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# CRYSTAL AND MOLECULAR STRUCTURE OF [3]FERROCENOPHANE-1,3-DIONE

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## Summary

The crystal structure of [3]ferrocenophane-1,3-dione has been determined by X-ray diffraction methods. This compound, $C_{13}H_{10}FeO_2$, crystallizes in the monoclinic space group $P2_1/c$. The unit cell contains four molecules and has the dimensions $a$ 7.775(8), $b$ 9.697(12) and $c$ 14.669(11) Å. The structure was solved by Patterson and Fourier syntheses and refined by the full-matrix least-squares method to $R = 0.036$ for 2087 independent reflections. The two cyclopentadienyl rings are tilted 9.8° with respect to each other. The average ring carbon–carbon bond distance is 1.428 Å and the average ring bond angle is 108°. The strain in the molecule is apparent by the fact that the bond angles in the bridge are less than normal by about 3–6°.

## Introduction

Internal strain has been observed in the case of some bridged ferrocene derivatives, [*m*]ferrocenophanes. This strain can be released, as was proved by X-ray structure analysis, either by distorting the parallelism of the cyclopentadienyl rings, e.g. ring tilting, or by combining the ring tilting and forcing the atom of the bridge

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out of coplanarity with the cyclopentadienyl ring. A ring tilt of 23.2° was observed in the case of 1,1,2,2-tetramethyl[2]ferrocenophane [1], 8.8° in the case of [3]ferrocenophane-1-one [2], 10° in the case of 3-phenyl[3]ferrocenophane-1-one [3], and 13.7° in the cation of [3]ferrocenophane [4]. A ring tilt of 5.7° was observed in 1,3-diselene[3]ferrocenophane [5].

On the other hand, a ring tilt of 16.6° was observed and the Ge atom was forced out of the plane of the cyclopentadienyl ring by 38° in the case of (1,1'-ferrocenediyl)diphenylgermane whilst the ring tilt in the case of (1,1'-ferrocenediyl)phenylphosphine was 26.7° and the P atom was forced out of the plane of the cyclopentadienyl ring by 32° [6]. [3]Ferrocenophane-1,3-dione was described several years ago [7], and the great ease of the bridge opening of this compound has been observed several times [7,8].

The main aim of this work was to determine the crystal structure of [3]ferrocenophane-1,3-dione and to find out whether the second carbonyl group (second $C_{sp^2}$) in the bridge causes greater ring tilting than in the case of [3]ferrocenophane-1-one, or whether the internal strain is released by distortion of the bond angles. The second aim was to give some explanation for the observed facile bridge opening of [3]ferrocenophane-1,3-dione.

## Results and discussion

The final positional and thermal parameters of the atoms are listed in Tables 1 and 2, respectively. The bond distances and angles are collected in Table 3 and the numbering scheme is shown in Fig. 1. The least-squares planes through each cyclopentadienyl ring, as well as through the other groups of atoms, are given in Table 4.

The three-carbon bridge $-CO-CH_2-CO-$ causes the two cyclopentadienyl rings to tilt. The dihedral angle between the rings, defined as the acute angle formed by the normals to the best planes, is 9.8°. Moreover, the two exocyclic bonds, C(11)-C(1) and C(21)-C(2), are bent 8.3 and 9.7°, respectively, from the ring

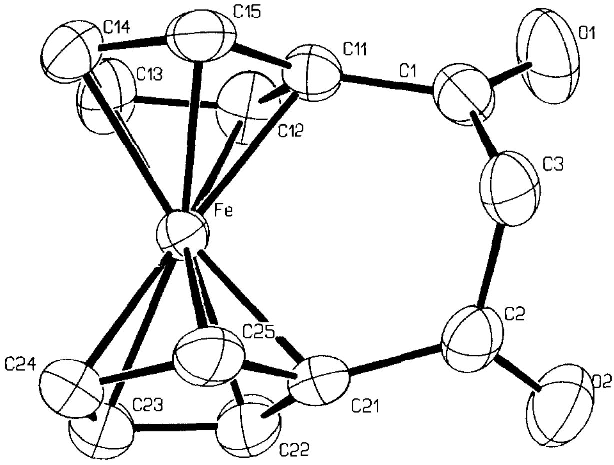

Fig. 1. ORTEP drawing of a molecule of $C_{13}H_{10}FeO_2$ showing the numbering scheme of the atoms.

TABLE 1

POSITIONAL PARAMETERS OF THE ATOMS ($\times 10^5$)

(The hydrogen atoms are numbered to correspond with the carbon atoms to which they are attached, e.g. H(12) is attached to C(12), H(31) and H(32) are attached to C(3), and so on.)

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Fe | 29276(5) | 23296(3) | 12730(2) |
| O(1) | −11394(30) | 3106(23) | 18468(17) |
| O(2) | −21979(28) | 23687(23) | −2036(15) |
| C(1) | −2451(39) | 13445(30) | 18566(19) |
| C(2) | −9881(38) | 27945(28) | 4613(20) |
| C(3) | −11432(37) | 27153(29) | 14807(20) |
| C(11) | 17513(37) | 12924(26) | 21121(18) |
| C(12) | 27277(41) | 3325(27) | 16997(22) |
| C(13) | 45704(39) | 7510(30) | 19802(22) |
| C(14) | 47535(40) | 19205(31) | 25750(20) |
| C(15) | 30201(40) | 22746(29) | 26572(17) |
| C(21) | 7754(37) | 32114(29) | 3586(18) |
| C(22) | 17337(41) | 24425(33) | −1702(18) |
| C(23) | 35253(42) | 29870(35) | 536(20) |
| C(24) | 36645(41) | 40883(32) | 6926(20) |
| C(25) | 19769(40) | 42406(28) | 8900(20) |
| H(12) | 21992 | −4874 | 12866 |
| H(13) | 55671 | 2912 | 17906 |
| H(14) | 59071 | 23994 | 29004 |
| H(15) | 27333 | 30570 | 30377 |
| H(22) | 12475 | 16572 | −6187 |
| H(23) | 45136 | 26618 | −2162 |
| H(24) | 47660 | 46762 | 9649 |
| H(25) | 16923 | 49501 | 13348 |
| H(31) | −4954 | 35035 | 18783 |
| H(32) | −24343 | 27252 | 14811 |

TABLE 2

ANISOTROPIC THERMAL PARAMETERS OF THE ATOMS

(The isotropic temperature factors of the hydrogen atoms were taken as 4.0 Å$^2$.)

| | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Fe | 2.07(1) | 2.29(2) | 1.98(1) | 0.04(1) | 0.57(1) | 0.00(1) |
| O(1) | 3.66(11) | 4.09(11) | 8.68(17) | −0.75(9) | 2.33(11) | 1.78(11) |
| O(2) | 3.12(10) | 5.80(12) | 4.29(10) | −0.34(9) | 0.01(8) | −0.54(10) |
| C(1) | 3.01(13) | 3.34(13) | 3.33(13) | 0.17(11) | 1.34(11) | 0.58(10) |
| C(2) | 2.56(11) | 2.82(12) | 3.65(13) | 0.56(10) | 0.54(10) | 0.39(10) |
| C(3) | 2.60(11) | 3.35(12) | 3.99(13) | 0.46(11) | 1.40(10) | −0.05(11) |
| C(11) | 2.80(12) | 2.51(11) | 2.86(12) | 0.06(10) | 0.83(10) | 0.74(9) |
| C(12) | 3.45(14) | 2.09(11) | 4.88(16) | 0.19(11) | 0.89(13) | 0.23(11) |
| C(13) | 2.57(13) | 3.00(13) | 5.28(17) | 0.80(11) | 0.81(12) | 0.58(12) |
| C(14) | 2.76(13) | 3.88(14) | 3.11(13) | −0.05(11) | −0.01(10) | 0.79(10) |
| C(15) | 3.56(13) | 3.30(12) | 2.15(10) | 0.00(11) | 0.68(9) | 0.52(10) |
| C(21) | 2.64(12) | 3.43(12) | 2.25(11) | 0.30(10) | 0.43(9) | 0.84(9) |
| C(22) | 3.37(13) | 5.98(18) | 2.11(10) | −0.60(14) | 0.54(9) | −0.50(12) |
| C(23) | 3.46(14) | 6.22(19) | 2.49(12) | −0.43(13) | 1.21(11) | 0.15(12) |
| C(24) | 3.26(14) | 4.41(15) | 3.09(13) | −0.72(12) | 0.78(11) | 1.12(11) |
| C(25) | 3.47(14) | 2.74(12) | 3.12(12) | 0.09(11) | 0.54(11) | 0.94(10) |

planes towards the iron atom. The carbonyl groups are not coplanar with the cyclopentadienyl rings, the oxygen atoms O(1) and O(2) being deviated outside the mean planes of the rings by 0.411 and 0.252 Å, respectively (Table 4).

In the crystal structure of ferrocene [9], the iron atom lies at the centre of symmetry and the rings are therefore staggered by exactly 36°. In [3]ferrocenophane-1,3-dione, the rings are staggered by only 6°. The degree of staggering is defined here as the angle between the mean planes through the atoms Fe–C(11)–C(1) and Fe–C(21)–C(2). The average ring C–C bond distance is 1.428 Å while the $C_\beta$–$C_\beta$ bonds in both rings are distinctly shorter than the others (1.412 and 1.404 Å, respectively). The average ring bond angle is 108° and the average Fe–C bond distance is 2.04 Å.

The strain in the molecule is apparent by the fact that the bond angles C(11)–C(1)–C(3), C(21)–C(2)–C(3) and C(1)–C(3)–C(2) in the bridge are less than normal by about 3–6° (Table 3). As a result, the carbon atom C(3) is deviated from the best plane through the atoms of C(11)–C(1)–C(2)–C(21) by 0.842 Å. The bond distances in the bridge appear to be normal [10] except for the two exocyclic bonds, which are significantly shorter (1.487 and 1.479 Å, repectively). This shortening is apparently caused by the presence of carbon–oxygen double bonds which are, at least partially, conjugated with the cyclopentadienyl rings.

It is evident from Fig. 1 and the data given in Table 4 that the molecule of

TABLE 3

SELECTED BOND DISTANCES (Å) AND ANGLES (°)

| | | | |
|---|---|---|---|
| Fe–C(11) | 2.005(3) | Fe–C(21) | 2.004(3) |
| Fe–C(12) | 2.055(3) | Fe–C(22) | 2.051(3) |
| Fe–C(13) | 2.068(3) | Fe–C(23) | 2.076(3) |
| Fe–C(14) | 2.058(3) | Fe–C(24) | 2.061(3) |
| Fe–C(15) | 2.011(3) | Fe–C(25) | 2.013(3) |
| C(11)–C(12) | 1.441(4) | C(21)–C(22) | 1.432(4) |
| C(12)–C(13) | 1.429(5) | C(22)–C(23) | 1.435(5) |
| C(13)–C(14) | 1.412(4) | C(23)–C(24) | 1.404(4) |
| C(14)–C(15) | 1.430(5) | C(24)–C(25) | 1.432(5) |
| C(15)–C(11) | 1.435(4) | C(25)–C(21) | 1.432(4) |
| C(1)–C(11) | 1.487(4) | C(2)–C(21) | 1.479(4) |
| C(1)–C(3) | 1.528(4) | C(2)–C(3) | 1.537(4) |
| C(1)–O(1) | 1.218(4) | C(2)–O(2) | 1.212(4) |
| C(12)–C(11)–C(15) | 107.58(24) | C(11)–C(1)–C(3) | 116.99(24) |
| C(13)–C(12)–C(11) | 107.61(25) | C(3)–C(1)–O(1) | 120.86(26) |
| C(14)–C(13)–C(12) | 108.50(26) | O(1)–C(1)–C(11) | 121.68(27) |
| C(15)–C(14)–C(13) | 108.53(26) | | |
| C(11)–C(15)–C(14) | 107.76(24) | C(21)–C(2)–C(3) | 116.85(24) |
| | | C(3)–C(2)–O(2) | 120.17(26) |
| C(22)–C(21)–C(25) | 107.33(24) | O(2)–C(2)–C(21) | 122.37(26) |
| C(23)–C(22)–C(21) | 107.96(26) | | |
| C(24)–C(23)–C(22) | 108.22(27) | C(1)–C(3)–C(2) | 103.71(23) |
| C(25)–C(24)–C(23) | 108.50(27) | | |
| C(21)–C(25)–C(24) | 107.97(25) | | |

TABLE 4

LEAST-SQUARES PLANES

| Plane | Atoms defining the plane | direction cosines | Other atoms | Deviation (Å) |
|---|---|---|---|---|
| 1 | C(11) | | Fe | 1.636(0) |
| | C(12) | 0.0733 | O(1) | −0.411(2) |
| | C(13) | 0.5870 | C(1) | 0.216(3) |
| | C(14) | −0.8063 | C(2) | 2.621(3) |
| | C(15) | | C(3) | 1.382(4) |
| 2 | C(21) | | Fe | −1.639(0) |
| | C(22) | −0.0840 | O(2) | 0.252(2) |
| | C(23) | 0.6376 | C(1) | −2.647(3) |
| | C(24) | −0.7658 | C(2) | −0.253(3) |
| | C(25) | | C(3) | −1.350(4) |
| 3 | C(11) | 0.2336 | | |
| | C(1) | −0.1478 | C(3) | 0.184(4) |
| | O(1) | −0.9610 | | |
| 4 | C(21) | −0.2883 | | |
| | C(2) | 0.9340 | C(3) | −0.212(3) |
| | O(2) | −0.2109 | | |
| 5 | Fe | 0.1135 | | |
| | C(11) | −0.8127 | | |
| | C(1) | −0.5715 | | |
| 6 | Fe | 0.1479 | | |
| | C(21) | −0.7483 | | |
| | C(2) | −0.6466 | | |
| 7 | C(11) | | | |
| | C(1) | 0.1423 | C(3) | −0.842(3) |
| | C(2) | −0.7947 | | |
| | C(21) | −0.5901 | | |

| | | | | |
|---|---|---|---|---|
| Dihedral angles between planes: | 1–2 | 9.8° | 1–7 | 88.8° |
| | 1–3 | 45.2° | 2–7 | 93.8° |
| | 2–4 | 38.6° | | |
| | 5–6 | 6.0° | | |

[3]ferrocenophane-1,3-dione is far from being symmetric. This can be seen, for example, from the different deviations of the atoms C(1), C(2), O(1), O(2) from the best planes of the cyclopentadienyl rings. All the above-mentioned observations can be taken as proof of considerable internal strain in the molecule under study, which is released by the facile opening of the bridge, as was observed previously [7].

## Experimental

### *X-Ray data collection*

A red-orange crystal of $C_{13}H_{10}FeO_2$, having dimensions of ca. 0.15 × 0.19 × 0.25 mm, was selected and mounted on a glass capillary. Diffraction measurements were recorded on a Syntex $P2_1$ four-circle automatic diffractometer using graphite-monochromatized Mo-$K_\alpha$ radiation ($\lambda$ 0.71069 Å). The unit cell dimensions were determined and refined from ten randomly selected reflections. Crystal data for

$C_{13}H_{10}FeO_2$ ($M = 254.07$): $a$ 7.775(8), $b$ 9.697(12), $c$ 14.669(11) Å, $\beta$ 107.01(7)°, $V$ 1057.5(2) Å$^3$, $d_c$ 1.596 g/cm$^3$, $Z = 4$, $\mu$ 14.4 cm$^{-1}$, space group $P2_1/c$ (from systematic absences).

A complete set of intensity data was collected within the range $0 < \theta < 25°$. The $\theta$–$2\theta$ scan technique was used with a variable scan rate, 5–29°/min. As a check for crystal stability, two standard reflections were remeasured after every 99 reflections. No significant change in the intensities of these reflections was observed during data collection. A total of 3111 independent reflections were collected, of which 2087 with $I > 2\sigma(I)$ were employed in the structure analysis. The intensities were corrected for Lorentz and polarization effects, but no absorption corrections were applied. The first absolute scale and the mean temperature factor were determined by Wilson's method.

*Structure determination and refinement*

The structure of $C_{13}H_{10}FeO_2$ was solved by the standard heavy-atom method. The initial positional parameters of the iron atom were determined from a Patterson map. A subsequent Fourier synthesis, calculated with the phases of this atom, revealed the positions of all the non-hydrogen atoms. The structure was refined by the full-matrix least-squares method with, initially, isotropic and then anisotropic thermal parameters, the function $\Sigma w\Delta^2$ ($w = 1/\sigma^2(F)$ and $\Delta = ||F_0| - |F_c||$) being minimized. The full anisotropic refinement converged with $R = \Sigma\Delta/\Sigma|F_0| = 0.036$ and $R_w = [\Sigma w\Delta^2/\Sigma|F_0|^2]^{1/2} = 0.035$ for 2087 observations.

The hydrogen atoms were placed at their geometrically calculated positions (considering the hybridization of carbon atoms with C–H distances of 1.1 Å) and were included in the final structure factor calculation. The positional and thermal parameters of the hydrogen atoms were not refined. The final difference Fourier map revealed no chemically significant features, the residual electron density being 0.14 e/Å$^3$.

All calculations were performed on a Nova 1200 computer using the XTL program system supplied by Syntex Corporation.

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