Tableau 1. *Coordonnées atomiques relatives, facteurs d'agitation thermique isotropes équivalents* ($Å^2$) *et écarts-type*

$B_{éq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (ab\cos\gamma)\beta_{12} + (ac\cos\beta)\beta_{13} + (bc\cos\alpha)\beta_{23}]$.

	x	y	z	$B_{éq}$
C(1)	0,3184 (2)	0,6405 (2)	0,1600 (1)	3,65 (3)
C(2)	0,4323 (2)	0,6514 (3)	0,1113 (2)	5,49 (4)
C(3)	0,1735 (2)	0,6260 (2)	0,0471 (2)	5,23 (4)
C(4)	0,3199 (3)	0,7629 (2)	0,2389 (2)	5,31 (5)
N(5)	0,3424 (1)	0,5138 (1)	0,2368 (1)	2,92 (2)
O(6)	0,3219 (2)	0,4015 (1)	0,1784 (1)	4,86 (3)
C(7)	0,4146 (1)	0,5080 (1)	0,3722 (1)	2,54 (2)
C(8)	0,3560 (1)	0,4492 (1)	0,4474 (1)	2,60 (2)
C(9)	0,5533 (1)	0,5564 (1)	0,4247 (1)	2,78 (2)
C(10)	0,2048 (1)	0,3913 (2)	0,4031 (1)	3,17 (3)
C(11)	0,1601 (1)	0,3861 (2)	0,5118 (2)	4,25 (3)
C(12)	0,0952 (2)	0,4781 (3)	0,3003 (2)	6,40 (5)
C(13)	0,2042 (2)	0,2444 (2)	0,3607 (2)	5,55 (4)

Tableau 2. *Longueurs* (Å), *angles des liaisons* (°) *et écarts-type*

C(1)—C(2)	1,529 (3)	C(7)—C(9)	1,398 (2)
C(1)—C(3)	1,538 (2)	C(8)—C(9)^{i}	1,395 (2)
C(1)—C(4)	1,519 (3)	C(8)—C(10)	1,549 (2)
C(1)—N(5)	1,501 (2)	C(10)—C(11)	1,534 (3)
N(5)—O(6)	1,275 (2)	C(10)—C(12)	1,527 (2)
N(5)—C(7)	1,442 (2)	C(10)—C(13)	1,534 (3)
C(7)—C(8)	1,397 (2)		
C(2)—C(1)—C(3)	108,9 (1)	C(8)—C(7)—C(9)	121,0 (1)
C(2)—C(1)—C(4)	111,3 (2)	C(7)—C(8)—C(9)^{i}	114,6 (1)
C(2)—C(1)—N(5)	109,0 (1)	C(7)—C(8)—C(10)	126,9 (1)
C(3)—C(1)—C(4)	110,5 (2)	C(9)^{i}—C(8)—C(10)	118,5 (1)
C(3)—C(1)—N(5)	107,0 (1)	C(7)—C(9)—C(8)^{i}	124,4 (1)
C(4)—C(1)—N(5)	110,0 (1)	C(8)—C(10)—C(11)	111,2 (1)
C(1)—N(5)—O(6)	117,2 (1)	C(8)—C(10)—C(12)	112,0 (1)
C(1)—N(5)—C(7)	124,8 (1)	C(8)—C(10)—C(13)	108,8 (1)
O(6)—N(5)—C(7)	116,6 (1)	C(11)—C(10)—C(12)	106,5 (1)
N(5)—C(7)—C(8)	123,2 (1)	C(11)—C(10)—C(13)	106,1 (2)
N(5)—C(7)—C(9)	115,6 (1)	C(12)—C(10)—C(13)	112,2 (1)

Code de symétrie: (i) $1-x, 1-y, 1-z$.

Les facteurs de structure ont subi une correction de décroissance linéaire en fonction du temps. La structure a été résolue avec le programme *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) et la Fig. 1 réalisée avec le programme *ORTEP*II (Johnson, 1976). Tous les programmes de calcul utilisés appartiennent au système *SDP* (B. A. Frenz & Associates, Inc., 1982). Les coordonnées atomiques relatives et les facteurs de température isotropes équivalents sont rapportés dans le Tableau 1, les longueurs et les angles des liaisons dans le Tableau 2. Les noms des atomes sont indiqués sur la Fig. 1.

Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope, des coordonnées des atomes d'hydrogène, des distances C—H, des distances des atomes au plan du cycle, des distances interatomiques intermoléculaires et des angles de torsion ont été déposées aux archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 55442: 13 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre. [Référence de CIF: PA1014]

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Structure of a Cyclotetradecadiene

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Abstract

In the title compound, (*E*,*Z*)-tetramethyl 3,8-cyclotetradecadiene-1,1,6,6-tetracarboxylate, the (*E*) and (*Z*) double-bond planes form a dihedral angle of 96.4 (3)° and their centers lie 4.429 (5) Å apart. The (*E*) C=C bond distance is 1.292 (5) Å, and the (*Z*) C=C bond distance is 1.320 (6) Å.

Comment

The title compound (1) is one of a series of compounds containing 13- and 14-membered rings recently prepared by a direct cyclization method (Brillon & Deslongchamps, 1987). A structure determination was undertaken in order to confirm the identity of the compound and to determine the conformation of the 14-membered ring. The conformation is approximately rectangular with the corners of the rectangle formed by the (*Z*) double bond, the two methoxycarbonyl-substituted C atoms and the central methylene C atom of the $(CH_2)_5$ chain. The endocyclic torsion angles are [beginning at the (*Z*) double bond and proceeding by the shortest route toward the (*E*) double bond] 5.3 (7), −111.9 (5), 66.7 (4), 60.7 (4), 151.1 (4), 172.0 (4), −114.8 (4), 54.5 (4), 64.4 (4), −172.0 (3), 70.3 (4), 77.2 (4), 176.4 (3) and 119.4 (5)°. The planes of the two

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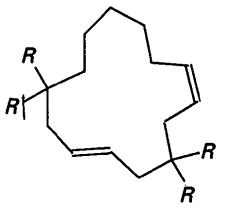
double bonds within the macrocycle are nearly orthogonal, forming a dihedral angle of 96.4 (3)°. The midpoints of these double bonds lie 4.429 (5) Å apart.



(1) R = $COOCH_3$

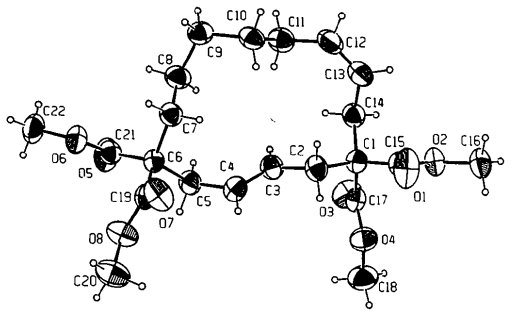


Fig. 1. View of the title compound showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level and H atoms shown with arbitrary radius.

Experimental

Crystal data

$C_{22}H_{32}O_8$
M_r = 424.5
Orthorhombic
Pbca
a = 22.669 (6) Å
b = 15.663 (6) Å
c = 12.995 (4) Å
V = 4614 (4) Å^3
Z = 8
D_x = 1.222 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 11–23°
μ = 0.73 mm^{-1}
T = 294 K
Needle
0.50 × 0.30 × 0.17 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical
T_{min} = 0.872, T_{max} = 1.000
4982 measured reflections
4469 independent reflections

3017 observed reflections [$I>\sigma(I)$]
θ_{max} = 75°
h = 0 → 28
k = 0 → 19
l = 0 → 16
3 standard reflections
frequency: 166.7 min
intensity variation: −2.0%

Refinement

Refinement on F
Final R = 0.080
wR = 0.073
S = 2.225
3017 reflections
272 parameters
H-atom parameters not refined
$w = 4F_o^2[\sigma^2(I)+(0.02F_o^2)^2]^{-1}$
$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: $(1+gI_c)^{-1}$ applied to F_c
Extinction coefficient: g = 2.6(2)×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
O1	0.7923 (1)	0.3359 (2)	0.4903 (2)	7.47 (8)
O2	0.8813 (1)	0.3133 (2)	0.4232 (2)	4.91 (6)
O3	0.8556 (1)	0.1504 (2)	0.2461 (2)	6.53 (7)
O4	0.8211 (1)	0.1340 (2)	0.4037 (2)	5.51 (7)
O5	0.5696 (1)	0.0989 (2)	−0.0395 (2)	6.55 (7)
O6	0.4873 (1)	0.1615 (2)	0.0161 (2)	5.06 (6)
O7	0.5140 (1)	0.1829 (2)	0.2852 (2)	6.38 (7)
O8	0.5190 (1)	0.0571 (2)	0.2059 (2)	5.89 (7)
C1	0.8016 (1)	0.2660 (2)	0.3251 (3)	3.99 (8)
C2	0.7335 (1)	0.2547 (2)	0.3298 (3)	4.79 (9)
C3	0.7080 (2)	0.2109 (2)	0.2385 (3)	4.84 (9)
C4	0.6608 (2)	0.1647 (3)	0.2369 (3)	4.72 (9)
C5	0.6318 (2)	0.1302 (2)	0.1426 (3)	4.72 (9)
C6	0.5685 (1)	0.1698 (2)	0.1255 (3)	3.81 (8)
C7	0.5707 (2)	0.2687 (2)	0.1239 (3)	4.54 (9)
C8	0.6060 (2)	0.3041 (2)	0.0339 (3)	5.4 (1)
C9	0.6156 (2)	0.3999 (2)	0.0396 (3)	5.13 (9)
C10	0.6579 (2)	0.4299 (2)	0.1239 (3)	4.98 (9)
C11	0.7227 (2)	0.4162 (3)	0.0976 (3)	5.5 (1)
C12	0.7622 (2)	0.4516 (2)	0.1793 (3)	5.9 (1)
C13	0.8013 (2)	0.4120 (3)	0.2376 (3)	6.2 (1)
C14	0.8206 (2)	0.3201 (3)	0.2322 (3)	4.98 (9)
C15	0.8220 (2)	0.3085 (2)	0.4224 (3)	4.67 (9)
C16	0.9085 (2)	0.3539 (3)	0.5108 (3)	6.0 (1)
C17	0.8304 (1)	0.1771 (2)	0.3188 (3)	4.20 (8)
C18	0.8454 (2)	0.0478 (3)	0.4072 (3)	7.3 (1)
C19	0.5301 (1)	0.1408 (2)	0.2145 (3)	4.12 (8)
C20	0.4846 (2)	0.0188 (3)	0.2874 (4)	7.5 (1)
C21	0.5439 (2)	0.1377 (2)	0.0251 (3)	4.32 (8)
C22	0.4585 (2)	0.1380 (3)	−0.0784 (3)	6.3 (1)

Table 2. *Geometric parameters* (Å, °)

C1—C2	1.554 (4)	C7—C8	1.523 (5)
C1—C14	1.538 (5)	C8—C9	1.518 (5)
C2—C3	1.488 (5)	C9—C10	1.530 (6)
C3—C4	1.292 (5)	C10—C11	1.524 (5)
C4—C5	1.493 (5)	C11—C12	1.494 (6)
C5—C6	1.579 (5)	C12—C13	1.320 (6)
C6—C7	1.549 (5)	C13—C14	1.506 (6)
C2—C1—C14	111.9 (3)	C7—C8—C9	113.5 (3)
C1—C2—C3	114.0 (3)	C8—C9—C10	115.4 (3)
C2—C3—C4	126.3 (3)	C9—C10—C11	113.6 (3)
C3—C4—C5	125.5 (3)	C10—C11—C12	111.4 (3)
C4—C5—C6	111.9 (3)	C11—C12—C13	129.4 (4)
C5—C6—C7	111.5 (3)	C12—C13—C14	128.2 (4)
C6—C7—C8	113.1 (3)	C1—C14—C13	114.2 (3)

Programs used include *SDP* (Frenz, 1978), *ORTEP* (Johnson, 1965) and *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55471 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1014]

The crystal was kindly provided by Professors K. N. Houk and P. Deslongschamps

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[12]aneS$_4$PdCl$_2$

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Abstract

The title compound, dichloro(1,4,7,10-tetrathiacyclododecane-S^1,S^4)palladium(II), has the metal coordinated in a square plane by the chloride ligands and by two of the four sulfur donors of the macrocycle. The conformation adopted by the macrocycle is unsymmetrical with one of the uncoordinated thia donors *endo* and the other *exo* with respect to the ring (these donors lie along an edge and at a corner respectively). The species may be regarded as an intermediate in the reaction between $PdCl_2$ and [12]aneS$_4$ which leads to the formation of [Pd([12]aneS$_4$)]$^{2+}$.

Comment

The conformation of the ring seen in this structure is different from that in the free ligand where all four sulfur donors are *exo* and lie at the corners of a square (Robinson & Sangokoya, 1988; Cooper, Foxman, Hartman, Storey & Wolf, 1987). It also differs from that in [Pd([12]aneS$_4$)]$^{2+}$ where the metal is displaced by 0.31 Å from the S$_4$ square plane, on the other side of which lie all the C atoms of the macrocycle (Blake & Schröder, 1990).

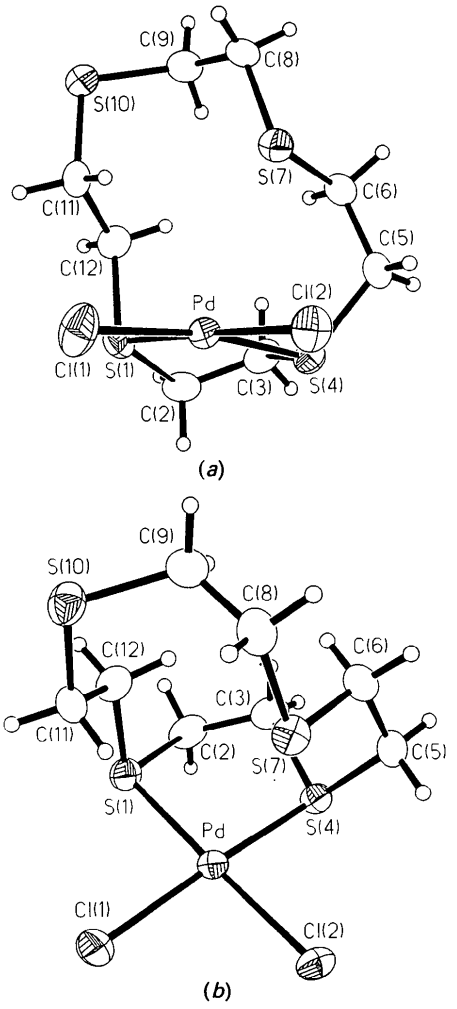

Fig. 1. Two views of the molecule: (*a*) and (*b*) are projections parallel and perpendicular to the square plane respectively. Thermal ellipsoids are drawn at the 30% probability level, except for those of H atoms which have been assigned arbitrary radii.

Experimental

Crystal data

$C_8H_{16}Cl_2PdS_4$
M_r = 417.7
Orthorhombic
$Pbc2_1$
a = 7.5289 (8) Å
b = 14.5526 (16) Å
c = 12.8578 (11) Å
V = 1408.8 Å^3
Z = 4
D_x = 1.970 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 57 reflections
θ = 9–11.5°
μ = 2.256 mm^{-1}
T = 277 K
Column
1.28 × 0.39 × 0.39 mm
Orange

Data collection

Stoe Stadi-4 four-circle diffractometer
ω–2θ scans
R_{int} = 0.007
θ_{max} = 22.5°
h = −8 → 8

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