

Short Communication

# Crystal Structure of 1-Ferrocenyl-3-(4'-nitrophenyl)-2-propen-1-one, C<sub>19</sub>H<sub>15</sub>FeNO<sub>3</sub>

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Lindeman, S. V., Bozak, R. E., Hicks, R. J. and Husebye, S., 1997. Crystal Structure of 1-Ferrocenyl-3-(4'-nitrophenyl)-2-propen-1-one, C<sub>19</sub>H<sub>15</sub>FeNO<sub>3</sub>. – Acta Chem. Scand. 51: 966–968. © Acta Chemica Scandinavica 1997.

As a continuation of the study of cytotoxic activity of enones with ferrocenyl substituents,<sup>1</sup> we wanted to study enones with the carbonyl group bonded directly to a ferrocenyl group. A convenient synthesis of such compounds is described by Boichard *et al.*<sup>2</sup>

## Experimental

*Preparation of 1-ferrocenyl-3-(4'-nitrophenyl)-2-propen-1-one.* The compound was made by adaptation of the literature method.<sup>2</sup> Sodium hydroxide (0.119 g, 2.97 mmol) was dissolved in 3.0 ml of ethanol. *p*-Nitrobenzaldehyde (0.352 g, 2.33 mmol) was added to the ethanolic NaOH solution. Acetylferrocene (0.532 g, 2.33 mmol) was dissolved in 5.0 ml of hot ethanol and filtered directly into the ethanolic NaOH solution while stirring. Stirring was continued for 20 min, and the reaction mixture was allowed to stand overnight at room temperature. The mixture was extracted with CHCl<sub>3</sub> (2 × 10 ml), washed with H<sub>2</sub>O, and the organic phase was dried with anhydrous MgSO<sub>4</sub>. The solvent was removed by rotary evaporation to yield 0.66 g (78.5%) of a dark-purple solid. The product was crystallized from ethanol to yield 0.583 g (69.3%) of dark-purple crystals, m.p. 189 × 190 °C. (lit. 190 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 4.25 (s, 5H), 4.70 (d, 2H), 4.98 (d, 2H), 7.25 (d, 1H), 7.85 (t, 3H), 8.39 (d, 2H) ppm (δ). IR (KBr) 3431.80, 1665.13, 1604.98, 1520.10, 1456.44, 1344.56, 1107.28 cm<sup>-1</sup>.

*Structure determination.* Cell dimensions (Table 1) were calculated from setting angles of 16 carefully centered reflections and their Friedel equivalents using a least squares procedure. Three standard reflections were

Table 1. Crystal and structure refinement data.

Empirical formula	C <sub>19</sub> H <sub>15</sub> FeNO <sub>3</sub>
Temperature/K	103(2)
Diffractometer	Enraf-Nonius CAD4
Wavelength/Å	0.710 69
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> /Å	5.878(3)
<i>b</i> /Å	10.507(8)
<i>c</i> /Å	12.633(8)
$\alpha$ /°	77.57(6)
$\beta$ /°	88.91(5)
$\gamma$ /°	82.71(5)
<i>V</i> /Å <sup>3</sup>	755.7(8)
Formula weight	361.17
<i>Z</i>	2
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.587
$\mu$ (MoK $\alpha$ )/mm <sup>-1</sup>	1.015
Crystal size/mm <sup>3</sup>	0.03 × 0.08 × 0.12
$\theta$ range ( $\omega/2\theta$ -scan)/°	2.0–27.0
Independent reflections collected	3292
Independent reflections observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	2353
Refinement method	Full-matrix least-squares on all <i>F</i> <sup>2</sup>
Data/restraints/parameters	3281/0/277
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.097
Final <i>R</i> -indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0513, <i>wR</i> <sub>2</sub> = 0.1284
<i>R</i> -indices (all data)	<i>R</i> <sub>1</sub> = 0.0882, <i>wR</i> <sub>2</sub> = 0.1543
Largest difference peak and hole/e Å <sup>-3</sup>	1.310 and –1.239
Wt. scheme	$w = 1/[s^2 F_o^2 + 0.1018 P^2]$ where $P = (F_o^2 + 2F_c^2)/3$

checked every 2 h during the data collection. Moderate crystal decay (4.3%) was observed. The intensity data were processed the usual way and corrected for Lorentz and polarization effects (not for absorption owing to a negligible  $\mu_R$  value, ca. 0.1). The structure was solved using direct methods<sup>3</sup> and refined by a full-matrix least

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**Table 2.** Atomic coordinates and equivalent isotropic displacement parameters (in Å<sup>2</sup>) for non-hydrogen atoms.

Atom	x	y	z	$U_{\text{eq}}^a$
Fe1	0.14358(9)	0.50955(5)	0.27911(4)	0.0135(2)
O1	0.5147(5)	0.7221(3)	0.0820(2)	0.0263(6)
O2	-0.6158(5)	1.1581(3)	-0.3970(2)	0.0255(6)
O3	-0.3440(5)	1.1337(3)	-0.5102(2)	0.0312(7)
N1	-0.4187(6)	1.1169(3)	-0.4185(3)	0.0182(6)
C1	0.2443(6)	0.6881(3)	0.2208(3)	0.0146(7)
C2	0.3973(6)	0.6148(3)	0.3064(3)	0.0160(7)
C3	0.2642(7)	0.5837(4)	0.4014(3)	0.0187(7)
C4	0.0337(6)	0.6376(3)	0.3767(3)	0.0161(7)
C5	0.0191(6)	0.7014(3)	0.2654(3)	0.0171(7)
C6	0.2958(7)	0.3411(4)	0.2387(4)	0.0253(9)
C7	0.1492(7)	0.4146(4)	0.1539(4)	0.0239(8)
C8	-0.0747(7)	0.4308(4)	0.1953(3)	0.0215(8)
C9	-0.0682(7)	0.3666(4)	0.3061(3)	0.0216(8)
C10	0.1629(7)	0.3104(4)	0.3325(4)	0.0251(9)
C11	0.3133(6)	0.7310(3)	0.1077(3)	0.0184(8)
C12	0.1274(6)	0.7887(4)	0.0279(3)	0.0184(7)
C13	0.1755(6)	0.8348(3)	-0.0756(3)	0.0171(7)
C14	0.0145(6)	0.9037(3)	-0.1617(3)	0.0149(7)
C15	0.0965(6)	0.9352(4)	-0.2671(3)	0.0175(7)
C16	-0.0447(6)	1.0055(3)	-0.3516(3)	0.0159(7)
C17	-0.2694(6)	1.0438(3)	-0.3287(3)	0.0157(7)
C18	-0.3572(7)	1.0159(4)	-0.2253(3)	0.0167(7)
C19	-0.2154(7)	0.9450(4)	-0.1416(3)	0.0182(7)

<sup>a</sup> $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

squares program<sup>4</sup> using anisotropic temperature factors for all non-hydrogen atoms. All hydrogens were found from difference maps and refined isotropically.

Crystallographic and structure refinement data are listed in Table 1. Eleven reflections were omitted from the last refinements because of unreasonably large differences between observed and calculated values. Coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms are listed in Table 2. The molecular structure is shown in Fig. 1. Further details of the structural work have been deposited with the Cambridge Crystallographic Data Centre, UK.

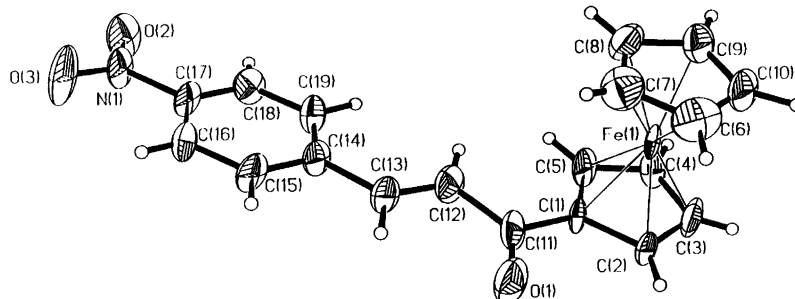
## Results and discussion

We have shown that 1-ferrocenyl-3-(4'-nitrophenyl)-2-propen-1-one has the expected composition. From

**Table 3.** Bond lengths (in Å) and selected bond angles (in °).

Fe1–C1	2.021(4)	C7–C8	1.410(6)
Fe1–C2	2.041(4)	C8–C9	1.417(6)
Fe1–C3	2.049(4)	C9–C10	1.426(6)
Fe1–C4	2.052(4)	C1–C11	1.468(5)
Fe1–C5	2.027(4)	C11–O1	1.219(5)
Fe1–C6	2.040(4)	C11–C12	1.479(5)
Fe1–C7	2.042(4)	C12–C13	1.332(5)
Fe1–C8	2.037(4)	C13–C14	1.459(5)
Fe1–C9	2.039(4)	C14–C15	1.393(5)
Fe1–C10	2.044(4)	C14–C19	1.402(5)
C1–C2	1.440(5)	C15–C16	1.383(5)
C1–C5	1.431(5)	C16–C17	1.375(5)
C2–C3	1.421(5)	C17–C18	1.381(5)
C3–C4	1.414(5)	C18–C19	1.380(5)
C4–C5	1.421(5)	C17–N1	1.463(4)
C6–C7	1.413(6)	N1–O2	1.231(4)
C6–C10	1.407(7)	N1–O3	1.216(4)
C2–C1–C5	107.6(3)	C12–C13–C14	127.2(4)
C1–C2–C3	107.5(3)	C13–C14–C15	118.4(3)
C2–C3–C4	108.6(3)	C13–C14–C19	122.6(3)
C3–C4–C5	108.4(3)	C15–C14–C19	119.0(3)
C4–C5–C1	107.9(3)	C14–C15–C16	121.3(4)
C7–C6–C10	108.1(4)	C15–C16–C17	118.1(4)
C6–C7–C8	108.2(4)	C16–C17–C18	122.6(3)
C7–C8–C9	108.1(4)	C16–C17–N1	117.8(3)
C8–C9–C10	107.5(4)	C18–C17–N1	119.5(3)
C9–C10–C6	108.0(4)	C17–C18–C19	118.9(4)
C1–C11–O1	121.2(3)	C18–C19–C14	120.2(4)
C1–C11–C12	116.7(3)	C17–N1–O2	117.8(3)
O1–C11–C12	122.1(3)	C17–N1–O3	119.0(3)
C11–C12–C13	120.6(4)	O2–N1–O3	123.2(3)

Fig. 1 one may see that except for iron and the upper cyclopentadienyl ring, the molecule is roughly planar (within 0.23 Å). The ferrocenyl group is eclipsed and ordered with average torsion angle C–ring centre–ring centre–C' = 1.1(4)°. The Cp rings are nearly parallel [dihedral angle 0.81(19)°]. The C–C bond lengths in the Cp rings range from 1.407(7) to 1.440(5) Å with an average of 1.420(10) Å. The Fe–C bond distances are 2.027(4)–2.052(4) Å with an average of 2.039(9) Å. The Fe to the centre of the Cp-ring distances are 1.638(1) and 1.648(1) Å for the substituted and unsubstituted rings, respectively; average 1.643(7) Å. These distances differ appreciably from the standard statistical values for those distances, 1.397(28), 2.080(35) and 1.706(39) Å,



**Fig. 1.** Perspective view of the molecule with labelling of the non-hydrogen atoms and 50% displacement ellipsoids. The Fe...C(Cp) distances are indicated by thin lines.

respectively.<sup>5</sup> However, they agree well with corresponding distances in monosubstituted ferrocenes whose structures are solved previously by us at low temperatures.<sup>1,6,7</sup> Also, these distances agree much better with the upper quartile of the aforementioned statistical data for C–C bonds (1.415 Å) and the lower quartiles for both the Fe–C bonds (2.052 Å) and the Fe-center of ring distances (1.662 Å).<sup>5</sup> Factors such as ring substitution and substituent–ring conjugation as well as unresolved disorders/large thermal motions in the bulk statistical material may be responsible for the above discrepancies.<sup>1</sup> The lower Cp ring (Fig. 1) is connected to the phenyl group through the C1–C11–C12=C13–C14 chain with the C=C bond length being 1.332(5) Å and the three single C<sub>sp<sup>2</sup></sub>–C<sub>sp<sup>2</sup></sub> bond lengths ranging from 1.459 to 1.479(5) Å. This range compares well with the statistical values for such bond lengths in conjugated C=C–C(=O)–C systems [1.464(18) Å] and for C<sub>sp<sup>2</sup></sub>–C<sub>aryl</sub> bonds (lower quartile 1.472 Å).<sup>8</sup> The structure of a related enone, 1-ferrocenyl-3-hydroxybut-2-en-1-one, has a C(ferrocenyl)–C(=O) bond length of 1.468(7) Å. However, this is the enol form of a diketone, so the C=O distances are closer to 1.30 Å.<sup>9</sup> The C=C bond length compares well with the values found for C=C–C=O conjugated systems [1.340(13) Å].<sup>8</sup> The observed *trans* conformation with respect to this double bond is the most reasonable for steric reasons.

The C=O bond length of 1.219(5) Å corresponds well with the statistical values for a carbonyl group conjugated to a C=C double bond [1.222(10) Å] or connected to an aromatic group [1.221(14) Å].<sup>8</sup> The phenyl group has an average C···C bond of 1.386(10) Å compared to statistical overall values for phenyl rings of 1.384(13) Å.<sup>8</sup> The C17–N1 bond length of 1.463(4) Å and the average

N–O bond length of 1.224(11) Å of the nitro group are also close to statistical values [1.468(14) and 1.217(11) Å, respectively].<sup>8</sup> The dihedral Ph/CNO<sub>2</sub> angle is 4.66(18)°, i.e. these groups are not quite coplanar.

Test results show that 1-ferrocenyl-3-(4'-nitrophenyl)-2-propen-1-one is relatively effective against mouse-cell leukemia with an ED<sub>50</sub> of 0.8 µg ml<sup>-1</sup> (DMSO). This compares with a corresponding value of 4.5 µg ml<sup>-1</sup> for ferrocenecarboxaldehyde. Further testing is being done.<sup>10</sup>

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Received January 16, 1997