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# 3,3,4,4-Tetrafluoro-2,3,4,5-tetrahydro-1,6-benzodioxocine-8-carbaldehyde

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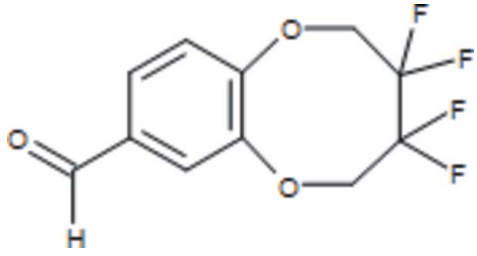
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.047; $wR$ factor = 0.146; data-to-parameter ratio = 12.2.

In the title compound, $C_{11}H_8F_4O_3$, the eight-membered dialkoxy ring adopts a highly puckered conformation. In the crystal, molecules are linked by weak C—H···O interactions.

## Related literature

For the applications of fluorinated mcarocyles, see: Babudri *et al.* (2007).




## Experimental

### Crystal data

$C_{11}H_8F_4O_3$
$M_r$ = 264.17
Monoclinic, $P2_1/n$
$a$ = 9.142 (5) Å
$b$ = 11.4935 (14) Å
$c$ = 10.928 (10) Å
$\beta$ = 104.109 (15)°
$V$ = 1113.6 (12) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.16 mm$^{-1}$
$T$ = 298 K
0.35 × 0.24 × 0.11 mm

### Data collection

Bruker SMART CCD diffractometer
5552 measured reflections
2000 independent reflections
972 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.044

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.146
$S$ = 0.97
2000 reflections
164 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.15 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C3—H3···O3$^{i}$ | 0.93 | 2.52 | 3.193 (5) | 130 |
| C8—H8$B$···O3$^{ii}$ | 0.97 | 2.43 | 3.343 (6) | 157 |

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+1, -y+1, -z+2$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

We are grateful to the Doctoral Program Foundation of the Natural Science Foundation of Guangdong Province, China (No. 5100430) and South China Normal University Grants (524002, 523467) for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5362).

## References

Babudri, F., Farinola, G. M., Naso, F. & Ragni, R. (2007). *Chem. Commun.* pp. 1003–1022
Bruker (2000). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

# supporting information

*Acta Cryst.* (2010). E**66**, o1137 [https://doi.org/10.1107/S1600536810014133]

## 3,3,4,4-Tetrafluoro-2,3,4,5-tetrahydro-1,6-benzodioxocine-8-carbaldehyde

**Zhuo Zeng, Jun-Wen Zhong, Hui Wang, Jin Wang and Wan-Wan Cao**

### S1. Comment

Fluorinated mcarocyles play an important role in the pharmaceutical, agrochemical and advanced materials fields (Babudri *et al.*, 2007). As part of our studies in this area, we now report the synthesis and structure of the title compound, (I).

The structure of this compound is shown in Fig. 1. The benzene ring is attached to a highly puckered eight-membered dialkoxy ring. The torsion angle at the fusion bond (O1—C8—C9—O2) is 3.27°. The C—C bond distances of the aromatic ring vary from 1.373 (3) to 1.407 (3) A, the latter being the C2—C7 fusion bond. The ring angles of the benzene ring also vary from 118.9 (8) to 120.8 (9)° indicating a slight distortion in this ring.

### S2. Experimental

A mixture of 3,4-dihydroxy-benzaldehyde (0.345 g, 2.5 mmol), potassium carbonate (3.453 g, 25 mmol) was refluxed in acetonitrile (20 ml) at 373 K for 45 min, then a solution of methanesulfonic acid, trifluoro-, 2,2,3,3-tetrafluoro-1,4-butanediylester in acetonitrile (5 ml) was added, the mixture was heated under reflux for 12 h. After cooling to room temperature, the inorganic salts was removed by filtration . The filtrate was concentrated under reduced pressure, The residue was purified by flash chromatography on silica gel to afford the title compound as a white solid, yield 467 mg (70.8%). Colourless blocks of (I) were grown by by slow evaporation from dichloromethane at room temperature.

### S3. Refinement

H-atoms were placed in calculated positions with C—H = 0.93–0.97 Å and refined as riding atoms.

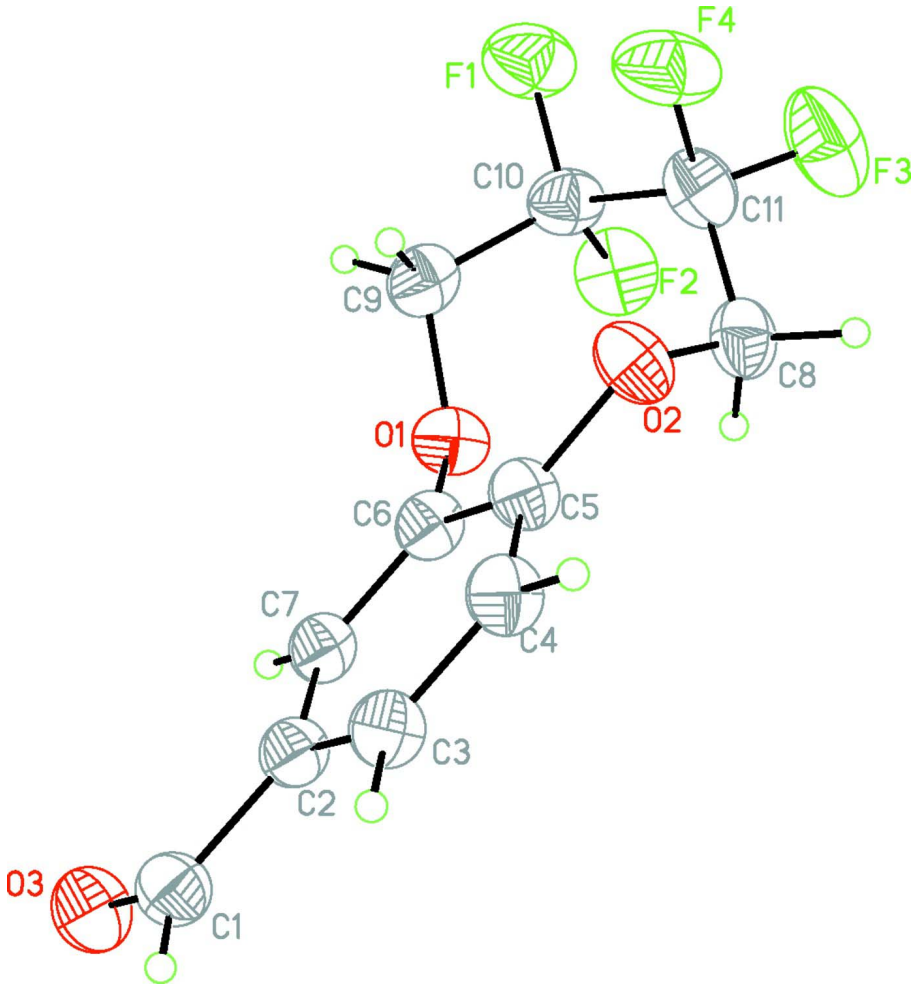



**Figure 1**

View of (I) showing displacement ellipsoids drawn at the 50% probability level.

### 3,3,4,4-Tetrafluoro-2,3,4,5-tetrahydro-1,6-benzodioxocine-8-carbaldehyde

*Crystal data*

$C_{11}H_8F_4O_3$
$M_r = 264.17$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 9.142\ (5)$ Å
$b = 11.4935\ (14)$ Å
$c = 10.928\ (10)$ Å
$\beta = 104.109\ (15)°$
$V = 1113.6\ (12)$ Å$^3$
$Z = 4$

$F(000) = 536.0$
$D_x = 1.576$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 733 reflections
$\theta = 3.2–20.1°$
$\mu = 0.16$ mm$^{-1}$
$T = 298$ K
Block, colourless
0.35 × 0.24 × 0.11 mm

*Data collection*

Bruker SMART CCD diffractometer
Radiation source: sealed tube
Graphite monochromator

$\omega$ scans
5552 measured reflections
2000 independent reflections
972 reflections with $I > 2\sigma(I)$

$R_{int}$ = 0.044
$\theta_{max}$ = 25.2°, $\theta_{min}$ = 2.6°
$h$ = −6→10
$k$ = −13→13
$l$ = −13→11

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.146
$S$ = 0.97
2000 reflections
164 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.4913P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.15 e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0047 (12)

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor wR and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) etc. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| F2 | 0.5814 (2) | 0.90137 (19) | 0.9443 (2) | 0.0901 (8) |
| F4 | 0.9709 (3) | 0.8853 (2) | 1.0613 (2) | 0.1040 (9) |
| F1 | 0.7668 (3) | 0.9585 (2) | 0.8674 (2) | 0.1008 (9) |
| F3 | 0.7960 (3) | 0.9756 (2) | 1.1293 (3) | 0.1194 (10) |
| C4 | 0.8950 (4) | 0.4731 (3) | 1.1272 (3) | 0.0599 (10) |
| H4 | 0.9789 | 0.4745 | 1.1953 | 0.072* |
| C7 | 0.6454 (3) | 0.4699 (3) | 0.9227 (3) | 0.0545 (9) |
| H7 | 0.5614 | 0.4689 | 0.8547 | 0.065* |
| C6 | 0.7048 (3) | 0.5746 (3) | 0.9715 (3) | 0.0535 (9) |
| C5 | 0.8301 (3) | 0.5770 (3) | 1.0754 (3) | 0.0552 (9) |
| C2 | 0.7096 (3) | 0.3650 (3) | 0.9738 (3) | 0.0549 (9) |
| C3 | 0.8354 (3) | 0.3678 (3) | 1.0779 (3) | 0.0590 (10) |
| H3 | 0.8785 | 0.2986 | 1.1136 | 0.071* |
| C10 | 0.7221 (4) | 0.8729 (4) | 0.9373 (4) | 0.0685 (11) |
| C8 | 0.8155 (4) | 0.7738 (3) | 1.1564 (3) | 0.0669 (11) |
| H8A | 0.8542 | 0.7957 | 1.2441 | 0.080* |
| H8B | 0.7108 | 0.7509 | 1.1445 | 0.080* |
| C1 | 0.6488 (4) | 0.2520 (4) | 0.9223 (4) | 0.0664 (11) |
| H1 | 0.6927 | 0.1853 | 0.9636 | 0.080* |
| C11 | 0.8265 (4) | 0.8762 (4) | 1.0718 (4) | 0.0741 (11) |

| | | | | |
|---|---|---|---|---|
| C9 | 0.7179 (4) | 0.7596 (3) | 0.8678 (3) | 0.0657 (10) |
| H9A | 0.6716 | 0.7710 | 0.7788 | 0.079* |
| H9B | 0.8197 | 0.7310 | 0.8761 | 0.079* |
| O2 | 0.9011 (2) | 0.6785 (2) | 1.1261 (2) | 0.0670 (7) |
| O1 | 0.6327 (2) | 0.6767 (2) | 0.9195 (2) | 0.0622 (7) |
| O3 | 0.5453 (3) | 0.2397 (2) | 0.8295 (3) | 0.0825 (9) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| F2 | 0.0728 (15) | 0.0924 (18) | 0.0987 (18) | 0.0255 (13) | 0.0085 (12) | 0.0057 (14) |
| F4 | 0.0709 (15) | 0.112 (2) | 0.116 (2) | −0.0292 (14) | −0.0040 (13) | 0.0202 (16) |
| F1 | 0.1117 (19) | 0.0856 (18) | 0.0951 (19) | −0.0162 (14) | 0.0061 (14) | 0.0252 (14) |
| F3 | 0.157 (2) | 0.0757 (18) | 0.103 (2) | 0.0154 (16) | −0.0126 (17) | −0.0179 (16) |
| C4 | 0.049 (2) | 0.073 (3) | 0.046 (2) | −0.0005 (19) | −0.0088 (15) | 0.0038 (19) |
| C7 | 0.0456 (19) | 0.070 (3) | 0.0410 (19) | −0.0046 (18) | −0.0020 (15) | 0.0014 (18) |
| C6 | 0.0420 (19) | 0.067 (3) | 0.046 (2) | 0.0014 (17) | 0.0012 (16) | 0.0051 (18) |
| C5 | 0.0449 (19) | 0.065 (3) | 0.049 (2) | −0.0042 (17) | −0.0011 (16) | −0.0010 (18) |
| C2 | 0.049 (2) | 0.065 (2) | 0.047 (2) | −0.0067 (17) | 0.0062 (16) | −0.0003 (18) |
| C3 | 0.056 (2) | 0.065 (3) | 0.049 (2) | 0.0014 (18) | 0.0010 (17) | 0.0049 (18) |
| C10 | 0.065 (2) | 0.070 (3) | 0.068 (3) | −0.003 (2) | 0.010 (2) | 0.013 (2) |
| C8 | 0.063 (2) | 0.079 (3) | 0.052 (2) | −0.001 (2) | 0.0015 (17) | −0.009 (2) |
| C1 | 0.064 (2) | 0.071 (3) | 0.063 (2) | −0.010 (2) | 0.012 (2) | −0.003 (2) |
| C11 | 0.070 (3) | 0.071 (3) | 0.074 (3) | 0.000 (2) | 0.004 (2) | −0.009 (2) |
| C9 | 0.058 (2) | 0.084 (3) | 0.049 (2) | 0.000 (2) | 0.0007 (16) | 0.011 (2) |
| O2 | 0.0481 (13) | 0.0678 (17) | 0.0733 (18) | −0.0011 (12) | −0.0077 (12) | −0.0091 (13) |
| O1 | 0.0472 (13) | 0.0663 (17) | 0.0647 (16) | 0.0009 (12) | −0.0025 (11) | 0.0115 (13) |
| O3 | 0.0749 (17) | 0.096 (2) | 0.0663 (18) | −0.0205 (16) | −0.0032 (14) | −0.0142 (15) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| F2—C10 | 1.347 (4) | C2—C1 | 1.469 (5) |
| F4—C11 | 1.357 (4) | C3—H3 | 0.9300 |
| F1—C10 | 1.368 (4) | C10—C9 | 1.504 (5) |
| F3—C11 | 1.365 (4) | C10—C11 | 1.545 (6) |
| C4—C3 | 1.381 (4) | C8—O2 | 1.432 (4) |
| C4—C5 | 1.392 (4) | C8—C11 | 1.515 (5) |
| C4—H4 | 0.9300 | C8—H8A | 0.9700 |
| C7—C6 | 1.374 (4) | C8—H8B | 0.9700 |
| C7—C2 | 1.397 (4) | C1—O3 | 1.215 (4) |
| C7—H7 | 0.9300 | C1—H1 | 0.9300 |
| C6—O1 | 1.398 (4) | C9—O1 | 1.430 (4) |
| C6—C5 | 1.402 (4) | C9—H9A | 0.9700 |
| C5—O2 | 1.383 (4) | C9—H9B | 0.9700 |
| C2—C3 | 1.407 (4) | | |
| | | | |
| C3—C4—C5 | 120.3 (3) | O2—C8—C11 | 109.4 (3) |
| C3—C4—H4 | 119.8 | O2—C8—H8A | 109.8 |

| | | | |
|---|---|---|---|
| C5—C4—H4 | 119.8 | C11—C8—H8A | 109.8 |
| C6—C7—C2 | 120.9 (3) | O2—C8—H8B | 109.8 |
| C6—C7—H7 | 119.6 | C11—C8—H8B | 109.8 |
| C2—C7—H7 | 119.6 | H8A—C8—H8B | 108.3 |
| C7—C6—O1 | 118.4 (3) | O3—C1—C2 | 124.6 (4) |
| C7—C6—C5 | 119.9 (3) | O3—C1—H1 | 117.7 |
| O1—C6—C5 | 121.6 (3) | C2—C1—H1 | 117.7 |
| O2—C5—C4 | 116.7 (3) | F4—C11—F3 | 106.6 (3) |
| O2—C5—C6 | 123.5 (3) | F4—C11—C8 | 108.8 (3) |
| C4—C5—C6 | 119.7 (3) | F3—C11—C8 | 108.5 (4) |
| C7—C2—C3 | 119.0 (3) | F4—C11—C10 | 108.1 (4) |
| C7—C2—C1 | 121.8 (3) | F3—C11—C10 | 108.1 (3) |
| C3—C2—C1 | 119.2 (3) | C8—C11—C10 | 116.4 (3) |
| C4—C3—C2 | 120.1 (3) | O1—C9—C10 | 109.0 (3) |
| C4—C3—H3 | 119.9 | O1—C9—H9A | 109.9 |
| C2—C3—H3 | 119.9 | C10—C9—H9A | 109.9 |
| F2—C10—F1 | 106.1 (3) | O1—C9—H9B | 109.9 |
| F2—C10—C9 | 109.4 (3) | C10—C9—H9B | 109.9 |
| F1—C10—C9 | 108.4 (3) | H9A—C9—H9B | 108.3 |
| F2—C10—C11 | 108.5 (4) | C5—O2—C8 | 120.5 (2) |
| F1—C10—C11 | 108.3 (3) | C6—O1—C9 | 118.1 (2) |
| C9—C10—C11 | 115.8 (3) | | |

| | | | |
|---|---|---|---|
| C2—C7—C6—O1 | −177.7 (3) | F2—C10—C11—F4 | −160.5 (3) |
| C2—C7—C6—C5 | −1.1 (5) | F1—C10—C11—F4 | −45.8 (4) |
| C3—C4—C5—O2 | −176.8 (3) | C9—C10—C11—F4 | 76.1 (4) |
| C3—C4—C5—C6 | −0.9 (5) | F2—C10—C11—F3 | −45.4 (5) |
| C7—C6—C5—O2 | 176.6 (3) | F1—C10—C11—F3 | 69.2 (4) |
| O1—C6—C5—O2 | −6.8 (5) | C9—C10—C11—F3 | −168.8 (3) |
| C7—C6—C5—C4 | 1.0 (5) | F2—C10—C11—C8 | 76.9 (4) |
| O1—C6—C5—C4 | 177.6 (3) | F1—C10—C11—C8 | −168.5 (3) |
| C6—C7—C2—C3 | 0.9 (5) | C9—C10—C11—C8 | −46.5 (5) |
| C6—C7—C2—C1 | −179.4 (3) | F2—C10—C9—O1 | −48.7 (4) |
| C5—C4—C3—C2 | 0.8 (5) | F1—C10—C9—O1 | −163.9 (2) |
| C7—C2—C3—C4 | −0.8 (5) | C11—C10—C9—O1 | 74.2 (4) |
| C1—C2—C3—C4 | 179.5 (3) | C4—C5—O2—C8 | −134.3 (3) |
| C7—C2—C1—O3 | 3.8 (6) | C6—C5—O2—C8 | 49.9 (5) |
| C3—C2—C1—O3 | −176.6 (4) | C11—C8—O2—C5 | −114.5 (3) |
| O2—C8—C11—F4 | −41.8 (4) | C7—C6—O1—C9 | −121.7 (3) |
| O2—C8—C11—F3 | −157.5 (3) | C5—C6—O1—C9 | 61.7 (4) |
| O2—C8—C11—C10 | 80.4 (4) | C10—C9—O1—C6 | −120.0 (3) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C3—H3···O3$^{i}$ | 0.93 | 2.52 | 3.193 (5) | 130 |

| | | | | |
|---|---|---|---|---|
| C8—H8*B*···O3$^{ii}$ | 0.97 | 2.43 | 3.343 (6) | 157 |

Symmetry codes: (i) $x+1/2, -y+1/2, z+1/2$; (ii) $-x+1, -y+1, -z+2$.