207 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.0750P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.544$
$\Delta\rho_{\max} = 0.10$ e Å^{-3}
$\Delta\rho_{\min} = -0.09$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = −0.17 (33)

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	$U_{\rm eq}$
N1	0.7501 (2)	0.12066 (13)	0.1047	0.0470 (4)
C2	0.8198 (3)	0.0273 (2)	0.0498 (2)	0.0501 (5)
C3	0.8165 (2)	0.0693 (2)	−0.0520 (2)	0.0502 (5)
C4	0.8669 (3)	0.0120 (2)	−0.1360 (2)	0.0618 (6)
C5	0.8417 (4)	0.0734 (3)	−0.2222 (2)	0.0730 (7)
C6	0.7692 (4)	0.1856 (3)	−0.2241 (2)	0.0711 (7)
C7	0.7196 (3)	0.2430 (2)	−0.1388 (2)	0.0616 (6)
C8	0.7459 (2)	0.1825 (2)	−0.0539 (2)	0.0499 (5)
C9	0.7058 (3)	0.2187 (2)	0.0469 (2)	0.0487 (5)
O10	0.8679 (2)	−0.06734 (13)	0.0813 (2)	0.0680 (5)
O11	0.6453 (2)	0.31108 (14)	0.0756 (2)	0.0677 (5)
C12	0.7293 (3)	0.1184 (2)	0.2071 (2)	0.0454 (4)
C13	0.6327 (3)	0.0286 (2)	0.2498 (2)	0.0545 (5)
C14	0.6110 (3)	0.0271 (2)	0.3484 (2)	0.0592 (5)
C15	0.6835 (3)	0.1149 (2)	0.4067 (2)	0.0549 (5)
C16	0.7780 (3)	0.2047 (2)	0.3621 (2)	0.0576 (5)
C17	0.8021 (3)	0.2071 (2)	0.2635 (2)	0.0533 (5)
C18	0.6605 (5)	0.1129 (4)	0.5151 (2)	0.0842 (9)

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

N1—C2	1.404 (3)	C7—C8	1.376 (3)
N1—C9	1.406 (3)	C8—C9	1.489 (3)
N1—C12	1.431 (2)	C9—O11	1.206 (3)
C2—O10	1.209 (3)	C12—C13	1.384 (3)
C2—C3	1.490 (3)	C12—C17	1.385 (3)
C3—C8	1.385 (3)	C13—C14	1.378 (3)
C3—C4	1.387 (3)	C14—C15	1.392 (3)
C4—C5	1.395 (4)	C15—C16	1.388 (3)
C5—C6	1.379 (5)	C15—C18	1.514 (3)
C6—C7	1.402 (4)	C16—C17	1.382 (3)
C2—N1—C9	111.6 (2)	C3—C8—C9	108.3 (2)
C2—N1—C12	124.7 (2)	O11—C9—N1	125.5 (2)
C9—N1—C12	123.7 (2)	O11—C9—C8	128.7 (2)
O10—C2—N1	125.4 (2)	N1—C9—C8	105.8 (2)
O10—C2—C3	128.9 (2)	C13—C12—C17	119.9 (2)
N1—C2—C3	105.7 (2)	C13—C12—N1	119.9 (2)
C8—C3—C4	121.4 (2)	C17—C12—N1	120.2 (2)
C8—C3—C2	108.5 (2)	C14—C13—C12	119.9 (2)
C4—C3—C2	130.2 (2)	C13—C14—C15	121.4 (2)
C3—C4—C5	116.9 (2)	C16—C15—C14	117.6 (2)
C6—C5—C4	121.7 (2)	C16—C15—C18	120.9 (3)
C5—C6—C7	120.9 (3)	C14—C15—C18	121.4 (3)
C8—C7—C6	117.2 (2)	C17—C16—C15	121.7 (2)
C7—C8—C3	121.9 (2)	C12—C17—C16	119.5 (2)
C7—C8—C9	129.8 (2)		

Data were corrected for Lorentz and polarization effects, but not for absorption. All the calculations were performed on a Dell 466De computer with the *CRYSRULER* (Rizzoli, Sangermano, Calestani & Andreetti, 1987) package.

Data collection: Belletti, Cantoni & Pasquinelli (1992). Cell refinement: Belletti, Cantoni & Pasquinelli (1992). Data reduction: Belletti, Cantoni & Pasquinelli (1992). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1133). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dimethyl 4,4-Bis(ethoxycarbonyl)-1,2-cyclopentanediylidenediacetate

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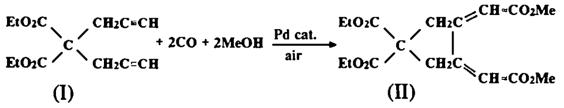
Abstract

The title compound, $C_{17}H_{22}O_8$, is an example of a product obtained from a cyclodicarbonylation reaction using diacetylenic substrates. The five-membered ring assumes a near-envelope conformation with the two acetate chains lying practically in the plane of the four coplanar ring atoms, C1, C2, C4 and C5, while the ethoxycarbonyl groups (attatched to the atom forming the 'flap') are oriented in opposite directions. The conjugated C═C—C═O chromophore systems are planar and are not parallel. Intramolecular interactions are in the range 2.43 (3)–2.60 (4) Å.

Comment

During recent years, much effort has been devoted to the carbonylation of olefins and alkynes, while little interest has been taken in diacetylenic substrates. A series of studies was carried out in our laboratories in order to characterize diacetylenic substrates, which can easily undergo cyclodicarbonylation reactions to form five-membered rings. It was found that high yields (70–85%) may be obtained using malonic substrates subjected to propynylation under mild conditions. The synthesis involves the reaction between the dipropynyl derivative (I) and a mixture of air, carbon monoxide and methanol in the presence of a Pd catalyst sealed in an autoclave at 323 K for a day, and results in the title compound, dimethyl 4,4-di(ethoxycarbonyl)-1,2-cyclopentanediylidenediacetate, (II).



The number of X-ray structure determinations of cyclopentane ring compounds connected through their 1 and 2 positions to aliphatic chains by double bonds is not sufficient to evaluate the magnitude of the geometrical deformations of the ring skeleton due to both the introduction of this kind of substituent and their steric interactions.

The five-membered ring assumes a conformation which is nearer envelope than twist, with atom C3 out of the mean plane of the remaining four atoms of the ring by 0.47 (1) Å. In terms of Cremer & Pople (1975) notation, the values of the amplitude phase pair are $Q = 0.30$ and $\varphi = 61.8°$. The two acetate chains lie practically in the plane of the four ring atoms mentioned above, whereas the ethoxycarbonyl side chains are oriented in opposite directions with respect to the plane formed by atoms C2, C3 and C4. The presence of the exocyclic double bonds C1═C6 and C5═C9 restricts the freedom of the ester groups to rotate about the C6—C7 and C9—C10 bonds. The planes of the two conjugated C═C—C═O chromophore systems also contain the two adjacent C atoms of the ring. The two C═C—C═O moieties are not parallel and have a dihedral angle of 12.0 (1)° between their mean planes. The five heavy atoms associated with the C1═C6 and C5═C9 π systems are coplanar to within 0.01 (1) and 0.02 (1) Å, respectively, or to within 0.04 (3) and 0.08 (4) Å when atoms H6 and H9 are included. The reciprocal chain orientations avoid mutual steric interactions between the methyl groups and the carbonyl O atoms. There are, however, short contacts between the H atoms attached to atoms C2 and C4, and the carbonyl O atoms of adjacent chains [these contacts range from 2.45 (3) to 2.55 (3) Å].

The packing of the molecules in the crystal is mainly determined by van der Waals interactions.

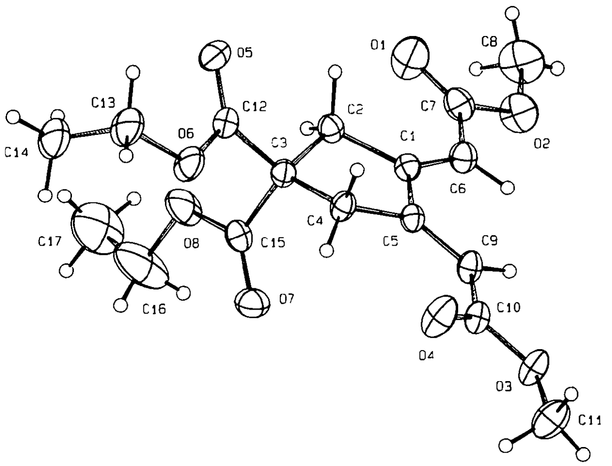


Fig. 1. Perspective view of the title molecule with the atomic labelling and 30% probability displacement ellipsoids.

Experimental

A solution of 8 g (0.05 mmol) of diethyl malonate in 70 ml of acetone was mixed with 20 g of potassium carbonate (anhydrated at 393 K for 2 h). After the rapid addition of 22.4 ml (0.2 mmol) of bromopropyne mixed (80%) with toluene and 30 ml of acetone, the mixture was stirred vigorously and heated under acetone reflux for 48 h. The solvent was removed at low pressure and the crude product eluted with ethyl ether after being washed with water. Concentration of the ethereal phase (dried on anhydrous Na_2SO_4) under vacuum, followed by distillation at reduced pressure yielded 10.03 g (85%) of the dipropynylic substrate. A methanolic solution (100 ml) of this substrate (1.652 g, 7.0 mmol) was added to KI (0.581 g, 3.5 mmol) and sealed in a steel autoclave in the presence of air and Pd/C (0.148 g, 0.14 mmol; 10%). Pressurization was obtained with air (3 bar) and CO (9 bar; 1 bar = 10^5 Pa). After stirring at 323 K for 24 h, the crude product was filtered and eluted with ethyl acetate. Careful chromatography was performed on silica gel to separate the products, a mixture of hexane and AcOEt (6:4) being used as eluant. Two isomers, *syn–syn* and *syn–anti* (4:1), were obtained in 81% yield (2.01 g). Addition of MeOH and cooling to 253 K yielded a pale yellow microcrystalline solid (1.51 g, 61%), which was the *syn–syn* isomer (m.p. 406–408 K).

Crystal data

$C_{17}H_{22}O_8$
$M_r = 354.35$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å

Triclinic
$P\bar{1}$
$a = 9.610\,(3)$ Å
$b = 11.468\,(3)$ Å
$c = 9.043\,(2)$ Å
$\alpha = 109.26\,(3)°$
$\beta = 98.36\,(2)°$
$\gamma = 73.59\,(3)°$
$V = 901.0\,(4)$ Å^3
$Z = 2$
$D_x = 1.306$ Mg m^{-3}

Cell parameters from 24 reflections
$\theta = 6.3–17.7°$
$\mu = 0.104$ mm^{-1}
$T = 295\,(2)$ K
Prism
0.26 × 0.16 × 0.12 mm
Pale yellow

Data collection

Philips PW1100 diffractometer
Lehmann & Larsen (1974) scans
Absorption correction: none
3931 measured reflections
3931 independent reflections
1480 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 27.0°$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 13$
$l = 0 \rightarrow 11$
1 standard reflection monitored every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0436$
$wR(F^2) = 0.1071$
$S = 0.700$
3930 reflections
315 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.420$
$\Delta\rho_{\max} = 0.224$ e Å^{-3}
$\Delta\rho_{\min} = -0.205$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0164 (21)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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	0.6764 (2)	0.43554 (15)	0.8778 (2)	0.0744 (6)
O2	0.5472 (2)	0.63244 (14)	0.8883 (2)	0.0585 (5)
O3	0.0449 (2)	0.4597 (2)	0.2959 (2)	0.0750 (6)
O4	0.1621 (2)	0.2554 (2)	0.2116 (2)	0.0857 (6)
O5	0.6037 (2)	−0.07073 (14)	0.3491 (2)	0.0640 (5)
O6	0.8064 (2)	−0.01125 (13)	0.4609 (2)	0.0667 (5)
O7	0.7624 (2)	0.2672 (2)	0.3629 (2)	0.0633 (5)
O8	0.7104 (2)	0.1003 (2)	0.1745 (2)	0.0841 (6)
C1	0.4931 (2)	0.3529 (2)	0.5884 (2)	0.0377 (5)
C2	0.6147 (3)	0.2360 (2)	0.5859 (3)	0.0436 (6)
C3	0.6113 (2)	0.1502 (2)	0.4152 (2)	0.0393 (5)
C4	0.4504 (2)	0.1834 (2)	0.3572 (3)	0.0431 (6)
C5	0.3887 (2)	0.3185 (2)	0.4552 (2)	0.0375 (5)
C6	0.4794 (2)	0.4689 (2)	0.6908 (3)	0.0455 (6)
C7	0.5793 (2)	0.5054 (2)	0.8258 (3)	0.0461 (6)
C8	0.6322 (4)	0.6831 (4)	1.0272 (4)	0.0733 (9)
C9	0.2603 (2)	0.3954 (2)	0.4296 (3)	0.0492 (6)
C10	0.1559 (2)	0.3592 (3)	0.3023 (3)	0.0561 (7)
C11	−0.0675 (4)	0.4363 (5)	0.1734 (6)	0.0948 (13)
C12	0.6691 (3)	0.0092 (2)	0.4011 (3)	0.0455 (6)
C13	0.8857 (4)	−0.1433 (3)	0.4487 (5)	0.0798 (9)
C14	0.9603 (4)	−0.2012 (4)	0.2999 (5)	0.0937 (12)
C15	0.7044 (2)	0.1814 (2)	0.3180 (3)	0.0473 (6)
C16	0.7892 (7)	0.1346 (7)	0.0683 (6)	0.146 (2)
C17	0.7626 (7)	0.0598 (8)	−0.0865 (6)	0.144 (2)

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

O1—C7	1.197 (2)	C1—C5	1.474 (3)
O2—C7	1.338 (2)	C1—C2	1.506 (3)
O2—C8	1.439 (3)	C2—C3	1.534 (3)
O3—C10	1.341 (3)	C3—C12	1.522 (3)
O3—C11	1.444 (4)	C3—C15	1.523 (3)
O4—C10	1.194 (3)	C3—C4	1.541 (3)
O5—C12	1.188 (2)	C4—C5	1.504 (3)
O6—C12	1.338 (3)	C5—C9	1.338 (3)
O6—C13	1.466 (3)	C6—C7	1.462 (3)
O7—C15	1.193 (2)	C9—C10	1.445 (3)
O8—C15	1.322 (3)	C13—C14	1.479 (5)
O8—C16	1.509 (5)	C16—C17	1.411 (6)
C1—C6	1.330 (3)		
C7—O2—C8	116.8 (2)	C1—C5—C4	108.4 (2)
C10—O3—C11	116.7 (3)	C1—C6—C7	125.8 (2)
C12—O6—C13	117.6 (2)	O1—C7—O2	122.8 (2)
C15—O8—C16	112.3 (2)	O1—C7—C6	127.0 (2)
C6—C1—C5	124.5 (2)	O2—C7—C6	110.2 (2)
C6—C1—C2	127.1 (2)	C5—C9—C10	124.5 (2)
C5—C1—C2	108.4 (2)	O4—C10—O3	122.0 (2)
C1—C2—C3	104.4 (2)	O4—C10—C9	126.9 (2)
C12—C3—C15	107.3 (2)	O3—C10—C9	111.2 (2)
C12—C3—C2	112.4 (2)	O5—C12—O6	124.6 (2)
C15—C3—C2	110.5 (2)	O5—C12—C3	126.4 (2)
C12—C3—C4	112.3 (2)	O6—C12—C3	109.0 (2)
C15—C3—C4	110.1 (2)	O6—C13—C14	109.3 (3)
C2—C3—C4	104.4 (2)	O7—C15—O8	124.5 (2)
C5—C4—C3	105.3 (2)	O7—C15—C3	125.5 (2)
C9—C5—C1	124.8 (2)	O8—C15—C3	110.0 (2)
C9—C5—C4	126.7 (2)	C17—C16—O8	107.2 (4)

Most of the H atoms were found in a ΔF map, the remainder were placed in calculated positions and all were refined isotropically. All calculations were performed on a Dell 466De personal computer with the *CRYSRULER* package (Rizzoli, Sangermano, Calestani & Andreetti, 1987).

Data collection: *FEBO* (Belletti, 1993). Cell refinement: *FEBO*. Data reduction: *FEBO*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1182). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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