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Dimethyl 2-[(acridin-9-yl)methylidene]-malonate

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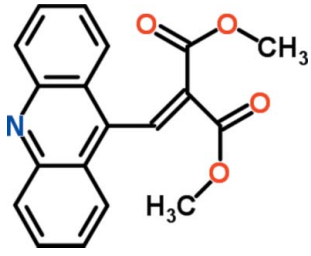
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.002 Å; R factor = 0.052; wR factor = 0.148; data-to-parameter ratio = 16.6.

In the title compound, $C_{19}H_{15}NO_4$, the acridine system is essentially planar (r.m.s. deviation = 0.015 Å). The crystal packing exhibits π–π interactions between pairs of centrosymmetric molecules, one of them between the central heterocyclic rings and others between the outer benzene rings of the acridine systems, with centroid–centroid distances of 3.692 (1) and 3.754 (1) Å, respectively. These pairs are further linked by additional π–π interactions along the a-axis direction through one of the two outer benzene ring of neighboring molecules, with a centroid–centroid distance of 3.642 (2) Å.

Related literature

For background to acridines, see: Kumar *et al.* (2012). For the biological activity of acridine derivatives, see: Pigatto *et al.* (2011); Das *et al.* (2011); Kumar *et al.* (2012). For the synthesis of acridines, see: Tomar *et al.* (2010). For related structures, see: Buckleton & Waters (1984).



Experimental

Crystal data

$C_{19}H_{15}NO_4$
M_r = 321.32
Triclinic, $P\overline{1}$
a = 8.3022 (2) Å
b = 9.0208 (3) Å
c = 12.0334 (4) Å
α = 96.468 (2)°
β = 93.652 (2)°
γ = 117.422 (2)°
V = 787.98 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 295 K
0.32 × 0.28 × 0.22 mm

Data collection

Nonius KappaCCD diffractometer
10674 measured reflections
3626 independent reflections
2805 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.148
S = 1.05
3626 reflections
218 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LR2094).

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supporting information

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Dimethyl 2-[(acridin-9-yl)methylidene]malonate

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S1. Comment

The pharmacological uses of acridine derivatives have been well documented (Kumar *et al.* 2012). Amongst these applications can be highlighted: Proflavin an antibacterial agent against many Gram positive bacteria; Bucricaine which is used topically for surface anesthesia (Kumar *et al.* 2012); Quinacrine and 9-aminoacridine that act as antimalarial and disinfectant agents respectively (Das *et al.* 2011); and several antitumor agents as nitracrina, amsacrine and 9-aryl-acridines which are potent topoisomerase inhibitors (Pigatto *et al.* 2011).

In this work, we report the structure of the title compound synthesized by the reaction between acridine-9-carbaldehyde and dimethyl malonate. The mean plane analysis of molecule shows that the acridine ring is essentially planar. The deviation observed is maximum for the C5 [(0.0311 (2) Å].The crystal packing exhibits π- π interactions between pairs of centrosymmetric molecules, one of them between the central heterocyclic rings and others between the side benzene rings of the acridine moieties, with centroid-centroid distances of 3.692 (1) and 3.754 (1) Årespectively. These pairs are further linked by additional π- π interactions along the *a* axis through one of the two side benzene ring of neighboring molecules, with centroid-centroid distance of 3.642 (2) Å.

S2. Experimental

In a Dean-Stark apparatus, acridine-9-carbaldehyde (0.1 mmol), dimethyl malonate (0.1 mmol) and morpholine (0.01 mmol) were refluxed in toluene (10 ml). The reaction mixture was refluxed at 383 K for 24 h, and the solvent was evaporated under reduced pressure. The title compound was purified by flash chromatography on silica gel (230–400 mesh) Merck (Germany), eluting with n-hexane/ethyl acetate (9.5:0.5) to give analytically pure yellow crystals of 2-acridin-9-yl-methylene-malonic acid dimethyl ester; yield 33%, *M*.p. 405–407 K. Crystals suitable for suitable for single-crystal X-ray diffraction were grown by slow evaporation at 289 K of a solution of the pure title compound in absolute ethanol.

FTIR (KBr, cm^{-1}) Umax: 2954, 2924, 1730, 1628, 1435, 1266, 1232, 1076, 785, 749. NMR ^{1}H (300 MHz, DMSO-d_6) δ 3.15 (s, 3H), 3.92 (s, 3H), 7.65 (m, 2H), 7.89 (m, 2H), 7.99 (d, 2H,,J = 8.6 Hz), 8.20 (d, 2H, J = 8.6 Hz), 8.70 (s, 1H). HRMS calcd for $C_{19}H_{15}NO_4$ = 321.1001, found = 322.0617.

S3. Refinement

All H-atoms were included in the refinement at calculated positions [C—H = 0.93 Å (aromatic) and 0.96 Å (methyl), with U_{iso}(H) = 1.2Ueq(aromatic C) or 1.5Ueq(methyl C)],also using a riding-model approximation. The maximum and minimum residual electron density peaks were located 0.16 and 0.77 Å, from the C9 and H14 atoms respectively.

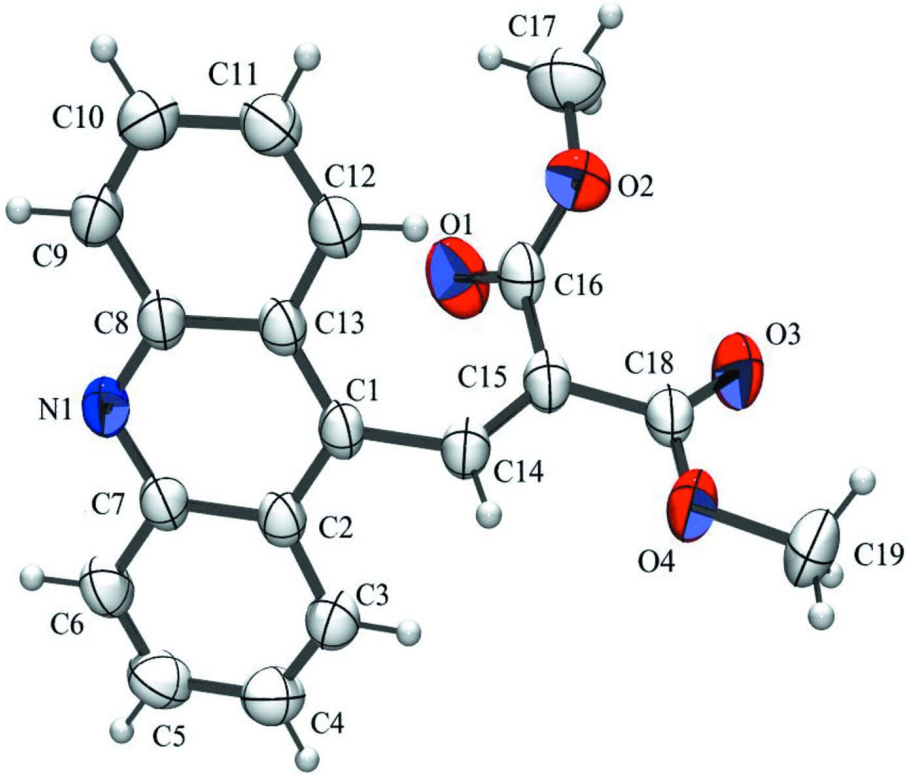

Figure 1

The molecular structure of the title compound. with the ellipsoids drawn at the 50% probability level.

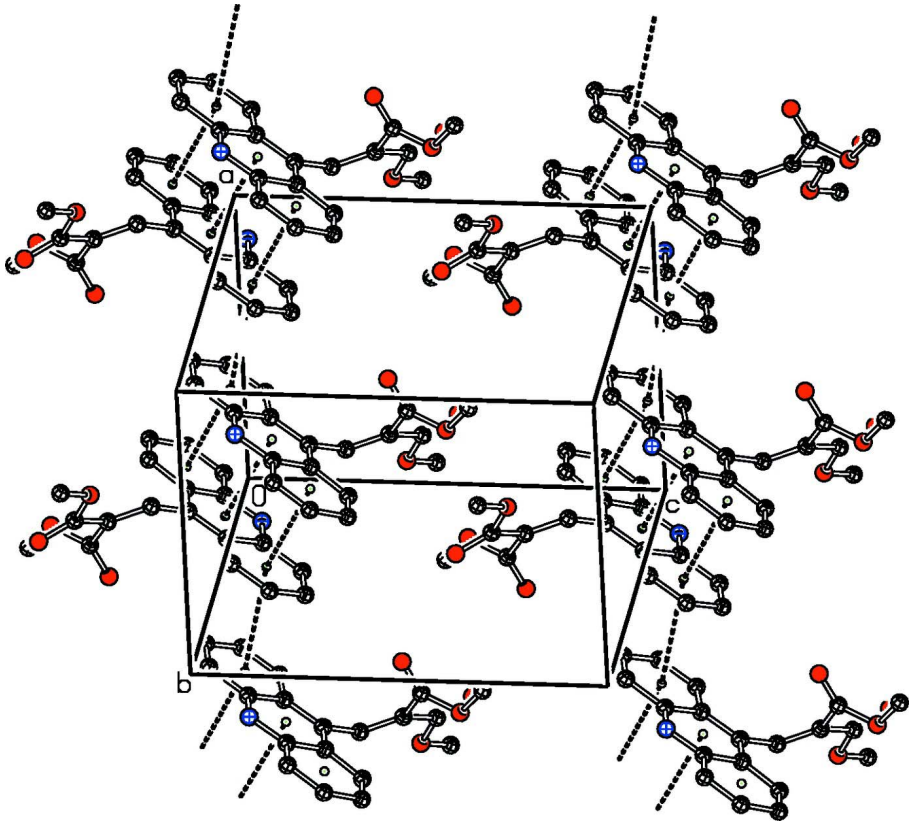

Figure 2

A partial view of the packing showing the π - π interactions.

Dimethyl 2-[(acridin-9-yl)methylidene]malonate

Crystal data

$C_{19}H_{15}NO_4$
M_r = 321.32
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.3022 (2) Å
b = 9.0208 (3) Å
c = 12.0334 (4) Å
α = 96.468 (2)°
β = 93.652 (2)°
γ = 117.422 (2)°
V = 787.98 (4) Å^3
Z = 2
$F(000)$ = 336
D_x = 1.354 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6418 reflections
θ = 2.5–27.5°
μ = 0.10 mm^{-1}
T = 295 K
Prism, yellow
0.32 × 0.28 × 0.22 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: Enraf Nonius FR590
Horizonally mounted graphite crystal monochromator
Detector resolution: 9 pixels mm^{-1}
CCD rotation images,thick slices scans
10674 measured reflections
3626 independent reflections
2805 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 27.5°, θ_{min} = 2.6°
h = −10→10
k = −11→10
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.148$
$S = 1.05$
3626 reflections
218 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
$w = 1/[\sigma^2(F_o^2) + (0.0817P)^2 + 0.1056P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.168 (19)

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.

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}
C2	0.18856 (17)	−0.04107 (16)	0.05238 (10)	0.0416 (3)
C8	0.27051 (18)	0.29435 (17)	0.10755 (11)	0.0439 (3)
C1	0.12960 (17)	0.00751 (16)	0.15015 (10)	0.0409 (3)
C16	0.25132 (19)	−0.00447 (18)	0.38809 (12)	0.0475 (3)
N1	0.32779 (16)	0.24918 (14)	0.01345 (9)	0.0477 (3)
C14	0.02296 (18)	−0.12607 (17)	0.21649 (11)	0.0455 (3)
H14	−0.0906	−0.2111	0.1815	0.055*
O4	−0.19557 (15)	−0.38893 (13)	0.31911 (9)	0.0630 (3)
C13	0.16978 (17)	0.17719 (16)	0.17992 (10)	0.0412 (3)
C12	0.11370 (19)	0.24024 (18)	0.27615 (11)	0.0484 (3)
H12	0.0464	0.1665	0.3236	0.058*
C11	0.1572 (2)	0.4058 (2)	0.29913 (12)	0.0544 (4)
H11	0.1202	0.4443	0.3625	0.065*
C6	0.3548 (2)	0.0411 (2)	−0.11100 (12)	0.0549 (4)
H6	0.4194	0.1228	−0.1546	0.066*
C9	0.3139 (2)	0.46746 (18)	0.13512 (13)	0.0538 (4)
H9	0.3808	0.5443	0.0892	0.065*
O2	0.22592 (15)	0.05138 (14)	0.48843 (9)	0.0593 (3)
O1	0.39648 (15)	0.04600 (18)	0.35414 (10)	0.0745 (4)
O3	0.02856 (18)	−0.31220 (15)	0.46082 (10)	0.0716 (4)
C7	0.28933 (18)	0.08723 (17)	−0.01311 (11)	0.0445 (3)
C18	−0.0314 (2)	−0.28576 (17)	0.37642 (11)	0.0488 (3)
C5	0.3247 (2)	−0.1193 (2)	−0.14145 (14)	0.0618 (4)

H5	0.3696	−0.1466	−0.2051	0.074*
C3	0.1592 (2)	−0.20857 (18)	0.01646 (12)	0.0508 (3)
H3	0.0939	−0.2935	0.0577	0.061*
C15	0.07425 (18)	−0.13590 (17)	0.32134 (11)	0.0452 (3)
C10	0.2585 (2)	0.52130 (19)	0.22792 (13)	0.0578 (4)
H10	0.2871	0.6345	0.2449	0.069*
C4	0.2252 (2)	−0.2462 (2)	−0.07701 (14)	0.0588 (4)
H4	0.2048	−0.3563	−0.0989	0.071*
C19	−0.3052 (3)	−0.5404 (2)	0.36533 (18)	0.0765 (5)
H19A	−0.4202	−0.6062	0.3179	0.115*
H19B	−0.3267	−0.5095	0.4398	0.115*
H19C	−0.2415	−0.6059	0.3690	0.115*
C17	0.3884 (3)	0.1685 (3)	0.56385 (16)	0.0767 (5)
H17A	0.3545	0.2006	0.6338	0.115*
H17B	0.4557	0.2672	0.5302	0.115*
H17C	0.4634	0.1156	0.5779	0.115*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.0385 (6)	0.0446 (7)	0.0367 (6)	0.0149 (5)	0.0014 (5)	0.0111 (5)
C8	0.0422 (7)	0.0438 (7)	0.0379 (6)	0.0126 (5)	0.0030 (5)	0.0124 (5)
C1	0.0387 (6)	0.0446 (7)	0.0350 (6)	0.0143 (5)	0.0027 (5)	0.0143 (5)
C16	0.0493 (7)	0.0517 (7)	0.0466 (7)	0.0249 (6)	0.0081 (6)	0.0219 (6)
N1	0.0484 (6)	0.0451 (6)	0.0397 (6)	0.0120 (5)	0.0080 (5)	0.0136 (5)
C14	0.0465 (7)	0.0429 (7)	0.0428 (7)	0.0157 (5)	0.0075 (5)	0.0136 (5)
O4	0.0636 (7)	0.0495 (6)	0.0614 (7)	0.0110 (5)	0.0127 (5)	0.0236 (5)
C13	0.0395 (6)	0.0448 (7)	0.0348 (6)	0.0153 (5)	0.0023 (5)	0.0117 (5)
C12	0.0506 (7)	0.0535 (8)	0.0411 (7)	0.0230 (6)	0.0081 (6)	0.0134 (6)
C11	0.0619 (9)	0.0575 (9)	0.0440 (7)	0.0291 (7)	0.0051 (6)	0.0058 (6)
C6	0.0510 (8)	0.0602 (9)	0.0419 (7)	0.0153 (6)	0.0115 (6)	0.0105 (6)
C9	0.0574 (8)	0.0425 (7)	0.0497 (8)	0.0127 (6)	0.0043 (6)	0.0139 (6)
O2	0.0593 (6)	0.0619 (7)	0.0536 (6)	0.0279 (5)	0.0027 (5)	0.0030 (5)
O1	0.0492 (6)	0.1023 (10)	0.0627 (7)	0.0255 (6)	0.0115 (5)	0.0222 (6)
O3	0.0931 (9)	0.0618 (7)	0.0579 (7)	0.0302 (6)	0.0085 (6)	0.0315 (5)
C7	0.0399 (6)	0.0491 (7)	0.0366 (6)	0.0137 (5)	0.0038 (5)	0.0109 (5)
C18	0.0622 (8)	0.0441 (7)	0.0440 (7)	0.0252 (6)	0.0168 (6)	0.0155 (6)
C5	0.0587 (9)	0.0693 (10)	0.0482 (8)	0.0241 (8)	0.0113 (7)	−0.0008 (7)
C3	0.0500 (8)	0.0477 (7)	0.0493 (8)	0.0180 (6)	0.0048 (6)	0.0107 (6)
C15	0.0502 (7)	0.0455 (7)	0.0425 (7)	0.0220 (6)	0.0119 (6)	0.0165 (5)
C10	0.0661 (9)	0.0442 (8)	0.0545 (8)	0.0204 (7)	0.0005 (7)	0.0048 (6)
C4	0.0603 (9)	0.0542 (8)	0.0561 (9)	0.0246 (7)	0.0041 (7)	0.0001 (7)
C19	0.0826 (12)	0.0459 (9)	0.0854 (13)	0.0120 (8)	0.0267 (10)	0.0254 (8)
C17	0.0776 (12)	0.0741 (11)	0.0667 (11)	0.0323 (9)	−0.0107 (9)	−0.0063 (9)

Geometric parameters (Å, º)

C2—C1	1.4037 (18)	C6—C5	1.351 (2)
C2—C3	1.425 (2)	C6—C7	1.427 (2)
C2—C7	1.4345 (17)	C6—H6	0.9300
C8—N1	1.3482 (18)	C9—C10	1.358 (2)
C8—C9	1.424 (2)	C9—H9	0.9300
C8—C13	1.4356 (17)	O2—C17	1.441 (2)
C1—C13	1.4049 (19)	O3—C18	1.1981 (17)
C1—C14	1.4823 (16)	C18—C15	1.4899 (18)
C16—O1	1.1940 (17)	C5—C4	1.415 (2)
C16—O2	1.3226 (18)	C5—H5	0.9300
C16—C15	1.497 (2)	C3—C4	1.358 (2)
N1—C7	1.3381 (18)	C3—H3	0.9300
C14—C15	1.3315 (18)	C10—H10	0.9300
C14—H14	0.9300	C4—H4	0.9300
O4—C18	1.3293 (19)	C19—H19A	0.9600
O4—C19	1.4474 (18)	C19—H19B	0.9600
C13—C12	1.4301 (19)	C19—H19C	0.9600
C12—C11	1.355 (2)	C17—H17A	0.9600
C12—H12	0.9300	C17—H17B	0.9600
C11—C10	1.419 (2)	C17—H17C	0.9600
C11—H11	0.9300		
C1—C2—C3	123.94 (12)	N1—C7—C6	117.91 (12)
C1—C2—C7	117.80 (12)	N1—C7—C2	123.52 (12)
C3—C2—C7	118.24 (12)	C6—C7—C2	118.55 (13)
N1—C8—C9	117.44 (12)	O3—C18—O4	124.20 (13)
N1—C8—C13	123.21 (12)	O3—C18—C15	123.33 (14)
C9—C8—C13	119.35 (12)	O4—C18—C15	112.42 (12)
C2—C1—C13	119.54 (11)	C6—C5—C4	120.40 (14)
C2—C1—C14	117.57 (12)	C6—C5—H5	119.8
C13—C1—C14	122.87 (12)	C4—C5—H5	119.8
O1—C16—O2	124.32 (15)	C4—C3—C2	121.06 (14)
O1—C16—C15	124.28 (14)	C4—C3—H3	119.5
O2—C16—C15	111.38 (11)	C2—C3—H3	119.5
C7—N1—C8	118.15 (11)	C14—C15—C18	122.41 (13)
C15—C14—C1	126.22 (12)	C14—C15—C16	122.17 (11)
C15—C14—H14	116.9	C18—C15—C16	115.18 (11)
C1—C14—H14	116.9	C9—C10—C11	120.38 (14)
C18—O4—C19	115.93 (13)	C9—C10—H10	119.8
C1—C13—C12	124.38 (12)	C11—C10—H10	119.8
C1—C13—C8	117.77 (12)	C3—C4—C5	120.61 (15)
C12—C13—C8	117.83 (12)	C3—C4—H4	119.7
C11—C12—C13	120.94 (13)	C5—C4—H4	119.7
C11—C12—H12	119.5	O4—C19—H19A	109.5
C13—C12—H12	119.5	O4—C19—H19B	109.5
C12—C11—C10	120.94 (14)	H19A—C19—H19B	109.5

C12—C11—H11	119.5	O4—C19—H19C	109.5
C10—C11—H11	119.5	H19A—C19—H19C	109.5
C5—C6—C7	121.14 (14)	H19B—C19—H19C	109.5
C5—C6—H6	119.4	O2—C17—H17A	109.5
C7—C6—H6	119.4	O2—C17—H17B	109.5
C10—C9—C8	120.55 (13)	H17A—C17—H17B	109.5
C10—C9—H9	119.7	O2—C17—H17C	109.5
C8—C9—H9	119.7	H17A—C17—H17C	109.5
C16—O2—C17	116.36 (13)	H17B—C17—H17C	109.5