

Comparison of Trifluoroacetyl Monostyryl and Distyryl Dyes: Effects of Chromophore Elongation on the Spectral Properties and Chemical Reactivity

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The trifluoroacetyl distyryl derivative 1-[4-(2-{4-[2-(4-dibutylaminophenyl)-vinyl]-phenyl}-vinyl)-phenyl]-2,2,2-trifluoroethanone was compared with the related monostyryl derivative 1-{4-[2-(4-dibutylaminophenyl)-vinyl]-phenyl}-2,2,2-trifluoroethanone with respect to spectral properties and sensitivity to amines. Both trifluoroacetyl derivatives had their absorbance maximum at around 445 nm. The fluorescence of the distyryl dye, however, was observed at significantly longer wavelengths than that of the monostyryl dye, indicating the effect of structural extension of the chromophore system. Furthermore, the distyryl dye exhibited significantly smaller quantum yields in polar solvents than the monostyryl dye. Both dyes were capable of chemically reacting with amines in that their trifluoroacetyl function was converted into a hemiaminal. Consequently, absorbance and fluorescence of both dyes were shifted to shorter wavelengths. The positions of the fluorescence maxima of the spectra when converting from trifluoroacetyl to hemiaminal form were shifted by an almost identical amount for both mono- and distyryl derivative. The hemiaminal form of the distyryl derivative, however, exhibited much larger quantum yields in both polar and nonpolar solvents than the hemiaminal form of the monostyryl dye. The structural extension of the chromophore affected the sensitivity to amines by enhancing the chemical reactivity of the distyryl dye over the monostyryl derivative.

KEY WORDS: Fluororeactand; styryl dyes; distyryl dyes; amines.

INTRODUCTION

Functional materials that perform (reversible) chemical reactions are currently attracting considerable interest because their physicochemical properties can be tailored according to demand. Lehn and coworkers, for example, presented dynamic covalent polymers composed of bis-hydrazides and dialdehydes [1,2]. The supramolecular structure of the resulting polyacylhydrazones was modified at room temperature by using acid catalysis.

Chemical reactions may also be used to detect anionic and neutral analytes. Accordingly, Swager and

coworker evaluated the chemical reaction of functional groups attached to conjugated polymers in order to detect fluoride [3]. In detail, a sensor system was created where the breakage of a Si–O bond was catalyzed by addition of fluoride. As a consequence of catalysis, a coumarin structure was formed which affected the optical properties of the conjugated polymer in terms of both fluorescence intensity and maximum.

In the last decade, we focused our research on the development and characterization of trifluoroacetyl dyes that interact reversibly with nucleophilic species. The absorbance and fluorescence of these dyes can be modified by appropriate reagent molecules [4], their structure and optical properties can be switched by illumination at selected wavelengths [5], and their chemical reactions may be used to detect (biogenic) amines, alcohols and thiols [6].

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To tailor the optical properties of chromogenic reactands, we synthesized azo dyes with donor and acceptor substituents, and bisazo dyes [7,8]. Elongation of the conjugated system via the synthesis of bisazo dyes is easily performed and often causes absorbance to shift to longer wavelengths [9]. Elongation of structurally related fluorogenic styryl dyes is synthetically less facile than in the case of azo dyes. However, in order to study the effect of elongation on absorbance and fluorescence of trifluoroacetyl styryl dyes, we synthesized a trifluoroacetyl distyryl derivative and compared its spectral properties with the parent monostyryl derivative [10].

EXPERIMENTAL

Apparatus

The absorbance spectra of the dissolved dyes were recorded on a Lambda 16 UV-Vis spectrometer (Perkin-Elmer) at $20 \pm 1^\circ\text{C}$. Fluorescence spectra of the dyes were recorded on a Jobin Yvon Spex Fluorolog 3 (Instruments S.A.). The fluorescence quantum yields were determined relative to quinine sulfate (p. a., Laborchemie Apolda) as fluorescence standard ($\phi_f = 0.55$, $n_{20}^D = 1.333$) according to ref. [11], giving relative standard deviations of $<10\%$. The determination of the quantum yields of the hemiaminal forms was less accurate (relative standard deviations of $<20\%$) than of the trifluoroacetyl form since, at high 1-butylamine concentrations, the hemiaminal showed decreasing intensity caused by chemical decomposition.

The equilibrium constants K_{equ} for the reaction of anhydrous amines in organic solvents (relative standard deviations $<10\%$) were determined by adding incremental aliquots of the respective amine to 3 mL of typically $10\mu\text{M}$ solutions of the dyes in a quartz UV/Vis cuvette at 20°C , and measuring signal changes at the absorbance maximum of the trifluoroacetyl form [12].

Chemicals and Reagents

All reagents were of analytical reagent grade. Quinine sulfate and 1-{4-[2-(4-dibutylaminophenyl)-vinyl]-phenyl}-2,2,2-trifluoroethanone (i.e., 4-*N,N*-dibutylamino-4'-trifluoroacetylstilbene, Fluka product number 28218) were obtained from Fluka AG (Buchs, Switzerland)(Fig. 1).

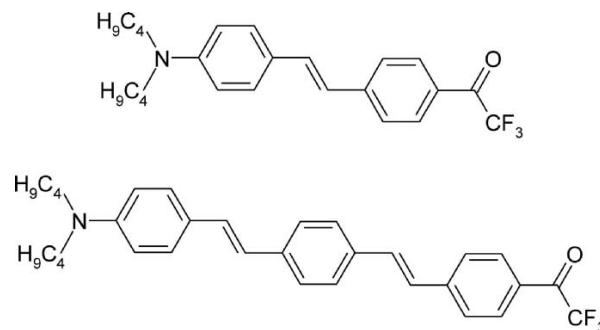


Fig. 1. Chemical structures of the monostyryl dye 1-{4-[2-(4-dibutylaminophenyl)-vinyl]-phenyl}-2,2,2-trifluoroethanone and the distyryl dye 1-[4-(2-{4-[2-(4-dibutylaminophenyl)-vinyl]-phenyl}-vinyl)-phenyl]-2,2,2-trifluoroethanone.

Synthesis of 1-[4-(2-{4-[2-(4-dibutylaminophenyl)-vinyl]-phenyl}-vinyl)-phenyl]-2,2,2-trifluoroethanone

A mixture composed of 0.2 g of 4-bromo-4'-*N,N*-dibutylaminostilbene (0.52 mmol) [10,13], 0.12 g of 4-trifluoroacetylstyrene (0.6 mmol) [14], 10 mg of dichlorobis-(triphenylphosphine)-palladium(II), 2 mL of tetrahydrofuran and 2 mL of triethylamine was heated to 115°C for 16 hr in a capped heavy-wall pyrex tube. To the cooled solution water was added, with 50 mL of dichloromethane. The aqueous layer was extracted two times with 50 mL of dichloromethane. The combined dichloromethane solutions were washed three times with 100 mL of distilled water, dried over magnesium sulfate and evaporated to dryness. Flash chromatography on silica gel 60 using hexane:dichloromethane (2:1) as the eluent gave 0.1 g of orange crystals, m.p. $182\text{--}184^\circ\text{C}$.

$^1\text{H-NMR}$ (CDCl_3): δ (ppm) 8.07 (d, 2H, =CH-), 7.64 (d, 2H, =CH-), 7.50 (m, 4H, =CH-), 7.36 (m, 3H, =CH-), 7.10 (m, 2H, =CH-), 6.88 (d, 1H, =CH-), 6.63 (d, 2H, =CH-), 3.31 (t, 4H, $-\text{CH}_2-$), 1.60 (m, 4H, $-\text{CH}_2-$), 1.36 (m, 4H, $-\text{CH}_2-$), 0.98 (t, 6H, $-\text{CH}_3$).

MS (ED): $m/z = 505$ [M], 420 [M - C_3H_7 and C_3H_6].

Calculated for $\text{C}_{32}\text{H}_{34}\text{F}_3\text{NO}$ (505.63): C, 76.02; H, 6.78; N, 2.77; found: C, 75.83; H, 6.30; N, 2.12.

RESULTS AND DISCUSSION

Comparing the Optical Properties of the Trifluoroacetyl Forms of the Mono- and the Distyryl Derivative

The absorbance maxima of the mono- and distyryl derivative in toluene are very close and are at 443 and

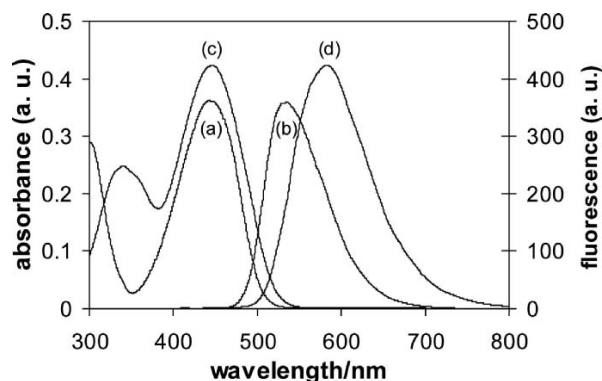


Fig. 2. Absorbance (a) and fluorescence (b) spectra of the trifluoroacetyl form of the monostyryl dye, and absorbance (c) and fluorescence (d) spectra of the distyryl dye, all in toluene as the solvent.

446 nm, respectively (Fig. 2). Obviously, the elongation does not provide much of a shift in absorbance as observed in the case of azo dyes, where elongation to a bisazo dye is very effective in causing the absorbance to shift to longer wavelengths [9]. In addition, only minor spectral changes (i.e., a weak positive solvatochromism) are observed when changing the solvent of the two dyes (Table I). However, both fluorescence maxima and quantum yields are significantly affected by organic solvents. The trifluoroacetyl form of the monostyryl dye in toluene emits at 536 nm, while the distyryl dye has its maximum at 584 nm. Here, chromophore elongation has a much stronger effect than in the case of the absorbance maxima. Although the triflu-

oroacetyl form of the monostyryl dye shows high quantum yield in almost any organic solvent, the fluorescence of the distyryl derivative is only strong in unpolar solvents, for example, hexane, toluene and diethyl ether. The fluorescence maxima of both dyes are significantly dependent on solvent polarity (in contrast to absorbance maxima) and a strong positive solvatochromism is observed for both derivatives although, as mentioned previously, the distyryl derivative is emissive only in relatively unpolar solvents.

Comparing the Optical Properties of the Hemiaminal Forms of the Mono- and the Distyryl Derivative

When reacting both the mono- and distyryl dye with the nucleophilic reagent 1-butylamine, then a shift in absorbance maximum from 443 to 362 nm in the case of the monostyryl derivative and from 446 to 400 nm in the case of the distyryl derivative is observed. This shift corresponds to a decrease in electron-acceptor strength of the trifluoroacetyl group upon conversion into a hemiaminal, which affects the electron delocalization within the chromophore/fluorophore. In the case of the monostyryl dye, the absorbance of the trifluoroacetyl and hemiaminal form are spectrally well-resolved by 81 nm (Fig. 3), while the elongation in conjugation of the distyryl fluorophore decreases this spectral resolution significantly (46 nm between the maxima of the trifluoroacetyl and hemiaminal forms) (Fig. 4).

Table I. Absorbance and Fluorescence Maxima, and Quantum Yields of the Trifluoroacetyl and Hemiaminal Forms of the Mono- and Distyryl Dye in Different Organic Solvents

	Trifluoroacetyl form			Hemiaminal form		
	λ_{abs}	λ_{em}	Φ	λ_{abs}	λ_{em}	Φ
Monostyryl derivative						
Hexane	431	476	0.21	359	395	0.12
Toluene	443	536	0.54	362	416	0.09
Diethyl ether	440	554	0.71	361	416	0.09
Ethyl acetate	446	596	0.64	363	430	0.06
Chloroform	452	618	0.51	364	434	0.06
Acetonitrile	447	674	0.04	367	455	0.09
Distyryl derivative						
Hexane	437	497	0.98	393	464	0.82
Toluene	446	584	0.79	400	467	0.81
Diethyl ether	433	620	0.43	394	482	0.70
Ethyl acetate	437	n.d.	n.d.	397	500	0.67
Chloroform	446	677	0.01	400	496	0.68
Acetonitrile	433	n.d.	n.d.	398	556	0.60

Note. λ_{abs} , λ_{em} , maximum wavelengths of absorption and fluorescence spectra (nm); n.d., not determined due to very weak fluorescence.

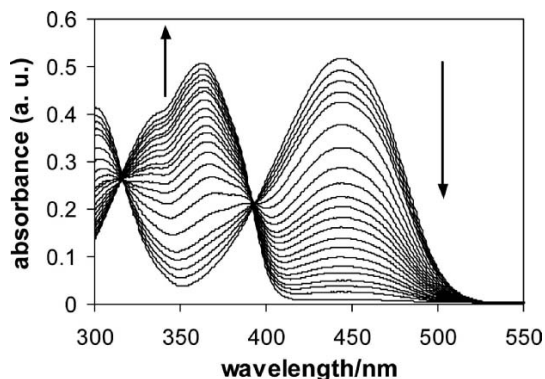


Fig. 3. Changes in absorbance of the monostyryl dye as a function of increasing amount of 1-butylamine (1, 2, 3, 4, 6, 8, 10, 12, 14, 16, 19, 22, 25, 30, 37, 47, 70, 100, 150, 200, and 300 μL) in 3 mL of toluene.

The effect of hemiaminal formation is also clearly visible when comparing the fluorescence of both dyes. When reacting both dyes with 1-butylamine in toluene, then the fluorescence of the monostyryl derivative at 536 nm decreases and a new fluorescence maximum at 416 nm is observed (Fig. 5). Similarly, the fluorescence of the distyryl derivative at 584 nm decreases while a new fluorescence maximum at 467 nm is encountered (Fig. 6). The spectral shift in going from the trifluoroacetyl to the hemiaminal form is very similar for both dyes (120 nm for the monostyryl and 117 nm for the distyryl dye). Interestingly, although in polar solvents such as acetonitrile or ethyl acetate the trifluoroacetyl form of the distyryl derivative is no longer emissive, the hemiaminal form still exhibits significant fluorescence intensity. In contrast, the trifluoroacetyl form of the monostyryl derivative is highly

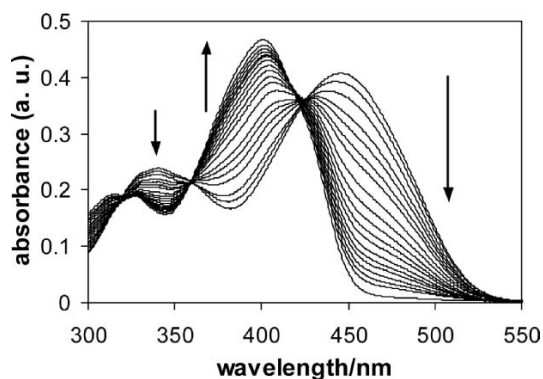


Fig. 4. Changes in absorbance of the distyryl dye as a function of increasing amount of 1-butylamine (1, 2, 3, 4, 6, 8, 10, 12, 14, 16, 19, 22, 25, 30, 37, 47, 70, 100, and 200 μL) in 3 mL of toluene.

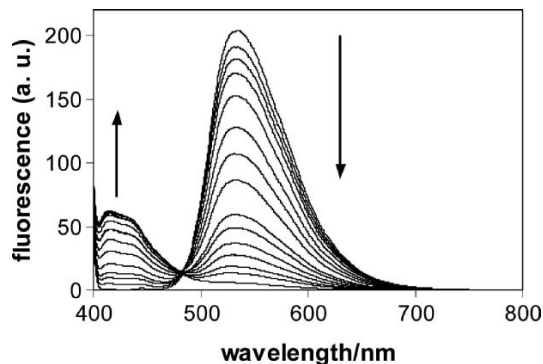


Fig. 5. Changes in fluorescence of the monostyryl dye as a function of increasing amount of 1-butylamine (1, 2, 4, 6, 8, 10, 15, 20, 25, 30, 40, 50, 65, 85, and 110 μL) in 3 mL of toluene (excitation set to 393 nm).

fluorescent in almost any organic solvent, while the hemiaminal is only weakly fluorescent (Table I).

For practical application, a ratiometric indicator dye with strong fluorescence of both the “free dye” and the “complex” is generally preferred over a photo-induced electron transfer dye as fluorescence readings are less affected by changes in light source intensity or detector fluctuations, and less prone to erroneous signals caused by concentration changes, leaching or bleaching [15]. However, in certain cases, analyte-dependent “off-on” fluorescent chemosensor dyes (such as the distyryl dye in polar solvents) may be of interest because they produce a visible signal out of a dark background which enhances the signal-to-noise ratio [16].

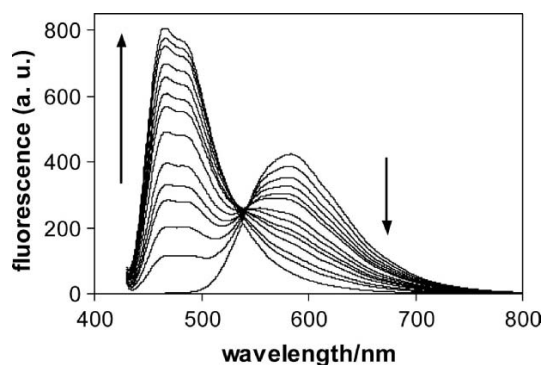


Fig. 6. Changes in fluorescence of the distyryl dye as a function of increasing amount of 1-butylamine (1, 2, 3, 4, 6, 8, 10, 12, 14, 16, 19, 22, 25, and 110 μL) in 3 mL of toluene (excitation set to 420 nm).

Calculating the Absorbance Characteristics of Trifluoroacetyl and Hemiaminal Forms of the Mono- and Distyryl Dye and Comparing Them with Measurements in Toluene

All quantum chemical calculations were performed using Gaussian 98 [17]. Structures were fully optimized on the B3LYP/6-31G(d) level. All geometries were confirmed as true minima by frequency calculations. The same model chemistry was used for the calculation of the transitions by TDDFT. For simplification, the *N,N*-dibutylamino groups were replaced with unsubstituted amino groups and the hemiaminal form was calculated as an ammonia derivative rather than as the 1-butylamino derivative. The resulting data (Table II) indicate that the calculated absorbance maxima are at shorter wavelengths for the monostyryl dye (minus of 30 and 22 nm for the trifluoroacetyl and hemiaminal form, respectively), while the maxima of the distyryl dye were calculated to be at longer wavelengths (plus of 53 and 16 nm for the trifluoroacetyl and hemiaminal form, respectively). The discrepancy between the predicted by DFT and experimental positions of the longest wavelength transitions is larger with the more extended compound. Although this may in part be due to methodological shortcomings, it also reflects the effect of the increased flexibility of the larger molecule. The distyryl dyes exhibit stronger deviations from the lowest energy geometry used for the calculation of the spectral transitions [18,19]. The shift in absorbance maximum in going from the trifluoroacetyl into the hemiaminal form is better represented in the case of the monostyryl dye (shift of 73 nm in the gas phase and 81 nm in toluene), while it is less accurate in the case of the distyryl dye with the overestimated shift in absorbance maximum of the triflu-

oroacetyl form (shift of 83 nm in the gas phase and 46 nm in toluene).

Comparing the Optical Properties of the Mono- and Distyryl Derivative upon Interaction with 1-Butylamine

The color change of both the mono- and distyryl dye upon interaction with 1-butylamine corresponds to an equilibrium where the trifluoroacetyl function reacts with a primary aliphatic amine to form a hemiaminal [12]. The equilibrium constants K_{equ} for the reaction of the monostyryl derivative with 1-butylamine were found to be 28, 70, and 80 M^{-1} in toluene, acetonitrile, and ethyl acetate, respectively, while for the distyryl derivative these are 35, 120, and 170 M^{-1} . The equilibrium constants for the reaction of the monostyryl derivative with 1-butylamine are slightly smaller than in the case of the distyryl derivative. This is due to the fact that enhanced electron donor strength in position *para* to the trifluoroacetylphenyl group reduces the chemical reactivity of the carbonyl function (i.e., its electrophilicity). The 4-*N,N*-dibutylaminophenylvinyl moiety is a slightly stronger electron donor than the corresponding distyryl moiety. A similar but more pronounced effect is observed for trifluoroacetyl monoazo and bisazo dyes [8].

The absorbance and fluorescence of both dyes are solvent-dependent and such is the chemical reactivity and the sensitivity upon interaction with 1-butylamine. The equilibrium constants are smaller in unpolar solvents such as toluene, while these are significantly larger in more polar solvents such as ethyl acetate or acetonitrile (Table II). It seems that the hemiaminal derivative is

Table II. Calculated and Measured Absorbance Maxima and Oscillator Strengths (f) [17] of the Trifluoroacetyl (TFA) and Hemiaminal (HA) Forms of the Mono- and Distyryl Dye, and Molar Extinction Coefficients ($\text{M}^{-1}\text{cm}^{-1}$, Given in Parentheses)

	Monostyryl dye		Distyryl dye		Monostyryl dye		Distyryl dye	
	In the gas phase—calculated				In toluene—experimental data			
	TFA	HA	TFA	HA	TFA	HA	TFA	HA
λ_{max} (nm)	413	340	499	416	443 (23200)	362 (43200)	446 (43200)	400
f	0.982	1.176	1.118	1.841				
λ_{max} (nm)	336	283	371	334	300		341	315
f	0.0001	0.029	1.142	0.337				
λ_{max} (nm)	297	227	346	299				
f	0.358	0.008	0.018	0.007				

Note. f , oscillator strength.

better stabilized in polar solvents than the trifluoroacetyl derivative although an opposite behavior is to be expected [20].

CONCLUSION

There is a significant effect of structural elongation on functional styryl-type donor–acceptor fluorophores, where the acceptor group can be switched in acceptor strength by a chemical reaction. Compared to the monostyryl dye, the distyryl derivative exhibits absorbance shifted only slightly to longer wavelengths while fluorescence is shifted much stronger. This effect is well understood because excitation renders molecules more rigid, that way enabling a larger conjugation length in the excited state. Elongation of the fluorophore also affects the quantum yield of the distyryl fluorophore in that in polar solvents, the hemiaminal form is still luminescent while the trifluoroacetyl form is not. Generally, the mono- and distyryl derivatives show significant color changes with 1-butylamine both with respect to absorbance and fluorescence. This color change can be used to detect not only 1-butylamine but also all nucleophilic species with related chemical functions, for example, biogenic aliphatic and aromatic amines, alcohols, and thiols as well as amino acids.

The color changes may also be used to tune the optical properties (e.g., the fluorescence) of the dyes in a spectral range from 400 to 800 nm by appropriate use of solvents and addition of nucleophiles.

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