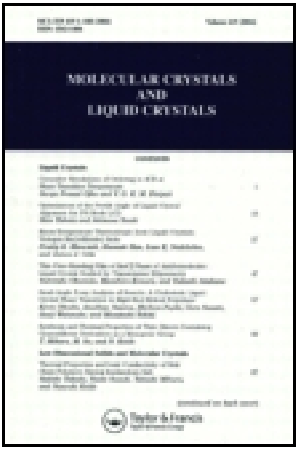

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EPR AND ELECTROCHEMICAL STUDIES OF RADICALS FROM PHOTOCHROMIC COMPOUNDS

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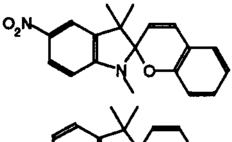
Abstract The radical anions of a number of nitrospirocompounds of the indolinic series have been generated by electrochemical or chemical reduction and studied by EPR spectroscopy. The oxidation and reduction peak potentials of the starting compounds have also been measured.

Spiro[indoline-benzopyrans] and spiro[indoline-naphthopyrans] are two important families of compounds exhibiting photochromic properties[1] owing to the equilibrium between their closed forms and the corresponding merocyanines. Several studies have also shown that the photochromic activity of these compounds can be somewhat modulated by the introduction of substituents in different positions of their molecular framework;[2] in particular it has been shown that nitro groups usually favour the ring opening and thus the photochromic process.[3]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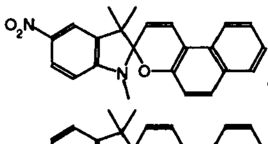
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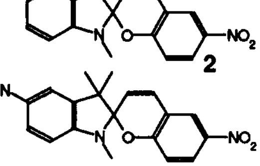
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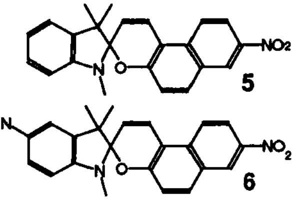
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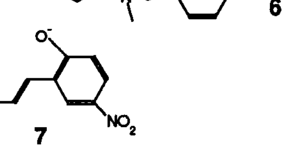
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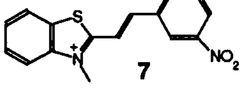
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As nitroaromatic compounds are easily reducible species, we have carried an EPR study on the radical anions obtained from 5-nitrospiro[indoline-benzopyran] **1**, 6'-nitrospiro[indoline-benzopyran] **2**, 5,6'-dinitrospiro[indoline-benzopyran] **3**, 5-nitrospiro[indoline-naphthopyran] **4**, 7'-nitrospiro[indoline-naphthopyran] **5**, 5,7'-dinitrospiro[indoline-naphthopyran] **6**, and of the merocyanine of the benzothiazolic series **7** as model of the open forms.

Cyclic voltammetry

Cyclic voltamperograms of compounds **1-7** were recorded in ACN using tetrabutylammonium hexafluorophosphate as supporting electrolyte at scan rates ranging from 0.1 to 10 V/s according to established procedures.[4] All the oxidation traces proved completely irreversible even at the highest scan rates, thus indicating that the resulting radical cations rapidly evolve in the medium to form species that are again electroactive: indeed in all cases a second oxidation peak was present at potentials around 2 V. The values collected in Table I indicate that compounds **2**, **5** and **7**, not bearing a nitrogroup on the indolinic or benzothiazolic moieties, are more readily oxidized then compounds **1** and **4** and, to an even greater extent, then compounds **3** and **6** bearing two nitro substituents. This indicates that oxidation proceeds through release of an electron from the heterocyclic nitrogen lone pair, the presence of a nitrogroup in the conjugated position 5 reducing its availability.

TABLE I Oxidation and reduction peak potentials *vs* SCE

Comp.	$E_{p_{ox}}$/V	I_{ox}/μA	$E'_{p_{red}}$/V	I'_{red}/μA	$E''_{p_{red}}$/V	I''_{red}/μA	Ref.
1	1.40	53.6	-1.52	-43.4			This work
2	1.05	65.1	-1.38	-44.2			This work
3	1.48	44.3	-1.24	-40.6	-1.50	-36.1	This work
4	1.24	36.9	-1.45	-26.9			5
5	1.02	25.7	-1.27	-25.3			5
6	1.36	20.0	-1.20	-20.0	-1.42	-17.8	5
7	1.00	25.7	-1.02	-26.3			This work

The reduction voltamperograms of compounds **1**, **2**, **4**, and **5** showed the complete and reversible uptake of one electron, indicating that the resulting radical anions are rather persistent species in line with expectation for nitroaromatic compounds. In particular the reduction of the nitroindolinic moiety appears to be more difficult than that of the nitrobenzopyranic or the nitronaphthopyranic units. Dinitro derivatives **3** and **6** showed two reduction peaks at potentials similar to those of the corresponding mononitro derivatives, thus suggesting the existence of little conjugative interaction, if any, between the two moieties of the spiro molecules. Finally, it is worthwhile pointing

Table II EPR spectral parameters for the radical anions from compounds **1-7**.[a]

Comp./ Solv.	a_{N_1}	a_{Me_1}	a_4	a_6	a_7	$a_{3'}$	$a_{4'}$	$a_{5'}$	$a_{6'}$	$a_{7'}$	$a_{8'}$	$a_{9'}$	$a_{10'}$	a_{NO_2}	g
1/DMSO	0.58	0.50	3.75	2.90	1.04									10.86	2.0045
1/ACN	0.61	0.53	4.00	31.0	1.10									11.62	2.0048
1/THF						no radical observed									
2/DMSO						----	0.32	2.46		3.59	0.67			14.15	2.0047
2/ACN						----	0.35	3.45		3.45	1.01			11.41	2.0048
2/THF						----	----	3.30		3.60	1.20			12.10	2.0048
3/DMSO	0.46	----	3.77	3.18	1.23									10.32	2.0046
3/ACN/LV[b]						----	0.40	3.43		3.43	1.20			11.11	2.0049
3/ACN/HV[c]	----	----	3.80	3.20	1.10									11.5	2.0048
3/THF					weak and unresolved signals										
4/DMSO[d]	0.49	----	3.46	3.00	1.08									10.89	2.0045
4/ACN	0.65	0.50	3.90	3.40	1.10									11.11	2.0048
4/THF[d]						no radical observed									
5/DMSO[d]						0.27	0.27	0.61	1.65		5.35	1.73	0.98	9.45	2.0047
5/ACN						0.25	0.25	0.65	1.60		5.28	1.75	1.00	9.71	2.0046
5/THF[d]						0.30	0.30	0.59	1.59		5.19	1.75	0.90	10.02	2.0047
6/DMSO[d]	0.42	----	3.72	3.21	1.10									10.77	2.0047
6/ACN/LV[b]						----	----	0.60	1.61		5.35	1.73	0.95	9.60	2.0047
6/ACN/HV[c]	----	----	3.85	3.42	1.01									11.12	2.0048
6/THF[d]						0.25	0.35	0.63	1.60		5.25	1.70	0.87	9.84	2.0047
7/DMSO						----	0.43	3.48		3.48	1.08			11.52	2.0046
7/ACN					overlapping spectra not interpreted										
7/THF						----	0.54	3.45		3.50	0.65			12.39	2.0046

[a] Coupling constants in Gauss = 10^{-4} Tesla. [b] LV = Low voltage ($E \geq -2.5V$). [c] HV = High voltage ($E \leq -3.0V$). [d] Ref. 5.

out that in the case of the open form **7** both the radical cation and the anion are very labile species. It would also appear that while **7** is oxidized at a potential similar to those characteristic of **2** and **5**, it can be reduced much more easily than these compounds.

EPR spectroscopy

The radical anions from **1-7** were produced either by electrochemical reduction in ACN directly inside the cavity of the EPR spectrometer, by chemical reduction with ^{t}BuOK in DMSO, or by chemical reduction with Bu_4NBH_4 in THF. The two former reactions were carried out under dark conditions, whereas the latter was photoinduced by UV irradiation.

The spectral parameters (see Table II) indicate that in all the radical anions the unpaired electron is confined in the molecular unit bearing the nitrogroup, providing further indication that no significative interannular conjugation is possible. The parameters measured for the anion of the permanent open compound **7** are quite similar to those measured for the anion of **2** under dark conditions (ACN) and under UV irradiation (THF): it would appear therefore impossible drawing any deduction about the structure of the observed radical anions based exclusively on the spectroscopic data.

The most striking feature to emerge from Table II is the odd behaviour of the two dinitroderivatives towards reduction. Actually, under mild conditions (low voltage electrochemical or photoinduced borohydride reduction) the observed spectra indicate that the unpaired electron is localised on the right-hand side of the molecule, consistent with expectation based on the reduction potentials, while under harder conditions (high voltage electrochemical or butoxide reduction) the unpaired electron appears to be located in an orbital essentially centred on the nitroindolinic unit. Although speculations are possible, we believe that a reliable explanation must await the results of further studies and theoretical calculations.

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