Ethyl Ester of 2-Nitro-3-ferrocenylacrylic Acid

By Ewa Skrzypczak-Jankun, Andrzej Hoser, Elżbieta Grzesiak and Zygmunt Kałuski

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

Abstract. $C_{15}H_{15}FeNO_4$, $M_r = 329 \cdot 1$, monoclinic, $P2_1/c$, $a = 10 \cdot 497$ (2), $b = 16 \cdot 655$ (3), $c = 8 \cdot 609$ (2) Å, $\beta = 108 \cdot 47$ (5)°, $Z = 4$, $D_x = 1 \cdot 531$ Mg m^{-3}. The structure was solved by direct methods. Refinement, by a full-matrix least-squares method, converged to $R_F = 0 \cdot 068$ ($R_w = 0 \cdot 037$) for 1944 observed reflections. The conjugated double-bond system cyclopentadienyl–C(11)=C(12)–C(13)=O(1) is not planar. The bonds C=C–C=O have the *s-cis* conformation with a torsion angle around the single bond of $-0 \cdot 9$ (5)°. The cyclopentadienyl rings in the ferrocenyl skeleton are within $1 \cdot 7$ (5)° from parallelism and $5 \cdot 0$ (5)° from eclipse.

Introduction. The title compound was synthesized and investigated in the Silesian University by Ratajczak and co-workers and supplied to us for a detailed description of the conjugated double-bond system.

A crystal suitable for X-ray analysis was obtained by slow evaporation of a saturated *n*-hexane solution. The unit-cell parameters were determined by least-squares calculation based on the angular settings for 15 automatically centred reflections with 2θ between 10 and 35°. Data were collected to $2\theta = 60°$ with Mo $K\alpha$ ($\lambda = 0 \cdot 71069$ Å) radiation, a graphite monochromator and the θ–2θ scan technique with scan speeds varying linearly between 2·00 and 29·30° min^{-1}, depending on the reflection intensity. Three control reflections were monitored every 50 measured intensities with no significant variation in intensity observed. Of the 4178 unique reflections, 1944 had $I > 1 \cdot 96\sigma(I)$ and were used in subsequent calculations. Intensities were corrected for Lp but not for absorption $[\mu_i(\text{Mo } K\alpha) = 1 \cdot 10$ mm$^{-1}]$.

The structure was solved by *MULTAN*. The Fe atom was located on an *E* map and the remaining atoms were found with the help of a Fourier synthesis. Full-matrix least-squares refinement, with anisotropic thermal parameters for all atoms, gave an *R* factor of 0·086. The H atoms were located on a difference map and were included in the refinement with all parameters fixed, except those for H(C11). The refinement converged to $R = 0 \cdot 068$ with a corresponding $R_w = \sum w^{1/2}|F_o - F_c|/\sum w^{1/2}|F_o| = 0 \cdot 037$ for 1944 reflections. The function minimized was $\sum w|F_o - F_c|^2$ with the weights $w = 1/\sigma^2(F_o)$. The *XTL/E-XTL* system of

Table 1. *Positional parameters* ($\times 10^5$ *for* Fe, $\times 10^4$ *for* C, N, O *and* $\times 10^3$ *for* H) *and isotropic temperature factors* B_i (Å^2)

	x	y	z	B_i
Fe	78911 (7)	13440 (4)	11612 (8)	2·71 (3)
C(1)	6506 (5)	747 (3)	−687 (5)	2·9 (2)
C(2)	6630 (5)	1567 (2)	−1149 (5)	3·1 (2)
C(3)	6281 (5)	2069 (3)	−14 (6)	3·6 (2)
C(4)	5956 (5)	1582 (3)	1165 (6)	3·8 (2)
C(5)	6130 (5)	765 (3)	773 (6)	3·2 (2)
C(6)	9829 (5)	1511 (4)	1204 (6)	4·5 (3)
C(7)	9671 (5)	734 (4)	1773 (7)	4·7 (3)
C(8)	9234 (5)	820 (4)	3160 (6)	4·3 (2)
C(9)	9110 (5)	1651 (4)	3443 (6)	4·2 (2)
C(10)	9485 (6)	2072 (3)	2227 (7)	4·8 (3)
C(11)	6706 (5)	2 (3)	−1465 (6)	2·8 (2)
C(12)	6928 (4)	−121 (3)	−2872 (5)	2·6 (2)
C(13)	6953 (5)	−925 (3)	−3579 (6)	3·7 (2)
C(14)	7192 (6)	−1648 (3)	−5859 (6)	4·6 (2)
C(15)	7508 (6)	−1470 (3)	−7385 (6)	5·3 (3)
O(1)	6787 (4)	−1533 (2)	−2915 (4)	4·6 (2)
O(2)	7173 (3)	−883 (2)	−5027 (4)	3·8 (1)
O(3)	8235 (4)	−855 (2)	−3502 (5)	5·8 (2)
O(4)	6144 (4)	798 (2)	−4970 (4)	5·7 (2)
N	7108 (5)	559 (2)	−3871 (5)	4·2 (2)
HC(2)	694	181	−222	5·0
HC(3)	612	267	−12	5·0
HC(4)	599	179	240	5·0
HC(5)	591	27	140	5·0
HC(6)	11	169	19	5·0
HC(7)	972	15	104	5·0
HC(8)	905	34	389	6·0
HC(9)	878	191	441	6·0
HC(10)	949	272	210	6·0
HC(11)	667 (2)	−47 (2)	−83 (4)	2·6 (9)
HC(141)	797	−203	−495	6·0
HC(142)	643	−208	−597	6·0
HC(151)	763	−199	−810	6·0
HC(152)	674	−109	−794	6·0
HC(153)	854	−115	−712	6·0

programs (Syntex, 1976) was used during the calculations. Positional parameters are listed in Table 1.*

Discussion. An *ORTEP* drawing of the molecule (Johnson, 1965) and the bond lengths and valency

C2–C1–C11–C12	−7·2(6)°
C1–C11–C12–C13	−172·6(6)°
C11–C12–C13–O1	−0·9(5)°
C11–C12–C13–O2	178·7(3)°

(a)

Fe–	C1	2·042(5)
	C2	2·044(5)
	C3	2·062(5)
	C4	2·071(5)
av. H C$_{a}$	1·09 Å	
∠ HCC	126°	C5	2·017(5)
H–C$_{a}$	1·09 Å	C6	2·042(6)
∠ HCC		C7	2·044(6)
∠ HCO } 109°		C8	2·044(5)
∠ HCH		C9	2·041(5)
		C10	2·035(6)

(b)
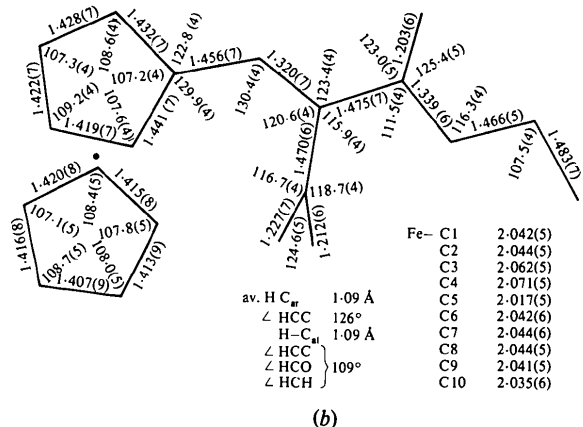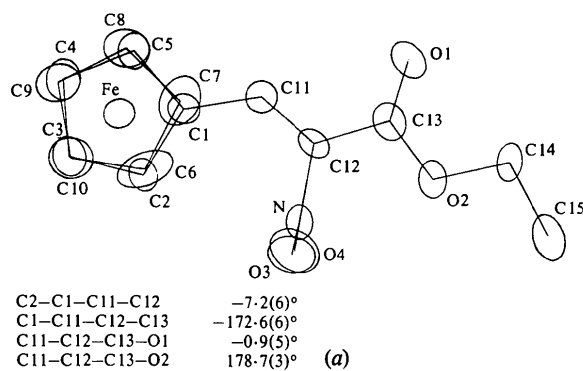
Fig. 1. (a) An ORTEP drawing with the atom numbering system and torsion angles with their e.s.d.'s. (b) Bond lengths (Å) and valency angles (°) with their e.s.d.'s.

angles with their e.s.d.'s are presented in Fig. 1. Examining the crystal structures of ferrocene derivatives (Kałuski & Skrzypczak-Jankun, 1978), we calculated mean values of 2·045 (13) Å for the Fe—C and 1·428 (14) Å for the C—C bonds in the cyclopentadienyl rings. Furthermore, we drew the conclusion that in the absence of very strong intramolecular strains or disorder in the crystalline state, the preferred geometry of the ferrocene skeleton should be eclipsed, or nearly so, with the conformational angles φ and ω both not greater than ~10°. In this structure the mean values of the Fe—C and C—C bonds in the ferrocenyl skeleton are 2·044 (15) and 1·421 (10) Å respectively. The two planar five-membered rings are tilted 1·7 (5)° from parallelism and twisted about 5·0 (5)° from the eclipsed conformation.

The remaining intramolecular distances and angles correspond to their expected values. The bond-angle enlargements at C(1) and C(11) to 130° (see Fig. 1) are due to a short intramolecular contact of 3·051 (6) Å between the atoms C(2) and N. A similar geometry of the vinyl substituent was observed in 2,2-dicyano-vinylferrocene (Krukonis, Silverman & Yannoni, 1972).
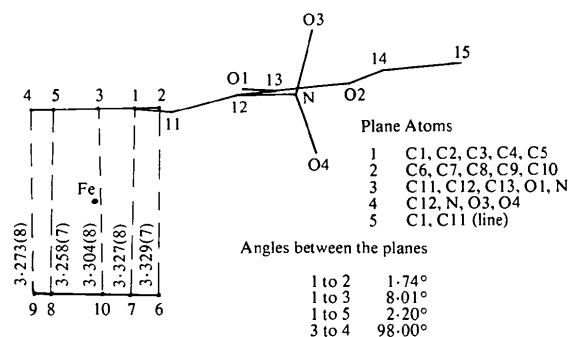

Fig. 2. View of the molecule (xOz projection) with the angles between the planes.

The C=C—C=O conjugated double bonds have the s-cis conformation. The bonds C(11)=C(12) and C(13)=O(1) have typical double-bond lengths and bonds C(12)—C(13) and C(1)—C(11) are only slightly shorter than a C_{sp^2}—C_{sp^2} single bond. This is in spite of the fact that the deviations from planarity are not large enough to prevent conjugation. The torsion angles (see Fig. 1) of −0·9 (5)° for C(11)=C(12)—C(13)=O(1) and −7·2 (6)° for C(2)=C(1)—C(11)=C(12) indicate that the s-cis double-bond system is planar, but not coplanar with the aromatic system of the ferrocenyl group. The vinyl substituent makes a dihedral angle of 8·0 (5)° with the C(1)–C(5) ring. The angles between the planes defined by the chosen groups of atoms are shown in Fig. 2 (the equations for the planes, and the individual distances from the planes and their e.s.d.'s have been deposited; see deposition footnote).

The intermolecular distances are all in the normal range, except 3·404 (8) Å for C(7)···C(13)-(−x,−y,−z) and 3·099 (7) Å for C(13)···O(4)(−x, −y, −z − 1).

References

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

KAŁUSKI, Z. & SKRZYPCZAK-JANKUN, E. (1978). Proceedings of the Pre-Congress Symposium on Organic Crystal Chemistry, 30 July–2 August, Dymaczewo, Poland.

KRUKONIS, A. P., SILVERMAN, J. & YANNONI, N. F. (1972). Acta Cryst. B28, 987–990.

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