Verdazyls. Part 30.[1] N-1,N-1'-Linked Biverdazyls (Bis-1,2,3,4-tetrahydro-*s*-tetrazin-1-yls) with a [2.2]Paracyclophanylene Bridge

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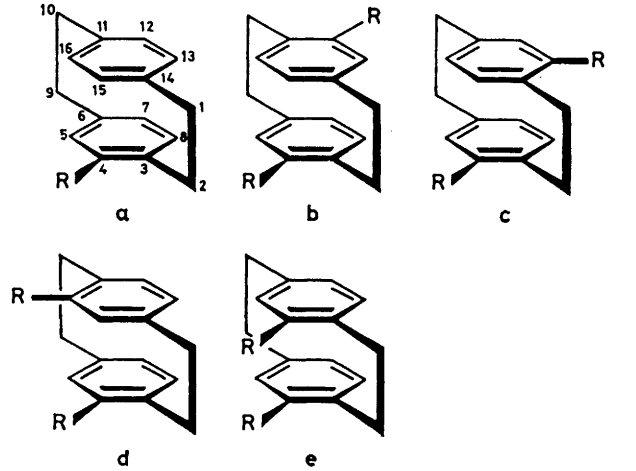
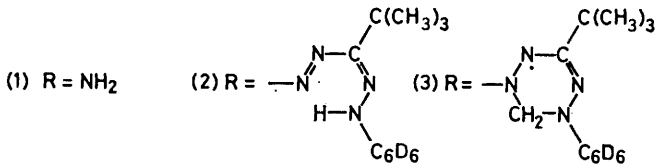
Three isomeric biverdazyls (3b—d) containing a [2.2]paracyclophanylene bridge have been prepared. The zero-field splitting parameter $|D'|$ could be evaluated from the e.s.r. spectra taken in liquid crystalline solution. The e.s.r. and n.m.r. results of (3b—d), which indicate $RT \gg |J| \gg a_N$, are discussed with respect to the structure and the distortion about the N–bridge bond.

N-1,N-1'-Linkage of verdazyls (tetrahydro-*s*-tetrazin-1-yls) through various conjugated bridges produces diffuse π-electron systems with interesting properties, *e.g.* strong interactions between both unpaired electrons.[2] Comparable effects might also appear, if there is no





direct bond between the two *N*-phenyl groups of the verdazyls but the possibility of a transannular interaction. The model of choice is the [2.2]paracyclophanylene bridge, in which *N*-phenyl groups of verdazyls are held face to face at a distance of *ca.* 3.1 Å. Forrester and Ramasseul have already synthesized binitroxides of this type.[3,4] In these compounds, however, the steric interaction between the $(CH_3)_3C(NO^{\bullet})$ substituent and the adjacent bridging methylene group causes the nitroxide substituent to be considerably twisted out of conjugation with the phenylene ring.[4,5] This is not observed in 3-t-butyl-1-([2.2]paracyclophan-4-yl)-5-phenylverdazyl, where the arrangement about the [2.2]-paracyclophan-4-yl–N-1 bond corresponds to that in 3-t-butyl-1,5-diphenylverdazyl.[1] Furthermore we intended to carry out a detailed n.m.r. study of [2.2]paracyclophanylene-linked biverdazyls, the results of which should reveal further information about transannular interactions in the paracyclophane bridge of such compounds.

Monosubstitution in each ring of [2.2]paracyclophane leads to the four isomers : pseudo-*para* (b), pseudo-*meta* (c), pseudo-*ortho* (d), and pseudo-geminal (e). The synthesis of the corresponding biverdazyls started out from dinitro[2.2]paracyclophanes.[6] Catalytic hydrogenation (Pd–$BaSO_4$) yielded the diamino-derivatives (1b—e). Each isomer exhibits a unique n.m.r. aromatic proton pattern (Table 1). In (1b) for the *ortho*- and pseudo-*meta*-protons the usual chemical upfield shift is observed (*ca.* +0.9 p.p.m. relative to the signal for the aromatic protons of [2.2]paracyclophane, δ 6.37) as in the case of aniline or the monoamino-derivative (1a).[7] The distinct downfield shift of the *meta* and pseudo-geminal protons in (1c) is mainly due to the deshielding effect of the pseudo-geminal amino-substituent.[7] Most of the observed effective shifts (Table 1), however, result from superimposed direct substituent and transannular effects. Compounds (1b—e) were diazotized and coupled with 2,2-dimethylpropanal [$^2H_5$]phenylhydrazone to yield the corresponding biformazans (2b—e). I.r. and n.m.r. spectra indicate that these biformazans, as well as the

Table 1

^{1}H N.m.r. chemical shifts [a] (δ) of amino-substituted [2.2]paracyclophanes

Compound	*ortho*	*meta*	*para*	pseudo-geminal	pseudo-*ortho*	pseudo-*meta*	pseudo-*para*	NH_2
(1a) [7,8]	5.39	6.27	6.08	7.14	~6.35	~6.35	6.58	3.35
(1b)	5.44	6.17	6.59	6.59	6.17	5.44		3.40
(1c) [7]	5.47	6.95	6.01	6.95	6.01		5.47	3.38
(1d)	6.16	6.35	6.02	6.16		6.02	6.35	3.35
(1e)	5.91	6.34	6.07		5.91	6.34	6.07	3.46

[a] Taken on a Bruker WP 80 on dilute solution (*ca.* 1%) in $CDCl_3$ with tetramethylsilane as internal standard.

monoformazan (2a), occupy a *trans-syn*-form, in which intramolecular hydrogen-bonding stabilizes the molecules in the *s-cis*-arrangement. When one compares the first absorption bands of (2b—e) with that of (2a) (Table 2), the pseudo-*ortho*-isomer (2d) shows a slight, and the pseudo-geminal compound (2e) a considerable, hypsochromic shift. These shifts are obviously caused by steric interactions between the substituents. In (2e) the formazanyl groups are considerably twisted out of conjugation with the phenylene rings of the bridge. The slight bathochromic shift observed for the pseudo-*para*-isomer (2b) suggests that transannular interactions also contribute to some extent. The biformazans (2b—d) were readily converted into the corresponding biverdazyls (3b—d) using the usual cyclisation method with formaldehyde.[9] In case of the biformazan (2e), however, all our attempts failed to obtain the pseudo-geminal biverdazyl (3e).

TABLE 2

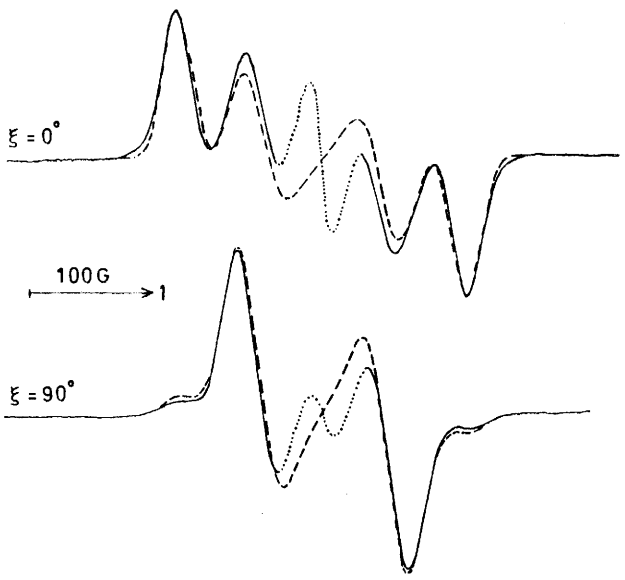
Electronic spectral data of formazans (2a—e) and verdazyls (3a—d) in dioxan solution; $\lambda_{max.}$/nm (log ε)

Compound	
(2a)	488 (4.27), 332 (3.62), 273s (3.99), 243sh (4.14)
(2b)	495 (4.54), 330sh (3.94), 253 (4.38)
(2c)	488 (4.52), 330sh (3.88), 240sh (4.40)
(2d)	481 (4.51), 345 (3.86), 242sh (4.42)
(2e)	457 (4.56), 330sh (3.94), 251 (4.35)
(3a) [1]	664 (3.72), 380sh (3.78), 329 (4.08), 272sh (3.85), 220sh (4.37)
(3b)	668 (4.05), 388 (4.09), 328 (4.37), 237sh (4.33)
(3c)	664 (4.03), 392 (4.10), 328 (4.36), 273 (4.11), 237 (4.40)
(3d)	657 (3.95), 383sh (4.03), 329 (4.36), 276 (4.07), 235sh (4.35)

sh = Shoulder.

The e.s.r. spectra of the biverdazyls (3b—d) in benzene at room temperature show a broad resonance line indicating a poorly resolved hyperfine structure with a spacing of *ca.* 2.9 G. This is typical for biverdazyls, in which the electron exchange parameter J, corresponding to the energy separation between singlet and triplet states, is considerably larger than the nitrogen splitting of *ca.* 5.9 G ($|J| \gg a_N$).[2] The line broadening is caused by the strong magnetic dipolar interaction of both unpaired electrons. The triplet state of (3b—d) is clearly confirmed by the e.s.r. spectra taken in liquid crystalline solutions (nematic phase 5; Merck) at 240 K (Figure). From these e.s.r. spectra only the zero-field splitting parameters $|D'|$ can be determined, the parameters $|E'|$ being apparently too small. Consequently in the computer simulations, employing a FORTRAN program,[10] only the parameter $|D'|$ has been considered. The results of the simulations, including linewidth and orientational distributions, are summarized in Table 3.

The zero-field splitting parameter $|D'|$ can be converted into a hypothetical average distance r between the two unpaired electrons using the two point model $|D'| = 3g\beta/4r^3$. The resulting distances r of the pseudo-*para*-biverdazyl (3b) and the pseudo-*meta*-compound (3c) agree almost with the distances between the midpoints of the verdazyl rings (see Table 3, footnote *c*). For the pseudo-*ortho*-biverdazyl (3d), however, the calculated distance r suggests that the average centres of the unpaired electrons are slightly shifted beyond the verdazyl midpoints, apparently a consequence of the steric arrangement in (3d). Due to the pseudo-*ortho*-substitution the verdazyl rings in (3d) are twisted out of



Experimental (——) and simulated (– – – –) e.s.r. spectra of (3d) in nematic phase 5 at 240 K. Signals in the centre of the spectra (· · · ·) are due to some monoradical impurity. ξ is the angle between the director of the liquid crystal and the magnetic field

TABLE 3

Compounds (3b—d) in a liquid crystal (nematic phase 5; Merck).[a] Zero-field splitting parameter $|D'|$, orientation-dependent linewidth OHB,[b] parameter A of the orientational distribution function,[10] order parameter $\bar{P}_2$, average distance r between the two unpaired electrons ($|D'| = 3g\beta/4r^3$), and molecular distance r' [c]

		OHB [b]					
Compound	$\|D'\|$/G	HB/G	F/G	A	P_2	r/Å	r'/Å
(3b)	56.2 ± 0.5	22.0	0	0.5	0.07	7.9	6.4—8.9
(3c)	68.2 ± 0.5	22.0	0	−0.3	−0.04	7.4	5.8—7.9
(3d)	111.8 ± 0.5	27.0	8.0	1.75	0.26	6.3	4.2—5.2

[a] θ = Angle between the principal axis of the zero-field splitting tensor and magnetic field, ξ = angle between director of the liquid crystal and magnetic field. [b] OHB = HB + $F\sin^2\theta$. [c] The molecular distances are estimated from X-ray structure analysis data of 1,3,5-triphenylverdazyl.[11] The lowest value in the range given for r' is the distance between the bridged N-1,N-1′ atoms; the highest value represents the distance between the midpoints of the verdazyl rings.

conjugation with the phenylene rings of the bridge to a large extent. This increased distortion about the N–bridge bond in (3d) is also indicated by the hypsochromic shift of the first absorption band, when one compares the data of the electronic spectra of (3a—d) in Table 1.

N.m.r. paramagnetic shifts (δ_p) of organic free radicals render directly the sign and the magnitude of electron-nuclei coupling constants (a_i).[12,13] Based on the Reitz–Weissman model[14,15] of the electronic structure of biradicals, δ_p is related to a_i by equation (1).[16] In

$$\delta_p = (H_d - H_p)/H_d = a_i g\beta\gamma_e/kT\gamma_i[3 + \exp(J/RT)] \quad (1)$$

biradicals satisfying $|J| \ll RT$ equation (1) is reduced to (2) which can be written $a_i = C_i(T)\delta_p$; C_H (300 K) = 1.35×10^{-2} G/p.p.m., C_D (300 K) = 2.08×10^{-3} G/p.p.m.

$$\delta_p = a_i g\beta\gamma_e/4kT\gamma_i \quad (2)$$

Equation (2) is in accord with the corresponding equation for monoradicals. Therefore the same paramagnetic shifts are expected for corresponding protons in biverdazyls satisfying $|J| \ll RT$ and in structurally related monoverdazyls.

The n.m.r. spectra of (3b—d) in di-t-butyl nitroxide[17] are sufficiently resolved and were analysed by comparison of the individual spectra and by analogy with the n.m.r. results of (3a).[1] The data obtained are listed in Table 4.

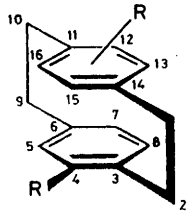
Comparing the n.m.r. results of (3b—d) with those of (3a),[1] excellent agreement is found for $a_{C(CH_3)_3\text{-}H} = 0.11$ (± 0.01), $a_{2',6'\text{-}D} = -0.160$ (± 0.003), $a_{3',5'\text{-}D} = 0.060$ (± 0.001), and $a_{4'\text{-}D} = -0.172$ (± 0.002) G. These results clearly show that the biverdazyls (3b—d) satisfy $RT \gg |J| \gg a_N$. Excellent agreement is also found for the aromatic bridge proton splittings of (3b and c) compared with the corresponding values of (3a): $a_{5,13\text{-}H}$(3b) $\approx a_{5,12\text{-}H}$(3c) $\approx a_{5\text{-}H}$(3a) $= -1.02$ (± 0.03) G, $a_{8,16\text{-}H}$(3b) $\approx a_{8,15\text{-}H}$(3c) $\approx a_{8\text{-}H}$(3a) $= 0.56$ (± 0.02) G, and $a_{7,15\text{-}H}$(3b) $\approx a_{7,16\text{-}H}$(3c) $\approx a_{7\text{-}H}$(3a) $= -1.03$ (± 0.01) G.

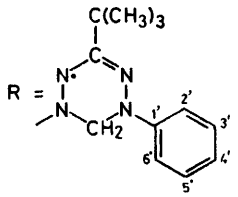
These data represent splittings of protons, which are directly connected with carbons bearing spin density (α to ρ_C). According to these splittings the varied bridging in (3a—c) apparently does not affect the spin density distribution in the phenylene rings of the bridge. The splittings $a_{2,10\text{-}H}$(3b) $\approx a_{1,2\text{-}H}$(3c) $\approx a_{2\text{-}H}$(3a) $= 0.77$ (± 0.06) or 0.20 (± 0.02) G stem from protons β to ρ_C [$a_H = (B_0 + B\cos^2\theta)\rho_C$]. Here the small deviations beyond the experimental error ($\pm 3\%$) may be connected, at least in part, with slight changes in the spatial arrangement (cos θ) of the [2.2]paracyclophanylene bridge caused by different verdazyl substitution. In (3d), however, the splittings of the [2.2]paracyclophanylene protons differ from those hitherto discussed. Obviously, due to the steric requirements of pseudo-*ortho*-substitution the verdazyl rings are twisted out of conjugation with the [2.2]paracyclophanylene bridge to a large extent [also indicated by $|D'|$ of (3d) and its absorption spectrum]. Consequently the spin density delocalisation into the phenylene rings of the bridge is reduced leading to smaller splittings of the aromatic protons. Additionally a distinct increase in one *ortho*-methylene proton splitting ($a_{2,10\text{-}H}$ 0.96 G) is observed. This increase of β-proton splitting with rising distortion angle about the N–bridge bond is apparently connected with an increasing long-range interaction. In particular homohyperconjugation[18,19] of the methylene proton *anti* to the verdazyl substituent would gain most from rising distortion about the N–bridge bond. Therefore we attribute the larger positive methylene proton splitting (a_H 0.96 G) to the *anti*-2,10-protons, for which spin polarisation, hyperconjugation, and homohyperconjugation reinforce each other.

Not only the n.m.r. results but also the $|D'|$ values of (3b—d) reveal no indication of a substantial transannular interaction within the [2.2]paracyclophanylene bridge of these compounds. Unfortunately we did not

TABLE 4

H and D paramagnetic shifts $\delta_p = (H_d - H_p)/H_d$ [a] and coupling constants a_H and a_D of (3b—d) in di-t-butyl nitroxide at 300 K





Compound	Assignment	δ_p (p.p.m.)	a_D/G	a_H/G
(3b)	1,1,9,9-H_4 [e]			
	2,10-H_2	52.7		0.71
	2,10-H_2	16.3		0.22
	5,13-H_2	−73.4		−0.99
	7,15-H_2	−77.0		−1.04
	8,16-H_2	43.0		0.58
	$[C(CH_3)_3]_2$-H_{18}	8.2		0.11
	(2′,6′)$_2$-D_4	−78.5	−0.163	−1.06
	(3′,5′)$_2$-D_4	28.9	0.060	0.39
	4′$_2$-D_2	−83.7	−0.174	−1.13
(3c)	1,2-H_2	60.9		0.82
	1,2-H_2	14.0		0.19
	5,7,12,16-H_4	−75.8		−1.02
	8,15-H_2	41.1		0.55
	9,10-H_2 [d]	−8.4		−0.11
	9,10-H_2 [e]			
	$[C(CH_3)_3]_2$-H_{18}	8.2		0.11
	(2′,6′)$_2$-D_4	−77.4	−0.161	−1.04
	(3′,5′)$_2$-D_4	28.7	0.060	0.39
	4′$_2$-D	−82.4	−0.171	−1.11
(3d)	1,9-H_2 [d]	−7.9		−0.11
	1,9-H_2 [d]	−4.3		−0.06
	2,10-H_2	71.4		0.96
	2,10-H_2	13.5		0.18
	5,15-H_2 [e]	−55.9		−0.75
	7,13-H_2 [e]	−67.7		−0.91
	8,12-H_2	37.3		0.50
	$[C(CH_3)_3]_2$-H_{18}	8.9		0.12
	(2′,6′)$_2$-D_4	−75.8	−0.158	−1.02
	(3′,5′)$_2$-D_4	28.5	0.059	0.38
	4′$_2$-D_2	−83.3	−0.173	−1.12

[a] Shift relative to the corresponding H or D resonance in the parent [2.2]paracyclophane derivative (2b—d). [b] Partly calculated from a_D; $a_H = 6.51a_D$. [c] These resonances could not be resolved or definitely assigned. [d] Measured in $CDCl_3$. [e] Tentatively assigned, may be in reverse order.

succeed in synthesizing the pseudo-geminal biverdazyl (3e), which would have been a neat example of a biverdazyl with an almost fixed molecular structure.

EXPERIMENTAL

N.M.R. of Compounds (3b—d).—The paramagnetic shifts were measured as described for (3a).[1] The n.m.r. spectra of the diamagnetic compounds were taken on a Bruker WP 80 spectrometer, the absorption spectra on a Cary 17 instrument.

4,12-*Diamino*[2.2]*paracyclophane* (1b).—4,12-Dinitro[2.2]paracyclophane [6] (3.0 g) in dioxan (80 ml) was hydrogenated (6 mol. equiv. H_2) in the presence of 10% Pd–$BaSO_4$ (1.0 g). After separation of the catalyst water was added to the filtrate to precipitate the product. Crystallisation from methanol yielded crystals (1.6 g, 67%), m.p. 288—289° (lit.,[7] 267—268°) (Found: C, 80.8; H, 7.85; N, 11.55. Calc. for $C_{16}H_{18}N_2$: C, 80.65; H, 7.6; N, 11.75%).

4,12-*Bis*(*acetamido*)[2.2]*paracyclophane*.—A solution of (1b) (30 mg) in acetic anhydride (0.5 ml) was heated to the b.p. *Crystals* from acetic acid had m.p. 356—357° (Found: C, 74.75; H, 6.9; N, 8.8. $C_{20}H_{22}N_2O_2$ requires C, 74.5; H, 6.9; N, 8.7%).

4,13-*Diamino*[2.2]*paracyclophane* (1c).—4.13-Dinitro[2.2]paracyclophane [6] (3.0 g) was hydrogenated as described for (1b), yielding crystals (2.1 g, 88%) from methanol, m.p. 256—257° (lit.,[7] 222—226°) (Found: C, 80.75; H, 7.45; N, 11.85%).

4,13-*Bis*(*acetamido*)[2.2]*paracyclophane*.—Acetylation of (1c) as described above gave *crystals*, m.p. 354—355° (Found: C, 74.65; H, 6.55; N, 8.95%).

4,16-*Diamino*[2.2]*paracyclophane* (1d).—4,16-Dinitro[2.2]paracyclophane [6] (3.0 g) was hydrogenated as described for (1b) to yield *crystals* (2.0 g, 84%) from methanol, m.p. 263—264° (Found: C, 80.35; H, 7.9; N, 11.8%).

4,16-*Bis*(*acetamido*)[2.2]*paracyclophane*.—Acetylation of (1d) as described above yielded *crystals*, m.p. 317—318° (Found: C, 74.45; H, 7.05; N, 8.95%).

4,15-*Diamino*[2.2]*paracyclophane* (1e).—4,15-Dinitro[2.2]paracyclophane [6] (1.5 g), 10% Pd–$BaSO_4$ (500 mg), and dioxan (40 ml) were treated as described for (1b). Brownish *crystals* (850 mg, 71%) from methanol–water had m.p. 245—247° (Found: C, 80.45; H, 7.85; N, 11.87%).

4,15-*Bis*(*acetamido*)[2.2]*paracyclophane*.—Acetylation of (1e) as described above gave crystals, m.p. 245—247° (Found: C, 74.65; H, 6.95; N, 8.75%).

4,12-*Bis*-(3-*t*-*butyl*-5-[$^2H_5$]*phenylformazan*-1-*yl*)[2.2]*paracyclophane* (2b).—The mixture of (1b) (1.5 g) in dimethylformamide (30 ml) and concentrated HCl (5 ml) was cooled to 0° and kept at this temperature while the solution of $NaNO_2$ (900 mg) in H_2O (10 ml) was added dropwise under stirring. This diazonium salt solution was added in small portions to the stirred mixture of 2,2-dimethylpropanal [$^2H_5$]phenylhydrazone (3.0 g) and sodium acetate (15 g) in dimethylformamide (40 ml) and methanol (15 ml) kept at −10°. Stirring was continued for 1 h. After addition of water (100 ml) the precipitated yellow azo-compound was collected, dissolved in dimethylformamide (50 ml), and rearranged by addition of methanolic KOH (saturated; 1 ml). After 15 min the biformazan was precipitated by addition of methanol and filtered. Crystallisation from dioxan–ethyl acetate–methanol yielded brown *crystals* (1.9 g, 48%), m.p. 203—204° (decomp.), δ ([$^2H_6$]DMSO; 80 MHz) 1.48 [18 H, s, $C(CH_3)_3$], 2.8—4.0 (8 H, m, CH_2), 6.0—7.0 6 H, m, aromatic H), and 14.15 (2 H, s, NH) (Found: C, 73.3; H + D, 8.9; N, 17.95. $C_{38}H_{34}D_{10}N_8$ requires C, 73.25; H + D, 8.75; N, 18.0%).

4,13-*Bis*-(3-*t*-*butyl*-5-[$^2H_5$]*phenylformazan*-1-*yl*)[2.2]*paracyclophane* (2c).—This was prepared from (1c) (1.5 g) as described above. Red-brown *crystals* (2.3 g, 59%) from dioxan–ethyl acetate–methanol, m.p. 181—182° (decomp.) δ ([$^2H_6$]DMSO; 80 MHz) 1.48 [18 H, s, $C(CH_3)_3$], 2.8—4.0 (8 H, m, CH_2), 6.42 (2 H, s, aromatic H), 6.83 (2 H, s, aromatic H), 8.01 (2 H, s, aromatic H), and 14.0 (2 H, s, NH) (Found: C, 73.15; H + D, 9.15; N, 17.8%).

4,16-*Bis*-(3-*t*-*butyl*-5-[$^2H_5$]*phenylformazan*-1-*yl*)[2.2]*paracyclophane* (2d).—This was prepared from (1d) (1.5 g) as described above. After the rearrangement the reaction mixture was partitioned between water and diethyl ether, the organic phase washed three times with water, dried ($MgSO_4$), and the solvent evaporated. The residue was purified by chromatography on Al_2O_3 (Brockmann), using cyclohexane as eluant, to yield red-brown *crystals* (1.3 g, 33%) from ethyl acetate–ethanol (1 : 2), m.p. 147—149° (decomp.), δ ([$^2H_6$]DMSO; 80 MHz) 1.25 [18 H, s, $C(CH_3)_3$], 2.8—4.0 (8 H, m, CH_2), 6.62 (2 H, s, aromatic H), 6.84 (4 H, s, aromatic H), and 13.41 (s, 2 H, NH) (Found: C, 73.45; H + D, 8.85; N, 17.85%).

4,15-*Bis*-(3-*t*-*butyl*-5-[$^2H_5$]*phenylformazan*-1-*yl*)[2.2]*paracyclophane* (2e).—Compound (1e) (600 mg) was treated as described for (2b) to yield red-brown crystals (600 mg, 38%) from ethyl acetate–ethanol (1 : 2), m.p. 195—196° (decomp.), δ ([$^2H_6$]DMSO; 80 MHz) 1.23 [18 H, s, $C(CH_3)_3$], 2.8—4.0 (8 H, m, CH_2), 6.76 (4 H, s, aromatic H), 6.83 (2 H, s, aromatic H), and 13.95 (2 H, s, NH) (Found: C, 73.35; H + D, 8.7; N, 17.9%).

4,12-*Bis*-(3-*t*-*butyl*-5-[$^2H_5$]*phenylverdazyl*-1-*yl*)[2.2]*paracyclophane* (3b).—Compound (2b) (1.5 g), $KHSO_4$ (2 g), and paraformaldehyde (500 mg) in dimethylformamide (70 ml) were stirred for 30 h. After filtration the solution was cooled to 0° and 40% aqueous formaldehyde (5 ml) added. Then 2N-NaOH was added dropwise to the stirred solution until the violet colour changed to green. The mixture was partitioned between benzene and water, the benzene layer washed three times with water, dried ($MgSO_4$), and the solvent evaporated. The residue was purified by chromatography on Al_2O_3 (Brockmann), using benzene as eluant, to yield black *crystals* (800 mg, 51%) from benzene–ligroin, m.p. 206—207° (decomp.), microhydrogenation, (3b) (4.85 mg) + 5% Pd–$BaSO_4$ (20 mg) in dimethylformamide (2 ml); 1.04 mol H_2 after 60 min (end value) (Found: C, 74.25; H + D, 9.1; N, 17.2. $C_{40}H_{36}D_{10}N_8$ requires C, 74.05; H + D, 8.7; N, 17.25%).

4,13-*Bis*-(3-*t*-*butyl*-5-[$^2H_5$]*phenylverdazyl*-1-*yl*)[2.2]*paracyclophane* (3c).—Compound (2c) (1.5 g) was treated as described above for (3b), giving black crystals (750 mg, 48%) from benzene–ligroin, m.p. 198—199° (decomp.), microhydrogenation, (3c) (7.21 mg) + 5% Pd–$BaSO_4$ (20 mg) in dimethylformamide (2 ml); 1.00 mol H_2 after 60 min (end value) (Found: C, 73.75; H + D, 8.95; N, 17.25%).

4,16-*Bis*-(3-*t*-*butyl*-5-[$^2H_5$]*phenylverdazyl*-1-*yl*)[2.2]*paracyclophane* (3d).—This was prepared from (2d) (1.2 g) as described for (3b). The residue was chromatographed on Al_2O_3 (Brockmann), using cyclohexane–benzene (4 : 1) as eluant, to yield black *crystals* (600 mg, 48%) from cyclohexane–ligroin, m.p. 181—182° (decomp.), microhydrogenation (3d) (8.96 mg) + 5% Pd–$BaSO_4$ (20 mg) in dimethylformamide (2 ml); 0.99 moles H_2 after 60 min (end value) (Found: C, 74.2; H + D, 8.8, N, 17.25%).

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