The Crystal Structure of Di-μ-phenylthio-bis(cyclopentadienylcarbonyliron) at −160°

By G. FERGUSON,* C. HANNAWAY, and K. M. S. ISLAM

(Department of Chemistry, University of Glasgow, Glasgow, W.2, Scotland)

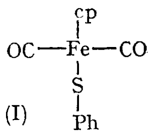
CONTROLLED dimerisation of $C_5H_5Fe(CO)_2SPh$ (I) results in two isomers of constitution $(C_5H_5FeCO{\cdot}SPh)_2$ (II), one of which (m.p. 170°) is thermodynamically more stable than the other (m.p. 166°).[1] At least five geometrical isomers of (II) can be formulated; although spectroscopic evidence did not allow an unequivocal establishment of stereochemistry, two of the possibilities can be eliminated from ^1H n.m.r. spectra. It was conceivable that the more stable isomer was the *all-trans*-system (III), but as this was by no means certain the more stable crystalline material† was examined by single-crystal *X*-ray methods.

The crystals are monoclinic, space group $P2_1/c$, with eight molecules of $C_{24}H_{20}Fe_2S_2O_2$ in a unit cell of dimensions $a = 10{\cdot}13$, $b = 23{\cdot}22$, $c = 17{\cdot}98$ Å, $\beta = 97{\cdot}3°$. 3700 *X*-ray intensity data were estimated visually from Weissenberg photographs of a crystal at −160° rotating about *a*. The iron and sulphur atoms of the two independent molecules in the asymmetric crystal unit were found by Patterson methods and the lighter atoms by

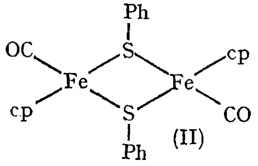
---

† This was kindly supplied by Dr. G. R. Knox, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, C.1.

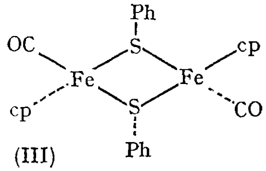
application of the heavy-atom method. Refinement by isotropic least-squares calculations has lowered R to 0·12.[2]



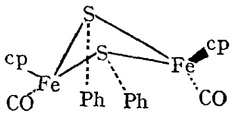
(I)



(II)



(III)



(IV)

Our results establish that the more stable isomer obtained on dimerisation of (I) has the *cis*-configuration (IV). The two independent molecules in the asymmetric unit have closely similar but not identical conformations; the small differences can be rationalised in terms of intermolecular packing effects. A detailed view of one of the molecules is given in the Figure.

In both molecules the Fe–S–Fe–S cycle is slightly puckered, equivalent, for example, to the ring being folded about a line through the Fe atoms through 16° in one molecule and 19° in the other. The mean length of the eight Fe–S bonds in the asymmetric unit is 2·262 ± 0·006 Å, close to the mean lengths in $[EtSFe(CO)_3]_2$ (2·259 ± 0·007 Å),[3] $[EtSFe(NO)_2]_2$ (2·27 ± 0·004 Å),[4] and to three of the bonds in $(C_5H_5FeS)_4$ (2·256 ± 0·002 Å).[5] The incorporation of the octahedral iron and tetrahedral sulphur atoms in a four-membered ring has resulted in the internal angles at these atoms being reduced by about 10° from the values appropriate to undisturbed tetrahedral and octahedral geometry; thus the S–Fe–S angles are all 81° while the Fe–S–Fe angles are 98°. The Fe · · · Fe intramolecular distance, 3·39 Å in both molecules, is too long to accommodate a 'bent' bond of the type found in the compound $[EtSFe(CO)_3]_2$,[3] but this kind of bond is, in any case, precluded here by consideration of the magnetic properties of (IV).

In each molecule the Fe–C–O bonds are, within experimental error, linear, parallel and therefore coplanar. The mean Fe–C and C–O distances of **1·71 ± 0·03** and **1·12 ± 0·03 Å** respectively compare well with distances reported for example in $[C_5H_5Fe(CO)_2]_2$ (1·75 ± 0·03 and 1·12 ± 0·04 Å).[6] The orientation of the phenyl rings in both molecules is almost identical and can be seen in the Figure. The mean S–C bond length and Fe–S–C angle are 1·76 ± 0·05 Å and 113° respectively. The mean distance of the iron atoms from the plane through the appropriate cyclopentadienyl ring is **1·71 Å**, intermediate between the values found for ferrocene (1·66 ± 0·02 Å)[7] and the somewhat larger values found for $[C_5H_5Fe(CO)_2]_2$ (1·75 ± 0·03 Å[6] and $(C_5H_5FeS)_4$ (1·757 ± 0·005 Å).[5]

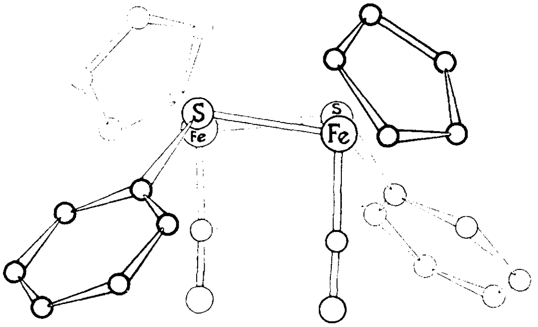


FIGURE. *A view of one molecule showing the folding of the* Fe-S *ring and the orientation of the cyclopentadienyl and phenyl rings.*

Disorder of cyclopentadienyl rings is not uncommon in ferrocene compounds at room temperature.[5] The intensity data used in our calculations were deliberately collected at −160° in an attempt to avoid such possible complications. However there is evidence from a difference synthesis and from thermal parameters that even at this low temperature a cyclopentadienyl ring of one molecule is disordered; the mean U_{iso} of its carbon atoms is 0·06 Å^2 compared with a mean of 0·03 Å^2 in the other cyclopentadienyl rings.

(*Received, July* 15*th*, 1968; *Com.* 951.)

---

[1] M. Ahmad, R. Bruce, and G. R. Knox, *J. Organometallic Chem.*, 1966, **6**, 1.

[2] C. Hannaway, B.Sc. Thesis, Glasgow, 1968.

[3] L. F. Dahl and C.-H. Wei, *Inorg. Chem.*, 1963, **2**, 328.

[4] J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Cryst.*, 1958, **11**, 599.

[5] R. A. Schunn, C. J. Fritchie, and C. T. Prewitt, *Inorg. Chem.*, 1966, **5**, 892.

[6] O. S. Mills, *Acta Cryst.*, 1958, **11**, 620.

[7] J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Cryst.*, 1956, **9**, 373.