J. prakt. Chem. 340 (1998) 214–222

Journal für praktische Chemie
Chemiker-Zeitung

Originalarbeiten · Full Papers

3,1'-Bridged 2-[2'-(4''-Dialkylaminophenyl)ethenyl] Pyrylium and 1-Benzopyrylium Dyes – Synthesis and Vis/NIR Absorption/Emission Behaviour

Peter Czerney, and Ulrich-W. Grummt

Jena, Institut für Physikalische Chemie, Friedrich-Schiller-Universität

Wolfgang Günther

Jena, Institut für Organische und Makromolekulare Chemie, Friedrich-Schiller-Universität

Received December 5th, 1997, respectively February 4th, 1998

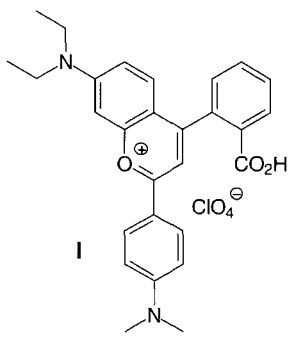
Dedicated to Prof. Dr. A. R. Katritzky on the Occasion of his 70th Birthday

Abstract. A series of new 3,1'-bridged 2-[2'-(4''-dialkylaminophenyl)ethenyl]-4,6-diarylpyrylium perchlorates (**3**), 2-[2'-(4''-dialkylaminophenyl)ethenyl]-7-diethylamino-1-benzopyrylium perchlorates **5**–**8**, 2-[4'-(4''-dialkylaminophenyl)butadien-1',3'-yl]-, and 2-[2'-(7''-diethylaminocoumar-3''-yl)ethenyl]-7-diethylamino-1-benzopyrylium perchlorates **10**–**12** were synthesized and characterized by means of elemental analysis, *m.p.*, Vis/NIR, and ^{1}H NMR spectra. Semiempirical MO calculations were performed to elucidate the essential features of the chromophores. The size of the bridging ring strongly affects the geometry of the chromophores which, in turn, determines the extent of charge transfer of the longest wavelength electronic transition. Increasing deviation from planarity causes the polymethine-like chromophore to become more polyene-like.

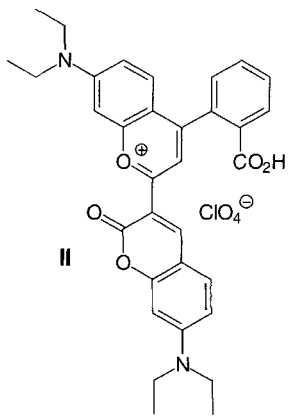
We presently witness an increasing interest in the chemistry and physics of functional dyes due to their potential application in various fields, *e.g.* nonlinear optics, chemical sensor techniques, solar energy conversion [1, 2]. Dyes absorbing or emitting in the red and near infrared spectral region (NIR) are of particular interest, among others, in chemical and biochemical sensing [3].

By substituting 2-aryl- or 2-styryl-1-benzopyrylium salts by two dialkylamino groups at positions with electron deficiency it is possible to obtain polymethine dyes, which absorb in the red and emit in the NIR with high quantum yields. Representative examples are the 2-(4'-dialkylaminophenyl)- and the 2-(7'-diethylaminocoumar-3''-yl)-7-diethyl-amino-1-benzopyrylium perchlorates **I** and **II**, the synthesis and Vis/NIR data of which we have recently reported [4, 5].

These compounds do not only exhibit high thermal and photochemical stability but additionally offer simple possibilities of derivatisation and immobilisation due to the carboxyphenyl substituent in the 4-position.



I



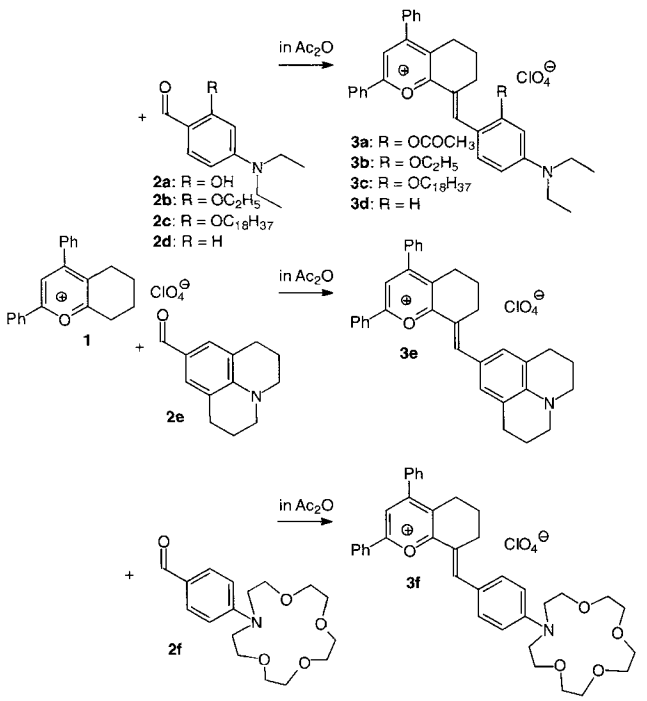
II

In this paper, we wish to report the synthesis and the Vis/NIR spectroscopic characterization of new 3,1'-bridged 2-[2'-(4''-dialkylaminophenyl)ethenyl]-pyrylium perchlorates **3**, 2-[2'-(4''-dialkylaminophenyl)ethenyl]-7-diethylamino-1-benzopyrylium perchlorates **5**–

8, and 2-[4'-(4''-dialkylaminophenyl)butadien-1',3'-yl]-7-diethylamino-1-benzopyrylium perchlorates **10**–**12**. In particular, we investigate the effect of the size of the alicyclic bridge in 3,1'-position (m = 1–4) and the length of the polymethine chain on the partial charge transfer character of the longest-wavelength electronic transition. The solvent dependence of absorption and emission spectra, ^{1}H NMR spectra, and quantum chemical calculations help to elucidate the electron distribution in the ground and first excited state of these dyes.

Results and Discussion

The educt **1** [6] allows the condensation with electrophilic compounds such as 4-dialkylaminobenzaldehydes **2** to obtain propylene-bridged pyrylium salts **3**. A general route for the synthesis of **3** is the condensation of equimolar amounts of **1** and **2** in acetic anhydride. The required benzaldehydes **2** are either commercial products or can be prepared by well known methods (see Experimental).



In case of the 4-diethylamino-2-hydroxybenzaldehyde **2a**, acylation of the hydroxy group takes place, and compound **3a** with R = $OCOCH_3$ can be isolated. Vis-spectroscopic data for the dyes **3a**–**f** are shown in Table 1.

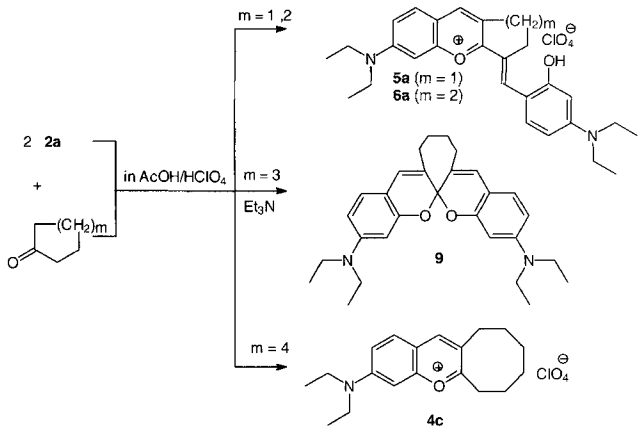
Three methods were used for synthesis of the differently 3,1'-bridged 2-[2'-(4''-dialkyl-aminophenyl)ethenyl]-7-diethylamino-1-benzopyrylium compounds **5**–**8**

Tab. 1 Vis/NIR absorption and emission data of the 3,1'-bridged 2-[2'-(4''-dialkylaminophenyl)ethenyl]-4,6-diphenylpyrylium perchlorates (**3**) in dichloromethane (D) and acetonitrile (A); $\Delta\tilde{\nu}_{D-A}$: solvent shift, $\Delta\tilde{\nu}_{a-f}$: *Stokes* shift

dye	solv.	λ_a (nm)	lg ε	$\Delta\tilde{\nu}_{D-A}$ (cm^{-1})	λ_f (nm)	$\Delta\tilde{\nu}_{a-f}$ (cm^{-1})
3a	D	680	4.59	846	825	2585
	A	643	4.58		932	4822
3b	D	698	4.75	488	835	2351
	A	675	4.72		930	4062
3c	D	702	4.60	483	a)	–
	A	679	4.58		a)	–
3d	D	693	4.75	791	840	2525
	A	657	4.69		938	4560
3e	D	727	4.70	470	a)	–
	A	703	4.65		1000	4286
3f	D	679	4.73	825	815	2458
	A	643	4.58		885	4253

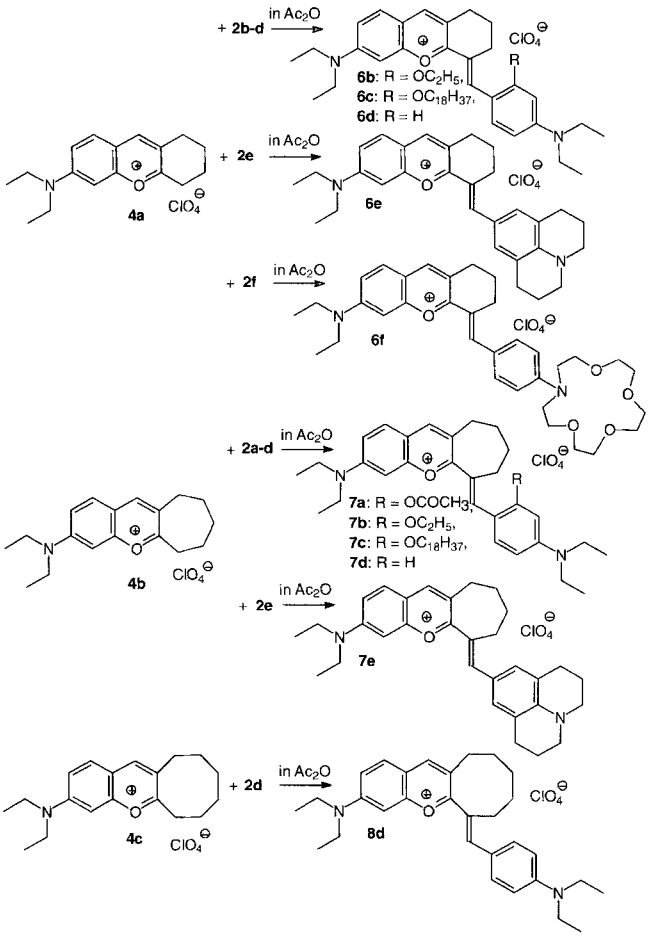
a) Not determined

(for mnemonic reasons the substance code was chosen to coincide with the size of the bridging ring). The first method has hitherto not been applied to **2a**. It consists in the 2:1 condensation of 4-diethylamino-2-hydroxybenzaldehyde **2a** with an alicyclic ketone (m = 1–4).



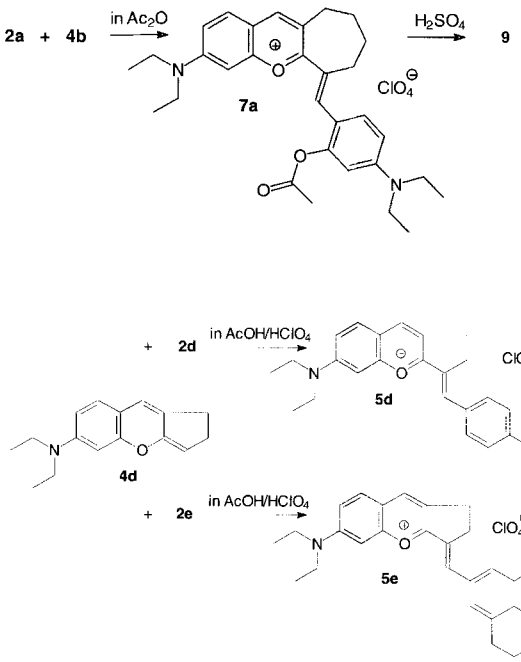
The applicability of this type of condensation is limited to a certain substituent pattern of the arylaldehyde **2a** to yield products of types **5a** and **6a**. In case of cycloheptanone (m = 3) as alicyclic ketone, we isolated a colorless, ring-closed product instead of the hydrolyzed dye **7** (R = OH), which was identified as the diperchlorate salt of spirobipyran **9**. Treatment of an alcoholic solution of this salt with triethylamine allows the free base **9** to be isolated. Condensation of **2a** with cyclooctanone under conditions analogous to the reaction for obtaining products **5a**, **6a** and **9** does not give the expected product. The 3,2-alicyclicbridged 7-diethylamino-1-benzopyrylium salt **4c** was formed instead of **8a**. As educts for the second method we used the new

3,2-alicyclic bridged 7-diethylamino-1-benzopyrylium salts **4a**, **4b** [7] and salt **4c** described above, which results from a 1:1 condensation of **2a** and cyclohexanone, cycloheptanone, or cyclooctanone. These salts allow access to new 2-[2'-(4''-dialkylaminophenyl) ethenyl]-7-diethylamino-1-benzopyrylium perchlorates **6**–**8** with substituent patterns similar to salts **3**.

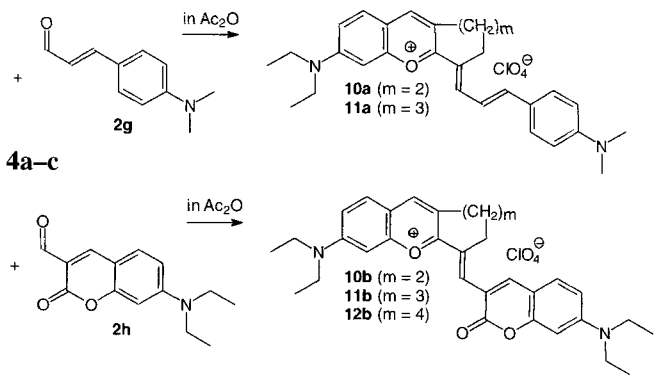


The dyes **6**–**8** were obtained in nearly quantitative yield by reaction of the appropriate arylaldehydes **2** and the 1-benzopyrylium salts **4** in acetic anhydride at elevated temperature. Attempts to synthesize compound **7** (R = unprotected OH-substituent) failed in this way. Instead of the expected hydroxy substituted salt we could only isolate the acylated product **7a** analogously to **3a**. Acid catalyzed hydrolysis of **7a** results in the cyclic product **9** (see preparations: synthesis of **9**, option B).

In a further reaction, we could show that there is a convenient access to the non-symmetrical 1-benzopyrylium salt **5.** We then used the new anhydro base **4d** [8] instead of the 1-benzopyrylium salts **4a**–**c**. The acid condensation of **4d** with **2d** and **2e** delivers the expected products **5d** and **5e** in good yields.



Condensation of salts **4a**–**c** with vinylogous arylaldehydes (4-dimethylaminocinnamaldehyde **2g** or 7-diethylamino-3-formylcoumarin **2h**) yields the 2-[4'-(4''-dialkylaminophenyl)butadien-1',3'-yl]-7-diethylamino-1-benzopyrylium perchlorates **10a** and **11a** or the 2-[2'-(7''-diethylaminocoumar-3''-yl)ethenyl]-7-diethylamino-1-benzopyrylium perchlorates **10b**–**12b**.



Vis/NIR spectroscopic data for the **10**–**12** are given in Table 3.

Structure Properties Relationships

It is particularly interesting to compare the Vis/NIR absorption and emission spectra of dyes **3**, **6**–**8**, and **10**–**12**, which all have the same substitution pattern.

Tab. 2 Vis/NIR absorption and emission data of the 3,1'-bridged 2-[2'-(4''-dialkylaminophenyl)ethenyl]-7-diethylamino-1-benzopyrylium perchlorates (**5**–**8**) in dichloromethane (D) and acetonitrile (A); $\Delta\tilde{\nu}_{D-A}$: solvent shift, $\Delta\tilde{\nu}_{a-f}$: *Stokes* shift

dye	solv.	λ_a (nm)	lg ε	$\Delta\tilde{\nu}_{D-A}$ (cm^{-1})	λ_f (nm)	$\Delta\tilde{\nu}_{a-f}$ (cm^{-1})
5a	D	723	a)	455	769	827
	A	700	4.26		766	1231
6a	D	721	4.78	437	778	1016
	A	699	4.78		783	1535
7a	D	668	4.64	1056	776	2083
	A	624	4.58		782	3238
6b	D	721	4.90	335	785	1131
	A	704	4.47		782	1417
7b	D	701	4.78	705	788	1575
	A	668	4.64		793	2360
6c	D	726	5.03	310	783	1003
	A	707	4.86		782	1297
7c	D	704	4.82	721	787	1498
	A	670	4.66		790	2267
5d	D	728	4.99	489	777	866
	A	703	4.94		779	1388
6d	D	711	4.99	533	774	1145
	A	685	4.83		783	1827
7d	D	677	4.73	805	784	2016
	A	642	4.63		788	2886
8d	D	701	4.77	750	781	1461
	A	666	4.63		787	2309
5e	D	760	4.98	448	800	657
	A	735	4.85		807	1214
6e	D	747	4.77	483	821	1207
	A	721	4.79		823	1719
7e	D	723	4.76	853	828	1754
	A	681	4.63		837	2737
6f	D	699	4.47	531	775	1403
	A	674	4.53		780	2016

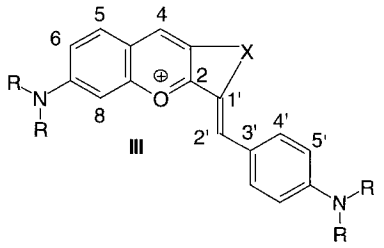
Tab. 3 Vis/NIR absorption and emission data of the 3,1'-bridged 2-[4'-(4''-dialkylaminophenyl)butadien-1',3'-yl]-7-diethylamino-1-benzopyrylium perchlorates (**10a**, **11a**) and 2-[2'-(7''-diethylaminocoumar-3''-yl)ethenyl]-7-diethylamino-1-benzopyrylium perchlorates **10b**, **11b** and **12b** in dichloromethane (D) and acetonitrile (A); $\Delta\tilde{\nu}_{D-A}$: solvent shift, $\Delta\tilde{\nu}_{a-f}$: *Stokes* shift

dye	solv. (nm)	λ_a	lg ε (cm^{-1})	$\Delta\tilde{\nu}_{D-A}$	λ_f (nm)	$\Delta\tilde{\nu}_{a-f}$ (cm^{-1})
10a	D	767	4.80	1187	857	1369
	A	703	4.66		878	2835
11a	D	712	4.66	1199	860	2417
	A	656	4.58		884	3932
10b	D	700	4.65	1146	811	1955
	A	648	4.62		828	3355
11b	D	645	4.62	944	808	3128
	A	608	4.56		834	4457
12b	D	653	4.42	1080	810	2968
	A	610	4.34		832	4374

The influence of the heterocycle and, in particular, the bridging (m = 1, 2, 3 or 4) is obvious (see λ_a and λ_f in Table 1–3).

Effect of Alkylene-Bridging on Vis/NIR Absorption and Emission Spectra

Bridging affects mainly the position of the absorption maxima. As shown in Figure 1, the absorption wavelength decreases in the series **5d**, **6d**, **8d**, and **7d**, whereas the fluorescence wavelength remains nearly unchanged. Additionally, the absorption wavelength decreases with increasing solvent polarity. The unbridged model compound **III** (X = H, H; R = CH_3) [9] is predicted to be planar as calculated by full geometry optimization with the AM1 *Hamiltonian*.



III

As shown by AM1 calculations, methylene (X = CH_2) or ethylene (X = CH_2–CH_2) bridges do not significantly change the geometry of the chromophore **III** (see **5d** in Table 2). A propylene bridge in compound **III** (*cf.* **6d** in Table 2) introduces a torsion of 23° of the aminophenyl ring, the 2'-1'- and 1'-2-bonds remaining virtually unaffected. The seven-membered ring in **III** (*cf.* **7d** in Table 2), however, introduces stronger distortions of 44 and 46° of the 3'-2'- and the 1'-2-bonds, respectively. There is, once again, almost no twisting of the 2'-1'-bond (4°). It becomes obvious from a grid search for compound **III** (X = H, H), that the rotational barrier around the 2'-1'-bond is considerably higher than those around the other bonds. The same result is obtained from reaction coordinate calculations of the isomerizations around either of the bonds if configuration interaction including doubly excited configuration is allowed (PECI = 6). The optimized lengths of the 3'-2'- and 2'-1'-bonds, respectively, are 142 and 137 pm for both the 5- and 6 membered species. The most significant alternation of the bond lengths is observed with the 7-membered compound: 144 and 136 pm, respectively. The 8-membered ring again allows (143 and 137 pm) a less distorted geometry of the polymethine like chromophor (bond lengths $r_{3'-2'}$ = 144 pm, $r_{2'-1'}$ = 137 pm). Thus, these compounds do not resemble "ideal polymethines", which should not exhibit π-bond order alternations nor bond length alternation along the chain, *cf.* reference

[10]; they are rather bis(dialkylamino) substituted 2-[2'-(aryl)ethenyl]-1-benzopyrylium salts with pronounced donor-acceptor behaviour. The donor-acceptor nature becomes obvious from a population analysis, see below.

The effect of torsion of the formal double bond (2'–1') is calculated to result in a bathochromic band shift, whereas torsion around the formal single bonds 1'–2 and 3'–2' yields a hypsochromic band shift. The bathochromic effect becomes significant only at a larger deviation from planarity. Calculated (PECI = 8) electronic spectral transitions: λ_{max} = 558, 562, 494, and 551 nm for X = $(CH_2)_2$ to $(CH_2)_5$ in **III** are at variance with the experimental ones (compare **5d–8d** in Table 2). However, the most distorted compound of type **III** (**7d**) is predicted to absorb at significantly shorter wavelength than all others in coincidence with experimental results.

If the chromophore is planar then the π-electron distribution is closest to the polymethinic state. Any deviation from planarity changes the nature of the chromophore towards the polyenic state. In the latter case one should expect a more pronounced charge-transfer character of the first electronic transition. This is in full accordance with the larger negative solvatochromism ($\Delta\tilde{\nu}_{D-A}$) if compounds of type **6** are compared to compounds of type **7** or **10** to **11**, see Tables 2 and 3. Arbitrary division of the molecules across the exocyclic double bond (position 2'–1' in **III**) into donor and acceptor parts reveals a significantly different distribution of the positive charge depending on sterical hindrance. For instance, 0.57 and 0.72 of the positive charge reside on the benzopyrylium moiety in the propylene- and butylene-bridged dyes, respectively. Formally, the dipole moment for an ion is undefined [11]. MOPAC6 allows the calculation of apparent "dipole moments" also for ions. They are defined in an accelerated molecule-fixed coordinate system, *cf.* [11, 12]. The "dipole moments" as calculated by MOPAC6 (AM1) amount to 3.35 and 3.29 D for the ground and first excited state of **6d**, respectively, whereas in the butylene-bridged analogue **7d**, values of 7.74 and 2.07 D are calculated with an opposite sign of the main component. If the *Stokes* shifts ($\Delta\tilde{\nu}_{a-f}$) (taken from the absorption and fluorescence maxima instead of from the unknown 00-transitions) are plotted against *Lippert*'s function of the solvent polarity [13], we can obtain rough experimental estimates of effective dipole moment differences between the ground and excited states, Figure 1.

If we approximate the polarizability volume of the molecules by 4.2 10^{-28} m^3 (from MM2-calculations) we obtain 15, 20, 13, and 19 D for **6b**, **7b**, **6d**, and **7d**, respectively. We will not discuss the absolute values of these "dipole moments". However, we realize that there is a significant difference of the charge redistribution

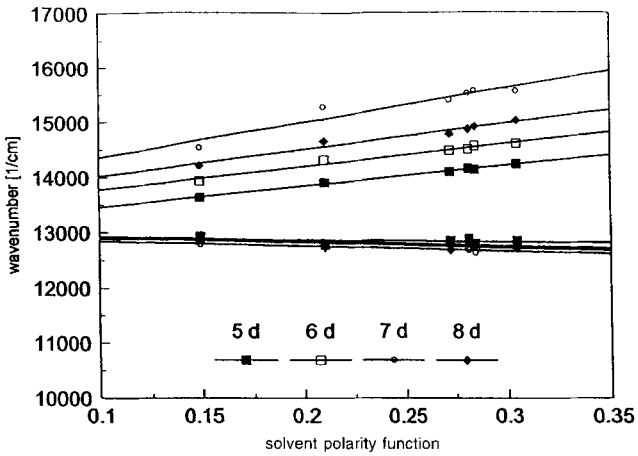


Fig. 1 Plot of the absorption and emission wavenumbers of dyes **5d–8d** against *Lippert's* function of solvent polarity (solvents: acetonitrile, acetone, propionitrile, *n*-butyronitrile, tetrahydrofuran and trichloromethane)

upon excitation between the propylene- and butylene bridged dyes **6** and **7**, which is in agreement with both the semiempirical MO calculations and the experimental solvatochromism.

The geometry changes calculated for the $S_1 \leftarrow S_0$ excitation are too small to account for the observed Stokes shifts. For instance, single point self-consistent reaction field calculation, with fully optimized S_0 and S_1 geometry of model compound **III**: X = $(CH_2)_3$, R_2 = H, gave a *Stokes* shift of $\Delta\tilde{\nu}$ = 325 cm^{-1} and 137 cm^{-1} (PECI = 8) using the dipole and quadrupole expansion for acetonitrile as solvent.

Fluorescence quantum yields of 5×10^{-2} down to 6×10^{-4} were obtained in dichloromethane solutions for compounds **5d** to **8d** (these yields have to be considered as rough estimates because the fluorescence spectrometer comes up against its limiting factors in that spectral region). Increasing size of the aliphatic bridge lowers systematically the fluorescence quantum yield. This is consistent with an increasing conformational flexibility of the chromophore. The yields are roughly one order of magnitude lower in acetonitrile as a solvent.

Exactly the same conclusions can be drawn from analogous calculations with vinylogous model compounds and their lactone-rigidized derivatives **10** and **11**.

Typical Vis/NIR absorption and emission spectra of compounds **7d** and **11b** with an unusually large *Stokes* shift are shown in Figure 2.

Our results show also, that increasing sterical hindrance can be used to tune a donor/acceptor chromophor system from a more polymethinic to a more polyenic nature. That way it should be possible to tune also the nonlinearoptical polarizabilities, as pointed out by

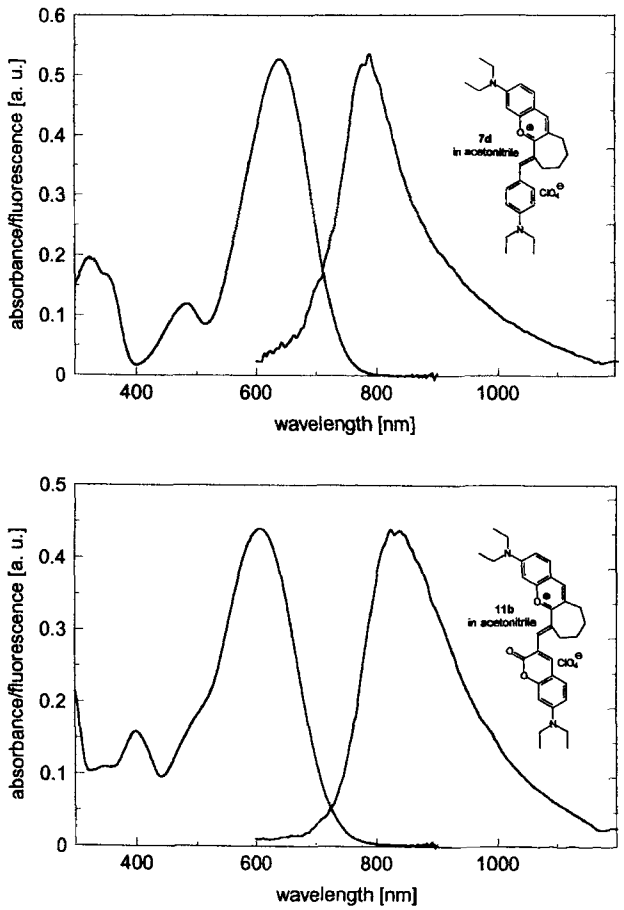


Fig. 2 Vis/NIR absorption and emission spectra of **7d** and **11b** in acetonitrile

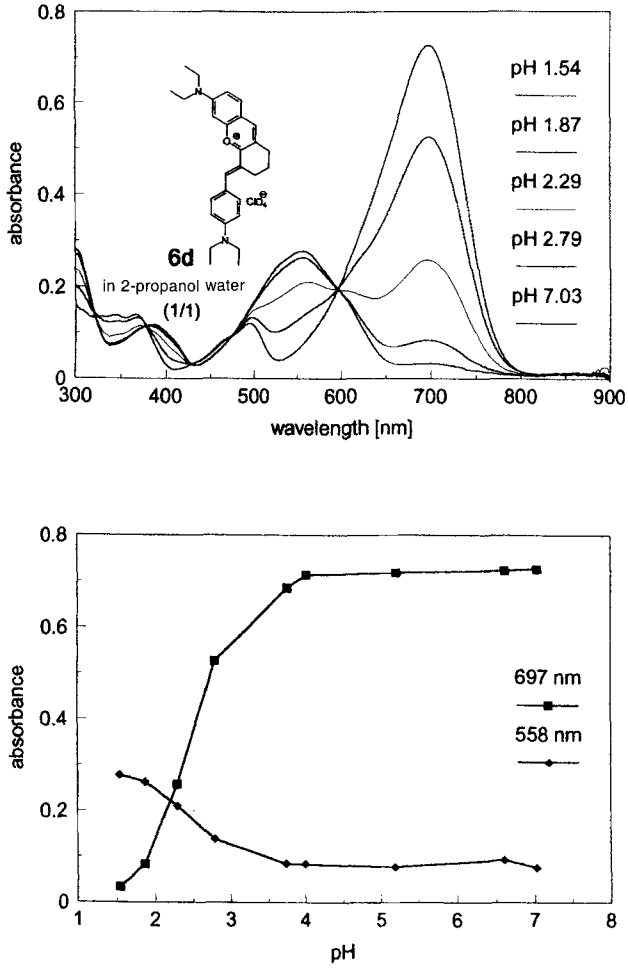


Fig. 3 Vis/NIR absorption spectra in dependence on pH value and pH titration plot of **6d** in 2-propanol/water (1/1, v/v)

Marder et al. [14]. Sum-over-states caclculations predict a variation of the static first hyperpolarization by a factor of 2 to 7 in the static and frequency dependent (1.03 eV) mode, respectively.

Acidochromic Behaviour

Protonation switches off the function of one dialkylamino group of the bis(dialkylamino) substituted 2-[2'-(aryl)ethenyl]-1-benzopyrylium salts **5**–**8** or the vinylogous salts **10**–**12**. The result is a hypsochromic shift of the long-wavelength absorption band. This behavior is called "inverse" acidochromism. As result of AM1 calculations the first protonation occurs at the dialkylamino function in 4-position, and is in accordance with line broadening of the ^{1}H NMR signals of the 4-dialkylaminophenyl ring by addition of CF_3CO_2D. For example the pK_a values for **6d** and **7d** in 2-propanol/water (1/1, v/v) are 2.46 and 2.90, respectively.

The dyes **5**–**8** and **10**–**12** are stable in acid and neutral solutions. Particularly in alkaline solution, the dyes decompose slowly due to nucleophilic attack of the HO^- ion to 2 or 4 position of **III**.

^{1}H NMR Chemical Shifts and Calculated Charge Densities

^{1}H- and ^{13}C-NMR chemical shifts have been shown to probe the charge residing on the carbon atom to which the hydrogens are attached [15, 16]. Fig. 4 shows a plot of the net charges obtained from PM3 calculations *versus* the experimental ^{1}H-NMR chemical shifts of the compounds **6d** and **7d**.

Due to the hardly managable interplay of diamagnetic and paramagnetic shielding effects one should not expect a very good correlation. Nevertheless, the positive correlation ($R^2 \approx 0.9$) is obvious.

P. C. and U.-W. G, greatly acknowledge financial support by the Fonds der Chemischen Industrie, Frankfurt/Main.

Experimental

Melting points were determined with a Kofler apparatus and are uncorrected. Satisfactory elemental analyses were obtained

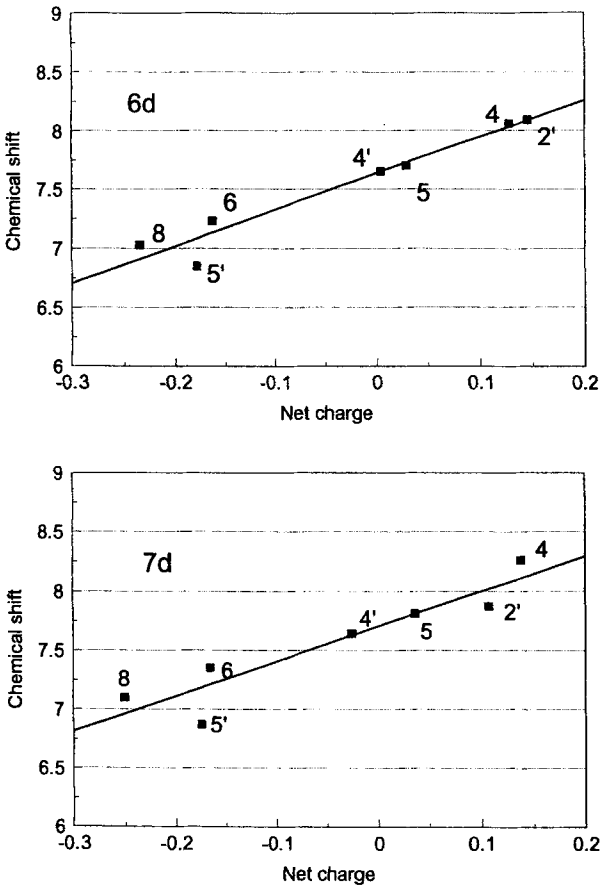


Fig. 4 Correlation of the calculated net charges (PM3) *versus* the experimental ^{1}H NMR chemical shifts of compounds **6d** and **7d** (in CD_3NO_2),(for positions of the H-atoms see **III**)

for all compounds. The solvents used were of spectrograde purity. The compounds dissolved in acetonitrile were stabilized by the addition of small amounts of 0.1% perchloric acid (there is definitely no protonation of the amino groups at this acid concentration). Vis/NIR absorption spectra were recorded by means of a Lambda 16 spectrophotometer (Perkin Elmer). Absorption spectra were recorded in the range from 10^{-5} – 10^{-4} M. The fluorescence spectra were measured on a home made NIR-emission spectrometer. The NIR-luminescence apparatus consists of a high pressure mercury lamp (HBO 200) with a high intensity monochromator (BAUSCH & LOMB) as excitation source and a grating monochromator type 01–001 (PHOTON TECHNOLOGY INTERNATIONAL), equipped with a liquid nitrogen cooled germanium detector EO-817 L (NORTHCOAST SCIENTIFIC CORP.) in a rectangular arrangement. Excitation was chopped with 35 Hz; a lock-in-amplifier model 223 (BENTHAM) was used with an optional muon-filter model 829 B (NORTHCOAST SCIENTIFIC CORP.). A photodiode or the detector of a pyroelectric radiometer RS-5900 (LASER PRECISION CORP.) were mounted opposite to the excitation source in order to control or to absolutely measure the irradiation and absorption.

^{1}H NMR spectra were measured in CD_3NO_2 with an DRX 400 (Bruker) and the signals were assigned with the help of two-dimensional TOCSY and NOESY spectra.

Semiempirical quantum chemical calculations were performed with the help of VAMP package [17] on a DEC ALPHA workstation and MOPAC6 on a PC. The AM *Hamiltonian* was applied for full structure optimization. The optimization of S_1-state geometries was performed using the keyword EXCITED which implies a minimal configuration interaction space equivalent to CI = 2.

General Procedure for Preparation of the 3,1'-Bridged 2-[2'-(4''-Dialkylamino-phenyl)ethenyl]-4,6-diaryl-pyrylium Perchlorates (3a–f)

2,4-Diphenyl-5,6,7,8-tetrahydro-1-benzopyrylium perchlorate **1** [6] (1.93 g, 5.0 mmol) and the corresponding 4-dialkylamino-benzaldehyde **2** (5.0 mmol,): 4-diethylamino-2-hydroxybenzaldehyde **2a** (0.97 g), 4-diethylamino-2-ethoxybenzaldehyde **2b** [18] (1.11 g), 4-diethylamino-2-*n*-octadecyloxybenzaldehyde **2c** [19] (2.23 g), 4-diethylaminobenzaldehyde **2d** (0.89 g), 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline-9-carbaldehyde **2e** [20] (0.99 g) or 4-(4',7',10',13'-tetraoxa-1-azacyclopentadecyl)benzaldehyde **2f** [21] (1.62 g) are dissolved in acetic anhydride (20 ml) and heated under reflux for 10 min. The precipitate separating soon after is filtered off and recrystallized from glacial acetic acid/nitromethane (10/1, v/v); *m.p.* 238 °C (**3a**), *m.p.* 231 °C (**3b**), *m.p.* 145–48 °C (**3c**), *m.p.* 239 °C (**3d**), *m.p.* 175–78 °C (**3e**) and *m.p.* 165–70 °C (**3f**).

General Procedure for Preparation of the 3,1'-Bridged 2-[2'-(4''-Diethylamino-2''-hydroxyphenyl)ethenyl]-7-diethylamino-1-benzopyrylium Perchlorates (5a, 6a)

To cyclopentanone or cyclohexanone (5.0 mmol) dissolved in glacial acetic acid (30 ml) and aqueous perchloric acid (1 ml, 70%), 4-diethylamino-2-hydroxybenzaldehyde **2a** (1.93 g, 10.0 mmol) is added. Then the reaction mixture is heated for 20 min on a boiling water bath. The blue/green precipitate separating after cooling is filtered off and recrystallized from glacial acetic acid/nitromethane (5/2, v/v); *m.p.* 135–40 °C (**5a**) and *m.p.* 176–80 °C (**6a**).

3,3'-Bridged 7,7'-Bis-diethylamino-2H-1-benzopyran-(2-spiro-2')-2H-1-benzopyran (**9**)

Option A: Analogously to the procedure mentioned before for preparation of the salts **5a** and **6a**, cycloheptanone (0.55 g, 5.0 mmol) is used as the alicyclic ketone. The white precipitate separating soon after heating is filtered, off washed with diethyl ether, and recrystallized from acetonitrile containing a few drops of triethylamine; *m.p.* 175 °C.

Option B: 3-Diethylamino-6-(4'-diethylamino-2'-acyloxy-benzylidene)-7,8,9,10-tetra-hydrobenzo[*b*]cyclohepta[*e*] pyrylium perchlorate **7a** (0.5 g) was dissolved in a mixture of water (25 ml), ethanol (25 ml), and conc. sulphuric acid (2.5 ml). The resulting solution was heated under reflux with stirring for 2 h and then poured into water (50 ml). The crude white product, which precipitated in quantitative yield, was filtered off, washed with water, and recrystallized from acetonitrile; *m.p.* 175 °C.

3-Diethylamino-benzo[b]cycloocta[e]pyrylium Perchlorate (**4c**)

Analogously to the above procedure for preparation of salts

5a and **6a**, cyclooctanone (0.64 g, 5.0 mmol) is used as the alicyclic ketone; *m.p.* 208 °C.

3,1'-Bridged 2-[2'-(4''-Dialkylaminophenyl)ethenyl]-7-diethylamino-1-benzopyrylium perchlorates (**6b–f**, **7a–e** and **8d**)

The appropriate 3,2-alicyclic bridged 7-diethylamino-1-benzopyrylium perchlorate **4a–c** [7] (5.0 mmol) and the 4-dialkylaminobenzaldehyde **2** (5.0 mmol): 4-diethylamino-2-hydroxybenzaldehyde **2a** (0.97 g), 4-diethylamino-2-ethoxybenzaldehyde **2b** [18] (1.11 g), 4-diethylamino-2-*n*-octadecyloxybenzaldehyde **2c** [19] (2.23 g), 4-diethylaminobenzaldehyde **2d** (0.89 g), 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline-9-carbaldehyde **2e** [20] (0.99 g), or 4-(4',7',10',13'-tetraoxa-1-azacyclopentadecyl)benzaldehyde **2f** [21] (1.62 g) are dissolved in acetic anhydride (20 ml) and heated under reflux for 10 min. The precipitate separating soon after is filtered off and recrystallized from glacial acetic acid/nitromethane (10/1, v/v); *m.p.* 205–08 °C (**6b**), *m.p.* 150 °C (**6c**), *m.p.* 198 °C (**6d**), *m.p.* 232–30 °C (**6e**), *m.p.* 125–30 °C (**6f**), *m.p.* 174 °C (**7a**), *m.p.* 195–98 °C (**7b**), *m.p.* 125 °C (**7c**), *m.p.* 148 °C (**7d**), *m.p.* 205–10 °C (**7e**) and *m.p.* 196–98 °C (**8d**). – ^{1}H NMR (**6b** in CD_3NO_2): δ/ppm = 1.24 (t, J = 7.1 Hz, 6H), 1.31 (t, J = 7.1 Hz, 6H), 1.54 (t, J = 6.9 Hz, 3H), 1.92–1.97 (m, 2H), 2.83–2.88 (m, 2H), 2.93–3.00 (m, 2H), 3.54 (q, J = 7.1 Hz, 4H), 3.66 (q, J = 7.1 Hz, 4H), 4.20 (q, J = 7.0 Hz, 2H), 6.29 (d, J = 2.0 Hz, 1H), 6.47 (dd, J = 2.0, J = 9.2 Hz, 1H), 6.85 (d, J = 2.0 Hz, 1H), 7.16 (dd, J = 2.0, J = 9.2 Hz, 1H), 7.63 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 9.3 Hz, 1H), 7.93 (s, 1H), 8.62 (s, 1H). – ^{1}H NMR (**6c** in CD_3NO_2): δ/ppm = 0.87 (t, J = 7.0 Hz, 3H), 1.14–1.42 (m, 38 H), 1.44–1.50 (m, 2H), 1.58–1.64 (m, 2H), 1.93–2.01 (m, 4H), 2.86–2.90 (m, 2H), 2.97–3.02 (m, 2H), 3.55 (q, J = 7.1 Hz, 4H), 3.66 (q, J = 7.1 Hz, 4H), 4.15–4.19 (m, 2H), 6.32 (d, J = 2.2 Hz, 1H), 6.49 (dd, J = 2.6, J = 9.2 Hz, 1H), 6.85 (d, J = 2.0 Hz, 1H), 7.18 (dd, J = 2.3, J = 9.2 Hz, 1H), 7.66 (d, J = 9.2 Hz, 1H), 7.67 (d, J = 9.2 Hz, 1H), 7.94 (s, 1H), 8.67 (s, 1H). – ^{1}H NMR (**6d** in CD_3NO_2): δ/ppm = 1.23 (t, J = 7.1 Hz, 6H), 1.32 (t, J = 7.1 Hz, 6H), 2.00–2.03 (m, 2H), 2.88–2.92 (m, 2H), 3.00–3.04 (m, 2H), 3.53 (q, J = 7.1 Hz, 4H), 3.69 (q, J = 7.1 Hz, 4H), 6.85 (d, J = 8.9 Hz, 2H), 7.03 (d, J = 2.0 Hz, 1H), 7.23 (dd, J = 2.0, J = 9.3 Hz, 1H), 7.65 (d, J = 9.0 Hz, 2H), 7.70 (d, J = 9.3 Hz, 1H), 8.06 (s, 1H), 8.09 (s, 1H). – ^{1}H NMR (**7a** in CD_3NO_2): δ/ppm = 1.20 (t, J = 7.1 Hz, 6H), 1.34 (t, J = 7.1 Hz, 6H), 1.94–2.00 (m, 4H), 2.43 (s, 3H), 2.96–3.03 (m, 4H), 3.48 (q, J = 7.1 Hz, 4H), 3.73 (q, J = 7.1 Hz, 4H), 6.53 (d, J = 2.7 Hz, 1H), 6.72 (dd, J = 2.7, J = 9.0 Hz, 1H), 6.93 (d, J = 1.9 Hz, 1H), 7.35 (dd, J = 2.4, J = 9.4 Hz, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.80 (s, 1H), 7.81 (d, J = 9.3 Hz, 1H), 8.28 (s, 1H). – ^{1}H NMR (**7b** in CD_3NO_2): δ/ppm = 1.21 (t, J = 7.1 Hz, 6H), 1.24 (t, J = 7.1 Hz, 6H), 1.34 (t, J = 7.0 Hz, 3H), 1.94–2.00 (m, 4H), 2.98–3.02 (m, 4H), 3.52 (q, J = 7.1 Hz, 4H), 3.71 (q, J = 7.1 Hz, 4H), 4.20 (q, J = 6.9 Hz, 2H), 6.32 (d, J = 2.0 Hz, 1H), 6.47 (dd, J = 2.0, J = 9.2 Hz, 1H), 6.89 (d, J = 2.0 Hz, 1H), 7.28 (dd, J = 2.2, J = 9.4 Hz, 1H), 7.62 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 9.3 Hz, 1H), 8.19 (s, 1H), 8.47 (s, 1H). – ^{1}H NMR (**7c** in CD_3NO_2): δ/ppm = 0.86 (t, J = 7.0 Hz, 3H), 1.13–1.42 (m, 38 H), 1.43–1.46 (m, 2H), 1.53–1.59 (m, 2H), 1.93–2.01 (m, 6H), 2.95–3.01 (m, 4H), 3.50 (q, J = 7.1 Hz, 4H), 3.71 (q, J = 7.1 Hz, 4H), 4.13–4.17 (m, 2H), 6.31 (d, J = 2.0 Hz, 1H), 6.43 (dd, J = 2.0, J = 9.2 Hz, 1H), 6.85 (d, J = 2.0 Hz, 1H), 7.28 (dd, J = 2.4, J = 9.3 Hz, 1H), 7.60 (d, J = 9.1 Hz, 1H), 7.74 (d, J = 9.3 Hz, 1H), 8.15 (s, 1H), 8.43 (s, 1H). – ^{1}H NMR (**7d** in CD_3NO_2): δ/ppm = 1.26 (t, J = 7.1 Hz, 6H), 1.37 (t, J = 7.1 Hz, 6H), 2.00–2.06 (m, 4H), 3.00–3.06 (m, 2H), 3.07–3.13 (m, 2H), 3.55 (q, J = 7.1 Hz, 4H), 3.76 (q, J = 7.1 Hz, 4H), 6.87 (d, J = 9.0 Hz, 2H), 7.10 (d, J = 2.1 Hz, 1H), 7.35 (dd, J = 2.3, J = 9.4 Hz, 1H), 7.64 (d, J = 9.0 Hz, 2H), 7.81 (d, J = 9.4 Hz, 1H), 7.87 (s, 1H), 8.27 (s, 1H). – ^{1}H NMR (**8d** in CD_3NO_2): δ/ppm = 1.22 (t, J = 7.1 Hz, 6H), 1.33 (t, J = 7.1 Hz, 6H), 1.70–1.76 (m, 2H), 1.98–2.04 (m, 2H), 2.05–2.09 (m, 2H), 3.25–3.33 (m, 4H), 3.51 (q, J = 7.1 Hz, 4H), 3.72 (q, J = 7.1 Hz, 4H), 6.84 (d, J = 8.7 Hz, 2H), 7.06 (d, J = 1.8 Hz, 1H), 7.30 (dd, J = 2.4, J = 9.3 Hz, 1H), 7.59 (d, J = 9.0 Hz, 2H), 7.76 (d, J = 9.3 Hz, 1H), 8.19 (s, 2H).

3-(4-Dialkylaminobenzylidene)-6-diethylamino-2,3-dihydro-1*H*-cyclopenta[*b*]-1-benzopyrylium Perchlorates 5d and 5e (General Procedure)

The methylene base **4d** [8] (1.21 g, 5.0 mmol) and 4-diethylaminobenzaldehyde **2d** (0.89 g, 5.0 mmol) or 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline-9-carbaldehyde **2e** [20] (0.99 g, 5.0 mmol), respectively, are dissolved in a mixture of acetic acid (20 ml) and aqueous perchloric acid (1 ml, 70%) and heated under reflux for 10 min. The precipitate separating soon after is filtered off and recrystallized from glacial acetic acid/nitromethane (10/1, v/v); *m.p.* 240–242 °C (**5d**) and *m.p.* 218–220 °C (**5e**). – ^{1}H NMR (**5d** in CD_3NO_2): δ/ppm = 1.26 (t, J = 7.1 Hz, 6H), 1.40 (t, J = 7.0 Hz, 6H), 3.30 (t, J = 3.9 Hz, 2H), 3.39 (t, J = 2.8 Hz, 2H), 3.77–3.85 (m, 8H), 7.19 (d, J = 1.8 Hz, 1H), 7.44 (dd, J = 2.3, J = 9.4 Hz, 1H), 7.67–7.75 (m, 3H), 7.90 (d, J = 9.5 Hz, 1H), 7.99 (d, J = 8.6 Hz, 2H), 8.45 (s, 1H).

3,1'-Bridged 2-[4'-(4''-Dialkylamino-phenyl)butadien-1',3'-yl]-7-diethylamino-1-benzopyrylium Perchlorates 10a, 11a and 2-[2'-(7''-Diethylaminocoumar-3''yl) ethenyl]-7-diethylamino-1-benzopyrylium Perchlorates (10b, 11b and 12b) (General Procedure)

The appropriate 3,2-alicyclic bridged 7-diethylamino-1-benzopyrylium perchlorate **4a–c** [7] (5.0 mmol) and 4-dimethylaminocinnamaldehyde **2g** (0.88 g, 5.0 mmol) or 7-diethylamino-3-formylcoumarin **2h** [22] (1.23 g, 5.0 mmol), respectively, are dissolved in acetic anhydride (20 ml) and heated under reflux for 10 min. The precipitate separating soon after is filtered off and recrystallized from glacial acetic acid/nitromethane (10/1, v/v); *m.p.* 254–258 °C (**10a**), *m.p.* 226–230 °C (**10b**), *m.p.* 150–152 °C (**11a**), *m.p.* 240 °C (**11b**) and *m.p.* 216 °C (**12b**). – ^{1}H NMR (**10a** in CD_3NO_2): δ/ppm = 1.38 (t, J = 7.1 Hz, 6H), 1.96–2.03 (m, 2H), 2.90–2.96 (m, 4H), 3.10 (s, 6H), 3.76 (q, J = 7.1 Hz, 4H), 6.79 (d, J = 8.9 Hz, 2H), 7.04 (d, J = 1.7 Hz, 1H), 7.23–7.31 (m, 3H), 7.58 (d, J = 9.0 Hz, 2H), 7.74 (d, J = 9.3 Hz, 1H), 7.94 (d, J = 9.4 Hz, 1H), 8.09 (s, 1H). – ^{1}H NMR (**10b** in CD_3NO_2): δ/ppm = 1.29 (t, J = 7.1 Hz, 6H), 1.38 (t, J = 7.1 Hz, 6H), 2.01–2.06 (m, 2H), 2.95–3.00 (m, 2H), 3.05–3.09 (m, 2H), 3.58 (q, J = 7.1 Hz, 4H), 3.79 (q, J = 7.1 Hz, 4H), 6.57 (d, J = 2.4 Hz, 1H), 6.83 (dd, J = 2.4, J = 9.0 Hz, 1H), 7.22 (d, J = 2.0 Hz,

1H), 7.40 (dd, J = 2.4, J = 9.4 Hz, 1H), 7.52 (d, J = 9.0 Hz, 1H), 7.83 (d, J = 9.4 Hz, 1H), 8.05–8.12 (m, 2H), 8.26 (s, 1H). – ^{1}H NMR (**11b** in CD_3NO_2): δ/ppm= 1.26 (t, J = 7.1 Hz, 6H), 1.36 (t, J = 7.1 Hz, 6H), 1.98–2.05 (m, 4H), 2.98–3.05 (m, 4H), 3.55 (q, J = 7.1 Hz, 4H), 3.77 (q, J = 7.1 Hz, 4H), 6.55 (d, J = 2.4 Hz, 1H), 6.80 (dd, J = 2.4, J = 9.0 Hz, 1H), 7.20 (d, J = 2.0 Hz, 1H), 7.41 (dd, J = 2.4, J = 9.4 Hz, 1H), 7.50 (d, J = 9.0 Hz, 7.81-7.87 (m, 2H), 8.06 (s, 1H), 8.34 (s, 1H).

References

[1] J. Fabian, H. Nakazumi, M. Matsuoka, Chem. Rev. **1992**, *92*, 1197

[2] J. Griffiths, Chem. in u. Zeit **1993**, *27*, 21

[3] O. S. Wolfbeis, G. Boisde in Sensors-A Comprehensive Survey, (Eds. W. Göpel, J. Hesse, J. N. Zemel), VCH, Weinheim, 1992, vol. 3, p. 867

[4] P. Czerney, G. Graneß, E. Birckner, F. Vollmer, W. Rettig, J. Photochem. Photobiol. A: Chem. **1995**, *89*, 31

[5] G. Haucke, P. Czerney, D. Steen, W. Rettig, H. Hartmann, Ber. Bunsenges. Phys. Chem. **1993**, *97*, 561

[6] H. D. Kirner, R. Wizinger, Helv. Chim. Acta **1961**, *44*, 1766

[7] P. Czerney, U.-W. Grummt, J. Chem. Res. (S) **1996**, 173

[8] A. Kanitz, H. Hartmann, P. Czerney, J. Prakt. Chem. **1998**, *340*, 34

[9] G. Haucke, P. Czerney, C. Igney, H. Hartmann, Ber. Bunsenges. Phys. Chem. **1989**, *93*, 805

[10] S. Dähne, Chimia **1991**, *45*, 19

[11] J. J. P. Stewart, MOPAC 93 Manual, Fujitsu Ltd. 1993, p. 110

[12] A. D. Buckingham, Quart. Rev. **1959**, *13*, 183

[13] C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, 2nd ed., VCH, Weinheim, 1990, p.311

[14] S. R. Marder, J. W. Perry, G. Bourhill, C. B. Gorman, B. G. Tiemann, K. Mansour, Science **1993**, *261*, 186

[15] R. Radeglia, S. Dähne, H. Hartmann, J. Prakt. Chem. **1970**, *312*, 1081

[16] M. Gruner, H. Hartmann, P. Czerney, R. Hultzsch, J. Prakt. Chem. **1990**, *332*, 461

[17] G. Rauhut, A. Alex, J. Chandrasekhar, T. Steinke, W. Sauer, B. Beck, M. Hutter, P. Gedeck, T. Clark, VAMP6.0, Oxford Molecular Ltd, The Medawar Centre, Oxford, Science Park, Oxford OX4 4GA, UK

[18] E. Jenny, Swiss.Pat. 350 277, (Chem. Abstr. **1961**, *55*, 27377)

[19] H. Lindauer, P. Czerney, U.-W. Grummt, J. Prakt. Chem. **1994**, *336*, 521

[20] P. A. S. Smith, T. Y. Yu, J. Org. Chem. **1952**, *17*, 1281

[21] J. P. Dix, F. Vögtle, Chem. Ber. **1980**, *113*, 457

[22] H. Harnisch, Ger. Offen. 2 413 371, (Chem. Abstr. **1976**, *84*, 46052f)

Address for correspondence:
Prof. Dr. U.-W. Grummt
Friedrich-Schiller-Universität Jena
Institut für Physikalische Chemie
Lessingstr. 10
D-07743 Jena
e-mail cug@rz.uni-jena.de