Crystal and Molecular Structure of the Cyclodimeric Propylene-1,3-phenylenediacetate and of Its Di-*n*-butyltin Dichloride Complex*

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As part of a systematic study on the synthesis and binding properties of a series of cyclophane ester hosts, the crystal structures of the cyclodimeric propylene-1,3-phenylenediacetate ($C_{26}H_{28}O_8$) and of its di-*n*-butyltin dichloride complex $\{(C_{26}H_{26}O_8) [SnCl_2(C_4H_9)_2]_2\}$ have been determined by X-ray analyses. The crystals of the free macrocycle are triclinic, space group $P\bar{1}$, with $a = 5.071(6)$, $b = 8.108(3)$, $c = 14.640(4)$ Å, $\alpha = 76.46(3)$, $\beta = 85.35(8)$, $\gamma = 86.04(7)°$, $Z = 1$. Similarly, the crystals of the complex belong to the $P\bar{1}$ space group of the triclinic system and have the following cell parameters: $a = 8.378(4)$, $b = 11.524(3)$, $c = 14.009(4)$ Å, $\alpha = 109.16(2)$, $\beta = 92.64(2)$, $\gamma = 100.93(3)°$, $Z = 1$.

The most important feature of the complex structure is represented by the unambiguous interaction between two cyclophane ester carbonyls and two molecules of Bu_2SnCl_2, the distance being 2.865(4) Å. The usual tetrahedral geometry of the organotin(IV) center is significantly influenced by the interaction, changing into a distorted trigonal bipyramid, with a longer apical distance, typical of the five-coordinate stannate complexes. Conformations of the cyclophane in the two structures have been analyzed in some detail.

Key words: tin complex, X-ray structure, cyclophane derivatives.

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* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

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INTRODUCTION

The use of cyclophanes as synthetic hosts for inclusion of a variety of guests, spanning from inorganic and organic cations and anions to neutral molecules, has recently attracted increasing attention.[1] Their inclusion properties are mainly determined by the presence of the electron-rich cavity created by the organized arrangement of aromatic rings. For example, the binding ability exerted toward quaternary ammonium cations has been ascribed to this structural requisite, which allows a cation–π interaction to be established between the cation's charge and the aromatic π orbitals.[2] This interaction has been shown to have relevant implications in the molecular recognition processes involving the neurotransmitter acetylcholine.[3] On the other hand, a number of natural and synthetic ionophores, *e.g.* the natural antibiotic class of nactins, feature the ester group as the binding functionality towards biologically relevant cations, like K^+, Na^+, NH_4^+.[4] In the search for new macrocyclic hosts, we thought that combining the structural features of cyclophanes with the binding ability of the ester functionality might lead to new »mixed donor« hosts with interesting receptor properties. Following this idea, we prepared a set of new cyclophane esters of the phenylenediacetic and phenylenedipropionic acids to be tested as hosts.[5] We report here crystallographic evidence that the ester groups in this family of cyclophanes do participate in the binding of appropriate guests of complementary coordinating properties.

EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were acquired at 200 and 50 MHz, respectively, on a Varian GEMINI 2000 spectrometer. Chemical shifts (δ) in $CDCl_3$ are given in ppm from the $CHCl_3$ signal at $\delta = 7.26$ for ^{1}H and from the $CDCl_3$ signal at $\delta = 77.00$ for [13]C. [119]Sn titrations were performed on a Varian VXR 300 instrument, equipped with a variable temperature apparatus. Electron Impact (EI) mass spectra were obtained at 70 eV on a Carlo Erba Instruments QMD 1000 spectrometer. Electrospray ionization mass (ESI-MS) spectra were recorded in the positive-ion mode on a Fisons Instruments VG-Platform benchtop mass spectrometer equipped with a pneumatically assisted electrospray LC/MS interface and a single quadrupole operating at 3.8 kV. Melting points were determined on a Büchi 510 Melting Point apparatus and are uncorrected. Microanalyses were obtained by combustion on a 245C Perkin Elmer Elemental Analyzer. Analytical thin-layer chromatography (TLC) was performed on MERCK Kieselgel 60 F-254 precoated silica gel plates. Flash column chromatography was carried out with Silica Gel 60 (0.032–0.063 mm) from ICN.

Materials

Chloroform (Carlo Erba RPE) was washed several times with water, dried over $CaCl_2$, and stored in the dark over 3A and 13X activated molecular sieves. Solvents used for chromatography, ethyl acetate and petroleum ether 40–70 °C, were distilled prior to use. Deuterochloroform (Merck, 99.8%) stored in the dark over 3A and 13X activated molecular sieves was used for the NMR measurements. Thionyl chloride was used freshly distilled. All other solvents and materials were commercial products used as received.

1,3-Phenylenediacetyl Chloride (2)

A suspension of 1,3-phenylenediacetic acid (2.51 g, 12.93 mmol) in freshly distilled thionyl chloride (10 mL) was gently refluxed to complete solution of the solid (*ca*.1 h), monitoring the evolution of HCl. The reaction was brought to completion by entraining residual HCl with a stream of nitrogen. Excess thionyl chloride was distilled under reduced pressure and the residue was crystallized from dry petroleum ether (100 mL) by keeping the solution overnight at 4 °C under nitrogen, to give pure 1,3-phenylenediacetyl chloride as pale yellow crystals (2.20 g, 73%; m.p. 39–40 °C, Lit.[6] 40–42 °C). ^{1}H NMR (0.2 M in $CDCl_3$) δ / ppm: 4.16 (s, 4 H, CH_2), 7.19–7.44 (m, 4 H, Ar); ^{13}C NMR (0.2 M in $CDCl_3$) δ / ppm: 52.76 (CH_2), 129.41 [$C_{4,6}$ (Ar)], 129.62 [C_5 (Ar)], 130.70 [C_2 (Ar)], 132.08 [$C_{1,3}$ (Ar)], 171.72 (CO).

Cyclodimeric n-*Propylene-1,3-phenylenediacetate (3)*

A suspension of 1,3-propanediol (0.85 g, 11.2 mmol) and dibutyltin oxide (2.73 g, 11.0 mmol) in toluene (40 mL) was refluxed overnight under nitrogen in a Dean-Stark apparatus with azeotropic removal of water. Toluene was evaporated under reduced pressure from the cooled suspension and dry chloroform (110 mL) was added to the white residue. To the resulting suspension, a 0.1 M solution of 1,3-phenylenediacetyl chloride (2.54 g, 11.0 mmol, 1 equiv.) in dry chloroform (110 mL) was added dropwise during 30 min under nitrogen at room temperature with magnetic stirring. The mixture was then refluxed for 1 h, cooled to room temperature and the solvent was evaporated under vacuum. The residue was washed with 3 portions of petroleum ether (50 mL each) to remove the dibutyltin dichloride formed in the reaction, affording 2.56 g of crude polyester mixture, which was separated by flash column chromatography on silica gel 60 with petroleum ether/EtOAc 1:1 as eluant to give pure cyclodimeric *n*-propylene-1,3-phenylenediacetate (**3**) as a white solid (593 mg, 23%), m.p. 80–82 °C; ^{1}H NMR (0.1 F in $CDCl_3$) δ / ppm: 1.92 (quint, J = 6.2 Hz, 4 H, CH_2CH_2O), 3.56 (s, 8 H, CH_2CO), 4.09 (t, J = 6.2 Hz, 8 H, CH_2O), 7.12–7.31 (m, 8 H, Ar); ^{13}C NMR (0.1 F in $CDCl_3$) δ / ppm: 27.70 (CH_2CH_2O), 41.28 (CH_2CO), 61.27 (CH_2O), 128.11 [$C_{4,6}$ (Ar)], 128.81 [C_5 (Ar)], 129.97 [C_2 (Ar)], 134.36 [$C_{1,3}$ (Ar)], 171.18 (CO); EI-MS m/z (rel. int.): 469 (22, M[+]), 468 (83), 467 (18), 336 (18), 234 (20), 207 (12), 206 (18), 205 (23), 179 (11), 169 (28), 158 (28), 149 (19), 131 (29), 117 (11), 105 (64), 104 (100), 103 (53), 91 (17), 78 (30), 77 (23), 57 (12), 55 (13); ESI-MS m/z: 508 (M[+] + K), 491 (M[+] + Na).

Anal. Calcd. for $C_{26}H_{28}O_8$: C, 66.66; H, 6.02%; found: C, 66.50; H, 6.14%.

Cyclodimeric n-*Propylene-1,3-phenylenediacetate / di-*n-*Butyltin Dichloride Complex (4)*

Large crystals of **4** (558 mg, 9%, m.p. 64–65 °C) separated on standing from the petroleum ether washings of the preparation of **(3)**, which were collected by filtration. ^{1}H NMR (0.1 M in CDCl$_3$) δ / ppm: 0.96 (t, J = 7.3 Hz, 6H, CH$_3$), 1.35–1.52 (m, 4H, CH$_3$CH$_2$), 1.77–1.86 (m, 8H, CH$_2$CH$_2$Sn), 1.93 (quint, J = 6.2 Hz, 2 H, CH$_2$CH$_2$O), 3.57 (s, 4 H, CH$_2$CO), 4.10 (t, J = 6.2 Hz, 4 H, CH$_2$O), 7.13–7.31 (m, 4 H, Ar).

Crystal Data and Refinement

Crystal data and refinement details of the structures of **3** and **4** are reported in Table I.

Unit cell parameters and intensity data were obtained on a Nonius CAD4 diffractometer for both two structures. Cell dimensions were determined by least-squares fitting of 25 centered reflections for every compound. Intensity data were corrected for Lorentz and polarization effects, an absorption correction was applied once the structures were solved by using the Walker and Stuart method.[7] The structures were solved by direct methods, using the SIR-92 program[8] and subsequently refined by the full-matrix least-squares program SHELXL-93.[9] The hydrogen atoms of the carbon atoms were introduced in calculated positions, with their coordinates »riding« on those of the linked atoms. Their overall isotropic thermal displacement parameters converged to U values of 0.084(4) and 0.114(4) Å^2 for **3** and **4,** respectively. Non-hydrogen atoms were refined anisotropically. Final ΔF Fourier syntheses showed no remarkable features. In compound **4,** the maximum electron density peak, which is only 0.85 Å apart from the tin atom, is rather high (0.763 e Å^{-3}). The maximum shift/error in the final refinement cycles was < 1 for both structures. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from Ref. 10. Geometrical calculations were performed by PARST93.[11] The molecular plots were produced by the ORTEP program.[12] Tables II and III report the atomic coordinates of the non-hydrogen atoms.*

RESULTS AND DISCUSSION

Synthesis

Cyclodimeric propylene-1,3-phenylenediacetate (**3**) was prepared by cyclooligomerization of dibutylstannylene acetal of 1,3-propanediol (**1**) with 1,3-phenylenediacetyl chloride (**2**) according to a well established method (Scheme I).[13] The dimeric cyclophane was isolated in good yield from the cyclooligomerization mixture by flash column chromatography and identified by ^{1}H, ^{13}C and ESI-MS spectra and elemental analysis.

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* Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK and can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 102299 and 102300.

TABLE I

Crystal data and refinement of compounds **3** and **4**

	3	**4**
Formula	$C_{26}H_{28}O_8$	$C_{42}H_{64}Cl_4O_8Sn_2$
M_r	468.48	1076.12
Crystal size / mm	$0.4 \times 0.5 \times 0.7$	$0.6 \times 0.5 \times 0.3$
Crystal system	Triclinic	Triclinic
Space group	$P\,\bar{1}$	$P\,\bar{1}$
a / Å	5.071 (6)	8.378 (4)
b / Å	8.108 (3)	11.524 (3)
c / Å	14.640 (4)	14.009 (4)
α / °	76.46 (3)	109.16 (2)
β / °	85.35 (8)	92.64 (3)
γ / °	86.04 (7)	100.93 (3)
V / Å^3	582.5 (7)	1245.9 (8)
Z	1	1
D_C / g cm^{-3}	1.336	1.434
Radiation	Mo-Kα graphite monochromated	Mo-Kα graphite monochromated
F (000)	248	548
μ / mm^{-1}	0.099	1.261
T_{min}, T_{max}	0.94, 0.96	0.53, 0.68
T / °K	293	293
2θ range / °	5–50	5–50
Scan mode	θ–2θ	θ–2θ
Tot. reflections measured	1811	4407
Unique observed reflections [$I > 2\sigma\,(I)$]	1730	4219
Refined parameters	156	257
R [obs. reflections]	$R1 = 0.0794$, $wR2 = 0.2306$	$R1 = 0.0398$, $wR2 = 0.1068$
Extinction parameter	0.04(2)	0.0014(9)
$\Delta\rho_{max,\ min}$ / e Å^{-3}	0.412, –0.461	0.763, –1.066
Max shift / e.s.d.	0.047	0.765

TABLE II

Atomic coordinates (x, y, $z \times 10^4$) and equivalent isotropic displacement
parameters ($U_{eq} \times 10^3$ / Å^2) for **3**

Atom	x	y	z	U_{eq}
O(1)	5547(5)	2518(3)	3509(2)	68(1)
O(2)	−78(8)	−3842(5)	1142(2)	113(2)
O(3)	−3275(6)	−2058(5)	560(2)	86(1)
O(4)	−3517(5)	−1843(3)	−2370(2)	57(1)
C(1)	3889(6)	1761(4)	3268(2)	45(1)
C(2)	1974(7)	669(4)	3940(2)	54(1)
C(3)	1406(6)	−989(4)	3718(2)	44(1)
C(4)	−351(6)	−1052(4)	3053(2)	44(1)
C(5)	−1003(6)	−2569(4)	2873(2)	46(1)
C(6)	201(8)	−4071(4)	3378(3)	59(1)
C(7)	1965(8)	−4024(4)	4027(3)	63(1)
C(8)	2582(7)	−2505(5)	4204(2)	55(1)
C(9)	−3018(7)	−2579(5)	2174(3)	57(1)
C(10)	−1895(6)	−2868(4)	1249(3)	52(1)
C(11)	−2698(8)	−2370(7)	−376(3)	75(1)
C(12)	−5291(7)	−2458(5)	−765(3)	56(1)
C(13)	−5069(7)	−3041(5)	−1668(3)	58(1)
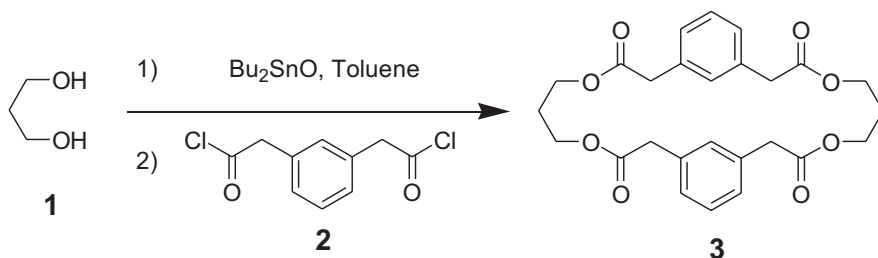
Scheme I.

When the crude cyclooligomerization mixture was washed with petro-
leum ether, cyclophane **3** (m.p. 80–82 °C), normally insoluble in this me-
dium, was extracted in solution together with the highly soluble dibutyltin
dichloride (DTC, m.p. 39–41 °C) formed in the course of the reaction. On
standing, large crystals (m.p. 64–65 °C) slowly separated from the clear so-
lution, that exhibited the ^{1}H NMR spectrum of a 1:2 mixture of **3** and DTC.

TABLE III

Atomic coordinates (x, y, $z \times 10^4$) and equivalent isotropic displacement
parameters ($U_{eq} \times 10^3$ / Å^2) for **4**

Atom	x	y	z	U_{eq}
Sn(1)	4382(1)	1079(1)	2373(1)	55(1)
Cl(1)	3988(2)	341(1)	3745(1)	72(1)
Cl(2)	6171(2)	−227(2)	1561(1)	96(1)
O(1)	2389(4)	3699(3)	6171(4)	94(1)
O(2)	7816(5)	7375(3)	6694(3)	86(1)
O(3)	10003(3)	7218(2)	5864(2)	55(1)
O(4)	9000(3)	8146(2)	3811(2)	57(1)
C(1)	2375(5)	2720(3)	6291(3)	52(1)
C(2)	3845(5)	2236(4)	6497(3)	58(1)
C(3)	5389(4)	3247(3)	6895(3)	48(1)
C(4)	6148(5)	3864(3)	6285(3)	50(1)
C(5)	7568(5)	4779(4)	6646(3)	54(1)
C(6)	8236(5)	5082(4)	7640(4)	65(1)
C(7)	7499(6)	4476(5)	8249(4)	73(1)
C(8)	6085(5)	3553(4)	7881(3)	61(1)
C(9)	8472(6)	5352(4)	5940(4)	69(1)
C(10)	8700(5)	6754(4)	6232(3)	55(1)
C(11)	10269(5)	8525(4)	5929(3)	59(1)
C(12)	11289(5)	8679(4)	5109(3)	58(1)
C(13)	10556(5)	7855(4)	4051(3)	59(1)
C(14)	6036(5)	2848(4)	2985(4)	66(1)
C(15)	6940(7)	3265(5)	2210(5)	87(2)
C(16)	5765(10)	3401(8)	1424(6)	120(2)
C(17)	6577(15)	4008(10)	743(7)	181(5)
C(18)	2281(7)	325(6)	1306(4)	90(2)
C(19)	1301(9)	−948(7)	1382(6)	119(2)
C(20)	−81(11)	−1572(9)	640(7)	142(3)
C(21)	−1004(12)	−2677(8)	801(8)	156(4)

Experimental evidence indicated that the enhanced solubility of **3** in petro-
leum ether was due to the interaction with DTC, producing a 1:2 adduct (**4**),
which crystallized from the solution.

Unambiguous structural assignment of adduct (**4**) was achieved by sin-
gle crystal X-ray analysis, which showed a complex in which DTC resides
outside the cyclophane ring because of the much too large size relative to

the ring size, but in which two of the four ester carbonyls clearly point to the tin atoms, arranged in the typical distorted trigonal bipyramid of the pentacoordinate tin.

Although ^{1}H NMR spectra of **4** in CDCl$_3$ showed no evidence of shift, as compared with the uncomplexed partners, an NMR titration of DTC with increasing amounts of **3**, following the shift of the ^{119}Sn signal, was performed in order to measure any detectable association constant. Absence of curvature in the plot of the ^{119}Sn signal shift *vs.* the host concentration demonstrated that in chloroform the association between **3** and DTC was below the detectable limit. This pointed to the conclusion that the interaction giving rise to **4** is strong enough in apolar solvents (petroleum ether), but too weak to form the complex in chloroform.

Structures

An ORTEP drawing of the X-ray structure of cyclophane **3** is reported in Figure 1. Bond distances and angles are reported in Table IV.
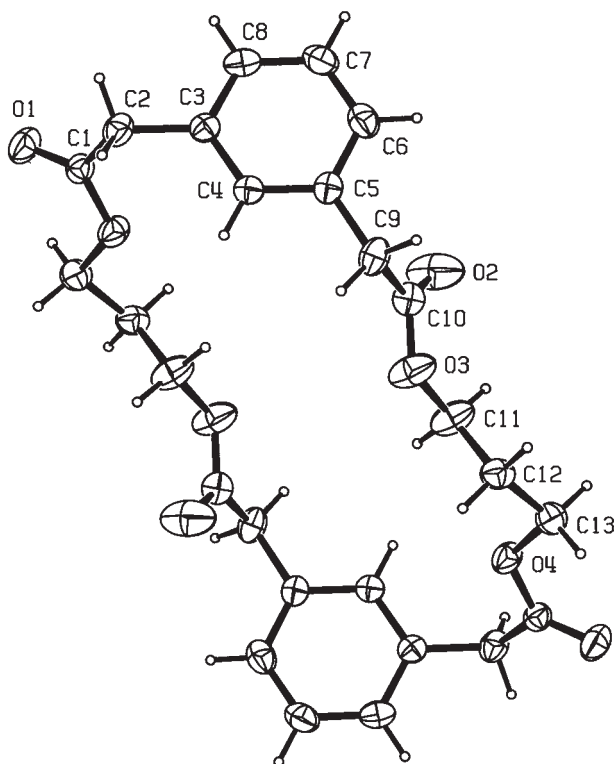

Figure 1. ORTEP drawing and atom numbering scheme of cyclophane **3**.

TABLE IV

Bond lengths / Å and angles / ° for **3**

Bond lengths / Å		Bond angles / °	
O(1)–C(1)	1.196(4)	O(1)–C(1)–O(4)'	122.9(3)
C(1)–O(4)'	1.329(4)	O(1)–C(1)–C(2)	123.8(3)
C(1)–C(2)	1.500(5)	O(4)'–C(1)–C(2)	113.2(3)
C(2)–C(3)	1.507(4)	C(1)–C(2)–C(3)	116.8(3)
C(3)–C(4)	1.384(4)	C(4)–C(3)–C(8)	118.4(3)
C(3)–C(8)	1.390(5)	C(4)–C(3)–C(2)	121.3(3)
C(4)–C(5)	1.383(4)	C(8)–C(3)–C(2)	120.3(3)
C(5)–C(6)	1.397(5)	C(5)–C(4)–C(3)	122.1(3)
C(5)–C(9)	1.506(5)	C(4)–C(5)–C(6)	118.0(3)
C(6)–C(7)	1.365(6)	C(4)–C(5)–C(9)	120.2(3)
C(7)–C(8)	1.378(5)	C(6)–C(5)–C(9)	121.8(3)
C(9)–C(10)	1.489(5)	C(7)–C(6)–C(5)	120.4(3)
C(10)–O(2)	1.197(5)	C(6)–C(7)–C(8)	121.0(3)
C(10)–O(3)	1.296(4)	C(7)–C(8)–C(3)	120.0(3)
O(3)–C(11)	1.454(5)	C(10)–C(9)–C(5)	115.0(3)
C(11)–C(12)	1.487(5)	O(2)–C(10)–O(3)	122.4(4)
C(12)–C(13)	1.498(5)	O(2)–C(10)–C(9)	125.2(3)
C(13)–O(4)	1.458(4)	O(3)–C(10)–C(9)	112.2(3)
O(4)–C(1)'	1.329(4)	C(10)–O(3)–C(11)	119.9(3)
		O(3)–C(11)–C(12)	106.8(3)
		C(11)–C(12)–C(13)	113.9(3)
		O(4)–C(13)–C(12)	108.4(3)
		C(1)'–O(4)–C(13)	116.9(2)

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

The centrosymmetric macrocycle exhibits an elongated shape, as it can be noted from distances between centrosymmetrically related atoms, ranging from 4.790(6) for O3 to 12.173(7) Å for C2. The displacements of the two pairs of carbonyl oxygen atoms with respect to the mean plane of the macrocycle, fitted on the atoms defining the ring, are 0.028(3) and 1.298(4) Å for O1 and O2, respectively, while the mean distance of the atoms defining the plane is 0.221(3) Å. The first carbonyl pair is therefore essentially coplanar with the ring, whereas the second lies significantly outside the ring plane. Phenyl rings lie instead on parallel planes, as requested by the crystallographic symmetry, which are staggered to each other in a staircase fashion.

Consequently, the macrocycle does not possess a preformed cavity, as it might be anticipated in consideration that a collapsed conformation minimizes empty space.

The structure of the centrosymmetric complex **4**, whose ORTEP drawing is reported in Figure 2, consists of one molecule of cyclophane **3** and two molecules of DTC. In Table V, intramolecular distances and angles are reported.
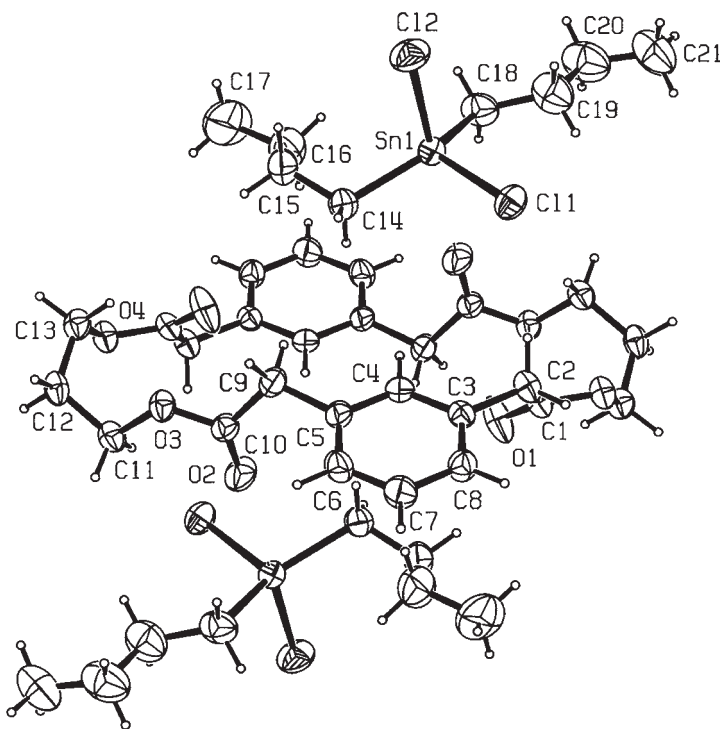

Figure 2. ORTEP drawing and atom numbering scheme of cyclophane / dibutyltin dichloride complex **4**.

The most relevant feature of the structure is the unambiguous evidence of an interaction between the tin atom of each DTC molecule and each carbonyl of one opposite pair of ester groups of the cyclophane. The Sn–O(2) distance is significantly shorter [2.865(4) Å] than the sum of tin's and oxygen's van der Waals radii (4.39 Å), and the geometry of DTC has been markedly changed by complexation, as shown by the bond angles around Sn, which have values intermediate between those of a tetrahedral and a trigonal-bipyramidal geometry (see Table V). In fact, the mean value of the

TABLE V

Bond lengths / Å and angles / ° for **4**

Bond lengths / Å		Bond angles / °	
Sn(1)–C(18)	2.100(5)	C(18)–Sn(1)–C(14)	135.5(2)
Sn(1)–C(14)	2.118(5)	C(18)–Sn(1)–Cl(1)	109.2(2)
Sn(1)–Cl(1)	2.3566(13)	C(14)–Sn(1)–Cl(1)	105.69(13)
Sn(1)–Cl(2)	2.387(2)	C(18)–Sn(1)–Cl(2)	100.8(2)
C(14)–C(15)	1.505(7)	C(14)–Sn(1)–Cl(2)	100.86(14)
C(15)–C(16)	1.509(9)	Cl(1)–Sn(1)–Cl(2)	97.88(5)
C(16)–C(17)	1.476(10)	C(15)–C(14)–Sn(1)	114.3(3)
C(18)–C(19)	1.579(9)	C(14)–C(15)–C(16)	110.9(5)
C(19)–C(20)	1.422(10)	C(17)–C(16)–C(15)	113.6(7)
C(20)–C(21)	1.449(12)	C(19)–C(18)–Sn(1)	111.2(4)
O(1)–C(1)	1.191(5)	C(20)–C(19)–C(18)	115.1(7)
C(1)–O(4)'	1.341(4)	C(19)–C(20)–C(21)	112.4(9)
C(1)–C(2)	1.499(5)	O(1)–C(1)–O(4)'	123.4(4)
C(2)–C(3)	1.509(5)	O(1)–C(1)–C(2)	126.1(4)
C(3)–C(8)	1.378(6)	O(4)'–C(1)–C(2)	110.4(3)
C(3)–C(4)	1.384(5)	C(1)–C(2)–C(3)	113.8(3)
C(4)–C(5)	1.379(5)	C(8)–C(3)–C(4)	118.8(4)
C(5)–C(6)	1.382(6)	C(8)–C(3)–C(2)	119.7(4)
C(5)–C(9)	1.515(5)	C(4)–C(3)–C(2)	121.5(3)
C(6)–C(7)	1.368(7)	C(5)–C(4)–C(3)	121.5(4)
C(7)–C(8)	1.381(6)	C(4)–C(5)–C(6)	118.8(4)
C(9)–C(10)	1.502(6)	C(4)–C(5)–C(9)	120.7(4)
C(10)–O(2)	1.193(5)	C(6)–C(5)–C(9)	120.3(4)
C(10)–O(3)	1.324(5)	C(7)–C(6)–C(5)	120.3(4)
O(3)–C(11)	1.451(5)	C(6)–C(7)–C(8)	120.7(4)
C(11)–C(12)	1.501(6)	C(3)–C(8)–C(7)	120.0(4)
C(12)–C(13)	1.498(6)	C(10)–C(9)–C(5)	115.6(3)
C(13)–O(4)	1.458(5)	O(2)–C(10)–O(3)	123.7(4)
		O(2)–C(10)–C(9)	125.8(4)
		O(3)–C(10)–C(9)	110.4(3)
		C(10)–O(3)–C(11)	118.1(3)
		O(3)–C(11)–C(12)	108.0(3)
		C(13)–C(12)–C(11)	114.6(3)
		O(4)–C(13)–C(12)	109.9(3)
		C(1)'–O(4)–C(13)	118.0(3)

Symmetry code ('): $-x + 1, -y + 1, -z + 1$.

angles between the Sn–Cl apical bond and the adjacent bonds in the complexed DTC, with respect to the corresponding angles in the uncomplexed molecule,[14] decreases from 102.8° to 99.9°; furthermore, the conformation of one of the two *n*-butyl chains substantially changes compared to free DTC, most likely in order to relieve steric hindrance between the chain and the aromatic ring of the macrocycle, giving rise to a short contact between one H atom on C15 and the non-binding carbonyl [H15b $\cdots$ O1 = 2.628(6) Å and C15–H15 $\cdots$ O1 = 137.8(6)°].

The distances of oxygen atoms O1 and O2 from the mean plane of the macrocycle, fitted on the atoms defining the ring, are 0.954(4) and 1.679(4) Å, respectively, while the mean distance of the atoms defining the plane is 0.3232(3) Å.

The terminal carbon atoms of the butyl chains are rather affected by thermal motion as provided by the significantly higher thermal displacement.

The cyclophane conformation is significantly affected by complexation as well. As can be seen in Table VI, the bigger differences for the dihedral angles, defining the ring of the free (**3**) and complexed (**4**) cyclodimeric propylene-1,3-phenylenediacetate macrocycle, concern the propyl chains which have an open shape in **3** and assume an U conformation in **4**.

Correspondingly, the most distant centrosymmetrically related atoms in **4** are the propylene C12 and C12′ (12.460(7) Å), as compared with the C2 and C2′ carbon atoms adjacent to the phenyl rings (12.173 Å) in the free host **3**. More important, the binding carbonyls assume an orientation roughly orthogonal to the adjacent phenyl rings, and point to the tin atoms

TABLE VI

Dihedral angles / ° defining the ring for compounds **3** and **4**

	3	**4**
C(1)–C(2)–C(3)–C(4)	−79.8(4)	−69.1(5)
C(2)–C(3)–C(4)–C(5)	−176.6(3)	−179.3(4)
C(3)–C(4)–C(5)–C(9)	177.2(3)	173.9(4)
C(4)–C(5)–C(9)–C(10)	104.5(4)	121.6(4)
C(5)–C(9)–C(10)–O(3)	−146.9(3)	154.1(4)
C(9)–C(10)–O(3)–C(11)	−171.5(3)	170.3(3)
C(10)–O(3)–C(11)–C(12)	137.7(4)	−155.6(4)
O(3)–C(11)–C(12)–C(13)	−171.0(3)	58.3(5)
C(11)–C(12)–C(13)–O(4)	−60.5(4)	61.2(5)
C(12)–C(13)–O(4)–C(1A)	−156.1(3)	111.4(4)
C(13A)–O(4A)–C(1)–C(2)	172.5(3)	−177.9(3)

along the direction of the apical Sn–Cl bond as a second apical ligand. This conformational change is achieved through a tilt of phenyl rings, (the angle between phenyl rings and the cyclophane mean plane shifts from 52.55(8)° in **3** to 26.32(9)° in **4**), inducing an overall flattening of the cyclophane mean plane, so as to adapt to the incoming ligand.

In conclusion, although the size of the cyclophane ring does not allow inclusion of the DTC molecule, complexation nevertheless occurs through the interaction of the ester carbonyl with the Lewis acidic tin center of the DTC ligand. The participation of the ester functionality in binding has thus been unambiguously demonstrated by crystallographic evidence.

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SAŽETAK

Kristalna i molekulska struktura ciklodimernog propilen-1,3-fenilendiacetata i njegova di-*n*-butilkositar dikloridnog kompleksa

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Kao dio sustavnog izučavanja priprave i vezujućih svojstava niza ciklofanskih estera difrakcijom rentgenskih zraka određena je kristalna struktura ciklodimernog propilen-1,3-fenilendiacetata, $(C_{26}H_{28}O_8)$ (**3**) i njegova di-*n*-butilkositrova dikloro--kompleksa, $\{(C_{26}H_{26}O_8)[SnCl_2(C_4H_9)_2]_2\}$ (**4**). Kristali makrocikličkog spoja (**3**) pripadaju triklinskom sustavu, prostornoj grupi $P\bar{1}$ s parametrima elementarne ćelije: $a = 5,071(6)$, $b = 8,108(3)$, $c = 14,640(4)$ Å, $\alpha = 76,46(3)$, $\beta = 85,35(8)$, $\gamma = 86,04(7)°$, $Z = 1$. Slično tomu, kositrov kompleksni spoj s propilen-1,3-fenilendiacetatom (**4**) kristalizira u istom kristalnom sustavu s istom prostornom grupom i parametrima elementarne ćelije: $a = 8,378(4)$, $b = 11,524(3)$, $c = 14,009(4)$ Å, $\alpha = 109,16(2)$, $\beta = 92,64(2)$, $\gamma = 100,93(3)°$, $Z = 1$.

Najvažnija značajka strukture kompleksa jest nedvojbeno međudjelovanje kisikovih i kositrovih atoma dvaju ciklofanskih esterskih karbonila i dviju molekula Bu_2SnCl_2, međusobno udaljenih $2,865(4)$ Å. To međudjelovanje znatno utječe na uobičajeno tetraedarsko okruženje organokositrova(IV) metalnog centra, mijenjajući ga u nepravilno trigonsko bipiramidsko s duljom apikalnom međuatomskom udaljenošću svojstvenom pentakoordiniranim stanatnim kompleksima. Konformacije ciklofana, kako u slobodnom ligandu tako i u metalnom kompleksu, potanko su opisane.