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Crystal structure of dimethyl 4,4′-(cyclopenta-3,5-diene-1,3-diyl)-bis(2,3,5,6-tetrafluorobenzoate), $C_{21}H_{10}F_8O_4$

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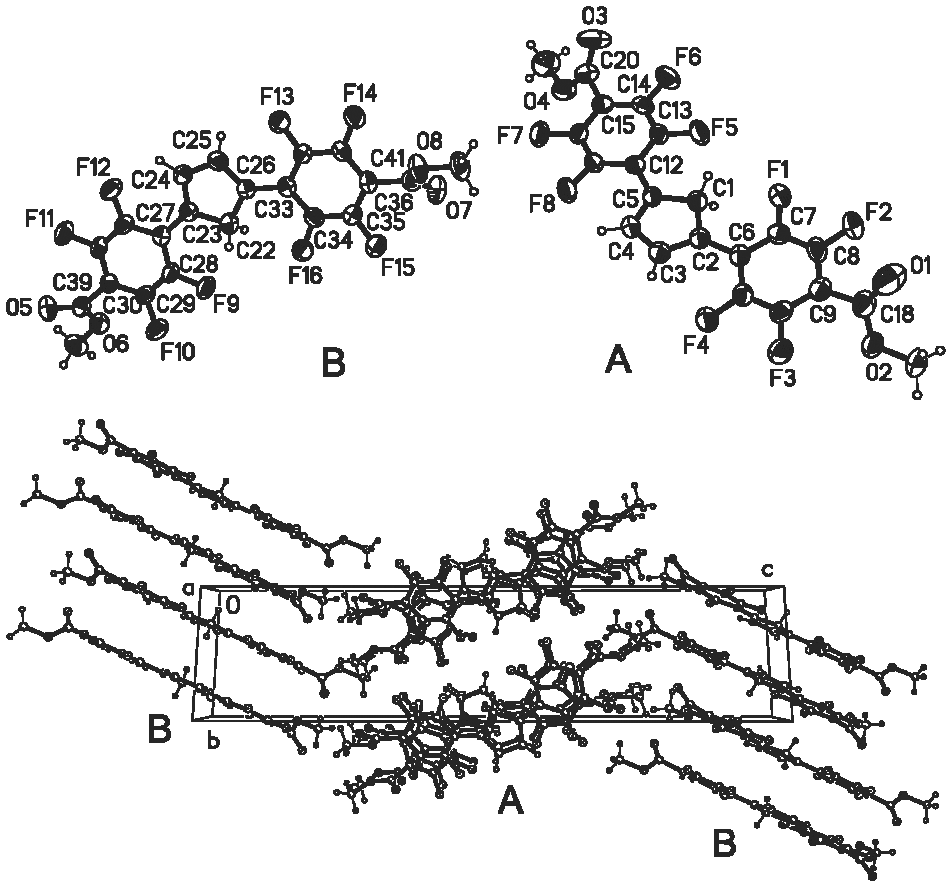

Abstract

$C_{21}H_{10}F_8O_4$, triclinic, $P\bar{1}$ (no. 2), a = 7.9194(2) Å, b = 8.0140(2) Å, c = 32.1570(8) Å, α = 89.179(2)°, β = 88.127(2)°, γ = 66.049(2)°, V = 1864.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.052, $wR_{ref}(F^2)$ = 0.122, T = 233 K.

Source of material

The title compound was obtained by reaction of sodium cyclopentadienide with methyl pentafluorobenzoate [1].

Experimental details

Hydrogen atoms were calculated and refined using a riding model. Low ratio $N_{gt}/N_{parameter}$ is caused by the small crystal with low diffraction and a long c-axis over 32 Å. Therefore, to obtain a good resolution of the reflections, the detector-crystal distance must be increased to a higher value.

Discussion

Two conformers A and B occupy the asymmetric unit (figure, top). Both have a nearly coplanar arrangement of the cyclopentadienyl ring and the arenes with torsion angles of 10.7(4)° and –3.4(4)° for A (C1–C2–C6–C7 and C1–C5–C12–C13) or –0.7(4)° and 2.5(4)° for B (C22–C23–C27–C28 and C22–C26–C33–C34), respectively. The bond lengths of the double bonds are 135.6(3) (C2—C3), 135.6(3) (C4—C5), 136.6(3) (C23—C24) and 134.9(3) pm (C25—C26). The difference between both confor-mers is the orientation of the ester groups. In A the methyl groups are on the same side of the main plane with torsion angles of 39.1(5)° and –44.8(4)° (O1–C18–C9–C8 and O3–C20–C15–C14), whereas in B they have opposite orientations with angles of 140.1(3)° and 46.7(4)° (O5–C39–C30–C29 and O7–C41–C36–C35), respectively. Interestingly, both conformers have the same intermolecular π-π stacking motif (figure, bottom); in each conformer the alternating enantiomeric molecules are connected *via* two types of π-π interactions. Conformer A stacks along [100] between the arenes

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(361 pm) and between a double bond of the cyclopentadienyl and an arene ring (358 pm). Conformer B stacks along [010] with distances of 350 and 374 pm; the shorter distance refers to the double bond to arene interaction. The reason for this separation is probably an inter-molecular repulsion between the methyl groups. Between the molecules with a distance of 374 pm, the methyl groups have a carbon-carbon distance of 413 pm, whereas this value increases to 695 pm for the molecules with a distance of 350 pm. In conformer A these intermolecular carbon-carbon distances are 440 and 542 pm. Finally, conformers A and B build up stacks that are connected along [001] by weak hydrogen bonds above 245 pm between the methyl hydrogens and the C=O oxygen atoms of the ester groups.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.03 × 0.04 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.69 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10882, 7207
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4326
$N(param)_{refined}$:	600
Programs:	SHELXS-97 [2], SHELXL-97 [3], SHELXTL [4]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	0.7277	1.1759	0.4978	0.049
H(1B)	2*i*	0.5722	1.1046	0.5106	0.049
H(3)	2*i*	0.9980	0.6574	0.4916	0.060
H(4)	2*i*	0.8406	0.7703	0.4240	0.058
H(19A)	2*i*	1.1877	0.9394	0.7545	0.096
H(19B)	2*i*	1.3682	0.7591	0.7464	0.096
H(19C)	2*i*	1.1791	0.7459	0.7591	0.096
H(21A)	2*i*	0.0877	1.5355	0.2519	0.129
H(21B)	2*i*	0.2629	1.5602	0.2327	0.129
H(21C)	2*i*	0.1271	1.7067	0.2643	0.129
H(22A)	2*i*	1.0328	0.3758	0.0165	0.050
H(22B)	2*i*	1.0824	0.1771	0.0355	0.050
H(24)	2*i*	0.6984	0.2181	–0.0384	0.057
H(25)	2*i*	0.5575	0.3569	0.0309	0.057
H(40A)	2*i*	1.7996	–0.2113	–0.1925	0.094
H(40B)	2*i*	1.7891	–0.0112	–0.1994	0.094
H(40C)	2*i*	1.6510	–0.0740	–0.2224	0.094
H(42A)	2*i*	0.7236	0.6958	0.2875	0.103
H(42B)	2*i*	0.5740	0.6157	0.2977	0.103
H(42C)	2*i*	0.5123	0.8151	0.2791	0.103

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	2*i*	0.8969(3)	0.9144(6)	0.71723(7)	0.071(2)	0.313(5)	0.044(1)	–0.076(2)	0.011(1)	0.002(2)
O(2)	2*i*	1.1910(3)	0.8211(3)	0.69984(5)	0.058(1)	0.083(1)	0.039(1)	–0.030(1)	–0.0032(9)	–0.0040(9)
O(3)	2*i*	0.0386(3)	1.5542(3)	0.33269(7)	0.041(1)	0.122(2)	0.085(2)	–0.011(1)	–0.003(1)	0.029(1)
O(4)	2*i*	0.2927(2)	1.4752(3)	0.29178(6)	0.051(1)	0.081(1)	0.049(1)	–0.021(1)	–0.0039(9)	0.012(1)
O(5)	2*i*	1.4815(3)	–0.2357(3)	–0.17569(6)	0.077(1)	0.056(1)	0.050(1)	–0.032(1)	0.010(1)	–0.011(1)
O(6)	2*i*	1.5868(2)	–0.0207(2)	–0.16218(5)	0.050(1)	0.059(1)	0.048(1)	–0.0287(9)	0.0112(8)	–0.0064(9)
O(7)	2*i*	0.7645(3)	0.8052(3)	0.21519(6)	0.089(2)	0.062(1)	0.055(1)	–0.043(1)	–0.005(1)	–0.007(1)
O(8)	2*i*	0.6339(3)	0.6185(3)	0.23697(5)	0.086(1)	0.059(1)	0.043(1)	–0.035(1)	0.016(1)	–0.0119(9)
C(1)	2*i*	0.6934(3)	1.0715(3)	0.49672(7)	0.037(1)	0.046(2)	0.043(2)	–0.021(1)	0.005(1)	–0.004(1)
C(2)	2*i*	0.8361(3)	0.9068(3)	0.51661(7)	0.040(1)	0.042(2)	0.041(2)	–0.022(1)	0.003(1)	–0.003(1)
C(3)	2*i*	0.9052(3)	0.7745(4)	0.48726(8)	0.050(2)	0.046(2)	0.045(2)	–0.011(1)	–0.003(1)	–0.002(1)
C(4)	2*i*	0.8159(3)	0.8393(4)	0.44860(8)	0.048(2)	0.052(2)	0.042(2)	–0.016(1)	0.001(1)	–0.007(1)
C(5)	2*i*	0.6909(3)	1.0146(3)	0.45265(7)	0.036(1)	0.043(2)	0.038(1)	–0.020(1)	0.005(1)	–0.006(1)
C(6)	2*i*	0.8874(3)	0.8983(3)	0.56023(7)	0.041(1)	0.051(2)	0.038(1)	–0.027(1)	0.004(1)	–0.003(1)
C(7)	2*i*	0.7871(3)	1.0330(4)	0.58925(8)	0.039(2)	0.060(2)	0.045(2)	–0.023(1)	0.001(1)	–0.004(1)
C(8)	2*i*	0.8340(4)	1.0237(4)	0.63014(8)	0.050(2)	0.071(2)	0.044(2)	–0.030(2)	0.014(1)	–0.016(2)
C(9)	2*i*	0.9829(4)	0.8821(4)	0.64613(8)	0.045(2)	0.076(2)	0.039(2)	–0.034(2)	0.004(1)	–0.001(1)
C(10)	2*i*	1.0865(3)	0.7462(4)	0.61789(8)	0.044(2)	0.063(2)	0.043(2)	–0.030(1)	–0.002(1)	0.005(1)
C(11)	2*i*	1.0388(3)	0.7547(4)	0.57687(8)	0.050(2)	0.050(2)	0.042(2)	–0.026(1)	0.006(1)	–0.005(1)
C(12)	2*i*	0.5702(3)	1.1305(3)	0.42093(7)	0.034(1)	0.042(2)	0.043(2)	–0.018(1)	0.002(1)	–0.001(1)
C(13)	2*i*	0.4358(3)	1.3060(4)	0.42884(8)	0.041(2)	0.049(2)	0.041(2)	–0.019(1)	0.008(1)	–0.007(1)
C(14)	2*i*	0.3191(3)	1.4117(3)	0.39957(8)	0.033(1)	0.046(2)	0.053(2)	–0.010(1)	0.008(1)	–0.003(1)
C(15)	2*i*	0.3287(3)	1.3548(3)	0.35868(8)	0.034(1)	0.048(2)	0.050(2)	–0.016(1)	–0.000(1)	0.004(1)
C(16)	2*i*	0.4602(3)	1.1822(4)	0.35008(8)	0.045(2)	0.053(2)	0.040(2)	–0.023(1)	–0.001(1)	–0.005(1)
C(17)	2*i*	0.5747(3)	1.0748(3)	0.37974(8)	0.041(2)	0.042(2)	0.044(2)	–0.014(1)	0.004(1)	–0.006(1)
C(18)	2*i*	1.0181(4)	0.8728(5)	0.69166(9)	0.052(2)	0.100(3)	0.044(2)	–0.040(2)	0.005(2)	–0.002(2)
C(19)	2*i*	1.2352(4)	0.8159(4)	0.74362(8)	0.081(2)	0.073(2)	0.040(2)	–0.032(2)	–0.015(1)	0.001(1)
C(20)	2*i*	0.2014(4)	1.4724(4)	0.32664(9)	0.043(2)	0.059(2)	0.060(2)	–0.022(1)	–0.005(1)	0.006(1)
C(21)	2*i*	0.1835(4)	1.5779(5)	0.25731(9)	0.081(2)	0.102(3)	0.056(2)	–0.018(2)	–0.015(2)	0.023(2)
C(22)	2*i*	0.9880(3)	0.2794(3)	0.02103(7)	0.049(2)	0.042(2)	0.038(1)	–0.021(1)	–0.000(1)	0.000(1)
C(23)	2*i*	0.9432(3)	0.2183(3)	–0.01932(7)	0.044(2)	0.038(1)	0.035(1)	–0.016(1)	0.000(1)	0.003(1)
C(24)	2*i*	0.7616(3)	0.2463(3)	–0.01724(8)	0.048(2)	0.050(2)	0.040(2)	–0.015(1)	–0.006(1)	–0.002(1)
C(25)	2*i*	0.6812(3)	0.3260(4)	0.02240(8)	0.042(2)	0.052(2)	0.042(2)	–0.012(1)	–0.000(1)	–0.003(1)
C(26)	2*i*	0.8084(3)	0.3501(3)	0.04562(7)	0.044(2)	0.037(1)	0.035(1)	–0.014(1)	–0.001(1)	0.002(1)
C(27)	2*i*	1.0771(3)	0.1386(3)	–0.05373(7)	0.044(2)	0.039(1)	0.034(1)	–0.018(1)	–0.001(1)	0.003(1)
C(28)	2*i*	1.2618(3)	0.1132(3)	–0.05233(7)	0.046(2)	0.052(2)	0.032(1)	–0.025(1)	–0.004(1)	–0.005(1)
C(29)	2*i*	1.3880(3)	0.0361(3)	–0.08420(8)	0.041(2)	0.054(2)	0.041(2)	–0.023(1)	–0.003(1)	–0.002(1)
C(30)	2*i*	1.3430(3)	–0.0238(3)	–0.12039(7)	0.046(2)	0.044(2)	0.034(1)	–0.023(1)	0.004(1)	–0.001(1)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(31)	2*i*	1.1596(3)	–0.0006(3)	–0.12242(7)	0.054(2)	0.054(2)	0.031(1)	–0.033(1)	–0.003(1)	–0.002(1)
C(32)	2*i*	1.0337(3)	0.0785(3)	–0.09075(7)	0.041(2)	0.053(2)	0.038(1)	–0.027(1)	–0.003(1)	–0.000(1)
C(33)	2*i*	0.7839(3)	0.4310(3)	0.08699(7)	0.045(2)	0.035(1)	0.037(1)	–0.015(1)	0.000(1)	0.003(1)
C(34)	2*i*	0.9260(3)	0.4565(3)	0.10712(8)	0.043(2)	0.044(2)	0.044(2)	–0.015(1)	0.005(1)	–0.003(1)
C(35)	2*i*	0.9011(3)	0.5377(3)	0.14551(8)	0.043(2)	0.045(2)	0.045(2)	–0.017(1)	–0.003(1)	–0.003(1)
C(36)	2*i*	0.7347(3)	0.5968(3)	0.16751(7)	0.053(2)	0.037(2)	0.036(1)	–0.017(1)	0.001(1)	–0.002(1)
C(37)	2*i*	0.5925(3)	0.5725(3)	0.14839(8)	0.046(2)	0.038(2)	0.041(2)	–0.016(1)	0.007(1)	–0.003(1)
C(38)	2*i*	0.6161(3)	0.4944(3)	0.10979(7)	0.047(2)	0.039(2)	0.041(2)	–0.020(1)	–0.003(1)	0.000(1)
C(39)	2*i*	1.4766(3)	–0.1083(4)	–0.15582(8)	0.049(2)	0.044(2)	0.036(1)	–0.019(1)	–0.002(1)	0.001(1)
C(40)	2*i*	1.7174(4)	–0.0846(4)	–0.19699(8)	0.052(2)	0.076(2)	0.057(2)	–0.023(2)	0.020(1)	–0.006(2)
C(41)	2*i*	0.7130(4)	0.6868(4)	0.20889(8)	0.051(2)	0.037(2)	0.045(2)	–0.012(1)	–0.005(1)	–0.001(1)
C(42)	2*i*	0.6089(4)	0.6924(4)	0.27879(8)	0.084(2)	0.075(2)	0.041(2)	–0.028(2)	0.012(2)	–0.017(2)
F(1)	2*i*	0.6355(2)	1.1772(2)	0.57772(5)	0.055(1)	0.065(1)	0.055(1)	–0.0108(8)	–0.0010(8)	–0.0127(8)
F(2)	2*i*	0.7265(2)	1.1640(2)	0.65489(5)	0.069(1)	0.096(1)	0.050(1)	–0.022(1)	0.0105(8)	–0.0261(9)
F(3)	2*i*	1.2355(2)	0.6023(2)	0.63013(5)	0.062(1)	0.073(1)	0.0501(9)	–0.0254(9)	–0.0092(8)	0.0051(8)
F(4)	2*i*	1.1489(2)	0.6157(2)	0.55216(5)	0.062(1)	0.054(1)	0.0502(9)	–0.0125(8)	–0.0047(7)	–0.0055(8)
F(5)	2*i*	0.4155(2)	1.3783(2)	0.46747(4)	0.066(1)	0.056(1)	0.0449(9)	–0.0099(8)	0.0060(7)	–0.0116(7)
F(6)	2*i*	0.1930(2)	1.5774(2)	0.41086(5)	0.058(1)	0.056(1)	0.063(1)	–0.0004(8)	0.0085(8)	–0.0044(8)
F(7)	2*i*	0.4739(2)	1.1116(2)	0.31195(5)	0.075(1)	0.062(1)	0.048(1)	–0.0243(8)	–0.0126(8)	–0.0078(8)
F(8)	2*i*	0.6961(2)	0.9078(2)	0.36774(4)	0.071(1)	0.050(1)	0.0482(9)	–0.0057(8)	–0.0061(8)	–0.0128(7)
F(9)	2*i*	1.3242(2)	0.1650(2)	–0.01837(4)	0.0532(9)	0.098(1)	0.0450(9)	–0.0372(9)	0.0004(7)	–0.0234(8)
F(10)	2*i*	1.5632(2)	0.0140(2)	–0.07827(5)	0.0457(9)	0.107(1)	0.0505(9)	–0.0381(9)	0.0007(7)	–0.0190(9)
F(11)	2*i*	1.1012(2)	–0.0553(2)	–0.15612(4)	0.063(1)	0.092(1)	0.0416(9)	–0.0451(9)	0.0010(7)	–0.0162(8)
F(12)	2*i*	0.8598(2)	0.0948(2)	–0.09644(4)	0.0486(9)	0.101(1)	0.0457(9)	–0.0395(9)	0.0004(7)	–0.0126(8)
F(13)	2*i*	0.4681(2)	0.4783(2)	0.09369(4)	0.0477(9)	0.070(1)	0.0511(9)	–0.0266(8)	0.0024(7)	–0.0129(7)
F(14)	2*i*	0.4244(2)	0.6320(2)	0.16697(4)	0.0521(9)	0.062(1)	0.0524(9)	–0.0237(8)	0.0129(7)	–0.0124(7)
F(15)	2*i*	1.0469(2)	0.5562(2)	0.16180(5)	0.0543(9)	0.081(1)	0.056(1)	–0.0279(8)	–0.0044(8)	–0.0156(8)
F(16)	2*i*	1.0954(2)	0.4014(2)	0.08886(5)	0.0449(9)	0.091(1)	0.055(1)	–0.0263(8)	0.0071(7)	–0.0214(9)

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