Radical Ions and Germyloxyaminoxyls from Nitrospiro[indoline-naphthopyrans]. A Combined Electrochemical and EPR Study

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The radical ions from 5-nitrospiro[indoline-2,3'-naphthopyran] **1**, 8'-nitrospiro[indoline-2,3'-naphthopyran] **2**, and 5,8'-dinitrospiro[indoline-2,3'-naphthopyran] **3** have been investigated electrochemically and by means of electron paramagnetic resonance spectroscopy.

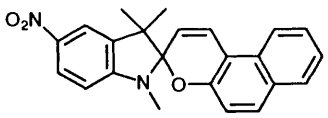
The first reduction potentials of these compounds reflect the position of the nitro groups and vary between -1.53_3 V for **1** and -1.27_2 V for **2** *vs.* SCE, while **3** exhibits two reduction waves at potentials similar to those of **1** and **2**, suggesting no or very little interaction between the two moieties of the molecules. The oxidation potentials are dominated by the indolinic moiety increasing in the order **2** < **1** < **3**.

The reduction with butoxide in DMF leads to the EPR observation of the expected radical anions of **1** and **2**, while the spectrum observed with **3** shows, against expectations, reduction of the indolinic moiety. Photoreduction with Bu_4NBH_4 in THF affords the radical anions of **2** and **3** but not of **1**, the measured hfs constants being similar to those measured in DMF without light. Addition of *in situ* generated triphenylgermyl radicals to **1**–**3** affords rather persistent germyloxyaminoxyls which give identical spectra both under UV irradiation and in the dark.

Photochromism is defined as the ability of a substance to undergo a detectable and reversible change of colour under the action of light, and because of this ability photochromic compounds have long since attracted the attention of many research groups world-wide. Actually, because of the wealth of possible applications of photochromic compounds in many fields, ranging from light sensitive sunglasses and 'smart windows' to electronic storage of data, compounds needed are characterised by a high durability, *i.e.* able to undergo a large number of photochromic cycles before undergoing irreversible degradation.

The observation of photochromism in spiro[indoline-benzopyrans] dates back to 1952:[1] since then an enormous amount of work has been devoted to synthesising new compounds with a potential industrial interest.[2] On the other hand the design of new active compounds has to be based on the best knowledge of the mechanism of the photochromic process. Although the large body of information collected on the mechanism of the photochromic process in spiro[indoline-benzopyrans] and structurally related compounds indicates the reversible, most likely heterolytic, cleavage of the bond between the heterocyclic oxygen and the carbon in position 2 as responsible for the observed change of colour,[3] we have recently shown *via* EPR double-trapping experiments that biradicals are present in the system during the process.[4] Although these biradicals do not seem likely to be involved in the actual photochromic process, they are believed to play a relevant role in the degradation of the photochromic compounds.

Previous studies have also shown that the presence of nitro-substituents in the spiromolecule usually enhances its photochromic activity;[5] with the aim of gaining information about their electronic properties, we have therefore studied the radical ions from some of these compounds, and we report here about the electrochemical reduction and oxidation of 5-nitrospiro[indoline-2,3'-naphthopyran] **1**, 8'-nitrospiro[indoline-2,3'-naphthopyran] **2**, and 5,8'-dinitrospiro[indoline-2,3'-naphthopyran] **3**, and about their chemical and photochemical reduction inside the cavity of an EPR spectrometer. In order to exclude effects due to the high polarity of the solvents employed in these reactions and to cancel out the effect of UV radiation, we have also studied the germyloxyaminoxyls obtained in benzene from compounds **1**–**3** both in the absence and in the presence of UV light.



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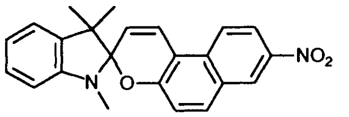

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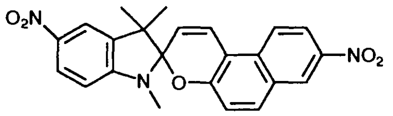


3

Results

Electrochemistry.—The reduction potentials of compounds **1**–**3** in acetonitrile (ACN) (see Table 1) indicate that the dinitro derivative **3** is reduced more readily than 5-nitrospiro-[indoline-naphthopyran] **1**, its reduction potential being very close to that of 8'-nitrospiro[indoline-naphthopyran] **2**. The voltammogram of compound **3**, however, shows a second wave at a potential close to that of the reduction of compound **1**. The voltammetric wave observed for compound **2** was estimated to be monoelectronic by comparison with the results obtained for

Table 1 Oxidation (E_{pa}) and reduction (E_{pc}) peak potentials for compounds **1**–**3** *vs.* SCE in ACN

	Peak 1				Peak 2					
Compounds	E'_{pf}/V	i'_{pf}/μA	E'_{pb}/V	i'_{pb}/μA	E''_{pf}/V	i''_{pf}/μA	E''_{pb}/V	i''_{pb}/μA	(i''_{pf}/C) μA dm^3 mol^{-1}	i'_{pf}/C μA dm^3 mol^{-1}
Oxidation										
1	1.24_7	36.9	—	—	1.84_0	33.6	—	—	23.1	21.0
2	1.02_0	25.7	—	—	1.88_4	23.3	—	—	29.0	26.5
3	1.36_7	19.3	—	—	2.11_6	24.64	—	—	24.1	30.8
Reduction										
1	-1.53_3	−26.9	-1.12_9	19.6	—	—	—	—	−21.2	—
2	-1.27_2	−25.3	-0.97_8	20.6	—	—	—	—	−22.8	—
3	-1.20_8	−20.0	-1.01_2	3.9[a]	-1.41_0	−12.4[a]	-1.18_0	8.9[a]	−25.0	15.5

[a] In this case the given current values are only indicative, owing to the overlapping of the two waves.

Table 2 EPR hyperfine spectral parameters for the radical anions from compounds **1**–**3**[a]

Comp.	Solvent	a_1[b]	a_4	a_5[c]	a_6	a_7	$a_{3'}$	$a_{4'}$	$a_{5'}$	$a_{6'}$	$a_{7'}$[c]	$a_{8'}$	$a_{9'}$	$a_{10'}$	g
1	DMF	0.49	3.46	10.89	3.00	1.08									2.0048
1	THF					No radical observed									
1	Calc.[d]	—	3.42	11.02	3.37	1.20									
2	DMF						0.27	0.27	0.61	1.65	9.45	5.35	1.73	0.98	2.0047
2	THF						0.30	0.30	0.59	1.59	10.02	5.19	1.75	0.90	2.0047
2	Calc.[d]						0.13	0.09	0.29	0.31	10.36	6.17	2.10	0.18	
3	DMF	0.42	3.72	10.77	3.21	1.10									2.0047
3	THF						0.25	0.35	0.63	1.60	9.84	5.25	1.70	0.87	2.0047

[a] Coupling constants in G = 10^{-4} T; [b] coupling with the heterocyclic nitrogen; [c] coupling with the nitrogen of nitro group; [d] by means of McLachlan spin density calculations.

N-phenyl-6′-nitrospiro[indoline-benzopyran];[6] compounds **1** and **3** are only slightly soluble, but the similarity of the peak currents measured for the three compounds in dilute solutions (0.8–1 mmol dm^{-3}) indicates that the process is also monoelectronic for compounds **1** and **3** and that in all cases the radical anions of the starting compounds are formed first.

The cyclic voltammetric traces at a scan speed of 1 V s^{-1} show the presence of an appreciable reverse peak after the reduction processes of compounds **1** and **2** (see Fig. 1), while for the dinitro derivative **3** reversibility might not be complete. A lifetime of at least several seconds can however be inferred for the species formed in the reduction of the three compounds.

The oxidation potentials of the investigated compounds increase according to the sequence **2** < **1** < **3** within the range 1.02_0 to 1.36_7 V (see Table 1). The number of exchanged electrons was again close to unity in all cases, and a second oxidation wave was always observed at higher potentials. These waves, characterised by a rather high intensity, present a structured pattern: in particular, in the oxidation of compound **2**, the second wave can be resolved into at least two components, while with compound **3** an unresolved convolution of waves is observed.

Cyclic voltammetric experiments showed no reverse peak for the first and second oxidation waves even at a scan speed of 10 V s^{-1}, thus indicating that the species formed in the oxidation reactions are much less persistent than those obtained upon reduction.

EPR Studies.—Two different techniques were used in the reduction of the spiro[indoline-naphthopyran]. When reduced with potassium butoxide in polar solvents such as dimethyl sulfoxide (DMSO) or dimethylformamide (DMF) compounds **1**–**3** lead to the observation of spectra whose hyperfine parameters are collected in Table 2. In particular, compounds **1** and **3** give identical spectra showing coupling of the unpaired electron with the nitrogen of a nitro group, three different hydrogen atoms and an additional small splitting from a nitrogen nucleus, while **2** affords a completely different spectrum indicating couplings with the nitrogen from the nitro group and seven unequivalent hydrogens.

Alternatively, the three spiro compounds were treated with tetrabutylammonium borohydride in tetrahydrofuran (THF), either in the dark or under UV irradiation. In the former case, no spectra are observed with any of the compounds; while the nitro derivative **1** does not afford any signal upon UV irradiation of the EPR cavity, under similar conditions the 8′-nitro- and 5,8′-dinitro compounds give an identical EPR spectrum (see Table 2) recalling that afforded by compound **2** in DMF.

Compounds **1**–**3** were also treated with triphenylgermyl radicals, $Ph_3Ge^•$. The attacking species were generated *in situ* through hydrogen abstraction from the corresponding hydride by butoxyl radicals obtained either by thermolysis of *tert*-butyl hyponitrite at 313 K or by photolysis of di-*tert*-butyl peroxide. In all cases, intense and well resolved spectra that can be attributed to germyloxyaminoxyl radicals are observed (see Table 3) independent of the route followed for the generation of the butoxyl radicals; as observed in the borohydride reduction in THF, compounds **2** and **3** led to the observation of identical spectra.

Discussion

The trend of the electrochemically measured first oxidation potentials of **1**–**3** collected in Table 1 appears to be dictated by the indolinic moiety present in the three spiro compounds, and suggests that in the oxidation the electron is taken from the indolinic nitrogen lone pair. Actually, taking into consideration the resonance structures **A** and **B**, the presence of an electron-withdrawing substituent such as the nitro-group in a position conjugated with the indolinic nitrogen must reduce the avail-

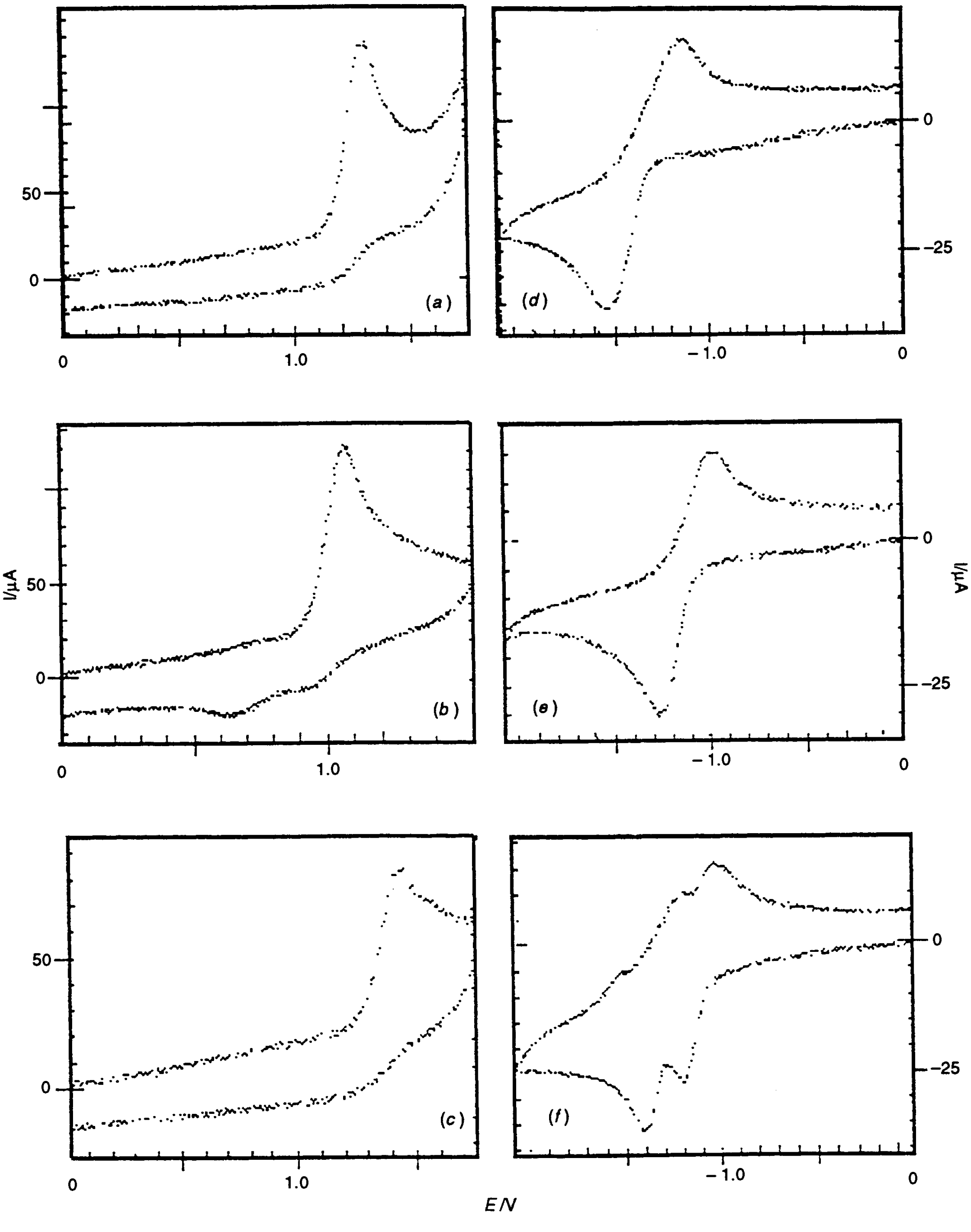
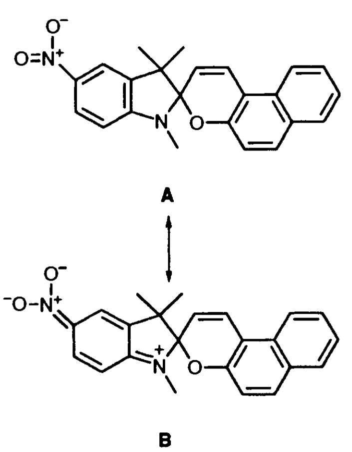


Fig. 1 Oxidation and reduction cyclic voltamperograms for compounds **1** (1.27 mmol dm^{-3} in ACN, diagrams *a* and *d*), **2** (1.11 mmol dm^{-3} in ACN, diagrams *b* and *e*) and **3** (0.8 mmol dm^{-3} in ACN, diagrams *c* and *f*) at voltage scan rate of 1 V s^{-1}



A

B

ability of its electrons, thus significantly increasing the oxidation potential; on the other hand conjugation through the spiro-linkage is not possible, and structures similar to **B** cannot be written for compounds where the nitro group is located on the naphthopyran unit. Consistently compound **1**, bearing the nitro group in position 5, is oxidized at a substantially higher potential than compound **2**, which carries a nitro group in position 8′, where it should not interact with the indolinic nitrogen. The fact that the dinitro compound **3** has the highest oxidation potential of the series is in line with the presence of two nitro groups; this however implies the existence of at least a slight interaction between the two units of the spiromolecule and suggests that the oxidation potential of compound **2** might be even lower in the absence of the nitro group in position 8′.

The number of exchanged electrons was estimated to be close to one for the three investigated compounds: the species formed

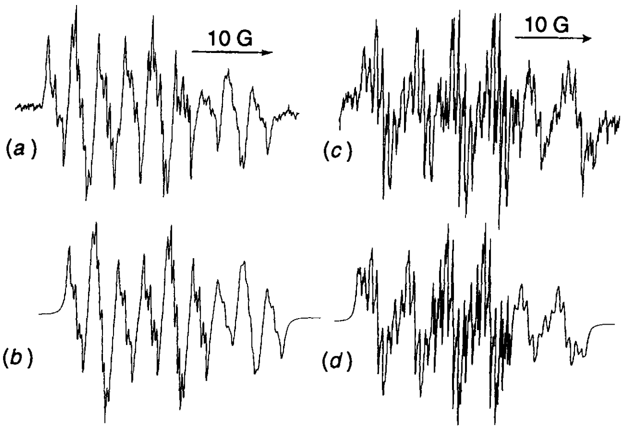


Fig. 2 EPR spectra of the radical anions observed by reducing compound 3 with Bu^{t}OK in DMF (*a*, experimental and *b*, simulated) and with Bu_4NBH_4 in THF (*c*, experimental and *d*, simulated)

in the first oxidation process should therefore be in all cases the radical cations. These species are very short lived, as indicated by the complete absence of a cathodic peak in their cyclic voltamperograms, even at the highest scan rate experimentally available (10 V s^{-1}). As to the second oxidation waves exhibited by compounds **1**–**3**, they might reflect further oxidation of the first formed radical cations. In view of the very high instability of the radical cations themselves, it cannot be excluded that the second waves might be due to species with a structure not necessarily related to the starting spiro compounds originating from degradation of the radical cations.

The reduction potentials of compounds **2** and **3** are rather low, while that of **1** is markedly more negative. This similarity of the first reduction potentials of compounds **2** and **3** is in line with expectation, as the reduction is dominated by the location of the nitro group in the molecular framework. A comparison between the reduction potentials of compounds **1** and **2** indicates that the latter compound has a greater electron affinity; for the dinitro derivative, in the absence of electronic interactions between the two sections of the molecule, the lowest energy acceptor level has therefore to be localised on the naphthopyran unit. This is actually what was found: compound **3** exhibits two reduction waves analogous to those observed for compounds **2** and **1** separately. Moreover, the slight interaction between the two molecular fragments observed in the oxidation is further substantiated by the fact that compound **3** exhibits reduction potential somewhat lower than those of compound **2** and, more noticeably, of compound **1**.

The three compounds were scarcely soluble in ACN, but in all cases it was possible to estimate that the number of exchanged electrons was one. The species resulting from the reduction of the three nitrospiro[indoline-benzopyran] compounds are therefore the corresponding radical anions. Additional evidence is provided by the reversibility of the process, as indicated by the presence of anodic peaks in the voltamperograms: radical ions of nitroaromatic derivatives are in fact expected to be rather persistent species in polar aprotic solvents such as ACN.

The radical anions of the three nitrospiro[indoline-naphthopyrans] have also been obtained in DMF by chemical reduction with potassium butoxide inside the cavity of an EPR spectrometer. The resulting spectra provide information on the MO orbital occupied by the unpaired electron which appears to be determined by the location of the nitro group; thus, in the case of **1** the unpaired electron is confined onto the nitroindoline moiety, coupling with the protons in positions 4, 6 and 7 and with the indolinic nitrogen being observed beside that with the nitrogen of the nitro group (see Fig. 2). The assignment of the splittings to the different positions given in Table 2 has been made on the basis of the results of McLachlan spin density calculations (see the Experimental section) that were found to be in very good agreement with the measured values. On the other hand, similar treatment of compound **2** led to a spectrum (Fig. 2) indicating a spin density distribution in line with the radical anion of a substituted β-nitronaphthalene; assignment of the splittings was therefore made by analogy to those reported in the literature for this radical anion,[7] although the agreement with calculated values was not as good as for the anion from compound **1**. In both cases the spectra were typical of isolated systems, showing the absence of interactions between the two entities in the molecules.

Aromatic nitro compounds can also be spontaneously reduced to their radical anions by reaction with tetrabutylammonium borohydride, Bu_4NBH_4, in THF provided their reduction potential is less negative than -1.15 V.[7] The reduction can be photoinduced for those compounds whose reduction potential falls in between -1.15 and -1.4 V,[8] but does not take place for derivatives characterised by a lower electron affinity. Both compounds **1** and **2** did not react spontaneously with Bu_4NBH_4; on the other hand, while compound **1** did not react with the borohydride even under UV irradiation, the reaction of compound **2** could be photoinduced resulting in the observation of the EPR spectrum of the radical anion $\mathbf{2}^{\bullet -}$. These results are in line with the measured electrochemical potentials for compounds **1** and **2** and provide further support for the identification of the species obtained in the electrochemical reduction as the radical anions.

The reduction of compound **3** is much less straightforward. When 5,8′-dinitrospiro[indoline-naphthopyran] was treated with Bu_4NBH_4 in THF no EPR signal developed spontaneously, although 'bumps' in the base line could be detected *ca.* 30 min after mixing. Upon UV irradiation of the EPR cavity an intense and well-resolved spectrum is observed, whose spectral pattern is almost identical with that detected by similar treatment of compound **2**. This indicates that the LUMO accommodating the extra electron is essentially centred on the nitronaphthopyran moiety, consistent with the expectations based on the similarity of the measured first reduction potential of compounds **3** (-1.20_8 V) and **2** (-1.27_2 V), and assuming no significant interactions between the moieties of the dinitro spiro compound. When, on the other hand, compound **3** is treated with potassium butoxide in DMF or in DMSO, an intense spectrum is again observed, but in this case the pattern closely resembles that of the radical anion from compound **1**; this indicates that the unpaired electron, at variance with what observed in THF, is now located in an orbital essentially centred on the nitroindoline unit. Although one might object that the species observed in DMF is in fact a radical trianion, hypothesising that reduction of the naphthopyran moiety takes actually place first followed by that of the nitroindoline unit which then uptakes a third electron, it appears quite unlikely that the MO accommodating the unpaired electron in the trianion should have the same atomic coefficients of the SOMO in the radical anion from compound **1**. The alternative of some kind of quantum-mechanical tunnelling between two radical anions differing for the orbital containing the unpaired electron seems equally unlikely as there is no reason why it should only take place in DMF and not in THF.

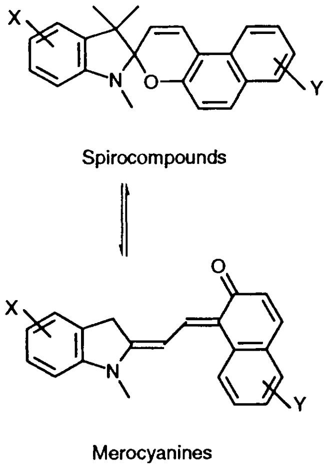
As mentioned in the introduction, the photochromism of the investigated compounds originates from the light induced opening of the pyran ring leading to the formation of the deeply coloured merocyanines which may be thermally reconverted into the starting closed spiro compounds. The question therefore arises as to whether the radical anions observed in the photoinduced reduction with Bu_4NBH_4 should be assigned the closed structure of the starting compounds or the open structure of the corresponding merocyanines. The spin density

Table 3 EPR hyperfine spectral parameters for the germyloxyaminoxyls from compounds **1**–**3**[a]

Comp.	a_1[b]	a_{Me}[c]	a_4	a_5[d]	a_6	a_7	$a_{3'}$	$a_{4'}$	$a_{5'}$	$a_{6'}$	$a_{7'}$[d]	$a_{8'}$	$a_{9'}$	$a_{10'}$	g
1	0.85	0.62	2.95	15.6	3.50	2.05									2.0042_4
2							0.20	0.24	0.56	1.26	14.37	4.72	1.80	1.03	2.0045_7
3							0.20	0.20	0.58	1.30	14.40	4.68	1.80	1.00	2.0045_9

[a] Coupling constants in G = 10^{-4} T; [b] coupling with the heterocyclic nitrogen; [c] coupling with the protons of the *N*-methyl group; [d] coupling with an aminoxyl nitrogen.

distribution should provide a means of discrimination as it should be significantly different in the two cases, the merocyanines being characterized, at variance with the spiro compounds, by an *ortho*-quinone-like structure.



An examination of the data collected in Table 2 indicates a close similarity of the spin density distribution in the radical anions obtained from compound **2** by butoxide reduction in DMF or by borohydride photoreduction in THF, suggesting the same structure for the observed species, *i.e.* the spiro-structure of the closed forms. However, as it has been reported that some photochromic compounds may be converted into the merocyanines by simply dissolving them in highly polar solvents,[9] doubts may be raised on the correctness of this assignment based on the assumption that the starting structure is retained by the radical in DMF in the absence of UV irradiation.

The only way of clearly determining the structure of the radicals is to generate them in the absence and in the presence of UV irradiation in an apolar solvent, *e.g.* benzene. It being difficult, even if possible, to generate the radical anions in benzene, we have considered the corresponding aminoxyls obtained by reacting triphenylgermyl radicals with the nitro-derivatives **1**–**3**, because the spin density distribution in these aminoxyls usually parallels that of structurally similar radical anions. The attacking triphenylgermyl radical can be obtained *in situ via* hydrogen abstraction from the related hydride by *tert*-butoxyl radicals; these, in turn, can be generated either by thermolysis of *tert*-butyl hyponitrite or by photolysis of di-*tert*-butyl peroxide.

$$\mathrm{Bu^tOOBu^t} \xrightarrow{h\nu} \mathrm{Bu^tO^{\cdot}} \xleftarrow{40\,^{\circ}\mathrm{C}} \mathrm{Bu^tO{-}N{=}N{-}OBu^t}$$

$$\mathrm{Bu^tO^{\cdot}} + \mathrm{Ph_3GeH} \longrightarrow \mathrm{Bu^tOH} + \mathrm{Ph_3Ge^{\cdot}}$$

$$\mathrm{Ph_3Ge^{\cdot}} + \mathrm{R{-}NO_2} \longrightarrow \mathrm{R{-}N(O^{\bullet})OGePh_3}$$

In Table 3 are collected the hyperfine spectral parameters for the germyloxyaminoxyls obtained from **1**–**3**: the same species were observed independently of the means of generation of the butoxyl radicals, either in the absence or in the presence of UV irradiation. As expected, in the aminoxyl from compound **1** the unpaired electron is only localised on the indoline moiety, while in that from compound **2** it resides only on the naphthopyran unit (see Fig. 3). The spectra observed when starting from compound **3** are superimposable on those obtained from compound **2**, indicating that the nitronaphthopyran fragment is more prone to radical addition than its nitroindolinic counterpart.

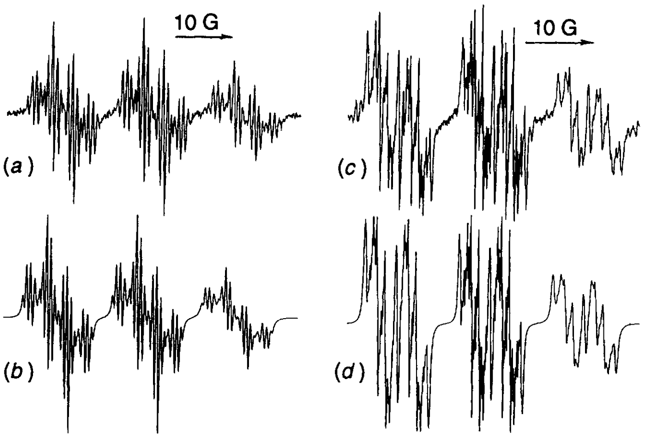


Fig. 3 EPR spectra of the triphenylgermyloxy aminoxyls observed by reacting triphenylgermyl radicals with compounds **1** (*a*, experimental and *b*, simulated) and **2** (*c*, experimental and *d*, simulated) in benzene solution at 40 °C

The fact that the same species are formed either under UV irradiation or in the dark at 40 °C can now be taken as acceptable evidence that in all cases the radicals should be assigned a spirostructure analogous to that of the starting compounds. The observation of only one germyloxyaminoxyl under UV irradiation of **3** suggests that radical addition must take place more readily at the nitro group of the spiro compounds than at that of the merocyanines and that, at variance with the starting compounds, the radicals do not exhibit photochromic properties, *i.e.*, do not undergo the photoinduced reversible opening of the pyran ring.

Experimental

Materials.—Compounds **1**–**3** were prepared as previously described[10] through condensation of the suitable 2-methyleneindolines and hydroxynaphthaldehydes, *tert*-butyl hyponitrite was obtained by reacting sodium hyponitrite and *tert*-butyl bromide in the presence of a Lewis acid,[11] while triphenylgermanium hydride was obtained by reducing the corresponding bromide with $LiAlH_4$ according to standard procedures.[12] All other chemicals were purchased and used as received or, in the case of solvents, carefully dried and distilled prior to use.

Electrochemistry.—Staircase cyclic voltammetric measurements were carried out in a cell equipped with a platinum disk as working electrode ($\o$ = 2 mm), a platinum wire as auxiliary electrode, and a saturated calomel electrode as reference. This was separated from the test solution by a compartment containing the supporting electrolyte and closed with a porous ceramic disk. A custom-built potentiostat and acquisition data system were also used.[13] Measurements were carried out on dry argon-purged acetonitrile solutions of the compounds (*ca.* 1 mmol dm^{-3}) and tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}). The latter was purchased from Fluka, twice crystallised from a mixture of ethyl acetate and pentane (20:80), and dried at 60 °C under reduced pressure.

EPR Spectroscopy.—EPR spectra were recorded using a Bruker ER200D X-band spectrometer, equipped with a standard variable temperature device, a Bruker NMR-Gaussmeter for field calibration and a Systron Donner 6245A frequency counter for the determination of g-factors that were corrected against that of perylene radical cation in concentrated sulfuric acid.[14] When necessary, UV irradiation was achieved by focusing on the EPR cavity the light from a Hanovia 1 kW high-pressure mercury lamp.

The radical anions were generated either by reduction of the spiro compounds with potassium butoxide in dried DMF in a capillary tube ($\o = 1$ mm), or by photoinduced reaction of the spiro compounds with $\mathrm{Bu_4NBH_4}$ in deoxygenated THF in a quartz tube ($\o = 4$ mm). The germyloxyaminoxyl were obtained either by photolysing degassed benzene solutions of the nitro compounds containing triphenylgermanium hydride and *tert*-butyl peroxide or by heating at 40–50 °C benzene solutions of the appropriate nitro compound, triphenylgermanium hydride and *tert*-butyl hyponitrite.

MO Calculations.—Spin density calculations were carried out according to the McLachlan method using the following parameters: $h_{\mathrm{N}}(\mathrm{NO_2}) = 2.2$, $k_{\mathrm{CN}}(\mathrm{NO_2}) = 1.2$, $h_{\mathrm{O}}(\mathrm{NO_2}) = 1.4$, $k_{\mathrm{NO}}(\mathrm{NO_2}) = 1.67$,[15] $k_{\mathrm{CC}}(\mathrm{C{=}C}) = 1.4$, $k_{\mathrm{CC}}(\mathrm{C{-}C}) = 0.8$,[16] h_{N}(indolinic) = 1.5, k_{CN}(indolinic) = 0.9.[17] The proton splittings were calculated through the usual McConnel equation $a(\mathrm{H}_\mu) = Q_{\mathrm{CH}}\rho(\mathrm{C}\mu)$ with a Q_{CH} value of -23 G, while the nitrogen splitting of the nitro group was calculated using the expression $a(\mathrm{N}) = 99\rho(\mathrm{N}_\pi) - 2[23.89\rho(\mathrm{O}_\pi)]$.[18]

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Paper 3/01942J
Received 30*th March* 1993
Accepted 21*st April* 1993