B3—B8	1.768 (9)	B3′—B8′	1.753 (8)
B4—B5	1.765 (9)	B4′—B5′	1.755 (8)
B4—B8	1.778 (10)	B4′—B8′	1.782 (8)
B4—B9	1.779 (9)	B4′—B9′	1.772 (8)
B5—B6	1.776 (9)	B5′—B6′	1.779 (8)
B5—B9	1.761 (10)	B5′—B9′	1.753 (9)
B5—B10	1.767 (8)	B5′—B10′	1.774 (8)
B6—B10	1.772 (10)	B6′—B10′	1.781 (9)
B6—B11	1.801 (9)	B6′—B11′	1.789 (8)
B7—B8	1.772 (10)	B7′—B8′	1.764 (9)
B7—B11	1.768 (9)	B7′—B11′	1.783 (7)
B7—B12	1.777 (10)	B7′—B12′	1.773 (9)
B8—B9	1.789 (10)	B8′—B9′	1.782 (9)
B8—B12	1.779 (10)	B8′—B12′	1.787 (9)
B9—B10	1.764 (11)	B9′—B10′	1.761 (9)
B9—B12	1.760 (10)	B9′—B12′	1.760 (9)
B10—B11	1.765 (9)	B10′—B11′	1.780 (8)
B10—B12	1.775 (11)	B10′—B12′	1.769 (9)
B11—B12	1.766 (10)	B11′—B12′	1.771 (9)
C41—P1—C31	105.2 (2)	C41′—P1′—C31′	106.5 (2)
C31—P1—C1	102.6 (2)	C31′—P1′—C1′	104.4 (2)
C41—P1—C1	103.6 (2)	C41′—P1′—C1′	102.8 (2)
B4—C1—P1	130.0 (4)	B4′—C1′—P1′	129.9 (3)
B6—C1—P1	113.1 (4)	B3′—C1′—P1′	118.7 (3)
B5—C1—P1	127.6 (3)	B5′—C1′—P1′	126.0 (3)
B3—C1—P1	116.6 (3)	B6′—C1′—P1′	112.2 (3)
C2—C1—P1	111.0 (3)	C2′—C1′—P1′	112.1 (3)

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraethyl (1Z,3Z)-Buta-1,3-diene-1,2,3,4-tetracarboxylate

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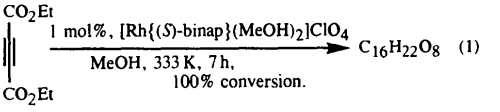
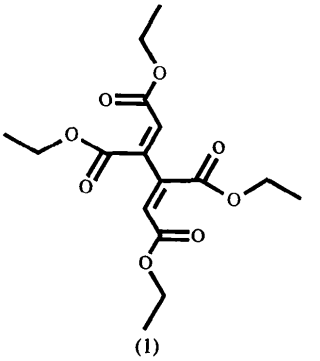
Abstract

The title compound, $C_{16}H_{22}O_8$, was obtained as the product of a cationic Rh^I-catalyzed hydridodimerization of diethyl acetylenedicarboxylate in methanol. The molecule lies on a crystallographic inversion centre. The diene moiety of the molecule possesses *s-trans* and *Z,Z* geometry.

Comment

The title compound, (1), has been synthesized by non-catalytic reactions (Bruce, Koutsantonis, Tiekink & Nicholson, 1991; Ryu, Kusumoto, Ogawa, Kambe & Sonoda, 1989; Neunhoeffer, Lehmann & Ewald, 1977); the *Z,Z* geometry, however, has been reported without X-ray analysis. We found an excellent cationic rhodium(I) catalyst containing the (*S*)-(−)-2,2′-bis-(diphenylphosphino)-1,1′-binaphthyl [(*S*)-binap] ligand which exhibited high catalytic activity for the hydridodimerization of acetylenic compounds. The synthetic details will be published elsewhere. The title compound was prepared according to the scheme shown below.





(1)

The reaction product was purified by distillation using a Kuhrgelrohr apparatus and subsequent recrystalliza-

tion. Suitable crystals for X-ray analysis were obtained from hexane. Molecular hydrogen was not used in this hydrogenation reaction system, methanol being the source of hydrogen for the diene moiety. The molecular structure of (1) is shown in Fig. 1. Both double bonds take the *Z* configuration. The bond lengths C1—C1^{i} and C1—C2, and the angle C1^{i}—C1—C2 of the diene moiety have values of 1.476 (6), 1.335 (6) Å and 122.8 (4)°, respectively [symmetry code: (i) $-x$, $-y$, $-z$]. These values are similar to those of buta-1,3-diene obtained from MO calculations; 1.467, 1.320 Å and 124°, respectively (Hehre, Radom, Schleyer & Pople, 1986). The plane defined by atoms C1, C2, C3, O1 and O2 is almost orthogonal to that defined by atoms C1, C6, O3 and O4 [dihedral angle 98.1 (1)°]. The torsion angles in the main and the side chains are given in Table 2. The main chain (C1, C2, C3, O2, C4, C5) and side chain (C1, C6, O4, C7, C8) both take zigzag forms. The diene moiety possesses a *trans*-planar conformation [C2—C1—C1^{i}—C2^{i} 180.0 (4)°].

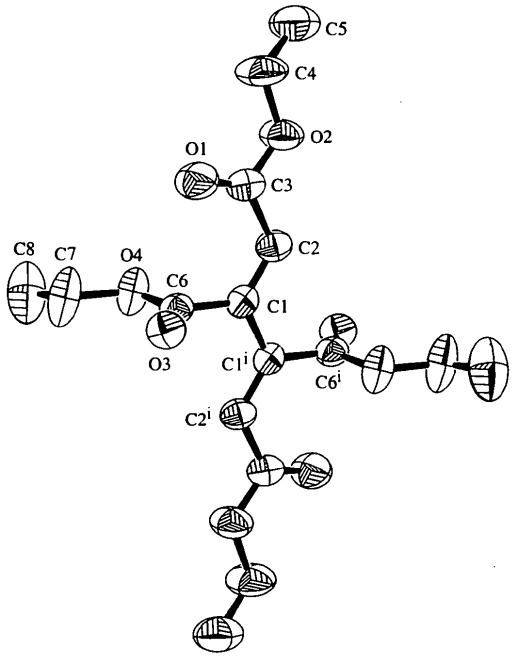


Fig. 1. View of $C_{16}H_{22}O_8$ showing the labelling of the non-H atoms. Displacement ellipsoids are plotted at the 50% probability level (*ORTEP*II; Johnson, 1976).

Experimental

Colourless crystals suitable for X-ray analysis were obtained from hexane (58% yield, m.p. 340.0–343.5 K).

Crystal data

$C_{16}H_{22}O_8$
M_r = 342.346
Cu $K\alpha$ radiation
λ = 1.54178 Å
Triclinic
$P\bar{1}$
a = 7.7523 (7) Å
b = 9.3535 (7) Å
c = 6.8139 (6) Å
α = 95.432 (8)°
β = 111.021 (7)°
γ = 99.112 (8)°
V = 449.19 (7) Å^3
Z = 1
D_x = 1.266 Mg m^{-3}
D_m not measured
Cell parameters from 25 reflections
θ = 22.9–30.2°
μ = 0.82 mm^{-1}
T = 293 (2) K
Prism
0.40 × 0.23 × 0.17 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.844, T_{max} = 0.985
1479 measured reflections
1349 independent reflections
939 observed reflections [$F > 3\sigma(F)$]
R_{int} = 0.023
θ_{max} = 60°
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 7$
3 standard reflections monitored every 200 reflections
frequency: 143 min
intensity decay: none

Refinement

Refinement on F
R = 0.0668
wR = 0.0558
S = 1.990
939 reflections
109 parameters
H atoms not refined
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max}$ = 0.00
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	U_{eq}
C1	0.0399 (5)	0.0785 (4)	0.0091 (7)	0.045 (2)
C2	0.0565 (5)	0.1795 (4)	0.1706 (7)	0.051 (2)
C3	0.1376 (6)	0.3372 (5)	0.1852 (8)	0.057 (2)
O1	0.1754 (5)	0.3915 (3)	0.0499 (5)	0.080 (2)
O2	0.1676 (5)	0.4094 (3)	0.3766 (5)	0.073 (2)
C4	0.2401 (8)	0.5675 (5)	0.4126 (9)	0.090 (3)
C5	0.3104 (7)	0.6197 (5)	0.6442 (9)	0.096 (3)
C6	0.0996 (6)	0.1187 (4)	−0.1714 (7)	0.049 (2)
O3	−0.0065 (4)	0.1377 (3)	−0.3394 (5)	0.060 (1)
O4	0.2830 (4)	0.1225 (3)	−0.1159 (5)	0.069 (2)
C7	0.3598 (7)	0.1583 (6)	−0.2791 (9)	0.095 (3)
C8	0.5389 (9)	0.1243 (7)	−0.2227 (10)	0.121 (4)

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

C1—C2	1.335 (6)	O2—C4	1.460 (6)
C1—C6	1.519 (6)	C4—C5	1.476 (8)
C1—C1^{i}	1.476 (6)	C6—O3	1.195 (5)
C2—C3	1.489 (6)	C6—O4	1.328 (6)
C3—O1	1.196 (6)	O4—C7	1.479 (7)
C3—O2	1.333 (6)	C7—C8	1.399 (9)

C2—C1—C6	121.9 (4)	C3—O2—C4	116.0 (4)
C2—C1—C1^i	122.8 (4)	O2—C4—C5	107.4 (3)
C6—C1—C1^i	115.4 (4)	C1—C6—O3	124.2 (3)
C1—C2—C3	121.7 (4)	C1—C6—O4	109.5 (4)
C2—C3—O1	125.9 (2)	O3—C6—O4	126.3 (2)
C2—C3—O2	109.4 (4)	C6—O4—C7	115.2 (4)
O1—C3—O2	124.6 (3)	O4—C7—C8	109.0 (5)

C6—C1—C2—C3	−1.1 (7)
C1^i—C1—C2—C3	180.0 (4)
C2—C1—C6—O3	−97.4 (6)
C2—C1—C6—O4	85.4 (5)
C1^i—C1—C6—O3	81.6 (6)
C1^i—C1—C6—O4	−95.7 (4)
C2—C1—C1^i—C2^i	180.0 (4)
C2—C1—C1^i—C6^i	−1.0 (6)
C1—C2—C3—O1	8.7 (8)
C1—C2—C3—O2	−169.6 (4)
C2—C3—O2—C4	−177.6 (4)
O1—C3—O2—C4	4.2 (7)
C3—O2—C4—C5	−165.3 (4)
C1—C6—O4—C7	179.1 (4)
O3—C6—O4—C7	1.9 (7)
C6—O4—C7—C8	−165.9 (5)

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

The $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included in the calculations for non-H atoms (Cromer, 1974). F_o data were collected at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University, Japan. All calculations were carried out on an NEC ACOS S3700 computer at the Research Center for Protein Engineering.

Data collection: Rigaku software. Cell refinement: Rigaku software. Data reduction: Rigaku software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *ANYBLK* (Imoto, 1990). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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10-(*N*-Carboxymethylcarbamoyl)-3,7-bis-(dimethylamino)phenothiazine (CCAP)–Ethanol (1/1), $C_{19}H_{22}N_4O_3S.C_2H_6O$

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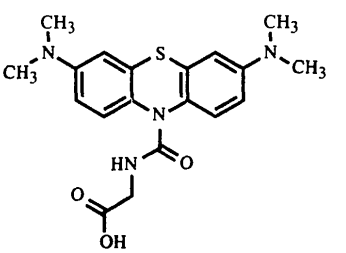
Abstract

In the title molecule, [3,7-bis(dimethylamino)phenothiazin-10-yl]-*N*-carbamoylacetic acid–ethanol (1/1), the phenothiazine ring adopts a boat conformation, with the S and N atoms occupying the bow and stern positions, respectively. The dihedral angle between the two phenyl rings is 131 (1)°. The system of conjugation in the molecule is remarkably different from that in methylene blue.

Comment

10-(*N*-Carboxymethylcarbamoyl)-3,7-bis(dimethylamino)phenothiazine (CCAP) is one of the functional dyes which have applications in clinical diagnostics. For example, it is used to measure the activity of lipase being converted in the presence of peroxidase and hydrogen peroxide to methylene blue. Effective conversion is essential for sensitive and accurate diagnosis. To understand the relationship between the efficiency of conversion and the molecular stereochemistry, the structure of CCAP has been determined as it ethanol solvate.



CCAP