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Crystal and molecular structure of a segment of a stacked face-to-face ferrocene polymer *

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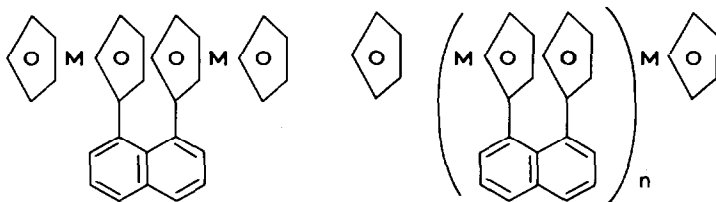
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Abstract

The crystal and molecular structure of a fragment of a face-to-face metallocene polymer, the [2,3]-oligomer(2a, $n = 2$) of 1,8-diferrocenylnaphthalene(1a), has been determined in order to better define the structural features of the polymer. The molecular structure of this compound shows the same form and magnitude of molecular distortions as those found in the monomeric unit 1a. An unusual feature of the oligomer is the *cis* arrangement of the two naphthalene nuclei, which brings several of the carbon centers on each naphthalene ring in close proximity. These structural aspects are discussed in the context of possible structures for the related polymer.

Single crystals comprising stacked arrays of donor-acceptor complexes represent solids of current interest as low dimensional organic conductors and superconductors [1]. Within this general structural class, a number of organometallic molecular systems, which possess such a columnar structure, through either bifacial metal coordination to a single unsaturated ligand or coordination to two such ligands joined in a stack, have been prepared [2]. We recently reported the synthesis of a new member of this class 1a and of polymers 2 derived from it, based on cyclopentadienylmetal complexes, in which the individual metallocene units are held proximate and cofacial as *peri* substituents on a naphthalene ring [3].



1a: M = Fe; 1b: M = Ru

2a: M = Fe; 2b: M = Ru

Although the crystal structures of 1a and 1b and of the monocation 1a⁺ have been determined [4], it was essential to gain some insight into the structure of the

* Dedicated to Professor P.L. Pauson on the occasion of his retirement.

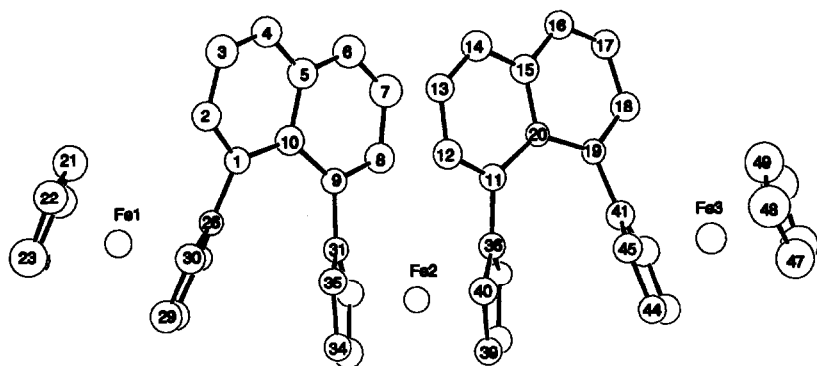


Fig. 1. Molecular structure of **2a**, showing atomic numbering.

polymeric system, since electronic band structure would be expected to be a sensitive function of the polymer structure, as well as the identity of both the metal and its oxidation state. Some inferences of chain mobility in oligomeric fragments of **1a** and **1b**, based on proton NMR spectra data, have been made [3], but these do not resolve the question of the polymer structure in the solid state. In the course of this work we had isolated and purified a number of oligomers of **1a**. We have now succeeded in crystallizing the [2,3]-oligomer, **2a** ($n = 2$), and report herein its crystal structure.

The molecular structure of this substance is shown in Fig. 1 and an edge-on view of the naphthalene plane is shown in Fig. 2. A salient feature of the oligomer structure is that it preserves the two significant molecular distortions found in the structures of 1,8-diferrocenylnaphthalene (**1a**) and 1,8-diruthenocenylnaphthalene (**1b**). These are the splaying of face-to-face cyclopentadienyl rings, and the rotation of these rings (including the ferrocene nucleus itself) from an orientation perpendicular to the average naphthalene ring. Both of these distortions are attributable to π -electron repulsive interactions of the face-to-face cyclopentadienyl rings, and their magnitudes are nearly identical in 1,8-diferrocenylnaphthalene (**1a**) and in the [2,3]-oligomer. Two further distortions which relieve electron repulsions are also observed in **1a**, **1b** and **2a**. These are the out-of-plane bending of naphthalene to cyclopentadienyl bonds and the distortion of the naphthalene ring itself. The data are summarized in Table 1, while bond distances and angles for the oligomer are presented in Table 2.

A further unusual feature of the oligomer molecular structure is the proximate, or *cis* arrangement of naphthalene nuclei, which brings several of the carbon centers on each naphthalene ring to within van der Waals contact distances. Thus, the

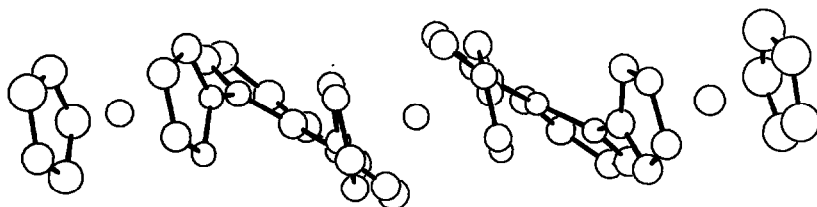


Fig. 2. View of the molecular structure of **2a** rotated 90° (relative to Fig. 1).

Table 1
Molecular distortions in 1,8-dimetallocenylnaphthalenes^a

Compound	Rotation of Cp ring from 90° orientation (°)	Cp ring splaying angle (°)	Displacement of <i>ipso</i> -Cp atoms from naphthalene best plane (Å)
1,8-Diferrocenylnaphthalene (1a)	45.0(1), 47.0(1)	29.1(1)	0.591(3) -0.611(3)
1,8-Diruthenocenylnaphthalene (1b)	42.0(1)	26.2(2)	±0.577(4)
Oligomer (2a)	48.5(4), 43.4(4) 44.8(4), 46.4(4)	28.0(4) 22.8(9)	-0.490(13) +0.415(13) -0.516(13) +0.512(13)

^a Numbers in parentheses in this and following tables are estimated standard deviations in the least significant digit.

distances separating C6–C14, C7–C14, C8–C12, C9–C12 fall within the range 3.32–3.46 Å. These are close to, but somewhat shorter than the equilibrium C–C distances derived for parallel stacked benzene dimers by Lii and Allinger from semiempirical molecular mechanics methods [5] (3.46–3.69 Å), or from the *ab initio* calculations of Karlström [6] (3.75 Å), but are better in accord with the equilibrium value of 3.44 Å calculated by Evans and Watts [7].

Inspection of the crystal structure (Fig. 3) reveals no unusually short intermolecular contacts. The only C–C contacts < 3.5 Å are: C12–C17 ($x-1, y, z$), 3.43 Å; C22–C46 ($x-1, y-1, z$), 3.44 Å; and C23–C46 ($x-1, y-1, z$), 3.38 Å. An infinite (but only partial) intermolecular overlap of the C11–C20 naphthalene rings along the relatively short *a* axis is indicated by the C12–C17 contact.

The *cis* structure may be stabilized by dispersion forces, but these cannot be very large. Estimates of the intermolecular potential between two stacked benzene rings range from -0.55 kcal mol⁻¹ from *ab initio* calculations [7], through 1.82 kcal mol⁻¹ for the most recent MM3 calculations [5], to 2.54 kcal mol⁻¹ from a semi-empirically derived potential function [6]. It appears unlikely that crystal lattice forces contribute significantly to the observed oligomer conformation in the solid state, since no unusually short contacts are observed (*vide supra*). The presence of the *trans* conformer in solutions of the [2,3]-oligomer is clearly evidenced by NMR spectral data, which shows only two proton resonances for each of the two structurally disparate substituted cyclopentadienyl rings. Each signal corresponds to a pair of α (C_{2,5}) and of β (C_{3,4}) protons on one of these cyclopentadienyl rings, which become chemically shift identical through synchronous rotation of the face-to-face cyclopentadienyl rings about their *ipso* carbon centers. Such rotation is not possible for the oligomer in the *cis* conformation, but is allowed in the *trans* isomer. Furthermore, the barrier for *cis*–*trans* interconversion must be small, since the ring rotational barrier in ferrocene itself is less than 5 kcal mol⁻¹ [8].

To the extent that dispersion forces may stabilize a *cis* conformation of ferrocene-based oligomers, such stabilization would be expected to be smaller in the oligomers based on ruthenocene [4] since the cyclopentadienyl ring separation in ruthenocene is 0.3 Å larger than in ferrocene and hence naphthalene ring overlap in

Table 2

Bond lengths (Å) and angles (°) for C₅₀H₃₈Fe₃

Fe1–C21	2.04(2)	Fe3–C50	2.04(2)	C22–C23	1.41(2)
Fe1–C22	2.04(1)	C1–C2	1.40(2)	C23–C24	1.39(2)
Fe1–C23	2.05(2)	C1–C10	1.43(2)	C24–C25	1.41(2)
Fe1–C24	2.02(2)	C1–C26	1.46(2)	C26–C27	1.43(2)
Fe1–C25	2.04(2)	C2–C3	1.41(2)	C26–C30	1.42(2)
Fe1–C26	2.08(1)	C3–C4	1.34(2)	C27–C28	1.42(2)
Fe1–C27	2.03(1)	C4–C5	1.40(2)	C28–C29	1.39(2)
Fe1–C28	2.05(1)	C5–C6	1.40(2)	C29–C30	1.41(2)
Fe1–C29	2.04(1)	C5–C10	1.44(2)	C31–C32	1.43(2)
Fe1–C30	2.04(1)	C6fs–C7	1.33(2)	C31–C35	1.41(2)
Fe2–C31	2.09(1)	C7–C8	1.42(2)	C32–C33	1.42(2)
Fe2–C32	2.07(1)	C8–C9	1.37(2)	C33–C34	1.38(2)
Fe2–C33	2.04(1)	C9–C10	1.45(2)	C34–C35	1.42(2)
Fe2–C34	2.03(1)	C9–C31	1.49(2)	C36–C37	1.41(2)
Fe2–C35	2.03(1)	C11–C12	1.38(2)	C36–C40	1.42(2)
Fe2–C36	2.08(1)	C11–C20	1.42(2)	C37–C38	1.44(2)
Fe2–C37	2.05(1)	C11–C36	1.50(2)	C38–C39	1.38(2)
Fe2–C38	2.04(1)	C12–C13	1.40(2)	C39–C40	1.42(2)
Fe2–C39	2.04(1)	C13–C14	1.33(2)	C41–C42	1.39(2)
Fe2–C40	2.05(1)	C14–C15	1.40(2)	C41–C45	1.40(2)
Fe3–C41	2.08(1)	C15–C16	1.39(2)	C42–C43	1.41(2)
Fe3–C42	2.04(1)	C15–C20	1.45(2)	C43–C44	1.38(2)
Fe3–C43	2.02(1)	C16–C17	1.35(2)	C44–C45	1.42(2)
Fe3–C44	2.03(1)	C17–C18	1.40(2)	C46–C47	1.41(2)
Fe3–C45	2.01(1)	C18–C19	1.38(2)	C46–C50	1.40(2)
Fe3–C46	2.05(2)	C19–C20	1.44(2)	C47–C48	1.38(3)
Fe3–C47	2.04(2)	C19–C41	1.49(2)	C48–C49	1.38(3)
Fe3–C48	2.05(2)	C21–C22	1.38(2)	C49–C50	1.35(2)
Fe3–C49	2.04(2)	C21–C25	1.42(2)		
C2–C1–C10	117.(1)	C12–C13–C14	119.(1)		
C2–C1–C26	118.(1)	C13–C14–C15	122.(1)		
C10–C1–C26	125.(1)	C14–C15–C16	120.(1)		
C1–C2–C3	123.(1)	C14–C15–C20	119.(1)		
C2–C3–C4	117.(1)	C16–C15–C20	121.(1)		
C3–C4–C5	124.(1)	C15–C16–C17	121.(1)		
C4–C5–C6	121.(1)	C16–C17–C18	120.(1)		
C4–C5–C10	118.(1)	C17–C18–C19	122.(1)		
C6–C5–C10	121.(1)	C18–C19–C20	119.(1)		
C5–C6–C7	122.(1)	C18–C19–C41	118.(1)		
C6–C7–C8	120.(1)	C20–C19–C41	123.(1)		
C7–C8–C9	121.(1)	C11–C20–C15	117.(1)		
C8–C9–C10	120.(1)	C11–C20–C19	127.(1)		
C8–C9–C31	116.(1)	C15–C20–C19	116.(1)		
C10–C9–C31	124.(1)	C22–C21–C25	108.(1)		
C1–C10–C5	118.(1)	C21–C22–C23	110.(1)		
C1–C10–C9	126.(1)	C22–C23–C24	106.(1)		
C5–C10–C9	116.(1)	C23–C24–C25	110.(1)		
C12–C11–C20	119.(1)	C21–C25–C24	106.(1)		
C12–C11–C36	117.(1)	C1–C26–C27	127.(1)		
C20–C11–C36	124.(1)	C1–C26–C30	128.(1)		
C11–C12–C13	122.(1)	C27–C26–C30	105.(1)		
C26–C27–C28	109.(1)	C37–C38–C39	109.(1)		

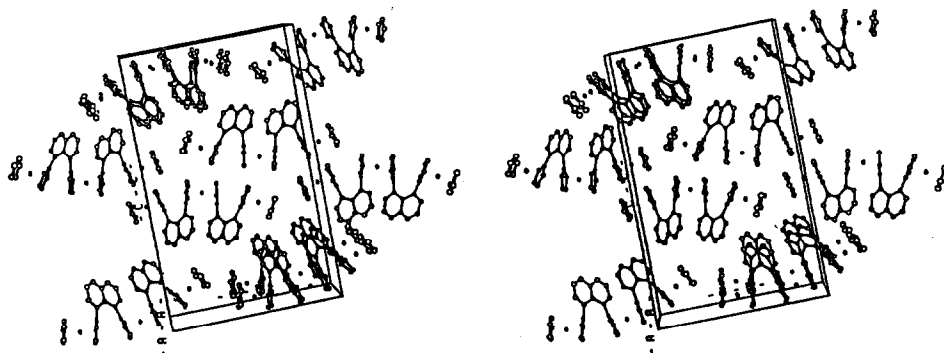
Table 2 (continued)

C27-C28-C29	108.(1)	C38-C39-C40	109.(1)
C28-C29-C30	108.(1)	C36-C40-C39	107.(1)
C26-C30-C29	109.(1)	C19-C41-C42	128.(1)
C9-C31-C32	124.(1)	C19-C41-C45	125.(1)
C9-C31-C35	128.(1)	C42-C41-C45	107.(1)
C32-C31-C35	108.(1)	C41-C42-C43	109.(1)
C31-C32-C33	106.(1)	C42-C43-C44	108.(1)
C32-C33-C34	111.(1)	C43-C44-C45	107.(1)
C33-C34-C35	107.(1)	C41-C45-C44	109.(1)
C31-C35-C34	108.(1)	C47-C46-C50	104.(1)
C11-C36-C37	128.(1)	C46-C47-C48	111.(2)
C11-C36-C40	124.(1)	C47-C48-C49	105.(2)
C37-C36-C40	109.(1)	C48-C49-C50	111.(2)
C36-C37-C38	106.(1)	C46-C50-C49	109.(2)

the *cis* conformation of the corresponding ruthenocene oligomer would be diminished.

Partially oxidized forms of these face-to-face oligomeric and polymeric metallocenes would also be expected to prefer a *trans* conformation, since oxidation of a metal center results in a decrease in electronic charge on the cyclopentadienyl rings and lowered repulsion of face-to-face rings [4]. This leads in turn to a smaller cyclopentadienyl twist angle (30° in $1a^+$ vs $\approx 45^\circ$ in $1a,b$ and $2a$), and consequently to poorer naphthalene ring overlap in the *cis* conformation of a partially oxidized oligomer or polymer.

Extrapolation of the molecular parameters observed in the oligomer to the structure of a *trans* polymer shows it to be roughly linear with respect to the ferrocene nuclei, with a small sinusoidal deviation from linearity due to the ring splaying distortion in the monomer unit. By contrast, a polymer derived from the *cis* form would be expected to adopt a helical structure as a consequence of the interplay of cyclopentadienyl ring splaying and the rotation of these rings through an angle of $\approx 45^\circ$ from an orientation perpendicular to the naphthalene nucleus. Based upon the structure of the oligomer, such a helix may be estimated to have a diameter of 68 Å with 16 monomer units per turn of the helix.

Fig. 3. Stereoview of the unit cell of $2a$.

Experimental

Preparation of the oligomer 2a ($n = 2$)

This compound was prepared according to the method of Arnold et al. [3], by the palladium-catalyzed coupling reaction of 1,1'-bis-(chlorozinc)ferrocene with 1,8-di-iodonaphthalene. The crude product containing various oligomeric fractions was purified by flash chromatography (silica/20% (v/v) CH_2Cl_2 in hexanes), and the fractions containing the component with $R_f = 0.32$ (by TLC, using silica/20% (v/v) CH_2Cl_2 in hexanes) were combined to yield 17 mg (1.8%) of the oligomer as an orange solid: $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 3.51–3.54 (t, 4H, J 2.0 Hz, H_b -inner

Table 3

Data for the X-ray diffraction study of $\text{C}_{50}\text{H}_{38}\text{Fe}_3$

Crystal data at 21(1)°C

Crystal system: monoclinic	$Z = 4$
Space group: $P2_1/c[C_2^2h]$; No. 14]	Crystal size: $0.36 \times 0.16 \times 0.08$ mm
a 6.396(3) Å	
b 18.797(9) Å	FW: 806.40
c 29.820(15) Å	ρ_{obs} 1.45(2) g cm^{-3}
β 93.48(5)°	ρ_{calc} 1.497 g cm^{-3}
V 3578.5(54) Å ³	μ 12.36 cm^{-1} (Mo- $K\alpha$)
Cell constant determination: 12 pairs of $\pm(hkl)$ and refined 2θ , ω , χ values in the range $17 \leq 2\theta \leq 26^\circ$ ($\lambda(\text{Mo-}K\alpha)$ 0.71073 Å)	

Measurement of intensity data

Radiation: Mo- $K\alpha$, graphite monochromator
 Reflections measured: $h, k, \pm l$ ($3 \leq 2\theta \leq 40^\circ$)
 Scan type, speed: ω , vble, 2.46–5.33° min^{-1}
 Scan range: 1.5°, with a 1.5° displacement in ω from $K\alpha$ position for background; $t_p/t_b = 0.5$
 No. of reflections measured: 4103; 3316 in unique set
 Standard reflections, period: 80; 113, 104, 025; variation $\leq \pm 3\sigma(I)$ for each
 Absorption correction; empirical, normalized transmission factors 0.827–1.000; 045; 1,6,10 reflections
 Data reduction: as before^b
 Statistical information: $R_{\text{av}} = 0.044$ ($0kl$ reflections)

Refinement

Refinement^c, with 1802 data for which $I \geq 1.96 \sigma(I)$
 Weighting of reflections: as before^c, $p = 0.04$
 Solution: Patterson, difference-Fourier
 Refinement^d: full-matrix least-squares, with:
 anisotropic temperature factors for Fe atoms;
 isotropic temperature factors for C, fixed H atoms;
 $R = 0.0693$; $R_w = 0.0629$; $SDU = 1.46$;
 R (structure factor calcn with all 3316 reflections) = 0.189
 Final difference map: 15 peaks, 0.40–0.83 e \AA^{-3} near Cp C atoms; other peaks random and ≤ 0.40 e \AA^{-3}

^a Measured by neutral buoyancy in KI– H_2O – $\text{C}_2\text{H}_5\text{OH}$ solution. ^b B.M. Foxman, P.L. Goldberg and H. Mazurek, Inorg. Chem., 20 (1981) 4368; all computations in the present work were carried out using the ENRAF–NONIUS Structure Determination Package. ^c P.W.R. Corfield, R.J. Doedens and J.A. Ibers, Inorg. Chem., 6 (1967) 197. ^d $R_{\text{av}} = \sum |I - I_{\text{av}}| / \sum I$; $R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$; $R_w = (\sum w[|F_o| - |F_c|]^2 / \sum w |F_o|^2)^{1/2}$; $SDU = (\sum w[|F_o| - |F_c|]^2 / (m - n))^{1/2}$ where m (= 1802) is the number of observations and n (= 228) is the number of parameters.

Table 4

Atomic coordinates for $C_{50}H_{38}Fe_3^a$

Atom	x	y	z	B (Å ²)
Fe1	-0.2645(3)	-0.0101(1)	0.42036(7)	2.87(5)
Fe2	0.0161(3)	0.3284(1)	0.44096(7)	2.57(5)
Fe3	0.3418(4)	0.6411(1)	0.37668(7)	3.67(5)
C1	-0.116(2)	0.1059(7)	0.3520(4)	2.6(3)
C2	-0.215(2)	0.0717(8)	0.3147(5)	3.7(3)
C3	-0.140(2)	0.0751(8)	0.2714(5)	4.4(4)
C4	0.039(2)	0.1103(8)	0.2666(5)	3.9(4)
C5	0.144(2)	0.1497(7)	0.3008(4)	3.3(3)
C6	0.327(2)	0.1872(8)	0.2933(5)	4.0(4)
C7	0.422(2)	0.2277(8)	0.3249(5)	4.2(4)
C8	0.330(2)	0.2378(7)	0.3664(5)	3.0(3)
C9	0.147(2)	0.2039(7)	0.3756(4)	2.2(3)
C10	0.054(2)	0.1527(7)	0.3439(4)	2.8(3)
C11	0.099(2)	0.3932(7)	0.3432(4)	2.2(3)
C12	-0.036(2)	0.3466(7)	0.3206(4)	3.0(3)
C13	-0.012(2)	0.3258(8)	0.2760(5)	3.5(3)
C14	0.155(2)	0.3486(8)	0.2554(5)	3.5(3)
C15	0.299(2)	0.3968(7)	0.2755(4)	3.0(3)
C16	0.475(2)	0.4168(8)	0.2537(5)	3.5(3)
C17	0.611(2)	0.4651(8)	0.2721(5)	3.4(3)
C18	0.565(2)	0.5010(8)	0.3116(4)	3.4(3)
C19	0.391(2)	0.4843(7)	0.3347(4)	2.2(3)
C20	0.260(2)	0.4256(7)	0.3195(4)	2.1(3)
C21	-0.215(2)	-0.0838(8)	0.3718(5)	4.0(4)
C22	-0.423(2)	-0.0840(8)	0.3816(5)	4.3(4)
C23	-0.441(2)	-0.1001(9)	0.4275(5)	5.0(4)
C24	-0.236(2)	-0.1098(8)	0.4454(5)	4.0(4)
C25	-0.094(2)	-0.1000(8)	0.4118(5)	4.4(4)
C26	-0.191(2)	0.0902(7)	0.3962(4)	2.1(3)
C27	-0.066(2)	0.0719(7)	0.4357(4)	1.9(3)
C28	-0.200(2)	0.0611(8)	0.4713(5)	3.8(4)
C29	-0.406(2)	0.0689(8)	0.4545(5)	3.6(4)
C30	-0.403(2)	0.0866(7)	0.4086(4)	2.7(3)
C31	0.055(2)	0.2241(6)	0.4183(4)	1.6(3)
C32	0.173(2)	0.2358(8)	0.4601(5)	3.0(3)
C33	0.025(2)	0.2548(8)	0.4914(5)	3.4(3)
C34	-0.174(2)	0.2584(8)	0.4707(5)	3.4(3)
C35	-0.157(2)	0.2405(7)	0.4248(4)	3.0(3)
C36	0.073(2)	0.4039(7)	0.3924(4)	2.4(3)
C37	0.232(2)	0.4051(7)	0.4275(4)	2.1(3)
C38	0.129(2)	0.4218(8)	0.4678(5)	3.0(3)
C39	-0.083(2)	0.4277(7)	0.4576(5)	3.1(3)
C40	-0.123(2)	0.4160(8)	0.4107(5)	3.0(3)
C41	0.340(2)	0.5308(7)	0.3731(4)	2.6(3)
C42	0.474(2)	0.5545(8)	0.4086(5)	3.4(4)
C43	0.358(2)	0.5954(8)	0.4380(5)	3.7(4)
C44	0.152(2)	0.5971(8)	0.4211(5)	3.2(3)
C45	0.142(2)	0.5588(7)	0.3799(5)	3.1(3)
C46	0.503(3)	0.735(1)	0.3829(6)	6.4(5)
C47	0.287(3)	0.7481(9)	0.3736(6)	6.2(5)
C48	0.217(3)	0.717(1)	0.3337(6)	6.7(5)
C49	0.393(3)	0.6879(9)	0.3167(6)	6.3(5)
C50	0.563(3)	0.6975(9)	0.3452(6)	5.8(4)

^a Atoms refined using anisotropic temperature factors are given in the form of the isotropic equivalent displacement parameter defined as: $1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + abc\cos\gamma B_{12} + accos\beta B_{13} + bccos\alpha B_{23}]$

Cp), 3.73–3.76 (t, 4H, J 2.0 Hz, H_a -inner Cp), 3.74–3.77 (t, 4H, J 2.0 Hz, H_b -outer Cp), 3.79–3.81 (t, 4H, J 2.0 Hz, H_a -outer Cp), 7.05–7.11 (dd, 2H, 3J 8.1, 7.2 Hz, H_3), 7.39–7.45 (dd, 2H, 3J 8.1, 7.2 Hz, H_6), 7.61–7.67 (m, 4H, $H_{2,4}$), 7.68–7.73 (dd, 2H, 3J 8.1, 4J 1.5 Hz, H_5), 8.00–8.04 (dd, 2H, 3J 7.2, 4J 1.5 Hz, H_7).

Structure determination of 2a

X-Ray quality crystals of this compound were grown by vapor diffusion from CH_2Cl_2 /hexanes at -20°C . An orange-red specimen, measuring $0.36 \times 0.16 \times 0.08$ mm, was mounted and used for the subsequent data collection. Laue photographs indicated the crystal (and all available samples) to be of only moderate quality; significant data were not observed beyond d 1 Å. The crystal was then transferred to a Supper No. 455 goniometer and optically centered on a Syntex $P2_1$ diffractometer. Operations were performed as described previously [9]. The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering for Fe were included in the calculations [10]. All computational work was carried out on a VAX 8650 computer using the Enraf–Nonius SDP software package. Details of the structure analysis, in outline form, are presented in Table 3. Atomic coordinates for all nonhydrogen atoms appear in Table 4. Tables S-I, Anisotropic displacement parameters, S-II, Hydrogen atomic coordinates and S-III, Observed and calculated structure amplitudes are available upon request from the authors.

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