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1-Ferrocenyl-2-phenylethanedione

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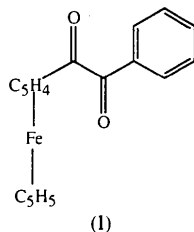
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Abstract

The title compound, [Fe(C₅H₅)(C₁₃H₉O₂)], crystallizes as chiral molecules in space group *P*2₁2₁2₁; in the crystal chosen for structure analysis, the molecules have the *S* configuration. The molecules are linked by weak C—H...O hydrogen bonds into chains parallel to the *b* axis and by C—H...π(C=C) interactions into chains parallel to the *a* axis.

Comment

Ferrocenyl-1,2-diketones Fc—CO—CO—R [Fc = (C₅H₅)—Fe(C₅H₄)] are important synthetic intermediates. As part of a wider study of these materials, we now report the structure of a representative example, 1-ferrocenyl-2-phenylethanedione, Fc—CO—CO—Ph (ferrocenylphenylglyoxal), (I).



1-Ferrocenyl-2-phenylethanedione crystallizes in the non-centrosymmetric space group *P*2₁2₁2₁ with a single molecule in the asymmetric unit (Fig. 1). Within these molecules the fragment C11—C1—O1 is almost coplanar with the substituted cyclopentadienyl ring C1*n* (*n* = 1–5) (Table 2), as typically found in simple acyl ferrocenes Fc—CO—R (Gyepes & Hanic, 1975; Sato, Iwai, Sano & Konno, 1984; Barnes, Bell, Glidewell & Howie, 1990); similarly, the fragment C31—C2—O2 is almost coplanar with the phenyl ring (Table 2). The mean value of the C1*n*—Cg1—Cg2—C2*n* twist angle (*n* = 1–5) is –20.0(4)°, essentially midway between the value for complete eclipsing of the rings, 0.0°, and the value for perfect staggering, 36.0° (Cg1 and Cg2 are the ring centroids).

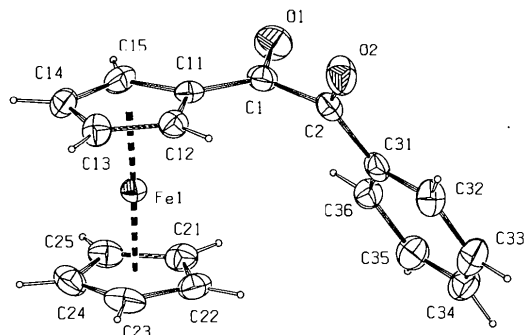


Fig. 1. A view of the *S* enantiomer of (I) with our numbering scheme. Ellipsoids are drawn at the 30% probability level.

The torsion angle O1—C1—C2—O2 is 109.1(5)°, so that the projections of the two carbonyl groups onto the plane normal to C1—C2 are almost orthogonal. Benzil, Ph—CO—CO—Ph, exhibits a similar value, 111.6°, for this torsion angle in the solid state (Brown & Sadanaga, 1965; More, Odou & Lefebvre, 1987), and similar torsion angles have been found for a range of 4,4'-disubstituted benzils (XC₆H₄CO)₂ (Kimura, McCluney & Watson, 1979; Crowley, Balanson & Mayerle, 1983). However, butane-2,3-dione, CH₃—CO—CO—CH₃ (Eriks, Hayden, Yang & Chan, 1983) and its 1,4-bis-diazo derivative (Hope & Black, 1972) are both centrosymmetric molecules in the solid state (*P*2₁/*n*, *Z* = 2) and hence adopt the *trans*-planar *C*_{2*h*} conformation; similarly, this conformer was the sole rotamer found in the gas phase even at 798 K (Danielson & Hedberg, 1979). The conformation found for (I) corresponds to molecular point group *C*₁, so that the molecules are chiral in the solid state, and all have the same handedness in *P*2₁2₁2₁; in the crystal chosen for study, the molecules have the *S* configuration. In solution, however, the NMR spectra indicate that *R/S* interconversion is fast at room temperature, so that crystallization in *P*2₁2₁2₁ represents a case of spontaneous resolution, or 'conglomerate crystallization'

(Bernal, 1985; Bernal, Cetrullo, Cai & Massoud, 1995). The intramolecular bond lengths and angles are unexceptional; the central C—C distance, 1.529 (5) Å, is very similar to the lengths found in butane-2,3-dione [gas-phase 1.524 (3) Å (Danielson & Hedberg, 1979), solid state 1.540 (6) Å (Eriks *et al.*, 1983)] and in benzil [trigonal high-temperature phase 1.523 (6) Å, monoclinic low-temperature phase 1.526 (13)–1.549 (16) Å, mean 1.536 Å (More *et al.*, 1987)].

Within the crystal structure there are a number of short intermolecular contacts. The atom O2 in the molecule at (*x*, *y*, *z*) makes contacts with H35 and C35 in the molecule at ($-x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$), with O··H and O··C distances of 2.73 and 3.327 (6) Å, respectively; these distances are both within the accepted criteria for attractive C—H··O hydrogen bonds (Desiraju, 1991; Steiner, 1994; Braga, Grepioni, Biradha, Pedireddi & Desiraju, 1995). Such C—H··O hydrogen bonds have been described (Braga *et al.*, 1995) as 'soft' hydrogen bonds, as opposed to N—H··O and O—H··O, both of which are 'hard'. Repetition of this interaction throughout the structure of (I) generates chains around the 2₁ axes parallel to the *b* axis. In addition, atom H12 in the molecule at (*x*, *y*, *z*) makes contacts of 2.88 and 2.79 Å with atoms C14 and C15 of the molecule at ($\frac{1}{2} + x$, $\frac{3}{2} - y$, $-z$). These distances are both less than the sum of the van der Waals radii (Bondi, 1964), and may represent a weak C—H··π(C=C) interaction; a number of examples of attractive C—H··π interactions with similar dimensions have been reported (Steiner, 1995). Repetition of the motif throughout the structure of (I) leads to the formation of chains around the 2₁ axes parallel to the *a* axis.

Experimental

Compound (I) was prepared by oxidation of phenacylferrocene, FcCH₂COPh, with manganese dioxide, and purified by chromatography on silica. Crystals suitable for single-crystal X-ray diffraction study were grown by slow evaporation of a solution in ethanol. Analysis: found C 68.3, H 4.8%; C₁₈H₁₄FeO₂ requires C 68.0, H 4.4%. NMR: δ_H 4.25 (*s*, 5H, C₅H₅), 4.65 (*m*, 2H) and 4.85 (*m*, 2H) (C₅H₄), 7.5–8.1 (*m*, 5H, C₆H₅); δ_C 71.1 (*d*), 74.6 (*d*) and 75.2 (*s*) (C₅H₄), 71.2 (*d*, C₅H₅); 129.5 (*d*), 130.6 (*d*), 133.6 (*s*) and 135.1 (*d*) (C₆H₅), 193.5 (*s*) and 199.6 (*s*) (2 × CO).

Crystal data

[Fe(C₅H₅)(C₁₃H₉O₂)]

M_r = 318.14

Orthorhombic

*P*2₁2₁2₁

a = 7.6430 (10) Å

b = 9.8349 (12) Å

c = 18.629 (2) Å

V = 1400.3 (3) Å³

Z = 4

D_x = 1.509 Mg m⁻³

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25

reflections

θ = 10.45–18.85°

μ = 1.077 mm⁻¹

T = 294 (1) K

Plate

0.44 × 0.42 × 0.14 mm

Orange

Data collection

Enraf–Nonius CAD-4

diffractometer

θ/2θ scans

Absorption correction:

four ψ scans at 4°

steps (North, Phillips &

Mathews, 1968)

T_{min} = 0.806, *T_{max}* =

0.999

1762 measured reflections

1762 independent reflections

1306 observed reflections

[*I* > 2σ(*I*)]

θ_{max} = 26.87°

h = 0 → 9

k = 0 → 12

l = 0 → 23

3 standard reflections

frequency: 120 min

intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.0319

wR(*F*²) = 0.0712

S = 0.977

1762 reflections

191 parameters

H atoms riding [SHELXL93

(Sheldrick, 1993) defaults,

C—H = 0.93 Å]

w = 1/[σ²(*F_o*²) + (0.0354*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.352 e Å⁻³

Δρ_{min} = -0.227 e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick,

1993)

Extinction coefficient:

0.0078 (10)

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Absolute configuration:

Flack (1983) parameter

= -0.05 (3)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U_{eq}</i> |
|-----|-------------|-------------|--------------|-----------------------|
| Fe1 | 0.04799 (6) | 0.99393 (5) | 0.04381 (2) | 0.0373 (2) |
| O1 | -0.2284 (4) | 0.8187 (4) | 0.1935 (2) | 0.0748 (10) |
| O2 | -0.0046 (4) | 0.5688 (3) | 0.13469 (15) | 0.0704 (10) |
| C1 | -0.1215 (6) | 0.7886 (4) | 0.1482 (2) | 0.0476 (10) |
| C2 | 0.0117 (5) | 0.6773 (4) | 0.1656 (2) | 0.0468 (10) |
| C11 | -0.1174 (5) | 0.8434 (4) | 0.0751 (2) | 0.0400 (9) |
| C12 | -0.0111 (5) | 0.7983 (4) | 0.0171 (2) | 0.0437 (10) |
| C13 | -0.0430 (6) | 0.8838 (3) | -0.0418 (2) | 0.0491 (9) |
| C14 | -0.1679 (5) | 0.9819 (4) | -0.0214 (2) | 0.0520 (10) |
| C15 | -0.2140 (5) | 0.9598 (4) | 0.0509 (2) | 0.0491 (10) |
| C21 | 0.1697 (5) | 1.0828 (4) | 0.1294 (2) | 0.0508 (10) |
| C22 | 0.2892 (5) | 1.0024 (5) | 0.0908 (2) | 0.0563 (10) |
| C23 | 0.2966 (6) | 1.0533 (5) | 0.0203 (3) | 0.0629 (13) |
| C24 | 0.1828 (6) | 1.1654 (4) | 0.0159 (2) | 0.0589 (12) |
| C25 | 0.1039 (5) | 1.1833 (4) | 0.0840 (2) | 0.0511 (11) |
| C31 | 0.1512 (6) | 0.7023 (4) | 0.2187 (2) | 0.0455 (10) |
| C32 | 0.2844 (7) | 0.6069 (5) | 0.2253 (2) | 0.0609 (12) |
| C33 | 0.4212 (7) | 0.6315 (5) | 0.2713 (2) | 0.0683 (14) |
| C34 | 0.4254 (7) | 0.7476 (5) | 0.3121 (2) | 0.0669 (13) |
| C35 | 0.2929 (7) | 0.8405 (5) | 0.3072 (2) | 0.0638 (13) |
| C36 | 0.1538 (6) | 0.8194 (4) | 0.2604 (2) | 0.0515 (10) |

Table 2. Selected geometric parameters (Å, °)

The pseudo-atoms Cg1 and Cg2 are the centroids of the two five-membered rings.

| | | | |
|-------------|-----------|-----------|-----------|
| Fe1—Cg1 | 1.648 (4) | C1—C11 | 1.466 (5) |
| Fe1—Cg2 | 1.657 (4) | C1—C2 | 1.529 (5) |
| O1—C1 | 1.211 (5) | C2—C31 | 1.474 (5) |
| O2—C2 | 1.219 (4) | | |
| Cg1—Fe1—Cg2 | 177.5 (2) | O2—C2—C1 | 117.3 (4) |
| O1—C1—C2 | 118.5 (4) | O2—C2—C31 | 122.5 (4) |
| O1—C1—C11 | 124.9 (4) | C1—C2—C31 | 120.2 (3) |
| C2—C1—C11 | 116.5 (4) | | |

| | | | |
|---------------|------------|---------------|------------|
| O1—C1—C2—O2 | 109.1 (5) | O1—C1—C11—C15 | 13.8 (6) |
| C11—C1—C2—O2 | -66.3 (5) | O2—C2—C31—C36 | -171.2 (4) |
| O1—C1—C2—C31 | -70.0 (5) | O2—C2—C31—C32 | 10.4 (6) |
| O1—C1—C11—C12 | -170.5 (4) | | |

Examination of the structure with *PLATON* (Spek, 1995) showed that there were no solvent-accessible voids in the crystal lattice. The structure was solved by the Patterson heavy-atom method.

Data collection: *CAD-4-PC* (Enraf–Nonius 1992). Cell refinement: *SET4* and *CELDIM* (Enraf–Nonius, 1991). Data reduction: *DATRD2* in *NRCVAX94* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to refine structure: *NRCVAX94* and *SHELXL93* (Sheldrick, 1993). Molecular graphics: *NRCVAX94* and *PLATON* (Spek, 1995). Software used to prepare material for publication: *NRCVAX94* and *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1043). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Racemic Bis(1-ferrocenylpropyl) Ether

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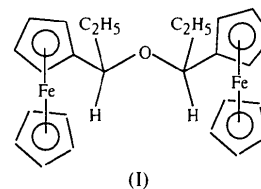
(Received 24 August 1995; accepted 1 November 1995)

Abstract

The title compound, [Fe₂(C₅H₅)₂(C₁₆H₂₀O)], formed by reduction of propionylferrocene and subsequent dehydration, crystallizes as a racemic mixture of *RR* and *SS* forms. In the central C—O—C fragment, the angle at the O atom is 115.7 (2)°.

Comment

The reaction between ferrocene and *p*-tolualdehyde in strongly acidic solution yields bis[ferrocenyl(*p*-tolyl)methyl] ether, [FcCH(C₆H₄CH₃)₂O], [Fc = (C₅H₅)Fe(C₅H₄)] (Matkovic-Calogovic, Ropic & Kovac, 1993). While each of the C atoms bonded to the O atom in this compound is a stereogenic centre, only a single product was isolated, which X-ray structure analysis identified as a racemic mixture of the *RR* and *SS* diastereoisomers (Matkovic-Calogovic *et al.*, 1993). No *RS* or *SR* product was observed. We have now observed that acid-catalysed dehydration of 1-ferrocenylpropan-1-ol, FcCH(OH)C₂H₅, yields bis[1-ferrocenylpropyl] ether, [FcCH(C₂H₅)₂O], (I), and have characterized the product as a similar racemic mixture of *RR* and *SS* forms.



Compound (I) crystallizes in the centrosymmetric triclinic space group *P* $\bar{1}$ with one molecule in the asymmetric unit: two enantiomeric forms are therefore present. Structure solution and refinement showed that these were the *RR* and *SS* forms and that each form has approximate twofold rotational symmetry (Fig. 1 and Table 2); no evidence was found for the occurrence of the *meso RS* (or *SR*) form of (I). In this respect, the structure of (I) resembles that of [FcCH(C₆H₄CH₃)₂O], in which the molecules lie on the twofold rotation axes