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(*E*)-2-(2-Adamantylidene)-3-(1-ferrocenylethylidene)succinic anhydride

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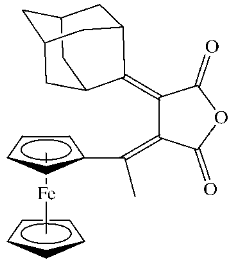
The title compound, [Fe(C_5H_5)($C_{21}H_{21}O_3$)], was obtained from successive Stobbe condensations between ketones and dimethyl succinate. The succinic anhydride five-membered ring is distorted significantly from planarity, with the butadiene moiety being twisted by 49.3 (2)° from planarity and the C atoms at the succinic anhydride end of the alkene bonds showing significant pyramidalization. The cyclopentadiene rings of the ferrocenyl moiety adopt an almost eclipsed conformation.

Comment

Organic fulgides with an aryl ring undergo photochromic ring closure to give highly coloured tricyclic dihydronaphthalene derivatives (Hart & Heller, 1972). The fulgides themselves can be synthesized using successive Stobbe condensations between ketones or aldehydes and a succinate diester (Heller & Szewczyk, 1974). Touchard & Dabard (1975) reported that Stobbe condensations can be carried out using acetylferrocene, without affecting the ferrocene nucleus. However, these organometallic fulgides, unlike organic fulgides, do not undergo photochromic ring closure, and molecular orbital calculations have shown that the ring closure is actually forbidden (McCabe *et al.*, 1993). Studies on the *E*/*Z* isomerization of ferrocenyl fulgides demonstrated that the preferred isomer was the *E* isomer in sterically hindered fulgide systems (McCabe *et al.*, 1993). In the present work, the sterically hindered title fulgide, (III), was synthesized and its crystal structure determined (Fig. 1).

In the solid state, the succinic anhydride five-membered ring of (III) is distorted significantly from planarity and adopts a half-chair conformation twisted on C12—C13, where atoms C12 and C13 are 0.122 (3) and −0.156 (3) Å, respectively, from the plane defined by atoms C14, O15 and C16. This has consequences for the torsion angles about the C11=C12 and C13=C18 double bonds, which deviate by up to 24° from the normally expected values of 0 or 180° in an alkene system (Table 1). In addition, atoms C12 and C13 show significant pryamidalization from the expected trigonal planar conformation, with atom C12 lying 0.120 (1) Å from the plane defined by atoms C11, C13 and C16, and atom C13 lying 0.124 (1) Å from the plane defined by atoms C12, C14 and C18. In contrast, atoms C11 and C18 have almost no pyramidalization, being only 0.020 (1) and 0.038 (1) Å, respectively, from the planes defined by their three surrounding atoms.



(III)

The torsion angle of the butadiene fragment is also severely skewed [C11—C12—C13—C18 = −49.3 (2)°]. This is commonly observed in fulgides and has been attributed to steric congestion imposed by the rigidity of the alkene substituents (Kaftory, 1984; Kaftory *et al.*, 1998). Of the 29 different fulgide structures currently stored in the Cambridge Structural Database (CSD; October 2002 release; Allen, 2002), the largest twist of the butadiene C—C bond is 56 (1)° in 2-(2-adamantylidene)-3-(9-fluorenylidene)succinic anhydride (Kaftory *et al.*, 1998), which is quite a sterically crowded molecule and is the only other reported fulgide structure in which an adamantylidene moiety is present. Kaftory *et al.* (1998) have discussed this twist in more detail, but an interesting additional observation is that the twist is closely correlated with the degree of pyramidalization of the C atoms at the succinic anhydride end of the alkene bonds. For the 29 known fulgide structures, the deviations of these C atoms from the planes defined by their three surrounding C atoms are in the range 0.00–0.16 Å, with the largest value again being observed in the structure of 2-(2-adamantylidene)-3-(9-fluorenylidene)succinic anhydride.

The steric congestion between the adamantylidene and ferrocene moieties causes opening of the C11—C12—C13 and C12—C13—C18 angles, although these are close to the mean values derived from the other fulgide structures, in which these angles are in the range 124–139°. The bond lengths within the butadiene moiety are also close to the mean values derived from the reported fulgide structures.

The cyclopentadiene rings of the ferrocenyl moiety are rotated by only 8.03 (11)° from an eclipsed conformation and are tilted very slightly with respect to one another, so that the centres of gravity of the cyclopentadiene rings subtend an angle of 177.83 (3)° at the Fe atom. The distances between the Fe atom and the centres of gravity of the cyclopentadiene rings containing atoms C1 and C7 are 1.6460 (6) and 1.6552 (7) Å, respectively.

When the title compound (1×10^{-4} *M* in toluene) was irradiated at 366 nm for 2 h, no change was observed in the

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UV absorption spectrum of the solution. This is consistent with the expected absence of a photochromic ring-closure reaction. When the same solution was irradiated for 24 h, slightly shorter UV absorption wavelengths (4 nm) were recorded, which is presumed to be an indication of the formation of a small amount of the *Z* isomer. McCabe *et al.* (1993) reported that the irradiation of various (*E*)-ferrocenyl fulgide derivatives resulted in the formation of a photostationary equilibrium with the corresponding *Z* isomers, which were found to absorb at slightly shorter or longer UV wavelengths than the *E* isomers, depending on the derivative.

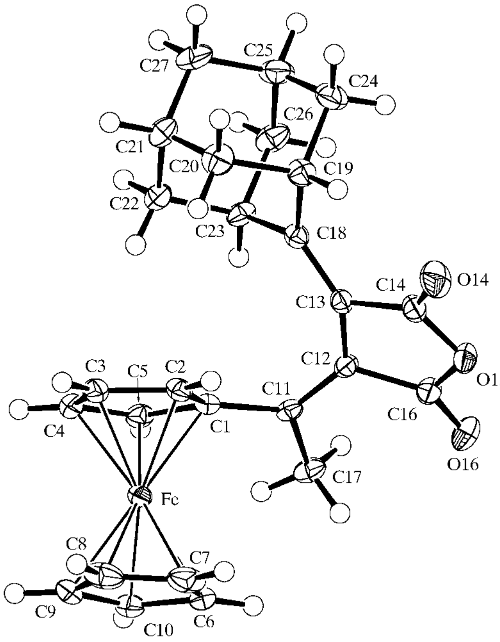

Figure 1
A view of the molecule of (III) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

Experimental

A mixture of dimethyl succinate (28 g, 0.2 mol), 2-adamantanone (36 g, 0.2 mol) and potassium *tert*-butoxide (22.4 g, 0.2 mol) in toluene (300 ml) was stirred at room temperature for 10 h. The resulting half-ester was then liberated by acidification with hydrochloric acid (5 *M*, 50 ml) and extracted with ether (3 × 50 ml). The combined extracts were dried ($MgSO_4$), and the ether was removed under reduced pressure to give the half-ester (38 g, 72%) as colourless cubes. Esterification of the half-ester (38 g) was conducted using acetyl chloride and methanol. The solvent was removed under reduced pressure and the residue was dissolved in ether and chromatographed on a short column (silica gel, light petroleum ether–diethyl ether, 2:1), to give dimethyl 2-(2-adamantylidene)succinate, (I), as a pale-yellow oil (27 g, 67%). Spectroscopic analysis, ^{1}H NMR (400 MHz, DMSO, δ, p.p.m.): 1.76–1.95, 2.84 (14H, *m*, adamantylidene H), 3.39 (2H, *s*, CH_2), 3.63 (3H, *s*, CH_3O), 3.68 (3H, *s*, CH_3O). A mixture of (I) (15 g, 0.05 mol), acetylferrocene (12 g, 0.05 mol) and potassium *tert*-butoxide (6.70 g, 0.06 mol) in toluene (200 ml) was stirred at room temperature for 10 h. Work-up gave the half-ester in quantitative yield as a red gum. The half-ester was hydrolysed by boiling in 10% KOH. The crude diacid, (II), was dissolved in dichloromethane (100 ml) to give a red solution, which was cooled in an ice–salt bath. Trifluoroacetic anhydride (3 ml) in dichloromethane (10 ml) was added dropwise and then stirred at room temperature for 3 h, after which the mixture was poured on to ice and extracted into ether. The ether solution was dried over $MgSO_4$ and evaporated to afford the title fulgide, (III), as red crystals (3.55 g, 16%), which were recrystallized from dichloromethane–light petroleum ether (1:3) (m.p. 486–487 K). Spectroscopic analysis, ^{1}H NMR (400 MHz, DMSO, δ, p.p.m.): 1.49–1.88 (14H, *m*, adamantylidene H), 2.50 (3H, *s*, CH_3), 4.25 (5H, *s*, Cp′ and 1H, *s*, Cp), 4.58 (3H, *s*, Cp); MS: *m*/*z* (ion, %*I*) 442 (M^+, 100); UV: λ_{max} 339.5 and 494 nm. Elemental analysis, calculated for $C_{26}H_{26}FeO_3$: C 70.59, H 5.88%; found: C 70.76, H 5.94%.

Crystal data

$[Fe(C_5H_5)(C_{21}H_{21}O_3)]$
$M_r = 442.33$
Triclinic, $P\overline{1}$
$a = 9.5997\ (1)$ Å
$b = 10.4336\ (1)$ Å
$c = 10.6348\ (2)$ Å
$\alpha = 72.0422\ (6)°$
$\beta = 85.3458\ (5)°$
$\gamma = 80.8752\ (6)°$
$V = 999.87\ (2)$ Å^3

$Z = 2$
$D_x = 1.469$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17 312 reflections
$\theta = 2.0–30.0°$
$\mu = 0.78$ mm^{-1}
$T = 160\ (1)$ K
Block, red
0.35 × 0.22 × 0.17 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.831$, $T_{max} = 0.880$
26 888 measured reflections

5825 independent reflections
5116 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 30°$
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 14$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.081$
$S = 1.06$
5824 reflections
272 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 0.3607P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C11—C12	1.3616 (17)	C13—C18	1.3558 (17)
C12—C13	1.4795 (17)		
C11—C12—C13	131.73 (11)	C18—C13—C12	130.26 (11)
C16—C12—C13	105.75 (11)	C18—C13—C14	122.51 (11)
C1—C11—C12—C16	156.74 (12)	C16—O15—C14—C13	−6.31 (14)
C17—C11—C12—C16	−20.47 (18)	C12—C13—C14—O15	14.85 (13)
C1—C11—C12—C13	−6.8 (2)	C14—O15—C16—C12	−4.98 (14)
C17—C11—C12—C13	175.98 (12)	C13—C12—C16—O15	14.16 (13)
C16—C12—C13—C14	−17.43 (13)		

The methyl H atoms were constrained to an ideal geometry (C—H = 0.98 Å), with $U_{iso}(H) = 1.5U_{eq}(C)$, but were allowed to rotate freely about the parent C—C bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.95–1.00 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. One low-angle reflection was omitted from the final cycles of refinement because its observed intensity was much lower than the calculated value as a result of being partially obscured by the beam stop.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1606). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Hart, R. J. & Heller, H. G. (1972). *J. Chem. Soc. Perkin Trans.* 1, pp. 1321–1324.

Heller, H. G. & Szewczyk, M. (1974). *J. Chem. Soc. Perkin Trans.* 1, pp. 1487–1492.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kaftory, M. (1984). *Acta Cryst.* C**40**, 1015–1019.

Kaftory, M., Goldberg, Y., Goldberg, S. & Botoshansky, M. (1998). *Acta Cryst.* C**54**, 683–687.

McCabe, R. W., Parry, D. E. & Saberi, S. P. (1993). *J. Chem. Soc. Perkin Trans.* 1, pp. 1023–1029.

Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Touchard, D. & Dabard, R. (1975). *Bull. Soc. Chim. Fr.* pp. 2567–2570.