cis- and trans-Dimethyl Spiro[(4',4'-dimethyl-2',6'-dioxacyclohexane)-1',3-(4-methylenebicyclo[3.3.0]octane)]-2,2-dicarboxylate

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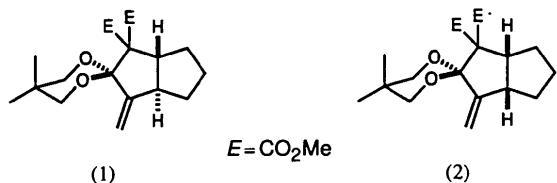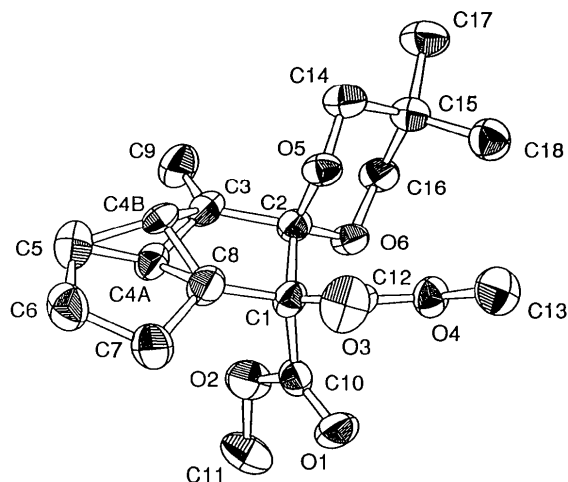Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

Fig. 1. Molecular structure and atomic numbering scheme for the mixed crystal, (I), containing cis and trans isomers (50% probability ellipsoids).

Abstract

The structures of the title compounds, $C_{18}H_{26}O_6$, were determined by X-ray analysis. The mixed crystals, with trans and cis isomers in a disordered structure, were obtained by recrystallization of the crude reaction mixture from hexane, while the crystals of the pure cis isomer were obtained after silica-gel chromatography and recrystallization. The mixed crystal is isomorphous with that of the pure cis isomer.

Comment

The title compounds were synthesized by the in-tramolecular [3+2] cycloaddition of a dipolar trimethyl-enemethane (Yamago, Ejiri, Nakamura & Nakamura, 1993) to an electron deficient olefin, as a mixture of different ratios of trans, (1), and cis isomers, (2). Re-crystallization of this mixture from hexane afforded the mixed crystals (I). Chromatographic purification of the crude mixture afforded crystals of the pure cis isomer, (II), after recrystallization from hexane.

Fig. 2. Molecular structure and atomic numbering scheme for crystal (II) (50% probability ellipsoids).

E = CO₂Me

(1)   (2)

The molecular structure within the crystal (I) is shown in Fig. 1. The ratio of the trans and cis isomers in a mixed crystal converged at 77:23. The molecular structure within the crystal (II) is shown in Fig. 2. It is clear that (II) comprises the cis isomer (2), which is the minor component in the crude mixture. The crystal structure of (II) is shown in Fig. 3. The crystal (I) has a structure isomorphous to that of (II), except that the C4 atom has two disordered positions. The similarity of the structural features of the cis and trans isomers may have caused them to crystallize in a mixed crystal.

Fig. 3. The packing of molecules in the crystal (II) viewed down the b axis.

Experimental

Crystal (I)

Crystal data

$C_{18}H_{26}O_6$
$M_r = 338.39$
Triclinic
$P\bar{1}$
$a = 8.960\,(4)$ Å
$b = 11.507\,(6)$ Å
$c = 8.889\,(7)$ Å
$\alpha = 97.29\,(5)°$
$\beta = 97.71\,(5)°$
$\gamma = 105.58\,(3)°$
$V = 862.0\,(9)$ Å^3
$Z = 2$
$D_x = 1.304$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.615–15.020°$
$\mu = 0.097$ mm^{-1}
$T = 296\,(2)$ K
Prismatic
$0.47 \times 0.34 \times 0.06$ mm
Colourless

Data collection

AFC-5R diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scan
  $T_{min} = 0.883$, $T_{max} = 1.000$
4219 measured reflections
3964 independent reflections
2101 observed reflections
  $[I > 2\sigma(I)]$

$R_{int} = 0.038$
$\theta_{max} = 27.50°$
$h = 0 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -11 \rightarrow 11$
3 standard reflections
  monitored every 100
  reflections
  intensity decay: 3.23%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.154$
$S = 1.109$
3963 reflections
231 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0919P)^2 + 0.2615P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Extinction correction: none
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) *for* (I)

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

	x	y	z	U_{eq}
O1	0.6669 (3)	0.4951 (2)	0.1061 (3)	0.057
O2	0.5262 (3)	0.4363 (2)	0.2856 (3)	0.055
O3	0.7536 (3)	0.2432 (2)	-0.0580 (3)	0.068
O4	0.9163 (2)	0.3771 (2)	0.1388 (2)	0.045
O5	0.7827 (2)	0.1732 (2)	0.2917 (2)	0.042
O6	0.7928 (2)	0.3620 (2)	0.4329 (2)	0.037
C1	0.6501 (3)	0.2964 (2)	0.1699 (3)	0.038
C2	0.6973 (3)	0.2582 (2)	0.3297 (3)	0.037
C3	0.5398 (4)	0.1896 (3)	0.3734 (4)	0.045
C4A	0.4098 (4)	0.1769 (4)	0.2417 (5)	0.038
C4B	0.4572 (15)	0.1096 (11)	0.2223 (7)	0.048
C5	0.2736 (4)	0.0675 (3)	0.1757 (4)	0.063
C6	0.2308 (4)	0.0827 (3)	0.0063 (4)	0.063
C7	0.3685 (4)	0.1859 (3)	-0.0257 (4)	0.055
C8	0.5005 (4)	0.1892 (3)	0.1022 (4)	0.050
C9	0.5112 (4)	0.1606 (3)	0.5072 (4)	0.059
C10	0.6175 (3)	0.4207 (3)	0.1824 (3)	0.039
C11	0.4818 (4)	0.5487 (3)	0.2971 (4)	0.062
C12	0.7770 (4)	0.3009 (3)	0.0693 (3)	0.041
C13	1.0449 (4)	0.3786 (4)	0.0571 (4)	0.065
C14	0.8612 (4)	0.1399 (3)	0.4243 (4)	0.046
C15	0.9756 (3)	0.2512 (3)	0.5299 (3)	0.041
C16	0.8828 (4)	0.3406 (3)	0.5680 (3)	0.043
C17	1.0413 (4)	0.2121 (3)	0.6768 (4)	0.057
C18	1.1112 (4)	0.3102 (3)	0.4502 (4)	0.056

Crystal (II)

Crystal data

$C_{18}H_{26}O_6$
$M_r = 338.39$
Triclinic
$P\bar{1}$
$a = 9.4915\,(11)$ Å
$b = 11.5618\,(14)$ Å
$c = 8.9687\,(9)$ Å
$\alpha = 98.806\,(9)°$
$\beta = 99.065\,(9)°$
$\gamma = 112.364\,(9)°$
$V = 874.0\,(2)$ Å^3
$Z = 2$
$D_x = 1.286$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 29.38–29.97°$
$\mu = 0.096$ mm^{-1}
$T = 296\,(2)$ K
Prismatic
$0.60 \times 0.30 \times 0.20$ mm
Colourless

Data collection

AFC-7R diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scan
  $T_{min} = 0.972$, $T_{max} = 1.000$
4273 measured reflections
4033 independent reflections
2259 observed reflections
  $[I > 2\sigma(I)]$

$R_{int} = 0.021$
$\theta_{max} = 27.49°$
$h = 0 \rightarrow 12$
$k = -15 \rightarrow 13$
$l = -11 \rightarrow 11$
3 standard reflections
  monitored every 100
  reflections
  intensity decay: 0.41%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.129$
$S = 1.129$
4033 reflections
295 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0674P)^2 + 0.1697P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
  from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
O1	0.6834 (2)	0.4923 (2)	0.1059 (2)	0.062
O2	0.5330 (2)	0.4158 (2)	0.2667 (2)	0.053
O3	0.7428 (2)	0.2375 (2)	-0.0715 (2)	0.078
O4	0.9126 (2)	0.3764 (2)	0.1420 (2)	0.050
O5	0.7414 (2)	0.1542 (2)	0.2715 (2)	0.045
O6	0.7938 (2)	0.3576 (1)	0.4205 (2)	0.044
C1	0.6454 (3)	0.2841 (2)	0.1524 (3)	0.041
C2	0.6829 (3)	0.2487 (2)	0.3106 (3)	0.040
C3	0.5219 (3)	0.1830 (2)	0.3443 (3)	0.044
C4	0.4095 (3)	0.1082 (2)	0.1906 (3)	0.048
C5	0.2482 (4)	0.1124 (4)	0.1586 (4)	0.066

C6	0.2078 (4)	0.1000 (3)	−0.0153 (4)	0.065
C7	0.3617 (3)	0.1890 (3)	−0.0449 (3)	0.058
C8	0.4874 (3)	0.1672 (2)	0.0640 (3)	0.046
C9	0.4860 (4)	0.1915 (3)	0.4811 (4)	0.059
C10	0.6259 (3)	0.4103 (2)	0.1728 (3)	0.042
C11	0.4975 (4)	0.5269 (3)	0.2844 (4)	0.063
C12	0.7700 (3)	0.2950 (2)	0.0597 (3)	0.046
C13	1.0408 (4)	0.3854 (4)	0.0688 (4)	0.068
C14	0.8017 (4)	0.1189 (3)	0.4058 (3)	0.054
C15	0.9370 (3)	0.2341 (3)	0.5164 (3)	0.051
C16	0.8750 (4)	0.3354 (3)	0.5567 (3)	0.050
C17	0.9890 (5)	0.1969 (4)	0.6646 (4)	0.072
C18	1.0754 (4)	0.2863 (4)	0.4418 (4)	0.069

Table 3. *Selected geometric parameters* (Å, °) *for* (II)

O5—C2	1.426 (3)	C3—C9	1.323 (3)
O5—C14	1.434 (3)	C3—C4	1.502 (4)
O6—C2	1.396 (3)	C4—C5	1.534 (4)
O6—C16	1.449 (3)	C4—C8	1.555 (3)
C1—C10	1.526 (3)	C5—C6	1.517 (4)
C1—C12	1.528 (3)	C6—C7	1.524 (4)
C1—C2	1.561 (3)	C7—C8	1.542 (4)
C1—C8	1.568 (3)	C14—C15	1.516 (4)
C2—C3	1.528 (3)	C15—C16	1.520 (4)
C2—O5—C14	112.2 (2)	C9—C3—C2	127.3 (2)
C2—O6—C16	116.7 (2)	C4—C3—C2	106.6 (2)
C10—C1—C12	107.8 (2)	C3—C4—C5	118.4 (2)
C10—C1—C2	112.3 (2)	C3—C4—C8	106.7 (2)
C12—C1—C2	113.2 (2)	C5—C4—C8	104.4 (2)
C10—C1—C8	111.3 (2)	C6—C5—C4	104.0 (2)
C12—C1—C8	109.7 (2)	C5—C6—C7	103.0 (2)
C2—C1—C8	102.5 (2)	C6—C7—C8	103.7 (2)
O6—C2—O5	112.4 (2)	C7—C8—C4	106.6 (2)
O6—C2—C3	117.5 (2)	C7—C8—C1	119.7 (2)
O5—C2—C3	108.8 (2)	C4—C8—C1	106.4 (2)
O6—C2—C1	110.1 (2)	O5—C14—C15	111.0 (2)
O5—C2—C1	102.8 (2)	C14—C15—C16	106.5 (2)
C3—C2—C1	103.8 (2)	O6—C16—C15	112.7 (2)
C9—C3—C4	126.0 (2)		
C8—C1—C2—C3	−36.2 (2)	C6—C7—C8—C1	−140.7 (2)
C1—C2—C3—C4	35.6 (2)	C3—C4—C8—C7	−131.9 (2)
C2—C3—C4—C5	−137.2 (2)	C5—C4—C8—C7	−5.9 (3)
C2—C3—C4—C8	−20.1 (3)	C3—C4—C8—C1	−3.1 (3)
C3—C4—C5—C6	148.2 (2)	C5—C4—C8—C1	123.0 (2)
C8—C4—C5—C6	29.9 (3)	C2—C1—C8—C7	144.9 (2)
C4—C5—C6—C7	−43.0 (3)	C12—C1—C8—C4	144.8 (2)
C5—C6—C7—C8	38.7 (3)	C2—C1—C8—C4	24.2 (2)
C6—C7—C8—C4	−20.1 (3)		

For crystal (I), H atoms were refined as riding on their associated atoms. The distance C4B—C3 was constrained.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structures: *TEXSAN* for (I); *SHELXS86* (Sheldrick, 1985) for (II). For both compounds, program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry for both structures have been deposited with the IUCr (Reference: AS1138). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,2-Diiod-1,2-bis(pentamethyl-cyclopentadienyl)diphosphan

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Abstract

The title compound, 1,2-diiodo-1,2-bis(pentamethyl-cyclopentadienyl)diphosphane, $C_{20}H_{30}I_2P_2$, is obtained as the *d,l*-diastereomer with a P—P distance of 2.234 (4) Å and a small I—P—P—I torsion angle of 13.0 (2)°.

Kommentar

Bei der Synthese der Titelverbindung aus dem Cyclo-triphosphan [(Me₅Cp)P]₃ (Jutzi, Kroos, Müller, Bögge & Penk, 1991) und elementarem Iod entstehen zwei Diastereomere, wobei sich die *meso*-Form innerhalb von ein bis zwei Stunden bei Raumtemperatur durch Inversion am Phosphor in die *d-l*-Form umwandelt. Wie Fig. 1 zeigt, hüllen die Pentamethylcyclopentadienyl (Pcp)-Liganden die Phosphoratome vollständig ein; das Diphosphan zeigt eine nahezu ekliptische Konformation mit einem Torsionswinkel I(1)—P(1)—P(2)—I(2) von 13,0 (2)°. Diese sterische Belastung führt zu einer Aufweitung der P—P—I-Winkel auf 109,9 (1) an P(1) bzw. 109,4 (1)° an P(2), verringert aber offenbar die erheblichen sterischen Wechselwirkungen zwischen den Iodatomen und den Pcp-Liganden, die bei einer gestaffelten Konformation aufträten.