Transition Metal Catalyzed Oxidations, 3[1]

Reaction of 4-Hydroxy[2.2]paracyclophane with the Mimoun Molybdenum Oxodiperoxo Complex $[Mo(O_2)_2O] \cdot Py \cdot HMPT$

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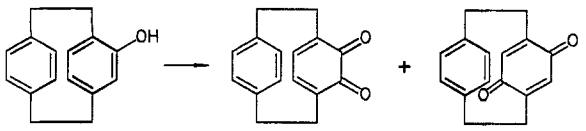
Treatment of 4-hydroxy[2.2]paracyclophane (**1**) with the Mimoun molybdenum oxodiperoxo complex $[Mo(O_2)_2O] \cdot Py \cdot HMPT$ gives 3,4-dihydro-3-hydroxy-4-oxo[2.2]paracyclophane (**4**). This dienone dimerizes at room temperature to afford the Diels-Alder adduct **5**, whose structure was confirmed by X-ray analysis.

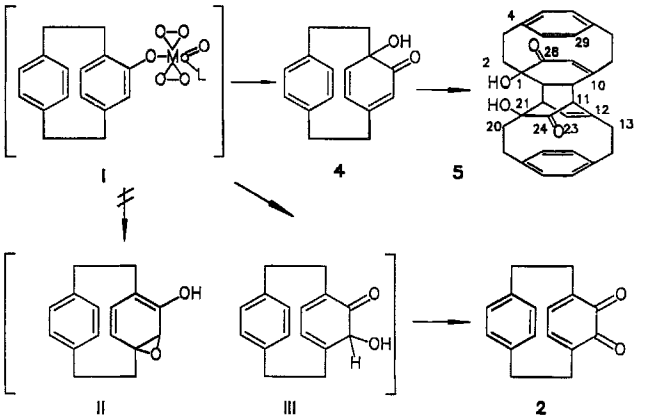
Recently, we have described the specific oxidation of phenols to *ortho*-quinones using *tert*-butyl hydroperoxide and transition metal complexes or the Mimoun molybdenum oxodiperoxo complex $[Mo(O_2)_2O] \cdot Py \cdot HMPT$[2]. This reaction is initiated by replacement of one ligand of the complex by the phenol, as depicted in **I**, followed by oxygenation and dehydrogenation processes[3]. The exact mechanism of the oxygen transfer is as yet unknown. In this paper the reaction of 4-hydroxy[2.2]paracyclophane (**1**) with $[Mo(O_2)_2O] \cdot Py \cdot HMPT$ is described; it provides insight into the nature of the oxygen-transfer step and yields a structurally new type of paracyclophane dimer.

Miyahara et al.[4] have described the isolation of a 1:1 mixture of the *ortho*-, **2**, and the *para*-quinone **3** obtained by the reaction of **1** with diphenylselenic anhydride (Barton's reagent[5]).



1 2 3

In an attempt to improve the yield of **2**, which is needed for further transformations, **1** was treated with the Mimoun molybdenum complex. However, only small amounts (< 1%) of the deep red *ortho*-quinone **2** are formed with two equivalents of $[Mo(O_2)_2O] \cdot Py \cdot HMPT$ at 0°C in CH_2Cl_2, the major part of the product mixture consisting of two polar colorless compounds. The ratio of the new products depends strongly on the reaction conditions and the workup procedure. It soon became clear from the mass spectra that the less polar product is monomeric and an intermediate in the formation of the stable, dimeric oxidation product. Traces of acid or Lewis acid catalyze the dimerization. For instance, the NMR measurements in $CDCl_3$ have to be carried out immediately after termination of the oxidation since the monomer decomposes under these conditions (ca. 40% after 14 h). The monomer is more stable if the workup is carried out under neutral rather than acidic conditions, the molybdenum catalyst being removed by rapid filtration through a column of silica gel. In this case the monomer can be isolated in 75% yield. On the basis of spectral data (see experimental section) this compound is assigned the structure **4**. Hydroxyketones of this type have previously been discussed as reaction intermediates in the epoxidation of various phanes[6,7], but they have never been isolated. Interestingly, related hydroxylation products have been identified recently by Effenberger et al.[8] in the autoxidation of phloroglucinophanes. The structural assignment of **4** is supported by the structure of the dimer as determined by X-ray analysis. As shown in Figure 1 this second compound has structure **5**, i.e. it is formally a Diels-Alder dimer of **4**. For the formation of **5**, whose very complex NMR spectral data (experimental section) clearly show its highly asymmetric nature, it must be assumed that the terminal double



I 4 5

II III 2

  0009–2940/90/0808–1729 $ 3.50+.25/0

bond of one molecule of **4** functions as the dienophile that adds to the conjugated system of a second hydroxyketone molecule.

The atomic coordinates and selected bond lengths and angles of **5** are listed in Tables 1 to 3[9]. The X-ray structure analysis confirms the formation of a dimeric product and establishes its connectivity (Figure 1). As is usual in cyclophanes, the aromatic rings are distorted; the bridgehead atoms C-4, C-7, C-15, C-18 lie 17–18 pm out of the plane defined by the other four ring atoms. The (formally sp^3) bond angles in cyclophane bridges involving further ring coupling are often widened to ca. 120°; here, we observe an asymmetric relaxation of the bridge strain in that the carbon atoms α to the aromatic rings display normal sp^3 angles (C-3 108.8, C-8 108.9, C-14 108.6, C-19 107.9°), whereas the corresponding angles α to the Diels-Alder-coupled rings are still very wide (C-2 122.3, C-9 116.6, C-13 119.1, C-20 120.4°). The formally single bonds C-1 ··· C-2 158.1, C-10a ··· C-11 159.6 and C-10a ··· C-22a 157.4 pm are long. The molecules are linked parallel to the *y* axis by hydrogen bonds, with O-3 ··· O-2 285, HO-3 ··· O-2 201 pm (symmetry operator of O-2: $x, -1+y, z$).

A reinvestigation of the reaction of **1** with diphenylselenic anhydride has revealed that **5** is also formed to some extent with Barton's reagent.

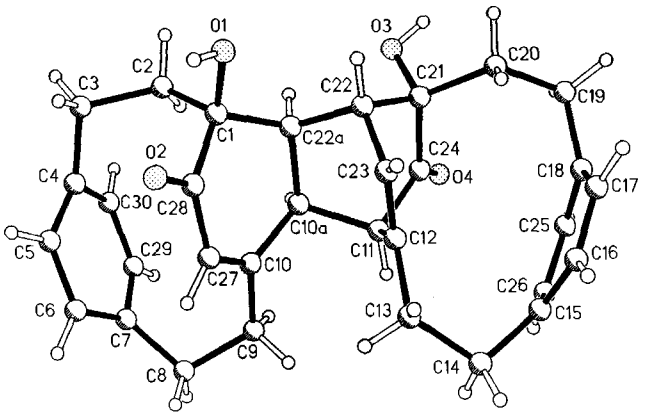


Figure 1. The molecule of compound **5** in the crystal

The formation of the α-hydroxy ketone **4** sheds some light on the nature of the oxygen-transfer step in the novel *ortho*-quinone synthesis[3]. The exclusive formation of the regioisomer **4** and small amounts of the *ortho*-quinone **2** shows that oxygen transfer occurs in both positions *ortho* to the phenolic group. The oxygenation of the *meta*-position, providing an intermediate such as **II** similar to those formed in the Sharpless epoxidation of allylic double bonds[10–13], can be ruled out. An analogy may be seen in the hydroxylation of enolates to α-hydroxy ketones using $[Mo(O_2)_2O]\cdot$ Py · HMPT, a reaction introduced by Vedejs[14] and exploited more recently by Tamm et al.[15] for asymmetric hydroxylations of chiral esters. The two possible reaction sites in *ortho*-position to the phenolic group of **1** differ markedly in reactivity. As is well-known from other reactions of [2.2]paracyclophanes, the bridgehead positions of these strained aromatic compounds are much more reactive than the non-alkylated carbon atoms[16]. Thus, oxygen transfer to yield **4** is the predominant reaction path. Although the hydroxylation of the bridgehead results in considerable release of strain[6,7,16], the reactivity of the dienone system is still high enough to induce a Diels-Alder reaction at room temperature to form **5**. For the formation of the *ortho*-quinone **2** we propose **III** as the reaction intermediate.

The facile hydroxylation of the phenolic paracyclophane **1** encourages further studies of the oxygenation of alkylated naphthols including the use of chiral molybdenum complexes[17,18].

Table 1. Atomic coordinates (× 10^4) and equivalent isotropic temperature factors ($pm^2 \times 10^{-1}$) for compound **5**

C(1)	6045(2)	5562(3)	1866(2)	39(1)
C(2)	6135(3)	5474(4)	2628(2)	51(1)
C(3)	6184(3)	6901(4)	3057(2)	55(1)
C(4)	7241(3)	7568(4)	3072(2)	50(1)
C(5)	7429(3)	8935(4)	2783(2)	48(1)
C(6)	8359(3)	9191(4)	2526(2)	46(1)
C(7)	9101(3)	8073(4)	2556(2)	46(1)
C(8)	9727(3)	7830(4)	1994(2)	52(1)
C(9)	9321(3)	6400(4)	1616(2)	48(1)
C(10)	8169(2)	6120(3)	1579(2)	35(1)
C(10A)	7821(2)	4504(3)	1579(2)	33(1)
C(11)	8116(2)	3767(3)	920(2)	34(1)
C(12)	7480(2)	4546(3)	376(2)	35(1)
C(13)	7922(3)	5594(4)	-113(2)	47(1)
C(14)	8676(3)	4942(4)	-574(2)	50(1)
C(15)	8401(3)	3332(4)	-711(2)	47(1)
C(16)	7443(3)	2978(5)	-1022(2)	53(1)
C(17)	6945(3)	1672(4)	-867(2)	52(1)
C(18)	7408(3)	690(4)	-401(2)	47(1)
C(19)	6736(3)	-192(4)	9(2)	51(1)
C(20)	6106(3)	942(4)	373(2)	46(1)
C(21)	6625(2)	1854(3)	956(2)	36(1)
C(22)	6172(2)	3467(3)	983(2)	36(1)
C(22A)	6643(2)	4201(3)	1622(2)	35(1)
C(23)	6477(2)	4371(4)	420(2)	38(1)
C(24)	7802(3)	2111(4)	989(2)	35(1)
C(25)	8448(3)	862(4)	-226(2)	50(1)
C(26)	8939(3)	2190(4)	-377(2)	50(1)
C(27)	7484(2)	7234(4)	1505(2)	36(1)
C(28)	6417(3)	7033(4)	1588(2)	37(1)
C(29)	9007(3)	6902(4)	2989(2)	56(1)
C(30)	8099(3)	6656(5)	3246(2)	60(2)
O(1)	4983(2)	5419(3)	1650(1)	56(1)
O(2)	5773(2)	8043(3)	1457(1)	54(1)
O(3)	6462(2)	1095(2)	1541(1)	50(1)
O(4)	8415(2)	1137(3)	1153(1)	48(1)

Table 2. Bond lengths (pm) for compound **5**

C(1)-C(2)	158.1 (5)	C(1)-C(22A)	154.8 (4)
C(1)-C(28)	152.4 (5)	C(1)-O(1)	142.6 (4)
C(2)-C(3)	154.5 (5)	C(3)-C(4)	150.1 (5)
C(4)-C(5)	138.4 (5)	C(4)-C(30)	140.2 (6)
C(5)-C(6)	139.0 (5)	C(6)-C(7)	138.5 (5)
C(7)-C(8)	150.3 (5)	C(7)-C(29)	138.6 (5)
C(8)-C(9)	155.9 (5)	C(9)-C(10)	152.1 (5)
C(10)-C(10A)	150.2 (4)	C(10)-C(27)	133.1 (4)
C(10A)-C(11)	159.6 (4)	C(10A)-C(22A)	157.4 (4)
C(11)-C(12)	150.9 (4)	C(11)-C(24)	153.5 (4)
C(12)-C(13)	152.9 (5)	C(12)-C(23)	133.1 (4)
C(13)-C(14)	155.0 (5)	C(14)-C(15)	149.2 (5)
C(15)-C(16)	139.0 (5)	C(15)-C(26)	138.3 (5)
C(16)-C(17)	138.0 (6)	C(17)-C(18)	139.8 (5)
C(18)-C(19)	149.9 (5)	C(18)-C(25)	138.2 (5)
C(19)-C(20)	154.1 (5)	C(20)-C(21)	156.0 (5)
C(21)-C(22)	154.9 (4)	C(21)-C(24)	155.0 (5)
C(21)-O(3)	142.3 (4)	C(22)-C(22A)	155.5 (4)
C(22)-C(23)	150.3 (5)	C(24)-O(4)	120.6 (4)
C(25)-C(26)	139.1 (5)	C(27)-C(28)	143.3 (5)
C(28)-O(2)	124.1 (4)	C(29)-C(30)	136.4 (6)

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Experimental

For general remarks see ref.[3]

4-Hydroxy[2.2]paracyclophane (**1**): Although several methods for the preparation of **1** have been described[19–21] none of these is satisfactory from the preparative viewpoint. The approach described here[22] allows the preparation of gram quantities of **1**; we also present the complete set of spectroscopic data of this important cyclophane intermediate, since the published data do not satisfy modern requirements. 1.14 g (4.0 mmol) of 4-bromo[2.2]paracyclophane[20] is placed into a 250-ml flask equipped with reflux condenser, septum, and magnetic stirring bar. Air and moisture in the reaction vessel are removed by several pumping and venting (with dry N_2) cycles, and finally 50 ml of dry ether is directly distilled into the flask from a supply flask where it has been refluxed over sodium/benzophenone. The solution is cooled to 0°C, and 5.33 ml of an *n*-butyllithium solution in hexane (1.5 M, 8 mmol) is added with a syringe. The solution turns yellow, and after stirring at room temp. for 20 min a white solid precipitates. The solution is cooled to 0°C again, and 0.90 ml (8 mmol) of trimethyl borate is added. After stirring at room temp. for 1 h the reaction mixture has become clear, and 2 ml of an 0.5 M aqueous solution of sodium hydroxide (1 mmol) is added, followed by 1.5 ml of 30% hydrogen peroxide solution (ca. 15 mmol). The temperature of the reaction mixture increases to about 40°C, and evolution of a gas is noted. After aqueous workup the raw product mixture is separated by column chromatography on silica gel using CH_2Cl_2 as eluent; fraction 1: [2.2]paracyclophane, 200 mg (24%); fraction 2: 4-hydroxy[2.2]paracyclophane (**1**), 660 mg (74%), m.p. 225°C (ref.[19] 225–229°C). – IR (KBr): $\tilde{\nu}$ = 3600–3200 cm^{-1} (br, OH), 2940 (vs), 1570 (m), 1420 (s), 1270 (m), 1170 (m), 1140 (m), 1100 (m), 1090 (m), 800 (m), 720 (s), 660 (m). – UV (ethanol): λ_{max} (lg ε) = 206 nm (4.26), 225 (4.15), 290 (2.87), 311 (2.81). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.60 bis 3.35 (m, 8H, 1-, 2-, 9-, 10-H), 5.50 (d, $J_{5,7}$ = 1.5 Hz, 1H, 5-H), 6.25 (dd, $J_{7,5}$ = 1.6, $J_{7,8}$ = 7.7 Hz, 1H, 7-H), 6.37 (d, $J_{8,7}$ = 7.7 Hz, 1H, 8-H), 6.38 (dd, $J_{12,13}$ = 7.8, $J_{12,16}$ = 1.9 Hz, 1H, 12-H), 6.43 (dd, $J_{13,12}$ = 7.8, $J_{13,15}$ = 1.9 Hz, 1H, 13-H), 6.54 (dd, $J_{16,15}$ = 7.8, $J_{16,12}$ = 1.9 Hz, 1H, 16-H), 6.98 (dd, $J_{15,16}$ = 7.8, $J_{15,13}$ = 1.9 Hz, 1H, 15-H). – ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 30.54 (t, C-2), 33.30, 34.27, 34.77 (3 × t, X-1, -9, -10), 122.03, 124.48, 124.91, 127.40, 131.32, 132.20, 133.04 (7 × d, C-5, -7, -8, -12, -13, -15, -16), 134.90, 138.27, 139.08, 141.44 (4 × s, C-3, -6, -11, -14), 153.14 (s, C-4).

3,4-Dihydro-3-hydroxy-4-oxo[2.2]paracyclophane (**4**): A solution of 224 mg (1.0 mmol) of **1** in 30 ml of dry CH_2Cl_2 is stirred at 0°C under nitrogen for 8 h with 868 mg (2.0 mmol) of $[Mo(O_2)_2O]\cdot$ Py · HMPA[2]. The solution is filtered through a short silica gel column to remove the molybdenum catalyst and then separated by thick-layer chromatography (silica gel, CH_2Cl_2, two developments) to afford 25 mg (10%) of the dimer **5** from the less polar fraction (data see below). The more polar zone contains 180 mg (75%) of hydroxy ketone **4**; m.p. 146°C (CH_2Cl_2/diethyl ether). – IR (KBr): $\tilde{\nu}$ = 3328 cm^{-1} (br, OH), 2941 (m), 2929, 1648 (vs), 1631 (vs), 1561 (m), 1389 (m), 1172 (m), 1049 (s), 870 (m), 582 (m). – UV (ethanol): λ_{max} (lg ε) = 229 nm (3.92), 307 (3.19). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.34–2.41 (m, 1H), 2.46–2.53 (m, 3H), 2.64–2.72 (m, 1H), 2.68 (s, 1H, OH), 2.81–2.88 (m, 1H), 3.02–3.08 (m, 1H), 3.15–3.22 (m, 1H), 5.17 (d, $J_{5,7}$ = 1.4 Hz, 1H, 5-H), 5.63 (d, $J_{7,8}$ = 9.7 Hz, 1H, 8-H), 5.73 (dd, $J_{7,8}$ = 9.7, $J_{5,7}$ = 1.4 Hz, 1H, 7-H), 6.87 (dd, J_{ortho} = 7.8, J_{meta} = 1.5 Hz, 1H, Ar-H), 6.94 (dd, J_{ortho} = 7.8, J_{meta} = 1.5 Hz, 1H, Ar-H), 7.01 (dd, J_{ortho} = 7.8, J_{meta} = 1.7 Hz, 1H, Ar-H), 7.15 (dd, J_{ortho} = 7.8, J_{meta} = 1.7 Hz, 1H, Ar-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 30.51, 33.43, 36.54, 45.81 (4 × t), 72.13 (s), 129.06, 129.88, 130.14, 130.87, 132.65, 134.41, 137.89 (7 × d), 139.52, 140.59, 152.96, 201.80 (4 × s). – MS (70 eV): *m/z* (%) = 240 (11) [M^+], 222 (2) [$M^+ - H_2O$], 212 (4), [M^+ – CO], 198 (3), 183 (2), 146 (48), 131 (5), 118 (20), 117 (28), 104 (100), 95 (15), 91 (12), 78 (15), 77 (13).

$C_{16}H_{16}O_2$ (240.3) Calcd. C 79.97 H 6.71
Found C 79.22 H 6.70

1,2,3,8,9,10a,11,13,14,19,20,21,22,22a-Tetradecahydro-1,21-dihydroxy-1,10-ethanylylidene-4,7:15,18-dietheno-11,21-methano-22,12-methylenocyclododecacyclotetradecene-24,28-dione (**5**): A solution of 284 mg (1.27 mmol) of **1** in 30 ml of dry CH_2Cl_2 is stirred under nitrogen at 0°C for 5 h with 1.101 g (2.54 mmol) of $[Mo(O_2)_2O]\cdot$ Py · HMPT[2]. After addition of 30 ml of 10% aqueous sulfuric acid the mixture is stirred at room temp. for another 1 h. The organic phase is separated and the aqueous phase extracted twice with 20 ml of CH_2Cl_2. The combined organic phases are dried ($MgSO_4$), the solvent is removed at reduced pressure and the residue separated by thick-layer chromatography. 69 mg (24%) of the starting material is recovered from the unpolar fraction. The polar fraction, containing a mixture of **4** and **5**, is kept in 5 ml of chloroform for 5 d, during which time the remaining monomer **4** dimerizes to **5**. Crystallization from diethyl ether affords 208 mg (74%) of **5**; m.p. 192°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3409 cm^{-1} (br, OH), 2916 (m), 1719 (s), 1635 (s), 1503 (w), 1438 (m), 1047 (m), 813 (m), 726 (m). – UV: λ_{max} (lg ε) = 208 nm (4.43), 232 (4.19), 255 (sh), 302 (sh). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.40–1.46 (m, 1H), 1.55–1.65 (m, 1H), 1.96–2.07 (m, 2H), 2.19–2.76 (m, 13H), 2.87–2.93 (m, 2H), 2.95 (s, 1H, OH), 3.18 (s, 1H, OH), 3.26–3.32 (m, 1H), 5.10 (s, 1H), 5.28–5.30 (m, 1H), 6.56 (dd, 1H, Ar-H), 6.81–7.05 (m, 7H, Ar-H). – ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 30.53, 30.94, 31.97, 33.41, 36.02, 37.56 (6 × t), 37.87 (d), 48.28 (d), 49.57 (t), 51.53 (t), 52.31 (d), 55.76 (d), 72.17 (s), 75.03 (s), 127.56, 128.26, 130.33, 130.62, 130.62, 131.12, 131.66 (7 × d), 132.00 (s), 132.00 (d), 133.30 (d), 133.50 (s), 134.11 (d), 139.21, 139.63, 140.21, 156.14 (4 × s). – MS (70 eV): *m/z* (%) = 480 (18) [M^+], 462 (2) [$M^+ - H_2O$], 452 (27) [M^+ – CO], 434 (8) [$M^+ - H_2O$, – CO], 330 (11), 240 (45), 224 (43), 146 (63), 123 (30), 118 (51), 117 (60), 104 (100), 91 (27). – MS [CI, pos. (NH_3)]: *m/z* (%) = 498 (24) [M + NH_4^+], 481 (44) [M + H^+], 463 (53) [M^+ – OH], 445 (29), 258 (79), 241 (100), 240 (98), 224 (23).

$C_{32}H_{32}O_4$ (480.6) Calcd. C 79.97 H 6.71
Found C 79.72 H 7.08

X-ray Structure Determination of Compound **5**: Colorless prisms are obtained from dichloromethane/petroleum ether. – *Crystal data:* $C_{32}H_{32}O_4$, M_r = 480.6. Monoclinic, space group $P2_1/c$, a = 1307.1(5), b = 886.1(4), c = 2080.2(8) pm, β = 95.33(2)°, U = 2.399 nm^3, Z = 4, D_x = 1.331 Mg m^{-3}, λ(Mo-K_α) = 71.069 pm, μ = 0.08 mm^{-1}, F(000) = 1024, T = 291 K. – *Data collection and reduction:* A crystal 0.5 × 0.25 × 0.25 mm was mounted in a glass capillary. 4162 intensities were measured on a Siemens R3 four-circle diffractometer using monochromatic Mo-K_α radiation (2 Θ_{max} 50°). Merging equivalents gave 4190 independent reflections (R_{int} 0.026), of which 2289 with $F > 3\sigma(F)$ were used for all calculations (program system „Siemens Shelx-Plus"). The orientation matrix was refined from diffractometer angles of 50 reflections in the 2Θ range 20–23°. – *Structure elucidation and refinement:* The structure was determined by direct methods and refined anisotropically to R = 0.049, wR = 0.054. Hydrogen atoms were included in the refinement using a riding model. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0006F^2$. 325 parameters, S = 1.1, max. Δ/σ 0.001, max. $\Delta\varrho$ 0.15 × 10^{-6} e pm^3. Final atomic coordinates are presented in Table 1, with derived bond lengths and angles in Tables 2 and 3.

Table 3. Bond angles (°) for compound **5**

C(2)-C(1)-C(22A)	107.3(3)	C(2)-C(1)-C(28)	115.2(3)
C(22A)-C(1)-C(28)	110.7(3)	C(2)-C(1)-O(1)	106.9(3)
C(22A)-C(1)-O(1)	109.5(2)	C(28)-C(1)-O(1)	107.0(2)
C(1)-C(2)-C(3)	122.3(3)	C(2)-C(3)-C(4)	108.8(3)
C(3)-C(4)-C(5)	122.4(3)	C(3)-C(4)-C(30)	119.4(3)
C(5)-C(4)-C(30)	116.5(4)	C(4)-C(5)-C(6)	120.4(3)
C(5)-C(6)-C(7)	120.0(3)	C(6)-C(7)-C(8)	119.8(3)
C(6)-C(7)-C(29)	117.4(3)	C(8)-C(7)-C(29)	119.1(3)
C(7)-C(8)-C(9)	108.9(3)	C(8)-C(9)-C(10)	116.6(3)
C(9)-C(10)-C(10A)	117.0(3)	C(9)-C(10)-C(27)	122.4(3)
C(10A)-C(10)-C(27)	120.4(3)	C(10)-C(10A)-C(11)	107.1(3)
C(10)-C(10A)-C(22A)	117.4(3)	C(11)-C(10A)-C(22A)	107.1(2)
C(10A)-C(11)-C(12)	107.3(2)	C(10A)-C(11)-C(24)	102.9(2)
C(12)-C(11)-C(24)	111.9(2)	C(11)-C(12)-C(13)	124.1(3)
C(11)-C(12)-C(23)	111.9(3)	C(13)-C(12)-C(23)	123.5(3)
C(12)-C(13)-C(14)	119.1(3)	C(13)-C(14)-C(15)	108.6(3)
C(14)-C(15)-C(16)	119.7(3)	C(14)-C(15)-C(26)	120.1(3)
C(16)-C(15)-C(26)	117.5(4)	C(15)-C(16)-C(17)	120.3(3)
C(16)-C(17)-C(18)	120.0(3)	C(17)-C(18)-C(19)	118.7(3)
C(17)-C(18)-C(25)	117.8(3)	C(19)-C(18)-C(25)	121.4(3)
C(18)-C(19)-C(20)	107.9(3)	C(19)-C(20)-C(21)	120.4(3)
C(20)-C(21)-C(22)	111.4(2)	C(20)-C(21)-C(24)	117.9(3)
C(22)-C(21)-C(24)	104.1(2)	C(20)-C(21)-O(3)	109.3(2)
C(22)-C(21)-O(3)	108.5(3)	C(24)-C(21)-O(3)	105.0(2)
C(21)-C(22)-C(22A)	107.1(2)	C(21)-C(22)-C(23)	109.5(3)
C(22A)-C(22)-C(23)	109.3(2)	C(1)-C(22A)-C(10A)	114.3(2)
C(1)-C(22A)-C(22)	115.8(2)	C(10A)-C(22A)-C(22)	109.5(3)
C(12)-C(23)-C(22)	116.7(3)	C(11)-C(24)-C(21)	114.2(3)
C(11)-C(24)-O(4)	122.3(3)	C(21)-C(24)-O(4)	122.6(3)
C(18)-C(25)-C(26)	119.8(3)	C(15)-C(26)-C(25)	120.6(3)
C(10)-C(27)-C(28)	123.0(3)	C(1)-C(28)-C(27)	120.0(3)
C(1)-C(28)-O(2)	117.8(3)	C(27)-C(28)-O(2)	122.1(3)
C(7)-C(29)-C(30)	120.5(4)	C(4)-C(30)-C(29)	120.7(4)

CAS Registry Numbers

1: 5628-11-5 / **1** (Br instead of OH): 1908-61-8 / **4**: 126255-65-0 / **5**: 126255-66-1 / MoOPH: 23319-63-3 / [2.2]paracyclophane: 1633-22-2

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