Cyclophanes, XLVI[+]

Oxidative Carbon−Carbon Bond Cleavage of a [2.2]Paracyclophane Derivative − Efficient Intramolecular Trapping of the Radical Cation

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4-(2,3,4,5-Tetraphenyl)phenyl[2.2]paracyclophane (**3**) has been prepared by cycloaddition of tetracyclone (**2**) to 4-ethynyl[2.2]paracyclophane (**1**). On treatment with $FeCl_3$ or $AlCl_3$ or $NOBF_4$ in nitromethane, **3** undergoes C–C bond cleavage by an electron transfer process to provide the double benzyl radical cation **10**. The phenyl groups of the aryl substituent are ideally oriented for intramolecular trapping and, in the presence of the Lewis acids, ring closure to the new phane system **5** takes place in good yield (65%). In the presence of $NOBF_4$, the half-cyclized aldehyde **6** (66%) is produced. For comparison, [2.2]paracyclophane (**7**) was also treated with the latter one-electron oxidant, providing bibenzyl-4,4′-dicarbaldehyde (**8**, 30%) and its monooxime **9** (35%). The structures of the new phane systems **3** and **5** have been determined by X-ray structural analysis, and the mechanisms leading to these products are discussed.

Introduction

Oxidative cleavage of the central C−C bond of 1,2-diarylethanes to give a benzyl radical and a benzyl cation (and subsequent products) is a well-known reaction that can be achieved by a variety of conditions involving chemical, electrochemical and photochemical activation.[2] [2.2]Paracyclophane is a special case of such a system in which the cleavage of the ethano bridge is thermodynamically substantially more favourable, due to ring opening and the release of associated strain.[3] The cleavage of the ethano bridge in this hydrocarbon can be accomplished by chemical (electrophilic), thermal and photochemical reactions, or under the oxidative conditions mentioned above.[4,5] Aryl-substituted derivatives of [2.2]paracyclophane, with strong nonbonded steric interaction with the ethano bridge (and hence still higher strain energy), are potential candidates for study of the oxidative cleavage of the ethano bridge in greater detail, because the resulting benzyl radical/benzyl cation pair could in principle be trapped intramolecularly by substitution reactions in the neighbouring aryl substituent(s).

A system containing phenyl groups well positioned for such an intramolecular trapping is 4-(2,3,4,5-tetraphenyl)phenyl[2.2]paracyclophane (**3**, Scheme 1), which is also an attractive precursor for the preparation (by cyclodehydrogenation) of the [2.2]paracyclophane system **4**, in which one "deck" consists of an extended polycyclic aromatic hydrocarbon (PAH). We have prepared several PAH phanes previously[6−8] and are presently interested in extending the size and complexity of the PAH subunit. Although attempts to achieve this latter goal have not yet been realised for **3** (see below), its chemistry with regard to oxidative cleavage of the cyclophane bridge and the intramolecular trapping of the resulting reactive benzylic intermediates have been studied successfully. Here we report on the synthesis, structural characterization and several bridge cleavage reactions of **3**.

Results and Discussion

Cycloaddition of ethynylparacyclophane (**1**) and tetracyclone (**2**) in diphenyl ether at 200−220 °C proceeded smoothly within 2 h to yield the desired starting material for the study; namely 2,3,4,5-tetraphenylphenyl[2.2]paracyclophane (**3**), in 85% yield (Scheme 1). In the ^1H NMR spectrum of **3**, the signal of the lone aromatic hydrogen atom on the phenyl ring directly attached to the phane appears at $\delta = 7.87$. From the X-ray structure (Figure 1) and the energy-minimized structure calculated using semi-empirical methods (PM3), it is clear that this hydrogen substituent is located between the two π planes of the phane moiety and hence is relatively more deshielded. It is also of importance that one of the phenyl rings lies just above the ethano bridge, the shortest distance between the bridging carbon atom and the ring being ca. 3.7 Å. This is crucial

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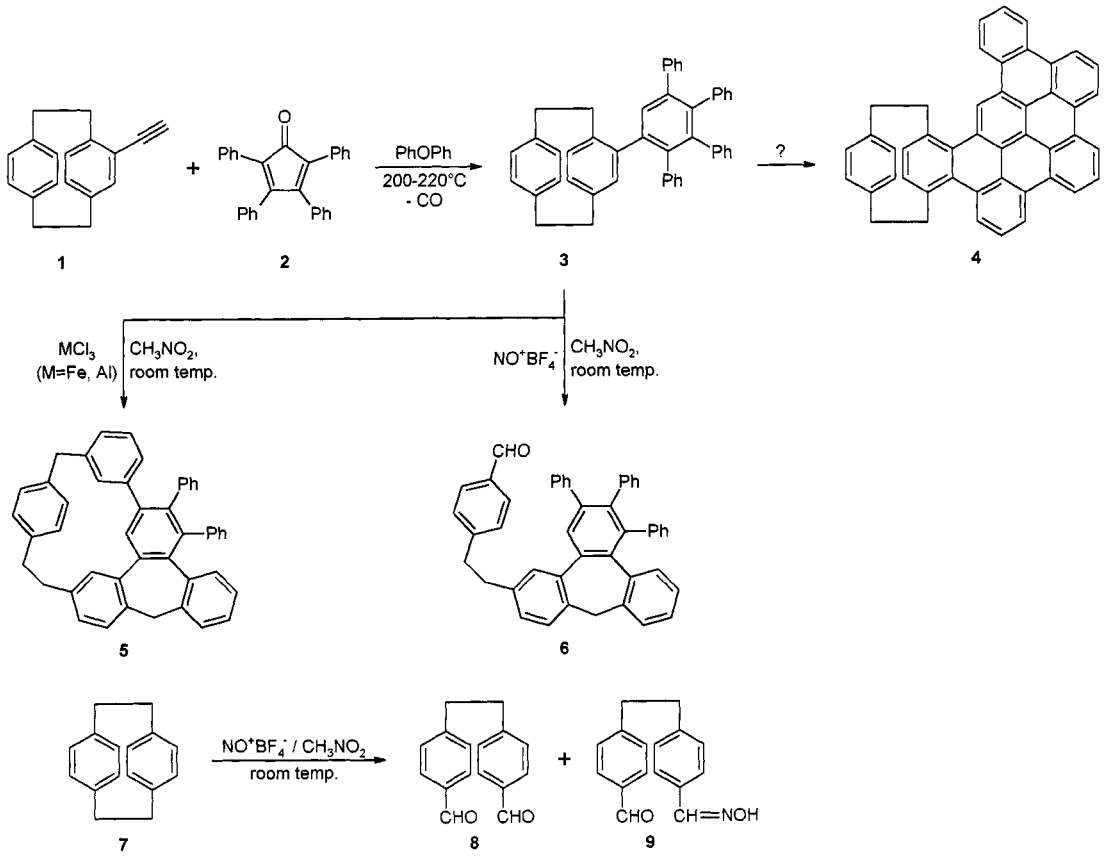


Scheme 1. Preparation of the cyclophane **3** and its bridge cleavage reactions

for the discussion of the reactivity of this molecule during oxidative cleavage (see below).

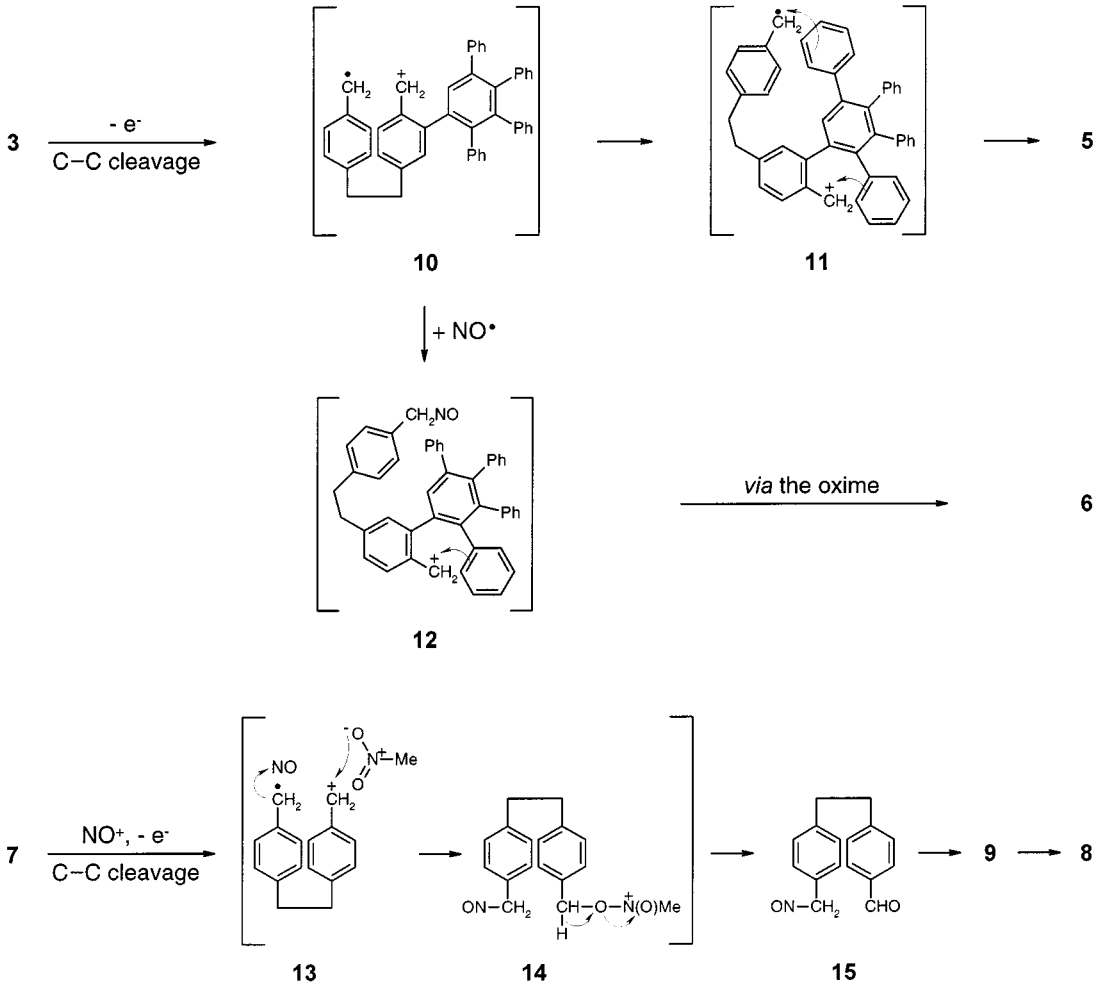
The attempted preparation of pentaphenylphenyl[2.2]paracyclophane (**3** with a pentaphenylphenyl substituent) from the reaction of phenylethynyl[2.2]paracyclophane with tetracyclone (**2**) under the above conditions did not yield any tractable product.

The geometries of the cyclophane fragments in **3** are very similar to the skeleton of the parent compound [2.2]paracyclophane. The interplanar angles in **3** between the planar ring systems are optimized so as to avoid steric repulsion between π-systems. The values are as follows (the carbon atoms of the respective planes are given in brackets): 50.87(7)° [the plane defined by the four coplanar carbon atoms C4, C5, C7, C8 and C23 to C28], 53.87(5)° [C23 to C28 and C29 to C34], 50.77(7)° [C29 to C34 and C35 to C40], and 61.76(5)° [C35 to C40 and C41 to C46].

Reaction of 3 with Anhydrous $FeCl_3$

The original objective of undertaking the synthesis of **3** was to carry out cyclodehydrogenation under Scholl reaction[9] conditions using a suitable Lewis acid and also to perform a photocyclization[10] of the stilbene-to-phenanthrene type to prepare the planarized derivative **4**. While the latter methodology, tried under various reaction conditions, failed completely, the Scholl reaction with $FeCl_3$ resulted in the formation of an interesting new cyclophane product. Thus, treatment of **3** with excess $FeCl_3$ in nitromethane/dichloromethane at room temperature yielded a mixture of products from which the major one was isolated in 65% yield by chromatographic separation and identified as **5** (Scheme 1) using spectroscopic data and single-crystal X-ray crystallography. The molecular structure shown in Figure 2 clearly indicates that one ethano bridge of the original cyclophane ring has been cleaved, leading to the formation of a tribenzocycloheptatriene ring and a 16-membered ring phane resulting from the intramolecular capture of the reactive intermediates of the C−C fragmentation (see below).

In compound **5**, the bond lengths of the single bonds in the cyclic fragment C1 to C28 are in the range of the respective standard bond lengths (these are given in brackets). $C(sp^3)-C(sp^3)$ bonds: 153.8(3) pm [153.9 pm] and $C(sp^3)-C(sp^2)$ bonds: 150.7(3) (C9−C10) to 152.0(3) pm (C1−C45) [151.0 pm]. The $C(sp^2)-C(sp^2)$ bonds C26−C41 (149.4(3) pm) and C12−C24 (149.1(3) pm) are slightly elongated in comparison with the standard bond length for conjugated aromatic systems [147.0 pm] due to the torsion of the aromatic systems and the consequent hindered conjugation. The interplanar angles of the cyclic fragment C1 to C28 indicate no interaction between the π-systems of the involved aromatic rings: 45.74(8)° [C2 to C7 and C10 to C15], 42.07(8)° [C10 to C15 and C23 to C28], 42.75(7)°



Scheme 2. Mechanism of the bridge cleavage of **3** and [2.2]paracyclophane (**7**)

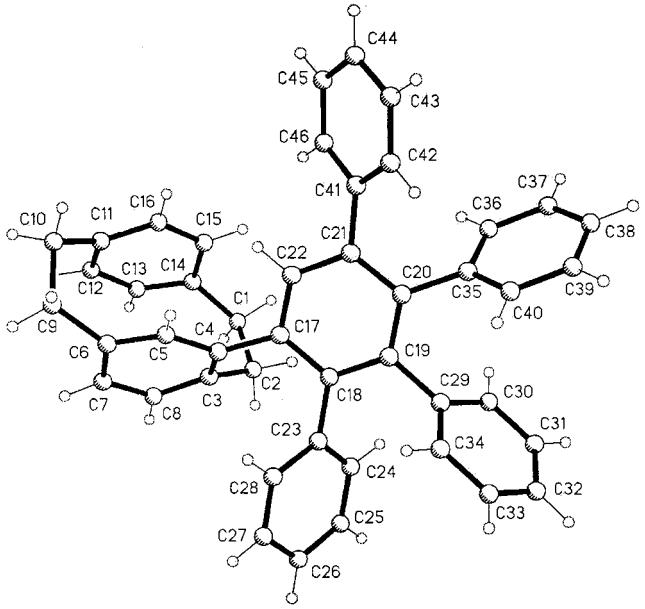


Figure 1. Single-crystal X-ray structure of **3**

[C23 to C28 and C41 to C46], 77.23(7)° [C2 to C7 and C23 to C28] and 65.09(7)° [C10 to C15 and C41 to C46]. The seven-membered ring in **5** adopts a boat conformation. The atoms C12, C13, C17 and C18 are coplanar, with a mean deviation of the plane of 0.53 pm. The other three carbon atoms are bent out of the plane by 72.8(3) (C16), 83.3(3) (C23) and 78.0(3) pm (C24).

In order to study further the viability of an electron transfer mechanism for the C−C bond cleavage, compound **3** was deliberately oxidised with $NOBF_4$, a well-known strong, one-electron oxidant ($E_{1/2}$ = 0.98 V vs. Cp_2Fe in CH_3NO_2),[11] known to form charge transfer complexes and undergo electron transfer reactions with aromatic hydrocarbons.[11] Thus, oxidation of **3** with $NOBF_4$ resulted in the formation of yet another product, identified as **6** (Scheme 1). The ^{1}H NMR spectrum of **6** shows an aldehyde signal at δ = 9.81 and an AB-quadruplet at δ = 3.96 and 3.66 (J = 12.6 Hz) characteristic of the methylene hydrogen atoms of the cycloheptatriene moiety (cf. the ^{1}H NMR spectrum of **5**, the structure of which was unambiguously established by the X-ray crystallographic data). The oxidative cleavage with ceric ammonium nitrate (another well-known electron transfer oxidant) of the ethano bridge in parent [2.2]paracyclophane (**7**) has been studied previously by Adam and co-workers.[5] For comparison, we oxidized **7** with $NOBF_4$ and isolated two major products, identified as bibenzyl-4,4′-dicarbaldehyde (**8**) and the corresponding

monooxime **9** (Scheme 1). The formation of these products with $NOBF_4$ is highly reminiscent of the products of oxidation by ceric ammonium nitrate.[5]

Mechanism

The cleavage, upon one-electron oxidation, of the C−C bond of the ethano bridge of [2.2]paracyclophane (**7**) to yield a benzyl radical/benzyl cation intermediate has been well established by chemical and electrochemical oxidation methods.[4,5] This radical ion intermediate is normally trapped by external nucleophiles, oxygen etc. The mechanism of formation of **5** and **6** is depicted in Scheme 2. Oxidation of **2** with either $FeCl_3$ or $NOBF_4$ leads to the formation of the radical cation, which readily undergoes C−C bond cleavage, leading to the intermediate double benzylic radical cation **10**.

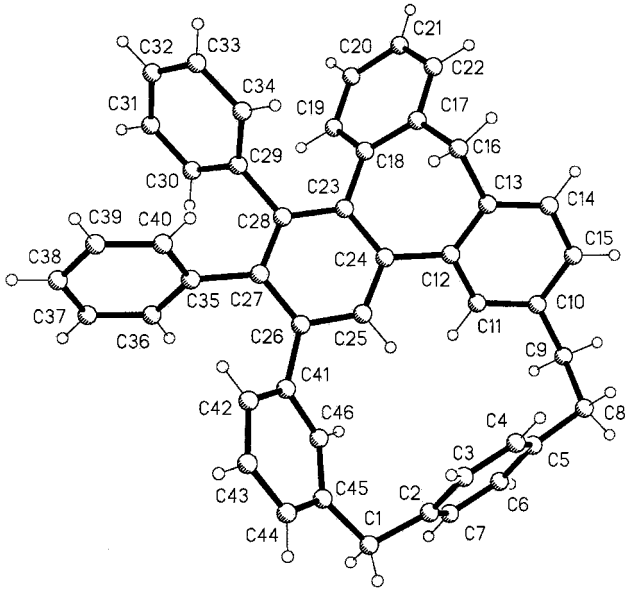


Figure 2. Single-crystal X-ray structure of **5**

With its eclipsed 1,2-diphenylethane conformation, this intermediate reduces its internal strain by rotation about the remaining ethano bridge, thus creating a more "open" structure, **11**. In this species, both reactive centres − the benzyl radical and the benzyl cation − face phenyl substituents, which can now fulfil their role as internal traps. Intramolecular Friedel−Crafts alkylation forms the seven-membered ring, while the benzyl radical attacks the other outer phenyl group of the *p*-terphenyl intermediate **11**. Alternatively, it is possible that, after formation of the cycloheptatriene ring, the intermediate benzyl radical is oxidized a second time by excess oxidant to provide a further benzyl cation intermediate, which can lead to **5** by a second Friedel−Crafts alkylation. In either case, the high yield of this new cyclophane system indicates that both ring-forming processes occur efficiently. When $NOBF_4$ is used as the oxidant, generation of the radical cation is accompanied by nitric oxide formation. Radical combination between the benzyl radical part of **10** and nitric oxide could lead to nitroso derivative **12**, which, after cyclization to the seven-membered ring, could tautomerize to the corresponding oxime. This, in turn, would be expected to hydrolyze to the aldehyde **6** during workup or chromatographic purification.

In the case of $NOBF_4$ oxidation, even though the initial intramolecular cyclization leading to the cycloheptatriene ring is still very efficient, the trapping of the benzyl radical by nitric oxide effectively competes with the second intramolecular cyclization, leading to the formation of the aldehyde **6** in good yield (66%).

In the case of the parent paracyclophane **7,** the oxidation with $NOBF_4$ leads to the double benzylic radical cation **13**. Since there is now no intramolecular trapping group, the radical part of **13** reacts with nitric oxide, whereas the cationic centre is intercepted by nitromethane.[12] The resulting intermediate **14** can subsequently fragment to nitrosomethane and **15**, from which the isolated products **9** and **8** would be produced during workup (Scheme 2).

Conclusions

Oxidation of the phenyl-substituted paracyclophane derivative **3** using $FeCl_3$ and $NOBF_4$ results in the cleavage of the C−C bridge; the resulting radical cation is trapped intramolecularly very efficiently, leading in the former case to the formation of a novel cyclophane **5** and, in the latter, the aldehyde **6**. The success of the intramolecular trapping is due to the proximity of one phenyl substituent lying just above the bridge of the cyclophane moiety, as shown by the X-ray crystal structure and the calculated structure of the starting material **3**.

Experimental Section

The spectroscopic methods used for structure elucidation have been described in the previous papers of this series.[1] Nitromethane was fractionally distilled and stored over freshly activated molecular sieves (type 4 Å). Dichloromethane was distilled from CaH_2 under nitrogen.

4-(2,3,4,5-Tetraphenyl)phenyl[2.2]paracyclophane (3): A mixture of 4-ethynyl[2.2]paracyclophane[13] (**1**, 1.16 g, 5 mmol) and tetracyclone (**2**, 1.92 g, 5 mmol) in diphenyl ether (10 mL) was heated at 200−220 °C for 2 h under nitrogen. The dark purple colour of the tetracyclone faded gradually and evolution of gas was observed. The reaction mixture was cooled to room temp. and then poured into 100 mL of methanol. The suspension was refluxed for 10 min, cooled to room temp., and the tan-coloured solid was removed by filtration and washed several times with methanol. The yield of the crude product was 2.5 g (86%), free of starting materials and diphenyl ether as shown by TLC analysis and the ^1H NMR spectrum. A small portion of the solid was dissolved in CH_2Cl_2 and treated with activated charcoal, and the solution was filtered and pentane added until slight turbidity appeared. The solution was cooled in a freezer (−25 °C) to yield analytically pure product as a colourless amorphous solid. When the above solution was very slowly concentrated from a loosely stoppered round bottomed flask, single crystals suitable for X-ray analysis were obtained (see below). − M.p. 310−315 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 2928 cm^{-1}, 1599, 697. − UV/

Vis ($CHCl_3$): λ_{max} (log ε) = 252 nm (4.60) 276 (sh, 4.39). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.33 (m, 1 H), 2.67 (m, 1 H), 2.80 (m, 1 H), 3.0 (m, 5 H), 6.01 (d, *J* = 7.8 Hz, 1 H), 6.30 (dd, *J* = 1.85 and 7.6 Hz, 1 H), 6.41 (d, *J* = 7.6 Hz, 1 H), 6.52 (d, *J* = 1.7 Hz, 1 H), 6.54 (d, *J* = 1.7 Hz, 1 H), 6.61 (m, 2 H), 6.63 (d, *J* = 1.8 Hz, 1 H), 6.70−7.05 (m, 15 H), 7.25 (m, 4 H), 7.87 (s, 1 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 34.15 (t), 35.26 (t), 35.3 (t), 35.4 (t), 125.04 (d), 125.1 (d), 125.5 (d), 126.16 (d), 126.2 (d), 126.4 (d), 126.6 (d), 126.8 (d), 127.8 (d), 129.6 (d), 129.9 (d), 131.36 (d), 131.4 (d), 131.6 (d), 131.7 (d), 131.8 (d), 131.9 (d), 132.1 (d), 132.5 (d), 132.9 (d), 133.3 (d), 134.1 (d), 138.5 (s) 138.6 (s), 139.02 (s), 139.3 (s), 140.05 (s), 140.1 (s), 140.2 (s), 140.56 (s), 140.6 (s), 140.7 (s), 140.8 (s), 141.2 (s),142.2 (s). − MS (EI, 70 eV); *m*/*z* (%): 590 (8) [M^+ + 2] , 589 (36) [M^+ + 1], 588 (68) [M^+] , 485 (10), 484 (54), 483 (100). − $C_{46}H_{36}$ (588.75): calcd. C 93.87, H 6.12; found C 93.74 H 6.13.

6,3-[2](1,2-Diphenyl-9*H*-tribenzo[*a*,*c*,*e*]cycloheptatrienyleno)[1](1,4-phen)yleno(1,3-phenyleno)phane (5): To a stirred solution of anhydrous $FeCl_3$ (0.48 g, 3 mmol) in dry nitromethane (2 mL) under nitrogen was added dropwise a solution of 4-(2,3,4,5-tetraphenyl)phenyl[2.2]paracyclophane (**3**, 0.15 g, 0.25 mmol) in dichloromethane (100 mL). The mixture was stirred at room temp. for 36 h, and water (100 mL) and saturated aqueous $NaHSO_3$ (25 mL) were added. The organic layer was separated, washed several times with water, dried with $MgSO_4$, and the solvent was removed under reduced pressure to yield a pale brown solid consisting of a mixture of products as shown by TLC and crude NMR analysis. Column chromatographic purification on silica gel with pentane/dichloromethane (1:1) yielded product **5** as a colourless solid (97 mg, 65%). Recrystallization by slow diffusion of pentane into a dichloromethane solution of **5** provided single crystals suitable for X-ray crystallography (see below). The preparation of **5** was also accomplished using $AlCl_3$ as follows, albeit in lower yield. To a solution of $AlCl_3$ (1 g) and NaCl (100 mg) (ground together as a fine powder prior to dissolution) in nitromethane (20 mL) was added a solution of **3** (0.1 g) in dichloromethane (50 mL) and the resulting mixture was stirred under nitrogen for 24 h. The solution turned dark green. Workup by addition of 1 M aqueous HCl (50 mL) followed by extraction with CH_2Cl_2 yielded a solid after solvent removal. On chromatographic separation as described above, **5** was isolated (30 mg, 30%) as a colourless solid; m.p. 278 °C. − IR (KBr): $\tilde{\nu}$ = 3022 cm^{-1}, 2919, 1599, 1433, 700. − UV/Vis ($CHCl_3$): λ_{max} (log ε) = 244 nm (4.43), 266 (4.61), 296 (sh, 4.34). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.65 (m, 1 H), 3.03 (m, 2 H), 3.30 (m, 1 H), 3.60 (d, *J* = 12.6 Hz, 1 H), 3.85 (d, *J* = 12.6 Hz, 1 H), 4.0 and 4.1 (AB-q, *J* = 15.5 Hz, 2 H), 6.25 (m, 1 H), 6.60 (m, 2 H), 6.70−7.0 (m, 13 H), 7.15 (m, 8 H),7.47 (s, 2 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 36.7 (t), 37.14 (t), 40.0 (t), 40.6 (t), 124.45 (d), 125.4 (d), 125.69 (d), 125.9 (d), 126.0 (d), 126.34 (d), 126.37 (d), 126.4 (d), 126.6 (d), 126.7 (d), 127.04 (d), 127.2 (d), 127.4 (d), 127.9 (d), 128.5 (d), 129.9 (d), 130.6 (d), 130.8 (d), 131.0 (d), 131.3 (d), 131.5 (d), 131.7 (d), 132.7 (d), 132.8 (d), 134.05 (d), 134.6 (d), 135.3 (s), 136.4 (s), 137.7 (s), 138.12 (s), 139.1 (s), 139.28 (s), 139.4 (s), 139.95 (s), 140.75 (s), 140.76 (s), 140.8 (s), 143.1 (s), 143.3 (s). − MS (EI. 70 eV); *m*/*z* (%): 588 (18) [M^+ + 2], 587 (48) [M^+ + 1], 586 (100) [M^+]. − HRMS; *m*/*z*: calcd. for $C_{46}H_{34}$ 586.26605; found 586.2651. − $C_{46}H_{34}$ (586.73): calcd. C 94.19, H 5.80; found C 94.37, H 5.61.

6-[2-(4-Formylphenyl)ethyl]-1,2,3-triphenyl-9*H*-tribenzo[*a*,*c*,*e*]cycloheptatriene (6): A solution of **3** (0.2 g, 0.3 mmol) in dry CH_2Cl_2 (100 mL) was added dropwise under nitrogen to a stirred solution of $NOBF_4$ (0.23 g, 2 mmol) in dry nitromethane. The solution initially turned wine-red, then brown. After stirring at room temp. overnight, the reaction mixture was quenched with water and the organic layer was dried with $MgSO_4$. Removal of the solvent under reduced pressure yielded a tan-coloured solid. Column chromatographic separation on silica gel with pentane and dichloromethane (1:1) yielded the major product as a pale yellow solid (0.12 g, 66%); m.p. 225−226 °C. − IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1}, 1698 (C=O), 1604, 701. − UV/Vis ($CHCl_3$): λ_{max} (log ε) = 244 nm (sh) (4.59), 262 (4.82), 284 (sh, 4.54). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.97 (m, 4 H), 3.66 and 3.96 (AB-q, *J* = 12.6 Hz, 2 H), 6.60−6.75 (m, 4 H), 6.85−7.10 (m, 12 H), 7.20 (m, 5 H), 7.42 (d, *J* = 1.4 Hz, 1 H), 7.52 (s, 1 H), 7.29 and 7.72 (AA′BB′-m, *J* = 8.0 Hz, 4H), 9.81 (s, 1 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 36.99 (t), 38.1 (t), 40.2 (t), 124.4 (d), 125.3 (d), 125.4 (d), 125.6 (d), 126.3 (d), 126.6 (d), 126.7 (d), 126.8 (d), 126.9 (d), 127.0 (d), 127.5 (d), 127.76 (d), 129.1 (d), 129.3 (d), 129.8 (d), 129.9 (d), 130.7 (d), 131.3 (d), 131.5 (d), 131.7 (d), 132.57 (d), 132.8 (d), 134.5 (s), 135.5 (s), 137.2 (s), 137.8 (s), 138.8 (s), 138.9 (s), 139.6 (s), 139.9 (s), 140.8 (s), 140.9 (s), 141.26 (s), 141.3 (s), 141.8 (s), 143.5 (s), 149.0 (s),191.9 (d). − MS (EI, 70 eV); *m*/*z* (%): 604 (16) [M^+ + 2], 603 (50) [M^+ + 1], 602 (100) [M^+], 485 (6), 484 (30), 483 (66). − HRMS; *m*/*z*: calcd. for $C_{46}H_{34}O$ 602.26096; found 602.2603. − A very minor product (5 mg) obtained as a yellow solid was identified as 6-[2-(4-hydroxymethylphenyl)ethyl]-1,2,3-triphenyl-9*H*-tribenzo[*a*,*c*,*e*]-cycloheptatriene from the following spectroscopic data. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.90 (m, 4 H), 3.6 (d, *J* = 11 Hz, 1 H), 3.9 (d, *J* = 11 Hz, 1 H), 4.5 (s, 2 H), 6.60 (m, 5 H), 6.9 (m, 14 H), 7.15 (m, 5 H), 7.45 (m, 3 H), 7.55 (s, 1 H). − MS (EI, 70 eV); *m*/*z* (%): 605 (14) [M^+ + 1], 604 (28) [M^+], 600 (52), 599 (100), 484 (40), 483 (92).

Oxidation of [2.2]Paracyclophane (7) with $NOBF_4$: The oxidation of **7** (0.21 g, 1 mmol) with $NOBF_4$ (0.34 g, 3 mmol) was carried out as described in the case of **3**. After stirring at room temp. for 48 h, the starting material had disappeared. Chromatographic separation of the crude product (0.23 g) on silica gel with CH_2Cl_2 and pentane (1:1) yielded bibenzyl-4,4′-dicarbaldehyde (**8,** 75 mg, 30%). Subsequent elution with CH_2Cl_2 provided the corresponding monooxime **9** (90 mg, 35%). Both compounds were identified by IR, NMR and MS analysis.

Bibenzyl-4,4′-dicarbaldehyde (8):[14] ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.06 (s, 4 H), 7.30 (d, *J* = 8.1 Hz, 4 H), 7.80 (d, *J* = 8.1 Hz, 4 H), 9.99 (s, 2 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 37.42 (t), 129.13 (d), 129.9 (d), 134.74 (s), 148.16 (s),191.8 (d). − MS (EI, 70 eV); *m*/*z* (%): 239 (10), 238 (50), 119 (92), 91 (100).

Bibenzyl-4,4′-dicarbaldehyde Monooxime (9): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.95 (br. s, 1 H), 2.98 (AA′BB′-m, 4 H), 7.15 (d, *J* = 8.1 Hz, 2 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.48 (d, *J* = 8.2 Hz, 2 H), 7.79 (d, *J* = 8.2 Hz, 2 H), 8.12 (s, 1 H), 9.96 (s, 1 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 37.13 (t), 37.68 (t), 127.08 (d), 128.86 (d), 129.16 (d), 129.92 (d), 130.0 (s), 134.6 (s), 143.0 (s), 148.6 (s), 150.1 (d), 192.0 (d). − MS (EI, 70 eV); *m*/*z* (%): 254 (4), 253 (24), 236 (14), 135 (10), 134 (100).

X-ray Crystallography of 3 and 5: A summary of crystal data, data collection and refinement parameters is given in Table 1. For the structure determination of **3** and **5**, a cut tablet was mounted on a glass fibre in inert oil and transferred to the cold gas stream of a Bruker SMART 1000 CCD diffractometer fitted with a Siemens LT-3 low-temperature attachment. Data were collected with ω-scans using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). An absorption correction using SADABS was applied in case of compound **5**. All unique data were used for calculations

(program SHELXL-97).[15] Both structures were solved by direct methods and refined anisotropically by full-matrix, least-squares on F^2. Hydrogen atoms were refined with a riding model. Compound **5** crystallizes with one molecule of dichloromethane. The solvent is severely disordered and badly resolved. Three alternative positions were refined isotropically without H atoms; the composition (and related parameters) should be regarded as tentative.

Table 1. Summary of crystal data, data collection, and refinement parameters for **3** and **5**

Compound	**3**	**5**·CH_2Cl_2
Formula	$C_{46}H_{36}$	$C_{47}H_{36}Cl_2$
M_r	588.75	671.66
Crystal habit	colourless tablet	colourless tablet
Crystal size (mm)	0.24 × 0.23 × 0.09	0.43 × 0.21 × 0.12
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	10.6882(14)	11.2468(10)
b (Å)	25.388(3)	11.0238(10)
c (Å)	11.8085(14)	28.040(2)
β (°)	98.781(6)	92.989(10)
V (Å^3)	3166.7	3471.8
Z	4	4
D_x (Mg m^{-3})	1.235	1.285
μ (mm^{-1})	0.070	0.221
Transmissions	–	0.876–1.000
F(000)	1248	976
T (°C)	−130	−130
$2\theta_{max}$	51	57
Refl. measured	29360	36748
Refl. unique	6489	8809
R_{int}	0.107	0.044
Parameters	415	448
Restraints	445	24
wR (F^2, all refl.)	0.117	0.173
R [F, > 4σ(F)]	0.048	0.058
S	0.89	0.98
max. Δρ (e Å^{-3})	0.25	0.83

Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-135530 (**3**) and -135531 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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