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cis,cis,cis-Tetramethyl 1,2,4,5-cyclohexanetetracarboxylate

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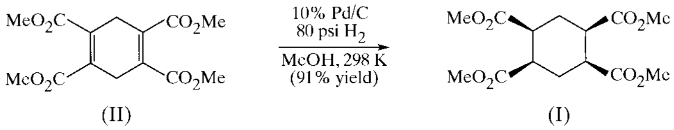
The title compound, $C_{14}H_{20}O_8$, was synthesized from the hydrogenation of tetramethyl 1,4-cyclohexadiene-1,2,4,5-tetracarboxylate with a catalytic amount of palladium/carbon. All four carbonyl moieties of the methyl ester groups are on the same face of the chair-conformed ring. The substantial ring distortion associated with the 1,3-diaxial methoxycarbonyl substituents is reflected in the large difference between bond angles as well as torsion angles, respectively, that in undistorted cyclohexanes would be approximately the same.

Comment

In our synthetic studies towards beltenes and cyclacenes (Stoddart, 1989), all-*cis* tetramethyl 1,2,4,5-cyclohexanetetracarboxylate, (I), was required. Although the synthesis of the *trans*,*cis*,*trans* isomer from the hydrogenation of tetrasodium pyromellitate at 423 K with hydrogen at 3000 p.s.i. (1 p.s.i. ≈ 6.895×10^3 Pa) and W-2 Raney nickel was reported, the stereochemistry was not well established (Longone, 1963; Bailey *et al.*, 1962). We synthesized (I) in 91% yield from the hydrogenation of tetramethyl 1,4-cyclohexadiene-1,2,4,5-tetracarboxylate, (II), with 10% palladium over carbon and 80 p.s.i. of hydrogen in methanol at 298 K (see Scheme). While the stereochemistry of (I) could not be determined from elemental and spectral analysis alone, its structure was unambiguously characterized by X-ray crystal structure analysis. Compound (II) was synthesized from the Diels–Alder reaction of dimethyl acetylenedicarboxylate and dimethyl 2,3-di(methylene)-1,4-butanedioate (Hamon & Spurr, 1981) in refluxing toluene.



(II) (I)

The molecular structure of (I) with the atom-numbering scheme (Fig. 1) shows it to have a chair conformation, with the methyl ester groups at C2 and C4 axially oriented and those at C1 and C5 equatorially oriented. All four carbonyl (C═O) moieties point in the same direction, towards C6 of the cyclohexane chair, an arrangement which reduces the steric methoxycarbonyl interaction among the four groups. The molecule has approximate non-crystallographic mirror symmetry. It can be seen from Table 1 that all the bond lengths within the ring are similar, with a mean distance of 1.534 (4) Å, which compares favorably with the mean C—C ring bond length [1.529 (4) Å] of *trans*-1,4-dicyanocyclohexane (Echeverria *et al.*, 1995). The largest endocyclic angle, C2—C3—C4, bearing the *cis*-diaxial C2- and C4-methoxycarbonyl groups, reflects classic 1,3-diaxial repulsion (Eliel & Wilen, 1994), the corresponding angle, C1—C6—C5, bearing these two substituents equatorially on the C1 and C5 atoms, being substantially smaller. The fact that the C4—C5—C6 angle is significantly larger than its corresponding C2—C1—C6 angle is a reflection of the asymmetric skeletal distortion associated with the repulsion noted above. The mean endocyclic angle [111.9 (3)°] is identical, within error, to the mean value [111.4 (4)°] of those in *trans*-1,4-cyclohexanedicarboxylic acid (Dunitz & Strickler, 1966; Von Luger *et al.*, 1972). The structural deformation caused by the 1,3-diaxial methoxycarbonyl groups in (I) is also quite evident from a comparison of the related torsion angles, *e.g.* C7—C1—C2—C11 is much larger than C15—C4—C5—C19, while C3—C4—C5—C6 is much smaller than C6—C1—C2—C3; C1—C2—C3—C4 is much larger than C2—C3—C4—C5; and C2—C1—C6—C5 is substantially larger than C4—C5—C6—C1.

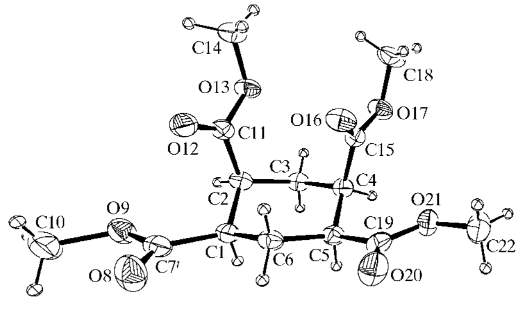


Figure 1
The molecular structure and atom-numbering scheme for (I) with displacement ellipsoids at the 30% probability level.

Experimental

A mixture of tetramethyl 1,4-cyclohexadiene-1,2,4,5-tetracarboxylate, (II) (0.817 g, 2.6 mmol), and 10% palladium (42 mg) on carbon in methanol (60 ml) was shaken at room temperature for 18 h in a bottle attached to a hydrogenator maintaining a pressure of 80 p.s.i. of hydrogen. The resulting mixture was diluted with ethyl acetate (150 ml), filtered through Celite, and the solids were carefully washed with ethyl acetate. The combined filtrates were concentrated and column chromatographed on silica gel, using a gradient mixture of hexane and diethyl ether as eluent, to give 0.752 g (91% yield) of compound (I). Recrystallization from diethyl ether provided long colorless needles (m.p. 388–391 K), which were used for the X-ray study.

Crystal data

$C_{14}H_{20}O_8$
$M_r = 316.3$
Monoclinic, *C*2/*c*
$a = 18.6901$ (19) Å
$b = 10.031$ (2) Å
$c = 17.781$ (2) Å
$\beta = 109.910$ (8)°
$V = 3134.3$ (9) Å^3
$Z = 8$
$D_x = 1.341$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.7$–11.9°
$\mu = 0.11$ mm^{-1}
$T = 296$ K
Plate, colorless
0.49 × 0.30 × 0.05 mm

Data collection

Rigaku AFC-5*S* diffractometer
ω scans (rate 2° min^{-1} in ω)
2864 measured reflections
2766 independent reflections
1039 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\rm max} = 25.02$°
$h = -22 \rightarrow 20$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 21$
3 standard reflections every 100 reflections intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.128$
$S = 0.958$
2766 reflections
203 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.15$ e Å^{-3}

The rotational orientations of the methyl groups were refined by the circular Fourier method available in *SHELXL*97 (Sheldrick, 1997). C—H riding distances for methyl, methylene and methine groups were fixed at 0.96, 0.97 and 0.98 Å, respectively. $U_{\rm iso}$ values for H atoms were calculated as $n \times U_{\rm iso}$ of their associated C atoms where $n = 1.5$ for methyl H atoms and $n = 1.2$ for methylene and methine H atoms. All H atoms are riding.

Data collection: *MSC*/*AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC*/*AFC Diffractometer Control Software*; data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SIR*92 (Burla *et al.*, 1989); program(s) used to refine structure: *LS* in *TEXSAN*, and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* in *TEXSAN* (Johnson, 1965); software used to prepare material for publication: *TEXSAN*, *SHELXL*97 and *PLATON* (Spek, 2000).

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.536 (4)	C4—C5	1.543 (4)
C2—C3	1.532 (4)	C5—C6	1.529 (4)
C3—C4	1.547 (4)	C1—C6	1.517 (5)
C2—C1—C6	110.9 (3)	C3—C4—C5	110.7 (3)
C1—C2—C3	108.9 (3)	C4—C5—C6	114.1 (3)
C2—C3—C4	114.6 (3)	C1—C6—C5	112.4 (3)
C7—C1—C2—C11	58.2 (4)	C1—C2—C3—C4	−56.1 (4)
C15—C4—C5—C19	−47.9 (4)	C11—C2—C3—C4	69.1 (4)
C2—C3—C4—C5	49.4 (4)	C2—C3—C4—C15	−76.9 (3)
C2—C1—C6—C5	−57.2 (4)	C19—C5—C6—C1	179.9 (3)
C3—C4—C5—C6	−45.6 (4)	C7—C1—C6—C5	172.3 (3)
C6—C1—C2—C3	58.7 (4)	C4—C5—C6—C1	50.9 (4)

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1298). Services for accessing these data are described at the back of the journal.

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