Electron-Transfer Chemistry and Redox-Switching of Stilbene-Like Heteroaromatic Compounds – Syntheses, Optoelectrochemical and ESR/ENDOR Studies☆

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Redox-active compounds, in which the electron donor and the acceptor subunits are covalently linked by a vinylene spacer group were synthesised and their properties were investigated by cyclovoltammetry, spectroelectrochemistry, and ESR/ENDOR spectroscopy. – 10-Methylphenothiazinyl, 10-methylphenoxazinyl, and phenoxathiinyl were used as electron-donating groups whereas 9,10-anthraquinon-2-yl and phenyl groups were employed as acceptors. The synthesis of the push-pull-substituted stilbenes **1a**, **1b**, **1c**, **2a**, **2b**, and **2c** was achieved by Wittig coupling of the heterocyclic aldehydes with the anthraquinoyl or phenyl phosphonium salts. The diastereoisomers were separated either by chromatography or by crystallization. – The redox potentials of the (*Z*) and (*E*) isomers differ only slightly. Spectroelectrochemical measurements indicate that the radical cations of the phenothiazine and phenoxazine derivatives undergo rearrangement from the (*Z*) to the (*E*) isomers. On the other hand, electron attachment leads to configurationally stable radical anions. This behaviour is rationalised in terms of the electron distribution reflected by the hyperfine data established by ESR/ENDOR spectroscopy.

Stilbenes are among the most intensively studied molecules in molecular switching especially due to their photodynamic behaviour[1]. Both (*E*)/(*Z*) isomerisation[2] and hexatriene/cyclohexadiene[3] cyclisation were established as reversible processes upon photochemical or thermal activation and have obtained widespread consideration in optoelectronic material science chemistry[4–8]. There are, however, only few reports on electron-transfer chemistry and electron-transfer-induced isomerisations of stilbenoid compounds[9].

The following study deals with the electron-transfer chemistry of push-pull-substituted stilbenes which can either be reversibly oxidised or reversibly reduced. To facilitate oxidation and to make the compounds more suitable for electrochemical and spectroelectrochemical investigations phenothiazinyl, phenoxazinyl, and phenoxathiinyl groups were introduced[10]. The anthraquinone and phenyl groups were used to improve the reductive electron transfer.

In this study we were mainly interested in the electrochemical and optical properties of these push-pull-substituted stilbenes (cf. Scheme 1) and in the properties of the radical ions and dianions. Investigations by cyclic voltammetry, spectroelectrochemistry, and ESR/ENDOR spectroscopy were undertaken. The long-term objective is to prepare molecular species which allow multimode switching as described in Scheme 2: The switching of stilbenoid compounds may occur in the electron transfer domain or in the photochemical or thermal isomerisation domain. All of these isomerisations may lead to characteristic changes of the optical and electrochemical properties[11].

Synthesis

Stilbenes **1a**, **2a**, **1b**, **2b**, **1c**, and **2c** were synthesised by Wittig reaction (Scheme 3): The carbaldehydes **4** of 10-methylphenothiazine, 10-methylphenoxazine, and phenoxathiine were treated with the appropriate phosphonium salts to yield the dihydroanthracenoid stilbene-like compounds as (*E*)/(*Z*) mixtures. Since the diastereomers were found to have almost the same R_f values in column chromatography on silica gel with common solvents, the analytically pure (*E*) isomers could be obtained by crystallisation (the (*E*) isomers have lower solubilities in common solvents). The pure (*E*) isomers could also be obtained by iodine-catalysed thermal isomerisation. Both diastereomers of **1a**, **2a** and **2b** were isolated in pure form. The phenoxathi-

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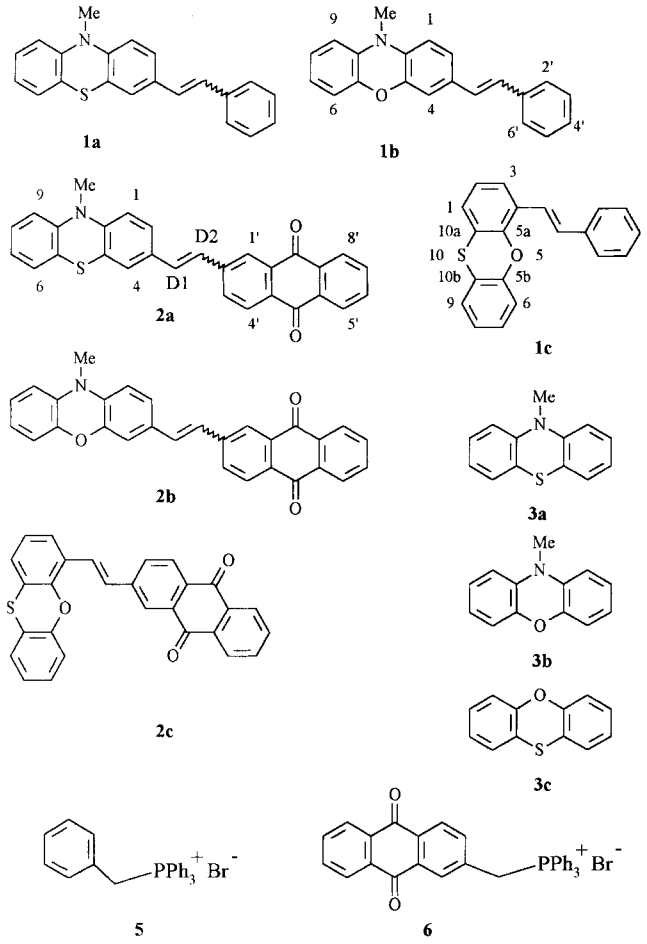
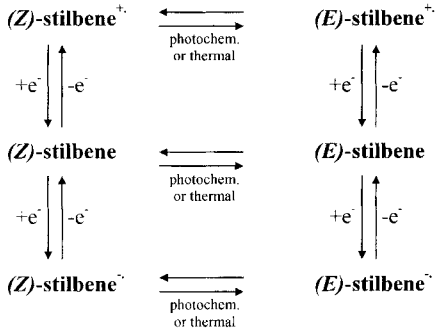
Scheme 1



Scheme 2. Schematic representation of the switching multifold of electron transfer-active stilbenoids



ine derivatives were obtained only as mixtures of (*E*)/(*Z*) isomers enriched in the (*Z*) isomer. Pure (*E*) isomers [(*E*)-**1c**, (*E*)-**2c**] were prepared by the iodine method. From the phenoxazine styryl compound **1b** we were only able to synthesise the pure (*E*) isomer.

Electrochemistry

The reversibility of the electron-transfer processes was investigated by cyclic voltammetry according to the following criteria: (a) the ratio of the reductive to the oxidative current, (b) the peak-to-peak separation of the forward and backward electron transfer, (c) multisweep experiments in a thin-layer electrochemicall cell. The results are summarised in Table 1.

Scheme 3. Synthesis of the push-pull-substituted stilbenes **1** and **2** (**a**–**c**)

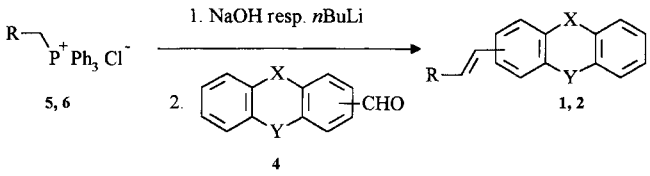


Table 1. Electrochemical data from cyclic voltammetry ($\tilde{\nu}$ = 250 mV/s; no significant changes by variation of the scan-speed between 50 to 1000 mV/s). $E_{1/2}$-values in mV vs FOC. Solvent: CH_3CN. Further details see experimental part

	1a	**1c**	**1b**	**2a**	**2c**	**2b**
(*Z*): $E_{1/2}$(ox)	+288	+805[c, d]	—	+315	+834[a]	+227
$E_{1/2}$(red1)	−2691	−2545	—	−1294	−1290	−1298
$E_{1/2}$(red2)	—	—	—	−1883	−1867	−1884
(*E*): $E_{1/2}$(ox)	+272	+811[d]	+164	+298	+833	+207[b]
$E_{1/2}$(red1)	−2662	−2506	−2681	−1291	−1274	−1338
$E_{1/2}$(red2)	—	—	—	−1835	−1826	−1907
ref. data: $E_{1/2}$(ox)	**3a**: +323		**3b**: +229		**3c**: +801	
	9,10-anthraquinone:		$E_{1/2}$(red1): −1321		$E_{1/2}$(red2): −1963	

[a] "(*Z*)-**2c**": ca. 16:5 (*Z*)/(*E*). – [b] Solvent: THF/CH_3CN (1:2). – [c] "(*Z*)-**1c**": ca. 5:2 (*Z*)/(*E*). – [d] Irreversible oxidation during thin layer examination.

All stilbenes except (*E*)-**1** and (*Z*)-**1c** undergo reversible one-electron oxidation leading to stable radical cations. On reduction the anthraquinone derivatives **2** exhibit reversible dianion formation in a two-step process whereas the phenyl-substituted derivatives **1** show only the reversible formation of the radical anion, similar to the unsubstituted 1,2-diphenylethene[12].

The differences between the oxidation potentials of the parent heteroarenes **3a**, **3b**, **3c**, and the corresponding push-pull stilbenoids **1** and **2** are less significant. For example, the oxidation potentials of the phenoxathiine-substituted compounds **1c** and **2c** are at most 30 mV higher than that of the parent heterocyclic compound **3c**. Otherwise, compounds **1a**–**b**, **2a**–**b** exhibit lower oxidation potentials (max. 70 mV) compared to **3a**–**b**. The reduction potentials of the stilbenes **2a**–**c** containing an anthraquinone subunit are shifted to less negative values by ca. 30 mV (first wave) and ca. 100 mV (second wave) compared to 9,10-anthraquinone itself.

As demonstrated in Table 1, the (*E*) and (*Z*) isomers show almost identical electrochemical behaviour leading to redox potentials of ca. 20 mV. In agreement with published data[9e], the *trans* forms are oxidised at slightly lower potential.

Spectroelectrochemistry

The spectroelectrochemical measurements were performed by application of the optical-transparent electrode (OTE) technique (Experimental). The pertinent absorption bands of the ionic species are summarised in Table 2.

As an example the spectroelectrogram obtained during the oxidation of (*E*)-**2a** is shown in Figure 1: the absorption bands of the neutral compound appear at 248 and 445 nm. Upon electrochemical oxidation (at 300 mV vs. *FOC*, see inset in Figure 1) these two bands decrease and the characteristic long-wave absorptions for the radical cations at 530, 666, and 926 nm arise together with a band at 307 nm.

ment with their instability already observed by thin-layer cyclic voltammetry (see above).

The quinoid stilbenes **2** can be reversibly reduced to their dianions in a two-step process. The dianions of the phenoxazine isomers **2b** could not be detected due to their low solubility. In contrast to the oxidation processes, (*Z*)/(*E*) isomerisation was not detected upon reduction of the

Table 2. Absorption data from spectroelectrochemistry λ_{max} in [nm]. m: medium, s: strong. Solvent as indicated in Table 1

		1a	**1b**	**2a**	**2c**[d]	**2b**
(*Z*):	$M^{\bullet-}$	—	—	1016, 613 (m)	950, 618 (m), 500 (m)	883, 559
	M^{2-}	—	—	717 (m), 567 (s)	780 (m), 593 (m)	[b]
	$M^{\bullet+}$	938, 667 (m), 508 (s)[c]	—	926, 666, 530 (s)[c]	[a]	840, 522 (m), 452 (m)[c]
(*E*):	$M^{\bullet-}$	—	—	1030, 671 (m), 541 (m)	950, 676 (m), 523 (m)	904, 693 (m), 619, 557 (m)
	M^{2-}	—	—	750 (m), 585 (m)	772 (m), 590 (m)	[b]
	$M^{\bullet+}$	930, 665 (m), 509 (s)	846, 651 (m), 489 (s)	906, 664, 529 (s), 307	[a]	900, 521 (m), 452 (m), 307
ref. data $M^{\bullet+}$:		**3a**: 846, 757, 510 (m)		**3b**: 660, 523 (s), 405 (m)		**3c**: 571 (s)
		9,10-anthraquinone	$M^{\bullet-}$: 980, 869, 540 (s), 404 (m)	M^{2-}:638 (m), 472 (s)		

[a] Radical cations not detectable. – [b] Reduction not reversible. – [c] Identical to the (*E*)-radical cation. – [d] "(*Z*)-**2c**": ca. 16:5 (*Z*)/(*E*).

Figure 1. Spectroelectrochemistry upon oxidation of (*E*)-**2a** to the corresponding radical cation. Solvent: CH_3CN. Inset: cyclic voltammetry, $\tilde{v}$ = 250 mV/s

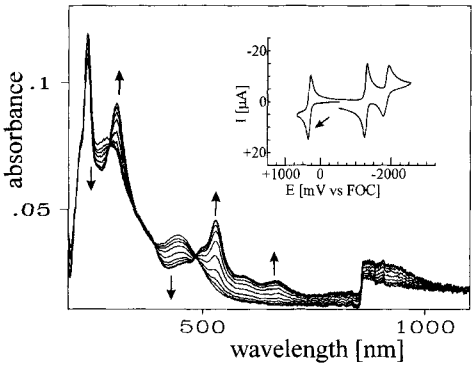
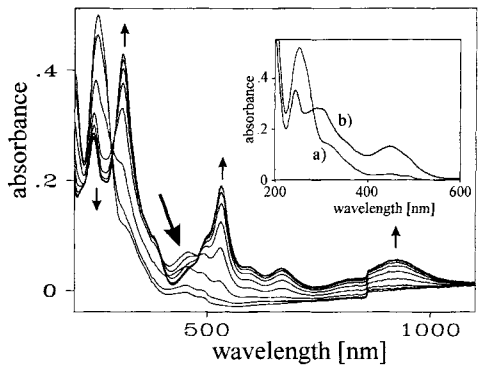


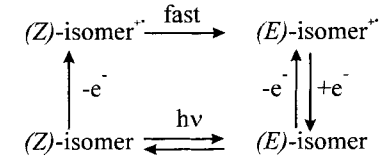
Figure 2. Spectroelectrochemistry upon oxidation of (*Z*)-**2a** to the radical cation of the (*E*) isomer (see text). The "larger arrow" indicates the formation of neutral (*E*) isomer as intermediate. Solvent: CH_3CN. Inset: Spectra before (a) and after (b) one complete redox cycle (oxidation/reduction)



Whereas the spectroelectrograms of the (*E*) isomers of the phenothiazine and phenoxazine derivatives **1**, **2** (**a**–**b**) show reversible behaviour as outlined above, the spectra of the (*Z*) isomers of **1a**, **2a**, and **2b** clearly indicate *cis*→*trans* isomerisation (Figure 2). The absorption spectrum of (*E*)-**2a** is recovered after one complete oxidation/reduction cycle (see inset in Figure 2) by starting from neutral (*Z*)-**2a**. The spectra obtained during the onset of the stepwise oxidation indicate a mixture containing the neutral forms of (*Z*)-**2a** and (*E*)-**2a** and the radical cation (*E*)-$\mathbf{2a}^{\bullet+}$. After a complete oxidative scanning the spectrum of pure (*E*)-$\mathbf{2a}^{\bullet+}$ is observed. Therefore, the (*Z*)→(*E*) isomerisation did occur at the radical cation stage as outlined in Scheme 4.

The electronic spectra of the stilbene radical cations $\mathbf{1}^{\bullet+}$, $\mathbf{2}^{\bullet+}$ exhibit almost the same characteristics as those of the parent heterocyclic compounds $\mathbf{3}^{\bullet+}$ with slightly red-shifted absorption bands readily rationalised by a slightly more extended conjugation. In the case of the phenoxathiine derivatives **1c** and **2c** we were unable to determine the radical cations by spectroelectrochemistry which again is in agree-

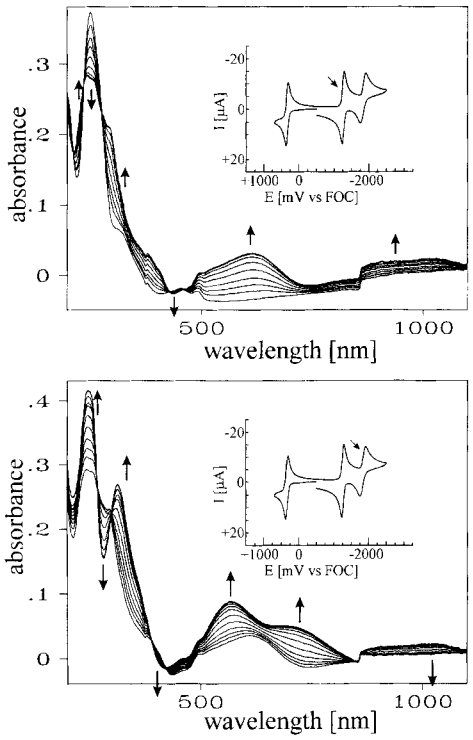
Scheme 4. Experimentally established interconversions of the push-pull-substituted stilbenoids **2**



anthraquinoid compounds, i.e., the radical anions and dianions are configurationally stable. As a representative example, the spectroelectrochemistry of the reduction of (*Z*)-**2a** to its radical anion and dianion is displayed in Figure 3. The presence of isosbestic points for both processes substantiates the configurational stability of the (*Z*) radical anions.

Within the time scale of the slow-scanning spectroelectrochemical experiment (ca. 0.5 h), the reduction of compounds **1** containing styryl groups is irreversible, presum-

Figure 3. Spectroelectrochemistry upon reduction of (*Z*)-**2a** to the corresponding radical anion (a); further reduction to the dianion (b). Insets: cyclic voltammetry, $\tilde{\nu}$ = 250 mV/s



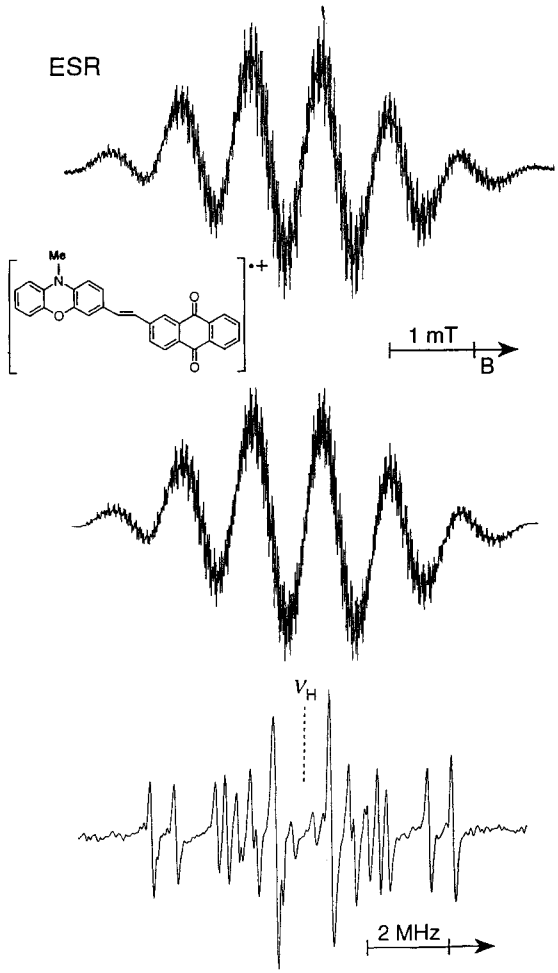
ably due to a dimerisation at the central double bond at the radical anion stage.

ESR and ENDOR Spectroscopy – Calculations

In order to gain more insight into the spectroelectrochemically established behaviour of the push-pull substituted stilbenes and to attain information about the electronic structure of the one-electron reduced and oxidised species, we investigated the radical ions of the (*E*) and (*Z*) isomers of **2a** and **2b** by ESR/ENDOR spectroscopy because of their particular persistence.

The radical cations were generated by oxidation with tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate[13] or thallium trifluoroacetate ($Tl(CF_3COO)_3$)[14] in a CH_2Cl_2 solution. Application of both methods to these two compounds leads to the appearance of identical ESR and ENDOR spectra for the (*E*) or (*Z*) isomers. In the temperature range from 203 to 298 K the ESR/ENDOR spectra are invariable. Figure 4 (top) exhibits the ESR spectrum of (*E*)-**2b**$^{\bullet+}$. The spectral pattern is dominated by six lines (spacing ca. 0.82 mT) which reveal further splittings. The corresponding ENDOR spectrum shows 9 pairs of lines between 11 and 18 MHz belonging to 9 proton hyperfine coupling constants, a_H, in the range from 0.019 to 0.259 mT. An additional line at 26.04 MHz marks the high-frequency signal belonging to an a_H of 0.82 mT[16]. The multiplicities of the a_H and the hyperfine coupling constant of the N atom in the donor part (a_N 0.839 mT) were determined by simulation of the ESR spectrum. The assignment of the major a_H (0.82 mT) to the three equivalent protons of the *N*-methyl group is straightforward because, together with the almost identical a_N, it causes the prominent 6-line pattern of the ESR signal. The remaining a_H were attributed to specific positions based on Hückel (HMO)-McLachlan calculations and a comparison with the hyperfine data of the 10-methylphenothiazine radical cation (see Table 3). The signs of the a_H were determined by general TRIPLE[15] spectroscopy. From Table 3 it can be anticipated that the ESR spectrum of [(*E*)/(*Z*)-**2a**]$^{\bullet+}$ possesses the same 6-line pattern as [(*E*)/(*Z*)-**2b**]$^{\bullet+}$, the dominating spacing being however ca. 0.7 mT [a_H (3H), 0.686 mT; a_N, 0.727 mT].

Figure 4. ESR spectrum (top), simulation (middle) and ENDOR spectrum (bottom) of [(*E*)-**2b**]$^{\bullet+}$. Solvents: CH_2Cl_2/CF_3COOH (2:1). Temp.: 253 K



Thus, in agreement with the HMO calculations the shapes of HOMOs of **2a** and **2b** are similar (Table 3). The spin population is predominantly concentrated inside the donor moieties. However, a considerable amount also resides at the olefinic double bond connecting the donor and the acceptor (Figure 5).

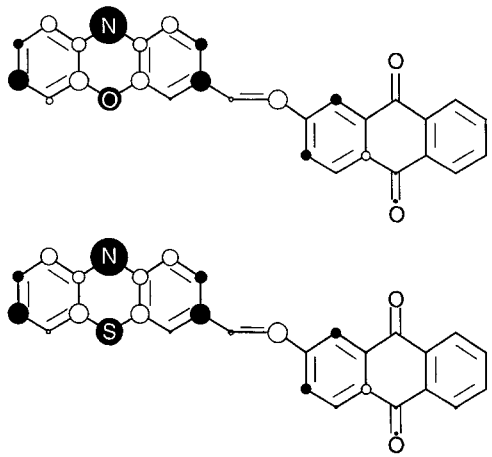
Reduction (K metal; solvent, DME/HMPA 2:1) of (*E*)- and (*Z*)-**2a** leads to the detection of two distinctly different ESR/ENDOR spectra as shown in Figure 6. In agreement with the spectroelectrochemical measurements, no isomerisation is detected at the radical anion stage. Analogous to the radical cations, the a_H determined by the ENDOR tech-

Table 3. Experimental and calculated[a] coupling constants a_H [mT] of radical cations

	(*E*)-**2a**		**3a**		(*E*)-**2b**	
	exp.	calcd.	exp.	calcd.	exp.	calcd.
1'	–0.084[f]	–0.07	—	—	–0.079[d]	–0.07
3'	–0.061[f]	–0.07	—	—	–0.048[d]	–0.07
4'	+0.013[g]	+0.02	—	—	+0.019[d]	+0.03
1	–0.092[e]	–0.13	–0.091	–0.15	–0.130[b]	–0.14
2	–0.033[g]	–0.04	–0.078	–0.01	–0.048[d]	–0.04
3	—	—	–0.210	–0.22	—	—
4	+0.084[f]	+0.09	+0.019	+0.06	+0.111[c]	+0.09
6	+0.024[g]	+0.05	+0.019	+0.06	+0.048[d]	+0.05
7	–0.154	–0.19	–0.210	–0.22	–0.210	–0.20
8	–0.033[g]	0.00	–0.078	–0.01	0.048[d]	0.00
9	–0.104[e]	–0.14	–0.091	–0.15	–0.146[b]	–0.14
D1	+0.061[f]	+0.07	—	—	+0.088[c]	+0.07
D2	–0.199	–0.26	—	—	–0.259	–0.26
CH_3	+0.686	+0.68	+0.719	+0.76	+0.827	+0.71
N	+0.726	—	+0.734	—	+0.839	—

[a] HMO-McLachlan calculation with:
$h_{C=O} = 1.2$ $h_{C-O-C} = 1.7$ $h_{C-S-C} = 1.2$ $h_N = 1.0$ $h_{C-Me} = -0.2$
$k_{C=O} = 1.56$ $k_{C-O} = 0.8$ $k_{C-S} = 0.65$ $k_{C-N} = 0.95$
for (*Z*)-isomers: $k_{3\text{-}D1} = k_{2'\text{-}D2} = 0.9$.
[b]–[g] Assignment interchangeable.

Figure 5. Shapes of the HOMOs of [(*E*)-**2a**] and [(*E*)-**2b**]



nique were assigned with the help of HMO-McLachlan calculations and by a comparison with the data of the 2-methylanthraquinone radical anion (Table 4). The HMO model with its graph-like handling of molecular geometries does not distinguish between (*E*) and (*Z*) isomers[16]. Therefore, a perturbation parameter, $k = 0.9\ \beta$, was introduced for the two bonds connecting the formal ethene and the donor and acceptor moieties in the case of the (*Z*) isomer to account for the slight deviation from planarity due to the sterical hindrance caused by the overlap of the *ortho* H atoms of the aromatic substituents. The comparison between calculated and experimental hyperfine data reveals that the above perturbation reproduces the experimentally established trends, particularly the decrease of the amount of a_H ascribed to the D2 and the increase ascribed to the D1 positions (Table 4). Interestingly, the ESR/ENDOR spectra of (*Z*) and (*E*)-**2b** are identical with those of the stilbenes with the phenothiazine donor. Therefore, we conclude that in the radical anions, no detectable spin population is delocalised into over the electron-rich donor moieties. The LUMOs representing the π-electron distribution in the radical anions of (*Z*) and (*E*)-**2a** and **2b** are displaced in Figure 7.

Figure 6. ESR spectra (top), simulation (middle) and ENDOR spectra (bottom) of [(*Z*)-**2a**]$^{\bullet-}$ (right) and [(*E*)-**2a**]$^{\bullet-}$ (left). Solvent: DME/HMPA (2:1); counter ion: K^+; temp.: 223 K

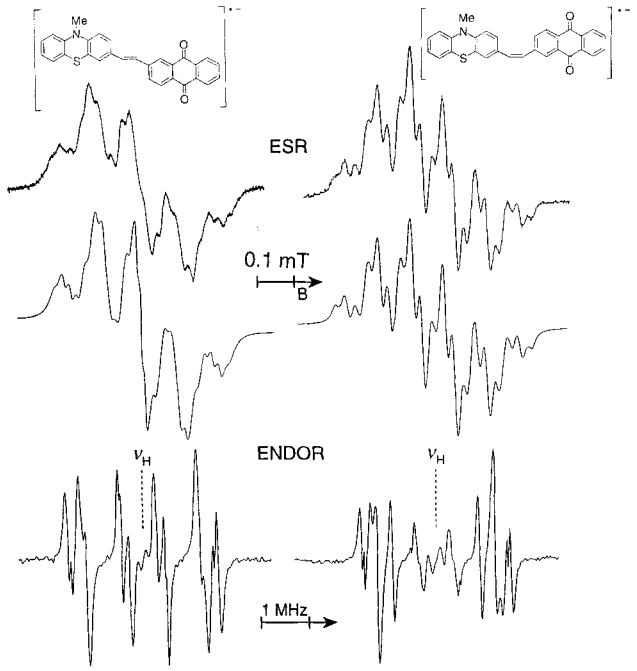


Figure 7. Shapes of the LUMOs of [(*Z*)-**2b**] (top) and [(*E*)-**2b**] (bottom)

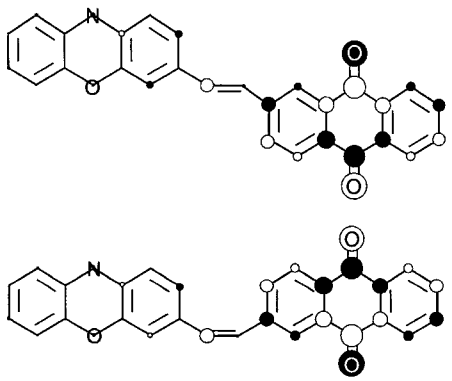


Table 4. Experimental and calculated[a] coupling constants a_H [mT] of radical anions

	2-Methylanthraquinone		(*E*)-**2a**		(*Z*)-**2a**	
	exp.	calcd.	exp.	calcd.	exp.	calcd.
1'	–0.040	–0.05	+0.006	+0.02	–0.009[c]	+0.01
2'	+0.092	+0.09	—	—	—	—
3'	–0.105	–0.08	–0.094[b]	–0.13	–0.097[d]	–0.13
4'	–0.020	–0.02	–0.020	–0.02	–0.022[c]	–0.02
5'	–0.020	–0.02	–0.020	–0.03	–0.030[c]	–0.03
6'	–0.105	–0.11	–0.085[b]	–0.08	–0.067[d]	–0.09
7'	–0.105	–0.10	–0.085[b]	–0.09	–0.087[d]	–0.10
8'	–0.031	–0.03	–0.020	–0.02	–0.022[c]	–0.02
D1	—	—	–0.114[b]	–0.16	–0.111[d]	–0.13
D2	—	—	+0.038	+0.04	+0.087	+0.03

[a] HMO-calculation with McLachlan-correction: see Table 3. – [b]–[d] Assignments are interchangeable.

The tendency to undergo (*E*)/(*Z*) isomerisation is mainly governed by the π bond order at the central olefinic molecular fragment. The a_H attributed to the D1 and D2 (see Scheme 1) positions are +0.088 and −0.259 mT for [(*E*)-**2b**]$^{\bullet+}$, and +0.061 and −0.199 for [(*E*)-**2a**]$^{\bullet+}$, respectively. For the radical anions the corresponding a_H are about half the size (Table 4). The a_H constants are related to the MO coefficients by the McConnell equation[17], $a_{H\mu} = Q \cdot \rho_\mu$ with $\rho_\mu = c_{j\mu}^2$, where Q is a constant (−2.5 mT), ρ_μ the π-spin population at a centre μ and $c_{j\mu}$ the coefficient at μ in the singly occupied MO (j). Based on the $c_{j\mu}$ values, the changes of the C(D1)−C(D2) π-bond order after electron removal or addition with respect to the neutral precursors can be estimated. In the HOMO the orbital coefficients at C(D1) and C(D2) posses the same sign (bonding interaction). Consequently, electron removal leads to a decrease of the π-bond order by $c_{HOMO(D1)} \cdot c_{HOMO(D2)}$ (J = HOMO). On the other hand, upon reduction the LUMO becomes the singly occupied MO and again the central π bond is weakened because $c_{LUMO(D1)} \cdot c_{LUMO(D2)}$ (j = LUMO) have opposite signs. The data in Table 5 illustrate that the π-bond order of the olefinic double bond (BO) is larger for the radical anions than for the radical cations.

Table 5. HOMO and LUMO coefficients for the D1 and D2 positions of the radical ions of (*E*)- and (*Z*)-**2a** and **2b** and decrease of the C(D1)−C(D2) π-bond orders (BO) related to the neutral compounds

	[(*E*)-**2b**]$^{\bullet+}$		[(*E*)-**2a**]$^{\bullet+}$		[(*E*)-**2a**]$^{\bullet-}$[a]		[(*Z*)-**2a**]$^{\bullet-}$[a]	
	D1	D2	D1	D2	D1	D2	D1	D2
c_μ	0.188	0.322	0.156	0.282	0.214	−0.123	0.211	−0.187
ΔBO	−0.060		−0.044		−0.026		−0.039	

[a] Same values for **2b**.

Conclusion

(*Z*)/(*E*) Isomerisation of the push-pull-substituted stilbenes can be achieved by one-electron oxidation. Reduction leads to configurationally stable radical anions. These findings, obtained from electrochemical and spectroelectrochemical investigations, can be rationalised by the shapes of the HOMOs and the LUMOs which were established by the ESR data of the radical cations and radical anions as well as HMO calculations. One particular factor responsible for the tendency to undergo (*E*)/(*Z*) isomerisation upon electron transfer is the amount of electron density at the olefinic C atoms. Moreover, the nodal properties of the singly occupied orbital have to be taken into account.

It will be interesting to investigate an extended palette of push-pull-substituted stilbenes with different amounts of electron delocalisation over the donor and acceptor moieties to obtain more detailed information about the delicate balance between configurational stability and isomerisation. Time-resolved optical and ESR techniques should help to establish the kinetics of these reactions. A further challenge is the study of the photochemical behaviour of the radical ions.

Experimental

Melting points: Uncorrected, Büchi SMP 20 and Reichert THERMOVAR. – UV/Vis: Perkin Elmer LAMBDA 9 Spectrophotometer. – IR: Beckman ACCULAB 1. – EI−MS: Varian CH-5. – NMR: Bruker ARX 400 spectrometers at frequencies of 400 and 101 MHz for ^{1}H and ^{13}C, respectively. Reference compounds are TMS (^{1}H) or $CDCl_3$ (^{13}C).

Electrochemistry: A standard one-compartment, three-electrode arrangement was used with a platinum disc as working electrode, a platinum wire as counter electrode and a pseudo Ag/AgCl reference electrode. The reversible oxidation signal of ferrocene (FOC) was used as internal standard. The solvents and the electrolyte (tetrabutylammonium hexafluorophosphate, TBAHFP) were purified or prepared according to standard procedures[18]. All measurements were undertaken under nitrogen. The electrochemical and spectroelectrochemical investigations of the (*Z*) isomers were performed with the exclusion of light.

Spectroelectrochemistry: After the measurements by cyclic voltammetry the solutions of the substrates were transferred by means of a syringe to the spectroelectrochemical cell which has been described previously[19]. The spectra were recorded by a Perkin-Elmer LAMBDA 9 spectrophotometer.

ESR/ENDOR: ESR: Varian E9 spectrometer. ENDOR/TRIPLE: Bruker-ESP-300 spectrometer. The solvents were dried over P_2O_5 (CH_2Cl_2) or potassium (dme, hmpa). Radical cations were generated by oxidation with $Tl(CF_3CO_2)_3$ or tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate at 203 K. Radical anions were produced by reduction on a potassium mirror.

Synthesis: Solvents and reagents were used as purchased without further purification unless stated otherwise: THF was dried and stored over Na and benzophenone under N_2. CH_2Cl_2 was dried over P_2O_5, benzene and Et_2O were dried over Na. Completion of the reactions was monitored by TLC.

10-Methyl-10H-phenothiazine-3-carboxaldehyde (**4a**)[20]: A solution of *N*-methylformanilide (14.0 g, 104 mmol), $POCl_3$ (14.4 g, 94 mmol) and 10-methyl-10H-phenothiazine (**3a**)[21] (20.0 g, 94 mmol) in *o*-dichlorobenzene (20 ml) was stirred at 100 °C for four hours with strict exclusion of water. Afterwards a 30% solution of NaAc in water (200 ml) was added and the reaction mixture was stirred for another one hour. The solvent and non-reacted formanilide were separated by steam distillation. The residue was extracted several times with toluene. Evaporation of the solvent from the combined extracts and purification of the crude product by vacuum distillation and recrystallisation from MeOH yielded yellow needles (12.57 g, 56%). – M.p. 80−82 °C (ref.[20] m.p. 89 °C). – IR (KBr): $\tilde{\nu}$ = 3060, 2880, 2820 cm^{-1} (C−H), 1670 (C=O), 1590 (ar). – UV/Vis (CH_3CN): λ_{max} (lg ε) = 375 nm (3.98), 283 (4.40), 269 (4.36), 235 (4.35). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.42 (s, 3H, N-CH_3), 6.84 (d, $J_{1,2}$ = 8.4 Hz, 1H, 1-H), 6.84 (dd, $J_{9,7}$ = 1.1, $J_{9,8}$ = 8.1 Hz, 1H, 9-H), 6.98 (dt, $J_{7,6} = J_{7,8}$ = 7.5, $J_{7,9}$ = 1.1 Hz, 1H, 7-H), 7.12 (dd, $J_{6,7}$ = 7.6, $J_{6,8}$ = 1.5 Hz, 1H, 6-H), 7.19 (ddd, $J_{8,6}$ = 1.6, $J_{8,7}$ = 7.4, $J_{8,9}$ = 8.1 Hz, 1H, 8-H), 7.60 (d, $J_{4,2}$ = 1.9 Hz, 1H, 4-H), 7.65 (dd, $J_{2,1}$ = 8.4, $J_{2,4}$ = 1.9 Hz, 1H, 2-H), 9.80 (s, 1H, CHO). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 190.1 (*C*HO), 35.8 (*C*H$_3$), 151.0 (quat.), 144.0 (quat.), 131.1 (quat.), 123.9 (quat.), 122.5 (quat.), 130.4 (tert.), 127.9 (tert.), 127.7 (tert.), 127.3 (tert.), 123.6 (tert.), 114.7 (tert.), 113.7 (tert.). – $C_{14}H_{11}NOS$ (241.3): calcd. C 69.68, H 4.59, N 5.80; found C 69.92, H 4.51, N 5.69. – MS (70 eV) *m/z* (%): 241 (100) [M$^+$], 226 (53) [M$^+$ − CH_3].

10-Methyl-10H-phenoxazine-3-carboxaldehyde (**4b**)[22]: The procedures were the same as in the synthesis of **4a**. Isolated yield: 66% green-yellow needles. – M.p.: 96 °C. – IR (KBr): $\tilde{\nu}$ = 3050, 2940,

2830 cm^{-1} (C–H), 1680 (C=O), 1600 (ar). – UV/Vis (CH_3CN): λ_{max} (lg ε) = 391 nm (4.06), 260 (4.26), 223 (4.22). – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.09 (s, 3H, N-CH_3), 6.53 (d, $J_{1,2}$ = 8.4 Hz, 1H, 1-H), 6.56 (dd, $J_{9,7}$ = 1.4, $J_{9,8}$ = 7.9 Hz, 1H, 9-H), 6.70 (dd, $J_{6,7}$ = 7.8, $J_{6,8}$ = 1.6 Hz, 1H, 6-H), 6.76 (dt, $J_{7,6}$ = $J_{7,8}$ = 7.7, $J_{7,9}$ = 1.4 Hz, 1H, 7-H), 6.86 (ddd, $J_{8,6}$ = 1.6, $J_{8,7}$ = 7.5, $J_{8,9}$ = 7.9 Hz, 1H, 8-H), 7.12 (d, $J_{4,2}$ = 1.9 Hz, 1H, 4-H), 7.34 (dd, $J_{2,1}$ = 8.3, $J_{2,4}$ = 1.9 Hz, 1H, 2-H), 9.67 (s, 1H, CHO). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 189.8 (*C*HO), 31.2 (*C*H_3), 145.6 (quat.), 145.0 (quat.), 140.6 (quat.), 132.8 (quat.), 130.0 (quat.), 128.8 (tert.), 124.0 (tert.), 122.5 (tert.), 115.6 (tert.), 114.1 (tert.), 112.2 (tert.), 110.7 (tert.). – $C_{14}H_{11}NO_2$ (225.2): calcd. C 74.66, H 4.92, N 6.22; found C 74.63, H 4.90, N 6.28. – MS (70 eV) *m/z* (%): 225 (100) [M^+], 210 (94) [$M^+ - CH_3$].

4-Phenoxathiinecarboxaldehyde (**4c**)[23]: A solution of phenoxathiine (**3a**) (5.00 g, 25.0 mmol) in dry THF (100 ml) was treated under N_2 with *n*BuLi (16 ml in *n*-hexane, 25 mmol) and stirred at 25°C for 1 d. The solution was cooled to –78°C and treated with DMF (1.83 g, 25 mmol). After 4 h (temperature had increased to 25°C) the reaction mixture was poured into ice/water/HCl (*c* = 2) and the mixture was extracted several times with CH_2Cl_2. The combined organic phases were concentrated and the residue was purified by two consecutive CCs (SiO_2; solvent: CH_2Cl_2). Recrystallisation from CH_2Cl_2/*n*-hexane (1:1) afforded **4c** as pale yellow crystals (2.85 g, 50%)[24]. – M.p.: 82–84°C. – IR (KBr): $\tilde{\nu}$ = 3060, 2900, 2780 cm^{-1} (C–H), 1690 (C=O), 1600 (ar). – UV (CH_3CN): λ_{max} (lg ε) = 350 nm (3.28), 270 (3.82), 228 (4.37). – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.07–7.16 (m, 4H, 2-H, 6-H, 8-H, 9-H), 7.20 (ddd, $J_{7,6}$ = 8.2, $J_{7,8}$ = 6.9, $J_{7,9}$ = 1.8 Hz, 1H, 7-H), 7.34 (dd, $J_{1,2}$ = 7.7 Hz, $J_{1,3}$ = 1.7 Hz, 1H, 1-H), 7.67 (dd, $J_{3,1}$ = 1.7, $J_{3,2}$ = 7.8 Hz, 1H, 3-H), 10.63 (s, 1H, CHO). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 188.3 (CHO), 154.6 (C-5b), 151.2 (C-5a), 125.1 (C-4), 121.9 (C-10a), 119.6 (C-10b), 132.4 (tert.), 128.1 (tert.), 127.0 (tert.), 126.1 (tert.), 125.4 (tert.), 124.4 (tert.), 117.8 (tert.). – $C_{13}H_8O_2S$ (228.3): calcd. C 68.40, H 3.53; found C 68.29, H 3.56. – MS (70 eV) *m/z* (%): 228 (100) [M^+], 199 (8) [$M^+ - CHO$].

Preparation of the Styryl Compounds[25]: A suspension of benzyltriphenylphosphonium chloride **5** (1.1 equivalents) in THF was cooled under N_2 to –78°C and treated with *n*BuLi (1.1 equivalents). After stirring for two hours the aldehyde was added and the reaction mixture was allowed to come to room temp. (time: about 16 hours). It was subsequently poured into ice/water and the product was extracted several times with CH_2Cl_2. Further workup by CC and recrystallisation[26].

3-(2-Phenylethenyl)-10-methyl-10H-phenothiazine (**1a**): Workup: several consecutive CCs (SiO_2; solvents: Et_2O/petroleum ether, 1:1; CH_2Cl_2/petroleum ether, 1:1; petroleum ether); the pure (*E*) isomer was recrystallized from methylcyclohexane. Isolated yields: (*E*) isomer 23% (yellow needles); (*Z*) isomer 23% (pale yellow powder).

(*E*)-**1a**: M.p.: 192–193°C. – IR (KBr): $\tilde{\nu}$ = 3060, 3030, 2930, 2900 cm^{-1} (C–H), 1595 (ar). – UV (CH_3CN): λ_{max} (lg ε) = 359 nm (4.26), 293 (4.54), 238 (4.26). – ^1H NMR (400 MHz, C_6D_6): δ = 2.69 (s, 3H, N-CH_3), 6.35 (d, $J_{1,2}$ = 8.3 Hz, 1H, 1-H), 6.37 (dd, $J_{9,7}$ = 1.1, $J_{9,8}$ = 8.1 Hz, 1H, 9-H), 6.72 (dt, $J_{7,6}$ = $J_{7,8}$ = 7.5, $J_{7,9}$ = 1.2 Hz, 1H, 7-H), 6.86, 6.90 (AB, J_{AB} = 16.3 Hz, 2H, H_{vinyl}), 6.92 (ddd, $J_{8,6}$ = 1.6, $J_{8,7}$ = 7.5, $J_{8,9}$ = 8.1 Hz, 1H, 8-H), 7.08 (dd, $J_{6,7}$ = 7.6, $J_{6,8}$ = 1.5 Hz, 1H, 6-H), 7.09 (m, 2H, 3′-H, 5′-H), 7.18 (m, 2H, 2-H, 4′-H), 7.28 (d, $J_{4,2}$ = 2.0 Hz, 1H, 4-H), 7.34 (m, 2H, 2′-H, 6′-H). – $C_{21}H_{17}NS$ (315.4): calcd. C 79.96, H 5.43, N 4.44; found C 79.70, H 5.80, N 4.53.

Z-**1a**: M.p.: 72–75°C. – IR (KBr): $\tilde{\nu}$ = 3050, 3010, 2920, 2860 cm^{-1} (C–H), 1595 (ar). – UV (CH_3CN): λ_{max} (lg ε) = 355 nm (sh, 3.68), 257 (4.32). – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.34 (s, 3H, N-CH_3), 6.45, 6.52 (AB, J_{AB} = 12.2 Hz, 2H, H_{vinyl}), 6.63 (d, $J_{1,2}$ = 8.9 Hz, 1H, 1-H), 6.80 (dd, $J_{9,7}$ = 1.1, $J_{9,8}$ = 8.1 Hz, 1H, 9-H), 6.92 (dt, $J_{7,6}$ = $J_{7,8}$ = 7.5, $J_{7,9}$ = 1.2 Hz, 1H, 7-H), 7.03 (dd, $J_{2,1}$ = 8.9, $J_{2,4}$ = 2.0 Hz, 1H, 2-H), 7.04 (d, $J_{4,2}$ = 1.9 Hz, 1H, 4-H), 7.11 (dd, $J_{6,7}$ = 7.6, $J_{6,8}$ = 1.4 Hz, 1H, 6-H), 7.16 (ddd, $J_{8,6}$ = 1.6, $J_{8,7}$ = 7.4, $J_{8,9}$ = 8.1 Hz, 1H, 8-H), 7.19–7.28 (m, 5H, H_{phenyl}).

3-(2-Phenylethenyl)-10-methyl-10H-phenoxazine (**1b**): Workup: several consecutive CCs (SiO_2; solvents: CH_2Cl_2/petroleum ether, 1:1; Et_2O/petroleum ether, 1:1); it was not possible to obtain the pure (*Z*) isomer. The (*E*) isomer was recrystallised from MeOH (36%, yellow needles).

E-**1b**: M.p. (decomp.): 164°C. – IR (KBr): $\tilde{\nu}$ = 3060, 3030, 2920, 2860 cm^{-1} (C–H), 1580 (ar). – UV (CH_3CN): λ_{max} (lg ε) = 379 nm (4.41), 283 (4.48), 237 (4.35), 210 (4.59). – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.08 (s, 3H, N-CH_3), 6.49 (d, $J_{1,2}$ = 8.1 Hz, 1H, 1-H), 6.54 [d (br), $J_{9,8}$ = 7.9 Hz, 1H, 9-H], 6.71, 6.72 (AB, J_{AB} = 16.1 Hz, 2H, H_{vinyl}), 6.84–6.93 (m, 4H, 4-H, 6-H, 7-H, 8-H), 6.95 (dd, $J_{2,1}$ = 8.1, $J_{2,4}$ = 2.0 Hz, 1H, 2-H), 7.22 (m, 1H, 4′-H), 7.34 (m, 2H, 3′-H, 5′-H), 7.47 (m, 2H, 2′-H, 6′-H). – $C_{21}H_{17}NO$ (299.4): calcd. C 84.25, H 5.72, N 4.68; found C 84.06, H 5.72, N 4.43.

4-(2-Phenylethenyl)phenoxathiine (**1c**): Workup: CC (SiO_2; solvent: CH_2Cl_2/petroleum ether, 1:1); it was not possible to separate the two isomers by CC. Evaporation of the solvent after CC gave a colourless oil consisting of the two isomers. Treatment of this oil with some MeOH caused precipitation of a colourless powder, which was recrystallised from MeOH to afford the pure (*E*) isomer (46%; colourless needles). Prolonged standing at –15°C yielded some more colourless powder from the first MeOH solution. This proved to be the enriched (*Z*) isomer (*Z*/*E* = 5:2). Yield: 14%.

(*E*)-**1c**: M.p.: 105–106°C. – IR (KBr): $\tilde{\nu}$ = 3060, 3020 cm^{-1} (C–H), 1570 (ar.). – UV (CH_3CN): λ_{max} (lg ε) = 297 nm (4.47), 266 (sh, 4.15), 225 (4.41). – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.00–7.19 (m, 6H, 1-H, 2-H, 6-H, 7-H, 8-H, 9-H), 7.18, 7.57 (AB, J_{AB} = 16.4 Hz, 2H, H_{vinyl}), 7.30 (m, 1H, 4′-H), 7.40 (m, 2H, 3′-H, 5′-H), 7.46 (dd, $J_{3,1}$ = 1.9, $J_{3,2}$ = 6.5 Hz, 1H, 3-H), 7.58 (m, 2H, 2′-H, 6′-H). – $C_{20}H_{14}OS$ (302.4): calcd. C 79.44, H 4.67; found C 79.54, H 4.75.

(*Z*)-**1c**: M.p.: 53–58°C. – IR (KBr): $\tilde{\nu}$ = 3080, 3020 cm^{-1} (C–H), 1570 (ar). – UV (CH_3CN): λ_{max} (lg ε) = 282 nm (4.16), 256 (4.20), 224 (4.42). – ^1H NMR (400 MHz, $CDCl_3$): δ = 6.74, 6.75 (AB, J_{AB} = 12.6 Hz, 2H, H_{vinyl}), 6.80 (t, $J_{2,1}$ = $J_{2,3}$ = 7.7 Hz, 1H, 2-H), 6.90 (dd, $J_{6,7}$ = 8.0, $J_{6,8}$ = 1.4 Hz, 1H, 6-H), 6.98–7.06 (m, 4H, 1-H, 3′-H, 4′-H, 5′-H), 7.08 (dd, $J_{9,7}$ = 1.8, $J_{9,8}$ = 7.9 Hz, 1H, 9-H), 7.11 (dd, $J_{3,1}$ = 1.8, $J_{3,2}$ = 7.4 Hz, 1H, 3-H), 7.14–7.21 (m, 2H, 7-H, 8-H), 7.25 (m, 2H, 2′-H, 6′-H). – $C_{20}H_{14}OS$ (302.4): calcd. C 79.44, H 4.67; found C 79.30, H 4.74.

Preparation of the Anthraquinone-Ethenyl Compounds[27]: A solution of the anthraquinone phosphonium salt[27] **6** in CH_2Cl_2 was treated with an excess of sodium hydroxide (50% in H_2O). After a few min. the aldehyde was added to the deep green solution. The mixture was stirred at room temperature until TLC. showed the end of the reaction. The solvent was evaporated; further work-up by CC and recrystallisation[26].

3-[2-{2-(9,10-Anthracenedionyl)}ethenyl]-10-methyl-10H-phenothiazine (**2a**): Workup: CC (SiO_2; solvent: CH_2Cl_2). Only the (*Z*) isomer was found. A part of the crude product was refluxed in *p*-xylene with a catalytic amount of I_2 to yield the (*E*) isomer which was purified by CC and recrystallised from CH_3CN to afford red

needles (52%). The (*Z*) isomer was also recrystallised from CH_3CN: orange powder (31%).

E-**2a**: M.p.: 204–205°C. – IR (KBr): $\tilde{\nu}$ = 3060, 2960, 2920, 2880 cm^{-1} (C–H), 1660 (C=O), 1580 (ar). – UV/Vis (CH_3CN): λ_{max} (lg ε) = 445 nm (4.06), 292 (4.41), 248 (4.44), 208 (4.32). – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.41 (s, 3H, N-CH_3), 6.82 (d, $J_{1,2}$ = 8.4 Hz, 1H, 1-H), 6.84 (dd, $J_{9,7}$ = 1.0, $J_{9,8}$ = 7.8 Hz, 1H, 9-H), 6.96 (dt, $J_{7,6}$ = $J_{7,8}$ = 7.5, $J_{7,9}$ = 1.2 Hz, 1H, 7-H), 7.08, 7.27 (AB, J_{AB} = 16.3 Hz, 2H, H_{vinyl}), 7.16 (dd, $J_{6,7}$ = 7.5, $J_{6,8}$ = 1.4 Hz, 1H, 6-H), 7.19 (ddd, $J_{8,6}$ = 1.6, $J_{8,7}$ = 7.4, $J_{8,9}$ = 8.1 Hz, 1H, 8-H), 7.35 (dd, $J_{2,1}$ = 8.3, $J_{2,4}$ = 2.0 Hz, 1H, 2-H), 7.36 (d, $J_{4,2}$ = 2.0 Hz, 1H, 4-H), 7.80 (m, 2H, 6′-H, 7′-H), 7.84 (dd, $J_{3',1'}$ = 1.8, $J_{3',4'}$ = 8.3 Hz, 1H, 3′-H), 8.28 (d, $J_{4',3'}$ = 8.2 Hz, 1H, 4′-H), 8.33 (m, 2H, 5′-H, 8′-H), 8.39 (d, $J_{1',3'}$ = 1.9 Hz, 1H, 1′-H). – $C_{29}H_{19}NO_2S$ (445.5): calcd. C 78.18, H 4.30, N 3.14; found C 77.79, H 4.62, N 3.37.

Z-**2a**: M.p.: 168–169°C. – IR (KBr): $\tilde{\nu}$ = 3070, 3010, 2970, 2880 cm^{-1} (C–H), 1665 (C=O), 1590 (ar). – UV/Vis (CH_3CN): λ_{max} (lg ε) = 440 nm (3.40), 324 (sh, 4.41), 256 (4.56), 208 (4.39). – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.35 (s, 3H, N-CH_3), 6.60, 6.67 (AB, J_{AB} = 12.2 Hz, 2H, H_{vinyl}), 6.63 (d, $J_{1,2}$ = 8.6 Hz, 1H, 1-H), 6.80 (dd, $J_{9,7}$ = 1.1, $J_{9,8}$ = 8.2 Hz, 1H, 9-H), 6.93 (dt, $J_{7,6}$ = $J_{7,8}$ = 7.5, $J_{7,9}$ = 1.2 Hz, 1H, 7-H), 7.02 (dd, $J_{2,1}$ = 8.9, $J_{2,4}$ = 2.0 Hz, 1H, 2-H), 7.04 (d, $J_{4,2}$ = 2.0 Hz, 1H, 4-H), 7.09 (dd, $J_{6,7}$ = 7.6, $J_{6,8}$ = 1.5 Hz, 1H, 6-H), 7.17 (ddd, $J_{8,6}$ = 1.6, $J_{8,7}$ = 7.4, $J_{8,9}$ = 8.1 Hz, 1H, 8-H), 7.69 (dd, $J_{3',1'}$ = 1.8, $J_{3',4'}$ = 8.1 Hz, 1H, 3′-H), 7.80 (m, 2H, 6′-H, 7′-H), 8.13 (d, $J_{4',3'}$ = 8.1 Hz, 1H, 4′-H), 8.21 (d, $J_{1',3'}$ = 1.8 Hz, 1H, 1′-H), 8.30 (m, 2H, 5′-H, 8′-H). – $C_{29}H_{19}NO_2S$ (445.5): calcd. C 78.18, H 4.30, N 3.14; found C 77.73, H 4.51, N 3.32.

3-[2-{2-(9,10-Anthracenedionyl)}ethenyl]-10-methyl-10H-phenoxazine (**2b**): Work-up: CC (SiO_2; solvent: CH_2Cl_2). The (*E*) isomer was recrystallised from CH_3CN to afford violet needles (49%). (*Z*) isomer: deep-red foamy powder (22%).

E-**2b**: M.p.: 220–222°C. – IR (KBr): $\tilde{\nu}$ = 3040, 3020, 2880 cm^{-1} (C–H), 1670 (C=O), 1580 (ar). – UV/Vis (CH_3CN): λ_{max} (lg ε) = 483 nm (4.03), 370 (4.08), 286 (4.35), 245 (4.40), 212 (4.41). – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.10 (s, 3H, N-CH_3), 6.52 (d, $J_{1,2}$ = 8.2 Hz, 1H, 1-H), 6.56 (d (br), $J_{9,8}$ = 7.8 Hz, 1H, 9-H), 6.74 (m, 2H, 6-H, 7-H), 6.86 (m, 1H, 8-H), 6.97 (d, $J_{4,2}$ = 2.0 Hz, 1H, 4-H), 7.01, 7.22 (AB, J_{AB} = 16.3 Hz, 2H, H_{vinyl}), 7.03 (dd, $J_{2,1}$ = 8.3, $J_{2,4}$ = 1.9 Hz, 1H, 2-H), 7.80 (m, 2H, 6′-H, 7′-H), 7.83 (dd, $J_{3',1'}$ = 1.7, $J_{3',4'}$ = 8.4 Hz, 1H, 3′-H), 8.28 (d, $J_{4',3'}$ = 8.1 Hz, 1H, 4′-H), 8.32 (m, 2H, 5′-H, 8′-H), 8.37 (d, $J_{1',3'}$ = 1.8 Hz, 1H, 1′-H). – $C_{29}H_{19}NO_3$ (429.5): calcd. C 81.10, H 4.46, N 3.26; found C 80.18, H 4.67, N 3.23. – MS (70 eV) *m/z* (%): 429 (62) [M^+], 414 (19) [$M^+ - CH_3$].

Z-**2b**: M.p.: 157–158°C. – IR (KBr): $\tilde{\nu}$ = 3060, 2920 cm^{-1} (C–H), 1665 (C=O), 1580 (ar). – UV/Vis (CH_3CN): λ_{max} (lg ε) = 467 nm (3.41), 330 (4.03), 272 (sh, 4.41), 248 (4.55), 207 (4.58). – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.03 (s, 3H, N-CH_3), 6.36 (d, $J_{1,2}$ = 8.2 Hz, 1H, 1-H), 6.51 (dd, $J_{9,8}$ = 7.9, $J_{9,7}$ = 1.4 Hz, 1H, 9-H), 6.55, 6.61 (AB, J_{AB} = 12.2 Hz, 2H, H_{vinyl}), 6.58 (d, $J_{4,2}$ = 2.0 Hz, 1H, 4-H), 6.62 (dd, $J_{6,7}$ = 7.9, $J_{6,8}$ = 1.6 Hz, 1H, 6-H), 6.67 (dt, $J_{7,6}$ = $J_{7,8}$ = 7.6, $J_{7,9}$ = 1.4 Hz, 1H, 7-H), 6.73 (dd, $J_{2,1}$ = 8.2, $J_{2,4}$ = 2.0 Hz, 1H, 2-H), 6.83 (ddd, $J_{8,6}$ = 1.6, $J_{8,7}$ = 7.4, $J_{8,9}$ = 7.9 Hz, 1H, 8-H), 7.74 (dd, $J_{3',1'}$ = 1.8, $J_{3',4'}$ = 8.1 Hz, 1H, 3′-H), 7.80 (m, 2H, 6′-H, 7′-H), 8.16 (d, $J_{4',3'}$ = 8.1 Hz, 1H, 4′-H), 8.22 (d, $J_{1',3'}$ = 1.8 Hz, 1H, 1′-H), 8.32 (m, 2H, 5′-H, 8′-H). – $C_{29}H_{19}NO_3$ (429.5): calcd. C 81.10, H 4.46, N 3.26; found C 80.63, H 4.38, N 3.25. – MS (70 eV) *m/z* (%): 429 (100) [M^+], 414 (30) [$M^+ - CH_3$].

4-[2-{2-(9,10-Anthracenedionyl)}ethenyl]phenoxathiine (**2c**): Workup: Several consecutive CCs (SiO_2; solvents: petroleum ether/THF, 1:1; petroleum ether/Et_2O, 5:1; CH_2Cl_2/petroleum ether, 1:1). It was not possible to obtain the pure (*Z*) isomer: only a small amount of enriched substance was isolated: 1% (yellow powder; (*Z*)/(*E*) = 16:5). The (*E*) isomer was washed with hot *n*-hexane: yellow needles (27%).

(*E*)-**2c**: M.p.: 225°C. – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} (C–H), 1665 (C=O), 1585 (ar). – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.05–7.12 (m, 3H, 2-H, 7-H, 8-H), 7.16 (dd, $J_{1,2}$ = 7.7, $J_{1,3}$ = 1.2 Hz, 1H, 1-H), 7.20 (m, 2H, 6-H, 9-H), 7.50 (dd, $J_{3,1}$ = 1.5, $J_{3,2}$ = 7.5 Hz, 1H, 3-H), 7.32, 7.83 (AB, J_{AB} = 16.5 Hz, 2H, H_{vinyl}), 7.83 (m, 2H, 6′-H, 7′-H), 7.97 (dd, $J_{3',1'}$ = 1.9, $J_{3',4'}$ = 8.1 Hz, 1H, 3′-H), 8.34 (d, $J_{4',3'}$ = 8.1 Hz, 1H, 4′-H), 8.32–8.36 (m, 2H, 5′-H, 8′-H), 8.48 (d, $J_{1',3'}$ = 1.9 Hz, 1H, 1′-H). – $C_{28}H_{16}SO_3$ (432.5): calcd. C 77.76, H 3.73; found C 77.74, H 4.09.

(*Z*)-**2c**: M.p.: 181–185°C. – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} (C–H), 1665 (C=O), 1580 (ar). – ^1H NMR (400 MHz, $CDCl_3$): δ = 6.83 (t, $J_{2,1}$ = $J_{2,3}$ = 7.7 Hz, 1H, 2-H), 6.85, 6.99 (AB, J_{AB} = 12.1 Hz, 2H, H_{vinyl}), 6.90 (dd, $J_{6,7}$ = 7.8, $J_{6,8}$ = 1.3 Hz, 1H, 6-H), 6.95 (dd, $J_{1,2}$ = 7.7, $J_{1,3}$ = 1.6 Hz, 1H, 1-H), 7.00 (dd, $J_{9,7}$ = 1.4, $J_{9,8}$ = 7.5 Hz, 1H, 9-H), 7.06 (m, 2H, 7-H, 8-H), 7.10 (dd, $J_{3,1}$ = 1.8, $J_{3,2}$ = 7.5 Hz, 1H, 3-H), 7.64 (dd, $J_{3',1'}$ = 1.8, $J_{3',4'}$ = 8.1 Hz, 1H, 3′-H), 7.79 (m, 2H, 6′-H, 7′-H), 8.10 (d, $J_{4',3'}$ = 8.1 Hz, 1H, 4′-H), 8.21 (d, $J_{1',3'}$ = 1.8 Hz, 1H, 1′-H), 8.29 (m, 2H, 5′-H, 8′-H). – $C_{28}H_{16}SO_3$ (432.5): calcd. 432.0820; found 432.0816. – MS (70 eV) *m/z* (%): 432 (100) [M^+].

☆ Dedicated to Prof. *M. Hanack* on the occasion of his 65th birthday.

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