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Crystal structure of bis(4-methoxyphenyl) malonate

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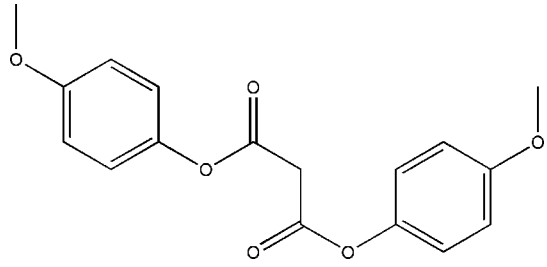
The complete molecule of the title compound, $C_{17}H_{16}O_6$, is generated by crystallographic twofold symmetry, with the central methylene C atom lying on the rotation axis. The carbonyl O atom is disordered over two adjacent positions in a 0.63 (3):0.37 (3) ratio and the dihedral angle between the benzene rings in the two halves of the molecule is 79.31 (12)°. In the crystal, molecules are connected by C—H···O hydrogen bonds, generating (110) sheets. Very weak intrasheet C—H···π interactions are also observed.

Keywords: crystal structure; orientational disorder; C—H···O interactions; C—H···π interactions.

CCDC reference: 1058073

1. Related literature

For the application of the 4-methoxyphenyl group in chemiluminescence, see: Teranishi *et al.*(1999). For its biological activity, see: Prasanna Kumar *et al.*, (2013).



2. Experimental

2.1. Crystal data

$C_{17}H_{16}O_6$
M_r = 316.30
Orthorhombic, *Pbcn*
a = 5.4307 (19) Å
b = 8.131 (3) Å
c = 36.149 (10) Å
V = 1596.3 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 296 K
0.18 × 0.16 × 0.14 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)
T_{min} = 0.982, T_{max} = 0.986
6486 measured reflections
1405 independent reflections
1008 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.162
S = 1.03
1405 reflections
121 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

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

*Cg*1 is the centroid of the benzene ring.

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9A···O3A^{i}	0.92 (3)	2.53 (3)	3.216 (6)	131 (3)
C4—H4···$Cg1^{ii}$	0.93	2.99	3.6957	134
C7—H7···$Cg1^{iii}$	0.93	2.99	3.6980	134

Symmetry codes: (i) $x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, z$; (iii) $-x-\frac{1}{2}, y-\frac{3}{2}, z$.

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7398).

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supporting information

Acta Cryst. (2015). E**71**, o330–o331 [https://doi.org/10.1107/S2056989015006891]

Crystal structure of bis(4-methoxyphenyl) malonate

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S1. Chemical context

4-Methoxyphenyl derivatives play significant role in synthesizing chemiluminescence (Teranishi *et al.*, 1999), biologically active materials (Prasanna Kumar *et al.*, 2013) and molecule-based magnetic materials etc., Keeping these things in mind, and our interest towards synthesizing liquid crystals bearing malonate moiety [–C(O)O—CH2—C(O)O-], we report here the crystal structure of the title compound.

S2. Structural commentary

The molecules of the title compound, $C_{17}H_{16}O_6$, show two fold rotation symmetry, for which the 2-fold rotation crystallographic axis passes through the C9 atom (with symmetry code -*x*, *y*, -*z*+1/2). The asymmetric unit of the title compound contains half molecule. The carbonyl oxygen atom is disordered over two positions due to crystallographic 2-fold rotation axis (orientational disorder), the occupancy ratio being 0.63 (3) : 0.37 (3). The dihedral angle between the benzene rings in the two halves of the molecule is 79.31 (12)º. Further, the dihedral angle between the central –CH_2–C(O)–O– segment and the phenyl ring is 86.41 (6)º. The methoxy group is approximately coplanar with the attached benzene ring, the C1—O1—C2—C3 torsion being 3.76 (1)º .

S3. Supramolecular features

In the crystal structure, the molecules are connected via C9—H9···O3 intermolecular interactions running into C(4) chains along crystallographic a and b axis, thus forming sheets in the ab plane. These sheets are further stabilized by C4—H4···pi and C7—H7···pi interactions (where Cg is the centroid of the phenyl ring)along [010], and thus, a two dimensional architecture is observed.

S4. Synthesis and crystallization

A mixture of malonic acid (1 mmol) and phosphorous oxychloride ($POCl_3$) was stirred for about an hour at 30°C . To this mixture, 4-methoxyphenol (2 mmol) was added and the reaction mixture was heated to 50°C for 30 minutes. The reaction mixture was poured into crushed ice and the solid obtained was thoroughly washed with water, dilute sodium hydroxide and again with water.

Colourless blocks of the title compound were obtained from slow evaporation technique using methanol as the solvent.

S5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 1. The H atoms were positioned with idealized geometry using a riding model with C—H = 0.95-0.99 Å. All H-atoms were refined with isotropic displacement parameters (set to 1.2-1.5 times of the U eq of the parent atom). The carbonyl oxygen atom is disordered over two sites and refined with site occupancy factors 0.63 (3) : 0.37 (3).

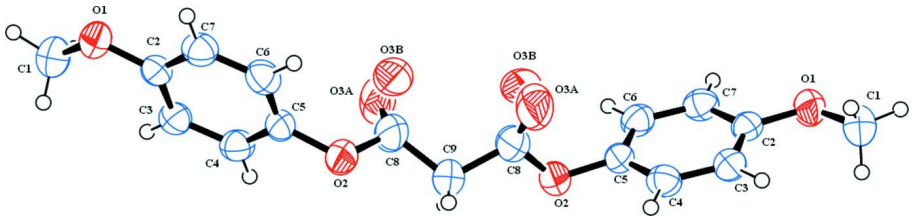

Figure 1

The molecular structure of the title compound, showing displacement ellipsoids drawn at the 50% probability level.

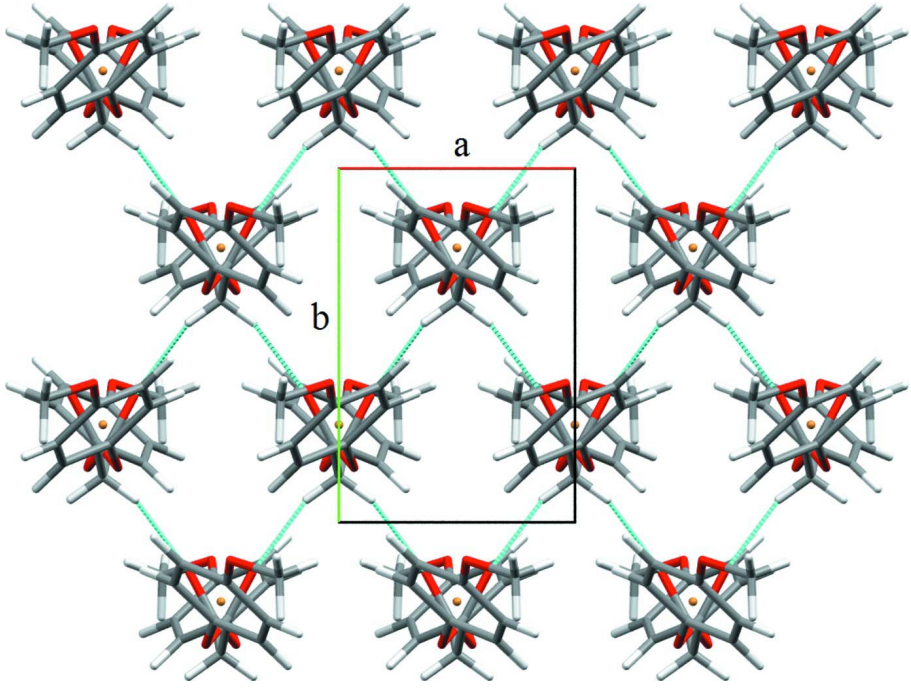

Figure 2

The molecular packing of the title compound when viewed along *c* axis. Dashed lines indicate intermolecular C—H···O interactions.

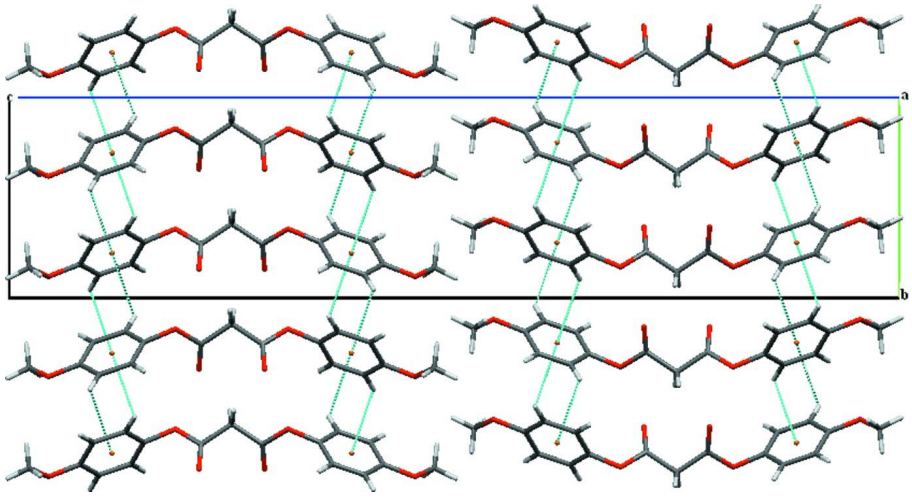

Figure 3

The molecular packing of the title compound when viewed along *a* axis. Dashed lines indicate intermolecular C—H···π interactions.

Bis(4-methoxyphenyl) malonate

Crystal data

$C_{17}H_{16}O_6$
M_r = 316.30
Orthorhombic, *Pbcn*
Hall symbol: -P 2n 2ab
a = 5.4307 (19) Å
b = 8.131 (3) Å
c = 36.149 (10) Å
V = 1596.3 (9) Å^3
Z = 4
F(000) = 664
Block
D_x = 1.316 Mg m^{-3}
Melting point: 465 K
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 1405 reflections
θ = 3.4–25.0°
μ = 0.10 mm^{-1}
T = 296 K
Block, colourless
0.18 × 0.16 × 0.14 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 2.09 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)
T_{min} = 0.982, T_{max} = 0.986
6486 measured reflections
1405 independent reflections
1008 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 25.0°, θ_{min} = 3.4°
h = −6→6
k = −9→8
l = −42→42

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.162
S = 1.03
1405 reflections
121 parameters
6 restraints
2 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1061P)^2 + 0.0364P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

Extinction correction: *SHELXL2014*/7 (Sheldrick 2014, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.019 (4)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O2	−0.0641 (3)	0.84493 (15)	0.31318 (4)	0.0610 (5)	
O1	0.0400 (3)	0.60669 (15)	0.45593 (4)	0.0591 (5)	
C8	0.0313 (6)	0.7692 (3)	0.28435 (6)	0.0854 (9)	
C1	0.2471 (4)	0.6502 (3)	0.47762 (6)	0.0697 (7)	
H1B	0.3947	0.6145	0.4654	0.105*	
H1A	0.2353	0.5983	0.5014	0.105*	
H1C	0.2515	0.7675	0.4807	0.105*	
C9	0.0000	0.8706 (5)	0.2500	0.0964 (15)	
C2	0.0277 (3)	0.66889 (19)	0.42034 (5)	0.0454 (5)	
C5	−0.0275 (3)	0.7785 (2)	0.34879 (5)	0.0468 (5)	
C4	0.1692 (3)	0.8324 (2)	0.36942 (5)	0.0511 (6)	
H4	0.2824	0.9052	0.3592	0.061*	
C7	−0.1689 (3)	0.6158 (2)	0.39913 (6)	0.0523 (5)	
H7	−0.2829	0.5430	0.4091	0.063*	
C6	−0.1967 (3)	0.6706 (2)	0.36313 (6)	0.0525 (6)	
H6	−0.3286	0.6348	0.3488	0.063*	
C3	0.1984 (3)	0.7778 (2)	0.40568 (5)	0.0499 (6)	
H3	0.3306	0.8138	0.4199	0.060*	
O3B	0.051 (3)	0.6253 (9)	0.2836 (3)	0.080 (4)	0.37 (3)
O3A	0.194 (5)	0.661 (2)	0.2893 (2)	0.152 (6)	0.63 (3)
H9A	−0.139 (6)	0.936 (4)	0.2521 (11)	0.150 (13)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0850 (11)	0.0534 (8)	0.0445 (10)	0.0136 (6)	−0.0043 (7)	0.0011 (6)
O1	0.0721 (10)	0.0615 (9)	0.0438 (9)	−0.0056 (6)	0.0010 (6)	0.0048 (6)
C8	0.147 (3)	0.0634 (16)	0.0460 (15)	0.0256 (15)	0.0084 (14)	−0.0017 (11)
C1	0.0823 (16)	0.0756 (14)	0.0514 (14)	0.0012 (11)	−0.0106 (12)	0.0041 (10)
C9	0.183 (5)	0.062 (2)	0.045 (2)	0.000	−0.010 (2)	0.000
C2	0.0547 (12)	0.0396 (9)	0.0418 (12)	0.0040 (7)	0.0041 (8)	−0.0033 (7)
C5	0.0602 (12)	0.0424 (10)	0.0380 (11)	0.0083 (8)	−0.0005 (8)	−0.0023 (7)
C4	0.0547 (12)	0.0448 (10)	0.0538 (13)	−0.0037 (7)	0.0023 (9)	0.0015 (8)
C7	0.0523 (12)	0.0483 (10)	0.0562 (13)	−0.0066 (8)	0.0061 (9)	−0.0019 (8)

C6	0.0509 (12)	0.0514 (11)	0.0553 (13)	−0.0006 (8)	−0.0072 (9)	−0.0071 (9)
C3	0.0529 (12)	0.0471 (10)	0.0497 (12)	−0.0045 (8)	−0.0054 (8)	−0.0016 (8)
O3B	0.140 (8)	0.043 (5)	0.057 (4)	0.026 (4)	0.001 (4)	−0.006 (2)
O3A	0.244 (14)	0.158 (7)	0.053 (3)	0.132 (9)	0.017 (5)	0.002 (3)

Geometric parameters (Å, º)

O2—C8	1.316 (3)	C9—H9A	0.92 (3)
O2—C5	1.410 (2)	C2—C7	1.383 (3)
O1—C2	1.384 (2)	C2—C3	1.387 (3)
O1—C1	1.416 (3)	C5—C6	1.372 (3)
C8—O3B	1.176 (9)	C5—C4	1.375 (3)
C8—O3A	1.262 (10)	C4—C3	1.393 (3)
C8—C9	1.500 (3)	C4—H4	0.9300
C1—H1B	0.9600	C7—C6	1.384 (3)
C1—H1A	0.9600	C7—H7	0.9300
C1—H1C	0.9600	C6—H6	0.9300
C9—C8^{i}	1.500 (3)	C3—H3	0.9300
C8—O2—C5	119.22 (16)	O1—C2—C3	123.81 (16)
C2—O1—C1	117.48 (15)	C7—C2—C3	120.20 (18)
O3B—C8—O2	121.3 (5)	C6—C5—C4	121.32 (17)
O3A—C8—O2	119.4 (4)	C6—C5—O2	119.70 (16)
O3B—C8—C9	122.6 (6)	C4—C5—O2	118.82 (16)
O3A—C8—C9	125.5 (5)	C5—C4—C3	119.79 (17)
O2—C8—C9	110.7 (2)	C5—C4—H4	120.1
O1—C1—H1B	109.5	C3—C4—H4	120.1
O1—C1—H1A	109.5	C2—C7—C6	120.35 (17)
H1B—C1—H1A	109.5	C2—C7—H7	119.8
O1—C1—H1C	109.5	C6—C7—H7	119.8
H1B—C1—H1C	109.5	C5—C6—C7	119.19 (17)
H1A—C1—H1C	109.5	C5—C6—H6	120.4
C8—C9—C8^{i}	113.4 (3)	C7—C6—H6	120.4
C8—C9—H9A	110 (2)	C2—C3—C4	119.15 (17)
C8^{i}—C9—H9A	107 (2)	C2—C3—H3	120.4
O1—C2—C7	116.00 (16)	C4—C3—H3	120.4
C5—O2—C8—O3B	32.7 (11)	C6—C5—C4—C3	−0.3 (3)
C5—O2—C8—O3A	−14.9 (17)	O2—C5—C4—C3	175.19 (14)
C5—O2—C8—C9	−172.58 (17)	O1—C2—C7—C6	−179.78 (15)
O3B—C8—C9—C8^{i}	6.5 (10)	C3—C2—C7—C6	0.1 (3)
O3A—C8—C9—C8^{i}	56.1 (17)	C4—C5—C6—C7	0.3 (3)
O2—C8—C9—C8^{i}	−147.9 (3)	O2—C5—C6—C7	−175.16 (15)
C1—O1—C2—C7	176.14 (16)	C2—C7—C6—C5	−0.2 (3)
C1—O1—C2—C3	−3.8 (3)	O1—C2—C3—C4	179.77 (16)

C8—O2—C5—C6	−91.6 (2)	C7—C2—C3—C4	−0.1 (3)
C8—O2—C5—C4	92.8 (2)	C5—C4—C3—C2	0.2 (3)

Symmetry code: (i) −*x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*A*···O3*A*^{ii}	0.92 (3)	2.53 (3)	3.216 (6)	131 (3)
C4—H4···*Cg*1^{iii}	0.93	2.99	3.6957	134
C7—H7···*Cg*1^{iv}	0.93	2.99	3.6980	134

Symmetry codes: (ii) *x*−1/2, *y*+1/2, −*z*+1/2; (iii) −*x*+1/2, *y*−1/2, *z*; (iv) −*x*−1/2, *y*−3/2, *z*.