Novel Transannular Reactions in the Acid Hydrolysis of Diazotized *syn*- and *anti*-4-Amino[2.2](1,4)naphthalenoparacyclophanes

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The diazonium ions derived from the title *syn*- and *anti*-4-aminocyclophanes **1a** and **4a** in aqueous solution undergo transannular reactions to give 17-hydroxy[2.2](1,4)naphthalenoparacyclophane **3a** and 9,10-dihydro-1,9:4,10-diethano-9,10-ethenoanthracene **6a**, respectively. Deuterium-tracer experiments suggest that the reaction of diazotized **1a** proceeds *via* a pathway involving transannular diazo coupling followed by generation of a 16,17-didehydro intermediate. On the other hand, the reaction pathway of diazotized **4a** involves dediazoniation followed by transannular electrophilic addition.

The anomalous rates and products of electrophilic substitutions of layered aromatics such as [2.2]paracyclophanes have been generally accepted as being due to transannular electronic interaction between the facing aromatic rings,[1] but it is not yet known whether such interactions exert an influence on nucleophilic substitutions. In the hope of clarifying this problem, we have studied the acid hydrolysis of [*n.n*]paracyclophanediazonium salts, since reactions of ordinary arenediazonium salts in aqueous acid proceed exclusively *via* an aryl cation mechanism, not *via* an aryne one.[2] Surprisingly, some [*n.n*]paracyclophanediazonium salts have been found to undergo transannular rearrangement or addition reactions,[3] which are not known in the cyclophane chemistry. We report here the results of a mechanistic investigation of the transannual reactions of diazotized *syn*- and *anti*-4-amino[2.2](1,4)-naphthalenoparacyclophanes **1a** and **4a** in aqueous solution.

Results and Discussion

Hydrolysis of Diazotized **1**.—Amine **1a** in dilute sulphuric acid, or in a mixture of dilute sulphuric acid and acetic acid, was diazotized with aqueous sodium nitrite and then hydrolysed at room temperature. After being worked up in the usual manner, the reaction mixture gave the corresponding *syn*-4-hydroxycyclophane **2a** and its 17-hydroxy isomer **3a** in 60 and 38% yields by GLC.

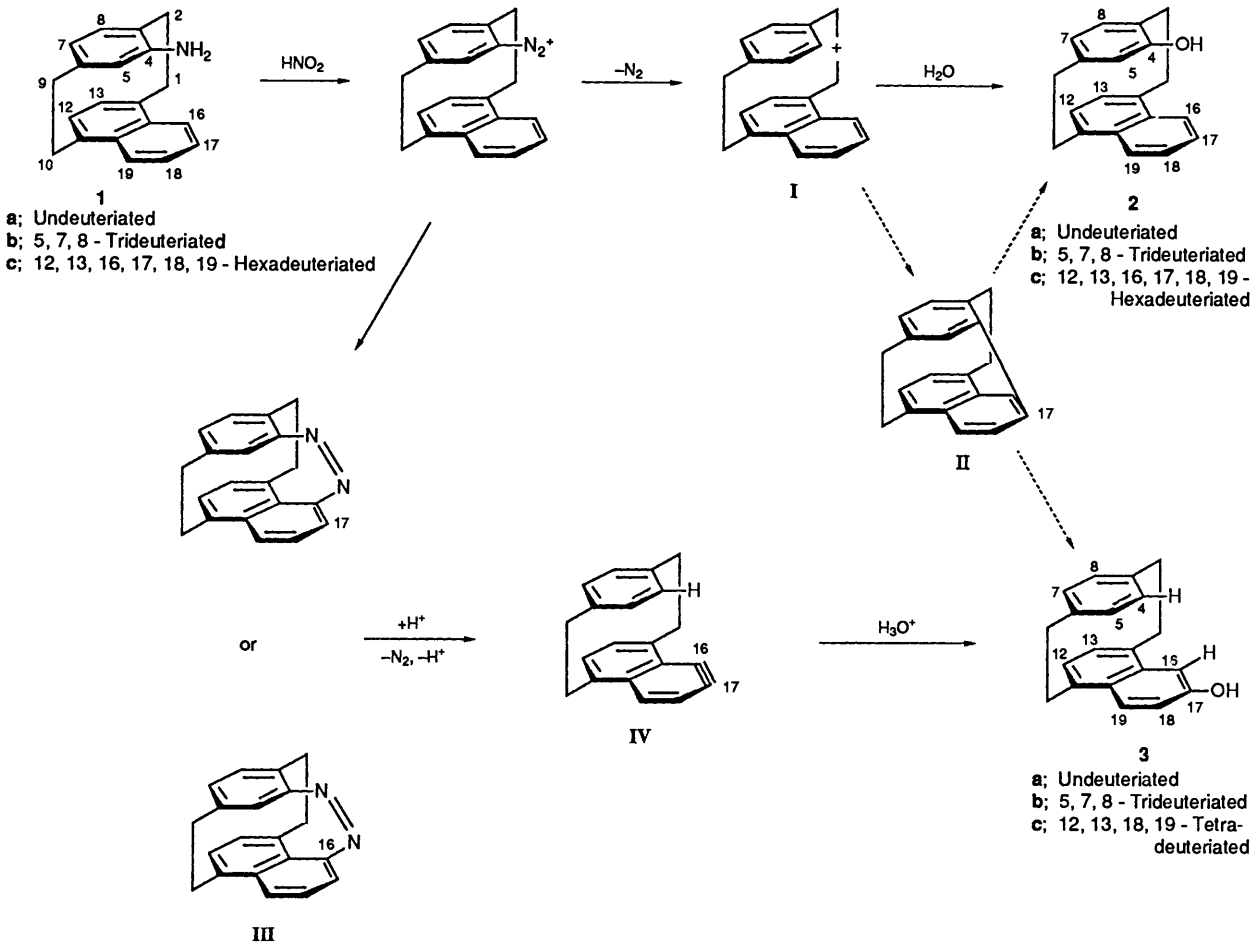
The rearrangement leading to **3a** is an anomalous reaction. For this reaction, two possible pathways were visualized. One involves transannular electrophilic attack on the 17-position by the aryl cation **I** arising from diazotized **1a**, followed by deprotonation with external bases such as water, to form an intermediate **II** having a direct bond between C-4 and C-17. This 4–17-bond is then cleaved with aqueous acid to give **2a** and **3a**. However, this pathway involving formation of **II** from **I** seems improbable on steric grounds. An examination of molecular models indicates that in **I** C-4 and C-17 lie in unfavourable positions for bonding with one another to give **II** and this molecule itself involves substantial distortion and strain. An alternative pathway involves transannular electrophilic attack by diazotized **1a** on the 17-position, followed by deprotonation, to form an azo intermediate **III** having an azo linkage between C-4 and C-17, as formulated in Scheme 1. This intermediate **III** undergoes protonation on either ring with loss of N_2 and addition of H_2O to give **2a** and **3a**. Formation of **III** from diazotized **1a** is more favourable on a steric basis than the former case. As can be seen from Scheme 1, the 4-position in **3a** and the 17-position in **2a** should have hydrogen atoms transferred from external acids. In order to test this hypothetical pathway, several deuterium-labelled starting materials were prepared and treated under similar conditions. From diazotized *syn*-4-amino-5,7,8-trideuterio[2.2](1,4)naphthalenoparacyclophane **1b**, the corresponding *syn*-4-hydroxycyclophane **2b** and its 17-hydroxy isomer **3b** were obtained. On the other hand, diazotized *syn*-4-amino-12,13,16,17,18,19-hexadeuterio[2.2]-(1,4)naphthalenoparacyclophane **1c** gave the corresponding *syn*-4-hydroxy cyclophane **2c** and a 17-hydroxy-12,13,18,19-tetradeuterio cyclophane **3c**. According to ^1H NMR spectroscopy, **3c** had 1.0 atoms of hydrogen at the 4-position and also at the 16-position. Diazotized **1c** did not give any isomers of **3c** such as a 16-hydroxy compound having hydrogen at the 17-position or a 17-hydroxy compound having hydrogen at the 18-position. These results allow us to suggest an aryne pathway in which the azo intermediate **III** undergoes protonation on C-4 and loss of N_2, followed by deprotonation to generate a 16,17-didehydro intermediate **IV**. This aryne **IV** undergoes regioselective addition of aqueous acid, due to a steric hindrance of the *peri*-bridge, to give **3c**. It should be noted that the azo-linking site is not necessarily C-17 but may be either C-16 or C-17. Aryne generation in aqueous acid is not yet known, but the aryne pathway described above may explain the formation of **3c** in a way consistent with the fact that treatment of 1- and 2-halonaphthalenes with base in non-aqueous solution generates exclusively the same 1,2-didehydronaphthalene to give preferentially 2-substituted naphthalenes.[4]

On the other hand, **2c** had no hydrogen atom either at the 16- or 17-position, indicating that **2** is produced *via* attack by H_2O on the aryl cation **I** (usual S_N1 process). This result does not exclude the azo-coupling pathway leading to **3**. It is reasonable that both processes take place competitively.

It is further noted that there was no generation of a 4,5-didehydro intermediate from **I**, since **2b** from **1b** had deuterium, not hydrogen, at the 5-position.

Hydrolysis of Diazotized **4**.—Hydrolysis of diazotized **4a** gave the corresponding *anti*-4-hydroxycyclophane **5a** and a bridged dibenzobarrelene (9,10-dihydro-1,9:4,10-diethano-9,10-ethenoanthracene) **6a** in 60 and 35% yield by GLC but no isomers of **5a**.

For the transannular addition leading to **6a**, two possible pathways were considered. One involves generation of a 4,5-didehydro intermediate **VI** from diazotized **4a** possibly *via* the aryl cation **V**. The aryne **VI** could undergo not only cycloaddition to give **6a**, but also addition of aqueous acid to give **5a**. Thus, **6a** should have no transferred hydrogen, but **5a**



Scheme 1.

should have a hydrogen atom transferred from external acid at the 5-position. Obviously **V** itself would undergo addition of H_2O. An alternative pathway involves transannular electrophilic attack by the aryl cation on the 14-position, followed by deprotonation, to give **6a**, as described in Scheme 2. Also in this case, **6a** has no transferred hydrogen atom at any position. In order to make a choice between the two possibilities, deuterium-tracer experiments were designed to show which of **V** and **VI** is an intermediate leading to **5a**. *anti*-4-Amino-5,7,8-trideuterio- and *anti*-4-amino-12,13,16,17,18,19-hexadeuterio[2.2](1,4)-naphthalenoparacyclophane **4b** and **4c**, were used as deuterium-labelled materials. Diazotized **4b** gave the corresponding *anti*-4-hydroxycyclophane **5b** and a 2,3-dideuterioanthracene **6b**. The product **5b** had no hydrogen atom at the 5-position, indicating that **5** was produced *via* the usual S_N1 process involving **V**. On this basis, it is presumed that **6** was produced *via* the latter pathway involving a σ complex **VII**, not *via* the former aryne pathway. On the other hand, diazotized **4c** gave the corresponding *anti*-4-hydroxycyclophane **5c** and a hexadeuterioanthracene **6c**, indicating that no deuterium-hydrogen exchange took place on the naphthalene ring.

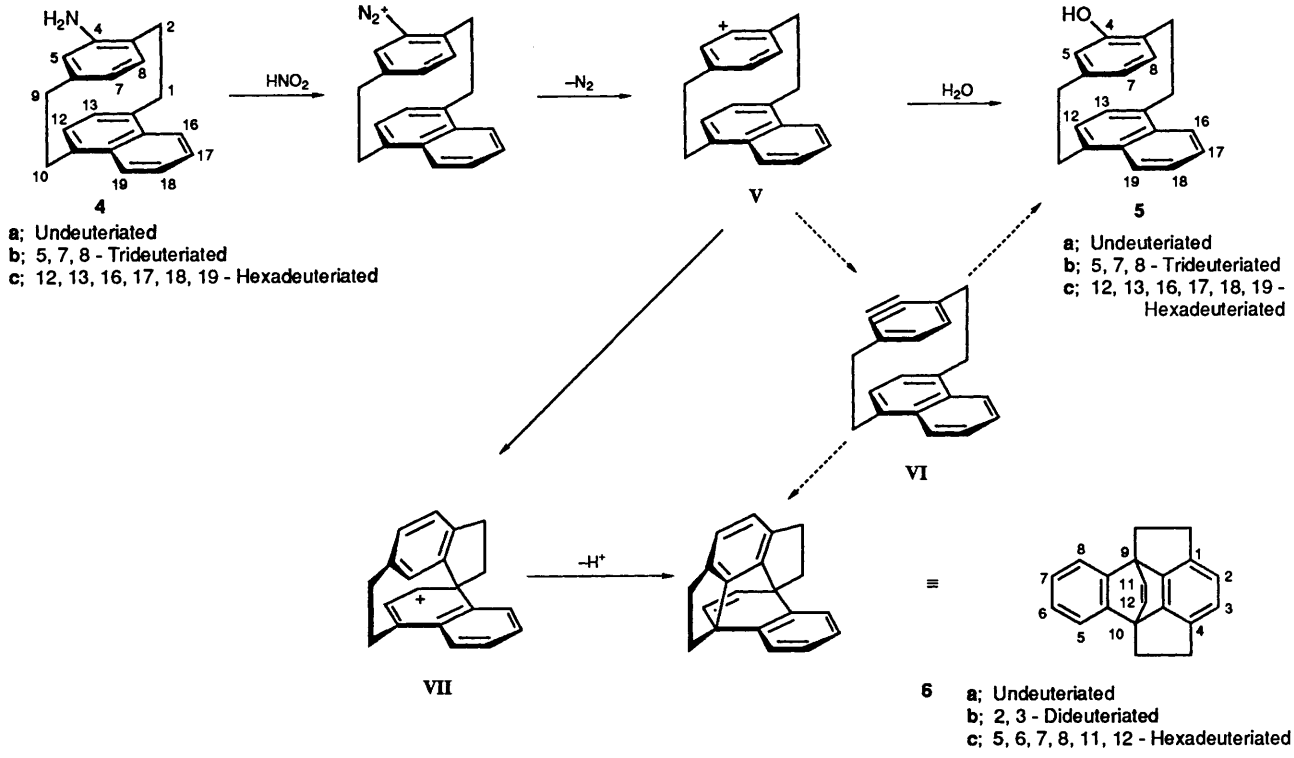
Finally, it should be noted that there are two known reactions in non-aqueous media leading to bridged benzobarrelenes similar to **6**. One is the reaction of 5-bromo[3.3]paracyclophane with potassium butoxide, which involves generation and subsequent cycloaddition of an aryne.[5] The other involves transannular Diels–Alder addition of 4,7-dimethoxy[2.2](9,10)-anthracenoparacyclophane, followed by acid-catalysed elimination of methanol.[6] It is interesting to note that these reaction pathways are different from one another and also from the present aryl cation pathway.

Experimental

General.—All m.p.s are uncorrected. GLC analyses were performed by using a Shimazu GC-4CM apparatus with a column of Silicone OV-17 (13%)-Chromosorb W (1.5 m) or Silicone SE-30 (10%)-Celite 545 (1.5 m) (N_2 as carrier gas). Preparative TLC treatments were carried out on glass plates (20 × 20 cm) coated with Merck Kieselgel $60PF_{254}$ (1.25 mm). IR spectra were measured on a Perkin-Elmer 1600 FT-IR spectrometer. ^1H NMR spectra were measured for $CDCl_3$ solutions containing tetramethylsilane on a JEOL JNM-FX 100 (100 MHz), JEOL JNM-GX 400 (400 MHz), or JEOL JNM-GSX 500 (500 MHz) spectrometer. Mass spectra [EI] were measured on a Hitachi M-80 spectrometer equipped with an M-003 data processor.

The observed NMR chemical shifts were assigned on the basis of coupling constants and patterns and/or by comparison with analogues. The structures of new compounds obtained were based upon extensive spectroscopic characterization except for the dibenzobarrelene **6a** which was further subjected to X-ray crystal structure diffraction, details of which were reported elsewhere.[7]

Preparation of **1a** *and* **4a**.—A solution of 2,5-bis(bromomethyl)nitrobenzene (**7a**; 11 g) and 1,4-bis(sulphydrylmethyl)-naphthalene[8] (**8a**; 3.09 g) in benzene (600 cm^3) was added



Scheme 2.

dropwise over 2 days to a rapidly stirred solution of KOH (11 g) in 95% ethanol (1.5 dm^3) at room temperature under nitrogen. After being stirred for 1 day, the solution was neutralized with acetic acid. Following removal of the solvent, the residue was extracted with $CHCl_3$ and the extract was washed with brine and dried over Na_2SO_4. Removal of the solvent and subsequent recrystallization of the yellow residue from $CHCl_3$ gave *anti*-5-nitro-2,11-dithia[3.3](1,4)naphthalenoparacyclophane (**10a**) as yellow crystalline powders (1.30 g). Silica gel column chromatograph of the mother liquor using benzene gave an additional crop of **10a** (0.28 g, total yield 43.1%) and its *syn*-isomer **9a** as yellow crystalline powders (0.7 g, 19%).

9a: m.p. 239.3–241.4 °C; δ(100 MHz) 3.71–4.64 (8 H, m), 6.77 (2 H, d, *J*/Hz: 2.0; 14-H and 15-H), 7.03 (2 H, d, *J*/Hz: 1.3; 8-H and 9-H), 7.13 (1 H, s, 6-H), 7.34–7.67 (2 H, m, 19-H and 20-H) and 7.86–8.08 (2 H, m, 18-H and 21-H).

10a: m.p. 257 °C (decomp.); δ(100 MHz) 3.47–4.53 (8 H, m), 6.52 (2 H, d, *J*/Hz: 2.5; 8-H and 9-H), 6.72 (2 H, s, 14-H and 15-H), 7.46–7.63 (2 H, m, 19-H and 20-H), 7.48 (1 H, s, 6-H) and 7.92–8.09 (2 H, m, 18-H and 21-H).

A solution of **9a** (450 mg) in $CHCl_3$ (200 cm^3) and acetic acid (40 cm^3) was mixed with 35% H_2O_2 (7 cm^3) at room temperature and stirred for 7 days, during which additional 35% H_2O_2 (6 cm^3) was added in six portions day by day. The resulting precipitate was isolated by filtration, washed successively with methanol and ether, and then dried *in vacuo*. In a flash-vacuum pyrolysis apparatus,[9] the bis-sulphone (600 mg) obtained was pyrolysed in six portions at 400 °C for 5 h with nitrogen-sweeping at 1 mmHg. The combined crude products were chromatographed on silica gel with benzene–hexane to give *syn*-4-nitro[2.2](1,4)naphthalenoparacyclophane **11a** as yellow prisms (24 mg, 5.7%) and its *anti*-isomer **12a** as yellow needles (59 mg, 14%). Similar results were obtained using **10a**.

11a: m.p. 197.2–202.1 °C; δ(400 MHz) 2.92–3.11 (3 H, m), 3.20–3.34 (2 H, m), 3.88–4.04 (2 H, m), 4.21–4.28 (1 H, m), 6.58 (1 H, d, *J*/Hz: 7.8; 8-H), 6.62 (1 H, d, *J*/Hz: 1.9; 5-H), 6.70 (1 H, dd, *J*/Hz: 1.9 and 7.8; 7-H), 6.77 (1 H, A of AB pattern, *J*/Hz: 7.3; 12-H or 13-H), 6.85 (1 H, B of AB pattern, *J*/Hz: 7.3; 13-H or 12-H), 7.28 (1 H, br d, *J*/Hz: 7.7; 17-H or 18-H), 7.47 (1 H, br d, *J*/Hz: 7.5; 18-H or 17-H), 7.71 (1 H, d, *J*/Hz: 8.3; 16-H or 19-H) and 7.77 (1 H, d, *J*/Hz: 8.3; 19-H or 16-H); *m*/*z* 303 (M^+, 15%), 154 (100) and 149 (3).

12a: m.p. 165.5–167.5 °C; δ(400 MHz) 2.50–3.40 (5 H, m), 3.58–4.10 (3 H, m) 5.63 (1 H, d, *J*/Hz: 7.8; 8-H), 5.82 (1 H, dd, *J*/Hz: 2.0 and 7.8; 7-H), 6.67 (1 H, A of AB pattern, *J*/Hz: 7.5; 12-H or 13-H), 6.76 (1 H, B of AB pattern, *J*/Hz: 7.5; 13-H or 12-H), 7.19 (1 H, d, *J*/Hz: 2.0; 5-H), 7.28–7.47 (2 H, m, 17-H and 18-H) and 7.52–7.69 (2 H, m, 16-H and 19-H); *m*/*z* 303 (M^+, 17%), 154 (100) and 149 (4).

The *syn*-nitro compound **11a** (110 mg) in methanol (5 cm^3) and ethyl acetate (7 cm^3) was hydrogenated in the presence of PtO_2 (*ca.* 10 mg) at room temperature under atmospheric pressure until hydrogen was no longer taken up. After being filtered, removal of the solvent gave **1a** as pale yellow crystals (100 mg, 100%), m.p. 135–139 °C; ν_{max}(KBr)/cm^{-1} 3380 and 3470 (NH_2). Similar hydrogenation of **12a** gave **4a** as pale yellow crystals in 100% yield, m.p. 162–164 °C; ν_{max}(KBr)/cm^{-1}: 3375 and 3470 (NH_2).

Preparation of **1b** *and* **4b**.—These were obtained starting from 2,5-bis(chloromethyl)-3,4,6-trideuterionitrobenzene **7b** and **8a** by almost the same method as described above. The compound **7b** was prepared from commercially available tetradeuterioterephthalic acid (98 atom% D) in the usual manner including its esterification with methanol, $LiAlH_4$ reduction of the dimethyl ester (m.p. 139.3–139.8 °C) in THF, chlorination of the diol (m.p. 117.4–117.8 °C) with 36% HCl, and nitration of the dichloride (m.p. 96.5–98.5 °C) with 96% H_2SO_4–60% HNO_3, pale yellow needles, m.p. 37.6–38.4 °C. In this process, deuterium–hydrogen exchange could not be detected by ^1H NMR spectroscopy.

Coupling of **7b** and **8a** with KOH gave *syn*-6,8,9-trideuterio-5-nitro-2,11-dithia[3.3](1,4)naphthalenoparacyclophane **9b** as

a pale yellow crystalline powder in 15.4% yield and its *anti*-isomer (**10b**) as a yellow crystalline powder in 38.4% yield.

9b: m.p. 232–235 °C; δ(500 MHz) 3.79 (1 H, d, *J*/Hz: 16.1), 3.85 (1 H, d, *J*/Hz: 15.4), 3.94 (1 H, d, *J*/Hz: 15.0), 3.95 (1 H, d, *J*/Hz: 15.4), 4.04 (1 H, d, *J*/Hz: 14.7), 4.44 (2 H, d, *J*/Hz: 16.1), 4.45 (1 H, d, *J*/Hz: 14.7), 6.74 (1 H, A of AB pattern, *J*/Hz: 7.3; 14-H or 15-H), 6.78 (B of AB pattern, *J*/Hz: 7.3; 15-H or 14-H), 7.58–7.61 (2 H, m, 19-H and 20-H), 8.03–8.05 (1 H, m, 18-H or 21-H) and 8.07–8.09 (1 H, m, 21-H or 18-H); *m*/*z* 370 (M^+, 100%), 154 (41) and 152 (18) (Found: M^+, 370.0891. $C_{20}H_{14}D_3NO_2S_2$ requires M, 370.0889).

10b: m.p. 255–258 °C (decomp.); δ(500 MHz) 3.81 (1 H, d, *J*/Hz: 15.0), 3.86 (2 H, d, *J*/Hz: 2.9), 4.01 (1 H, d, *J*/Hz: 15.0), 4.05 (1 H, d, *J*/Hz: 14.7), 4.47 (1 H, d, *J*/Hz: 10.6), 4.50 (1 H, d, *J*/Hz: 10.3), 4.59 (1 H, d, *J*/Hz: 15.0), 6.79 (1 H, A of AB pattern, *J*/Hz: 7.0; 14-H or 15-H), 6.84 (1 H, B of AB pattern, *J*/Hz: 7.0; 15-H or 14-H), 7.50 (1 H, m, 19-H or 20-H), 7.62 (1 H, m, 20-H or 19-H), 7.98 (1 H, d, *J*/Hz:, 8.4; 18-H or 21-H) and 8.06 (1 H, d, *J*/Hz: 8.4; 21-H or 18-H); *m*/*z* 370 (M^+, 100%), 306 (14), 154 (51) and 152 (22) (Found: M^+, 370.0899).

H_2O_2 oxidation and subsequent pyrolysis of **9b** or **10b** gave *syn*-5,7,8-trideuterio-4-nitro[2.2](1,4)naphthalenoparacyclophane **11b** in 8% yield and its *anti*-isomer **12b** in 25% yield.

11b: m.p. 155–158 °C; δ(500 MHz) 2.93–3.10 (3 H, m), 3.23 (1 H, m), 3.31 (1 H, m), 3.91 (1 H, dd, *J*/Hz: 9.9 and 13.6), 4.00 (1 H, m), 4.26 (1 H, m), 6.77 (1 H, A of AB pattern, *J*/Hz: 7.3; 12-H or 13-H), 6.85 (1 H, B of AB pattern, *J*/Hz: 7.3; 13-H or 12-H), 7.28 (1 H, m, 17-H or 18-H), 7.47 (1 H, m, 18-H or 17-H), 7.71 (1 H, d, *J*/Hz: 8.1; 16-H or 19-H) and 7.77 (1 H, d, *J*/Hz: 8.4; 19-H or 16-H); *m*/*z* 306 (M^+, 11%), 154 (100) and 152 (8) (Found: M^+, 306.1448. $C_{20}H_{14}D_3NO_2$ requires M, 306.1448).

12b: m.p. 165–166 °C; δ(500 MHz) 2.78–2.84 (1 H, m), 2.91–2.97 (1 H, m), 3.07–3.19 (2 H, m), 3.21–3.28 (1 H, m), 3.77–3.87 (2 H, m), 4.00 (1 H, dd, *J*/Hz: 9.5 and 13.2), 6.76 (1 H, A of AB pattern, *J*/Hz: 7.0; 12-H or 13-H), 6.79 (1 H, B of AB pattern, *J*/Hz: 7.3; 13-H or 12-H), 7.44–7.48 (2 H, m, 17-H and 18-H) and 7.69–7.73 (2 H, m, 16-H and 19-H); *m*/*z* 306 (M^+, 16%), 154 (100) and 152 (8) (Found: M^+, 306.1458).

Catalytic hydrogenation of **11b** and **12b** performed in the presence of PtO_2 or 10% Pd–C gave **1b** and **4b**, respectively, in quantitative yield.

1b: m.p. 137–138 °C; ν_{max}(KBr)/cm^{-1}: 3378 and 3456 (NH_2).

12b: m.p. 170–173 °C; ν_{max}(KBr)/cm^{-1}: 3365 and 3458 (NH_2).

Preparation of **1c** *and* **4c**.—These were obtained starting from **7a** and 2,3,5,6,7,8-hexadeuterio-1,4-bis(sulphydrylmethyl)-naphthalene **8c** in a similar manner. The compound **8c** was prepared starting from commercially available octadeuterionaphthalene (98 atom% D) by almost the same method as for **8a**; m.p. 78–80 °C; δ(100 MHz) 1.87 (2 H, t, *J* 7.0 Hz) and 4.17 (4 H, d, *J*/Hz: 8.0); ν_{max}(KBr)/cm^{-1} 2550 (SH).

Coupling of **7a** and **8c** gave a mixture of *syn*-14,15,18,19,20,21-hexadeuterio-5-nitro-2,11-dithia[3.3](1,4)naphthalenoparacyclophane **9c** and its *anti*-isomer **10c** in 47% yield. Preparative TLC treatment of a sample of the mixture gave **9c** and **10c**.

9c: m.p. 199–103 °C; δ(100 MHz) 3.74–4.68 (8 H, m), 7.09 (2 H, d, *J*/Hz: 1.0) and 7.20 (1 H, s).

10c: m.p. 202–205 °C; δ(100 MHz) 3.34–4.56 (8 H, m), 6.60 (2 H, d, *J* 2.5 Hz) and 7.58 (1 H, s).

H_2O_2 oxidation and subsequent pyrolysis of the mixture of **9c** and **10c** gave *syn*-12,13,16,17,18,19-hexadeuterio-4-nitro-[2.2](1,4)naphthalenoparacyclophane **11c** as yellow prisms (7.1% yield) and its *anti*-isomer **12c** as yellow needles (21.7%).

11c: m.p. 147–151 °C; δ(400 MHz) 2.95–3.12 (3 H, m), 3.21–3.36 (2 H, m), 3.89–4.04 (2 H, m), 4.20–4.30 (1 H, m), 6.59 (1 H, d, *J*/Hz: 7.9, 8-H), 6.62 (1 H, d, *J*/Hz: 1.5; 5-H) and 6.71 (1 H, dd, *J*/Hz: 7.5 and 1.5; 7-H); *m*/*z* 309 (M^+, 20%), 160 (100) and 149 (3).

12c: m.p. 149–151.5 °C; δ(400 MHz) 2.77–2.85 (1 H, m), 2.91–2.98 (1 H, m), 3.07–3.30 (3 H, m), 3.76–3.87 (2 H, m), 3.98–4.03 (1 H, m), 5.71 (1 H, d, *J*/Hz: 7.6; 8-H), 5.88 (1 H, dd, *J*/Hz: 7.7 and 2.1; 7-H) and 7.26 (1 H, d, *J*/Hz: 2.0; 5-H); *m*/*z* 309 (M^+, 20%), 160 (100) and 149 (3).

Catalytic hydrogenation of **11c** and **12c** gave **1c** and **4c**, respectively, as pale yellow crystals in quantitative yield.

1c: m.p. 128–133 °C; ν_{max}/cm^{-1}: 3380 and 3460 (NH_2).

4c: m.p. 143–150 °C; ν_{max}/cm^{-1}: 3360 and 3460 (NH_2).

Hydrolysis of Diazotized **1**.—The amine **1a** (50 mg, 0.18 mmol) in a mixture of H_2O (3 cm^3), H_2SO_4 (2 cm^3) and $MeCO_2H$ (2 cm^3) was diazotized with aq. $NaNO_2$ (24 mg, 0.34 mmol) at 0 °C for 30 min, treated with a small amount of urea and then stirred at 20–25 °C for 2 h. The solution was neutralized with aq. $NaHCO_3$ and extracted into CH_2Cl_2. The extract was washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue contained two main products, **2a** and **3a**, in 60 and 38% distribution (GLC). Preparative TLC with CH_2Cl_2 gave **2a** as colourless needles (12 mg, 24%) and **3a** as colourless plates (7 mg, 14%).

2a: m.p. 164–166 °C; δ(400 MHz) 2.66–2.75 (1 H, m), 2.78–2.83 (1 H, m), 2.99–3.09 (2 H, m), 3.17–3.24 (1 H, m), 3.43–3.50 (1 H, m), 3.79–3.94 (2 H, m), 3.19 (1 H, s, OH), 4.87 (1 H, d, *J*/Hz: 1.6; 5-H), 6.22 (1 H, dd, *J*/Hz: 1.7 and 7.8; 7-H), 6.41 (1 H, d, *J*/Hz: 7.8; 8-H), 6.69 (1 H, A of AB pattern, *J*/Hz: 7.3; 12-H or 13-H), 6.73 (1 H, B of AB pattern, *J*/Hz: 7.1; 13-H or 12-H), 7.31 (1 H, m, 17-H or 18-H), 7.43 (1 H, m, 18-H or 17-H), 7.76 (1 H, d, *J*/Hz: 8.1; 16-H or 19-H) and 8.06 (1 H, d, *J*/Hz: 8.3; 19-H or 16-H); *m*/*z* 274 (M^+, 50%), 154 (100) and 120 (74); ν_{max}(CCl_4)/cm^{-1} 3598 (OH) (Found: M^+, 274.1364. $C_{20}H_{18}O$ requires M, 274.1358).

3a: m.p. 171–173 °C; δ(400 MHz) 2.83–2.93 (2 H, m), 2.98–3.13 (4 H, m), 3.62–3.75 (2 H, m), 4.88 (1 H, s, OH), 5.63 (1 H, dd, *J*/Hz: 1.7 and 7.7; 7-H or 8-H), 5.75 (1 H, dd, *J*/Hz: 1.7 and 7.6; 8-H or 7-H), 6.42 (1 H, dd, *J*/Hz: 1.7 and 7.8; 4-H or 5-H), 6.46 (1 H, dd, *J*/Hz: 1.7 and 7.8; 5-H or 4-H), 6.63 (1 H, A of AB pattern, *J*/Hz: 7.3; 12-H or 13-H), 6.69 (1 H, B of AB pattern, *J*/Hz: 7.3; 13-H or 12-H), 6.99 (1 H, dd, *J*/Hz: 2.6 and 8.8; 18-H), 7.04 (1 H, d, *J*/Hz: 2.5; 16-H) and 7.57 (1 H, d, *J*/Hz: 8.8; 19-H); *m*/*z* 274 (M^+, 23%), 170 (100) and 104 (18); ν_{max}(CCl_4)/cm^{-1} 3608 (OH) (Found: M^+, 274.1352).

In a similar manner, diazotization and subsequent hydrolysis of **1b** gave **2b** and **3b** in 32 and 16% yield, respectively.

2b: m.p. 145.5–148.0 °C; δ(500 MHz) 2.70 (1 H, ddd, *J*/Hz: 4.8, 10.6 and 13.6), 2.78–2.82 (1 H, m), 3.00–3.08 (2 H, m), 3.18 (1 H, s, OH), 3.20 (1 H, ddd, *J*/Hz: 3.30, 10.6 and 13.6), 3.46 (1 H, ddd, *J*/Hz: 3.30, 9.9 and 13.6), 3.79–3.85 (1 H, m), 3.90 (1 H, ddd, *J*/Hz: 4.8, 9.9 and 13.6), 6.69 (1 H, A of AB pattern, *J*/Hz: 7.0; 12-H or 13-H), 6.73 (1 H, B of AB pattern, *J*/Hz: 7.0; 13-H or 12-H), 7.30 (1 H, ddd, *J*/Hz: 1.5, 7.0 and 8.1; 17-H or 18-H), 7.42 (1 H, ddd, *J*/Hz: 1.5, 7.0 and 8.1; 18-H or 17-H), 7.76 (1 H, d, *J*/Hz: 8.1; 16-H or 19-H) and 8.06 (1 H, d, *J*/Hz; 8.1; 19-H or 16-H); *m*/*z* 277 (M^+, 78%), 154 (100) and 123 (58); ν_{max}(CCl_4)/cm^{-1} 3597 (OH) (Found: M^+, 277.1544. $C_{20}H_{15}D_3O$ requires M, 277.1546). The NMR spectrum showed no benzene-proton signals.

3b: 164–168 °C; δ(500 MHz) 2.83–2.93 (2 H, m), 2.98–3.13 (4 H, m), 3.63–3.75 (2 H, m), 4.94 (1 H, s, OH), 5.75 (1 H, s, 4-H), 6.63 (1 H, A of B pattern, *J*/Hz: 7.3; 12-H or 13-H), 6.69 (1 H, B of AB pattern, *J*/Hz: 7.0; 13-H or 12-H), 7.00 (1 H, dd, *J*/Hz: 2.6 and 8.8; 18-H), 7.04 (1 H, d, *J*/Hz: 2.6; 16-H) and 7.57 (1 H, d, *J*/Hz: 8.8; 19-H); *m*/*z* 277 (M^+, 40%), 170 (100) and 107 (13); ν_{max}(CCl_4)/cm^{-1} 3607 (OH) (Found: M^+, 277.1545). By NMR spectroscopy, the 4-H of the sample integrated as 1.0 H, indicating 100% hydrogenation of that position.

In a similar manner, diazotized **1c** gave **2c** and **3c** in 25 and 15% yield.

2c: m.p. 124–130 °C; δ(400 MHz) 2.66–2.74 (1 H, m), 2.77–

2.82 (1 H, m), 2.99–3.09 (2 H, m), 3.17–3.24 (1 H, m), 3.43–3.50 (1 H, m), 3.78–3.93 (2 H, m), 3.18 (1 H, s, OH), 4.87 (1 H, d, *J*/Hz: 1.8; 5-H), 6.22 (1 H, dd, *J*/Hz: 1.6 and 7.6; 7-H) and 6.41 (1 H, d, *J*/Hz: 7.6; 8-H); *m/z* 280 (M^+, 69%), 160 (100) and 120 (58) (Found: M^+, 280.1744. $C_{20}H_{12}D_6O$ requires M, 280.1735).

3c: m.p. 130–134 °C; δ(400 MHz) 2.83–2.93 (2 H, m), 2.98–3.13 (4 H, m), 3.62–3.75 (2 H, m), 5.03 (1 H, br s, OH), 5.63 (1 H, A of AB pattern, *J*/Hz: 7.8; 7-H or 8-H), 5.75 (1 H, B of AB pattern, *J*/Hz: 7.8; 8-H or 7-H), 6.42 (1 H, A of AB pattern, *J*/Hz: 7.8; 4-H or 5-H), 6.46 (1 H, B of AB pattern, *J*/Hz: 7.8; 5-H or 4-H) and 7.04 (1 H, s, 16-H); *m/z* 278 (M^+, 31%), 174 (100) and 104 (16) (Found: M^+, 278.1616. $C_{20}H_{14}D_4O$ requires M, 278.1609). By NMR spectroscopy, the 4-H and 16-H of the sample integrated as 1.0 H.

Hydrolysis of Diazotized **4**.—Diazotization and subsequent hydrolysis of amines **4** were carried out in a manner similar to that described for **1**. The reaction of **4a** gave **5a** and **6a** in 60 and 37% yield, respectively, by GLC. Preparative TLC of the crude product with CH_2Cl_2 gave **5a** as colourless needles in 23% yield and **6a** as colourless plates in 17% yield.

5a: m.p. 135–138 °C; δ(400 MHz) 2.56–2.67 (1 H, m), 2.78–2.86 (1 H, m), 2.94–3.06 (2 H, m), 3.18–3.28 (2 H, m), 3.68–3.85 (2 H, m), 4.40 (1 H, s, OH), 5.26 (1 H, dd, *J*/Hz: 1.7 and 7.8; 7-H), 5.46 (1 H, d, *J*/Hz: 7.7; 8-H), 5.59 (1 H, d, *J*/Hz: 1.6; 5-H), 6.69 (1 H, A of AB pattern, *J*/Hz: 7.3; 12-H or 13-H), 7.16 (1 H, B of AB pattern, *J*/Hz: 7.3; 13-H or 12-H), 7.35–7.42 (2 H, m, 17-H and 18-H), 7.66 (1 H, dd, *J*/Hz: 2.3 and 7.2; 16-H or 19-H) and 7.73 (1 H, dd, *J*/Hz: 2.3 and 7.2; 19-H or 16-H); *m/z* 274 (M^+, 46%), 154 (100) and 120 (76); $\nu_{max}(CCl_4)/cm^{-1}$ 3607 (OH) (Found: M^+, 274.1349. $C_{20}H_{18}O$ requires M, 274.1358).

6a: m.p. 137–139 °C; δ(400 MHz) 2.79–2.88 (2 H, m), 3.24–3.38 (6 H, m), 6.79 (2 H, s, vinyl protons), 6.80 (2 H, s, 2-H and 3-H), 6.94 (2 H, dd, *J*/Hz: 3.1 and 5.3; 6-H and 7-H) and 7.32 (2 H, dd, *J*/Hz: 3.1 and 5.3; 5-H and 8-H); *m/z* 256 (M^+, 100%), 228 (17), 202 (7), 120 (5) and 113 (7) (Found: M^+, 256.1271. $C_{20}H_{16}$ requires M, 256.1253).

Diazotized **4b** gave **5b** and **6b** as colourless crystals in 32 and 26% yield, respectively.

5b: m.p. 168.5–169.7 °C; δ(500 MHz) 2.58–2.64 (1 H, m), 2.78–2.84 (1 H, m), 2.94–3.05 (2 H, m), 3.19–3.27 (2 H, m), 3.68–3.74 (1 H, m), 3.82 (1 H, br t, *J*/Hz: 11.2), 4.41 (1 H, s, OH), 6.69 (1 H, d, *J*/Hz: 7.1; 12-H or 13-H), 7.16 (1 H, d, *J*/Hz: 7.1; 13-H or 12-H), 7.35–7.41 (2 H, m, 17-H and 18-H), 7.65–7.67 (1 H, m, 16-H or 19-H) and 7.72–7.74 (1 H, m, 19-H or 16-H); *m/z* 277 (M^+, 46%), 154 (100) and 123 (63) (Found: M^+, 277.1543. $C_{20}H_{15}D_3O$ requires 277.1546).

6b: m.p. 173.5–175.5 °C; δ(500 MHz) 2.82–2.87 (2 H, m), 3.25–3.38 (6 H, m), 6.79 (2 H, s, vinyl protons), 6.94 (2 H, dd, *J*/Hz: 3.1 and 5.3; 6-H and 7-H) and 7.31 (2 H, dd, *J*/Hz: 3.1 and 5.3; 5-H and 8-H); *m/z* 258 (M^+, 100%), 232 (21), 204 (8), 121 (7) and 114 (8) (Found: M^+, 258.1378. $C_{20}H_{14}D_2$ requires M, 258.1378).

From diazotized **4c** were obtained **5c** and **6c** in 26 and 24% yield, respectively.

5c: m.p. 99.5–103.5 °C; δ(400 MHz) 2.58–2.66 (1 H, m), 2.79–2.85 (1 H, m), 2.95–3.07 (2 H, m), 3.20–3.29 (2 H, m), 3.69–3.86 (2 H, m), 4.41 (1 H, s, OH), 5.27 (1 H, dd, *J*/Hz: 1.5 and 7.6; 7-H), 5.47 (1 H, d, *J*/Hz: 7.6; 8-H) and 5.61 (1 H, d, *J*/Hz: 1.5; 5-H); *m/z* 280 (M^+, 58), 160 (100) and 120 (69) (Found: M^+, 280.1752. $C_{20}H_{12}D_6O$ requires M, 280.1735).

6c: m.p. 120–121.5 °C; δ(400 MHz) 2.82–2.89 (2 H, m), 3.24–3.39 (6 H, m) and 6.80 (2 H, s, 2-H and 3-H); *m/z* 262 (M^+, 100), 234 (19), 206 (5), 122 (2) and 115 (3) (Found: M^+, 262.1654. $C_{20}H_{10}D_6$ requires M, 262.1629).

References

1 D. J. Cram and M. J. Cram, *Acc. Chem. Res.*, 1971, **4**, 204.
2 A. F. Hegarty, in *Kinetics and Mechanisms of Reactions Involving Diazonium and Diazo Groups*, in *The Chemistry of Diazonium and Diazo Groups*, Part 2, ed. S. Patai, Wiley, New York, 1978, p. 511.
3 For preliminary reports, see N. Mori and T. Tachibana, *J. Am. Chem. Soc.*, 1984, **106**, 6115; N. Mori, T. Takemura and K. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1988, 575.
4 R. H. Hales, J. S. Bradshaw and D. R. Pratt, *J. Org. Chem.*, 1971, **36**, 314; J. S. Bradshaw and R. H. Hales, 1971, **36**, 318.
5 D. T. Longone and J. A. Gladysz, *Tetrahedron Lett.*, 1976, 4559.
6 Y. Fukuzawa, M. Kikuchi, O. Kajita and S. Ito, *Tetrahedron Lett.*, 1984, **25**, 1505.
7 H. Matsuzawa, K. Kozawa, T. Uchida, K. Tsuchiya and N. Mori, *Acta Crystallogr., Sect. C*, 1989, **45**, 1389.
8 Henkel & Cie. G.m.b.H., B.P. 807,720/1959 (*Chem. Abstr.*, 1960, **54**, 412g). For 1,4-bis(halomethyl)naphthalenes, see G. Lock and R. Schneider, *Chem. Ber.*, 1958, **91**, 1770; C. S. Marvel and B. D. Wilson, *J. Org. Chem.*, 1958, **23**, 1483.
9 S. A. Sherrod, R. L. da Costa, R. A. Barnes and V. Boekelheide, *J. Am. Chem. Soc.*, 1974, **96**, 1965.

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