



Crystal structure of 5-[4-(diethylamino)benzylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione

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Received 17 September 2015

Accepted 21 September 2015

Edited by D.-J. Xu, Zhejiang University (Yuquan Campus), China

Keywords: crystal structure; arylidene Meldrum's acid; 5-arylmethylene-2,2-dimethyl-1,3-dioxane-4,6-dione; organic synthesis; intramolecular hydrogen bonding

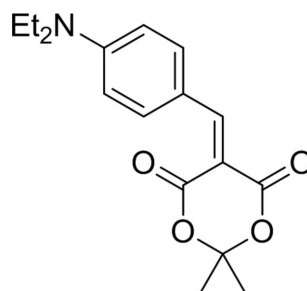
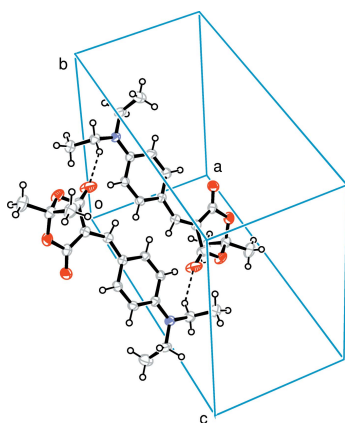
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The title compound, C₁₇H₂₁NO₄, consists of substituted Meldrum's acid with a [4-(diethylamino)phenyl]methylidene fragment attached to the fifth position. The heterocycle assumes a distorted boat conformation. The planar part of heterocycle is almost coplanar with the benzene ring due to the presence of a long conjugated system in the molecule. This leads to the formation of C—H···O-type intramolecular contacts. As a result of the absence of hydrogen-bond donors in the structure, the crystal packing is controlled by van der Waals forces and weak C—H···O interactions, which associate the molecules into inversion dimers.

1. Chemical context

Arylidene Meldrum's acids (5-arylmethylidene-2,2-dimethyl-1,3-dioxane-4,6-diones) are attractive building blocks in organic chemistry: these compounds are used for the synthesis of different heterocycles. Recent examples include: pyrazolidinones (Pair *et al.*, 2014), lactames (Zhang *et al.*, 2013), carbocycles (*e.g.* Trost & Maruniak, 2013) and aliphatic compounds (*e.g.* Mohite & Bhat, 2013). Arylidene Meldrum's acids can be easily converted to arylmethyl Meldrum's acids [for a description of a typical procedure, see Mierina *et al.* (2015)], which serve as starting compounds for the synthesis of various valuable compounds [for a mini-review, see Mierina (2014)]. Apart from their wide application in syntheses, these derivatives of Meldrum's acid have been studied as platelet aggregation inhibitors (El Maatougui *et al.*, 2012), antimalarial agents and anti-oxidants (Sandhu *et al.*, 2010) and photostable UV-filters for cosmetic applications (Habeck & Krause, 1999).



2. Structural commentary

The title compound, C₁₇H₂₁NO₄, consists of substituted Meldrum's acid with a [4-(diethylamino)phenyl]methylidene fragment attached to fifth position (Fig. 1). The heterocycle assumes a distorted boat conformation. Atoms C2 and C5

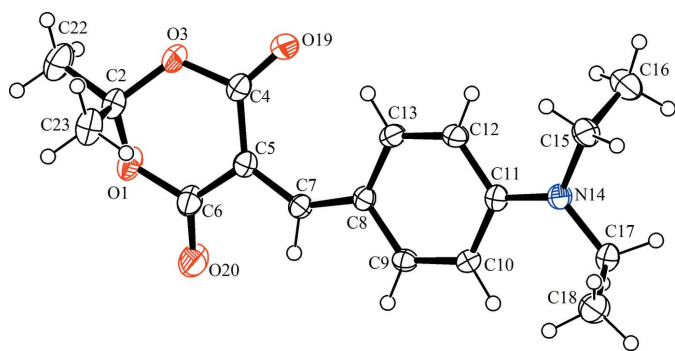


Figure 1
The molecular structure the title compound, showing 50% probability displacement ellipsoids and the atomic numbering

deviate from the least-squares plane [maximum deviations ± 0.013 (1) Å] calculated for the other four atoms of the heterocycle by 0.549 (3) and 0.154 (3) Å, respectively. The planar part of heterocycle is nearly coplanar with the benzene ring [dihedral angle = 8.05 (10)°] due to the presence of a long conjugated system in the molecule. This leads to the formation of C—H...O-type intramolecular contacts (Table 1).

π - π stacking interactions are also observed between conjugated systems of the molecules. The distance between the corresponding least-square planes is 3.54 (su?) Å.

The crystal structure of the zwitterionic form of 5-[4-(diethylamino)benzyl]-2,2-dimethyl-1,3-dioxane-4,6-dione has

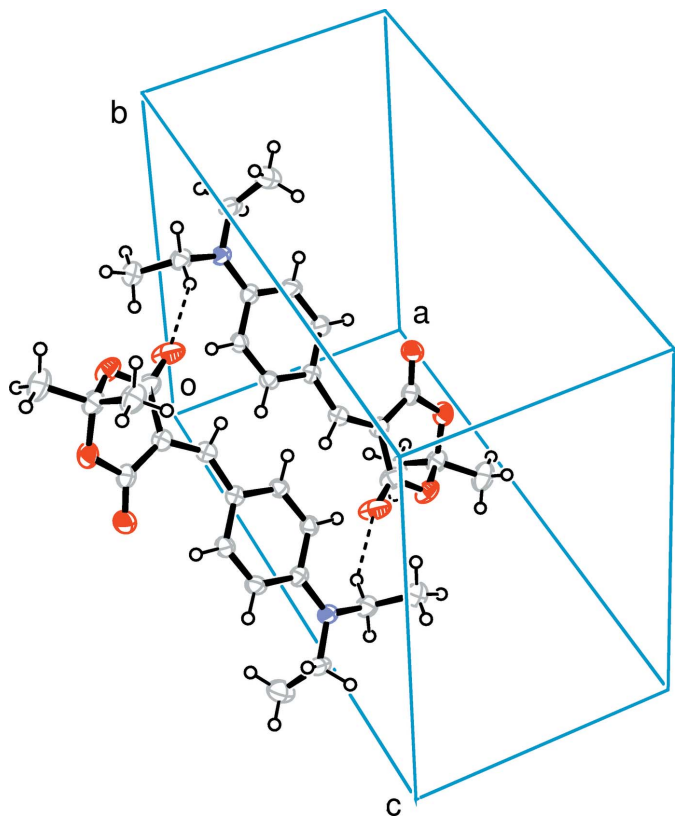


Figure 2
The crystal packing of the title compound, viewed along the *b* axis. Hydrogen bonds are shown as dashed lines (see Table 1 for details).

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C13—H13...O19	0.93	2.13	2.915 (2)	141
C17—H17B...O20 ⁱ	0.97	2.39	3.268 (3)	151

Symmetry code: (i) $-x, -y + 1, -z + 1$.

been already reported (Mierina *et al.*, 2015). The title compound differs from this by the presence of a double bond between atoms C5 and C7.

3. Supramolecular features

Because of the absence of hydrogen-bond donors in the structure, the crystal packing is controlled by van der Waals forces and weak C—H...O interactions, which associate molecules into inversion dimers (Fig. 2, Table 1).

4. Database survey

Several 5-arylidene-2,2-dimethyl-1,3-dioxane-4,6-diones (Huck *et al.*, 1995; Gould *et al.*, 1998; Novoa de Armas *et al.*, 2000; O'Leary *et al.*, 2001; O'Leary & Wallis 2006; Crawford & McNab, 2009; Wilsily & Fillion, 2009; Zeng, 2010*a,b*, 2011*a,b,c*, 2013; Jie, 2012; García-Álvarez *et al.*, 2013; Dey *et al.*, 2015) and their spiro-analogues (Sato *et al.*, 1989; Zeng, 2011*d,e,f*; Zeng *et al.* 2013) have been characterized by X-ray analysis. However, information on the crystal structure of 5-arylmethylidene-2,2-dimethyl-1,3-dioxane-4,6-diones containing an amino functionality on the aromatic ring is not available.

5. Synthesis and crystallization

5-[4-(Diethylamino)phenylmethylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione was obtained from Meldrum's acid (1.00 g, 6.9 mmol) and 4-diethylaminobenzaldehyde (1.27 g, 6.9 mmol) by heating in water (50 ml) at 348 K for 2 h, followed by cooling to room temperature and filtration of the formed precipitate and recrystallization from ethanol (1.62 g, 80%) analogously to the method described previously (Mierina *et al.*, 2015). The spectroscopic and physical data correspond to those in the literature (Mierina *et al.*, 2015). X-ray quality single crystals were obtained by slow evaporation from ethanol.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound H atoms were positioned geometrically and refined as riding on their parent atoms: C—H = 0.93–0.98 Å with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for other H atoms.

Acknowledgements

IM thanks the European Social Fund for a scholarship within the project ‘Support for the implementation of doctoral studies at Riga Technical University’.

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Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₇ H ₂₁ NO ₄
<i>M_r</i>	303.35
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.8662 (2), 11.4601 (3), 18.1517 (6)
β (°)	96.858 (1)
<i>V</i> (Å ³)	1624.62 (8)
<i>Z</i>	4
Radiation type	Mo Kα
μ (mm ⁻¹)	0.09
Crystal size (mm)	0.26 × 0.19 × 0.09
Data collection	
Diffractometer	Nonius KappaCCD
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	6627, 3705, 2183
<i>R</i> _{int}	0.054
(sin θ/λ) _{max} (Å ⁻¹)	0.649
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.055, 0.127, 1.00
No. of reflections	3705
No. of parameters	203
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.18, -0.19

Computer programs: *KappaCCD Server Software* (Nonius, 1997), *HKL DENZO* and *SCALEPACK* (Otwinovski & Minor, 1997), *SIR2011* (Burla *et al.*, 2012), *ORTEP-3 for Windows* (Farrugia, 2012), *SHELXL97* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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supporting information

Acta Cryst. (2015). E71, 1242-1244 [doi:10.1107/S2056989015017673]

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Computing details

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *HKL SCALEPACK* (Otwinovski & Minor, 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinovski & Minor, 1997); program(s) used to solve structure: *SIR2011* (Burla *et al.*, 2012); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

5-[4-(Diethylamino)benzylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione

Crystal data

$C_{17}H_{21}NO_4$

$M_r = 303.35$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.8662$ (2) Å

$b = 11.4601$ (3) Å

$c = 18.1517$ (6) Å

$\beta = 96.858$ (1)°

$V = 1624.62$ (8) Å³

$Z = 4$

$F(000) = 648$

$D_x = 1.240$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 15405 reflections

$\theta = 1.0$ – 27.5 °

$\mu = 0.09$ mm⁻¹

$T = 173$ K

Plate, red

$0.26 \times 0.19 \times 0.09$ mm

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

CCD scans

6627 measured reflections

3705 independent reflections

2183 reflections with $I > 2\sigma(I)$

$R_{int} = 0.054$

$\theta_{max} = 27.5$ °, $\theta_{min} = 2.3$ °

$h = -10$ → 10

$k = -14$ → 13

$l = -23$ → 23

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.055$

$wR(F^2) = 0.127$

$S = 1.00$

3705 reflections

203 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

$$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 0.0774P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.57779 (16)	0.16291 (12)	0.51388 (7)	0.0404 (4)
O19	0.65514 (15)	0.45154 (13)	0.40080 (8)	0.0407 (4)
O3	0.73309 (14)	0.27588 (11)	0.43789 (8)	0.0390 (4)
C8	0.2432 (2)	0.50423 (15)	0.40398 (10)	0.0252 (4)
C10	-0.0015 (2)	0.63516 (16)	0.37433 (10)	0.0266 (4)
H10	-0.1138	0.6545	0.3804	0.032*
O20	0.33160 (19)	0.21986 (13)	0.54631 (9)	0.0584 (5)
N14	0.02179 (17)	0.80169 (13)	0.29384 (9)	0.0307 (4)
C12	0.2607 (2)	0.66959 (17)	0.32158 (11)	0.0317 (5)
H12	0.3242	0.7124	0.2910	0.038*
C9	0.0729 (2)	0.53919 (16)	0.40930 (10)	0.0259 (4)
H9	0.0078	0.4944	0.4382	0.031*
C11	0.0910 (2)	0.70529 (16)	0.32900 (10)	0.0266 (4)
C4	0.6131 (2)	0.36263 (18)	0.42864 (11)	0.0310 (5)
C13	0.3340 (2)	0.57427 (17)	0.35789 (11)	0.0309 (5)
H13	0.4465	0.5550	0.3521	0.037*
C7	0.3028 (2)	0.40397 (16)	0.44569 (10)	0.0275 (4)
H7	0.2188	0.3745	0.4725	0.033*
C15	0.1135 (2)	0.86883 (18)	0.24297 (11)	0.0386 (5)
H15A	0.0311	0.9075	0.2070	0.046*
H15B	0.1801	0.8159	0.2161	0.046*
C5	0.4505 (2)	0.33863 (16)	0.45730 (10)	0.0292 (4)
C6	0.4436 (3)	0.23885 (18)	0.50801 (11)	0.0377 (5)
C2	0.6814 (2)	0.16029 (17)	0.45458 (12)	0.0363 (5)
C18	-0.2946 (2)	0.7988 (2)	0.25955 (13)	0.0473 (6)
H18A	-0.2752	0.8057	0.2085	0.071*
H18B	-0.3967	0.8406	0.2673	0.071*
H18C	-0.3077	0.7180	0.2716	0.071*
C17	-0.1429 (2)	0.84969 (17)	0.30887 (12)	0.0349 (5)
H17A	-0.1415	0.9336	0.3019	0.042*
H17B	-0.1577	0.8348	0.3603	0.042*
C21	0.8427 (3)	0.0962 (2)	0.48418 (14)	0.0551 (6)

H21A	0.8967	0.1357	0.5274	0.083*
H21B	0.9195	0.0943	0.4469	0.083*
H21C	0.8146	0.0179	0.4971	0.083*
C22	0.5872 (3)	0.1025 (2)	0.38720 (12)	0.0460 (6)
H22A	0.5555	0.0247	0.3997	0.069*
H22B	0.6600	0.0994	0.3484	0.069*
H22C	0.4860	0.1465	0.3706	0.069*
C16	0.2319 (3)	0.9596 (2)	0.28194 (14)	0.0533 (6)
H16A	0.1656	1.0166	0.3047	0.080*
H16B	0.2950	0.9971	0.2465	0.080*
H16C	0.3102	0.9224	0.3194	0.080*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0464 (8)	0.0385 (9)	0.0367 (8)	0.0179 (6)	0.0058 (6)	0.0069 (7)
O19	0.0303 (7)	0.0382 (9)	0.0546 (10)	0.0026 (6)	0.0093 (6)	0.0078 (7)
O3	0.0274 (7)	0.0354 (8)	0.0538 (9)	0.0093 (6)	0.0033 (6)	0.0008 (7)
C8	0.0267 (9)	0.0252 (10)	0.0236 (10)	0.0011 (7)	0.0025 (7)	-0.0030 (8)
C10	0.0229 (9)	0.0296 (11)	0.0276 (10)	0.0014 (7)	0.0039 (7)	-0.0005 (9)
O20	0.0643 (10)	0.0510 (11)	0.0666 (11)	0.0218 (8)	0.0352 (9)	0.0286 (9)
N14	0.0289 (8)	0.0294 (9)	0.0341 (10)	0.0030 (7)	0.0042 (7)	0.0077 (7)
C12	0.0287 (9)	0.0320 (12)	0.0357 (12)	-0.0004 (8)	0.0096 (8)	0.0068 (9)
C9	0.0263 (9)	0.0292 (11)	0.0229 (10)	-0.0026 (7)	0.0058 (7)	-0.0004 (8)
C11	0.0291 (9)	0.0257 (10)	0.0241 (10)	0.0014 (8)	-0.0003 (7)	-0.0027 (8)
C4	0.0285 (10)	0.0321 (12)	0.0315 (11)	0.0051 (8)	0.0000 (8)	-0.0043 (10)
C13	0.0243 (9)	0.0335 (11)	0.0359 (12)	0.0028 (8)	0.0077 (8)	0.0029 (9)
C7	0.0292 (9)	0.0266 (11)	0.0279 (11)	0.0007 (8)	0.0082 (7)	-0.0034 (9)
C15	0.0417 (11)	0.0358 (12)	0.0389 (12)	0.0026 (9)	0.0070 (9)	0.0156 (10)
C5	0.0303 (9)	0.0279 (11)	0.0293 (11)	0.0026 (8)	0.0033 (7)	-0.0022 (9)
C6	0.0430 (11)	0.0346 (12)	0.0364 (12)	0.0103 (9)	0.0086 (9)	0.0034 (10)
C2	0.0360 (11)	0.0324 (12)	0.0403 (13)	0.0108 (9)	0.0033 (9)	0.0005 (10)
C18	0.0347 (11)	0.0472 (14)	0.0580 (15)	0.0033 (9)	-0.0029 (10)	0.0115 (12)
C17	0.0342 (10)	0.0286 (11)	0.0421 (12)	0.0069 (8)	0.0057 (8)	0.0037 (10)
C21	0.0446 (12)	0.0548 (16)	0.0634 (17)	0.0220 (11)	-0.0038 (11)	0.0016 (13)
C22	0.0522 (12)	0.0397 (14)	0.0441 (14)	0.0123 (10)	-0.0023 (10)	-0.0057 (11)
C16	0.0518 (13)	0.0419 (14)	0.0670 (17)	-0.0090 (10)	0.0103 (11)	0.0091 (12)

Geometric parameters (Å, °)

O1—C6	1.363 (2)	C7—H7	0.9300
O1—C2	1.426 (2)	C15—C16	1.514 (3)
O19—C4	1.201 (2)	C15—H15A	0.9700
O3—C4	1.368 (2)	C15—H15B	0.9700
O3—C2	1.429 (2)	C5—C6	1.473 (3)
C8—C9	1.413 (2)	C2—C22	1.506 (3)
C8—C13	1.413 (2)	C2—C21	1.509 (3)
C8—C7	1.424 (2)	C18—C17	1.519 (3)

C10—C9	1.366 (2)	C18—H18A	0.9600
C10—C11	1.413 (3)	C18—H18B	0.9600
C10—H10	0.9300	C18—H18C	0.9600
O20—C6	1.205 (2)	C17—H17A	0.9700
N14—C11	1.357 (2)	C17—H17B	0.9700
N14—C15	1.457 (2)	C21—H21A	0.9600
N14—C17	1.463 (2)	C21—H21B	0.9600
C12—C13	1.367 (3)	C21—H21C	0.9600
C12—C11	1.418 (2)	C22—H22A	0.9600
C12—H12	0.9300	C22—H22B	0.9600
C9—H9	0.9300	C22—H22C	0.9600
C4—C5	1.463 (2)	C16—H16A	0.9600
C13—H13	0.9300	C16—H16B	0.9600
C7—C5	1.377 (2)	C16—H16C	0.9600
C6—O1—C2	117.50 (15)	O20—C6—C5	125.78 (18)
C4—O3—C2	119.35 (14)	O1—C6—C5	117.29 (17)
C9—C8—C13	115.46 (16)	O1—C2—O3	110.09 (15)
C9—C8—C7	116.56 (16)	O1—C2—C22	110.63 (16)
C13—C8—C7	127.97 (16)	O3—C2—C22	111.13 (17)
C9—C10—C11	120.46 (16)	O1—C2—C21	105.88 (17)
C9—C10—H10	119.8	O3—C2—C21	106.15 (16)
C11—C10—H10	119.8	C22—C2—C21	112.74 (18)
C11—N14—C15	121.78 (15)	C17—C18—H18A	109.5
C11—N14—C17	122.20 (15)	C17—C18—H18B	109.5
C15—N14—C17	115.86 (15)	H18A—C18—H18B	109.5
C13—C12—C11	122.18 (17)	C17—C18—H18C	109.5
C13—C12—H12	118.9	H18A—C18—H18C	109.5
C11—C12—H12	118.9	H18B—C18—H18C	109.5
C10—C9—C8	123.61 (16)	N14—C17—C18	113.34 (17)
C10—C9—H9	118.2	N14—C17—H17A	108.9
C8—C9—H9	118.2	C18—C17—H17A	108.9
N14—C11—C10	122.12 (16)	N14—C17—H17B	108.9
N14—C11—C12	121.31 (16)	C18—C17—H17B	108.9
C10—C11—C12	116.57 (16)	H17A—C17—H17B	107.7
O19—C4—O3	116.57 (16)	C2—C21—H21A	109.5
O19—C4—C5	127.27 (17)	C2—C21—H21B	109.5
O3—C4—C5	116.09 (17)	H21A—C21—H21B	109.5
C12—C13—C8	121.68 (16)	C2—C21—H21C	109.5
C12—C13—H13	119.2	H21A—C21—H21C	109.5
C8—C13—H13	119.2	H21B—C21—H21C	109.5
C5—C7—C8	137.58 (17)	C2—C22—H22A	109.5
C5—C7—H7	111.2	C2—C22—H22B	109.5
C8—C7—H7	111.2	H22A—C22—H22B	109.5
N14—C15—C16	112.95 (18)	C2—C22—H22C	109.5
N14—C15—H15A	109.0	H22A—C22—H22C	109.5
C16—C15—H15A	109.0	H22B—C22—H22C	109.5
N14—C15—H15B	109.0	C15—C16—H16A	109.5

C16—C15—H15B	109.0	C15—C16—H16B	109.5
H15A—C15—H15B	107.8	H16A—C16—H16B	109.5
C7—C5—C4	126.92 (18)	C15—C16—H16C	109.5
C7—C5—C6	115.10 (16)	H16A—C16—H16C	109.5
C4—C5—C6	117.86 (16)	H16B—C16—H16C	109.5
O20—C6—O1	116.90 (18)		
C11—C10—C9—C8	0.8 (3)	C8—C7—C5—C4	4.4 (4)
C13—C8—C9—C10	-1.4 (3)	C8—C7—C5—C6	-179.8 (2)
C7—C8—C9—C10	178.19 (17)	O19—C4—C5—C7	13.2 (3)
C15—N14—C11—C10	-175.52 (17)	O3—C4—C5—C7	-170.14 (18)
C17—N14—C11—C10	9.3 (3)	O19—C4—C5—C6	-162.49 (19)
C15—N14—C11—C12	4.1 (3)	O3—C4—C5—C6	14.2 (2)
C17—N14—C11—C12	-171.03 (17)	C2—O1—C6—O20	160.50 (19)
C9—C10—C11—N14	-179.51 (17)	C2—O1—C6—C5	-21.3 (2)
C9—C10—C11—C12	0.8 (3)	C7—C5—C6—O20	-10.3 (3)
C13—C12—C11—N14	178.48 (18)	C4—C5—C6—O20	166.0 (2)
C13—C12—C11—C10	-1.8 (3)	C7—C5—C6—O1	171.75 (17)
C2—O3—C4—O19	-165.89 (17)	C4—C5—C6—O1	-12.0 (3)
C2—O3—C4—C5	17.1 (2)	C6—O1—C2—O3	50.5 (2)
C11—C12—C13—C8	1.3 (3)	C6—O1—C2—C22	-72.7 (2)
C9—C8—C13—C12	0.4 (3)	C6—O1—C2—C21	164.84 (18)
C7—C8—C13—C12	-179.18 (18)	C4—O3—C2—O1	-48.8 (2)
C9—C8—C7—C5	179.1 (2)	C4—O3—C2—C22	74.2 (2)
C13—C8—C7—C5	-1.4 (4)	C4—O3—C2—C21	-162.94 (17)
C11—N14—C15—C16	-85.9 (2)	C11—N14—C17—C18	-89.7 (2)
C17—N14—C15—C16	89.6 (2)	C15—N14—C17—C18	94.8 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C13—H13...O19	0.93	2.13	2.915 (2)	141
C17—H17B...O20 ⁱ	0.97	2.39	3.268 (3)	151

Symmetry code: (i) -x, -y+1, -z+1.