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Preparation and X-Ray Structure of [2.2](5,6)Indanocyclophane

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The title compound **3** was prepared by pyrolysis of the corresponding bis-sulfone **2** and subjected to X-ray structural analysis; space group $P\bar{1}$, $a = 477.0(1)$, $b = 625.6(2)$, $c = 1363.6(3)$ pm, $\alpha = 82.79(2)$, $\beta = 83.43(2)$, $\gamma = 78.18(3)^\circ$, $Z = 1$, $R = 0.058$ for 900 reflections. The molecule contains a crystallographic symmetry centre, thus confirming the *anti* configuration.

Although there is some controversy in the literature concerning the preferred conformation of [3.3]orthocyclophanes, recent investigations increasingly favour the *anti*-arrangement, as shown for 2,11-dithia-[3.3](5,6)indano-orthocyclophane (**1**) [1]; see Fig. 1, top). In order to investigate the influence of shorter molecular bridges on the geometry of phanes of this general type [1, 2] we prepared the [2.2]orthocyclophane (**3**) by the pyrolysis of its sulfone (**2**) [2]. The results of an X-ray structure analysis of **3** are reported here.

Experimental

Preparation of [2.2](5,6)indanocyclophane (**3**)

2.96 g (7.11 mmol) of the bis-sulfone (**2**) [2] was pyrolysed in a double oven system as described by

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Staab and Haenel [3]. The temperature of the preheating zone was gradually increased from 250 to 400 °C in the course of the pyrolysis, whereas the decomposition zone was heated to 530 °C. The pyrolysis system was connected *via* two cold traps (maintained at liquid nitrogen temperature) to a high-vacuum line that held a pressure of 10^{-1} to 10^{-2} torr throughout the decomposition process. The raw pyrolysate was dissolved in chloroform and purified by silica gel chromatography using dichloromethane/cyclohexane (1:1) as the eluent. Yield: 0.76 g (37%) of **3** as colourless needles from pentane, m.p. 255–257 °C.

^1H NMR (CDCl_3 , 400.1 MHz, int. TMS): $\delta = 6.93$ (s, 4H, H-4, H-7, H-12, H-15), 2.96 (s, 8H, H-1, H-2, H-9, H-10), 2.81 (t, 8H, $J_{17,18} = J_{18,19} = J_{20,21} = J_{21,22} = 7.4$ Hz, H-17, H-19, H-20, H-22), 2.01 (4H, t, $J_{17,18} = J_{18,19} = J_{20,21} = J_{21,22} = 7.4$ Hz, H-18, H-21). – ^{13}C NMR (CDCl_3 , 100.6 MHz, int. CDCl_3): $\delta = 141.88$ (s, C-5, C-6, C-13, C-14), 139.40 (s, C-3, C-8, C-11, C-16), 125.65 (d, C-4, C-7, C-12, C-15), 35.94 (t, C-1, C-2, C-9, C-10), 32.46 (t, C-17, C-19, C-20, C-22), 25.45 (t, C-18, C-21). – IR (KBr): $\nu = 3000$ m, 2950 s, 2925 m, 2895 m, 2860 m, 2840 m, 1488 m, 1452 m, 1438 m, 880 s cm^{-1} . – UV (acetonitrile): λ_{max} ($\lg \epsilon$) = 283 (3.71), 277 (3.65), 273 (3.67), 268 (3.57), 265 (3.51, sh), 217 (4.36, sh), 206 nm (4.60). – MS (70 eV): m/z (%) = 288 (65, M^+), 274 (23), 273 (100), 259 (22), 156 (23), 145 (88), 144 (37), 143 (36), 129 (55), 128 (54), 116 (20), 115 (40).

$\text{C}_{22}\text{H}_{24}$ (288.43)

Calcd C 91.61 H 8.39,

Found C 91.51 H 8.34.

X-Ray structure determination of **3**

Recrystallization of **3** from ethanol/benzene (1:1) provided single crystals in the form of flat needles. *Crystal data*: Triclinic, space group $P\bar{1}$, $a = 477.0(1)$, $b = 625.6(2)$, $c = 1363.6(3)$ pm, $\alpha = 82.79(2)$, $\beta = 83.43(2)$, $\gamma = 78.18(3)^\circ$, $U = 0.3934$ nm 3 , $Z = 1$, $D_x = 1.22$ Mg m $^{-3}$, $F(000) = 156$, $\lambda(\text{Mo-K}\alpha) = 71.069$ pm, $\mu = 0.06$ mm $^{-1}$, $T = 293$ K.

Data collection and reduction: A crystal $0.85 \times 0.36 \times 0.04$ mm was mounted on a glass fibre. 2405 intensities were recorded on a Siemens four-circle diffractometer (type R3) using monochromated Mo-K α radiation ($2\theta_{\text{max}} 50^\circ$). Merging equivalents gave 1398 unique reflections ($R_{\text{int}} 0.034$), of which 900 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens SHELXTL PLUS). Cell constants were refined from 29 values

of 29 reflections in the range $20-22^\circ$, measured on a Stoe-Siemens diffractometer.

Structure solution and refinement: The structure was solved by routine direct methods and subjected to anisotropic full-matrix refinement on F . Hydrogen atoms were included using a riding model. The final R value was 0.058, with R_w 0.061. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0007 F^2$. 100 parameters, S 1.8, max. Δ/σ 0.001, max. $\Delta\rho$ $0.22 \times 10^{-6} \text{ e pm}^{-3}$.

Final atom coordinates are given in Table I, with derived bond lengths and angles in Table II*.

* Further details may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, by quoting the Registry-No. CSD 54435, the names of the authors and the journal citation.

Table I. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for compound **3**.

	x	y	z	$U(\text{eq})^*$
C(2)	-1878(5)	7268(4)	4406(2)	39(1)
C(3)	595(5)	6462(4)	3672(2)	35(1)
C(4)	1560(6)	7927(4)	2914(2)	40(1)
C(5)	3828(6)	7230(4)	2227(2)	42(1)
C(6)	5198(6)	5046(4)	2291(2)	42(1)
C(7)	4272(5)	3573(4)	3042(2)	39(1)
C(8)	1982(5)	4243(4)	3738(2)	35(1)
C(9)	1041(6)	2580(4)	4541(2)	38(1)
C(17)	5177(7)	8527(5)	1360(2)	61(1)
C(18)	7198(8)	6807(5)	799(2)	68(1)
C(19)	7631(6)	4670(5)	1481(2)	52(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

C(2)–C(3)	150.3(3)	C(2)–C(9i)	155.2(4)
C(3)–C(4)	139.5(3)	C(3)–C(8)	140.7(3)
C(4)–C(5)	138.4(3)	C(5)–C(6)	138.5(4)
C(5)–C(17)	150.7(4)	C(6)–C(7)	138.5(3)
C(6)–C(19)	151.1(4)	C(7)–C(8)	139.4(3)
C(8)–C(9)	150.9(3)	C(17)–C(18)	151.1(4)
C(18)–C(19)	152.1(4)		
C(3)–C(2)–C(9i)	115.0(2)	C(2)–C(3)–C(4)	120.0(2)
C(2)–C(3)–C(8)	121.1(2)	C(4)–C(3)–C(8)	118.9(2)
C(3)–C(4)–C(5)	121.2(2)	C(4)–C(5)–C(6)	119.9(2)
C(4)–C(5)–C(17)	129.5(2)	C(6)–C(5)–C(17)	110.6(2)
C(5)–C(6)–C(7)	119.6(2)	C(5)–C(6)–C(19)	110.8(2)
C(7)–C(6)–C(19)	129.6(2)	C(6)–C(7)–C(8)	121.3(2)
C(3)–C(8)–C(7)	119.0(2)	C(3)–C(8)–C(9)	121.4(2)
C(7)–C(8)–C(9)	119.5(2)	C(8)–C(9)–C(2i)	115.4(2)
C(5)–C(17)–C(18)	104.3(2)	C(17)–C(18)–C(19)	107.9(2)
C(6)–C(19)–C(18)	103.7(2)		

Table II. Bond lengths (pm) and angles ($^\circ$) for compound **3**.

Symmetry operator (i): $-x, 1-y, 1-z$.

Discussion

The molecule of **3** is exactly centrosymmetric, and its *anti* configuration is clearly recognizable in Fig. 1. The aromatic rings are parallel (by symmetry); in **1** the corresponding dihedral angle is 2° .

The bond lengths of **3** are normal; the rather short single bonds in the five-membered ring mirror similar values in **1**. Since the thermal parameters are not unusually large (all $< 700 \text{ pm}^2$), no extreme libration effects would be expected. Attempts to apply a rigid-body libration correction were unsuccessful, presumably because of appreci-

able flexibility of the molecule (R_{lib} 0.1). The bond angles in the bridges ($115.0, 115.4^\circ$) are wider than standard sp^3 angles, but this is a general feature of cyclophanes; in some [2.2]paracyclophane derivatives angles as large as 120° are observed.

The packing diagram (Fig. 2) shows that the molecules of **3** are related by translation only. There are no intermolecular $\text{C}\cdots\text{C}$ contacts $< 360 \text{ pm}$.

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Fig. 1. The structures of **1** ([1], top) and **3** (this work, bottom) in the crystal, showing the *anti* configuration and (for **3**) the numbering scheme of the asymmetric unit. (The extended numbering scheme, including the second half of the molecule, is used for the spectroscopic data in the text.) Radii are arbitrary.

Fig. 2. Stereographic packing diagram of **3** viewed along the short *a* axis. H atoms omitted for clarity; radii arbitrary.

[1] For a summary of the relevant literature see Part 33: G. Bodwell, L. Ernst, H. Hopf, and P. G. Jones, *Tetrahedron Lett.* **30**, 6005 (1989).

[2] G. Bodwell, Ph. D. Dissertation, Braunschweig (1989).

[3] H. A. Staab and M. W. Haenel, *Chem. Ber.* **106**, 2190 (1973); cf. M. W. Haenel and A. Flatow, *Chem. Ber.* **112**, 249 (1979).