organic papers

Tetramethyl 2,6-dioxoadamantane-1,3,5,7-tetracarboxylate

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Key indicators

Single-crystal X-ray study
$T = 110$ K
Mean σ(C–C) = 0.001 Å
R factor = 0.042
wR factor = 0.127
Data-to-parameter ratio = 55.6

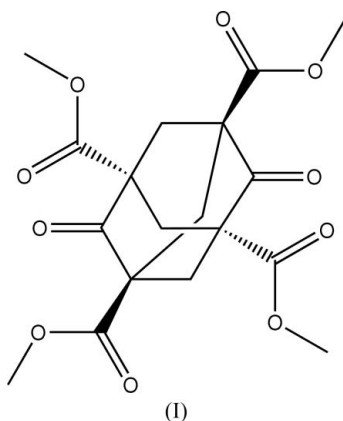For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{18}H_{20}O_{10}$, has crystallographically imposed $\bar{4}$ molecular symmetry. It is a dioxoadamantane with its two C=O bonds lying along the twofold axis. It is symmetrically substituted with four methoxycarbonyl groups, and the ester groups form CH$_2$—C—C=O torsion angles of 26.21 (7)° with the adamantane core.

Comment

Prior to our convenient three-step synthesis (Newkome *et al.*, 1992) of adamantanetetracarboxylic acid, there was only one difficult and lengthy procedure reported (Landa & Kamvcek, 1959), a modification of the original route (Stetter *et al.*, 1956). A key component to understanding the multi-step procedure was the isolation of the title compound, (I).

(I)

The crystal structure of one other 2,6-dioxoadamantane has been reported (Ayres *et al.*, 1994), but it is asymmetric. Ermer (1988) characterized adamantane-1,3,5,7-tetracarboxylic acid [Cambridge Structural Database (CSD, Version 5.27; Allen, 2002) refcode GEJVEW], and he and others have characterized several of its derivatives: CSD refcodes GIMSIE (Ermer & Lindenberg, 1988), KENVUU (Ermer & Lindenberg, 1990), UNIBIC (Fleischman *et al.*, 2003), VOBDOF, VOBFOH and VOBFUN (Ermer & Lindenberg, 1991). Four of these (GEJVEW, VOBFOH, VOBFUN AND KENVUU) display the same crystallographically imposed $\bar{4}$ molecular symmetry as the title compound.

Experimental

Meerwein's ester (tetramethyl 2,6-dioxobicyclo[1.3.3]nonane-1,3,5,7-tetracarboxylate; Meerwein & Schurmann, 1913) (10 g) was treated with CH$_2$Br$_2$ (16 ml) in the presence of sodium methoxide (1.4 g sodium and 18 ml dry MeOH) in a sealed tube according to the

original procedure of Böttger (1937). Heating for 10 h at 403 K produced the colorless crystalline dione tetraester in 31% isolated yield. Recrystallization from 1:2 dioxane–MeOH produced crystals suitable for diffraction analysis (m.p. 559 K, literature m.p. 556.5–557.5 K).

Crystal data

$C_{18}H_{20}O_{10}$	$D_x = 1.494$ Mg m^{-3}
$M_r = 396.34$	Mo $K\alpha$ radiation
Tetragonal, $I4_1/a$	$\mu = 0.12$ mm^{-1}
$a = 12.7635$ (8) Å	$T = 110$ K
$c = 10.8158$ (6) Å	Bicapped square prism, colorless
$V = 1761.97$ (18) Å^3	$0.43 \times 0.40 \times 0.40$ mm
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler	22791 measured reflections
	3672 independent reflections
	2858 reflections with $I > 2\sigma(I)$
ω scans with κ offsets	$R_{int} = 0.024$
Absorption correction: none	$\theta_{max} = 45.3°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.063P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 0.5219P]$
$wR(F^2) = 0.127$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
3672 reflections	$\Delta\rho_{max} = 0.45$ e Å^{-3}
66 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.2144 (9)	C1—C2	1.5310 (6)
O2—C4	1.2092 (7)	C2—C4	1.5274 (6)
O3—C4	1.3329 (6)	C2—C3	1.5432 (6)
O3—C5	1.4489 (7)	C2—C3^i	1.5467 (7)
C4—O3—C5	115.21 (5)	C1—C2—C3^i	109.66 (3)
O1—C1—C2^{ii}	123.79 (3)	C3—C2—C3^i	109.37 (3)
C2^{ii}—C1—C2	112.41 (5)	C2—C3—C2^{iii}	110.25 (4)
C4—C2—C1	109.60 (4)	O2—C4—O3	123.90 (5)
C4—C2—C3	112.76 (4)	O2—C4—C2	123.39 (4)
C1—C2—C3	107.05 (3)	O3—C4—C2	112.71 (4)
C4—C2—C3^i	108.38 (4)		
C3^i—C2—C4—O2	26.21 (7)		

Symmetry codes: (i) $-y + \frac{5}{4}, x + \frac{1}{4}, -z + \frac{5}{4}$; (ii) $-x + 1, -y + \frac{3}{2}, z$; (iii) $y - \frac{1}{4}, -x + \frac{5}{4}, -z + \frac{5}{4}$.

The coordinates are relative to the origin at the $\bar{1}$ position, $(0, \frac{1}{4}, \frac{1}{8})$ from the alternate $\bar{4}$ origin. All H atoms were placed in idealized positions, with C—H = 0.98–0.99 Å, and thereafter treated as riding. A torsional parameter was refined for the methyl group. Isotropic displacement parameters of the H atoms were assigned as $1.2U_{eq}(C)$ or $1.2U_{eq}(methyl\ C)$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:
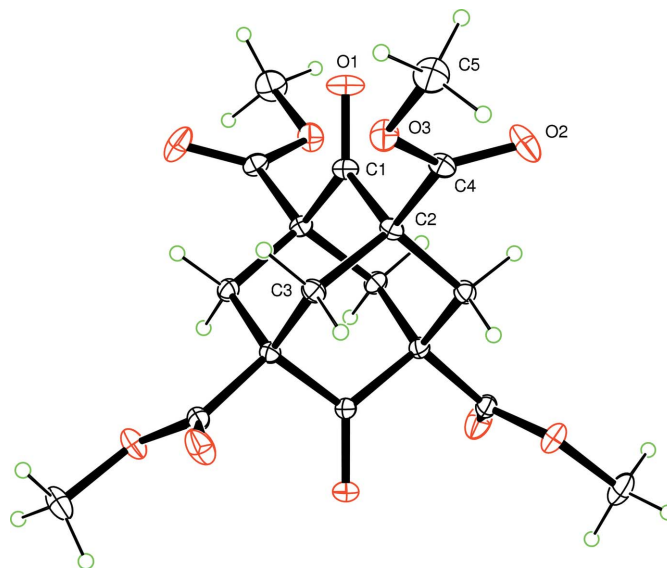

Figure 1
View of (I) (50% probability displacement ellipsoids) with the asymmetric unit labeled. Unlabeled atoms are related by the three symmetry codes given in Table 1.

ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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