

The Structure of 1,4-(1,1'-Ferrocenediyl)butan-1-one ([4]-Ferrocenophan-1-one)

BY T. STANLEY CAMERON AND RUTH E. CORDES

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

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Abstract. $C_{14}H_{14}FeO$, orthorhombic, $P2_12_12_1$, $a = 5.785$ (3), $b = 11.090$ (3), $c = 17.115$ (8) Å; $Z = 4$, $D_c = 1.537$ Mg m⁻³, Cu $K\alpha_1$ (carbon monochromator), $\mu = 10.64$ mm⁻¹, $\lambda = 1.54051$ Å. The structure was solved by the heavy-atom method and refined by a full-matrix least-squares procedure to $R = 0.04$ for 791 reflections. The planes of the two cyclopentadienyl groups are essentially parallel and the molecular configuration suggests considerable steric strain in the bridging group. The structure is poorly resolved, probably because of high thermal motion.

Introduction. It has been suggested (Watts, 1967; Barr, Boulton, Lentzner & Watts, 1969) that the anomalous reactivity of the 4-ferrocenophanes compared with the 3- and 5-ferrocenophanes can be attributed either to an unusual angle of tilt between the planes of the two cyclopentadienyl rings or to the steric strain induced in the bridging group by the planes of the two cyclopentadienyl groups remaining parallel. In the 3-ferrocenophanes the bite of the bridging group comfortably spans the two cyclopentadienyl groups without too much distortion of the bridging group or of the ferrocene moiety (Jones, Marsh & Richards, 1965), while the bridging group of the 5-ferrocenophanes is sufficiently long to adjust to the preferred, parallel ring planes, conformation of the ferrocene fragment (Shul'pin & Rybinskaya, 1974, and references therein). In the 4-ferrocenophanes, the bridging group is too long to accommodate and too short to adjust easily to an undistorted ferrocene. The structure of the title compound was determined in order to examine in particular the molecular configuration of this bridging group.

The crystals, which were prepared by W. E. Watts, are orange translucent prisms. From these a small piece was cut and carefully ground until it was approximately spherical with a diameter of 0.13 mm. The crystals slowly evaporate in the X-ray beam, so the needle was sealed in a Lindemann-glass capillary tube. The crystal system and approximate cell dimensions were determined from Weissenberg photographs. Systematic extinctions $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, $00l$, $l = 2n + 1$ uniquely indicated space group $P2_12_12_1$. The cell dimensions were refined from 12 general reflections with 2θ between 70–75° on a Picker FACS-

1 four-circle diffractometer. With Cu $K\alpha_1$ radiation (carbon monochromator) 923 independent reflections were measured, with 2θ between 0 and 120°, of which 791 had $I > 3\sigma(I)$. The pulse-height discriminator on the radiation analyser of the diffractometer was set to exclude the fluorescent Fe radiation. The data were reduced to a standard scale by comparison with the intensities of three standard reflections which were measured after every 58 reflections and which showed a slight (6–10%) decrease over the data collection. The steady decrease in the intensities of the standard reflections could be fitted to a first-order decay with a deviation of 0.008. The actual deviation, in these intensities, from the counting statistics, is 0.012. The

Table 1. Atomic parameters ($\times 10^4$, except $\times 10^3$ for hydrogen)

	x	y	z
Fe	3367 (2)	3915 (1)	8312 (0)
C(1)	3447 (14)	5635 (6)	7982 (4)
C(2)	2101 (13)	4987 (7)	7443 (4)
C(3)	3500 (15)	4068 (7)	7117 (4)
C(4)	5743 (12)	4177 (7)	7434 (4)
C(5)	5786 (12)	5135 (6)	7968 (4)
C(11)	3001 (15)	3831 (6)	9489 (3)
C(12)	851 (14)	3651 (7)	9116 (5)
C(13)	1035 (16)	2644 (8)	8643 (5)
C(14)	3301 (19)	2187 (6)	8727 (4)
C(15)	4464 (14)	2929 (7)	9247 (4)
C(21)	3789 (25)	4768 (7)	10071 (4)
C(22)	3229 (25)	6014 (8)	9970 (4)
C(23)	3894 (14)	6761 (6)	9286 (4)
C(24)	2499 (13)	6445 (6)	8571 (4)
O(1)	535 (10)	6838 (5)	8509 (4)
H(2)	44 (5)	492 (8)	728 (4)
H(3)	285 (12)	344 (5)	676 (3)
H(4)	708 (12)	358 (6)	738 (5)
H(5)	722 (7)	545 (6)	823 (4)
H(12)	-50 (9)	420 (5)	918 (4)
H(13)	-10 (16)	220 (10)	830 (6)
H(14)	426 (19)	151 (8)	850 (6)
H(15)	605 (8)	275 (9)	943 (6)
H(211)	358 (11)	458 (7)	1065 (2)
H(212)	543 (4)	501 (8)	995 (4)
H(221)	331 (19)	644 (8)	1050 (5)
H(222)	186 (20)	538 (13)	992 (8)
H(231)	552 (6)	654 (7)	914 (5)
H(232)	379 (16)	766 (2)	934 (8)

data were corrected for Lorentz, polarization, and primary-extinction effects.

The position of the Fe atom was established from a Patterson function, and the locations of the remaining non-hydrogen atoms from an F_o synthesis phased on the position of this heavy atom. After three cycles of full-matrix least-squares refinement [$\sum \omega(\Delta F)^2 = \min.$] with isotropic temperature factors on all atoms R was 0.09. The H atom positions were determined from the geometry of the molecule and refinement was continued with anisotropic temperature factors on all but these H atoms, which had a common temperature factor. It converged with $R = 0.041$ [$wR = 0.043$ for 785 reflections (6 reflections were removed because of extinction effects)]. The weights were calculated from $w = (\sigma^2|F_o|^2 + 0.0008F^2)^{-1}$ where σ is the standard deviation for each reflection, and was derived from the diffractometer counting statistics. A similar refinement with the alternative enantiomorph converged at $R = 0.06$.

The scattering factors used were taken from *International Tables for X-ray Crystallography* (1974) and were corrected for anomalous dispersion. The refinement was performed with the *X-ray System* of Sheldrick (1976).

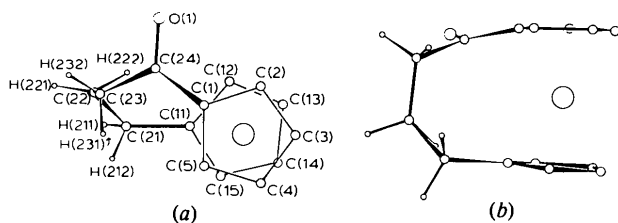


Fig. 1. The individual molecule viewed (a) perpendicular and (b) parallel to the C(1)–C(5) plane.

Table 2. Interatomic distances (Å) and interbond angles (°)

C(1)–C(2)	1.404 (10)	C(2)–C(1)–C(5)	107.9 (6)
C(1)–C(5)	1.463 (10)	C(2)–C(1)–C(24)	124.1 (7)
C(1)–C(24)	1.457 (10)	C(5)–C(1)–C(24)	126.4 (6)
C(2)–C(3)	1.417 (11)	C(1)–C(2)–C(3)	108.1 (6)
C(3)–C(4)	1.411 (10)	C(2)–C(3)–C(4)	108.1 (6)
C(4)–C(5)	1.401 (10)	C(3)–C(4)–C(5)	109.4 (6)
C(11)–C(12)	1.412 (11)	C(1)–C(5)–C(4)	106.4 (6)
C(11)–C(15)	1.374 (10)	C(12)–C(11)–C(15)	107.6 (7)
C(11)–C(21)	1.510 (12)	C(12)–C(11)–C(21)	131.4 (7)
C(12)–C(13)	1.385 (12)	C(15)–C(11)–C(21)	121.0 (7)
C(13)–C(14)	1.413 (12)	C(11)–C(12)–C(13)	108.1 (7)
C(14)–C(15)	1.387 (11)	C(12)–C(13)–C(14)	107.6 (7)
C(21)–C(22)	1.432 (14)	C(13)–C(14)–C(15)	107.6 (7)
C(22)–C(23)	1.484 (13)	C(11)–C(15)–C(14)	109.1 (7)
C(23)–C(24)	1.507 (10)	C(11)–C(21)–C(22)	121.2 (8)
C(24)–O(1)	1.221 (9)	C(21)–C(22)–C(23)	125.2 (9)
		C(22)–C(23)–C(24)	111.8 (7)
		C(1)–C(24)–C(23)	120.2 (6)
		C(1)–C(24)–O(1)	120.7 (7)
		C(23)–C(24)–O(1)	119.0 (7)

Table 1 gives the atomic parameters; the interatomic distances and interbond angles are given in Table 2. The molecule is shown in Fig. 1 and the packing diagram in Fig. 2.*

Discussion. The crystal is constructed from isolated molecules which pack (Fig. 2) with the methylene groups of a pair of molecules adjacent and the plane of a cyclopentadienyl group of another molecule close to the 'open' side of the ferrocene sandwich. In the molecule itself the angle between the planes of the two cyclopentadienyl groups is $4.4(1)^\circ$ and the two C_5 rings are almost exactly staggered (Fig. 1a). The angle between the planes, such as it is, does not occur in the general direction of the bridging group, but is approximately at right angles to it. This bridging group spans the minimum distance for a staggered ferrocene so that it revolves through approximately one tenth of a turn around the cp–Fe–cp axis. Atom C(21) of the methylene group bonded to the cyclopentadienyl is 0.02 \AA from the least-squares plane through that ring. C(24) (the carbonyl C atom) however is 0.33 \AA from the plane of the ring to which it is bonded and the angle between the plane through atoms C(1), C(23), and O(1) and the ring plane is $18.3(1)^\circ$. The steric strain therefore in this 4-ferrocenophane occurs at the carbonyl junction between the bridge and the cyclopentadienyl group while the ferrocene fragment remains practically undistorted. With the plane of the carbonyl group inclined at 18° to that of the ring, there will be considerable conjugation between the π systems of this group and the ring, and it is possible that this specifically strained junction is a consequence of the carbonyl conjugation.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34140 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

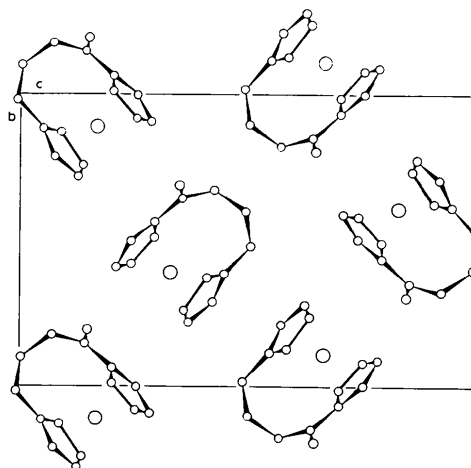


Fig. 2. The unit cell projected along a .

The reliability of the dimensions of this compound is disappointingly low; indeed the data reported here are the third attempt with the sample. Previously the crystals had required absorption corrections and the refinements had converged at $R = 0.07$, with a needle-shaped fragment cut from a larger crystal and $R = 0.09$ with a less-regular fragment. Although R is 0.04 in this third attempt, the resolution of the structure is not much improved.

It seems therefore that there is some other factor inherent in the crystal structure which is causing the poor resolution. The two most likely possibilities are either some static disorder, or large molecular librations. The molecule possesses an approximate C_2 axis (Fig. 1a) which passes through the Fe atom and bisects the C(22)–C(23) bond. Operation around this axis would exchange O(1) with H(211) and H(212) with the π electrons on C(24) but otherwise would interchange similar atoms. The space actually occupied by C(24)–O(1) and C(21)–H(211) with C(21)–H(212) is approximately equivalent so an attempt was made to refine the structure with the two possible orientations present simultaneously. Both orientations were refined as rigid bodies (André, Fourme & Renaud, 1972) with each given a single occupation factor. The value of each occupation factor was refined and the sum of them both was kept equal to one. The refinement converged with one occupation factor at one and the other zero. The difference Fourier series at this stage had no unusual features, so that significant static disorder is unlikely.

The temperature factors of C(13), C(14), C(21) and C(22) are unusually large, and this suggests a libration of the C(11)–C(15) ring pivoting somewhere close to C(11) and involving the atoms on either side [*i.e.* C(13), C(14) in the ring and C(21), C(22) attached to it]. A van der Waals plot (Watkin, 1972) shows that the molecules are not as closely packed as is usual although there are no gross interstices. This absence of strong intermolecular attractions fits in with the observed significant vapour pressure of the crystal and is not inconsistent with large molecular librations. These librations therefore are the most reasonable explanation for the poor resolution of the structure.

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Two Modifications of Bis[(2-thienyl)methyldithiophosphinato]nickel(II)

BY H. WUNDERLICH AND H.-G. WUSSOW

Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, Universitätsstrasse 1, 4000 Düsseldorf, Federal Republic of Germany

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Abstract. $Ni(C_5H_6PS_2)_2$, $C_{10}H_{12}NiP_2S_6$, monoclinic, $P2_1/c$, $Z = 2$, $M_r = 445.25$. Modification A: $a = 8.499$ (4), $b = 6.513$ (4), $c = 16.413$ (7) Å, $\beta = 108.91$ (4)°, $D_m = 1.70$, $D_x = 1.72$ Mg m⁻³, $\mu(Mo K\alpha) = 2.04$ mm⁻¹. Modification B: $a = 7.964$ (4), $b = 11.640$ (10), $c = 9.439$ (3) Å, $\beta = 106.52$ (3)°, $D_m = 1.67$, $D_x = 1.76$ Mg m⁻³, $\mu(Mo K\alpha) = 1.99$ mm⁻¹. The crystal structures of modifications A and B were refined to $R = 0.04$. Both molecules are centrosymmetric with Ni at $\bar{1}$; thus the thienyl and methyl groups are *trans* with respect to the plane of the four-coordinated Ni

atoms. The thienyl rings show a twofold disorder with the predominating orientation opposite in both structures.

Introduction. The crystal structures of several $Ni(S_2PR^1R^2)_2$ complexes with identical substituents R have been reported: CH_3 (Jones, Ansell & Katz, 1969), C_2H_5 (Shetty & Fernando, 1969), C_6H_5 (Porta, Sgamellotti & Vinciguerra, 1968), CH_3O (Kastalsky & McConnell, 1969), and C_2H_5O (McConnell & Kastalsky, 1967). In all these structures there is a planar