Dimethyl dispiro[tricyclo[3.3.1.1^{3,7}]-decane-1,2'-bicyclo[1.1.0]butane-4',1''-tricyclo[3.3.1.1^{3,7}]decane]-1',3'-dicarboxylate, a strain-enhanced bicyclo[1.1.0]butane with a very short intramolecular C—H···H—C contact

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The title molecule, $C_{26}H_{34}O_4$, shows a very short repulsive intramolecular C—H···H—C contact, with an H···H distance of only 1.71 Å. The flap angle φ of the bicyclo[1.1.0]butane group is widened to 131.23 (8)°. Both methylene C atoms show tilt angles of 6.1°. Bond lengths in the fused cyclopropane rings range from 1.501 (1) to 1.542 (1) Å and are influenced by π interactions with the carboxylate substituents.

Comment

The angle φ between the two cyclopropane rings in the title compound, (I), is 131.23 (8)°. This is the largest flap angle observed for a bicyclo[1.1.0]butane derivative. A value of 121.7 (5)° has been observed for the parent bicyclo[1.1.0]-butane by microwave spectroscopy (Cox *et al.*, 1969). The Cambridge Structural Database (Allen & Kennard, 1993) revealed seven different non-bridged bicyclobutane derivatives; five of these have been reviewed by Allen (1984). Two *exo,exo*-dicarboxylic acid derivatives have rather small φ angles of 112.8 and 113.4°. The remaining compounds have φ angles between 121.2 and 128.7°. This large range of φ values shows the bicyclobutane skeleton to be rather flexible. This flexibility has been confirmed by theoretical calculations (Gassman *et al.*, 1983).

(I)
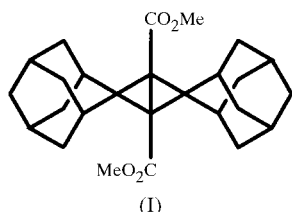
The large φ value in (I) may result from an intramolecular repulsive interaction. There is a very short intramolecular

repulsive C—H···H—C interaction between the two adamantyl groups; the H8···H18 distance is only 1.71 Å. This short distance is not an artefact resulting from the use of constraints on the H-atom parameters in the least-squares refinement. Refining the positional and displacement parameters of H8 and H18 gave an H8···H18 distance of 1.76 (2) Å. This steric interaction results in a deformation of the bond angles at the methylene C7 and C17 atoms. The C8—C7—C4, C8—C7—C3, C18—C17—C3 and C18—C17—C4 angles are about 10° larger than the corresponding C14—C7—C4, C14—C7—C3, C24—C17—C3 and C24—C17—C4 angles. A methylene tilt angle can be defined as the angle between the line bisecting the C_{adam}–$C_{methylene}$–C_{adam} angle and the plane of the attached three-membered ring; it is 6.1° for both C7 and C17. Steric repulsions between *endo* substituents may in part explain the larger φ values in the *endo,endo*-disubstituted bicyclobutanes compared with the *exo,exo*-disubstituted analogues. A short intramolecular H···C contact with a distance of only 2.40 Å is found between the *endo* substituents in a compound with $\varphi = 125.1°$ reported by Padwa *et al.* (1983). Allen (1984) has shown the geometry of the bicyclobutane group to depend also on the nature of the bridgehead substituents. Conjugational effects may result in a lengthening of the central C—C bond and a corresponding increase of the flap angle φ. An empirical relationship derived by Allen (1984) for the central C—C bond length as a function of φ and the bridgehead-substituent valence angle gives a value of 1.517 Å, which is in very good agreement with the observed distance of 1.518 (1) Å for the C3—C4 bond.

The lateral C—C bond lengths in the cyclopropane rings show considerable differences; C4—C7 and C3—C17 are about 0.04 Å shorter than the corresponding C3—C7 and C4—C17 bonds. Conjugation with the π system of the carboxylate groups may be responsible for these differences. The bond-length asymmetry of a cyclopropane ring due to carboxylate substituents has been analysed by Allen (1980). Transfer of electron density from the cyclopropane ring to the
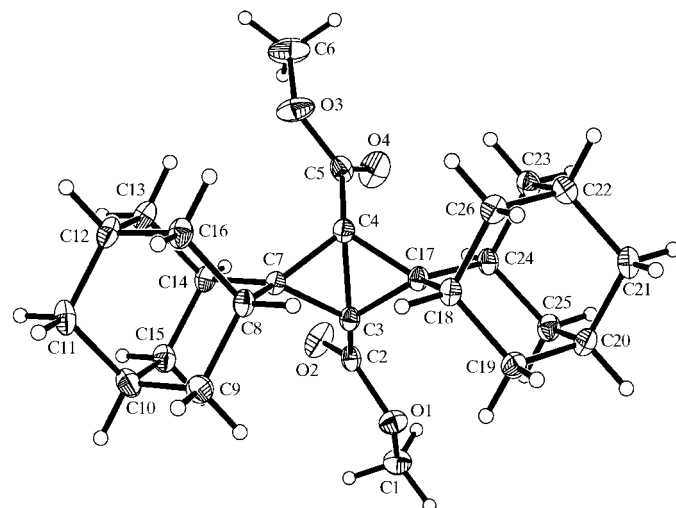

Figure 1
The structure of (I) with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

organic compounds

π system of the carboxylate group may occur for a parallel arrangement of a cyclopropane Walsh $3e'$ orbital with the π orbitals of the carboxylate group (Hoffmann & Davidson, 1971).

Maximum overlap occurs if the torsion angle $X_{n,m}$—C—C=O is 0 or 180° and results in a shortening of the distal C—C bond and a lengthening of the vicinal C—C bonds ($X_{n,m}$ is the midpoint of the distal Cn—Cm bond). A torsion angle $X_{n,m}$—C—C=O near 90° would have no effect on the cyclopropane bond lengths. Values for this torsion angle in the title compound are $X_{4,7}$—C3—C2—O2 = 4.9 (2)°, $X_{4,17}$—C3—C2—O2 = −75.6 (2)°, $X_{3,7}$—C4—C5—O4 = −76.1 (2)° and $X_{3,17}$—C4—C5—O4 = 1.9 (2)°. Using the arguments of Allen (1980), the C4—C7 and C3—C17 bonds should be shorter than the C3—C7 and C4—C17 bonds, in agreement with our observation. The orientations of the carboxylate groups are stabilized by four intramolecular C—H···O interactions (Table 1).
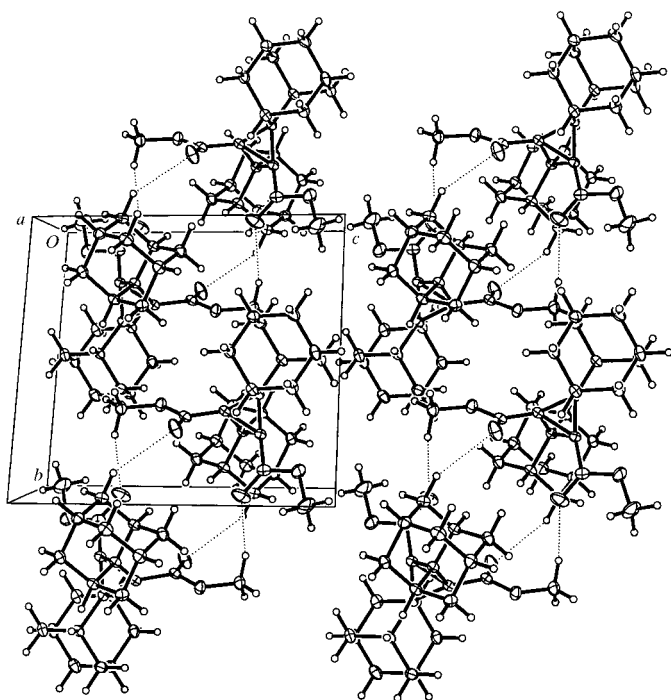

Figure 2
The crystal packing of (I) viewed down **a**. Intermolecular C—H···O interactions are shown as dotted lines.

The molecules crystallize as centrosymmetric dimers connected by weak intermolecular C—H···O interactions between a methoxy C—H bond and a keto group (Table 1 and Fig. 2). A second intermolecular C—H···O interaction within the dimer has an H···O distance of 2.71 Å and consequently is rather weak (Desiraju & Steiner, 1999). There are no other significant intermolecular contacts. The final difference density at the bicyclobutane group shows a good qualitative agreement with the deformation density for this group calculated by Eisenstein & Hirshfeld (1983); deformation density maxima of the lateral bonds are found outside the ring and the deformation density peak of the bridging bond is displaced to the exocyclic side of the molecule.

Experimental

Compound (I) was prepared by a procedure similar to that described by Jefferson & Warkentin (1992) for other compounds. 1-Acetyl-2-adamantylidenehydrazone was prepared by refluxing for 24 h a solution of acetylhydrazine (2.47 g, 33.3 mmol) and adamantanone (5.00 g, 33.3 mmol) in 20 ml ethanol with addition of Na_2SO_4 (4.00 g, 28.2 mmol) and catalytic amounts of acetic acid (0.1 ml, 1.75 mmol). The solvent was removed under vacuum and the residue was recrystallized from ethanol to afford the acetylhydrazone (4.77 g, 23.1 mmol) in 69% yield as a mixture of E and Z isomers. Reaction of the latter acetylhydrazone (4.47 g, 21.7 mmol) and lead tetraacetate (10.0 g, 22.6 mmol) in absolute methanol (94 ml) afforded 5-methoxy-5-methylspiro[Δ^3-1,3,4-oxadiazoline-2,2′-tricyclo[3.3.1.1^{3,7}]-decane] (1.43 g, 6.05 mmol, 28%) as a racemic mixture. A solution of the latter oxadiazoline (1.00 g, 4.23 mmol) and dimethyl acetylenedicarboxylate (1.50 g, 10.6 mmol) in diethyl ether (200 ml) was irradiated with a medium-pressure mercury lamp at room temperature for 11 h. After the volatiles had been removed *in vacuo*, column chromatography (silica gel, hexane/ethyl acetate = 30:1) provided 180 mg (20%) of (I). Single crystals were obtained by slow evaporation of a solution in pentane/dichloromethane at 273 K.

Crystal data

$C_{26}H_{34}O_4$	$Z = 2$
$M_r = 410.53$	$D_x = 1.315$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.710$ (2) Å	Cell parameters from 154
$b = 10.3412$ (12) Å	reflections
$c = 11.051$ (2) Å	$\theta = 3$–23°
$\alpha = 89.442$ (11)°	$\mu = 0.087$ mm^{-1}
$\beta = 82.317$ (14)°	$T = 143$ (2) K
$\gamma = 70.628$ (8)°	Block, colorless
$V = 1036.7$ (3) Å^3	$0.48 \times 0.40 \times 0.28$ mm

Data collection

Siemens SMART diffractometer	$R_{int} = 0.039$
ω scans	$\theta_{max} = 31°$
Absorption correction: numerical	$h = -13 \rightarrow 13$
using 7 indexed faces	$k = -15 \rightarrow 14$
(*SHELXTL*; Sheldrick, 1996)	$l = -14 \rightarrow 15$
$T_{min} = 0.952$, $T_{max} = 0.979$	299 standard reflections
18 851 measured reflections	frequency: 600 min
5993 independent reflections	intensity decay: none
5005 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.05P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 0.3P]$
$wR(F^2) = 0.108$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.060$	$(\Delta/\sigma)_{max} < 0.001$
5993 reflections	$\Delta\rho_{max} = 0.37$ e Å^{-3}
274 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.010 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1B···O4^i	0.98	2.53	3.288 (2)	134
C13—H13A···O3	0.99	2.39	3.194 (2)	138
C14—H14···O2	1.00	2.41	3.039 (2)	120
C23—H23A···O2^i	0.99	2.71	3.482 (2)	135
C24—H24···O4	1.00	2.34	3.000 (2)	122
C25—H25A···O1	0.99	2.52	3.320 (2)	138

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

The H atoms were taken from a difference Fourier synthesis and were refined with fixed individual displacement parameters $[U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $U(\text{H}) = 1.6U_{\text{eq}}(\text{C}_{\text{Me}})]$ using a riding model with fixed distances of H—C(methyl) = 0.98 Å, H—C(secondary) = 0.99 Å and H—C(primary) = 1.00 Å. Torsion angles about the C—O bonds of the methoxy groups were refined.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *CIF* in *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1443). Services for accessing these data are described at the back of the journal.

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