

Ring Transformations of Heterocyclic Compounds. **XXIII** [1].
 The UV Irradiation Product of Photochromic 2,4,6-Triaryl-1-(spiro[2*H*-1-benzopyran-2,2'-indoline]-6-yl)pyridinium Salts - A Phenolate Betaine or a Pyridinium Substituted Merocyanine Dye?

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The synthesis of the novel 2,4,6-triaryl-1-(spiro[2*H*-1-benzopyran-2,2'-indoline]-6-yl)pyridinium perchlorates **4** by reaction of 5-nitrosalicylaldehydes **6** with 1,3,3-trimethyl-2-methyleneindoline (**7**) to 6-nitro-spiro[2*H*-1-benzopyran-2,2'-indolines] **1**, their stannous chloride reduction to the 6-amino derivatives **8**, followed by a 2,6-[C₅+N] ring transformation with 2,4,6-triarylpyrylium perchlorates **9**, is reported. UV irradiation experiments in twenty solvents of different polarity prove their photochromic properties and show that the photochemically generated negative solvatochromic dyes **5**, formed by ring opening of the benzopyran moiety of **4**, are rather merocyanine than pyridinium phenolate betaine dyes.

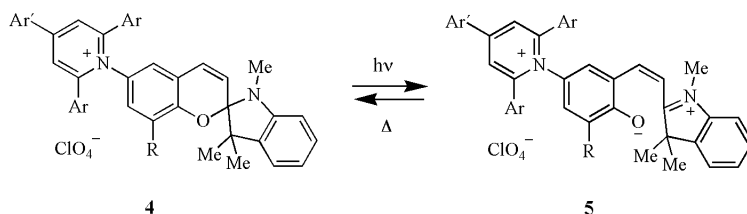
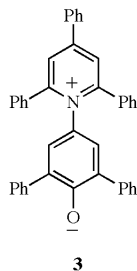
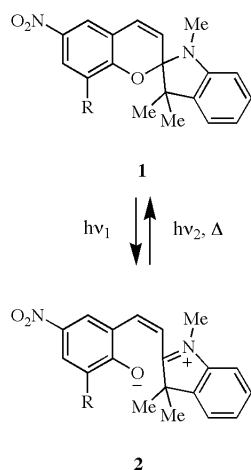
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In recent years, photochromism, *i.e.* the reversible transformation of chemical species, induced in one or both directions by electromagnetic radiation between two states showing observable light absorptions in different regions has been intensively studied. The aim of these studies has been to improve our knowledge of this phenomenon and to obtain new photochromic systems for practical applications [2].

The 2*H*-1-benzopyrans, possessing a second ring, usually heterocyclic, attached to the 2-carbon atom in a *spiro* manner ("spirochromenes") are one of the main classes of photochromic compounds [2]. In the well established compounds of the type **1**, an indoline moiety is *spiro* connected

with the benzopyran. The uv irradiation of the colourless **1** leads to the merocyanine **2** which can be recycled by heat or visible light to the starting spirobenzopyran **1**. For an efficient formation of the photoproduct **2** the presence of the electron attracting nitro group at C-6, stabilizing the negative charge at the oxygen, is essential [2]. The merocyanine **2** shows a slightly negative solvatochromism, *i.e.* a shift of the longest absorption maximum to shorter wavelengths by enhancing the polarity of the solvent, which can be characterized by Reichardt's E_T(30) empirical parameters based on the solvatochromism of the pyridinium phenolate betaine dye **3** [3].

Substitution of the nitro group in the spirobenzopyran **1** by a 2,4,6-triarylpyridinium moiety, having also a high electron attracting capability, would result in the pyridinium derivatives of the type **4**. Their uv irradiation should give rise to the ring-opened isomers **5** possessing a phenolate betaine as well as a merocyanine substructure. On the basis of investigations on the solvatochromism of the dyes **5** it can be decided which type of substructure preferentially determines the properties of **5**. If it is the phenolate betaine moiety, a high degree of solvatochromism as in the case of the structurally related Reichardt's dye **3** should be found [3] whereas if the merocyanine unit predominates a much lower solvatochromism should be detectable. In this paper we wish to report on the synthesis of the 2,4,6-triaryl-1-(spiro[2*H*-1-benzopyran-2,2'-indoline]-6-yl)pyridinium salts **4**, on their photochromic properties and on the nature of the photochemically obtained dyes **5**, based on studies of their solvatochromism.



For the synthesis of the pyridinium salts **4** a strategy was chosen based on the commercially available or easily accessible salicylaldehydes **6a-c**. They were reacted in ethanol with 1,3,3-trimethyl-2-methyleneindoline (**7**) (Fischer base) [4] according to known methods to give the 6-nitro substituted spiro[2*H*-1-benzopyran-2,2'-indolines] **1a-c** [5,6]. A critical step of the envisaged reaction sequence was their reduction to the 6-amino derivatives **8a-c**, since it has to be performed chemoselectively at the nitro group under neutral conditions. By testing various reducing agents and solvents it was found that stannous chloride dihydrate in boiling ethanol [7] gave the best results. Applying this method, the 6-aminospiro[2*H*-1-benzopyran-2,2'-indolines] **8a-c** were obtained in good yield as air-sensitive oils. Hence, they were immediately reacted with the 2,4,6-triarylpyrylium salts **9a-i** [8] and anhydrous sodium acetate in ethanol to afford by the well known 2,6-[C₅+N] [9] pyrylium ring transformation, where the oxygen atom is replaced by nitrogen, the desired 2,4,6-triaryl-1-(spiro[2*H*-1-benzopyran-2,2'-indoline]-6-yl)pyridinium perchlorates **4a-k** in 53-64% yield.

The results of the elemental analyses and the spectroscopic data are in agreement with the structure of the pyridinium salts **4a-k** (*cf.* Tables 1 and 2). In the ¹H NMR spectra the diastereotopic protons of the two methyl groups at

C-3' are responsible in **4a** for one and in **4b,c** for two singlets at 0.89-1.03 ppm. Another singlet at 2.30-2.38 ppm can be attributed to the protons of the *N*-bonded methyl group. The olefinic proton at C-3 of the benzopyran moiety resonates at 5.72-5.90 ppm as a doublet with a coupling constant of 9.8-10.4 Hz. The protons of the benzene rings cause the multiplet at 6.38-8.60 ppm that usually masks the doublet of the olefinic proton at C-4 of the benzopyran. A singlet at 8.56-8.78 ppm shows the presence of the two protons bonded at the pyridinium ring [10]. In the FAB mass spectra, recorded for **4a-c**, the mass peaks of the corresponding cations were found. A characteristic feature of the uv spectra, recorded in acetonitrile, are strong absorption bands at 242-249 nm and 296-352 nm.

To study the photochromic properties of the 2,4,6-triaryl-1-(spiro[2*H*-1-benzopyran-2,2'-indoline]-6-yl)pyridinium perchlorates **4** solutions of **4a-k** in methanol were uv irradiated and the changes monitored by running the uv-vis spectra (details see Experimental part). In all cases the formation of a blue dye was observed, the longest wavelength absorption maxima of which are compiled in Table 3. The figures show that the substitution of the hydrogen atom at C-8 in **4a** by a methyl group (**4b**) or by a phenyl ring (**4c**) is accompanied by a shift of this absorption maximum to longer wavelengths whereas the varia-

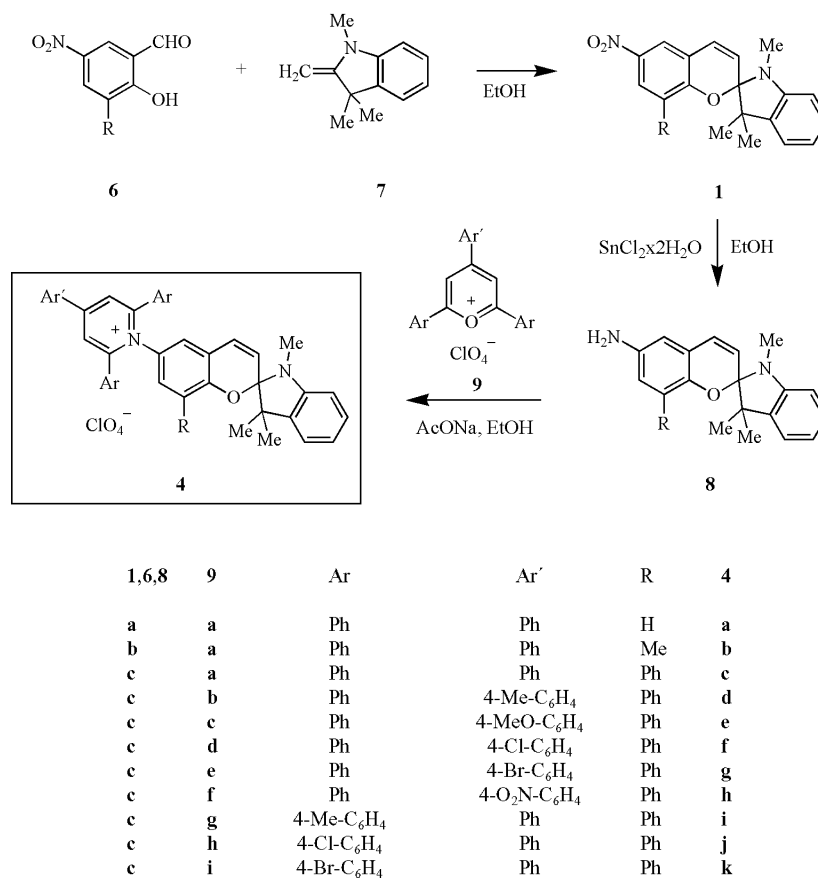


Table 1
Physical and Analytical Data for the 2,4,6-Triaryl-1-(spiro[2*H*-1-benzopyran-2,2'-indoline]-6-yl)pyridinium Perchlorates 4

No.	-pyridinium Perchlorate	Yield [a] (%)	Mp (°C)	Molecular Formula (Molecular Weight)	Analysis (%)		
					Calcd./Found	C	H N
4a	1-(1',3',3'-Trimethylspiro[2 <i>H</i> -1-benzopyran-2,2'-indoline]-6-yl)-2,4,6-triphenyl-	58	181-182 [b]	C ₄₂ H ₃₅ ClN ₂ O ₅ (683.2)	73.84 73.81	5.16 5.20	4.10 4.08
4b	1-(1',3',3',8-Tetramethylspiro[2 <i>H</i> -1-benzopyran-2,2'-indoline]-6-yl)-2,4,6-triphenyl-	53	193-194 [b]	C ₄₃ H ₃₇ ClN ₂ O ₅ (697.2)	74.08 74.21	5.35 5.40	4.02 4.12
4c	1-(1',3',3'-Trimethyl-8-phenylspiro[2 <i>H</i> -1-benzopyran-2,2'-indoline]-6-yl)-2,4,6-triphenyl-	53	195-196 [b]	C ₄₈ H ₃₉ ClN ₂ O ₅ (759.3)	75.93 76.00	5.18 5.06	3.69 3.75
4d	4-(4-Methylphenyl)-1-(1',3',3'-trimethyl-8-phenylspiro[2 <i>H</i> -1-benzopyran-2,2'-indoline]-6-yl)-2,6-diphenyl-	63	294-295	C ₄₉ H ₄₁ ClN ₂ O ₅ (773.3)	76.10 76.08	5.34 5.40	3.62 3.48
4e	4-(4-Methoxyphenyl)-1-(1',3',3'-trimethyl-8-phenylspiro[2 <i>H</i> -1-benzopyran-2,2'-indoline]-6-yl)-4,6-diphenyl-	61	270-271	C ₄₉ H ₄₁ ClN ₂ O ₆ (789.3)	74.56 74.70	5.24 5.18	3.55 3.53
4f	4-(4-Chlorophenyl)-1-(1',3',3'-trimethyl-8-phenylspiro[2 <i>H</i> -1-benzopyran-2,2'-indoline]-6-yl)-4,6-diphenyl-	55	305-306	C ₄₈ H ₃₈ Cl ₂ N ₂ O ₅ (793.8)	72.63 72.58	4.83 4.72	3.53 3.62
4g	4-(4-Bromophenyl)-1-(1',3',3'-trimethyl-8-phenylspiro[2 <i>H</i> -1-benzopyran-2,2'-indoline]-6-yl)-2,6-diphenyl-	58	299-300	C ₄₈ H ₃₈ BrClN ₂ O ₅ (838.2)	68.78 68.90	4.57 4.60	3.34 3.40
4h	1-(1',3',3'-Trimethyl-8-phenylspiro[2 <i>H</i> -1-benzopyran-2,2'-indoline]-6-yl)-4-(4-nitrophenyl)-2,6-diphenyl-	56	199-200	C ₄₈ H ₃₈ ClN ₃ O ₇ (804.3)	71.68 71.47	4.76 4.70	5.22 5.30
4i	2,6-Bis(4-methylphenyl)-1-(1',3',3'-trimethyl-8-phenylspiro[2 <i>H</i> -1-benzopyran-2,2'-indoline]-6-yl)-4-phenyl-	53	291-292	C ₅₀ H ₄₃ ClN ₂ O ₅ (787.4)	76.27 76.30	5.50 5.41	3.56 3.48
4j	2,6-Bis(4-chlorophenyl)-1-(1',3',3'-trimethyl-8-phenylspiro[2 <i>H</i> -1-benzopyran-2,2'-indoline]-6-yl)-4-phenyl-	64	310-311	C ₄₈ H ₃₇ Cl ₃ N ₂ O ₅ (828.2)	69.61 69.45	4.50 4.58	3.38 3.45
4k	2,6-Bis(4-bromophenyl)-1-(1',3',3'-trimethyl-8-phenylspiro[2 <i>H</i> -1-benzopyran-2,2'-indoline]-6-yl)-4-phenyl-	57	297-298	C ₄₈ H ₃₇ Br ₂ ClN ₂ O ₅ (917.1)	62.86 62.90	4.07 4.12	3.05 3.18

[a] Yields for the final reaction step $8 + 9 \rightarrow 4$ are given. [b] In some cases the compounds tend to separated as amorphous solids leading to low melting points.

Table 2
Spectral Data for the 2,4,6-Triaryl-1-(spiro[2*H*-1-benzopyran-2,2'-indoline]pyridinium Perchlorates 4

Compound	UV (CH ₃ CN) λ _{max} (nm) (log ε)	¹ H-NMR (dimethyl-d ₆ sulfoxide) [a] δ (ppm)
4a [b][c]	226 (4.67), 242 sh (4.57), 306 (4.59), 370 sh (3.50)	0.95 (s, 6H, 3',3'-(CH ₃) ₂), 2.38 (s, 3H, 1'-CH ₃), 5.72 (d, J = 10.3 Hz, 1H, 3-H), 6.38-8.30 (m, 23H, 4-H, arom-H), 8.59 (s, 2H, 3-H, 5-H)
4b [b][c]	230 (4.68), 246 sh (4.60), 304 (4.61), 370 sh (3.80)	0.94 (s, 3H, 3'-CH ₃), 0.98 (s, 3H, 3'-CH ₃), 1.52 (s, 3H, 8-CH ₃), 2.33 (s, 3H, 1'-CH ₃), 5.73 (d, J = 10.2 Hz, 1H, 3-H), 6.45-8.31 (m, 22H, 4-H, arom-H), 8.60 (s, 2H, 3-H, 5-H)
4c [b][c]	246 (4.67), 306 (4.65), 373 sh (3.48)	0.91 (s, 3H, 3'-CH ₃), 1.02 (s, 3H, 3'-CH ₃), 2.33 (s, 3H, 1'-CH ₃), 5.86 (d, J = 10.0 Hz, 1H, 3-H), 6.47-8.34 (m, 27H, 4-H, arom-H), 8.65 (s, 2H, 3-H, 5-H)
4d	244 (4.67), 323 (4.64), 385 sh (3.51)	0.89 (s, 3H, 3'-CH ₃), 1.00 (s, 3H, 3'-CH ₃), 2.30 (s, 3H, 1'-CH ₃), 2.37 (s, 3H, 4-CH ₃ C ₆ H ₄), 5.84 (d, J = 10.0 Hz, 1H, 3-H), 6.45-8.26 (m, 26H, 4-H, arom-H), 8.60 (s, 2H, 3-H, 5-H)
4e	244 (4.71), 352 (4.58)	0.89 (s, 3H, 3'-CH ₃), 1.01 (s, 3H, 3'-CH ₃), 2.30 (s, 3H, 1'-CH ₃), 3.85 (s, 3H, 4-CH ₃ OC ₆ H ₄), 5.85 (d, J = 10.0 Hz, 1H, 3-H), 6.46-8.38 (m, 26H, 4-H, arom-H), 8.57 (s, 2H, 3-H, 5-H)
4f	244 (4.68), 313 (4.68), 370 sh (3.42)	0.90 (s, 3H, 3'-CH ₃), 1.01 (s, 3H, 3'-CH ₃), 2.31 (s, 3H, 1'-CH ₃), 5.85 (d, J = 10.4 Hz, 1H, 3-H), 6.45-8.38 (m, 26H, 4-H, arom-H), 8.66 (s, 2H, 3-H, 5-H)
4g	244 (4.68), 316 (4.67), 370 sh (3.48)	0.89 (s, 3H, 3'-CH ₃), 1.00 (s, 3H, 3'-CH ₃), 2.31 (s, 3H, 1'-CH ₃), 5.85 (d, J = 10.2 Hz, 1H, 3-H), 6.45-8.29 (m, 26H, 4-H, arom-H), 8.65 (s, 2H, 3-H, 5-H)
4h	245 (4.68), 296 (4.68), 400 sh (3.46)	0.91 (s, 3H, 3'-CH ₃), 1.02 (s, 3H, 3'-CH ₃), 2.32 (s, 3H, 1'-CH ₃), 5.87 (d, J = 9.8 Hz, 1H, 3-H), 6.46-8.60 (m, 26H, 4-H, arom-H), 8.78 (s, 2H, 3-H, 5-H)
4i	249 (4.67), 306 (4.62), 394 sh (3.28)	0.91 (s, 3H, 3'-CH ₃), 1.02 (s, 3H, 3'-CH ₃), 2.23 (s, 6H, 2,6-(CH ₃ C ₆ H ₄) ₂), 2.32 (s, 3H, 1'-CH ₃), 5.87 (d, J = 10.2 Hz, 1H, 3-H), 6.48-8.29 (m, 25H, 4-H, arom-H), 8.56 (s, 2H, 3-H, 5-H)
4j	243 (4.68), 309 (4.64), 388 sh (3.37)	0.92 (s, 3H, 3'-CH ₃), 1.03 (s, 3H, 3'-CH ₃), 2.36 (s, 3H, 1'-CH ₃), 5.89 (d, J = 10.3 Hz, 1H, 3-H), 6.49-8.31 (m, 25H, 4-H, arom-H), 8.68 (s, 2H, 3-H, 5-H)

Table 2 (continued)

Compound	UV (CH ₃ CN) $\lambda_{\max}$ (nm) (log ϵ)	¹ H-NMR (dimethyl-d ₆ sulfoxide) [δ] δ (ppm)
4k	243 (4.73), 310 (4.68), 388 sh (3.97)	0.93 (s, 3H, 3'-CH ₃), 1.03 (s, 3H, 3'-CH ₃), 2.37 (s, 3H, 1'-CH ₃), 5.90 (d, J = 10.0 Hz, 1H, 3-H), 6.46-8.31 (m, 25H, 4-H, arom-H), 8.68 (s, 2H, 3-H, 5-H)

[a] 3-H, 5-H denote the protons in 3-/5-position of the pyridinium moiety, 3-H, 4-H the protons in 3-/4-position of the benzopyran system and arom-H the protons bonded to the benzene rings; [b] ¹³C nmr (dimethyl-d₆ sulfoxide) **4a** 17.7 (3'-CH₃), 23.6 (3'-CH₃), 26.4 (1'-CH₃), 49.3 (C-3'), 102.2 (C-2'), 104.8, 112.5, 116.8, 117.1, 119.3, 123.0, 124.7, 125.5, 126.0, 126.8, 127.6, 129.5, 130.4, 131.3, 131.4, 133.9, 145.3, 152.3, 153.4, 154.5 (olefin, benzene, and pyridinium carbons), **4b** 12.5 (8-CH₃), 17.8 (3'-CH₃), 23.6 (3'-CH₃), 26.5 (1'-CH₃), 49.0 (C-3'), 102.0 (C-2'), 104.8, 116.2, 117.1, 118.9, 119.3, 121.6, 122.4, 123.0, 125.4, 126.0, 126.2, 126.3, 126.8, 127.6, 127.7, 127.8, 128.5, 128.9, 130.5, 131.1, 131.2, 131.4, 134.0, 145.2, 149.8, 153.3, 154.6 (olefin, benzene, and pyridinium carbons), **4c** 17.7 (3'-CH₃), 23.4 (3'-CH₃), 26.6 (1'-CH₃), 48.5 (C-3'), 102.4 (C-2'), 104.8, 112.5, 117.3, 117.9, 118.4, 119.1, 123.0, 123.8, 124.5, 125.4, 125.6, 126.0, 126.1, 126.3, 126.8, 127.7, 127.8, 127.9, 128.3, 129.7, 130.5, 131.3, 131.4, 132.7, 134.1, 145.1, 148.7, 153.6, 154.5, 154.6 (olefin, benzene, and pyridinium carbons); [c] Mass spectra (FAB): m/z **4a** 583 [C₄₂H₃₅N₂O⁺], **4b** 597 [C₄₃H₃₇N₂O⁺], **4c** 659 [C₄₈H₃₉N₂O⁺].

tion of the substitution pattern of Ar and Ar' in **4c-k**, i.e. the introduction of an electron attracting or releasing substituent in *p*-position, has practically no influence. Storing in the dark, the blue colour of the solutions vanishes and it could be regenerated by repeated uv irradiation. After the five coloration/decoloration cycles tested no significant decomposition was detected. The observations made are characteristic behaviour of a photochromic compound and can be explained by a uv initiated electrocyclic ring opening of the benzopyran moiety of the pyridinium perchlorates **4** to give the coloured isomers **5** and their thermal back reaction to the starting salts **4** [2].

Table 3

Substitution Pattern of R and Ar/Ar' together with the Longest Wavelength Absorption Maxima $\lambda_{\max}$ of the Dyes **5a-k** Obtained by UV Irradiation of the Pyridinium Salts **4a-k** in Methanol

Compound	Substitution Pattern of			$\lambda_{\max}$
	R	Ar	Ar'	(nm)
5a	H	4-H	4-H	553
5b	Me	4-H	4-H	567
5c	Ph	4-H	4-H	581
5d	Ph	4-H	4-Me	581
5e	Ph	4-H	4-MeO	581
5f	Ph	4-H	4-Cl	582
5g	Ph	4-H	4-Br	579
5h	Ph	4-H	4-O ₂ N	579
5i	Ph	4-Me	4-H	580
5j	Ph	4-Cl	4-H	575
5k	Ph	4-Br	4-H	576

To get information on the nature of the photochemically generated blue dyes **5** their solvatochromism, i.e. the dependence of the position of the longest wavelength absorption maximum from the polarity of the solvent, in which it is generated, was studied. Table 4 contains maxima of these dyes **5a-c** obtained by uv irradiation of the pyridinium perchlorates **4a-c** in twenty selected solvents of different polarity characterized by Reichardt's

empirical $E_T(30)$ parameters. In addition, the molar transition energies E_T were calculated from the absorption maxima according to equation (1) [2].

$$E_T/(\text{kcal}\cdot\text{mol}^{-1}) = h \cdot c \cdot N_A/l \quad (1)$$

h : Planck's constant, c : velocity of the light, N_A : Avogadro's number, l : wavelengths of the longest absorption maximum.

From figures it can be seen that the enhancement of the solvent polarity on going from toluene to methanol causes a shift of the absorption maxima to shorter wavelengths. Hence, compounds **5a-c** must be classified as negative solvatochromic dyes. Another interesting observation was that only in alcohols was the dye formation found to be a reversible process. In all the other solvents used, after the first irradiation a more-or-less decomposition caused by a thermal reaction was observed.

Besides the qualitative interpretation of the data a linear regression analysis on the dependence of the transition energies E_T of **5a-c** from the solvent polarity $E_T(30)$ was performed giving rise to the following equations and correlation coefficients (R) (2) - (4):

$$\mathbf{5a}: E_T/(\text{kcal}\cdot\text{mol}^{-1}) = 0.286 \cdot E_T(30)/(\text{kcal}\cdot\text{mol}^{-1}) + 35.809 \quad R = 0.990 \quad (2)$$

$$\mathbf{5b}: E_T/(\text{kcal}\cdot\text{mol}^{-1}) = 0.226 \cdot E_T(30)/(\text{kcal}\cdot\text{mol}^{-1}) + 37.753 \quad R = 0.982 \quad (3)$$

$$\mathbf{5c}: E_T/(\text{kcal}\cdot\text{mol}^{-1}) = 0.230 \cdot E_T(30)/(\text{kcal}\cdot\text{mol}^{-1}) + 36.510 \quad R = 0.989 \quad (4)$$

The data show a good quantitative correlation between E_T and $E_T(30)$. The slope does not differ so much for **5a** ($R = H$), **5b** ($R = Me$) and **5c** ($R = Ph$) and its magnitude indicates that the susceptibility to changes of the solvent polarity is much lower for **5a-c** than for the classical pyridinium phenolate betaine dye **3**. On the other hand, the shift of the absorption maximum to shorter wavelengths on going from the less polar toluene to the more polar ethanol (**5a**: 57 nm, **5b**: 45 nm, **5c**: 53 nm) is comparable to that determined for the 6-nitrospiro[2*H*-1-benzopyran-2,2'-indoline] (**1a**) (65 nm) [2] in which instead of the 2,4,6-tri-

Table 4

Longest Wavelength Absorption Maxima $\lambda_{\max}$ and Resulting Transition Energies E_T of the Dyes **5a-c** Formed by UV Irradiation of the Pyridinium Salts **4a-c** in 20 Solvents of Different Polarity Characterized by their $E_T(30)$ Parameters

No.	Solvent	$E_T(30)$	5a $\lambda_{\max}$ (nm)	E_T	5b $\lambda_{\max}$ (nm)	E_T	5c $\lambda_{\max}$ (nm)	E_T
1	Toluene	33.9	624	45.8	628	45.5	645	44.3
2	Benzene	34.3	626	45.7	628	45.5	642	44.5
3	1-Methylnaphthalene	35.3	623	45.9	624	45.8	645	44.3
4	1,4-Dioxane	36.0	619	46.2	616	46.4	640	44.7
5	Diethylene glycol diethyl ether	37.5	615	46.5	623	45.9	628	45.5
6	Ethyl acetate	38.1	611	46.8	618	46.3	626	45.7
7	Diethylene glycol dimethyl ether	38.6	611	46.8	618	46.3	630	45.4
8	Pyridine	40.5	608	47.0	615	46.5	628	45.5
9	<i>N,N</i> -Dimethylformamide	43.8	598	47.8	596	48.0	618	46.3
10	2-Butanol	47.1	579	49.4	587	48.7	607	47.1
11	1-Octanol	48.3	583	49.0	593	48.2	603	47.4
12	2-Propanol	48.4	572	50.0	582	49.1	596	48.0
13	1-Heptanol	48.5	576	49.6	586	48.8	599	47.7
14	3-Methyl-1-butanol	49.0	572	50.0	580	49.3	592	48.3
15	1-Pentanol	49.1	574	49.8	587	48.7	597	47.9
16	1-Butanol	50.2	568	50.3	586	48.8	596	48.0
17	Ethanol	51.9	567	50.4	583	49.0	592	48.3
18	2-Methoxyethanol	52.3	567	50.4	579	49.4	592	48.3
19	Methanol	55.4	553	51.7	567	50.4	581	49.2
20	1,2-Ethanediol (Glycol)	56.3	546	52.4	563	50.8	576	49.6

arylpyridinium moiety a nitro group is bonded at C-6. These results clearly indicate that the dyes **5a-c** formed by uv irradiation of the pyridinium salts **4a-c** should be classified not as pyridinium phenolate betaine but as merocyanine type dyes.

EXPERIMENTAL

The melting points were measured on a Boëtius hot stage apparatus. The ^1H nmr and ^{13}C nmr spectra were recorded on a Varian Gemini 200 spectrometer (^1H : 199.975 MHz, ^{13}C : 50.289 MHz) and on a Varian Gemini 2000 spectrometer (^1H : 200.041 MHz, ^{13}C : 50.305 MHz) in dimethyl- d_6 sulfoxide at 25° with hexamethyl disiloxane as internal standard. The uv spectra were obtained on a Zeiss M 40 instrument (acetonitrile, 25°) or on a Shimadzu UV-2101 PC scanning spectrophotometer (various solvents, 25°). Mass spectra were determined on a VG ZAB HSEQ Analytical Instruments spectrometer (FAB, matrix: 3-nitrobenzyl alcohol). For the irradiation experiments a Müller Elektronik/Optik ELL 1000 apparatus (mercury high pressure lamp) was used. The salicylaldehydes **6b** [11], **6c** [6] and the pyrylium perchlorates **9a** [12], **9b** [13], **9c** [14], **9d,f** [15], **9e** [16], **9g-i** [17] were synthesized according to literature procedures. 5-Nitrosalicylaldehyde (**6a**), 1,3,3-trimethyl-2-methyleneindoline (**7**) and stannous chloride dihydrate were purchased from Aldrich. All solvents used were of analytical grade and anhydrous.

Preparation of the 6-Nitrospiro[2*H*-1-benzopyran-2,2'-indolines] **1a-c**.

The 6-nitrospiro[2*H*-1-benzopyran-2,2'-indolines] **1a-c** were prepared by the reaction of the 6-nitrosalicylaldehydes **6a-c** with

1,3,3-trimethyl-2-methyleneindoline (**7**) in boiling ethanol as described in the literature [5,6].

Reduction of the 6-Nitrospiro[2*H*-1-benzopyran-2,2'-indolines] **1a-c** to the 6-Amino Derivatives **8a-c** [7].

To 40 ml ethanol 6 mmoles 6-nitrospiro[2*H*-1-benzopyran-2,2'-indoline] **1** and 6.77 g (30 mmoles) stannous dichloride dihydrate were added. The reaction mixture was then refluxed and magnetically stirred under nitrogen for one hour. A dark brown precipitate formed in some cases and was separated by suction and the resulting solution was poured into a stirred mixture of 100 ml sodium hydroxide in water (5%) and of 50 ml chloroform. After transfer into a separatory funnel the chloroform layer was separated, the aqueous layer extracted with chloroform (30 ml), the combined chloroform solutions washed with water (100 ml) and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* on a water bath at 40° to give the 6-aminospiro[2*H*-1-benzopyran-2,2'-indoline] (**8a**) (80%), the 6-amino-8-methylspiro[2*H*-1-benzopyran-2,2'-indoline] (**8b**) (60%) and the 6-amino-8-phenylspiro[2*H*-1-benzopyran-2,2'-indoline] (**8c**) (85%), respectively, as dark brown air sensitive oils which were reacted immediately with the pyrylium salts **9**. A thin layer chromatographic analysis carried out on silica gel with acetone/n-hexane (v:v = 3:1) as eluent showed that the reduction was complete and only traces of by-products were formed.

Synthesis of the 2,4,6-Triaryl-1-spiro[2*H*-1-benzopyran-2,2'-indoline]-6-ylpyridinium Perchlorates **4a-k** from the 6-Aminospiro[2*H*-1-benzopyran-2,2'-indolines] **8a-c** and the 2,4,6-Triarylpyrylium Perchlorates **9a-i** [8].

General Procedure (cf. Tables 1 and 2).

To absolute ethanol (30 ml) 5 mmoles 6-aminospiro[2*H*-1-benzopyran-2,2'-indoline] **8**, 5 mmoles 2,4,6-triarylpyrylium perchlorate **9** and 0.82 g (10 mmoles) anhydrous sodium acetate

were added. The resulting reaction mixture was then refluxed for two hours under nitrogen. The pyridinium salts **4** formed crystallized in some cases from the hot solutions. Otherwise their crystallization was initiated by cooling. They were filtered by suction and washed with water and ethanol. For purification the compounds **4a** and **4b** were recrystallized from ethanol whereas the 8-phenyl derivatives **4c-k** were dissolved in a minimal amount of chloroform (in the case of scarcely soluble compounds acetonitrile was added) and precipitated by dropwise addition of absolute ethanol.

UV Irradiation Experiments.

Solutions of the 2,4,6-triaryl-1-(spiro[2H-1-benzopyran-2,2'-indoline]-6-yl)pyridinium perchlorates **4** ($2 \times 10^{-5} \text{ mol} \cdot \text{l}^{-1}$) in the solvents given in Table 4 were irradiated with a mercury high pressure lamp in a quartz cell (1 cm) thermostated at 5°. After 5 min and 30 min formation of the blue dyes **5** was verified by transferring the cell to the uv-vis spectrophotometer and running the spectra. After the intensity of the longest wave length absorption of **5** had reached a maximum the irradiation was stopped, the solutions were stored for 30 min in the dark and another spectrum was recorded to obtain information on the result of the thermal back reaction. Then, the next irradiation was started. To elucidate the reversibility of the coloration/decoloration up to five cycles were monitored.

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