Molecular Materials containing Donor and Acceptor Groups. Synthesis, Structure and Spectroscopic Properties of Ferrocenyl Schiff Bases†

Andrew Houlton,[a] **Naseralla Jasim,**[a] **Roger M. G. Roberts,**[a] **Jack Silver,***[,a] **Desmond Cunningham,**[b] **Patrick McArdle**[b] **and Tim Higgins**[b]

[a] *Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, UK*

[b] *Department of Chemistry, University College Galway, Galway, Ireland*

Ferrocenyl Schiff-base derivatives of the form [Fe(η-C_5H_5)(η-$C_5H_4CH{=}NR$)] [R = NCH($C_6H_4NO_2$-*p*) **1**, C_6H_4CN-*p* **2**, $C_6H_4NO_2$-*p* **3**, C_6H_4F-*p* **4**, C_6H_4Cl-*p* **5**, C_6H_4Br-*p* **6**, $C_6H_4NO_2$-*m* **7**, NH($C_6H_4NO_2$-*o*) **8**, NH($C_6H_4NO_2$-*p*) **9** or NH(C_6F_5) **10**], have been prepared from ferrocenecarbaldehyde. Proton, ^{13}C NMR, UV/VIS and ^{57}Fe Mössbauer spectroscopic data are presented. A number of these derivatives contain the donor–π-acceptor-(D–π-A) structural motif desired for non-linear optical materials. The behaviour of the ferrocenyl moiety as a donor is compared to that of the 4-dimethylaminophenyl group. The UV/VIS spectra of compound **1** showed considerable solvatochromism. As a result of this and its extended donor–π-acceptor nature, **1** was tested for non-linear optical properties, specifically, second harmonic generation. The results, however, were negative. A single-crystal X-ray study revealed **1** to crystallize in a centrosymmetric space group $P2_1/n$, with a = 5.885(1), b = 30.745(3), c = 8.662(1) Å, β = 96.40(2)° and Z = 4. The most striking feature of the molecular structure is the coplanarity of the substituent group with the η-C_5H_4 ring of the ferrocenyl moiety. The crystal structure reveals stacks of ferrocenyl, phenyl, phenyl, ferrocenyl moieties with inter-ring distances of 3.529 Å between the C_5–C_6 rings and 3.478 Å between the C_6–C_6 ring planes. The observation of a DAAD in contrast to a DADA stack is discussed.

We have previously reported on our initial attempts to prepare redox-active ligands based on ferrocenyl Schiff bases,[1] and have since widened this study with the aim of producing a series of ferrocenyl derivatives that would have applications in non-linear optics and other areas of molecular electronics. A number of recent studies have utilized ferrocene-containing molecules in this general area. Among these have been (*a*) 'ferrocene sensors' in which the ferrocene properties have been used to sense the presence of metals in another part of the molecule,[2,3] (*b*) non-linear optical materials where the ferrocenyl moiety is the donor part of a donor–π-acceptor system (D–π-A),[4–7] (*c*) as molecular switches in controlling supramolecular assembly,[8] and (*d*) molecular magnetic materials based on ferrocenium salts.[9]

We report here the synthesis and spectroscopic data of a series of Schiff-base derivatives of ferrocenecarbaldehyde [Fe(η-C_5H_5)(η-$C_5H_4CH{=}NR$)], where R = NCH($C_6H_4NO_2$-*p*) **1**, C_6H_4CN-*p* **2**, $C_6H_4NO_2$-*p* **3**, C_6H_4F-*p* **4**, C_6H_4Cl-*p* **5**, C_6H_4Br-*p* **6**, $C_6H_4NO_2$-*m* **7**, NH($C_6H_4NO_2$-*o*) **8**, NH($C_6H_4NO_2$-*p*) **9** or NH(C_6F_5) **10**. A number of these exhibit donor–π-acceptor frameworks. In order to compare the effectiveness of the ferrocenyl moiety with other common donor groups, a series of organic derivatives containing the 4-dimethylaminophenyl group replacing the ferrocenyl group in compounds **1**–**6** were synthesised. A single-crystal X-ray study of [Fe(η-C_5H_5){η-$C_5H_4CH{=}NN{=}CH(C_6H_4NO_2$-*p*)}] **1** is presented and the molecular structure and solid-state arrrangement are discussed.

Experimental

Compound Preparation.—All materials were purchased from Aldrich Chemical. Ethanol was dried over 3 Å molecular sieve prior to use.

Reactions involved refluxing ferrocenecarbaldehyde with a slight excess of the appropriate base in ethanol for ≈ 1 h in the presence of molecular sieve. Reduction of the volume (≈ 15 cm^3) and storing overnight at 4 °C gave the corresponding Schiff base which was filtered off and air dried. Exceptions to this involved replacing ethanol with toluene and refluxing for 24 h in the case of compound **2** and 48 h in the case of **3** using Dean Stark apparatus. The organic derivatives were prepared similarly from 4-(dimethylamino)benzaldehyde. Elemental analysis was performed at the University of Manchester. [Found (Calc.) for **1**: C, 60.2 (59.8); H, 4.1 (4.1); N, 11.5 (11.6). **2**: C, 68.3 (68.6); H, 4.7 (4.45); N, 8.9 (8.9). **3**: C, 60.9 (61.1); H, 4.1 (4.2); N, 8.2 (8.40). **4**: C, 66.5 (66.5); H, 4.9 (4.6); N, 4.6 (4.55). **5**: C, 63.0 (62.85); H, 4.6 (4.30); N, 4.2 (4.30). **6**: C, 55.9 (55.85); H, 3.9 (3.7); N, 3.7 (3.7). **7**: C, 61.3 (60.9); H, 4.4 (4.2); N, 8.4 (8.35). **8**: C, 58.2 (58.5); H, 4.2 (4.3); N, 11.8 (12.0). **9**: C, 58.0 (58.5); H, 4.3 (4.3); N, 11.7 (12.0). **10**: C, 51.6 (51.8); H, 2.6 (2.80); N, 6.8 (7.10). *p*-$Me_2NC_6H_4CHNC_6H_4NO_2$-*p* **11**: C, 64.95 (64.85); H, 5.85 (5.40); N, 18.85 (18.90). *p*-$Me_2NC_6H_4CHNC_6H_4CN$-*p* **12**: C, 76.3 (77.1); H, 6.3 (6.00); N, 16.8 (16.9). *p*-$Me_2NC_6H_4CHNNCHC_6H_4NO_2$-*p* **13**: C, 64.85 (64.95); H, 5.40 (5.60); N, 18.90 (18.85). *p*-$Me_2NC_6H_4CHNC_6H_4F$-*p* **14**: C, 74.1 (74.40); H, 6.4 (6.2); N, 11.5 (11.55). *p*-$Me_2NC_6H_4CHNC_6H_4Cl$-*p* **15**: C, 69.65 (69.4); H, 5.8 (6.0); N, 10.85 (10.8). *p*-$Me_2NC_6H_4CHNC_6H_4Br$-*p* **16**: C, 59.4 (59.4); H, 4.95 (5.1); N, 9.2 (9.2)%].

Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 5 spectrometer, ^{57}Fe Mössbauer spectra on a spectrometer previously described[10] at 80 K with isomer shifts (δ/mm s^{-1}) referred to natural iron at room temperature. Selected materials were prepared as thin films using an Edwards 306A vacuum sublimator.

Single-crystal X-Ray Diffraction Study of Compound **1**.—

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Crystal and intensity-collection parameters for compound **1**

Formula	$C_{18}H_{15}FeN_3O_2$
Crystal system	Monoclinic
Space group	$P2_1/n$
M	361.182
a/Å	5.885(1)
b/Å	30.745(3)
c/Å	8.662(1)
β/°	96.40(2)
U/Å^3	1560.11
Z	4
D_c/g cm^{-3}	1.54
μ/cm^{-1}	91.9
F(000)	744
Orienting reflections, θ range/°	25, $13 < \theta < 20$
T/°C	22
Data collection range/°	$2 < 2\theta < 48$
No. unique data	2853
Observed $[I > 2\sigma I]$	1541
No. parameters fitted	114
R^a	0.0484
R'^b	0.0421
Largest shift/esd, final cycle	<0.001
Largest positive and negative peak/e Å^{-3}	0.22, −0.17

[a] $R = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$. [b] $R' = \{[\Sigma w(|F_o - F_c|)^2]/[\Sigma w(|F_o|)^2]\}^{\frac{1}{2}}$; $w = 1/(\sigma F_o)^2$.

Table 2 Fractional atomic co-ordinates for compound **1**

Atom	*x*	*y*	*z*
Fe	0.800 93(11)	0.186 66(2)	0.463 35(8)
O(1)	1.794 8(9)	−0.131 6(2)	1.047 2(6)
O(2)	1.494 1(10)	−0.127 5(2)	1.163 2(6)
N(1)	1.057 0(8)	0.071 1(1)	0.541 8(5)
N(2)	1.099 4(8)	0.040 2(1)	0.661 8(5)
N(3)	1.610 6(9)	−0.115 9(2)	1.064 8(6)
C(1)	0.777 8(8)	0.121 1(2)	0.430 0(6)
C(2)	0.896 6(9)	0.141 0(2)	0.315 2(6)
C(3)	0.750 0(9)	0.171 4(2)	0.231 7(6)
C(4)	0.538 6(10)	0.170 9(2)	0.297 9(7)
C(5)	0.553 4(9)	0.140 5(2)	0.420 4(6)
C(11)	0.863 7(9)	0.089 3(2)	0.546 3(6)
C(12)	1.296 2(9)	0.023 2(2)	0.664 0(6)
C(13)	1.375 1(8)	−0.011 8(2)	0.772 3(6)
C(14)	1.239 0(9)	−0.027 9(2)	0.879 4(6)
C(15)	1.313 5(10)	−0.061 4(2)	0.978 2(6)
C(16)	1.527 1(9)	−0.079 3(2)	0.963 4(6)
C(17)	1.665 7(9)	−0.064 3(2)	0.858 3(6)
C(18)	1.589 7(9)	−0.030 3(2)	0.761 8(6)
C(19)	1.061 8(11)	0.200 6(2)	0.636 0(8)
C(20)	1.065 4(11)	0.230 6(2)	0.511 8(8)
C(21)	0.852 3(11)	0.252 8(2)	0.493 4(8)
C(22)	0.717 1(11)	0.236 4(2)	0.606 2(8)
C(23)	0.846 5(11)	0.204 2(2)	0.694 3(8)
C(19′)	0.723 0(16)	0.218 4(2)	0.659 4(11)
C(20′)	0.939 9(16)	0.197 8(4)	0.685 3(11)
C(21′)	1.079 9(16)	0.214 9(4)	0.576 6(11)
C(22′)	0.949 4(16)	0.246 0(4)	0.483 5(11)
C(23′)	0.728 9(16)	0.248 1(4)	0.534 7(11)

Table 3 Iron-57 Mössbauer data (80 K)

Compound	δ*/mm s^{-1}	Δ/mm s^{-1}
1	0.53(1)	2.28(1)
2	0.53(1)	2.31(1)
3	0.53(1)	2.25(1)
4	0.53(1)	2.31(1)
5	0.54(1)	2.29(1)
6	0.54(1)	2.31(1)
7	0.52(1)	2.27(1)
8	0.53(1)	2.26(1)
9	0.53(1)	2.28(1)
10	0.53(1)	2.33(1)
$[Fe(C_5H_5)(C_5H_4CHO)]$	0.53(1)	2.25(1)

* Shifts referred to natural iron at room temperature.

Crystals (purple in colour) were prepared as described above. Crystal data are presented in Table 1. Diffraction intensities were collected by the ω–2θ method on an Enraf-Nonius CAD4F diffractometer with Mo-Kα radiation (λ = 0.7093 Å). The structure was solved by direct methods, SHELXS 86,[11] and refined by full-matrix least squares using SHELX 76.[12] Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions with fixed thermal parameters. The iron and oxygen atoms were refined anisotropically. The thermal parameters were terms U_{ij} of $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. The atomic scattering factors for the non-hydrogen and hydrogen atoms were taken from the literature.[13–15] The unsubstituted η-C_5H_5 ring is disordered between staggered and eclipsed positions with respect to the substituted ring. The staggered position (shown in the figures) is present to the extent of 60%. All calculations were performed on a VAX 8700 computer. The ORTEP program was used to obtain the drawings.[16] Positional parameters are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond distances and angles.

Second Harmonic Generation Measurements.—The testing of powder samples for second harmonic generation was performed at the University of Durham in collaboration with Professor D. Bloor and Dr. G. Cross.

Results and Discussion

Iron-57 Mössbauer Spectroscopic Data.—Table 3 presents the iron-57 Mössbauer spectroscopic data for the compounds studied and ferrocenecarbaldehyde. All the isomer shifts are within experimental error and typical of ferrocenyl derivatives, at ≈0.52(1) mm s^{-1}. The quadrupole splitting (q.s.) values are lower than for ferrocene (q.s. = 2.37 mm s^{-1} at 80 K) as expected for electron-withdrawing substituents, the lowest being equal to that for ferrocenecarbaldehyde (see Table 3).[17,18] Compounds **3** and **7** show the smallest q.s. values. This might have been expected for **3**, but is somewhat surprising for **7** which contains an NO_2 group non-conjugated with the ferrocenyl moiety. However, we have observed such an effect before[19] and also draw attention to the discussion on through-space field effects in the following section. From the data for compounds **2** and **4**–**6** it is apparent that in these molecules CN shows a comparable effect on the q.s. to that of the halogens. The extension of the conjugation by the addition of an N=C link between the ferrocenyl and *p*-nitrophenyl groups, as in **1**, diminishes the electron-withdrawing effect of the latter as expected. Compounds **8**–**10** differ from the previous compounds in that the phenyl ring cannot be in resonance with the ferrocenyl group. However, the electronic effect of the nitro group is such, that even when limited to a direct field effect (see below), its influence is considerable, especially in the *ortho* position. The q.s. of **10** is the largest for the compounds studied and is difficult to rationalize since it has similar electronic effects to a nitro group. A general point observed is that the replacement of the C=O by a C=NR group reduces the electron withdrawal felt at the iron nucleus unless R contains a sufficiently strong acceptor group (*i.e.* NO_2).

NMR Spectroscopic Studies.—The numbering schemes shown in Fig. 1 have been adopted for the NMR analyses. The ^1H and ^{13}C data appear in Tables 4–7. For the strictly organic

Table 4 Proton NMR shifts* for ferrocenyl Schiff bases [$Fe(C_5H_5)(C_5H_4CH{=}NR)$] in $(CD_3)_2CO$

R	H^2	H^3	C_5H_5	$H^{2'}$	$H^{3'}$	$H^{4'}$	$H^{5'}$	$H^{6'}$	CH=
Ph	4.85(t) (2.0)	4.48(t) (2.0)	4.26(s)	7.2(m)	7.2(m)	7.2(m)	7.2(m)	7.2(m)	8.42(s)
4 C_6H_4F-*p*	4.78(m)	4.46(m)	4.21(s)	7.2(m)	7.2(m)	7.2(m)	7.2(m)	7.2(m)	8.38(s)
5 C_6H_4Cl-*p*	4.79(d) (1.9)	4.49(d) (1.9)	4.23(s)	7.14(d) (9.0)	7.34(d) (9.0)	—	7.34(d) (9.0)	7.14(d) (9.0)	8.40(s)
6 C_6H_4Br-*p*	4.82(d) (1.8)	4.52(d) (1.81)	4.26(s)	7.10(d) (8.7)	7.50(d) (8.7)	—	7.50(d) (8.7)	7.10(d) (8.7)	8.43(s)
3 $C_6H_4NO_2$-*p*	4.83(br s)	4.57(br s)	4.27(s)	7.29(d) (8.7)	8.21(d) (8.7)	—	8.21(d) (8.7)	7.29(d) (8.7)	8.49(s)
7 $C_6H_4NO_2$-*m*	4.84(t) (2.0)	4.54(t) (2.0)	4.26(s)	7.90(s)	—	7.91(d) (3.0)	7.59(t) (14.7)	7.59(d) (14.7)	8.55(s)
2 C_6H_4CN-*p*	4.81(t) (1.7)	4.54(t) (1.7)	4.25(s)	6.69(d) (8.3)	7.71(d) (8.3)	—	7.71(d) (8.3)	6.69(d) (8.3)	8.43(s)
C_6H_4OMe-*p*	4.76(t) (1.8)	4.43(t) (1.8)	4.20(s)	7.12(d) (9.0)	6.89(d) (9.0)	—	6.89(d) (9.0)	7.12(d) (6.0)	8.38(s)
8 $NH(C_6H_4NO_2$-*p*)	4.60(br s)	4.36(br s)	4.16(s)	—	8.08(d) (7.9)	6.71(t)	7.44(t)	7.81(s)	7.81(s)
9 $NH(C_6H_4NO_2$-*p*)	4.63(br s)	4.35(br s)	4.16(s)	7.09(d) (8.5)	8.07(d) (8.5)	—	8.07(d) (8.5)	7.09(d) (8.5)	7.87(s)
10 $NH(C_6F_5)$	4.56(br s)	4.34(br s)	4.20(s)	—	—	—	—	—	7.59(s)
1 $N{=}CH(C_6H_4NO_2$-*p*)	4.69(br s)	4.46(br s)	4.19(s)	7.90(d) (8.1)	8.21(d) (8.1)	—	8.21(d) (8.1)	7.90(d) (8.1)	8.56(s) (2 H)

* In ppm from $SiMe_4$; s = singlet, br = broad, d = doublet, t = triplet, m = multiplet; coupling constants (*J*/Hz) in parentheses.

Table 5 Hydrogen-1 chemical shifts[a] of Schiff bases of the type *p*-$Me_2NC_6H_4CH{=}NC_6H_4Y$-*p* in $(CD_3)_2CO$

Y	H^2	H^3	$H^{2'}$	$H^{3'}$	$H^{4'}$	Me_2N	CH=
H	6.72(d) (9.0)	7.76(d) (9.0)	7.5(m)	7.5(m)	7.5(m)	3.04(s)	8.31(s)
14 F	6.79(m)	7.76(m)	7.12(d) (2.6)[b]	7.20(d) (5.0)[c]	—	3.04(s)	8.38(s)
15 Cl	6.78(d) (9.0)	7.76(d) (9.0)	7.18(d) (9.0)	7.34(d) (9.0)	—	3.04(s)	8.37(s)
16 Br	6.79(d) (9.0)	7.77(d) (9.0)	7.12(d) (9.0)	7.51(d) (9.0)	—	3.05(s)	8.38(s)
Br[d]	6.70(d) (8.9)	7.74(d) (8.9)	7.04(d) (8.6)	7.45(d) (8.6)	—	3.03(s)	8.26(s)
12 CN[d]	6.71(d) (8.8)	7.75(d) (8.8)	7.18(d) (8.5)	7.62(d) (8.5)	—	3.06(s)	8.23(s)
13 NO_2	6.73(d) (9.0)	7.77(d) (9.0)	7.21(d) (9.1)	8.22(d) (9.1)	—	3.05(s)	8.28(s)
11[e]	6.77(d) (9.1)	7.71(d) (9.1)	8.10(d) (8.7)	8.30(d) (8.7)		*f*	8.57(s) 8.70(s)

[a] In ppm from $SiMe_4$; coupling constants (*J*/Hz) in parentheses. [b] $^2J_{HF}$. [c] $^3J_{HF}$. [d] In solvent $CDCl_3$. [e] *p*-$Me_2NC_6H_4CH{=}N{-}N{=}CHC_6H_4NO_2$-*p*. [f] Masked by water in solvent.

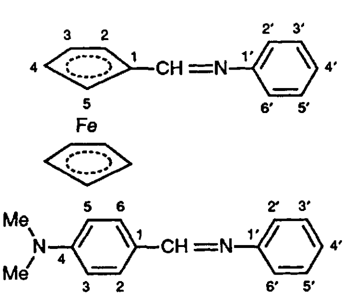

Fig. 1 Numbering scheme used for the analysis of the NMR data

compounds *p*-$Me_2NC_6H_4CHNC_6H_4Y$ ^1H NMR assignments were made by reference to the *p*-fluoro derivative. Here hydrogen–fluorine coupling enables the protons in the Y-substituted ring to be distinguished from those in the NMe_2-substituted ring. This affords an easy method of assigning the ring protons in the other derivatives since the protons of the NMe_2-substituted ring will not be very susceptible to changes in the remote substituent Y. A similar approach was adopted for the ^{13}C NMR assignments. The ^{13}C shifts (δ_i) of the iminyl carbons of the imines show some dependence on the nature of Y for both ferrocenyl and dimethylaminophenyl systems. This is apparent in the reasonably linear correlation between δ_i and the Hammett substituent parameters σ_p.[20] The slope of the correlation of the ferrocenyl series is over twice that of the purely organic system. This can be understood in terms of the relative electronic effects of the $Me_2NC_6H_4$ and $C_5H_5FeC_5H_4$ groups. The latter has reported σ_p values of -0.18[21] and -0.01.[22] There appear to be no σ values listed for the former group. However, it has been shown[23] that in 4'-substituted biphenylcarboxylic acids the substituent effect of the 4' substituent is attenuated by 37% from pK_a measurements of the carboxylic acid. The σ_p value for the NMe_2 group is -0.83, giving a value of -0.31 for the $Me_2NC_6H_4$ group. This group is therefore better than ferrocenyl at stabilizing any positive charge built up on the iminyl carbon. The fully charge-separated canonical form **II** (Fig. 2) therefore contributes to a greater extent in the organic molecule than in the ferrocenyl derivative.

Table 6 Carbon-13 chemical shifts[a] of ferrocenyl Schiff bases $[Fe(C_5H_5)(C_5H_4CH{=}NR)]$ in $(CD_3)_2CO$

	R	C^1	C^2	C^3	C_5H_5	$C^{1'}$	$C^{2'}$	$C^{3'}$	$C^{4'}$	$C^{5'}$	$C^{6'}$	CH=	Others
	Ph	81.41	69.39	71.47	69.57	153.50	120.97	129.47	125.34	129.47	120.97	161.24	
4	C_6H_4F-*p*	81.25	69.31	71.47	69.49	149.74[b]	122.46[c]	115.91[d]	160.91[e]	115.91	122.46	161.42	
5	C_6H_4Cl-*p*	81.01	69.40	71.56	69.51	152.22	122.56	129.37	130.10	129.37	122.56	162.21	
6	C_6H_4Br-*p*	81.53	70.04	72.09	69.94	153.10	123.47	132.84	118.39	132.84	123.47	162.70	
2	C_6H_4CN-*p*	81.01	70.17	72.51	70.17	157.88	122.39	134.11	108.72	134.11	122.39	164.62	CN 199.62
3	$C_6H_4NO_2$-*p*	—	69.81	72.24	69.75	—	121.65	125.22	—	125.22	121.65	164.75	
7	$C_6H_4NO_2$-*m*	80.19	69.39	71.67	69.36	154.22	115.07	—	119.36	130.34	127.32	164.19	
	C_6H_4OMe-*p*	81.73	69.08	71.11	69.39	146.28	122.02	114.60	158.10	114.60	122.02	159.25	CH_3 55.20
8	$NH(C_6H_4NO_2$-*o*)	—	67.56	70.31	69.27	—	—	125.89	117.48	136.03	116.03	144.56	
9	$NH(C_6H_4NO_2$-*p*)	80.45	67.53	70.16	69.33	139.08	126.27	111.15	151.11	111.15	126.27	142.91	
10	$NH(C_6F_5)$	78.78	67.37	69.97	69.11	—	—	—	—	—	—	144.43 165.93	
1	$N{=}CH(C_6H_4NO_2$-*p*)	—	69.24	71.77	69.56	140.48	128.73	123.99	148.86	123.99	128.73	157.25	

[a] In ppm from $SiMe_4$. [b] $^4J_{CF}$ 2.4 Hz. [c] $^3J_{CF}$ 7.3 Hz. [d] $^2J_{CF}$ 23.2 Hz. [e] $^1J_{CF}$ 240.5 Hz.

Table 7 Carbon-13 chemical shifts[a] of Schiff bases of the type *p*-$Me_2NC_6H_4CH{=}NC_6H_4Y$ in $(CD_3)_2CO$

Y	C^1	C^2	C^3	C^4	$C^{1'}$	$C^{2'}$	$C^{3'}$	$C^{4'}$	=CH	Me_2N
H[b]	—	111.58	130.43	124.96	—	120.92	128.99	—	160.22	40.15
	153.63	112.36	131.11	125.42	—	123.12[c]	116.29[d]	161.40[e]	160.57[f]	40.15
Cl	153.81	112.36	131.34	125.22	152.67	123.30	129.81	—	161.23	40.15
Cl[b]	—	111.54	130.60	123.99	—	122.25	129.07	—	160.54	40.15
Br	153.84	112.36	131.34	125.25	153.22	123.73	132.81	118.22	161.23	40.15
Br[b]	152.65	111.53	130.62	124.00	151.88	124.00	132.02	118.15	160.56	40.16
CN[b]	152.99	111.48	131.01	123.49	—	121.64	133.16	107.80	161.71	40.05
NO_2[b]	152.09	111.44	131.11	123.43	158.88	121.28	124.92	144.69	162.01	40.01
g[b]	152.82	111.64	130.71	121.11	140.71	128.70	123.95	148.75	164.57 157.25	40.08

[a] In ppm from $SiMe_4$. [b] In solvent $CDCl_3$. [c] $^3J_{CF}$ 8.1 Hz. [d] $^2J_{CF}$ 22.7 Hz. [e] $^1J_{CF}$ 241.1 Hz. [f] $^6J_{CF}$ 1.5 Hz. [g] *p*-$Me_2NC_6H_4CH{=}N{-}N{=}CHC_6H_4NO_2$-*p*.

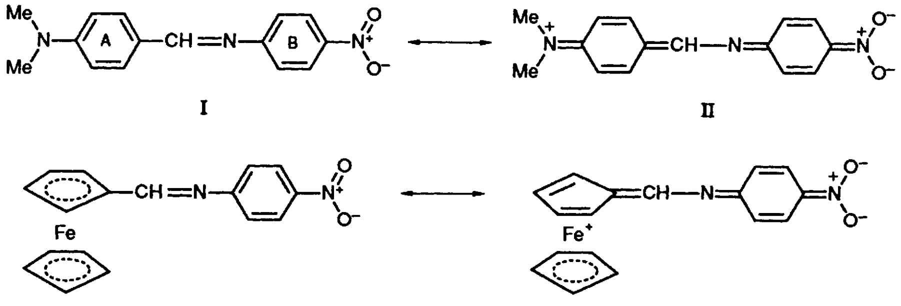

Fig. 2 Canonical forms for the ferrocenyl and dimethylaminobenzene compounds

Thus the sensitivity of δ_i to substituents in ring B will be lower for the purely organic system.

It should be noted that for the ferrocenyl imines the δ_i values for the *m*-N_2O and *p*-NO_2 derivatives are very similar, both being significantly deshielded relative to the unsubstituted compound. It is now generally recognized that electrostatic field effects play a dominant role in the transmission of polar effects other than those of resonance.[24] Since the *m*-NO_2 substituent is not involved in any through resonance, the observed deshielding is probably due to a direct through-space field effect.* This may well also account for the observed similarity of the Mössbauer quadrupole splittings of compounds **3** and **7**. The δ_i values for the hydrazones[26] appear markedly upfield from those of the imines. This is a consequence of through conjugation in the latter structures. However, even in the hydrazones remote substituents have some effect on δ_i. The higher δ_i value for the *o*-NO_2 compared with the *p*-NO_2 derivative also suggests the operation of direct field effects since in this series the iminyl carbon is not conjugated with the phenyl ring.

The data for compound **1** are significant in the light of the established coplanarity of the conjugated system in the solid state (see below). The δ_i values of the two iminyl carbons differ by 8.68 ppm. Through resonance from the ferrocenyl iminyl carbon to the nitro group would reduce the electron density on this carbon atom with a concomitant increase in electron density on the aryl iminyl carbon. This indicates that the conjugated system is also likely to be coplanar in solution. A similar effect is apparent for *p*-$Me_2NC_6H_4CH{=}N{-}N{=}CHC_6H_4NO_2$-*p*. Here the difference in the iminyl shifts is smaller (7.32 ppm) which again reflects greater release by the $Me_2NC_6H_4$ group compared to the ferrocenyl substituent.

Electronic Absorption Spectra.—The current interest in the uses of organic[27,28] and organometallic[4] materials in optical processing, particularly in second harmonic generation (s.h.g.), prompted us to determine the suitability of these ferrocenyl derivatives as possible non-linear optics molecular materials. Solvation effects on the solution electronic spectra can be a

---

* Carbon-13 substituent chemical shifts (s.c.s.s) of positive-pole nitrogen substituents are revealing in this context. The s.c.s for the NH_3^+ substituent is +2.2 ppm for the *para*-carbon and −5.8 ppm for the *ortho*-carbon (solvent CF_3CO_2H).[25] Comparable data for the NO_2 group are +7.0 (*para*) and −4.9 ppm (*ortho*). This suggests that direct field effects contribute to the overall NO_2 substituent effect.

Table 8 Electronic absorption data for $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CHNR)]$

Compound	λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1}) dmf	Et$_2$O	$\Delta\lambda$[a]
1	505[b]	486 (0.58)	+19
	326 (12.6)	320 (1.8)	
2	470[b] (1.0)	471 (0.95)	−1
	370 (15.0)	—	
	301 (9.8)	298 (9.0)	+3
3	500[b]	471 (7.1)	+13
	407 (2.0)	—	
		≈321[b]	
4	456 (0.9)	459 (0.7)	−3
	305 (8.8)	309 (7.5)	−4
5	460 (1.1)	459 (1.1)	+1
	308 (10.4)	311 (10.3)	−3
6	463 (1.0)	461 (1.9)	+2
	312 (10.5)	312 (18.0)	0
8	464 (5.6)	451 (7.1)	+13
	319 (14.6)	320 (16.1)	−1
9	417 (1.5)[c]	392 (21.0)	+25
10	505[b]	446 (2.3)	+1
	309 (19.7)	305 (28.5)	+4

[a] $\Delta\lambda = \lambda_{dmf} - \lambda_{Et_2O}$. [b] Band was a shoulder on a more intense band. [c] $\Gamma_{\frac{1}{2}}$ = 70 nm.

Table 9 Electronic absorption data for p-$Me_2NC_6H_4CH{=}NC_6H_4Y$-p

Y	λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1}) dmf	Et$_2$O	$\Delta\lambda$
F	257 (2.3)	347 (2.6)	+10
Cl	361 (3.4)	352 (2.3)	+9
Br	363 (3.1)	353 (2.3)	+10
CN	375 (3.9)	361 (2.7)	+14
NO$_2$	408 (2.6)	387 (3.4)	+21
*	422 (3.2)	410 (3.0)	+12

* p-$Me_2NC_6H_4CH{=}N{-}N{=}CHC_6H_4NO_2$-$p$.

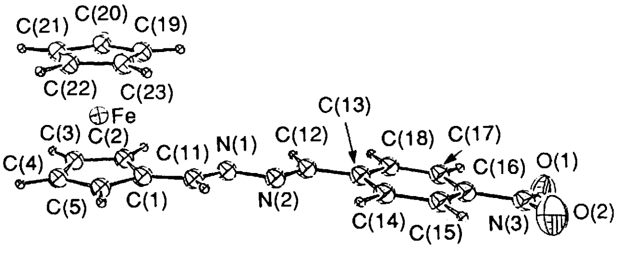

Fig. 3 Molecular structure of compound **1** including numbering scheme. The angle between the η-C_5H_4 ring and the planar substituent group is 3.54°

useful indicator of potential non-linear optics properties.[4,29] Table 8 presents data for the electronic absorption spectra in polar and non-polar solvents [dimethylformamide (dmf) and diethyl ether respectively] in the range 300–750 nm for the compounds prepared. For the ferrocenyl derivatives there are essentially two bands in this range, present in both solvents at ≈450 and ≈310 nm. Exceptions to this are seen for compound **2** which shows three bands in dmf, **9** which has only one broad band ($\Gamma_{\frac{1}{2}}$ = 100 nm) at ≈400 nm in both solvents, and **3** which exhibits an absorbance at 407 nm and a shoulder at ≈500 nm. However, for **3** in $CHCl_3$, bands are seen at 490 ($\varepsilon = 3 \times 10^3$) and 332 nm ($\varepsilon = 2.2 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

Generally, smaller shifts in λ are observed on change of solvent for the high-energy band, whilst quite large solvatochromic shifts are observed for the low-energy band. Compound **9** shows the largest effect, however this compound is not a D–π–A type structure. Of the D–π–A type complexes, **1** and **3** showed the largest $\Delta\lambda$ values. Compounds **4**–**6** show an increasingly positive shift in $\Delta\lambda$ ($\lambda_{dmf} - \lambda_{Et_2O}$) with the increased ease of polarization of the halogen, rather than increasing electronegativity. Very recently Calabrese *et al.*[30] have reported studies on the optical non-linearities of metallocenes of the form $[M(C_5X_5)\{C_5H_4\text{–}(CH{=}CH)_n\text{–}C_6H_4Y\text{-}p\}]$ (M = Fe or Ru; X = Me or H; n = 1 or 2, Y = CN or NO_2). The visible absorption spectra of these compounds also showed two bands. From extended-Hückel molecular orbital calculations[30] the lower-energy transition was tentatively assigned to metal (d_{z^2}, $d_{x^2-y^2}$, d_{xy}) to ligand (cyclopentadienyl + $d_{x^2-y^2}$, d_{xz} + C=C) charge transfer; the higher-energy transition was assigned to essentially ligand $\pi \longrightarrow \pi^*$ transitions (with some metal character).[30] As a result of the overall similarities of these compounds and their absorption spectra to those reported here it is reasonable to suppose that similar orbitals are involved in the transitions of the present compounds, particularly **1**–**6**.

For the organic derivatives (Table 9) $\Delta\lambda$ is always positive indicating that this transition produces a polar excited state. The magnitude of $\Delta\lambda$ increases as the acceptor strength increases, with the halogens having approximately the same effect. The exception to this is p-$Me_2NC_6H_4CHNNCHC_6H_4NO_2$-$p$ for which $\Delta\lambda$ = +12 nm.

These observations are particularly interesting in light of the conclusions of Calabrese *et al.*[30] They proposed that the poor coupling between the metal centre and substituent in their compounds was a consequence of the fact that the metal is not in the same plane as the π-system. This then makes it a less effective donor than might have been anticipated. The fact that the dimethylaminobenzene donor in the compounds reported here produces generally greater solvatochromic shifts affirms this statement, as the dimethylamino group would be expected to be in the plane of the π system. This is also in keeping with the relative electron-donor strengths of the $Me_2NC_6H_4$ and ferrocenyl groups as discussed previously.

Of the ferrocenyl derivatives, **1** proved potentially the most interesting in view of its D–π–A nature and relatively extended π system, so a single-crystal X-ray study was undertaken.

Molecular Structure of Compound **1**.—The structure of compound **1** is depicted in Fig. 3, with selected bond lengths and angles in Table 10. All the bond lengths are typical. The unsubstituted C_5H_5 ring is disordered between the staggered and eclipsed positions with respect to the substituted ring. There is a very small ring tilt of 1.53°. The iron distances to the substituted and unsubstituted rings are 1.654 and 1.673 Å, respectively. Comparison with other ferrocenyl Schiff bases[1,31] reveals slight differences; *cf* N–N and C=N bond lengths at 1.384 and 1.289 Å respectively for $[Fe\{C_5H_4C(Me)NNHC_5H_4NH\}_2]^{2+}2MeCO_2^-$ and C=N at 1.278 Å for $[Fe(C_5H_5)(C_5H_4NHCC_6H_4O)]$.[31]

The most striking feature of the structure is the almost complete planarity of the $C_5H_4CHNNCHC_6H_4NO_2$ fragment (the angle between the C_5H_4 and the planar substituent group is only 3.54°). While all the aromatic bond lengths are within the expected ranges, certain bonds [C(4)–C(5), C(2)–C(3), C(17)–C(18), C(14)–C(15)] are amongst the shortest, and indicate some resonance between the two extreme forms **I** and **II** (Fig. 2). From the planarity of the conjugation pathway between the donor and the acceptor groups, and the noted solvatochromic behaviour, hyperpolarizability would be expected for this type of molecule.

Molecular Packing of Compound **1**.—The solid-state arrangement of compound **1** is best considered as centrosymmetrically related pairs of molecules (see Fig. 4). Stacking of these related pairs occurs with continuous staggering (along the a axis). The staggering leaves a ferrocenyl moiety almost perfectly above the nitrophenyl group of the neighbouring centrosymmetrically

Table 10 Selected bond lengths (Å) and angles (°) for compound **1**

Fe–ring(C_5H_5)	1.673	N(2)–C(12)	1.270(8)
Fe–ring(C_5H_4)	1.654	N(3)–C(16)	1.479(8)
Fe–C(C_5H_5)$_{av}$	2.040(5)	C–C(C_5H_5)	1.420*
Fe–C(C_5H_4)$_{av}$	2.066(7)	C–C(C_5H_4)$_{av}$	1.423(8)
N(1)–N(2)	1.410(6)	N–O$_{av}$	1.210(7)
C(11)–N(1)	1.272(7)		
C(1)–C(11)–N(1)	121 (0.5)	N(1)–N(2)–C(12)	112 (0.5)
C(11)–N(1)–N(2)	111 (0.5)	N(2)–C(12)–C(13)	122 (0.5)

* Bond lengths fixed due to disorder (see text).

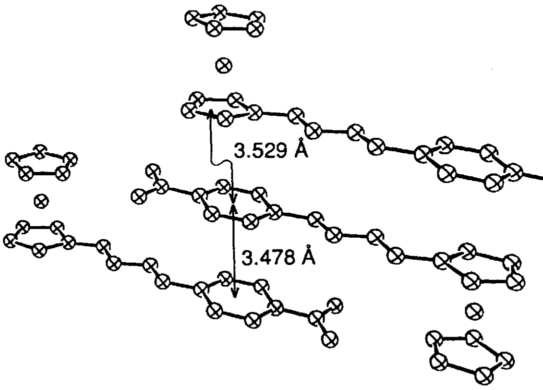

Fig. 4 Profile view of the stacked arrangement observed in compound **1**. The ring–ring distances are indicated

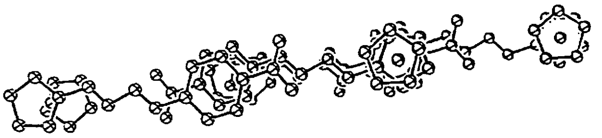

Fig. 5 View down a typical DAAD sandwich stack of six aromatic rings with the two iron atoms superimposed

related pair (see Fig. 5). Perfectly aligned stacking sequences of this type extend throughout the lattice with their *a* axes parallel. The overall stacking sequence generates an infinite two-dimensional ribbon which repeats at units of translation of *b*, but the immediately adjacent ribbon forms a herringbone pattern to the first.

The staggering of the molecules generates the discrete DAAD structural motif rather than a DADA type stack that might have been anticipated. The ring–ring distances (see Fig. 4) within the stack are 3.529 Å between the C_5–C_6 rings and 3.478 Å between C_6–C_6 ring planes. These distances are within the range associated with π–π interactions.

Hunter and Sanders[32] have recently considered the nature of π–π interactions using a simple model consisting of a σ framework and a separate π system. They draw on experimental data from porphyrin chemistry and cite intermolecular distances in the range 3.4–3.6 Å as interesting. Their series of calculations are based on an intermolecular plane–plane distance of 3.4 Å, and are obviously useful for discussions here. Their conclusions for non-polarized π systems are summarized as (*a*) π–π repulsion dominates in a face-to-face stacked geometry, and (*b*) π–σ attraction dominates in an offset stacked arrangement. These rules are able to account for the offset stacking that is observed in many molecular compounds. Of greater significance to the present work is their finding that the intermolecular geometry is affected considerably by the presence of strongly polarizing groups. An attractive face-to-face stacking is predicted for acceptor–acceptor interactions such as those of the nitrophenyl groups in the structure of compound **1**. For such molecules the interaction between π-deficient groups can be more favourable than that between π-poor and π-rich groups. This is observed in the crystal structure of **1**, with the face-to-face stacking of the phenyl groups at a distance that is slightly closer than the approach of the C_5–C_6 rings. Interestingly, it might be considered that because the C_5 and C_6 rings cannot eclipse each other then they are not strictly stacking face-to-face in the same sense as the phenyl groups. In this way the π–π repulsions between the donor and acceptor groups would be reduced and permit their close approach in the stack.

The DAAD structural motif has been reported before for the 1:1 salt of decamethylferrocenium and tetracyanoquinodimethane $[Fe(C_5Me_5)_2]_2[tcnq]_2$.[33] As in compound **1** the DAAD units do not form an infinite chain. However, it should be noted that in this salt the components are all individual molecules involved in just one stack compared to each molecule taking part in two stacks as is the case in **1**. In $[Fe(C_5Me_5)_2]_2[tcnq]_2$ the interplanar spacings are 3.554 Å for $C_5 \cdots$ tcnq and 3.147 Å for tcnq ⋯ tcnq, however the tcnq rings are offset along the short molecular axis. We also note the recent structural report of 4-ferrocenyl-2′-methyl-4′-nitroazobenzene.[34] This compound crystallizes in a centrosymmetric arrangement ($P2_1/c$) and features a head-to-tail pairing of the molecules. However the packing of the molecules does not produce the DAAD motif observed in **1**.

No second harmonic generation (s.h.g.) was observed in keeping with compound **1** exhibiting a centrosymmetric solid-state structure. As mentioned previously, in addition to the absence of a centre of symmetry, s.h.g. requires molecules which contain polarizable dipoles.[28] In common with many cases where the synthesis of molecules with large optical non-linearities is desired, it is tempting to ascribe the failure to achieve parallel alignment of the molecules as due to dipole–dipole interactions in the crystal. However, Whitesell *et al.*[35] have shown that the high preference for organic molecules to crystallize in centrosymmetric arrangements cannot be attributed to such interactions.

Another strategy to promote s.h.g. properties is to incorporate the compound of interest in a host matrix that is either itself non-centrosymmetric or produces a head-to-tail alignment of the guest molecules. It is established that ferrocenyl derivatives can act as guests to cyclodextrins which are of course chiral.[36] Similar host matrices, particularly thiourea, have been used to yield materials exhibiting s.h.g. from guests that are themselves non-active.[37] Unfortunately attempts to incorporate **1** into α,β and γ-cyclodextrin failed.

Thin Film Studies.—While ferrocene readily sublimes, it is difficult to produce good-quality films, as large single crystals grow preferentially on the substrate. We have found that the introduction of substituent groups onto the ferrocenyl moiety allows the facile preparation of good-quality thin films *via* sublimation. Thin films of compounds **1**, **8** and **9** were prepared on optically transparent electrodes and the visible and reflectance IR spectra recorded. The essential features of the visible solution spectra are retained although the λ_{max} values are shifted to longer wavelength and the bands are broader. In the case of **1** this shift is considerable (≈60 nm). The film appears purple (like the crystals) in contrast to the red colour of **1** in solution. This is undoubtedly due to the solid-state interactions described above.

Conclusion

A series of ferrocenyl Schiff bases have been reported along with a number of purely organic equivalents, some of which possess the donor–π-acceptor motif necessary for non-linear optical properties. Testing of one of these materials, **1**, revealed an absence of s.h.g. As with so many molecular solids, crystallization of the compound occurred in a centrosymmetric space group. Attempts to circumvent this, through the incorporation of **1** in cyclodextrins, failed.

We are currently investigating other techniques to fabricate such materials in non-centrosymmetric phases. With the ability to produce thin films of these compounds, *via* sublimation, the production of orientated films is being explored, as are different matrices in order to produce active compounds.

In common with other recent studies[6,30] this work indicates that the apparent potential of the ferrocenyl group is difficult to fully exploit as a donor in materials for non-linear optics. It is nonetheless a useful substituent in many areas of molecular electronics.[2–9]

References

1 A. Houlton, J. R. Dilworth, R. M. G. Roberts, J. Silver and M. G. B. Drew, *Polyhedron*, 1990, **9**, 2751.
2 P. D. Beer, J. E. Nation, S. W. L. McWhinnie, M. E. Harman, M. B. Hursthouse, M. I. Ogden and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1991, 2485.
3 A. Houlton, S. K. Ibrahim, J. R. Dilworth and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1990, 2421.
4 M. L. H. Green, S. R. Marder, M. E. Thompson, J. A. Bandy, D. Bloor, P. V. Kolinsky and R. J. Jones, *Nature (London)*, 1987, **330**, 360.
5 B. J. Coe, C. J. Jones, J. A. McCleverty, D. Bloor, P. V. Kolinsky and R. J. Jones, *J. Chem. Soc., Chem. Commun.*, 1989, 1485.
6 S. Ghosal, M. Samoc, P. N. Prasad and J. J. Tufariello, *J. Phys. Chem.*, 1990, **94**, 2847.
7 G. Doisneau, G. Balavoine, T. Fillebeen-Kahn, J.-C. Clinet, J. Delaire, I. Ledoux, R. Loucif and G. Puccetti, *J. Organomet. Chem.*, 1991, **421**, 299.
8 J. C. Medina, I. Gay, Z. Chen, L. Echegoyen and G. W. Gokel, *J. Am. Chem. Soc.*, 1991, **113**, 365.
9 J. S. Miller, A. J. Epstein and W. M. Reiff, *Chem. Rev.*, 1988, **88**, 201.
10 M. Y. Hamed, R. C. Hider and J. Silver, *Inorg. Chim. Acta*, 1982, **66**, 13.
11 G. M. Sheldrick, SHELXS 86, Package for Crystal Structure Determination, University of Göttingen, 1986.
12 G. M. Sheldrick, SHELX 76, Package for Crystal Structure Determination, University of Cambridge, 1976.
13 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
14 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
15 D. T. Cromer and D. J. Liberman, *J. Chem. Phys*, 1970, **53**, 1891.
16 C. K. Johnson, ORTEP, Oak Ridge National Laboratory, TN, 1965; revised 1971.
17 A. Houlton, J. R. Miller, R. M. G. Roberts and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1990, 2181.
18 A. Houlton, J. R. Miller, R. M. G. Roberts and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1991, 467.
19 R. M. G. Roberts, J. Silver, B. M. Yamin, M. G. B. Drew and U. Eberhardt, *J. Chem. Soc., Dalton Trans.*, 1988, 1549.
20 C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165 and refs. therein.
21 A. N. Nesmeyanov, E. G. Perevalova, S. P. Gubin, K. I. Granberg and A. G. Kozlovsky, *Tetrahedron Lett.*, 1966, 2381.
22 R. M. G. Roberts, J. Silver and B. Yamin, *J. Organomet. Chem.*, 1984, **270**, 221.
23 E. Berliner and E. A. Blommers, *J. Am. Chem. Soc.*, 1951, **73**, 2479.
24 K. Bowden, *J. Chim. Phys., Phys.-Chem. Biol.*, in the press.
25 D. F. Ewing, *Org. Magn. Reson.*, 1979, **12**, 499.
26 N. Naulet, M. L. Filleux, G. J. Martin and J. Pornet, *Org. Magn. Reson.*, 1975, **7**, 326.
27 D. Pugh and J. N. Sherwood, *Chem. Br.*, 1988, 544.
28 D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 690.
29 P. D. Beer and H. Sikanyika, *Polyhedron*, 1990, **9**, 1091.
30 J. C. Calabrese, L. Cheng, J. C. Green, S. R. Marder and W. Tam, *J. Am. Chem. Soc.*, 1991, **113**, 7227.
31 M. Bracci, C. Ercolani, B. Floris, M. Bassetti, A. Chiessi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1990, 1357.
32 C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525.
33 A. H. Reis, jun., L. D. Preston, J. M. Williams, S. W. Peterson, G. A. Candela, L. J. Swartzendruber and J. S. Miller, *J. Am. Chem. Soc.*, 1979, **101**, 2756.
34 B. J. Coe, J.-D. Foulon, T. A. Hamor, C. J. Jones and J. A. McCleverty, *Acta Crystallogr., Sect. C*, 1991, **47**, 2032.
35 J. K. Whitesell, R. E. Davis, L. L. Saunders, R. J. Wilson and J. P. Feagins, *J. Am. Chem. Soc.*, 1991, **113**, 3267.
36 Y. Odagaki, K. Hirotsu, T. Higuchi, A. Harada and S. Takahashi, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1230.
37 D. F. Eaton, A. G. Anderson, W. Tam and Y. Wang, *J. Am. Chem. Soc.*, 1987, **109**, 1886.

Received 21*st February* 1992; *Paper* 2/00920J