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# Dimethyl dipropargylmalonate

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**Key indicators**

Single-crystal X-ray study
*T* = 173 K
Mean σ(C–C) = 0.002 Å
*R* factor = 0.028
*wR* factor = 0.078
Data-to-parameter ratio = 11.6

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



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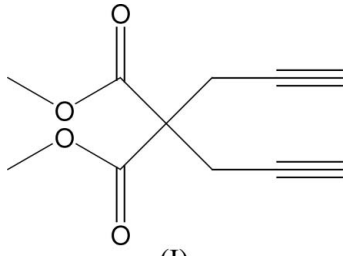
Geometric parameters of the title compound, $C_{11}H_{12}O_4$, are in the normal ranges. The crystal packing is stabilized by two weak C—H···O hydrogen bonds.

## Comment

Dimethyl dipropargylmalonate, (I), is a frequently used building block for organic synthesis [for selected examples, see Yamamoto *et al.* (2005), Trost & Rudd (2005), Grigg *et al.* (2003), Hashmi *et al.* (1998) and Hashmi *et al.* (1997)]. The related dimethyl monopropargylmalonate is even more popular, but a selective monopropargylation is difficult; usually in the known procedures significant amounts of the dimethyl dipropargylmalonate as a side product cannot be avoided (Atkinson & Grimshire, 1986; Brillon, 1986; Curran *et al.*, 1991; Dötz *et al.*, 1987; Llerena *et al.*, 1998).



(I)

A perspective view of (I) is shown in Fig. 1. Bond lengths and angles can be regarded as normal (Cambridge Structural Database, Version 1.6 plus three updates; *MOGUL*, Version 1.0; Allen, 2002). Compound (I) can be described as being composed of two nearly planar halves: C33/O32/C31/O31/C1/C21–C23 (r.m.s. deviation = 0.062 Å) and C43/O42/C41/O41/C1/C11–C13 (r.m.s. deviation = 0.036 Å). The dihedral angle between these two planes is 87.05 (4)°. The crystal packing is stabilized by two weak C—H···O hydrogen bonds (Table 2 and Fig. 2).

## Experimental

From the distillation of products resulting from a synthesis of dimethyl monopropargylmalonate (Atkinson & Grimshire, 1986; Brillon, 1986; Curran *et al.*, 1991; Dötz *et al.*, 1987; Llerena *et al.*, 1998) a fraction enriched with dimethyl dipropargylmalonate was obtained. After storage in the refrigerator for several months, single crystals of the title compound had precipitated.

*Crystal data*

$C_{11}H_{12}O_4$
$M_r$ = 208.21
Monoclinic, *Pc*
*a* = 8.260 (1) Å
*b* = 9.706 (1) Å
*c* = 7.770 (1) Å
$\beta$ = 117.45 (1)°
*V* = 552.80 (11) Å$^3$
*Z* = 2
$D_x$ = 1.251 Mg m$^{-3}$
Mo *K*$\alpha$ radiation
Cell parameters from 8192 reflections
$\theta$ = 4.2–23.5°
$\mu$ = 0.10 mm$^{-1}$
*T* = 173 (2) K
Block, colourless
0.37 × 0.35 × 0.28 mm

*Data collection*

Siemens SMART CCD three-circle diffractometer
$\omega$ scans
Absorption correction: none
12526 measured reflections
1609 independent reflections
1499 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.030
$\theta_{max}$ = 30.6°
*h* = −11 → 11
*k* = −13 → 13
*l* = −10 → 11

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.078
*S* = 1.07
1609 reflections
139 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 0.0043P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.17 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.14 e Å$^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.031 (9)

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| C12—C13 | 1.196 (2) | C31—O32 | 1.3318 (16) |
| C22—C23 | 1.186 (3) | C41—O41 | 1.1975 (16) |
| C31—O31 | 1.2008 (16) | C41—O42 | 1.3327 (15) |

**Table 2**
Hydrogen-bond geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C13—H13···O41$^{i}$ | 0.95 | 2.27 | 3.1247 (19) | 150 |
| C33—H33*A*···O31$^{ii}$ | 0.98 | 2.45 | 3.3969 (19) | 162 |

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

H atoms were located in a difference Fourier map, but refined with fixed individual displacement parameters [$U_{iso}$(H) = 1.2$U_{eq}$(C) or 1.5 $U_{eq}$(methyl C)], using a riding model, with C—H distances ranging from 0.95 and 0.99 Å. In addition, the methyl groups were allowed to rotate but not to tip. In the absence of significant anomalous scattering, Friedel pairs were merged.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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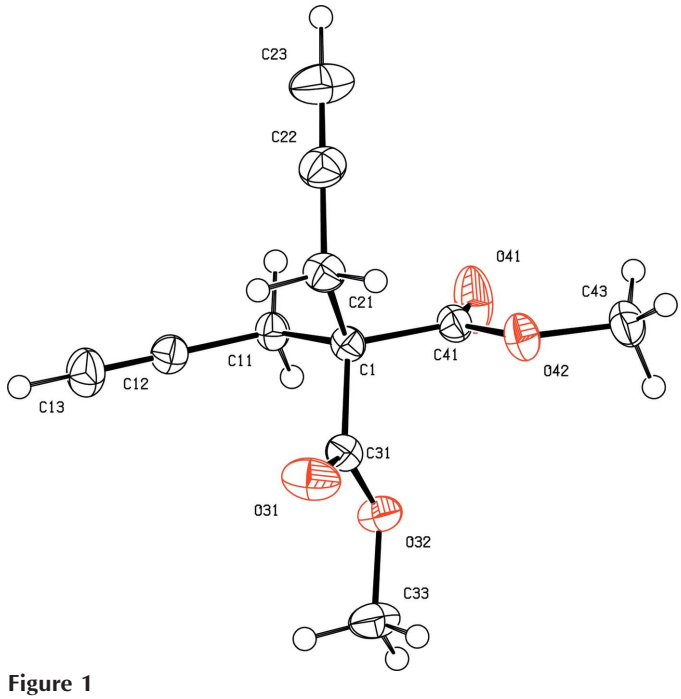


**Figure 1**
Perspective view of the title compound with the atom numbering; displacement ellipsoids are drawn at the 50% probability level.

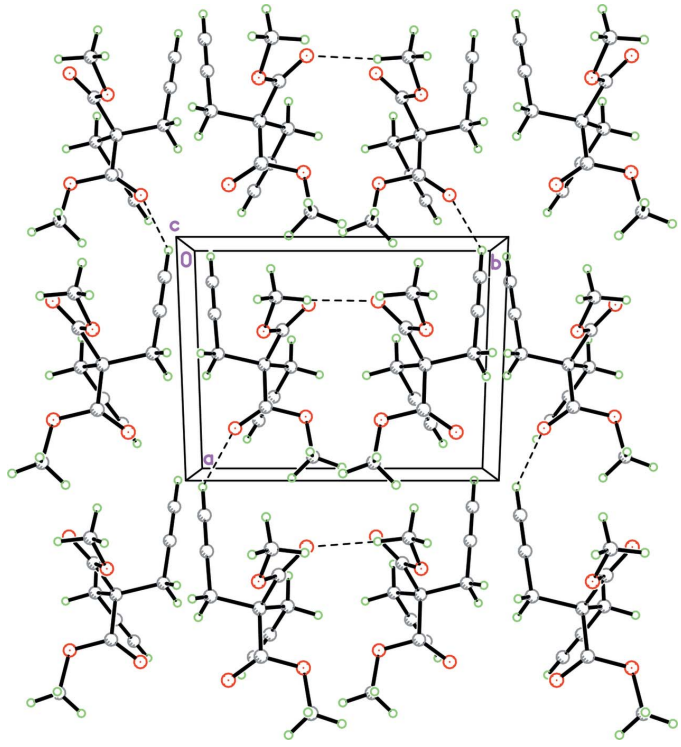


**Figure 2**
Packing diagram of the title compound, viewed along the *c*-axis direction. Hydrogen bonds are drawn as dashed lines.

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