Thionation of 1,1′-Dibenzoylferrocene: Crystal and Molecular Structure of 1,4-Diphenyl-1,4-epithio-2,3-dithia[4](1,1′)ferrocenophane†

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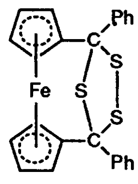
1,1′-Dibenzoylferrocene reacts with tetraphosphorus decasulphide to yield, in addition to the expected 1,1′-bis(thiobenzoyl)ferrocene, a minor, yellow by-product (**1**) of composition $C_{24}H_{18}FeS_3$. Crystals of (**1**) are monoclinic, space group $P2_1/n$ with $a = 11.769(3)$, $b = 11.750(4)$, $c = 14.835(2)$ Å, $\beta = 98.63(1)°$, and $Z = 4$; the structure was refined from diffractometer data to an R value of 0.041. The structure was found to be that of 1,4-diphenyl-1,4-epithio-2,3-dithia[4](1,1′)-ferrocenophane, in which the two rings of the ferrocene nucleus are spanned by a 1,2,4-trithiolane ring.

Monoacylferrocenes $[Fe(C_5H_5)(C_5H_4COR)]$ can readily be thionated to the corresponding thioacylferrocenes $[Fe(C_5H_5)(C_5H_4CSR)]$ by use of tetraphosphorus decasulphide, P_4S_{10}, in dichloromethane solution, in the presence of sodium hydrogencarbonate.[1] Extension to the 1,1′-diacylferrocenes is generally straightforward, except that the deep purple-black bis(thioacyl) derivatives $[Fe(C_5H_4CSR)_2]$ are sometimes accompanied by very small quantities of a pale yellow by-product. For the case of R = Ph, we have now isolated and purified this by-product, albeit in yields of less than 1%, and have characterised it analytically, spectroscopically, and crystallographically as 1,4-diphenyl-1,4-epithio-2,3-dithia[4](1,1′)ferrocenophane, (**1**), which contains the rather uncommon 1,2,4-trithiolane ring.



(**1**)

Experimental

Diethyl ether and light petroleum (b.p. 40—60 °C) were dried by reflux over sodium diphenylketyl; dichloromethane was dried by reflux over calcium hydride. Elemental analysis was by the Microanalytical Laboratory of this Department. Infrared spectra were measured using a Perkin-Elmer model 1710 (FTIR) spectrometer, and ^1H and ^{13}C n.m.r. spectra were measured using a Bruker AM 300 spectrometer.

Reaction of 1,1′-Dibenzoylferrocene with Tetraphosphorus Decasulphide.—1,1′-Dibenzoylferrocene (0.40 g, 1.0×10^{-3} mol) was dissolved in a mixture of dichloromethane (50 cm³) and diethyl ether (50 cm³). Tetraphosphorus decasulphide (11.3 g, 25.5×10^{-3} mol) was added with vigorous stirring, and the mixture was refluxed during 1 h. The resulting mixture was filtered twice through Hyflo-supercel, and the deep purple filtrate was reduced to small volume and chromatographed on silica, with toluene eluant, to remove the last traces of P_4S_{10}. The toluene eluate was reduced to small volume, and rechromatographed on alumina. Elution with ether gave first (**1**), in a yield of less than 1% (Found: C, 62.7; H, 3.9. $C_{24}H_{18}FeS_3$ requires C, 62.9; H, 4.0%). N.m.r.: $\delta_H(CD_2Cl_2)$ 4.26 (m, 2 H), 4.30 (m, 2 H), 4.32 (m, 2 H), 4.33 (m, 2 H) ($2 \times C_5H_4$), 7.2—7.3 (m, 6 H), and 7.7—7.8 (m, 4 H) (C_6H_5); $\delta_C(CDCl_3)$ 69.0 (d), 70.3 (d), 71.7 (d), 74.6 (d), 83.0 (s) (C_5H_4); 96.6 (s, $>C<$), 128.1 (d, Ph, C^2 or C^3), 128.6 (d, C^4), 129.0 (d, C^3 or C^2), and 137.1 p.p.m. (s, C^1), (C_6H_5). The i.r. spectrum (CCl_4 solution) showed no absorption assignable to ν(C=O) or ν(C=S). This was followed by purple 1,1′-bis(thiobenzoyl)ferrocene, yield *ca.* 40%.

X-Ray Crystallography.—Crystals suitable for *X*-ray examination were grown from CH_2Cl_2–light petroleum.

Crystal data. $C_{24}H_{18}FeS_3$, $M_r = 458.45$, monoclinic, $a = 11.769(3)$, $b = 11.750(4)$, $c = 14.835(2)$ Å, $\beta = 98.63(1)°$, $U = 2\,028(1)$ Å³, $Z = 4$, $D_c = 1.50$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 10.5$ cm^{-1}, $\lambda = 0.710\,73$ Å, $F(000) = 944$, space group $P2_1/n$ (no. 14) (from systematic absences: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$).

Data collection. Cell dimensions were determined by least-squares refinement using the setting angles for 22 reflections in the range $7 \leqslant \theta \leqslant 20°$. Intensity data were measured at 21 °C using a CAD4 diffractometer with graphite-monochromated Mo-K_α radiation, in the ω—2θ scan mode; the ω-scan rate was 1—7° min^{-1}, the ω-scan width was $(0.70 + 0.35 \tan\theta)°$, and the maximum value of 2θ was 54°. A total of 4 950 reflections were measured, of which 3 176 were unique and 3 146 had $I \geqslant 3\sigma(I)$. Lorentz and polarisation corrections were applied, together with a numerical absorption correction: maximum and minimum transmission coefficients were 0.683 and 0.561.

Structure solution and refinement. The structure was solved using the Patterson heavy-atom method which revealed the position of the iron atom, followed by difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically: hydrogen atoms were visible in difference maps and were included in the refinement as riding atoms with d(C–H) = 0.95 Å and B_{iso} fixed at 5 Å². The final residuals were R, 0.041 and R', 0.053.

Scattering factor data were taken from refs. 2—4. All calculations were performed on a PDP-11/73 computer using SDP-Plus.[5] Final refined atom co-ordinates are given in Table 1; bond lengths and selected bond angles are given in Table 2. A

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Positional parameters for complex (**1**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe	0.034 44(3)	0.230 62(4)	0.031 42(3)	C(25)	0.129 0(3)	0.180 8(3)	−0.065 9(2)
S(1)	−0.225 37(7)	0.162 93(7)	−0.174 24(5)	C(26)	−0.016 4(2)	0.317 4(2)	−0.167 9(2)
S(2)	−0.074 24(7)	0.185 21(7)	−0.228 04(5)	C(31)	−0.328 7(2)	0.308 8(3)	−0.071 3(2)
S(3)	−0.137 60(6)	0.393 00(6)	−0.132 26(4)	C(32)	−0.395 9(3)	0.374 9(3)	−0.135 4(2)
C(11)	−0.137 1(2)	0.230 5(2)	0.004 3(2)	C(33)	−0.505 9(3)	0.405 5(4)	−0.124 3(3)
C(12)	−0.100 2(3)	0.301 4(3)	0.081 4(2)	C(34)	−0.551 8(3)	0.367 8(4)	−0.050 2(3)
C(13)	−0.036 2(3)	0.233 9(3)	0.149 6(2)	C(35)	−0.487 7(3)	0.300 4(4)	0.013 6(2)
C(14)	−0.034 2(3)	0.121 4(3)	0.116 5(2)	C(36)	−0.376 0(3)	0.271 6(3)	0.003 5(2)
C(15)	−0.097 6(3)	0.118 4(3)	0.027 7(2)	C(41)	0.032 6(2)	0.391 7(3)	−0.237 3(2)
C(16)	−0.206 7(2)	0.272 8(2)	−0.083 5(2)	C(42)	0.147 6(3)	0.403 5(4)	−0.235 8(2)
C(21)	0.072 9(2)	0.287 7(2)	−0.087 2(2)	C(43)	0.191 2(3)	0.471 6(5)	−0.298 4(3)
C(22)	0.114 8(3)	0.365 5(3)	−0.015 3(2)	C(44)	0.119 0(3)	0.529 1(4)	−0.363 0(3)
C(23)	0.193 4(3)	0.305 6(3)	0.049 9(2)	C(45)	0.004 0(4)	0.517 2(4)	−0.367 0(2)
C(24)	0.201 3(3)	0.192 6(3)	0.019 6(2)	C(46)	−0.040 2(3)	0.447 7(3)	−0.305 3(2)

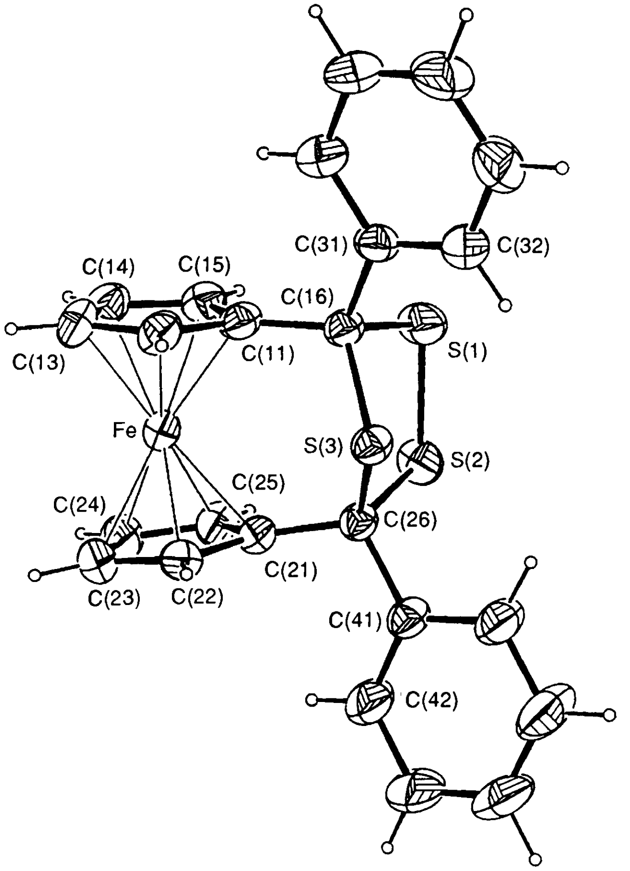


Figure 1. Perspective view of the molecule, showing the atom-numbering scheme

perspective view of the molecule, showing the atom-numbering scheme is in Figure 1.

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

Results and Discussion

Thionation of 1,1′-dibenzoylferrocene with tetraphosphorus decasulphide produced 1,1′-bis(thiobenzoyl)ferrocene in yields around 40%, together with a chromatographically homogeneous by-product (**1**) in yields never more than *ca.* 1%. The use of sodium hydrogencarbonate, as recommended earlier[6] for the thionation of organic ketones, effected no improvement in the yield of either product, but merely rendered the work-up more complex.

The yellow colour of (**1**) suggested that it contained no C=S bonds, and the i.r. spectrum showed no absorption assignable to either C=O or C=S stretches. The ^{1}H n.m.r. spectrum of (**1**) showed, in addition to the absorption characteristic of a monosubstituted phenyl group, four resonances in the cyclopentadienyl region, each of which had an intensity equivalent to one proton for each phenyl group present. Since monosubstituted cyclopentadienyl ligands normally provide just two proton resonances, the observation of four such signals initially suggested the presence of two non-equivalent cyclopentadienyl ligands. The ^{13}C n.m.r. spectrum, in addition to the usual signals from a monosubstituted phenyl ring of local C_{2v} symmetry, showed six other resonances, of which four were shown by DEPT n.m.r. spectroscopy to arise from C–H groups, while the remaining two were from carbons not attached to hydrogen. Again the observation of four C–H resonances in the cyclopentadienyl region suggested the presence of two distinct cyclopentadienyl ligands; together the ^{1}H and ^{13}C spectra indicated that the initial C_5H_4–C–C_6H_5 fragment was retained.

Microanalysis supported a C:H atomic ratio of 12:9 as required by this fragment: on the assumption of two cyclopentadienyl ligands per iron atom, the analytical data indicated a relative molar mass per iron atom of 459, consistent with the formulation $C_{24}H_{18}FeS_3$ (M_r, 458.4). This deduction was fully supported by the results of a single crystal *X*-ray structure determination.

Crystal and Molecular Structure.—The crystal structure revealed a molecular unit in which the two carbon atoms which originally formed the carbonyl groups in 1,1′-dibenzoylferrocene had been incorporated into a five-membered C_2S_3 ring; since the resulting 1,2,4-trithiolane ring is connected, at carbon, to the two cyclopentadienyl rings, the compound (**1**) is thus a bridged ferrocenophane.

Rather few derivatives containing 1,2,4-trithiolane rings have been structurally characterised: the known examples (**2a**)—(**2g**)[7–13] all have two exocyclic double bonds.

In compound (**1**) on the other hand there are no double bonds exocyclic to the trithiolane ring, whose carbon atoms are both essentially tetrahedral: accordingly the C–S bond lengths in (**1**) [range 1.825(3)—1.868(3) Å] are significantly longer than those found in compounds (**2**), in which the C–S bond lengths cluster around 1.74 Å.

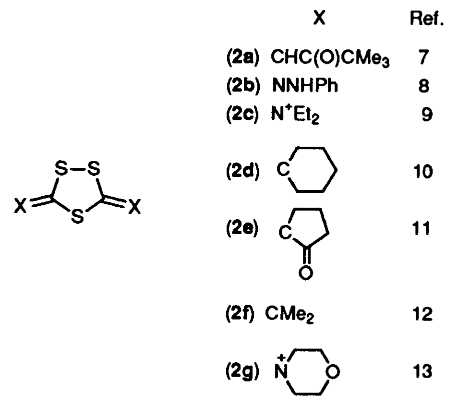
The overall molecular symmetry of (**1**) is approximately *m* (C_s), although no symmetry is imposed crystallographically. The two cyclopentadiene rings are not parallel: the rings are

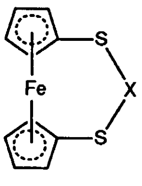
Table 2. Bond lengths (Å) and angles (°) for complex (**1**) with e.s.d.s in parentheses

Fe–C(11)	1.998(3)	C(16)–C(31)	1.534(4)
Fe–C(12)	2.026(3)	C(21)–C(22)	1.435(4)
Fe–C(13)	2.051(3)	C(21)–C(25)	1.431(4)
Fe–C(14)	2.050(3)	C(21)–C(26)	1.511(3)
Fe–C(15)	2.032(3)	C(22)–C(23)	1.421(4)
Fe–C(21)	1.997(3)	C(23)–C(24)	1.409(5)
Fe–C(22)	2.021(3)	C(24)–C(25)	1.424(4)
Fe–C(23)	2.048(3)	C(26)–C(41)	1.528(4)
Fe–C(24)	2.046(3)	C(31)–C(32)	1.381(4)
Fe–C(25)	2.037(3)	C(31)–C(36)	1.385(5)
S(1)–S(2)	2.072(1)	C(32)–C(33)	1.378(5)
S(1)–C(16)	1.854(3)	C(33)–C(34)	1.369(6)
S(2)–C(26)	1.868(3)	C(34)–C(35)	1.370(5)
S(3)–C(16)	1.831(3)	C(35)–C(36)	1.387(5)
S(3)–C(26)	1.825(3)	C(41)–C(42)	1.356(5)
C(11)–C(12)	1.429(4)	C(41)–C(46)	1.387(4)
C(11)–C(15)	1.422(4)	C(42)–C(43)	1.382(6)
C(11)–C(16)	1.515(4)	C(43)–C(44)	1.362(6)
C(12)–C(13)	1.412(4)	C(44)–C(45)	1.353(6)
C(13)–C(14)	1.411(5)	C(45)–C(46)	1.386(5)
C(14)–C(15)	1.414(4)		

C(11)–Fe–C(12)	41.6(1)	Fe–C(21)–C(26)	123.6(2)
C(11)–Fe–C(15)	41.3(1)	C(22)–C(21)–C(25)	107.4(2)
C(12)–Fe–C(13)	40.5(1)	C(22)–C(21)–C(26)	124.2(3)
C(13)–Fe–C(14)	40.3(1)	C(25)–C(21)–C(26)	128.3(2)
C(14)–Fe–C(15)	40.5(1)	C(21)–C(22)–C(23)	107.8(3)
C(21)–Fe–C(22)	41.8(1)	C(22)–C(23)–C(24)	108.4(3)
C(21)–Fe–C(25)	41.5(1)	C(23)–C(24)–C(25)	108.5(3)
C(22)–Fe–C(23)	40.9(1)	C(21)–C(25)–C(24)	107.8(3)
C(23)–Fe–C(24)	40.3(1)	S(2)–C(26)–S(3)	107.4(1)
C(24)–Fe–C(25)	40.8(1)	S(2)–C(26)–C(21)	110.3(2)
S(2)–S(1)–C(16)	100.1(1)	S(2)–C(26)–C(41)	107.5(2)
S(1)–S(2)–C(26)	101.2(1)	S(3)–C(26)–C(21)	111.3(2)
C(16)–S(3)–C(26)	98.7(1)	S(3)–C(26)–C(41)	107.9(2)
Fe–C(11)–C(12)	70.2(2)	C(21)–C(26)–C(41)	112.2(2)
Fe–C(11)–C(15)	70.6(2)	C(16)–C(31)–C(32)	121.5(3)
Fe–C(11)–C(16)	124.9(2)	C(16)–C(31)–C(36)	120.2(3)
C(12)–C(11)–C(15)	107.2(2)	C(32)–C(31)–C(36)	118.2(3)
C(12)–C(11)–C(16)	123.9(3)	C(31)–C(32)–C(33)	121.0(3)
C(15)–C(11)–C(16)	128.9(3)	C(32)–C(33)–C(34)	120.2(3)
C(11)–C(12)–C(13)	108.2(3)	C(33)–C(34)–C(35)	119.9(3)
C(12)–C(13)–C(14)	108.1(3)	C(34)–C(35)–C(36)	120.0(4)
C(13)–C(14)–C(15)	108.3(3)	C(31)–C(36)–C(35)	120.6(3)
C(11)–C(15)–C(14)	108.2(3)	C(26)–C(41)–C(42)	121.5(3)
S(1)–C(16)–S(3)	105.2(1)	C(26)–C(41)–C(46)	120.4(3)
S(1)–C(16)–C(11)	112.7(2)	C(42)–C(41)–C(46)	118.1(3)
S(1)–C(16)–C(31)	105.5(2)	C(41)–C(42)–C(43)	121.2(3)
S(3)–C(16)–C(11)	112.2(2)	C(42)–C(43)–C(44)	120.3(4)
S(3)–C(16)–C(31)	108.2(2)	C(43)–C(44)–C(45)	119.6(4)
C(11)–C(16)–C(31)	112.6(2)	C(44)–C(45)–C(46)	120.3(4)
Fe–C(21)–C(22)	70.0(2)	C(41)–C(46)–C(45)	120.5(3)
Fe–C(21)–C(25)	70.7(2)		

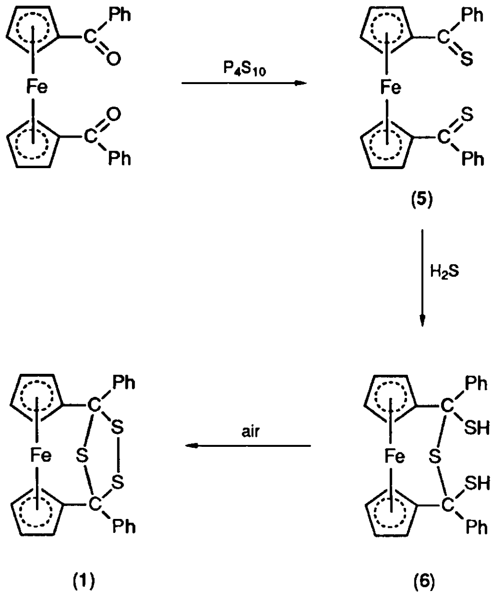
inclined at an angle of 8.5°, while the ring centroids subtend an angle at iron of 174.9°. Thus as well as a bending at iron, there is also a simple tilting of the rings about their centroids, as shown by the variation of the Fe–C bond lengths (Table 2). The bending at iron is much more than observed in the two derivatives (**3**)[14] and (**4**);[15] in (**3**) the ring centroids subtend an angle of 177.1° at iron, while in (**4**) the angle is 177.6°. In compound (**1**) the rings are twisted by 2.6(2)° from the fully eclipsed conformation, as compared with 0.1 and 1.5° in (**3**) and (**4**) respectively.





(**3**) X = S
(**4**) X = Se

The observed n.m.r. spectra in solution are readily interpreted in terms of the structure revealed by *X*-ray analysis, provided only that the rotation of the phenyl rings about bonds C(16)–C(31) and C(26)–C(41) is not restrained. The presence of the trithiolane ring renders distinct each of the four C–H fragments in the cyclopentadienyl rings, although the two cyclopentadienyl rings are equivalent; hence the observation of four signals due to cyclopentadienyl C–H fragments in the ^{1}H and ^{13}C n.m.r. spectra. The molecule contains two types of quaternary carbon atoms, other than in the phenyl rings, with δ_C 83.0 and 96.6 p.p.m.: we tentatively assign the resonance at higher frequency to the carbon bound to two sulphur atoms and that at lower frequency to the carbon in the cyclopentadienyl ring.



Scheme. Possible route for formation of complex (**1**)

While the mechanism of formation of (**1**) is not established, a reasonable route is that shown in the Scheme: thionation gives 1,1′-bis(thiobenzoyl)ferrocene (**5**) as the major isolated product, but H$_2$S (produced by the action of traces of moisture with P$_4$S$_{10}$) could add across the two thioketone groups to give the dithiol (**6**), oxidation of which provides (**1**) as the isolable byproduct.

Acknowledgements

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