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NMR STUDY OF 3-t-BUTYL-1-([2.2]PARACYCLOPHAN-4-YL)-5-PHENYLVERDAZYL[1]

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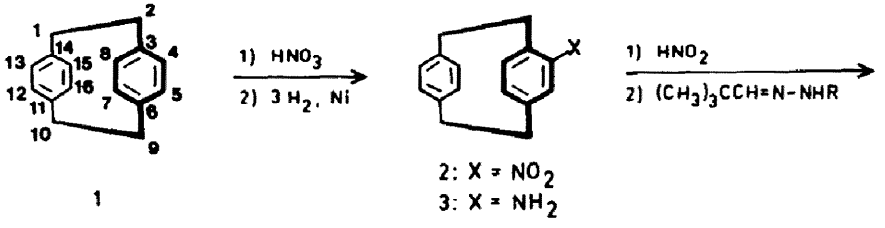
Abstract—NMR measurements on the title verdazyl **5a** and on specifically deuterated derivatives **5b–5f** gave clear assignments of the proton hyperfine coupling constants. There is no substantial interaction of the unpaired electron with transannular protons.

The fixed framework of [2.2]paracyclophanes, in which the slightly bent aryl rings are held face to face at a distance of *ca* 3.1 Å, makes them interesting models for studying transannular electronic interactions, e.g. charge transfer.[2] Derivatives with radical substituents (nitroxide,[3] verdazyl[4]) can be used as intramolecular spin probes to study transannular interactions between the unpaired spin densities on the C atoms of the ring bearing the radical substituent and the corresponding "pseudogeminal" carbons of the other ring. The interpretation of the complex NMR results, however, requires a clear assignment of the proton hyperfine coupling constants, which can be achieved by studying deuterated derivatives.

The synthesis of the verdazyls **5c–5f** is based on the selectively deuterated [2.2]paracyclophanes **1c–1f** as starting materials. These compounds were obtained by following the reaction pathway of Brink.[5] In the sub-



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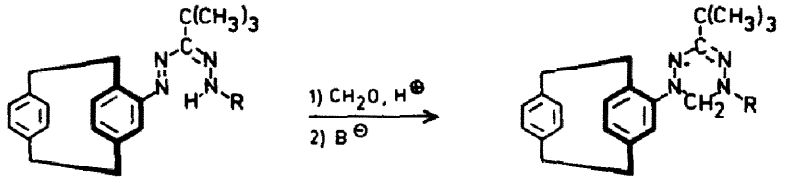


4 5

1a		2a, 3a[6]	
1c	4,5,7,8,12,13,15,16-D_8	2c, 3c	5,7,8,12,13,15,16-D_7
1d	1,1,2,2,9,9,10,10-D_8	2d, 3d	1,1,2,2,9,9,10,10-D_8
1e	2,2,9,9-D_4, 4-OCH_3	2e, 3e	2,2,9,9-D_4, 7-OCH_3
1f	2,2-D_2, 5-OCH_3	2f, 3f	2,2-D_2, 7-OCH_3

		R
4a, 5a		C_6H_5
4b, 5b		C_6D_5
4c, 5c	5,7,8,12,13,15,16-D_7	C_6H_5
4d, 5d	1,1,2,2,9,9,10,10-D_8	C_6H_5
4e, 5e	2,2,9,9-D_4, 7-OCH_3	C_6D_5
4f, 5f	2,2-D_2, 7-OCH_3	C_6H_5

sequent nitration[6] the OMe groups of **1e** and **1f** direct the entering nitro substituents preferentially into the deuterated aryl moiety. Hydrogenation[6] of the nitro compounds **2c–2f** gave the corresponding amino derivatives **3c–3f**, which were diazotized and coupled with 2.2 - dimethylpropanal phenylhydrazone. The resulting formazans **4a–4f** were converted to the corresponding verdazyls **5a–5f** by the usual procedure.[7] Likewise the verdazyl **6** was obtained, which was prepared for comparison.

NMR paramagnetic shifts (δ_p) of organic free radicals[8,9] render directly both the sign and the size of the electron-nuclei coupling constants (a_i). In addition small coupling constants below the resolution of ESR can frequently be measured. This second advantage makes NMR particularly useful for the study of radicals such as **5a–5f**, where a whole series of slightly different small coupling constants have to be determined. The NMR spectra of **5a–5f** are sufficiently resolved (Fig. 1) and exhibit resonance lines for all aliphatic and aromatic protons (D), except for those whose signals are obscured by the intense resonance of the solvent di-t-butyl nitroxide (DBNO)[10] or are too much broadened to be clearly observed. This concerns the CH_2 protons of the verdazyl ring. Their signals are often additionally broadened due to the ring inversion occurring in the verdazyl ring.[11] The resonance lines were assigned by comparison of the individual spectra of **5a–5f** and by analogy with NMR data obtained previously for verdazyls.[12] The values of the paramagnetic shifts and the resulting coupling constants are listed in Table 1.

The D NMR spectrum of **5b** identifies the signals of the N-phenyl protons (2'–6') in **5a**. The coupling constants of these protons as well as that of the t-Bu protons agree well with corresponding data of the reference verdazyl **6** (Table 1). The NMR signals of 5-H, 7-H and 8-H are likewise assigned by comparing the spectra of **5a**, **5b** and **5c**. 5-H and 7-H appear as one signal at high field; 8-H is observed at low field (**5b**, **5c**). The coupling constants of these protons have nearly the same sizes as the corresponding ones of the N-phenyl ring (2',4',5') indicating that there are only small deviations in the spatial arrangement of the N-substituents towards the verdazyl system. Therefore the degree of distortion about the N-phenyl bond and the N - [2.2]paracyclophan - 4 - yl bond in **5a** can be assumed to be almost the same. This differs from the situation in the reference verdazyl **6**, where significantly smaller values of $a_{6\text{-H}}$, $a_{4\text{-H}}$ and $a_{3\text{-H}}$ with respect to $a_{2'\text{-H}}$, $a_{4'\text{-H}}$ and $a_{5'\text{-H}}$ indicate a considerably higher degree of distortion about the N-xylyl bond than about the N-phenyl bond. This view is supported by the hypsochromic shift of the first absorption max of **6** (641 nm) with respect to that of **5a** (664 nm).

The D NMR spectra of **5d** and **5e** demonstrate that all further coupling constants > |0.05| G represent methylene protons of the aryl ring bearing the verdazyl substituent. In accordance with the reference verdazyl **6** and confirmed by **5f** the positive coupling constants are assigned to 2,2-H_2 (β to positive $\rho_{3\text{-C}}$) and the coupling constants to 9,9-H_2 (β to negative $\rho_{6\text{-C}}$). The 2,2-H_2 coupling constants are remarkably different. We tentatively attribute the larger splitting of 0.75 G to the anti 2-H with respect to the verdazyl group, for which spin polarisation, hyperconjugation ($\rho_{3\text{-C}}$) and homohyperconjugation[13,14] (the verdazyl ring is twisted out (~25°) of the aryl plane for steric reasons) reinforce each other. A further argument for this assignment is the dependence of the larger 2-H coupling constant on the distortion angle about the N-phenyl bond. Biverdazyls with a [2.2] - paracyclophanylene bridge show an increase of this coupling constant with rising distortion angle.[15]

Most interesting are the paramagnetic shifts of the protons in the attached 1,4-xylene system. The D NMR spectra of **5c** and **5d** clearly reveal the positions of the corresponding NMR signals (D-1,10,12,13,15,16). As a

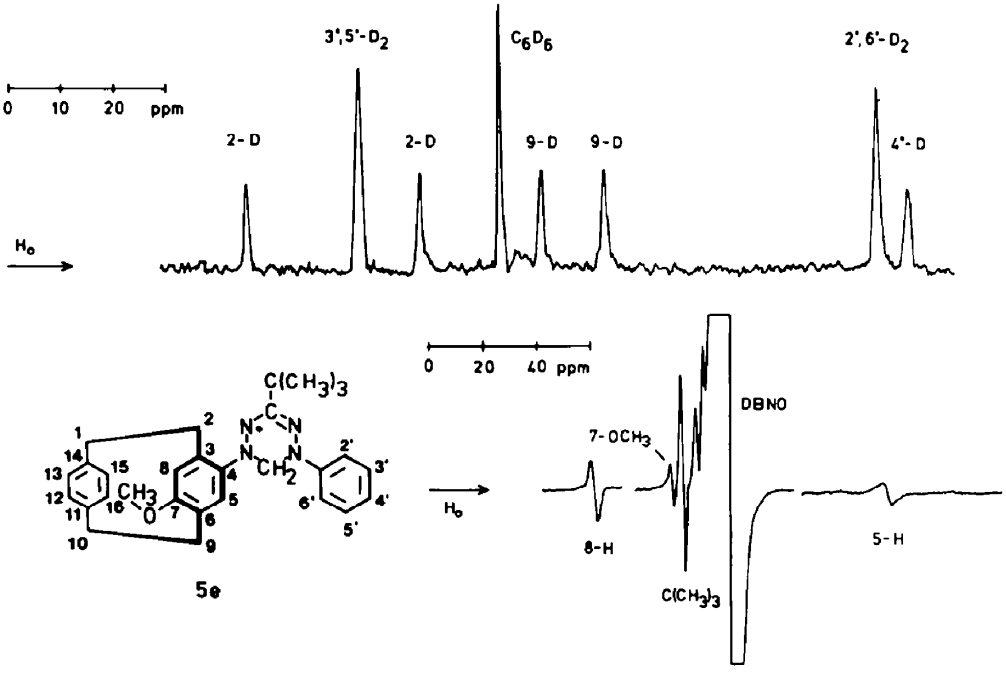
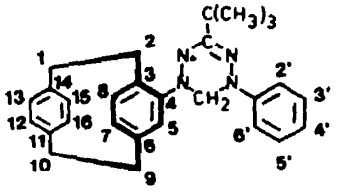
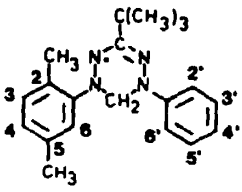


Fig. 1. D and H NMR spectrum of **5e** in di - t - butyl nitroxide (DBNO).

Table 1. H and D paramagnetic shifts $\delta_p = (H_d - H_p)/H_d$[a] and coupling constants a_H and a_D of 5a–5f and 6 at 300 K



5a



6

	Solvent	Assignment	δ_p [ppm]	a_D [G]	a_H [G][b]
5a	DBNO	1,1,10,10,12,13,15,16-H_8[c]			
		2,2-H_2	55.8		0.75
			13.7		0.19
		5,7-H_2	-76.8		-1.04
		8-H	41.2		0.56
		9,9-H_2[c]			
		$C(CH_3)_3$	8.9		0.12
		2',6'-H_2	-76.8		-1.04
		3',5'-H_2	28.0		0.38
		4'-H	-82.6		-1.12
5b	DBNO	1,1,10,10,12,13,15,16-H_8[c]			
		2,2-H_2	56.3		0.76
			14.4		0.19
		5,7-H_2	-74.6		-1.01
		8-H	41.3		0.56
	$CDCl_3$	9,9-H_2	-9.0		-0.12
			-5.0		-0.07
		$C(CH_3)_3$	8.8		0.12
		2',6'-D_2	-76.0	-0.158	-1.03
		3',5'-D_2	28.8	0.060	0.39
		4'-D	-81.8	-0.170	-1.11
5c	DBNO	5,7-D_2	-74.0	-0.154	-1.00
		8-D	41.8	0.087	0.56
		12,13,15,16-D_4	2.6 (2D)	0.005	0.04
			-2.3 (2D)	-0.005	-0.03
5d	DBNO	1,1,10,10-D_4	2.2 (2D)	0.005	0.03
			0.6	0.001	0.01
			-1.8	-0.004	-0.02
		2,2-D_2	54.8	0.114	0.74
			13.4	0.028	0.18
		9,9-D_2	-8.8	-0.018	-0.12
			-5.8	-0.012	-0.08
5e	DBNO	1,1,10,10,12,13,15,16-H_8[c]			
		2,2-D_2	52.1	0.108	0.70
			19.1	0.040	0.26
		5-H	-74.3		-1.00
		7-OCH_3	9.6		0.13

Table 1. (*Contd*)

			5a	6	
	Solvent	Assignment	δ_p [ppm]	a_D [G]	a_H [G][b]
		8-H	34.1		0.46
		9,9-D_2	-16.3	-0.034	-0.22
			-4.2	-0.009	-0.06
		$C(CH_3)_3$	8.2		0.11
		2',6'-D_2	-72.0	-0.150	-0.97
		3',5'-D_2	26.6	0.055	0.36
		4'-D	-78.3	-0.163	-1.06
5f	DBNO	2,2-D_2	53.3	0.111	0.72
			20.0	0.042	0.27
6	DBNO	$C(CH_3)_3$	9.2		0.12
		2-CH_3	35.8		0.48
		3-H	16.5		0.22
		4-H	-48.5		-0.65
		5-CH_3	-13.7		-0.18
		6-H	-43.7		-0.58
		2',6'-H_2	-82.1		-1.10
		3',5'-H_2	30.5		0.41
		4'-H	-87.0		-1.16

[a] Shift relative to the corresponding H(D) resonance in the parent [2.2]paracyclophane. [b] Partly calculated from a_D; $a_H = 6.51\ a_D$.
[c] These resonances could not be resolved or definitely assigned.

result only small ($<|3|$ ppm) paramagnetic shifts are observed. The sizes of these shifts have a considerable relative experimental error, since the positions of the diamagnetic reference signals (multiplets not resolved) can only be measured to within ± 1 ppm.

The detailed NMR study of **5a** and its derivatives **5b–5f** yields an almost complete assignment of all paramagnetic shifts. The analysis of the experimental data reveals no substantial transannular interaction of the unpaired electron delocalised in the aryl ring bearing the verdazyl substituent with protons of the attached 1,4-xylene part. There is also no substantial direct interaction between 15-H and the pseudogeminally fixed nitrogen of the verdazyl substituent. The small coupling constants of the protons (1,10,12,13,15,16 $<|50|$ mG) in the attached 1,4-xylene system probably arise from weak long range interactions.

EXPERIMENTAL

NMR of **5a–5f** and **6**: The magnitude of the paramagnetic shift δ_p is related to the hyperfine coupling constant a_i by $\delta_p = (H_d - H_p)/H_d = a_i g\beta\gamma_e/4kT\gamma_i$, which can be written as $a_i = C_i(T)\delta_p$. $C_H(300\ K) = 1.35 \times 10^{-2}$ G/ppm; $C_D(300\ K) = 2.08 \times 10^{-3}$ G/ppm. Nuclei with lines shifted to low field have positive coupling constants, those with lines shifted to high field positive ones.

H NMR spectra were measured using the broad line technique (Bruker Spectrospin HX-90 MHz, 30 Hz modulation, phase sensitive detection). Each spectrum was recorded several times with linear field sweep and checked by 2 kHz control distances. D NMR spectra were recorded with a Bruker Spectrospin HX-360 MHz instrument.

H NMR spectra of the diamagnetic compounds were run on Bruker Spectrospin WP 80 or HX-360 MHz. Mass spectra were obtained with a Du Pont 21-492 spectrometer.

1,4 - *Bis(chloromethyl)* - $[D_4]$ - *benzene* was prepared from $[D_6]$ - benzene, formaldehyde and HCl as described in the literature for the undeuterated compound,[16] m.p. 99–100°. H NMR (80 MHz, $CDCl_3$): $\delta = 4.54$ (s, CH_2).

1,4 - *Bis(hydroxy* - $[D_2]$ - *methyl)benzene.* The soln of dimethyl terephthalate (97 g) in THF (1 l.) was slowly added (~1 hr) to the stirred suspension of $LiAlD_4$ (25 g) in THF (500 ml). Then the mixture was heated under reflux for 1 hr. After addition of EtOAc (20 ml) and 2 N H_2SO_4 (~100 ml) at room temp the mixture was filtered and the residue washed with THF. The combined filtrates were evaporated. Crystallisation of the residue from water yielded colorless needles (59 g, 71%), m.p. 112–113 (undeuterated compound m.p. 113–114°). H NMR (80 MHz $CDCl_3$): $\delta = 1.58$ (s, 2H, OH), 7.29 (d, J = 10 Hz, 4 H aromatic)

1,4 - *Bis(hydroxy* - $[D_2]$ - *methyl)* - 2 - *methoxybenzene* Dimethyl 2 - methoxyterephthalate (56 g) in THF (500 ml) $LiAlD_4$ (12 g) in THF (300 ml) were treated as described above Crystallisation of the residue from EtOAc/hexane yielded colorless crystals (27 g, 63%), m.p. 83–84°. H NMR (80 MHz, $CDCl_3$ $\delta = 2.11$ (s, 2 H, OH), 3.81 (s, 3 H, OCH_3), 6.8–7.3 (m, 3 aromatic). (Found: C, 62.80; H + D, 9.43, $C_9H_8D_4O_3$ requires: C 62.77; H + D, 9.36%).

Methyl 4 - *hydroxymethyl* - 3 - *methoxybenzoate.* $LiAlH_4$ (0.60 g) was added to the soln of dimethyl 2 - methoxyterephthalate (5.6 g) in diethyl ether (200 ml) and the mixture stirred room temp for 3 hr. After addition of 2 N H_2SO_4 (~5 ml) the mixture was filtered, the filtrate washed with water and dri

($MgSO_4$). After evaporation of the solvent, the residue was chromatographed on silica gel, using CH_2Cl_2 as eluent, to yield colorless needles (2.1 g, 43%) from MeOH, m.p. 99–100°. H NMR (360 MHz, $CDCl_3$): $\delta = 2.36$ (br. s, 1 H, OH), 3.90 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 4.71 (s, 2 H, CH_2), 7.37 (d, $J_{5,6} = 7.9$ Hz, 4-H), 7.52 (d, $J_{2,6} = 1.4$ Hz, 2-H), 7.63 (q, 6-H).

Methyl 4 - *acetoxymethyl* - 3 - *methoxybenzoate.* The mixture of methyl 4 - hydroxymethyl - 3 - methoxybenzoate (10 g) in Ac_2O (25 ml) was refluxed for 2 min. After hydrolysis of the remaining Ac_2O with ice water the product was collected. Crystallisation from MeOH yielded colorless needles (7.5 g, 62%), m.p. 59–60°. H NMR (360 MHz, $CDCl_3$): $\delta = 2.13$ (s, 3 H, CCH_3), 3.89 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 5.19 (s, 2 H, CH_2), 7.37 (d, $J_{5,6} = 7.9$ Hz, 5-H), 7.54 (d, $J_{2,6} = 1.4$ Hz, 2-H), 7.64 (q, 6-H). (Found: C, 60.33; H, 6.17. $C_{12}H_{14}O_5$ requires: C, 60.50; H, 5.92%).

1 - *Hydroxymethyl* - 4 - *hydroxy* - [D_2] - *methyl* - 2 - *methoxybenzene.* Methyl 4 - acetoxymethyl - 3 - methoxybenzoate (7.1 g) in THF (100 ml), $LiAlD_4$ (1.7 g) in THF (100 ml) were treated as described for 1,4 - bis(hydroxy - [D_2] - methyl)benzene. The residue yielded from EtOAc/hexane colorless crystals (2.9 g, 57%), m.p. 83–84°. MS: $m/e = 170$ (M^+). H NMR (80 MHz, $CDCl_3$): $\delta = 2.25$ (s, 2 H, OH), 3.84 (s, 3 H, OCH_3), 4.65 (s, 2 H, CH_2), 6.8–7.4 (m, 3 H aromatic).

1,4 - *Bis(chloro* - [D_2] - *methyl)benzene.* $SOCl_2$ (70 ml) was slowly added to the stirred soln of 1,4 - bis(hydroxy - [D_2 - methyl)benzene (50 g) in CH_2Cl_2 (300 ml). After stirring for 1 hr the soln was treated with water and the separated organic phase evaporated. The residue yielded colorless prisms (48 g, 79%) from cyclohexane, m.p. 100–101° (undeuterated compound, m.p. 100°).[16] H NMR (80 MHz, $CDCl_3$): $\delta = 7.39$ (s, H aromatic).

1,4 - *Bis(chloro* - [D_2] - *methyl)* - 2 - *methoxybenzene.* 1,4 - Bis(hydroxy - [D_2] - methyl) - 2 - methoxybenzene (26 g) in CH_2Cl_2 (200 ml) and $SOCl_2$ (30 ml) were treated as described above. The residue was distilled. The fraction, b.p. 144–146°/10^{-2} Torr, crystallized (18 g, 57%), m.p. 62–64°. H NMR (80 MHz, $CDCl_3$): $\delta = 3.87$ (s, 3 H, OCH_3), 6.8–7.4 (m, 3 H aromatic). (Found: C, 51.56; H + D, 6.56. $C_9H_6Cl_2D_4O$ requires: C, 51.69; H + D, 6.74%).

1 - *Chloromethyl* - 4 - *chloro* - [D_2] - *methyl* - 2 - *methoxybenzene.* 1 - Hydroxymethyl - 4 - hydroxy - [D_2] - methyl - 2 - methoxybenzene (5 g) in CH_2Cl_2 (100 ml) and $SOCl_2$ (6 ml) were treated as described above, to yield colorless crystals (3.4 g, 56%), m.p. 63–64°. H NMR (80 MHz, $CDCl_3$): $\delta = 3.87$ (s, 3 H, OCH_3), 4.63 (s, 2 H, CH_2), 6.8–7.4 (m, 3 H aromatic).

5 - *Methoxy* - 2,11 - *dithia*[3,3,10,10 - D_4] [3.3] *paracyclophane.* Solutions: (a) 1,4 - Bis(chloro - [D_2] - methyl) - 2 - methoxybenzene (8.35 g) in benzene (500 ml); (b) 1,4 - bis(mercaptomethyl)benzene[5] (7.1 g) in EtOH (500 ml); (c) KOH (4.7 g) in EtOH (500 ml). These solns were added dropwise simultaneously and equally within 6 hr to boiling EtOH (3 l.), which was vigorously stirred.

After the addition heating under reflux was continued for 1 hr. Evaporation of the mixture gave a colorless residue, which was extracted (twice) with boiling toluene. This soln was again evaporated and the residue purified by chromatography on Al_2O_3 (Brockmann), using toluene as eluent, to yield colourless prisms (6.3 g, 51%) from EtOH, m.p. 140–141°. MS: $m/e = 306$ (M^+). (Found: C, 66.95; H + D, 7.16. $C_{17}H_{14}D_4OS_2$ requires C, 66.62; H + D, 7.23%).

6 - *Methoxy* - 2,11 - *dithia* - [3,3 - D_2] [3.3] *paracyclophane.* The solutions: (a) 1 - Chloromethyl - 4 - chloro - [D_2] - methyl - 2 - methoxybenzene (4.15 g) in benzene (500 ml); (b) 1,4 - bis(mercaptomethyl)benzene[5] (3.6 g) in EtOH (500 ml); (c) KOH (2.4 g) in EtOH (500 ml); and EtOH (2 l.) were treated as above. Colorless prisms (4.0 g, 66%) from EtOH, m.p. 139–140°. MS: $m/e = 304$ (M^+).

[4,5,7,8,12,13,15,16 - D_8] [2.2] *Paracyclophane* (1c). 1c was prepared from 1,4 - bis(chloromethyl) - [D_4] - benzene as described in the lit.[5] for the undeuterated compound: m.p. 286–287°. MS: $m/e = 216$ (M^+). H NMR (80 MHz, $CDCl_3$): $\delta = 3.08$ (s, CH_2).

[1,1,2,3,9,9,10,10 - D_8] [2.2] *Paracyclophane* (1d). This was prepared from 1,4 - bis(chloro - [D_2] - methyl)benzene as above:[5] m.p. 285–287°. MS: $m/e = 216$ (M^+). H NMR (80 Hz, $CDCl_3$): $\delta = 6.46$ (s, H aromatic).

4 - *Methoxy*[2,2,9,9 - D_4] [2.2] *paracyclophane* (1e). The stirred soln of 5 - methoxy - 2,11 - dithia - [3,3,10,10 - D_4] [3.3] paracyclophane (4 g) in trimethyl phosphite (1.5 l.) was photolyzed in the Rayonet reactor 85 (300 nm) for 6 hr, the progress of the photolysis being checked by tlc. The soln was evaporated. Crystallisation of the residue from EtOH yielded colourless crystals (2.6 g, 82%), m.p. 113–115° (undeuterated compound, m.p. 116–117°).[17] MS: $m/e = 242$ (M^+).

5 - *Methoxy*[2,2 - D_2] [2.2] *paracyclophane* (1f). 6 - Methoxy - 2,11 - dithia - [3,3 - D_2] [3.3] paracyclophane (4 g) in trimethyl phosphite (1.5 l.) was treated as above to yield colorless crystals (2.4 g, 76%), m.p. 113–114° (undeuterated compound, m.p. 116–117°).[17] MS: $m/e = 240$ (M^+).

4 - *Nitro* - [5,7,8,12,13,15,16 - D_7] [2.2] *paracyclophane* (2c), m.p. 154–155°, MS: $m/e = 260$ (M^+), and 4 - *nitro* - [1,1,2,2,9,9,10,10 - D_8] [2.2] *paracyclophane* (2d), m.p. 155–156°, MS: $m/e = 261$ (M^+), were prepared from the corresponding cyclophanes 1c and 1d as described in the lit.[6] for the undeuterated compound, m.p. 155.5–156.5°.

7 - *Methoxy* - 4 - *nitro* - [2,2,9,9 - D_4] [2.2] *paracyclophane* (2e). Conc HNO_3 (1.5 ml) was added to the soln of 1e (2.6 g) in AcOH (25 ml). After stirring at room temp for 1 hr, the mixture was partitioned between benzene and water, the benzene layer washed 3 times with water, dried ($MgSO_4$), and the solvent evaporated. The residue was chromatographed on silica gel, using CH_2Cl_2 as eluent, to yield yellow prisms (800 mg, 26%) from ethanol, m.p. 170–171°. MS: $m/s = 287$ (M^+). (Found: C, 70.82; H + D, 7.66; N, 5.12. $C_{17}H_{13}D_4NO_3$ requires: C, 71.06; H + D, 7.36; N, 4.87%).

7 - *Methoxy* - 4 - *nitro* - [2,2 - D_2] [2.2] *paracyclophane* (2f). This was prepared from 1f as described above; m.p. 170–171°. MS: $m/e = 285$ (M^+).

4 - *Amino* - [5,7,8,12,13,15,16 - D_7] [2.2] *paracyclophane* (3c), m.p. 242–244°, MS: 230 (M^+), and 4 - *amino* - [1,1,2,2,9,9,10,10 - D_8] [2.2] *paracyclophane* (3d), m.p. 243–244°, MS: $m/e = 231$ (M^+), were prepared from the corresponding nitro compounds 2c and 2d as described in the lit.[6] for the undeuterated compound, m.p. 239–241.5°.

4 - *Amino* - 7 - *methoxy* - [2,2,9,9 - D_4] [2.2] *paracyclophane* (3e). 2e (1.8 g) in EtOAc (50 ml) was hydrogenated (~3 H_2) in the presence of Raney Ni (1 g). The catalyst was collected, and the filtrate evaporated. The residue yielded colourless plates (1.2 g, 74%) from EtOH, m.p. 165–166°. MS: $m/e = 257$ (M^+).

4 - *Amino* - 7 - *methoxy* - [2,2 - D_2] [2.2] *paracyclophane* (3f). This was prepared from 2f as described above, m.p. 164–165°, MS: $m/e = 255$ (M^+).

3 - *t* - *Butyl* - 1 - ([2.2]*paracyclophan* - 4 - *yl*) - 5 - *phenylformazan* (4a). The mixture of 4 - amino - [2.2] paracyclophane[6] (2 g) in dimethylformamide (25 ml) + H_2O (2.5 ml) + conc HCl (2.5 ml) was cooled to 0° and kept at this temp while the soln of $NaNO_2$ (620 mg) in H_2O (10 ml) was added dropwise under stirring. A soln of phenylhydrazine (2.1 g) and 2,2 - dimethylpropanal (1.7 g) in MeOH (20 ml) was heated to the b.p. After addition of NaOAc (10 g) this mixture was cooled and kept at 0° while the diazonium salt soln was added in small portions with stirring. Stirring was continued for 1 hr, then the product was separated by adding water to the mixture. The collected product was dissolved in DMF (20 ml) + methanolic KOH (saturated, 1 ml); rearrangement. 15 min later the product was precipitated by adding water, collected and purified by chromatography on Al_2O_3 (Brockmann), using cyclohexane/benzene 2:1 as eluent, to yield redbrown crystals (2.3 g, 63%) from EtOAc/MeOH, m.p. 168–169° (dec). (Found: C, 78.71; H, 7.51; N, 13.58. $C_{27}H_{30}N_4$ requires: C, 78.99; H, 7.37; N, 13.65%).

3 - *t* - *Butyl* - 1 - ([2.2] *paracyclophan* - 4 - *yl*) - 5 - [D_5] - *phenylformazan* (4b). This was prepared as described above using [D_5] - phenylhydrazine,[11] m.p. 168–169° (dec). (Found: C, 78.29; H + D, 8.65; N, 13.25. $C_{27}H_{25}D_5N_4$ requires: C, 78.03; H + D, 8.49; N, 13.48%).

3 - *t* - *Butyl* - 1 - ([5,7,8,12,13,15,16 - D_7] [2.2] *paracyclophan* - 4 - *yl*) - 5 - *phenylformazan* (4c). This was prepared from 3c as described for 4a; m.p. 165–167° (dec).

3 - *t* - *Butyl* - 1 - ([1,1,2,2,9,9,10,10 - D_8] [2.2] *paracyclophan* - 4 - *yl*) - 5 - *phenylformazan* (**4d**). This was prepared from **3d** as described for **4a**; m.p. 166–168° (dec).

3 - *t* - *Butyl* - 1 - (7 - *methoxy*[2,2,9,9 - D_4] [2.2] *paracyclophan* - 4 - *yl*) - 5 - [D_5] - *phenylformazan* (**4e**). This was prepared from **3e** and [D_5] - phenylhydrazine[11] as described for **4a**; red-brown plates (42%), m.p. 141–142° (dec). (Found: C, 74.77; H + D, 9.36; N, 12.29. $C_{28}H_{23}D_9N_4O$ requires: C, 74.79; H + D, 9.19; N, 12.46%).

3 - *t* - *Butyl* - 1 - (7 - *methoxy*[2,2 - D_2] [2.2] *paracyclophan* - 4 - *yl*) - 5 - *phenylformazan* (**4f**). This was prepared from **3f** as described for **4a**; m.p. 140–142° (dec).

3 - *t* - *Butyl* - 1 - ([2.2] *paracyclophan* - 4 - *yl*) - 5 - *phenylverdazyl* (**5a**). **4a** (1.8 g) + $KHSO_4$ (2 g) + paraformaldehyde (500 mg) in DMF (50 ml) were stirred for 24 hr. The mixture was filtered, the filtrate cooled to 0°, 40% aqueous formaldehyde (5 ml) was added, and then dropwise 2 N NaOH until the colour of the mixture changed to green. The mixture was partitioned between benzene and water, the benzene layer washed 3 times with water, dried ($MgSO_4$) and the solvent evaporated. The residue was chromatographed on Al_2O_3 (Brockmann), using benzene as eluent, to yield green needles (1.3 g, 70%) from EtOAc/hexane, m.p. 119–120° (dec). Microhydrogenation: **5a** (9.75 mg) + 5% Pd/$BaSO_4$ (20 mg) in DMF (2 ml); 0.49 moles H_2 after 60 min (end value). UV (dioxane): λ_{max} (log ϵ) = 664 (3.72), 380 s (3.78), 329 (4.08), 272 s (3.85), 220 s nm (4.37). (Found: C, 79.12; H, 7.66; N, 12.97. $C_{28}H_{31}N_4$ requires: C, 79.40; H, 7.38; N, 13.23%).

3 - *t* - *Butyl* - 1 - ([2.2] *paracyclophan* - 4 - *yl*) - 5 - [D_5] - *phenylverdazyl* (**5b**). This was prepared from **4b** as described above; m.p. 120–121° (dec). (Found: C, 78.29; H + D, 8.65; N, 13.25. $C_{28}H_{26}D_5N_4$ requires: C, 78.46; H + D, 8.46; N, 13.07%).

3 - *t* - *Butyl* - 1 - ([5,7,8,12,13,15,16 - D_7] [2.2] *paracyclophan* - 4 - *yl*) - 5 - *phenylverdazyl* (**5c**). This was prepared from **4c** as described above; m.p. 120–121° (dec).

3 - *t* - *Butyl* - 1 - ([1,1,2,2,9,9,10,10 - D_8] [2.2] *paracyclophan* - 4 - *yl*) - 5 - *phenylverdazyl* (**5d**). This was prepared from **4d** as described above; m.p. 122–123° (dec).

3 - *t* - *Butyl* - 1 - (7 - *methoxy*[2,2,9,9 - D_4] [2.2] *paracyclophan* - 4 - *yl*) - 5 - [D_5] - *phenylverdazyl* (**5e**). This was prepared from **4e** as described above. From ligroin green plates, m.p. 138–139° (dec). (Found: C, 75.41; H + D, 9.10; N, 11.90. $C_{29}H_2D_9N_4O$ requires: C, 75.28; H + D, 9.15; N, 12.11%).

3 - *t* - *Butyl* - 1 - (7 - *methoxy*[2,2 - D_2] [2.2] *paracyclophan* - 4 - *yl*) - 5 - *phenylverdazyl* (**5f**). This was prepared from **4f** as described above; m.p. 137–139° (dec).

3 - *t* - *Butyl* - 1 - (2,5 - *dimethylphenyl*) - 5 - *phenylformazan*. 2,5 - Xylidine (2.4 g) in H_2O (5 ml) + conc HCl (5 ml); $NaNO_2$ (1.4 g) in H_2O (10 ml); phenylhydrazine (2.1 g) + 2,2 - dimethylpropanal (1.7 g) in MeOH (20 ml); NaOAc (5 g) + DMF (25 ml) were reacted as described for **4a** to yield brown crystals (2.4 g, 39%) from EtOH, m.p. 109–110° (dec). (Found: C, 73.75; H, 7.98; N, 17.92. $C_{19}H_{24}N_4$ requires: C, 73.99; H, 7.84; N, 18.17%).

3 - *t* - *Butyl* - 1 - (2,5 - *dimethylphenyl*) - 5 - *phenylverdazyl* (**6**). 3 - t - Butyl - 1 - (2,5 - dimethylphenyl) - 5 - phenylformazan (2 g) in DMF (50 ml) + paraformaldehyde (0.5 g) + $KHSO_4$ (2 g) were treated as described for **5a**. From ligroin blue crystals (1.1 g, 53%), m.p. 61–62° (dec). UV (dioxane): λ_{max} (log ϵ) = 641 (3.71), 375 s (3.66), 372 (4.13), 280 (4.00), 243 nm (4.11). (Found: C, 74.77; H, 8.09; N, 17.44. $C_{20}H_{25}N_4$ requires: C, 74.73; H, 7.84; N, 17.43%).

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