), 153.0 (s), 153.6 (s) and 154.6 (s) (phenyl and quinoxalyl); 166.2 (s) COOH. The resolution of the aromatic resonances requires resolution enhancement. Both the carboxyl carbons appear at the same position, and two of the quaternary carbons of the aromatic/quinoxaline moieties are superimpose on other peaks in that region and hence are not visible in the spectrum.

Synthesis of ferrocenylphenylnitroquinoxaline

Ferrocenylphenylethanedione **1** (0.22 g, 0.69 mmol), 4-nitro-1,2-diaminobenzene **6** (0.12 g, 0.76 mmol) and toluene (5 cm^3) were refluxed, as above, under a gentle stream of nitrogen for 3 h; the reaction was monitored by TLC. The solvent was evaporated after this time. After cooling, the solid residue was redissolved in dichloromethane, filtered, concentrated and chromatographed over silica gel using dichloromethane as the mobile phase to yield ferrocenylphenylnitroquinoxaline **7** (0.22 g, 73%) as a dark purple solid. The compound crystallises as a hemi-hydrate as shown by the elemental analysis and integration of the ^1H NMR spectrum gave an isomer ratio of 3:1. An attempt to separate the two isomers on silica using dichloromethane as eluent yielded a pure fraction of the more abundant isomer, together with a mixture of both the isomers. Anal. found (isomer mixture) C 65.1, H 3.9, N 9.1; $C_{24}H_{17}FeN_3O_2$ requires C 66.2, H 3.9, N 9.6; $C_{24}H_{17}FeN_3O_2.0.5H_2O$ requires C 64.9, H 4.1, N, 9.4%. NMR (major isomer pure, minor isomer from spectrum of mixture) δ(H) (major isomer) 4.01 (5H, s, C_5H_5); 4.40 (2H, m) and 4.57 (2H, m) (C_5H_4); 7.5–7.6 (5H, m, Ph); 8.18 (1H, d; *J*, 9.5), 8.44 (1H, dd; *J*, 9.5 and 2.4) and 8.98 (1H, d; *J*, 2.4) (quinoxalyl); (minor isomer) 4.00 (5H, s, C_5H_5); 4.43 (2H, m) and 4.60 (2H, m) (C_5H_4); 7.5–7.6 (5H, m, Ph); 8.16 (1H, d; *J*, 9.4), 8.48 (1H, dd; *J*, 9.4 and 2.4) and 8.98 (1H, d; *J*, 2.4) (quinoxalyl); δ(C) (major isomer) 69.9 (d, C_5H_5); 70.8 (d), 71.1 (d) and 80.8 (s) (C_5H_4); 121.8 (d), 124.7 (d), 128.4 (d), 128.9_0 (d), 129.5 (d), 130.5 (d), 138.9 (s), 140.4 (s), 142.0 (s), 147.9 (s), 144.8 (s) and 157.1 (s) (phenyl and quinoxalyl); (minor isomer) 70.0 (d, C_5H_5); 71.2_5 (d), 71.2_8 (d) and 80.7 (s) (C_5H_4); 123.2 (d), 125.6 (d), 128.2 (d), 128.8_7 (d), 129.4 (d), 129.6 (d), 138.0 (s), 138.9 (s), 144.1 (s), 146.7 (s), 145.2 (s) and 158.1 (s) (phenyl and quinoxalyl).

Synthesis of ferrocenylphenylmethylquinoxaline

In a similar manner, ferrocenylphenylethanedione **1** (0.5 g, 1.57 mmol), 2,3-diaminotoluene (0.22 g, 1.8 mmol) and chlorobenzene (5 cm^3) were refluxed in an oil bath at 150°C under a gentle stream of nitrogen. The reaction was monitored by TLC and after 4 h the reaction was complete. The two regio-isomers had distinguishable R_f values, but the less polar isomer

had almost the same value as the diketone, so that it was sometimes difficult to differentiate between diketone and this isomer of the product. When the reaction was complete, the solvent was removed and the solid residue was redissolved in dichloromethane, filtered, concentrated and chromatographed over silica gel using dichloromethane/petrol as the mobile phase to yield ferrocenylphenylmethylquinoxaline **8** (0.6 g, 95%) as a dark purple solid. The relative yield of the regioisomers as calculated from the ^{1}H NMR integration is 3:2. Another column was run to separate the two isomers from each other; this yielded first the pure less-polar isomer, then the mixture of two isomers and finally a small portion of the more-polar isomer. Anal. found C 74.0, H 5.0, N 6.7; $C_{25}H_{20}FeN_2$ requires C 74.3, H 5.0, N 6.9%. NMR δ(H) (major isomer) 2.95 (3H, s, CH_3); 4.02 (5H, s, C_5H_5); 4.32 (2H, m) and 4.55 (2H, m) (C_5H_4); 7.4–7.7 (7H, m) and 7.94 (1H, d) (phenyl and quinoxalyl); (minor isomer) 2.82 (3H, s, CH_3); 4.00 (5H, s, C_5H_5); 4.32 (2H, m) and 4.55 (2H, m) (C_5H_4); 7.4–7.7 (7H, m) and 7.94 (1H, d) (phenyl and quinoxalyl); δ(C) (major isomer) 17.1 (q, CH_3); 69.7 (d, C_5H_5); 69.7 (d), 70.8 (d) and 82.9 (s) (C_5H_4); 126.8 (d), 128.1 (d), 128.5_0 (d), 128.5_5 (d), 129.1 (d), 129.5 (d), 136.5 (s), 139.6 (s), 139.8 (s), 140.8 (s), 152.1 (s) and 152.4 (s) (phenyl and quinoxalyl); (minor isomer) 17.0 (q, CH_3); 69.6 (d, C_5H_5); 69.6 (d), 70.7 (d) and 82.7 (s) (C_5H_4); 126.2 (d), 127.9 (d), 128.4 (d), 128.6 (d), 129.2 (d), 129.4 (d), 137.3 (s), 138.8 (s), 140.2 (s), 141.4 (s), 151.4 (s) and 152.9 (s) (phenyl and quinoxalyl).

Synthesis of 2-*ferrocenyl*-3-*phenyl*-5-*azaquinoxaline*

Ferrocenylphenylethanedione **1** (0.32 g, 1.0 mmol), 2,3-diaminopyridine (0.22 g, 2.0 mmol) and 1,4-dioxan (2 cm^3) were heated, as above, in an oil bath at 110°C under a slow stream of nitrogen until dryness. The temperature was then increased to 150°C and held for 30 min. After cooling, the mixture was dissolved in dichloromethane, filtered, concentrated and chromatographed on silica gel to give pure ferrocenylphenylazaquinoxaline **9** (0.26 g, 67%) as a dark purple solid. The product contained both regio-isomers of the azaquinoxaline, confirmed by ^{1}H and ^{13}C NMR. The two isomers which were not separable on silica gel were found to be separable on alumina by very careful elution using dichloromethane as eluting solvent. Any slight increase in the polarity of the mobile phase (e.g. one drop of methanol in 100 cm^3 of dichloromethane) elutes both the isomers at the same time. Integration of the ^{1}H NMR spectrum gave an isomer ratio of *ca.* 3:2. Anal. found C 69.8, H 4.6, N 10.1; $C_{23}H_{17}FeN_3$ requires C 70.6, H 4.4, N 10.7%. NMR δ(H) (major isomer) 4.02 (5H, s, C_5H_5); 4.38 (2H, m) and 4.62 (2H, m) (C_5H_4); 7.4–7.7 (6H, m, phenyl and quinoxalyl), 8.42 (1H, d × d) and 9.10 (1H, d) (quinoxalyl); (minor isomer) 4.06 (5H, s, C_5H_5); 4.40 (2H, m) and 4.68 (2H, m) (C_5H_4); 7.4–7.8 (6H, m, phenyl and quinoxalyl), 8.46 (1H, d × d) and 9.15 (1H, d) (quinoxalyl); δ(C) (major isomer) 69.6 (d, C_5H_5); 70.2 (d), 70.8 (d) and 81.8 (s) (C_5H_4); 124.8 (d), 127.8 (d), 128.9 (d), 129.2 (d), 136.2 (s), 136.8 (d), 138.8 (s), 148.4 (s), 152.5 (d), 155.3 (s) and 155.5 (s) (phenyl and quinoxalyl); (minor isomer) 69.8 (d, C_5H_5); 70.7 (d), 71.0 (d) and 80.5 (s) (C_5H_4); 123.7 (d), 128.2 (d), 128.7 (d), 128.9 (d), 134.2 (s), 137.7 (d), 139.2 (s), 150.0 (s), 153.6 (d), 154.1 (s), 157.8 (s) (phenyl and quinoxalyl).

Synthesis of di(*ferrocenyl*)*diphenylbiquinoxaline*

In a similar manner, ferrocenylphenylethanedione **1** (0.30 g, 0.94 mmol), 3,3′,4,4′-biphenyltetramine **10** (0.40 g, 1.87 mmol) and 1,4-dioxan (2 cm^3) were heated in an oil bath at 110°C under a gentle stream of nitrogen until all the solvent had evaporated. The temperature of the oil bath was then raised to 150°C and the mixture was kept at this temperature for 45 min. After cooling, the solid residue was dissolved in dichloromethane. TLC analysis showed the presence of two purple quinoxaline spots. As three regioisomers of the product **11** could be formed in this reaction, it is possible that the two of these isomers have virtually identical R_f values. As the R_f values of the two distinguishable components are very closely similar, attempts to separate the isomers have not so far been successful.

Synthesis of ferrocenyl-phenyl-6-(3′,4′-*diaminophenyl*)*quinoxaline*

Ferrocenylphenylethanedione **1** (0.10 g, 0.314 mmol), 3,3′,4,4′-biphenyltetramine (0.13 g, 0.61 mmol), sodium sulfite (0.06 g, 0.48 mmol) and potassium carbonate (0.06 g, 0.43 mmol) were dissolved in 50% (v/v) aqueous ethanol (50 cm^3). The mixture was refluxed with stirring for 2 h. After this time, TLC of the organic extract showed two highly polar components of very similar R_f values, in addition to traces of the bis-quinoxaline **11** and unreacted biphenyltetramine. During the course of the reaction some solid product precipitated out; this was filtered off and the filtrate extracted with diethyl ether. The combined solids were purified by chromatography on neutral alumina using 20% (v/v) methanolic diethyl ether as eluent to yield ferrocenylphenyl-6-(3′,4′-diaminophenyl)quinoxaline **12** (0.12 g, 77%). Anal. found C 71.6, H 4.8, N 11.0; $C_{30}H_{24}FeN_4$ requires C 72.6, H 4.9, N 11.3%; $C_{30}H_{24}FeN_4.0.5(H_2O)$ requires C 71.3, H 5.0, N 11.1%.

Electrochemistry

materials and apparatus for electrochemistry have been described elsewhere [13, 15]. All the potential

values are referred to the saturated calomel electrode (S.C.E.).

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