2201 measured reflections
2021 independent reflections
1960 observed reflections
[$F > 2\sigma(F)$]

4 standard reflections
monitored every 100 reflections
intensity variation: ±1%

Refinement

Refinement on F
$R = 0.055$
$wR = 0.080$
$S = 1.285$
1828 reflections
264 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\text{max}} = 0.52$

$\Delta\rho_{\text{max}} = 0.38$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.42$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N(1*a*)	0.6867 (3)	0.0556	0.0524 (4)	0.077 (2)
C(1)	0.7384 (5)	0.0255 (6)	0.1416 (5)	0.084 (3)
O(1)	0.8051 (5)	−0.0337 (6)	0.1467 (5)	0.114 (4)
C(2)	0.7134 (5)	0.0698 (6)	0.2402 (5)	0.083 (3)
N(2)	0.6491 (4)	0.1485 (5)	0.2346 (4)	0.079 (3)
C(3)	0.7490 (7)	0.0367 (9)	0.3393 (6)	0.113 (5)
S(3)	0.7047 (2)	0.1049 (4)	0.4274 (1)	0.126 (2)
C(4)	0.6396 (5)	0.1760 (7)	0.3271 (5)	0.083 (3)
C(5)	0.5756 (5)	0.2612 (7)	0.3478 (4)	0.087 (3)
C(6)	0.6202 (6)	0.3621 (7)	0.3296 (6)	0.102 (5)
C(7)	0.7197 (6)	0.369 (1)	0.3979 (8)	0.122 (6)
C(8)	0.555 (1)	0.4466 (8)	0.349 (1)	0.138 (8)
N(2*a*)	0.4859 (4)	0.2465 (6)	0.2753 (4)	0.084 (3)
C(9)	0.4010 (5)	0.2513 (7)	0.3067 (5)	0.091 (4)
O(9)	0.3909 (4)	0.2745 (8)	0.3937 (3)	0.130 (4)
C(10)	0.3164 (5)	0.2357 (6)	0.2212 (4)	0.082 (3)
N(10)	0.3383 (4)	0.1817 (5)	0.1292 (4)	0.078 (3)
C(11)	0.2377 (5)	0.1745 (7)	0.2603 (5)	0.093 (4)
O(11)	0.2344 (3)	0.0852 (5)	0.1933 (3)	0.087 (2)
C(12)	0.1443 (8)	0.223 (1)	0.241 (1)	0.143 (8)
C(13)	0.2910 (4)	0.1023 (6)	0.1238 (4)	0.069 (3)
C(14)	0.2937 (6)	0.0188 (6)	0.0455 (6)	0.093 (4)
C(15)	0.3621 (7)	−0.0667 (8)	0.0830 (7)	0.114 (6)
C(16)	0.316 (1)	−0.138 (1)	0.147 (2)	0.18 (1)
C(17)	0.364 (2)	−0.231 (1)	0.153 (4)	0.31 (3)
C(18)	0.443 (1)	−0.0345 (9)	0.134 (1)	0.15 (1)
O(1)*W*†	1/2	0.1868 (7)	0	0.109 (5)
O(1)Et†	0.452 (1)	0.383 (1)	0.051 (2)	0.17 (1)
C(1)Et†	1/2	0.553 (4)	0	0.29 (4)
C(2)Et†	1/2	0.446 (2)	0	0.51 (7)

† *W* and Et denote water and ethanol molecules, respectively. The occupancy factor of O(1)Et is 0.5.

Table 2. *Selected torsion angles* (°)

Thiazole	
N(1*a*)—C(1)—C(2)—N(2)	−9.2 (6)
C(14)′—N(1*a*)—C(1)—C(2)	178.9 (8)
Valine	
C(9)—N(2*a*)—C(5)—C(4)	132.3 (7)
N(2*a*)—C(5)—C(4)—N(2)	45.7 (5)
N(2*a*)—C(5)—C(6)—C(7)	−173.3 (8)
N(2*a*)—C(5)—C(6)—C(8)	61.1 (7)
Oxazoline	
N(10)—C(10)—C(9)—N(2*a*)	21.9 (6)
C(10)—C(9)—N(2*a*)—C(5)	179.1 (8)
Isoleucine	
C(1)′—N(1*a*)′—C(14)—C(13)	−133.0 (6)
N(1*a*)′—C(14)—C(13)—N(10)	−31.1 (9)
N(1*a*)′—C(14)—C(15)—C(16)	−151 (1)
N(1*a*)′—C(14)—C(15)—C(18)	85 (1)
C(14)—C(15)—C(16)—C(17)	161 (2)

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). The structure refinement by full-matrix least-squares methods was carried out using *SHELX*76 (Sheldrick, 1976). During the last stage of refinement, all H atoms, except those of solvents, were placed at assumed positions and included in the refinement. The y coordinate of N(1*a*) was fixed to define the origin during the refinement. The molecular conformation was drawn using *ORTEP*II (Johnson, 1971).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1088). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dimethyl Cubane-1,4-dicarboxylate

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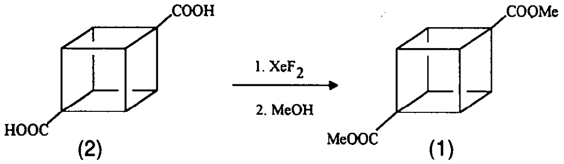
Abstract

In the crystal, dimethyl pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]-octane-1,4-dicarboxylate, $C_{12}H_{12}O_4$, has crystallographic $2/m$ symmetry. The carbonyl group takes an eclipsed orientation with respect to the skeleton bond C1—C3, as well as to the methoxy O2—C5 bond. The ester group is tilted in the direction of the opposite C atom C3″ about its staggered orientation relative to the skele-

ton bonds C1—C2 and C1–C2′. The valence angles within the ester group, C4—O2—C5, O1—C4—C1 and O1—C4—O2, are expanded to 116.9 (2), 126.2 (2) and 123.5 (2)°, respectively. These enlargements cause a narrowing of the bond angle O2—C4—C1 to 110.4 (2)°.

Comment

In the course of our studies of strained polycyclic compounds (Irngartinger & Oeser, 1994), we investigated the crystal and molecular structure of the dimethyl cubane-1,4-dicarboxylate (1) (Eaton & Cole, 1964; Chapman, Key & Toyne, 1970; Luh & Stock, 1972). We obtained the title compound (1), from chloroform, as colourless monoclinic crystals *via* treatment of cubane-1,4-dicarboxylic acid (2) with xenon difluoride followed by solvolysis with methanol.



The dimethyl ester (1) is fixed in the crystal with $2/m$ molecular symmetry; the space group is $C2/m$ with $Z = 2$. The methyl carboxylate groups and the diagonal plane through the cubane skeleton lie on a crystallographic mirror plane.

The carbonyl fragment of the ester group exhibits an eclipsed orientation with respect to the C1—C3 bond of the cube (Schweizer & Dunitz, 1982), as well as to the O2—C5 bond of the ester group (Fig. 1). The repulsive interactions along the 1···4 distances O1···C3 [3.143 (3) Å] and O1···C5 [2.663 (3) Å] generate the enlarged bond angles O1—C4—C1 [126.2 (2)°], O1—C4—O2 [123.5 (2)°] and C4—O2—C5 [116.9 (2)°] (Table 2). The staggered conformation of the ester group relative to the skeleton bonds C1—C2 and C1—C2′ render these bond-angle distortions, and give rise to the compressed bond angle O2—C4—C1 [110.4 (2)°]. This kind of angle distortion is quite usual for carboxylic esters (Kroon & Kanters, 1973; Borthwick, 1980).

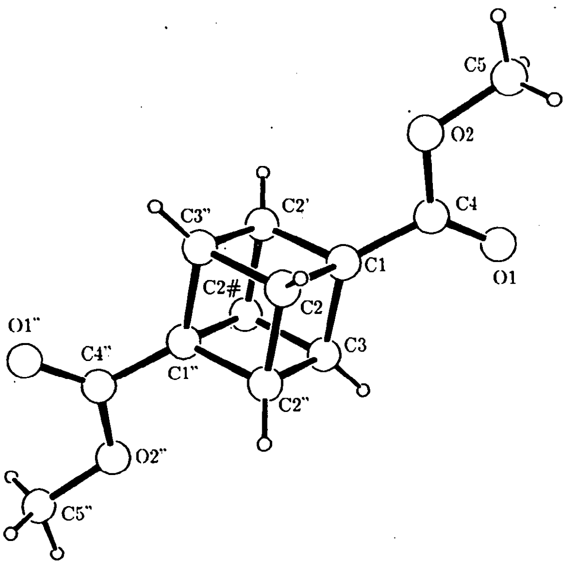


Fig. 1. View of the diester (1) with atomic labelling.

The torsion angles and the bond angles of the skeleton show only very small distortions from cubic symmetry. As a result of the increased *s* character of the exocyclic bonds (Eaton & Cole, 1964; Della, Hine & Patney, 1977) the bond length C1—C4 [1.481 (3) Å] is shortened, as calculated and observed in several cubane derivatives (Schleyer & Bremer, 1989; Gilardi, Maggini & Eaton, 1988; Ermer & Lex, 1987; Moriarty, Khosrowshahi, Miller, Flippen-Andersen & Gilardi, 1989; Ammon & Bashir-Hashemi, 1993). The corresponding averaged bond length in acyclic esters is 1.497 Å (Allen *et al.*, 1987). The C1—C4 bond length is similar to the length of the corresponding bond in the diacid (2) [1.480 (1) Å; Ermer & Lex, 1987]. Thus, the repulsive interactions described above do not cause a bond lengthening but a tilting of the ester group in the direction of C3″ about the staggered orientation [C3—C1—C4 127.3 (2) compared to C2—C1—C4 124.5 (1)°]. The average bond length [1.563 (3) Å] of the cubane skeleton vicinal to the substituent is expanded only slightly compared to the average bond length [1.551 (3) Å] of cubane (Fleischer, 1964).

Experimental

Compound (1) was synthesized by addition of 3 eq. of XeF_2 to a suspension of the diacid (2) in CCl_4 at 301 K under an Ar atmosphere. After stirring for 18 h at this temperature, the insoluble residue was filtered off, dried in vacuum and dissolved in methanol. After stirring for 72 h at room temperature and evaporation of the solvent, the crude diester (1) was isolated and purified by column chromatography on silica gel, eluting with diethyl ether. M.p. 430–433 K (434–435 K; Eaton & Cole, 1964); ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 3.70$ (*s*, 6H), 4.20 p.p.m. (*s*, 6H) [$\delta = 3.70$ p.p.m. (*s*), 4.22 (*s*); Edward, Farrell & Langford, 1976]. Slow crystallization from chloroform afforded single crystals of (1).

Crystal data

$C_{12}H_{12}O_4$
$M_r = 220$
Monoclinic
$C2/m$
$a = 13.580$ (2) Å
$b = 6.437$ (1) Å
$c = 5.895$ (1) Å
$\beta = 92.12$ (1)°
$V = 515.0$ (2) Å^3
$Z = 2$
$D_x = 1.42$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–20°
$\mu = 0.101$ mm^{-1}
$T = 293$ K
Irregular pyramids
0.45 × 0.45 × 0.25 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
698 measured reflections
671 independent reflections
528 observed reflections [$I \geq 2.5\sigma(I)$]

$R_{\rm int} = 0.011$
$\theta_{\rm max} = 28°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 8$
$l = -7 \rightarrow 7$
3 standard reflections
frequency: 60 min
intensity variation: 0.1%

Refinement

Refinement on F
$R = 0.049$
$wR = 0.059$
$S = 2.79$
528 reflections
60 parameters
All H-atom parameters refined

$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\rm max} < 0.01$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.36$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
O1	0.7286 (1)	0	−0.0582 (3)	0.055 (1)
O2	0.7827 (1)	0	0.3044 (2)	0.048 (1)
C1	0.9018 (1)	0	0.0334 (3)	0.038 (1)
C2	0.9769 (1)	0.1710 (3)	0.1187 (2)	0.045 (1)
C3	0.9491 (1)	0	−0.2030 (4)	0.044 (1)
C4	0.7955 (1)	0	0.0807 (3)	0.037 (1)
C5	0.6830 (2)	0	0.3772 (4)	0.058 (1)

Table 2. *Selected geometric parameters* (Å, °)

O1—C4	1.199 (2)	C1—C3	1.556 (3)
O2—C4	1.336 (2)	C1—C4	1.481 (3)
O2—C5	1.436 (3)	C2—C2″	1.555 (2)
C1—C2	1.570 (2)	C2—C3″	1.559 (2)
O1···C3	3.143 (3)	C4···C3″	3.517 (3)
O1···C5	2.663 (3)	O2···C2	3.095 (2)
O1—C4—O2	123.5 (2)	C2—C1—C4	124.5 (1)
O1—C4—C1	126.2 (2)	C2—C1—C2′	89.0 (1)
O2—C4—C1	110.4 (2)	C2—C2″—C3	90.6 (1)
C1—C2—C2″	89.5 (1)	C2—C3″—C2′	89.8 (1)
C1—C2—C3″	90.6 (1)	C3—C1—C4	127.3 (2)
C1—C3—C2″	89.8 (1)	C4—O2—C5	116.9 (2)
C2—C1—C3	90.1 (1)		

The selection of the space group *C2/m* is based on statistics of the reflection intensities. Structure solution was carried out using *MULTAN*11/82 (Main *et al.*, 1982).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SE1048). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*Z*)-2-(2-Methoxyphenoxy)-3-(4-methoxyphenyl)propenoic Acid

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Abstract

The structure of (*Z*)-2-(2-methoxyphenoxy)-3-(4-methoxyphenyl)propenoic acid, $C_{17}H_{16}O_5$, was