New podands with terminal chromogenic moieties derived from formazans

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Synthesis of several new podands, bearing various terminal chromophoric functions of formazan (9–11), verdazyl (18–20) and verdazylium salt (21–23) types and having a different length of oligooxyethylene bridge between chromophoric units, is developed. Calculated (Alchemy-2000) and found (EPR data) distances between spin centers in bis-radicals 18–20 correlate well. Such spin-labeled species could be good models for the EPR study of host–guest interactions involving ethylene glycol-based podands.

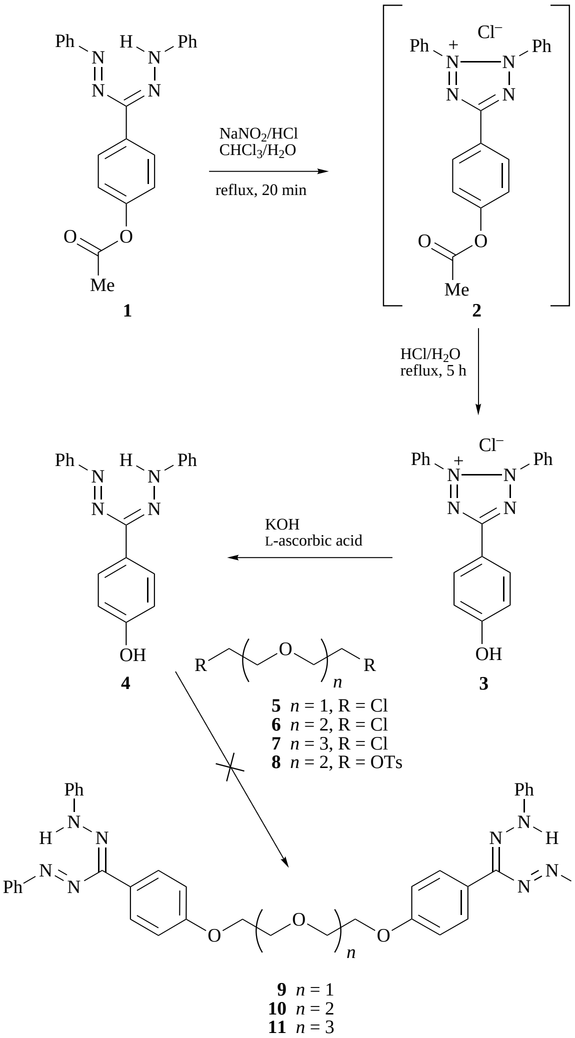
Introduction

Podands, as open-chain ligands, usually possess ionophoric properties intermediate between those typical for cyclic crown ethers and those for glymes.[1,2] Crown ethers and cryptands possess cavities specific for a single size of cation or neutral host, whereas the 'wrap-around' capability of podands having terminal functionalities allows them to create cavities of the appropriate sizes during complexation with metal cations or neutral molecules in a manner unique among ligands.[3] Podands containing a terminal quinolin-8-yloxy moiety have been studied for the complexation of metal cations and neutral hosts.[1,2,4–7] Such podands containing both 'hard' (oxygen) and 'soft' (nitrogen) donor sites were suggested both for alkali metal ion complexation[7] and transition metal ion[6] solvent extraction.

The use of terminal functionalities containing several heteroatoms, in particular nitrogen atoms, should improve the selectivity/efficiency of host binding by the podand molecule. Formazans, compounds containing four nitrogen atoms and a carbon atom in a conjugated chain, are selective and efficient reagents for the determination and separation of transition metal cations, such as Pd, Pt, Ru, Os, V, Mo, Hg, Ag, Th, La, as well as Se, Bi, *etc.* (for a recent review, see ref. 8). Formazans are closely related to several classes of nitrogen-containing heterocycles, *e.g.* verdazyls,† verdazylium salts and 1,2,4,5-tetrazines,[9] but complexation of metal cations by these related heterocycles is hardly known, although it holds great promise. Apart from some initial attempts,[10] design and synthetic strategy for the preparation of ligands carrying such heterocycles is undeveloped. We recently prepared a lariat crown formazan containing a terminal electron-donating dimethylamino group,[11] and now report the new bis-formazans **9**–**11** (Scheme 2) together with analogous bis-verdazyls **18**–**20** (Scheme 3) as novel potential podands with terminal chromogenic moieties.

Results and discussion

The preparation of podands **9**–**11** was attempted by two alternative routes. First, we attempted to build a formazan backbone containing a hydroxy (phenolic) functionality and to link two formazan moieties by a flexible oligooxyethylene bridge (Scheme 1). 3-(4-Hydroxyphenyl)-1,5-diphenylformazan (**4**) was prepared starting from the *O*-acetylated formazan **1**. Traditional formazan assembly, *i.e.* azo-coupling of a diazonium salt with an arylaldehyde arylhydrazone, is not suitable in the case of phenolic formazans of type **4** because azo-coupling occurs predominantly into the aromatic nucleus activated by the hydroxy group.[12] Therefore, we utilized the combination of acetyl group/tetrazolium salt protection, which was previously applied in the preparation of aminophenyl-substituted formazans.[13] The formazan backbone is sensitive to acids,[12] and direct hydrolysis of acetoxy-derivative **1** into the corresponding



Scheme 1

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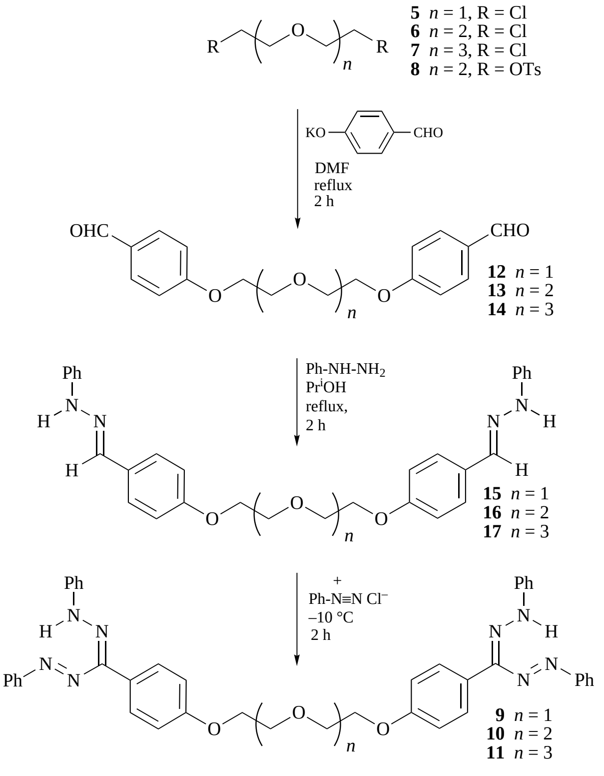
† The IUPAC name for verdazyl is 3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl.

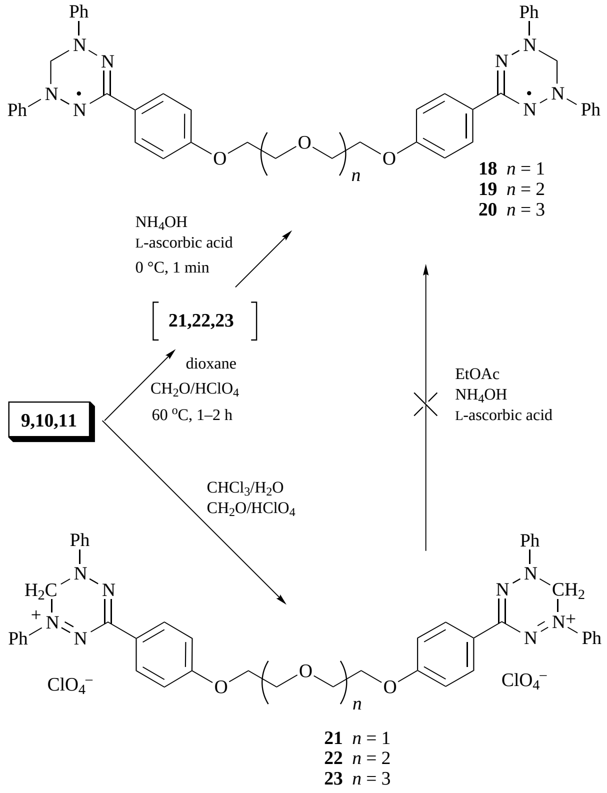
hydroxy-formazan **4** is not possible. Therefore, the acetoxy-formazan **1** was oxidized into the acid-stable tetrazolium salt **2**, which was easily hydrolyzed yielding hydroxy-containing tetrazolium salt **3**. Reduction of salt **3** to formazan **4** was accomplished by L-ascorbic acid in a basic medium. However, condensation of formazan **4** (2 equiv.) with α,ω-dichloro-oligooxyethylene glycols **5**–**7** or α,ω-ditosylate **8** failed to give the desired podands **9**–**11** either (*i*) in DMF in the presence of KOH with heating (70 °C), or (*ii*) under phase-transfer conditions (NaOH/tetrabutylammonium hydrogen sulfate, methylene chloride/water). All these attempts gave instead complex reaction mixtures, possibly because of competitive alkylation of the NH-group in formazan **4**.

Our second route comprised the preparation of bis-aldehydes **12**–**14** by reaction of the potassium salt of 4-hydroxybenzaldehyde with α,ω-dichlorooligooxyethylene glycols **5**–**7** in refluxing DMF (Scheme 2).[14] Aldehydes **12**–**14** were subsequently reacted with phenylhydrazine to afford the bis-phenylhydrazones **15**–**17** in good yields. Treatment of hydrazones **15**–**17** with phenyldiazonium chloride gave the expected deep ruby-red bis-formazans **9**–**11**. The physical and spectral characteristics of bis-aldehydes **12**–**14**, bis-phenylhydrazones **15**–**17** and bis-formazans **9**–**11** are shown in Tables 1 and 2. UV–VIS spectra of bis-formazans **9**–**11** contain intense (log ε 61 4.56–4.57, dioxane) maxima in the visible range, at 498, 504 and 505 nm for **9**, **10** and **11**, respectively. Therefore, compounds **9**–**11** are potential chromoionophores for colorimetric studies in host–guest chemistry.



Scheme 2

Cyclization of podands **9**–**11** with formaldehyde in the presence of perchloric acid, carried out in a two-phase (CHCl$_3$/water) system, according to our recently reported method,[15] led to the precipitation of the corresponding black–blue bis-verdazylium perchlorates **21**–**23** as oily or sticky solids, which were hard to isolate. Attempted reduction of **21**–**23** with L-ascorbic acid in two-phase liquid/liquid media at pH 9–10 did not lead to the isolation of bis-radicals **18**–**20**, possibly because of the presence of hard-to-separate traces of perchloric acid contained in the crude salts **21**–**23**, which caused the decomposition of **21**–**23** during reduction in basic medium. However, similar cyclization of **9**–**11**, carried out in dioxane, gave deep-blue verdazylium salt solutions. In this case, the crude salts **21**–**23** were successfully separated, treated with L-ascorbic acid, and then basified with aqueous ammonia, which resulted in their reduction to bis-verdazyls **18**–**20** in good yields (Scheme 3). Data for bis-radicals **18**–**20** are collected in Tables 1 and 3.



Scheme 3

Radical podands **18**–**20** are dark-green crystalline substances with low melting points, soluble in most organic solvents, but sparingly soluble in alcohols and insoluble in water. After purification by column chromatography, solid samples of the verdazyls **18**–**20** were stored at −10 °C, since at room temperature they start to decompose after several days. Nevertheless, solutions of bis-radicals **18**–**20** in organic solvents (benzene, toluene, dioxane, CH$_2$Cl$_2$) can be stored for several weeks without noticeable changes in their optical densities. The UV–VIS spectra of podands **18**–**20** in dioxane contain a long-wave absorption maximum at *ca.* 733 nm (Table 3), similar to that characteristic for many mono-verdazyl radicals. However, the new bis-radicals have much higher extinction coefficients than many mono- or bis-verdazyls: for instance, typical log ε values for mono-verdazyls are 3.4–3.9, while for bis-verdazyls with non-conjugated bridge systems they are 3.8–3.9 and for bis-verdazyls with conjugated bridge systems they are 3.8–4.4.[9]

The EPR spectra of the bis-radicals **18**–**20** were studied both in solution and in the solid state. The spectra of **18**–**20** in toluene at room temperature each show the nine-line splitting pattern with coupling constants a^N = *ca.* 5.8 ± 0.1 G and *g*-factor = *ca.* 2.0033 ± 0.0002, typical for mono-verdazyls, thus indicating that there is little, if any, conjugation between the two parts of the molecule that bear unpaired electrons. Compared to those of the mono-verdazyls, the spectra of the bis-radicals **18**–**20** are much less well-resolved, regardless of whether or not their solutions are degassed. This can be ascribed to the faster spin–spin relaxation processes resulting from spin–dipolar interactions in the bis-radicals. The observation that the hyperfine structure corresponds to just nine lines is direct proof that no strong magnetic coupling exists between the two radical centers of the bis-radical, otherwise the number

Table 1 Preparation of podand-aldehydes **12**–**14**, -phenylhydrazones **15**–**17**, -formazans **9**–**11** and -verdazyls **18**–**20**

Compound	Yield (%)	Mp/°C (solvent)	Molecular formula	Elemental analysis Found (%) (Required)	
				C	H
12	60	140–141 (142–143)[a] (EtOAc)	$C_{18}H_{18}O_5$		
13	54	74–75 (75–76)[a] (aq. MeOH)	$C_{20}H_{22}O_6$		
14	52	43–44 (aq. MeOH)	$C_{22}H_{26}O_7$	*b*	
15	85	154–155 (EtOH)	$C_{30}H_{30}N_4O_3$	72.60 (72.84)	6.25 (6.12)
16	94	127–129 (EtOH)	$C_{32}H_{34}N_4O_4$	71.07 (71.34)	6.44 (6.37)
17	72	84–86 (Et_2O)	$C_{34}H_{38}N_4O_5$	69.74 (70.07)	6.83 (6.58)
9	77	142–143 (aq. dioxane)	$C_{42}H_{38}N_8O_3$	71.95 (71.76)	5.36 (5.45)
10	85	178–179 (aq. dioxane)	$C_{44}H_{42}N_8O_4$	70.89 (70.75)	5.88 (5.67)
11	56	115–116 (aq. dioxane)	$C_{46}H_{46}N_8O_5$	70.06 (69.84)	6.12 (5.87)
18	35	55–56[c]	$C_{44}H_{40}N_8O_3$	*d*	
19	58	48–50[c]	$C_{46}H_{44}N_8O_4$	*e*	
20	83	39–40[c]	$C_{48}H_{48}N_8O_5$	*f*	

[a] Lit. mp, ref. 14. [b] Found: 403.1754 [M + 1]; calc.: 403.1756 [M + 1]. [c] Purified by column chromatography (Al_2O_3 basic, eluent: EtOAc). [d] Found: 729.3338 [M + 1]; calc.: 729.3302 [M + 1]. [e] Found: 773.3558 [M + 1]; calc.: 773.3564 [M + 1]. [f] Found: 817.3839 [M + 1]; calc.: 817.3826 [M + 1].

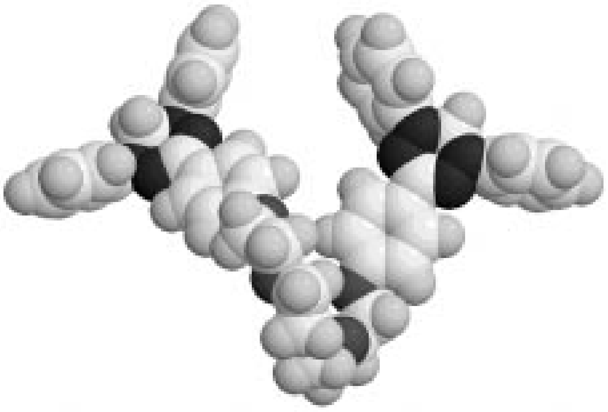


Fig. 1 Space-filling model of bis-radical **20**

of the lines should be 17. Solid samples of bis-radicals **18**–**20** exibit a single-lined Lorentz-type absorption with peak-to-peak width (ΔH_s) of *ca.* 18–20 G, which is considerably wider than in the case of a crown ether bearing a single verdazyl moiety (4.9 G[10]), and of all other mono-verdazyls.[9,16]

Based on this result and using the simple point dipole approximation,[17] we calculated the average approximate distance between the two spin centers of radicals **18**–**20** to be *ca.* 11.6 Å. Using the molecular mechanics program implemented in the 'Alchemy-2000' minimizer,[18] we calculated the effective distance between the spin centers in bis-radical **18** as 18.6 Å for the extended molecule ('rod'-type), and 13.9 Å for the bent molecule ('loop'-type). For the 'loop' conformations of bis-radicals **19** and **20** these distances were calculated to be 10.9 and 9.3 Å, respectively, which indicates that for **20**, where the podand molecule contains four oxyethylene units, it is wrapped in an essentially helical manner (Fig. 1). Comparison of these results suggests that in the solid state the bis-radicals **18**–**20** exist preferentially in the arched forms. Although these calculations are only preliminary, they demonstrate the potential utility of the EPR method in host–guest interaction studies of podands containing spin labels: based on the EPR results (ΔH_s measurements of the ligands and their complexes with neutral and charged guests) and molecular modeling, one can estimate the approximate conformations of both the host and the complex.

Conclusions

We prepared a new series of podands bearing nitrogen-containing chromophoric terminal functionalities derived from formazans and related heterocycles (verdazyl radicals, verdazylium salts). Although bis-verdazyls **18**–**20** demonstrated very little, if any, intramolecular spin–spin interaction both in solution and in the solid state, their tendency to exist in the arched or helical form in the solid state suggests that these and similar compounds could be promising models for the EPR study of host–guest interactions in podands.

Experimental

For general information see ref. 16. The EPR spectra were measured at the X-band (9.4–9.5 GHz) frequencies, using a Varian E112 spectrometer. Concentrations of the radical solutions in toluene used for EPR measurements were 1 mmol dm^{-3}. The *g*-values were measured relative to the radical standard, 1,1-diphenyl-2-picrylhydrazyl ($g = 2.0037$). ^{1}H NMR spectra were recorded at 300 MHz, and ^{13}C NMR spectra at 75 MHz in $CDCl_3$ (unless otherwise specified). ^{1}H and ^{13}C NMR spectra for **7** and UV–VIS and EPR spectra for compounds **18**, **19** and **20** are available as supplementary material (SUPPL. NO. 57337, 11 pp.). For details of the Supplementary Publications Scheme see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, available *via* the RSC Web page (http//www.rsc.org/authors).

General procedure for the preparation of bis-aldehydes 12, 13 and 14

To a stirred under nitrogen solution of 4-hydroxybenzaldehyde potassium salt (12.8 g, 0.08 mol) in dry DMF (40 cm^3) a solution of the corresponding ethylene glycol dichloride **5**–**7** (0.04 mol) in dry DMF (15 cm^3) was added dropwise at reflux within 5 min. The stirring was continued at reflux for 2 h, the resulting yellow–brownish mixture was cooled and poured onto ice–

Table 2 NMR data for podand-aldehydes **12**–**14**, -phenylhydrazones **15**–**17** and -formazans **9**–**11**

Compound	δ_H, *J*/Hz	δ_C
12	9.88 (2 H, s), 7.82 (4 H, d, *J* 8.7), 7.01 (4 H, d, *J* 8.7), 4.25 (4 H, t, *J* 4.7), 3.97 (4 H, t, *J* 4.7)	190.7, 163.7, 131.9, 130.2, 114.9, 69.8, 67.8
13	9.88 (2 H, s), 7.82 (4 H, d, *J* 8.7), 7.01 (4 H, d, *J* 8.7), 4.21 (4 H, t, *J* 4.7), 3.90 (4 H, t, *J* 4.7), 3.76 (4 H, s)	190.7, 163.8, 131.9, 130.1, 114.9, 70.9, 69.6, 67.8
14	9.88 (2 H, s), 7.82 (4 H, d, *J* 8.8), 7.01 (4 H, d, *J* 8.8), 4.20 (4 H, t, *J* 4.7), 3.88 (4 H, t, *J* 4.7), 3.67–3.76 (8 H, m)	190.8, 163.8, 131.9, 130.1, 114.9, 70.9, 70.7, 69.5, 67.7
15	10.13 (2 H, s), 7.82 (2 H, s), 7.57 (4 H, d, *J* 8.5), 7.19 (4 H, t, *J* 7.7), 7.03 (4 H, d, *J* 8.2), 6.98 (4 H, d, *J* 8.5), 6.71 (2 H, t, *J* 7.2), 4.15 (4 H, t, *J* 4.0), 3.83 (4 H, t, *J* 4.0)	158.4, 145.5, 136.5, 128.9, 128.5, 126.9, 118.2, 114.7, 111.8, 69.0, 67.2
16	10.13 (2 H, s), 7.81 (2 H, s), 7.56 (4 H, d, *J* 8.8), 7.20 (4 H, t, *J* 7.7), 7.03 (4 H, d, *J* 7.7), 6.96 (4 H, d, *J* 8.8), 6.71 (2 H, t, *J* 7.3), 4.11 (4 H, t, *J* 4.5), 3.76 (4 H, t, *J* 4.5), 3.63 (4 H, s)	158.5, 145.5, 136.5, 128.9, 128.5, 126.9, 118.2, 114.7, 111.7, 69.9, 68.9, 67.2
17	10.13 (2 H, s), 7.81 (2 H, s), 7.56 (4 H, d, *J* 8.8), 7.19 (4 H, t, *J* 7.8), 7.03 (4 H, d, *J* 8.0), 6.96 (4 H, d, *J* 8.8), 6.71 (2 H, t, *J* 7.3), 4.12 (4 H, t, *J* 4.5), 3.75 (4 H, t, *J* 4.5), 3.54–3.65 (8 H, m)	158.5, 145.5, 136.5, 128.9, 128.5, 126.9, 118.3, 114.7, 111.8, 69.9, 69.8, 68.9, 67.2
9	8.05 (4 H, d, *J* 8.8), 7.58–7.80 (8 H, m), 7.41–7.55 (8 H, m), 7.23–7.36 (4 H, m), 6.80–7.15 (4 H, m), 4.18–4.27 (4 H, m), 3.90–4.10 (4 H, m)	158.6, 148.0, 141.2, 137.2, 130.4, 129.2, 127.2, 118.7, 114.6, 70.1, 67.7
10	8.03 (4 H, d, *J* 8.9), 7.64 (8 H, d, *J* 7.5), 7.43 (8 H, t, *J* 7.5), 7.25 (4 H, t, *J* 7.3), 6.98 (4 H, d, *J* 8.9), 4.21 (4 H, t, *J* 5.0), 3.92 (4 H, t, *J* 5.0), 3.81 (4 H, s)	158.7, 147.9, 141.2, 137.2, 129.4, 129.4, 127.2, 118.7, 114.6, 70.9, 69.9, 67.5
11	8.02 (4 H, d, *J* 8.9), 7.63 (8 H, d, *J* 7.5), 7.42 (8 H, t, *J* 7.5), 7.24 (4 H, t, *J* 7.3), 6.97 (4 H, d, *J* 8.9), 4.18 (4 H, t, *J* 5.0), 3.89 (4 H, t, *J* 5.0), 3.68–3.77 (8 H, m)	158.7, 147.9, 141.2, 137.2, 130.3, 129.3, 127.2, 118.7, 114.5, 70.9, 70.7, 69.8, 67.5, 67.1

Table 3 Spectral properties of bis-verdazyls **18**–**20**

Radical	λ_{max}/nm (log ε)[a]	*g*-value	ΔH_s/G[b]	a^N/G[c]
18	733 (4.55)	2.0032	20.0	5.9
19	732 (4.51)	2.0033	18.0	5.7
20	733 (4.29)	2.0033	18.5	5.7

[a] 1×10^{-5} mol dm^{-3}, dioxane. [b] Linewidth between points of maximum slope (solid samples). [c] ^{14}N Hyperfine coupling due to four nitrogens (in toluene).

water (1 dm^3). The oily product formed was left standing overnight, the solid obtained was filtered, washed with water, air-dried and recrystallized from the corresponding solvent (Table 1). Physical and spectral data of 1,5-bis(4-formylphenoxy)-3-oxapentane (**12**), 1,8-bis(4-formylphenoxy)-3,6-dioxaoctane (**13**) and 1,11-bis(4-formylphenoxy)-3,6,9-trioxaundecane (**14**) are shown in Tables 1 and 2.

General procedure for the preparation of bis-hydrazones 15, 16 and 17

To a stirred suspension of the corresponding bis-aldehyde **12**–**14** (21 mmol) in propan-2-ol (100 cm^3) phenylhydrazine (5.4 g, 50 mmol) was added dropwise at 50–60 °C. The solution was heated at reflux for 5–15 min, by which time a precipitate started to form. The suspension was stirred at reflux for an additional 2 h, cooled, the precipitate was filtered, washed with the corresponding organic solvent (propan-2-ol for **15**, diethyl ether for **16**, **17**), and air-dried to give bis-phenylhydrazone **15**–**17** as white microcrystals. The analytical samples of bis-phenylhydrazones **15**, **16** were recrystallized from ethanol. Physical and spectral data of 1,5-bis[4-(phenylhydrazonomethyl)phenoxy]-3-oxapentane (**15**), 1,8-bis[4-(phenylhydrazonomethyl)phenoxy]-3,6-dioxaoctane (**16**) and 1,11-bis[4-(phenylhydrazonomethyl)phenoxy]-3,6,9-trioxaundecane (**17**) are shown in Tables 1 and 2.

General procedure for the preparation of bis-formazans 9, 10 and 11

To a stirred solution of the corresponding bis-phenylhydrazone **15**–**17** (7.1 mmol) in pyridine (70 cm^3) at −15 °C a solution of phenyldiazonium chloride (freshly prepared from 25 mmol of aniline) was added dropwise. During addition the temperature was kept below −10 °C. After addition of the diazonium salt the formed suspension was stirred at −15 °C for 2 h and then at room temperature overnight. The precipitate was filtered, washed with 10% HCl (3 × 20 cm^3), water (2 × 25 cm^3), and air-dried. The solid obtained was recrystallized from aqueous dioxane. Physical and spectral data of 1,5-bis[4-(1,5-diphenylformazan-3-yl)phenoxy]-3-oxapentane (**9**), 1,8-bis[4-(1,5-diphenylformazan-3-yl)phenoxy]-3,6-dioxaoctane (**10**) and 1,11-bis[4-(1,5-diphenylformazan-3-yl)phenoxy]-3,6,9-trioxaundecane (**11**) are shown in Tables 1 and 2.

General procedure for the preparation of bis-verdazyls 18, 19 and 20

A stirred mixture of the corresponding formazan **9**–**11** (0.7 mmol), dioxane (30 cm^3), and aqueous formaldehyde (37%, 4.2 cm^3) was warmed up to 60 °C, followed by dropwise addition of $HClO_4$ (70%, 1.4 cm^3). A dark-blue mixture (the color indicates formation of the corresponding verdazylium perchlorate **21**–**23**) was vigorously stirred at room temperature for up to 2 h, until complete consumption of the starting formazan was established by TLC. Chloroform (50 cm^3) was added, the organic phase was extensively washed with water, separated, cooled to 0 °C, and the solution of L-ascorbic acid (0.9 g) in water (20 cm^3) was added in one portion, followed by the dropwise addition of aqueous ammonia (25%, 2 cm^3) to a vigorously stirred mixture. After *ca.* 1 min, the color of the mixture became emerald-green, indicating formation of the radical **18**–**20**. The organic layer was quickly separated, washed with ice-cold water (2 × 50 cm^3), and dried over anhydrous Na_2SO_4. After removal of the solvent, the dark-green oil was purified by column chromatography (Al_2O_3 basic Brockman Activity I, eluent: EtOAc) to give the corresponding bis-verdazyl **18**–**20** (**18**, deep-green plates; **19**, dark-green microcrystals; **20**, green oil, which crystallized after trituration with hexanes). Physical and spectral data of 1,5-bis[4-(2,4-diphenylverdazyl-6-yl)phenoxy]-3-oxapentane (**18**), 1,8-bis[4-(2,4-diphenylverdazyl-6-yl)phenoxy]-3,6-dioxaoctane (**19**), and 1,11-bis[4-(2,4-diphenylverdazyl-6-yl)phenoxy]-3,6,9-trioxaundecane (**20**) are collected in Tables 1 and 3.

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Paper 7/07561H
Received 20*th October* 1997
Accepted 21*st November* 1997