that the local anesthetics compete for the calcium binding sites on the phosphate group.

We gratefully acknowledge the support of this work by a grant, PCM76-23288, from the National Science Foundation.

References

Baker, R. W., Chothia, C. H., Pauling, P. J. & Petcher, T. J. (1971). *Nature (London)*, **230**, 439–445.

Blaustein, M. P. & Goldman, D. E. (1966). *J. Gen. Physiol.* **49**, 1043–1063.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

DeTitta, G. T. & Craven, B. M. (1973). *Acta Cryst.* B**29**, 1354–1357.

Elder, M., Hitchcock, P., Mason, R. & Shipley, G. (1977). *Proc. R. Soc. London Ser. A*, **354**, 157–170.

Hughes, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1737–1352.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Keith, A. D., Snipes, W. & Chapman, D. (1977). *Biochemistry*, **16**, 634–641.

Main, P., Woolfson, M. M. & Germain, G. (1971). *MULTAN. A Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Pauling, L. (1960). *The Nature of the Chemical Bond*, p. 260. Ithaca: Cornell Univ. Press.

Sax, M. & Pletcher, J. (1969). *Science*, **166**, 1546–1548.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Sundaralingam, M. (1968). *Nature (London)*, **217**, 35–37.

Sundaralingam, M. (1972). *Ann. NY Acad. Sci.* **195**, 324–355.

Sundaralingam, M. & Arora, S. K. (1972). *J. Mol. Biol.* **71**, 49–70.

Acta Cryst. (1979). B**35**, 2699–2702

Ethyl Ester of (*Z*)-2-Ferrocenyl-2-methylcyclopropanecarboxylic Acid

By Z. Kałuski and E. Skrzypczak-Jankun

Institute of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 *Poznań, Poland*

and M. Cygler

Institute of Chemistry, University of Łódź, Nowotki 18, 91-416 *Łódź, Poland*

(*Received* 27 *February* 1979; *accepted* 6 *July* 1979)

Abstract. $C_{17}H_{20}FeO_2$, $M_r = 312{\cdot}2$, triclinic, $P\bar{1}$, $a = 7{\cdot}580\,(2)$, $b = 11{\cdot}121\,(3)$, $c = 10{\cdot}187\,(3)$ Å, $\alpha = 100{\cdot}48\,(5)$, $\beta = 103{\cdot}85\,(5)$, $\gamma = 111{\cdot}85\,(5)°$, $d_m = 1{\cdot}39$, $Z = 2$, $d_x = 1{\cdot}40$ Mg m^{-3}, $V = 738{\cdot}2$ Å^3. The structure was solved by heavy-atom methods and refined to $R_F = 0{\cdot}033$ for 2512 reflexions. X-ray analysis confirmed the *Z* configuration of the title compound. The cyclopentadienyl rings in the ferrocenyl skeleton are parallel within 1·3° and twisted about 3·8° from the eclipsed conformation.

Introduction. Although most ferrocene derivatives have been explored, little is known about the chemistry of the ferrocenylcycloalkanes. This work is an example of an X-ray study of the structural properties of the smallest ring, *i.e.* cyclopropane, combined with a ferrocenyl substituent. The X-ray investigations were undertaken in order to determine unequivocally the configuration and the preferable conformation of the ethyl ester of (*Z*)-2-ferrocenyl-2-methylcyclopropanecarboxylic acid.

Crystals suitable for X-ray analysis were obtained by slow cooling of a saturated petroleum ether solution. The crystal chosen was cut and formed into the shape of a barrel 0·2 mm in diameter and height. The measurements were performed on a Syntex $P2_1$ four-circle diffractometer with Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å) graphite-monochromated radiation. The data set ($2\theta_{\max} = 60°$, θ–2θ scan, scan speeds varying linearly between 2·0 and 29·30° min^{-1}) contained 3033 reflexions, of which 2518 with $I > 3\sigma(I)$ were used in the calculations. Intensities were corrected for Lorentz and polarization effects but not for absorption ($\mu_l = 1{\cdot}05$ mm^{-1}).

Structure analyses attempted in space groups $P1$ and $P\bar{1}$ showed the latter to be correct. Firstly, as the piezo effect was ambiguous, space group $P1$ was chosen on the basis of *E* statistics. The structure was solved by heavy-atom methods and refined by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms to $R = 0{\cdot}049$. The H atoms were easily located from a difference map, and were included in the calculations with fixed parameters. The *R* value fell to 0·033 but convergence in the refinement process could not be reached and a model of the molecular

0567-7408/79/112699-04$01.00

structure was unsatisfactory. For instance, the lengths of the chemically equivalent C—C bonds in the cyclopentadienyl rings varied from 1·316 to 1·506 Å; however, the mean value of 1·422 Å agrees very well with the expected value. The same was observed for the other bond distances and angles. The origin was shifted, therefore, and the calculations were carried out for the alternative space group $P\bar{1}$. The structure was refined by full-matrix least squares, dividing the molecule into two parts: (I) Fe, C(1)–C(11), and (II) C(11)–C(15), O(1), O(2), C(16), C(17). A difference Fourier map clearly showed all the H atoms which were included in the refinement and their parameters were allowed to vary. The final agreement factor was $R_F = 0{\cdot}033$ with a corresponding $R_w = \sum w^{1/2}|F_o - F_c|/\sum w^{1/2}|F_o| = 0{\cdot}039$ for 2512 reflexions (six reflexions suffering from extinction were removed from the last stages of refinement). The function minimized was $\sum w|F_o - F_c|^2$, with the weights $w = k/[\sigma^2(F_o) + gF_o^2]$, where the coefficients k and g were refined and converged at $k = 0{\cdot}2547$, $g = 0{\cdot}005391$. Neutral-atom scattering factors were taken from Cromer & Mann (1968). The final difference map was featureless and contained a maximum peak of 0·3 e $Å^{-3}$. The molecular structure for space group $P\bar{1}$ was chemically reasonable so this solution was accepted as correct. On the basis of Hamilton's test we can assert that this hypothesis could not be rejected without committing an error exceeding 50%.

Positional parameters are listed in Table 1.* The *XTL/E-XTL* (Syntex, 1976) and *SHELX* (Sheldrick, 1976) systems were used for the calculations.

Discussion. X-ray analysis confirmed the *Z* configuration; this was previously predicted by chemical and spectroscopic methods (Ratajczak, Czech & Zyzik, 1975; Ratajczak & Zyzik, 1975).

Table 1. *Positional parameters* ($\times 10^5$ *for* Fe, $\times 10^4$ *for the other atoms*) *and approximate isotropic temperature factors* ($Å^2$)

	x	y	z	B_i
Fe	5725 (4)	23232 (3)	21608 (3)	2·8
C(1)	758 (3)	2192 (2)	4160 (2)	2·8
C(2)	1037 (4)	1127 (2)	3367 (3)	3·4
C(3)	2720 (4)	1696 (3)	2927 (3)	3·6
C(4)	3494 (4)	3118 (3)	3443 (3)	3·9
C(5)	2290 (4)	3425 (2)	4201 (2)	3·0
C(6)	−2135 (5)	2328 (4)	1291 (3)	5·6
C(7)	−2009 (4)	1205 (3)	491 (3)	4·2
C(8)	−372 (5)	1690 (3)	−6 (3)	4·4
C(9)	511 (5)	3117 (3)	496 (3)	4·6
C(10)	−570 (5)	3519 (3)	1287 (3)	5·0
C(11)	−856 (3)	2013 (2)	4790 (2)	3·3
C(12)	−279 (4)	2567 (3)	6402 (3)	3·9
C(13)	−1174 (5)	3205 (3)	5427 (3)	4·8
C(14)	−2684 (4)	671 (3)	4123 (3)	4·3
C(15)	1858 (4)	3294 (2)	7292 (2)	3·8
O(1)	2912 (3)	4455 (2)	7508 (2)	5·0
O(2)	2476 (3)	2444 (2)	7833 (2)	4·0
C(16)	4584 (5)	2994 (4)	8700 (3)	5·0
C(17)	5905 (5)	3090 (4)	7825 (4)	5·4
H(21)	239 (38)	237 (28)	3194 (27)	3·2
H(31)	3179 (49)	1292 (35)	2244 (37)	5·8
H(41)	4629 (47)	3786 (32)	3312 (33)	4·9
H(51)	2250 (48)	4254 (34)	4532 (35)	5·4
H(61)	−2852 (66)	2429 (46)	2000 (48)	9·6
H(71)	−2771 (51)	359 (35)	327 (35)	5·1
H(81)	120 (54)	1110 (39)	−476 (40)	6·4
H(91)	1794 (47)	3751 (33)	365 (34)	5·4
H(101)	−219 (50)	4488 (37)	1922 (37)	5·5
H(121)	−1107 (43)	1989 (30)	6816 (31)	4·6
H(131)	−143 (55)	4150 (38)	5558 (37)	6·0
H(132)	−2385 (65)	3020 (43)	5362 (43)	8·0
H(141)	−3267 (49)	569 (33)	3180 (39)	4·7
H(142)	−2341 (59)	−56 (41)	4319 (40)	7·2
H(143)	−3621 (60)	646 (40)	4549 (42)	7·7
H(161)	5026 (48)	3898 (35)	9292 (35)	4·9
H(162)	4611 (51)	2489 (35)	9283 (39)	5·6
H(171)	5881 (49)	3822 (35)	7355 (37)	5·6
H(172)	7247 (57)	3431 (35)	8491 (38)	5·9
H(173)	5610 (65)	2444 (48)	7227 (48)	11·7

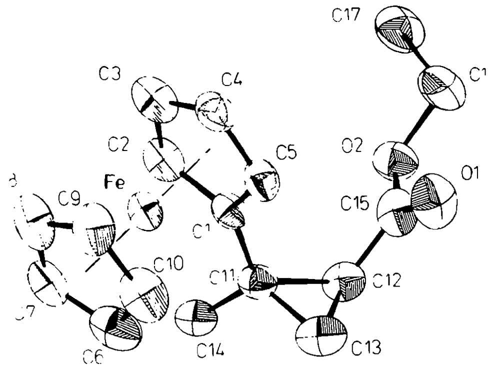


Fig. 1. An *ORTEP* diagram of the molecule.

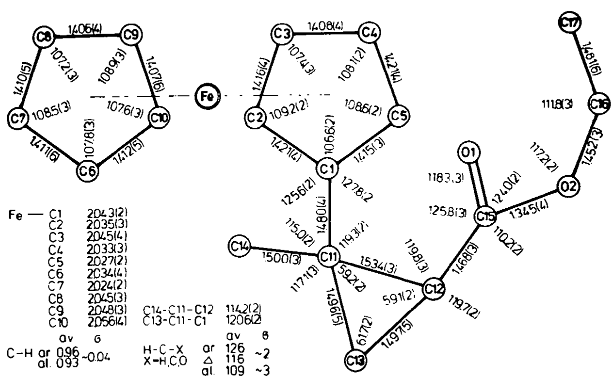


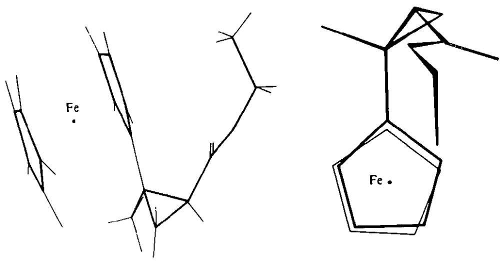
Fig. 2. Schematic drawing of the molecule with distances (Å) and angles (°).

---

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34591 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

An *ORTEP* (Johnson, 1965) drawing is shown in Fig. 1. The intramolecular distances and angles are given in Fig. 2. Bond lengths and valency angles in the ferrocenyl skeleton agree well with values recently cited for other 1-substituted ferrocenes (diffractometrically measured intensities, H atoms included in the refinement; Hall & Brown, 1971; Sime & Sime, 1974; Brown & Hall, 1977). The average values are 1·413 [15] Å* for C—C in cyclopentadienyl (Cp) rings and 2·039 [10] Å for Fe—C. These are consistent with the mean values 1·428 [14] and 2·045 [13] Å calculated for ferrocene derivatives mentioned in *Molecular Structures and Dimensions* (1970 1977) and in other works cited elsewhere in this paper. The remaining bond lengths and valency angles agree with their expected values.

In accordance with the fact that the cyclopropane ring behaves chemically much like a double bond, the C(1)—C(11) and C(12)—C(15) bonds are comparable with a single bond in a conjugated system. Such a great difference in bond lengths as that between C(11)—C(12) and C(11)—C(13), C(12)—C(13) is frequently observed in cyclopropane rings (for instance: Heller, Dreiding, Grieb & Niggli, 1972; Saenger, Schwalbe, Fellenberger & Schöllkopf, 1973; Eraker & Rømming, 1967; Carlström, 1975; Herbstein & Kaftory, 1977; Martínez, Cano & García-Blanco, 1977). There is evidence for shortening of the C—C bond in the cyclopropane ring opposite a C atom to which an unsaturated group is attached (Hoffmann, 1970, 1971; Lauher & Ibers, 1975). In the present structure the C(11)—C(12) bond of 1·534 (3) Å, opposite the unsubstituted C(13), is the longest in the cyclopropane ring. The other two bonds, C(11)—C(13) opposite the carboxyl and C(12)—C(13) opposite the ferrocenyl group, are definitely shorter and equal to each other, 1·496 (5), 1·497 (5) Å respectively. The same difference in bond lengths is observed in a similarly substituted cyclopropane ring in (*R*)-(—)-2,2-diphenylcyclopropanecarboxylic acid and *R*-(+)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid (Chiang, Lin, Wang, Curtin & Paul, 1977).



(*a*) (*b*)

Fig. 3. Views of the molecule: (*a*) *yz* projection, (*b*) projection on the plane of the unsubstituted Cp ring.

The five-membered rings are planar; no atom of either ring is displaced more than ±0·001 Å (±0·003 Å) from the least-squares best plane through the substituted (unsubstituted) Cp ring. The intramolecular contacts between the atoms in the two rings are as follows (e.s.d.'s = 0·004 Å): C(1)···C(6) = 3·274, C(2)···C(7) = 3·305, C(3)···C(8) = 3·324, C(4)···C(9) = 3·297, C(5)···C(10) = 3·274 Å.

As for most ferrocene derivatives (Kałuski & Skrzypczak-Jankun, 1978) the conformational angles φ and ω are both less than 10°. The two ring planes are inclined at 1·33° to each other and the Cp rings are twisted from the eclipsed conformation by about 3·8°.

The best planes calculated through the atoms: (I) C(1)–C(5); (II) C(11), C(12), C(13); (III) C(12), C(15), O(1), O(2), form the angles I/II = 78·8, II/III = 115·2, I/III = 67·2°.

The intermolecular distances associated with the van der Waals contacts are all in the normal range. Two views of the molecule are in Fig. 3.

We wish to thank Professor A. Ratajczak and Dr H. Zyzik, Silesian University, Katowice, for supplying the substances. This work was supported by the Polish Academy of Sciences in the framework of project MRI-9,1.13.3.

References

Brown, G. M. & Hall, L. H. (1977). *Acta Cryst.* B**33**, 876–879.

Carlström, D. (1975). *Acta Cryst.* B**31**, 2185–2188.

Chiang, C. C., Lin, C.-T., Wang, A. H.-J., Curtin, D. Y. & Paul, I. C. (1977). *J. Am. Chem. Soc.* **99**, 6303–6308.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Eraker, J. & Rømming, C. (1967). *Acta Chem. Scand.* **21**, 2721–2726.

Hall, L. H. & Brown, G. M. (1971). *Acta Cryst.* B**27**, 81–90.

Heller, J., Dreiding, A. S., Grieb, R. & Niggli, A. (1972). *Angew. Chem.* **2**, 170–172.

Herbstein, F. H. & Kaftory, M. (1977). *Acta Cryst.* B**33**, 3318–3321.

Hoffmann, R. (1970). *Tetrahedron Lett.* p. 2907.

Hoffmann, R. (1971). *Proc. Int. Congr. Pure Appl. Chem.* **2**, 233.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Kałuski, Z. & Skrzypczak-Jankun, E. (1978). *On the Conformation of Ferrocene Type π-Complex Compounds.* Pre-Congress Symposium on Organic Crystal Chemistry, Dymaczewo, Poland, 30 July–2 August, 1978.

Lauher, J. W. & Ibers, J. A. (1975). *J. Am. Chem. Soc.* **97**, 561.

Martínez, M. L., Cano, F. H. & García-Blanco, S. (1977). *Acta Cryst.* B**33**, 3913–3915.

Molecular Structures and Dimensions (1970–1977). *Bibliographies.* Vol. 2 – Vol. 8. Utrecht: Bohn, Scheltema & Holkema.

---

* Values in square brackets are root-mean-square deviations.

Ratajczak, A., Czech, B. & Zyzik, H. (1975). *Rocz. Chem.* **49**, 953–958.

Ratajczak, A. & Zyzik, H. (1975). *Rocz. Chem.* **49**, 945–951.

Saenger, W., Schwalbe, C. H., Fellenberger, K. & Schöllkopf, U. (1973). *Chem. Ber.* **106**, 2883–2889.

Sheldrick, G. M. (1976). *SHELX*. A program for crystal structure determination. Univ. of Cambridge, England.

Sime, R. L. & Sime, R. J. (1974). *J. Am. Chem. Soc.* **96**, 892–898.

Syntex (1976). *The Syntex XTL/E-XTL Structure Determination System*. Syntex Analytical Instruments, Inc., 10040 Bubb Road, Cupertino, California 95014, USA.

Acta Cryst. (1979). B**35**, 2702–2704

Structure of *cis*-Bis(2,2′-bipyridine)dimethylcobalt(III) Tetraethylaluminate

By Sanshiro Komiya,* Takakazu Yamamoto* and Akio Yamamoto

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 *Nagatsuta, Midori-ku, Yokohama* 227, *Japan*

and Akio Takenaka and Yoshio Sasada

Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, 4259 *Nagatsuta, Midori-ku, Yokohama* 227, *Japan*

(*Received* 11 *May* 1979; *accepted* 10 *July* 1979)

Abstract. $[Co(CH_3)_2(C_{10}H_8N_2)_2][Al(C_2H_5)_4]$, $C_{22}H_{22}CoN_4^+.C_8H_{20}Al^-$, monoclinic, $P2_1/c$, $Z = 4$, $a = 14{\cdot}010\,(1)$, $b = 19{\cdot}462\,(2)$, $c = 11{\cdot}081\,(1)$ Å, $\beta = 99{\cdot}15\,(1)°$, at room temperature; $D_x = 1{\cdot}19_2$, $D_m = 1{\cdot}21$ Mg m^{-3} (flotation). The crystal contains bis(2,2′-bipyridine)dimethylcobalt cations and tetraethylaluminium anions. The cation has an octahedral coordination, the two methyl groups lying at *cis* positions. The Co—N coordination distance shows the significant *trans* influence of the methyl group.

Introduction. A series of dialkylbis(2,2′-bipyridine)cobalt(III) cations have been prepared (Komiya, Bundo, Yamamoto & Yamamoto, 1979; Yamamoto, Bundo & Yamamoto, 1977). To confirm the *cis* configuration, an X-ray analysis of bis(2,2′-bipyridine)dimethylcobalt(III) tetraethylaluminate, $[Co(bpy)_2(CH_3)_2]^+[Al(C_2H_5)_4]^-$, has been performed.

Red prisms of the complex, suitable for X-ray diffraction studies, were obtained from a THF–diethyl ether–hexane solution. They are stable in dry air for at least 1 month, but they slowly decompose with moisture. The diffraction experiment was undertaken with a crystal $0{\cdot}05 \times 0{\cdot}06 \times 0{\cdot}06$ mm sealed in an N_2-filled capillary.

Intensity data were collected on a Rigaku automated four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). The ω–2θ scan mode was employed with a scan width of 1·5° (in ω) plus α_1–α_2 divergence at a scan speed of 8° (in 2θ) min^{-1}. Intensities of four monitored reflexions gradually decreased by up to 15% throughout the experiment. Out of 5250 independent reflexions in the range $2 < 2\theta < 50°$, 1326 weak reflexions with counts less than the background were considered as zero-reflexions. Intensities were corrected for Lorentz and polarization factors but not for absorption effects. The standard deviation for each reflexion was estimated by $\sigma^2(F) = \sigma_p^2 + qF_o^2$, where σ_p is from counting statistics and q is $9{\cdot}38 \times 10^{-4}$, derived from the variation of the monitored reflexions (McCandlish, Stout & Andrews, 1975).

The structure was solved by the heavy-atom method and atomic parameters were refined by block-diagonal least squares with the weight $1/\sigma(F)$. All the H atoms in the cation were found on a difference map, but they were not included in the least-squares calculations. The zero-reflexions were included in the least-squares calculation by assuming $F_o = F_{\rm lim}$ where $F_{\rm lim}$ was 5·76, an observational threshold value, but those for which $|F_c| < F_{\rm lim}$ were omitted. The final R value was 0·106 [$R = 0{\cdot}090$ for $F_o > 3\sigma(F)$]. The final atomic parameters are listed in Table 1.† Atomic scattering factors

---

* Authors to whom correspondence should be addressed.

† Lists of structure factors, thermal parameters, bond lengths, and the least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34608 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/79/112702-03$01.00