280. Synthesis, Structure and Photochemical Properties of 4,4′,7,7′-Tetra-substituted 1,1′,3,3′-Tetraethylbenzimidazolotriazatrimethine Cyanines

by **Rudolf Naef** and **Heinz Balli**

Institut für Farbenchemie der Universität Basel

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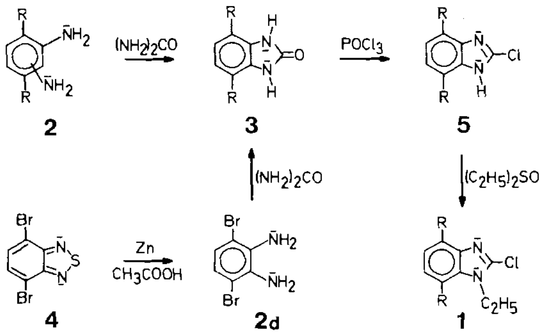
Summary

The synthesis of sterically hindered 1,1′,3,3′-tetraethylbenzimidazolotriazatrimethine cyanine dyes, their electron absorption spectra and that of their photoproducts (inverse photochromism) is described. Kinetic data of the thermally reversed reaction of the photo-bleached compounds are given. The differences of the electron absorption spectra in this series of dyes are explained by the different degree of distortion of the π-systems which is confirmed by an X-ray investigation.

Introduction. - Various syntheses of triazatrimethine dyes have been described [1-3]. Reaction of azidinium salts with azide ion [4] allows the synthesis of a wide variety of symmetrical dyes of this kind (*e.g.* [2] [5-8]), their long wave absorption maxima ranging from *ca.* 425 nm to 622 nm. *Kalk* [9] observed photochromic properties of some benzimidazole triazacyanines at low temperatures, analogous to the trimethine cyanines [10]. A thorough reinvestigation of several known and some as yet unknown triazacyanines [11] shows wide differences in their spectral, photochemical and kinetic behaviour. This paper reports the dependence of the absorption spectra and the kinetic data on the structural and electronic effects influencing the triazatrimethine cyanine chromophore.

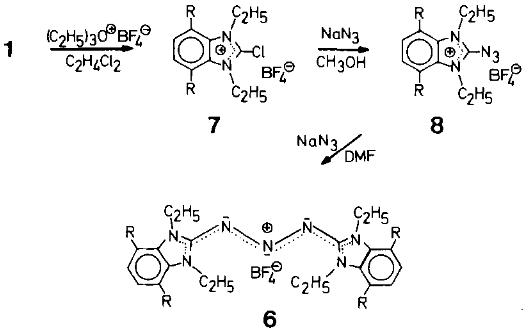
1. Syntheses. - *4,7-Disubstituted 2-chloro-1-ethylbenzimidazoles.* The basic compound **1a** (R = H) is known [8].



a R = H
b R = CH_3
c R = OCH_3
d R = Br

The preparation of compounds **1b** and **1c** started from *p*-xylene and *p*-dimethoxybenzene which were nitrated in 2 steps to yield a mixture of 2,3-, 2,5- and 2,6-dinitro-*p*-xylenes [12] and -*p*-dimethoxybenzenes [13] respectively. Hydration of the mixtures afforded the diamines **2b** [14] and **2c** [15]. Heating the diamine mixtures without separation in the presence of urea gave the benzimidazolones **3b** and **3c** [16] in moderate yields. Starting material for the synthesis of **3d** (R = Br) was pure 2,5-dibromo-*o*-phenylendiamine (obtained from metallic reduction [17] of 4,7-dibromo-2,1,3-benzothiadiazole (**4**) [18]), the procedure being the same as for **3b** and **3c**, but resulting in a much higher yield. Boiling **3** in phosphorus oxychloride to give the 2-chlorobenzimidazoles **5** (for **5c** see [15]) and subsequent alkylation with diethylsulfate in basic media afforded the 2-chloro-1-ethylbenzimidazoles **1**.

Triazatrimethine cyanines. The synthetic course from **1** to the dyes **6a**–**6d** followed the known steps [8]:

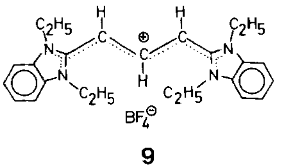


quaternisation of **1** by triethyloxonium tetrafluoroborate gave the symmetrical 2-chloro-1,3-diethylbenzimidazolium salts **7** in good yields, substitution of chloride by azide ion afforded the azidinium salts **8** which, without further purification, were converted into the final products **6a**–**6d** through reaction with sodium azide in dimethylformamide. The mechanism of the latter reaction is well documented [19].

2. Electron absorption spectra. - *Method.*

All absorption spectra of dyes **6a**–**6d** were taken in ethanol/methanol/2-propanol (90:5:5) at concentrations of about 10^{-4} mol/l. It was controlled that *Beer-Lambert*'s law was observed.

Results and discussion. A comparison of the absorption spectra of the analogous trimethine cyanine **9** [20] and **6a** shows a strongly hypsochromic shift from 485 nm [20] to 435 nm *(Table 1)*, which was interpreted by *Balli* [2] as a superposition of 2



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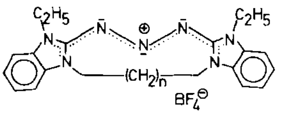
perturbational effects: a hypsochromic shift due to replacement of the carbon atoms adjacent to the benzimidazole groups by nitrogen [21], partially compensated through the bathochromic effect of a substitution of the central carbon atom by nitrogen.

Table 1. *Electron absorption maxima of* **6a**-**6d**, **9** [20] *and* **10** [9] *at 25°*

Compound	λ_{max_1} (nm)	λ_{max_2} (nm)	logε	$\Delta\nu$(cm^{-1})
6a	435		4.43	5200
		370 sh	4.26	
6b	413		4.32	3900
		356	4.30	
6c	410		4.36	3700
		356	4.33	
6d	414		4.31	3700
		359	4.35	
9	485		5.13	980
		463 sh	4.91	
10a	405		4.18	6300
		323	4.38	
10b	413	-	4.51	-
10c	434		4.45	4600
		362	4.33	
10d	427		4.33	5400
		347	4.31	

A significant difference of the structure of the long-wave absorption band *(Fig. 1)* can be observed on comparing the spectrum of the 'unsubstituted' triazacyanine **6a** with those of the 4,4′,7,7′-tetrasubstituted dyes **6b**-**6d**. Apart from a general hypso- and hypochromic shift, the substituted dyes **6b**-**6d** exhibit a distinctly enhanced second maximum at the position of the shoulder on the short-wave side of the spectral band of **6a**.



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10a n = 3
10b n = 4
10c n = 6
10d n = 8

Kalk [9] found the same features with the bridged triazacyanines **10** in ethanol *(Table 1)*; while **10b** shows a practically symmetrical long-wave band with λ_{max} = 413 nm, the band structures of the remaining compounds are formed with strong second maxima resembling those of **6b**-**6d**.

The appearance of the second band in the absorption spectra near 360 nm can be explained in some ways: a) aggregation, b) addition of solvent molecule, c) different vibrational states, d) equilibrium of 2 conformations A and B, e) 2 different electronic transitions.

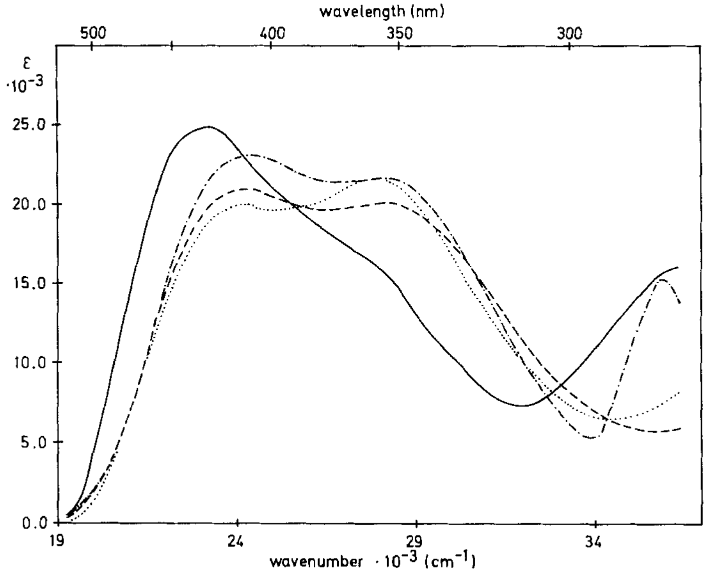


Fig. 1. *Electron absorption spectra of triazatrimethine cyanines* **6a–6d** *at 25° in ethanol/methanol/2-propanol 90:5:5;* ——— **6a**, - - - - - **6b**, -·-·-·- **6c**, ······· **6d**

a) Aggregation, which shows unexpected new bands in the absorption spectra of polymethine dyes [22], can be excluded by the fact that neither the *Beer-Lambert* law is violated at very different concentrations, nor is there any significant dependence of the relative intensities of the 2 bands on temperature (see d));

b) From mechanistic investigations of the alkaline hydrolysis of triazatrimethine cyanines [23], it is known that nucleophilic attack on these dyes in ethanolic solutions occurs in neutral to basic media at C(2) of the heteroaromatic group, resulting in stable adducts which show long-wave absorption bands lying approximately in the same spectral region as the short-wave bands of **6b–6d**. The suspicion that the latter band simply represents solvolysis product being at equilibrium with its starting material can be allayed by the observation that addition of hydrochloric acid (which should shift the equilibrium towards the starting materials) has no influence on the spectra;

c) Vibrational fine structure in electron absorption spectra in conjugated systems shows spacings of usually 600–1500 cm^{-1} (the maximum lying at 2350 cm^{-1} for tetraacetylene) [24]. Comparison of these values with those in the last column of *Table 1* proves that the double bands of **6** and **10** (but not of **9**) cannot be ascribed to vibrational states;

d) Assuming an equilibrium between conformations A and B of the triazacyanine absorbing at different wave-lengths, and expecting them to have different enthalpies, the equilibrium and hence the ratio of the oscillator strengths of the 2 absorption bands as well as their absolute oscillator strengths should depend on temperature. Since the oscillator strength of absorption bands – especially superimposed ones – do not correlate with their extinction maxima but with their integrated area, it was necessary to deconvolute these bands.

In a typical experiment the electron absorption spectrum of an ethanolic solution of **6d** was taken from +60° to −70°. The double band at each temperature was then deconvoluted by means of an optimization program based on the least square method (*Marquardt*-method) on a table computer (HP 9830A) simulating the single spectral bands by equations (1) and (2) [25].

$$E_{\nu_{I},J} = E_{\max,J} \cdot \exp\left(-\left[\frac{\nu_{\max,J}}{\nu_{I,J}} \cdot \frac{\nu_{\max,J} - \nu_{I,J}}{B_J}\right]^2\right) \qquad J = 1,2 \qquad (1)$$

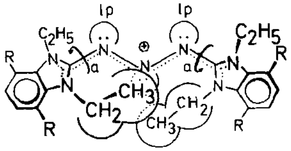
$$E_I = \sum_{J=1}^{2} E_{\nu_{I},J} \qquad (2)$$

$$F_J = \sum_{\nu} E_{\nu,J} \cdot \Delta\nu \qquad (3)$$

Having evaluated extinction $E_{\max,J}$, wave number $\nu_{\max,J}$ and 'band width'-factor B_J of each absorption band J (standard errors $s \approx 1\%$), their respective area F_J was calculated numerically by equations (1) and (3).

The results of the calculations showed no temperature dependence, either of the absolute intensity ($\equiv F_J$) of the bands (standard error $s = 2.6\%$), or of their ratio ($s = 4\%$) in the region of +60° to −72°. These facts exclude the existence of an equilibrium;

e) To explain the different shape of the electron absorption spectra of **10a**, **10c** and **10d** compared with **10b**, *Kalk* [9] supposed an influence of the length of the methylene chains on the planarity of the chromophoric system. From *Stuart-Briegleb-* and *Dreiding*-models he found that only the tetramethylene-bridged cyanine **10b** is nearly planar, whereas the remaining dyes **10a**, **10c** and **10d** are distorted to an extent dependent on the chain length. The same assumption is valid for the tetrasubstituted cyanines **6b**–**6d**, considering the fact that the substituents R (methyl, methoxy and bromine) force the ethyl groups towards the center of the molecule **11** (buttressing effect), thus increasing steric crowding in this region which the system avoids through distortion around bond 'a' (see chapter 4).



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At this point the question arises as to what kind of transition is so extremely sensitive to distortion of the π-system. Three possibilities may be discussed: bathochromic shift of the second π,π^*-transition, increased transition probably of either a π,π^*- or an n,π^*-transition.

In *Table 2* SCF-CI-calculations are compared with experimental data.

These computations were carried out according to the *Pariser-Parr-Pople*-method (PPP) [27], programmed in *Zahradnik*'s version [28]. The 2-center integrals were calculated in accordance with the method of *Mataga & Nishimoto* [29]. *Zahradnik*'s parameter was used, and all Z_{core}-values were taken equal to 1 except

Table 2. *Experimental and calculated electron absorption spectra of* **6d**

Experimental			Calculated[a])	
λ_{max} (nm)	$\lambda^{b)}_{max}$ (nm)	$\varepsilon \cdot 10^{-3}$	λ (nm)	f
414	429	20.8	435	1.44
359	352	21.5	-	-
272	-	9.5	291	0.14

[a]) C-N bond angles $a = 35°$. [b]) After deconvolution.

for the 4 benzimidazole nitrogen atoms for which 1.75 (instead of 2) was chosen. Calculations were based on ideal geometry (bond length 140 pm). Changes of β_{C-N} of the distorted C,N-bonds were considered by equation (4), a being the distortion angle.

$$\beta = \beta_0 \cos a \tag{4}$$

Several SCF-calculations indicated practically no influence of the various substituents and/or rotation around bonds 'a' on the first 2 π,π^*-transitions. No transition - either allowed or forbidden - around 360 nm was found *(Table 2)*. Since the PPP-program used only accounts for π,π^*-absorptions, the results give rise to the assumption that the bond at 360 nm represents an n,π^*-transition. Usually having low oscillator strengths, the latter may increase through distortion of the π-system as in the present case, where rotation around bond 'a' in **11** allows strong interaction of the 'lone-pair'-orbital (lp) with the π^*-orbitals similar to imines [30], where the non-planarity of the π-system is responsible for strong n,π^*-absorption (resulting from interaction of the 'lone-pair'-orbital of the nitrogen atom with the π^*-orbital of the adjacent phenyl ring which is turned out of plane).

3. Investigation of inverse photochromism. - *Electron absorption spectra of photoconversion products. - a) Method.*

Solutions of **6a-6d** in ethanol/methanol/2-propanol 90:5:5 were cooled to −90° to −110° and irradiated for about 30 s at a suitable wave length to obtain total photoconversion. At these temperatures thermal reversibility was suppressed and the spectra of the colourless forms were recorded.

b) Results: Dyes **6a-6d** proved to be photochromic at low temperatures, *i.e.* they underwent photo-bleaching when irradiated with visible light, this conversion being completely thermally reversible. EA-Spectra of the photoconverted forms (denoted as **$6a^{ph}$-$6d^{ph}$**) are collected in *Figure 2.*

A comparison of the spectral data of **$6a^{ph}$-$6d^{ph}$** with those of **$10a^{ph}$-$10d^{ph}$** [9] *(Table 3)* exhibits striking similarities as well as large differences. While **$10c^{ph}$** and **$10d^{ph}$** absorb at the same wavelength as **6^{ph}**, the spectrum of **$10b^{ph}$** experiences only minute hypso- and hypochromic shifts compared with **10b**. The subdivision of **$10a^{ph}$** into **$10a,1^{ph}$** and **$10a,2^{ph}$** needs further explanation. *Kalk* [9] succeeded in separating electrophoretically 2 conformeric species of **10a**, having quite different spectra. Component **10a,1** shows an intense narrow band at 322 nm and a broad weak one at 425 nm, whereas the bands of **10a,2** are of the same intensity, the one at 399 nm still being about twice as broad as the second at 323 nm [9]. It can be seen from *Table 3* that **10a,1** is bleached totally, whereas **10a,2** only exhibits minor changes in the spectrum on irradiation.

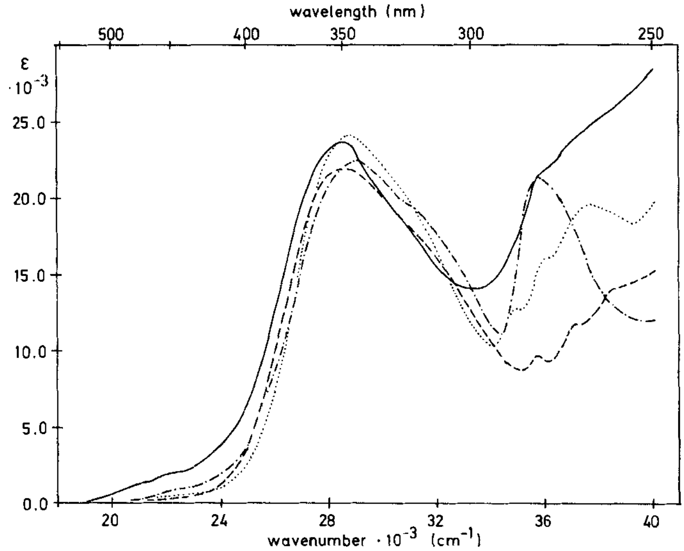


Fig. 2. *Electron absorption spectra of photoproducts* **6a**^{ph}-**6d**^{ph} *in ethanol/methanol/2-propanol 90:5:5 (reduced to 25°);* ——— **6a**^{ph} (−110°), - - - - - **6b**^{ph} (−93°), -·-·-·- **6c**^{ph} (−88°), ······· **6d**^{ph} (−113°)

Kinetics of the thermally reversed reaction. - a) Method.

At various temperatures (ranging from 180-240 K), dyes **6a-6d** and **10b-10d** (**10a** was no longer available) in the solvent mixture mentioned above were irradiated for about 10 s, and the time-dependent spectral change indicating the thermal reaction was recorded at a suitably fixed wave-length immediately after irradiation.

b) Results: kinetic data of the thermal reaction of **6a**^{ph}-**6d**^{ph} and **10b**^{ph}-**10d**^{ph} are collected in *Table 4*. The measurements were repeated in the presence of 0.05 M HCl (10 μl of 7.5 M HCl added to 1.5 ml of dye solution) and showed no significant change. The reactions are purely first order, the *Arrhenius* plots showing excellent linearity (correlation coefficient $r \geq 0.9999$).

Discussion. However different the structure of the starting materials **6a-6d** may be, the structure of the final products **6**^{ph} and **10**^{ph} are alike, except for **10a,2**^{ph} and **10b**^{ph} *(Fig. 2)*.

Table 3. *Electron absorption data of* **6a**^{ph}-**6d**^{ph} *and* **10a**^{ph}-**10d**^{ph} *at low temperatures after maximum photoconversion*

Compound	λ_{max}(nm), (logε)						Temp (K)
6a^{ph}		352 (4.37),		279 (3.99),	271 (4.00)		163
6b^{ph}		349 (4.39),		280 (4.03),	269 (4.12)		180
6c^{ph}		345 (4.40),		280 (4.37)			185
6d^{ph}		348 (4.44)		286 (4.15),	277 (4.26),	265 (4.34)	160
10a, 1^{ph}[a]		350 (3.62),	326 (4.43),		277 (3.73),	270 (3.73)	148
10a,2^{ph}	402 (4.05),		326 (4.20),		278 (3.69),	272 (3.61)	148
10b^{ph}	404 (4.41),			290 (4.00),			123
10c^{ph}		346 (4.40),		281 (4.02),	273 (4.02)		123
10d^{ph}		351 (4.29),		280 (3.85)			123

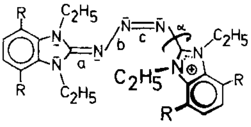
[a]) ph = photoconverted forms; **10a,1**, **10a,2**: see text.

Table 4. *Activation energy* E_A, *action constant* A, *free activation energy* ΔG^*, *activation enthalpy* ΔH^* *and activation entropy* ΔS^* $(\pm\sigma)$ *of the thermal coloration of photo-generated compounds* **6a**$^{\mathrm{Ph}}$-**6d**$^{\mathrm{Ph}}$ *and* **10b**$^{\mathrm{Ph}}$-**10d**$^{\mathrm{Ph}}$ [9] *at 173 K*

Compound	E_A		ΔG^*	ΔH^*	ΔS^*
	(kJ/mol)	log A	(kJ/mol)	(kJ/mol)	(J/mol · deg)
6a$^{\mathrm{Ph}}$	47.41 ± 0.15	11.09 ± 0.04	52.27 ± 0.20	45.97 ± 0.15	-36.4 ± 0.8
6b$^{\mathrm{Ph}}$	51.28 ± 0.52	11.26 ± 0.13	55.58 ± 0.68	49.84 ± 0.52	-33.2 ± 2.5
6c$^{\mathrm{Ph}}$	53.34 ± 0.43	11.63 ± 0.10	56.41 ± 0.55	51.90 ± 0.43	-26.1 ± 2.0
6d$^{\mathrm{Ph}}$	47.39 ± 0.16	11.62 ± 0.04	50.50 ± 0.22	45.95 ± 0.16	-26.3 ± 0.9
10b$^{\mathrm{Ph}}$	37.54 ± 0.26	11.54 ± 0.09	40.91 ± 0.39	36.10 ± 0.26	-27.9 ± 1.7
10c$^{\mathrm{Ph}}$	50.30 ± 0.20	11.42 ± 0.05	54.07 ± 0.26	48.86 ± 0.20	-30.0 ± 0.97
10d$^{\mathrm{Ph}}$	45.29 ± 0.32	10.44 ± 0.08	52.31 ± 0.42	43.85 ± 0.32	-49.0 ± 1.6

Solvent addition is excluded by the fact that the rate of the reverse reaction is not influenced by the presence of hydronium ions. The same holds for the assumption of photo-induced aggregation or dimerization because the decay of the aggregates or dimers would most probably depend on the steric hindrance of the substituents on the chromophores, thus favouring the decay of the most hindered compounds **6b**$^{\mathrm{Ph}}$-**6d**$^{\mathrm{Ph}}$, **10c**$^{\mathrm{Ph}}$ and **10d**$^{\mathrm{Ph}}$ resulting in the lowest activation energy. This is not the case *(Table 4)*.

From similar work on polymethine dyes [10] [22], one may assume *trans/cis*-isomerization for triazacyanines to occur on irradiation. *Stuart-Briegleb*-models, on the other hand, predict a very strained conformation of the *cis*-forms (**12**) with a high torsion angle a (except for **10b**$^{\mathrm{Ph}}$, for which *Kalk* [9] postulates a somewhat differently distorted all-*trans*-form because of the extraordinarily high rigidity of **10b**).



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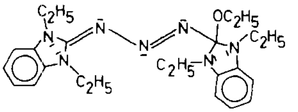
The positive charge is mainly located on the heterocycle turned out of plane leaving a benzimidazolinylidene triazene chromophore. From SCF-CI-calculations, small a-values have little effect on the position of the long-wave band which lies roughly at the same place as that of the all-*trans*-form. Only at greater distortion ($a > 50°$), a distinct hypsochromic shift can be observed. In *Table 5* the spectrum of **6a**$^{\mathrm{Ph}}$ is compared with a calculated one of **12**, where complete decoupling of the triazene- and the benzimidazolium-π-systems is assumed, *i.e.* $a = 90°$. The strong inductive acceptor effect of the second on the first π-system was not taken into consideration. However, it can be shown by means of simple HMO-calculation that electron withdrawing substituents on the terminal N-atom exhibit bathochromic shift of the long-wave band. This, and the unrealistically high a, might explain the gap between calculated and experimental values.

Table 5. *Experimental and calculated electron absorption spectrum of* **6a^{ph}** *and* **12** *(α = 90°) respectively*

Experimental (**6a^{ph}**)		Calculated (**12**)	
λ_{max} (nm)	$\varepsilon \cdot 10^{-3}$	λ(nm)	f
352	23.3	330	1.23
279	9.8	279	0.21
271	10.1	276[a]), 269	0.07[a]), 0.01

[a]) From benzimidazolium part.

Compounds **13** and **14** [9] indicate the general correctness of this picture. *Kalk* [9] ascribed the different EA spectra of **10a,1** and **10a,2**, as being attributed to strained *trans*- and *cis*-forms respectively which are not interconvertible. The photochromic behaviour of these conformers, however, could not be explained.



λ max: 344nm

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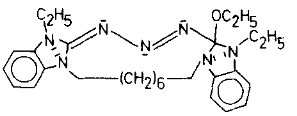

360nm

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The mechanism of the photo-conversion of the remaining dyes can be understood on the basis of an SCF-CI-calculation. *Figure 3* shows electron densities and bond orders in the ground state and their change on excitation into the S$_1$-state. (There is no proof to date, however, that photo-conversion occurs *via* the singlet state and not *via* the triplet state, but the SCF-CI-calculation showed the same general characteristics of the bond orders for the T$_1$-state as for the S$_1$-state).

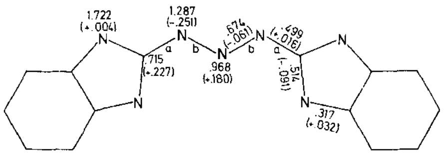
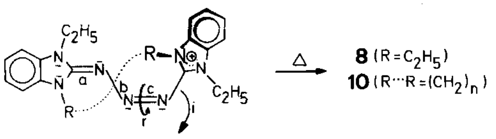


Fig. 3. *Charge density and bond orders in ground state and change (added in brackets) on* S_0*-*S_1*-transition*

Excitation thus strengthens bonds 'a' and at the same time weakens bonds 'b' by this means facilitating rotation around one of the central N,N-bonds.

Calculation of the benzimidazolinylidene triazene part in **12** showed that bonds 'a' and 'c' are weakened, whereas bond 'b' is strengthened. These results suggest that these dyes are photoconvertible in both directions which is in accordance with the fact that **6** and **10** can be restored at low temperatures on irradiation of their photobleached analogues with light of appropriate wave-length. This recovery of the initial dyes is limited, however, at the photo-stationary state [31].

Thermal reconversion of the photo-bleached dyes may proceed either *via* inversion i [30] or *via* rotation r (see **15**). Model considerations allow for both reaction paths except for **10b**^{ph} and **10a**^{ph}. The path of the former, however, begins at a different point *(Table 3)*.



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Kinetic data are ambiguous; the values of the activation energies are in the same range as those for trimethine cyanines [10e] [32] which might lead to the assumption that the mechanism is similar, *i.e.* rotational isomerization might take place. The activation energy of this mechanism would be clearly affected by the bond order of the N,N-bond around which rotation occurs (bond 'c' in **15**). HMO-calculations of the benzimidazolinylidene triazene part in **12** with various substituents R nevertheless yielded no electronic influence at all of R on this bond order. This and the difference of activation energies of **10c**^{ph} and **10d**^{ph} indicate that the variation of E_A in this series is caused by steric effects. However, this does not allow a clear distinction between the 2 mechanisms mentioned above.

4. X-ray investigations. - *Method.*

Dye **6d** was chosen for X-ray measurements because it yielded well-developed crystals. An optically pure, well-formed monoclinic prism of 0.26 · 0.18 · 0.15 mm^3 was used for irradiation. The structure was solved by direct methods (MULTAN-program) using successively structural factor computation and *Fourier* synthesis to localise the non-hydrogen atoms. Block-diagonal least square refinements, first with isotropic, then with anisotropic temperature factors, converged at R = 0.075 for observed reflections and at 0.079 when unobserved reflections ($F_0 > 2\sigma(F_0)$) were included.

Results and discussion. Figure 4 shows a 3-dimensional view of the dye cation. The molecule was projected in a position where one benzimidazole ring lies in the plane of drawing. *Figures 5, 6* and *7* give bond lengths (Å), bond- and torsional angles (degrees) respectively. Estimated standard deviations from least square refinements amount to 0.015-0.020 Å for bond lengths and 1.0-1.3° for angles.

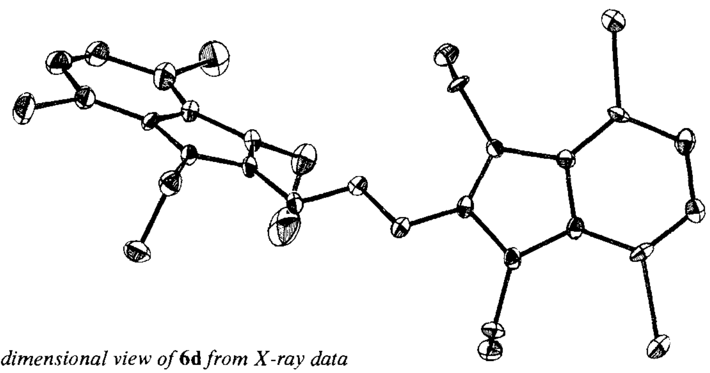

Fig. 4. *Three-dimensional view of* **6d** *from X-ray data*

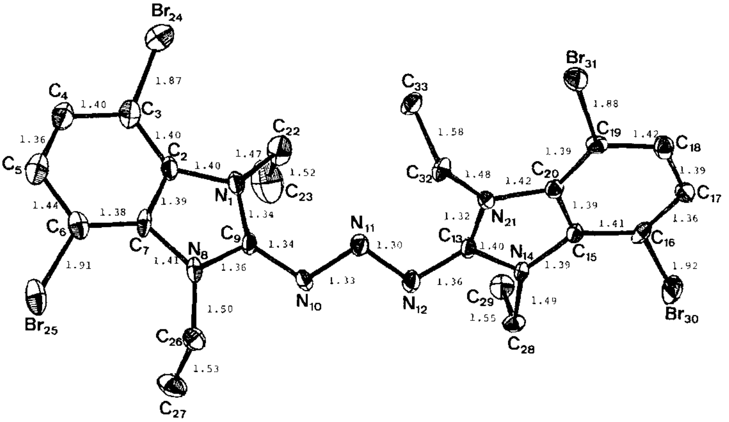

Fig. 5. *Bond lengths of* **6d**

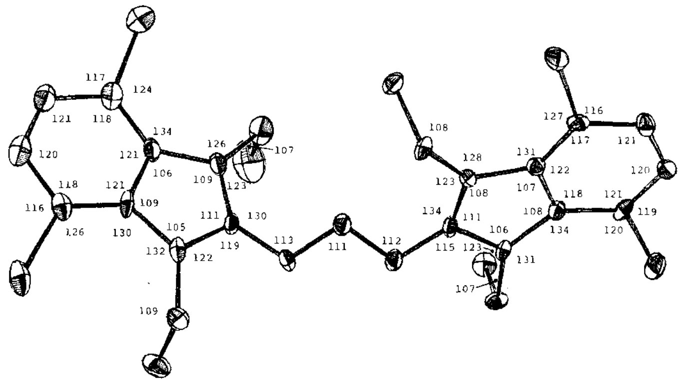

Fig. 6. *Bond angles of* **6d**

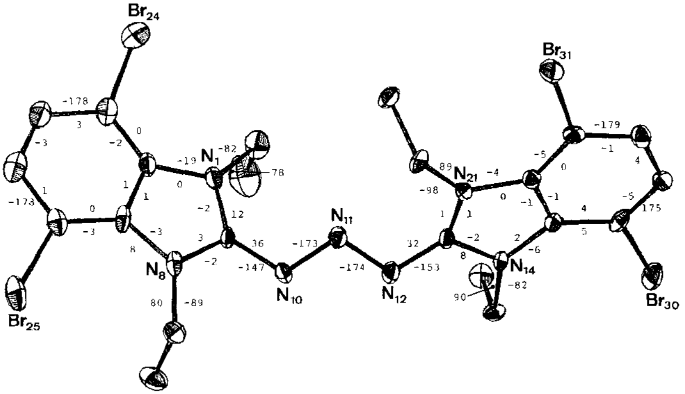

Fig. 7. *Dihedral angles of* **6d**

Obviously the molecule is highly distorted: the centers of the π-system lie in 3 different planes, A, B and C; A and C being formed by the 2 benzimidazole parts and B by the triazatrimethine chain (C(9)–N(10)–N(11)–N(12)–C(13)). The angles between the adjacent planes are about 35°, and 67° between A and C.

Figure 8 shows the content of an elementary cell, projected on the (a,c)-plane. The elementary cell is monoclinic, the measurements being $a = 1752.2 \pm 0.2$ pm, $b = 933.5 \pm 0.2$ pm, $c = 1732.0 \pm 0.42$ pm, $\alpha = \gamma = 90°$, $\beta = 97.33 \pm 0.02°$ and contains 4 molecules.

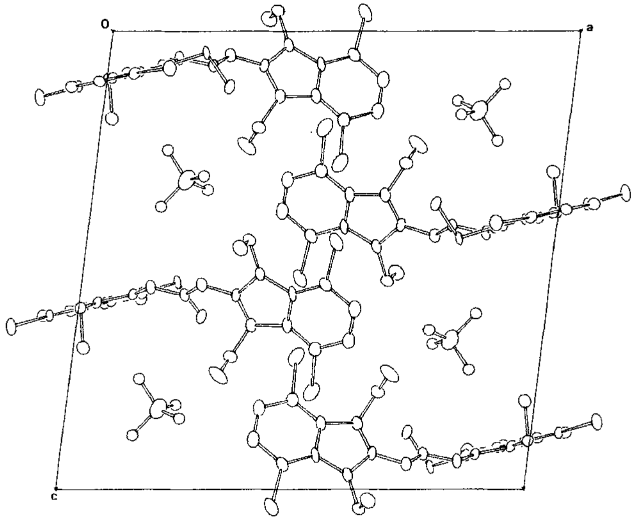

Fig. 8. *Content of an elementary cell of* **6d**, *projected on the (a,c)-plane*

A comparison of these findings with X-ray investigations of analogous, but sterically unhindered planar trimethine cyanines [33], shows that there are at least 2 reasons for the strong distortion of the triazacyanines in question: the first is the evident buttressing effect of the bromine atoms on the neighbouring ethyl group, which can be made out in *Figure 6* to cause a widening of the following angles: C(2)–C(3)–Br(24) (124°), C(7)–C(6)–Br(25) (126°), C(20)–C(19)–Br(31) (127°), all instead of 120°, and C(7)–N(8)–C(26) (132°), C(15)–N(14)–C(28) (131°), C(20)–N(21)–C(32) (128°), instead of ideally 126°. The second reason is the considerably shorter total length of the central chain in the triazacyanines than in the trimethine cyanines caused by both the shorter C,N- and N,N-bonds than the C,C-bonds and the generally smaller bond angles in the central chain (112° ± 1° compared to > 120° in the trimethine chain [33]). The resulting steric hindrance of the internal 2 ethyl groups is minimized mainly by rotation of both benzimidazole parts in opposite directions, and to a lesser degree by enlarging the angles N(1)–C(9)–N(10) and N(12)–C(13)–N(21), *i.e.* bending the heteroaromatic group apart *(Fig. 5)*. Although there is no proof, it seems reasonable to assume that the triazatrimethine dye **6d** retains its distorted conformation in solution. This supports the picture outlined in the discussion of the EA-spectra (chapter 2). The relative size of the second band in these spectra is thus an indicator of the degree of distortion of these π-systems; **6b-6d** are similarly strained, whereas **6a** is much less (but still) distorted, this being caused by the shorter length of the central chain compared with the totally planar trimethine cyanines as mentioned above.

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Experimental Part

General. Electron absorption spectra at room and low temperatures as well as kinetic measurements were recorded on a *Beckman* Acta M-IV spectrophotometer. Cooling device was an *Oxford* Instruments DN-704 cryostat with Digital Temperature Controller DTC-2. Light source was an *Osram* HBO 200 W high-pressure Hg lamp, filtered by *Balzers* K1 and K2 filters. Spectroscopic quality solvents were used. - X-ray measurements were executed on a *Picker* single crystal diffractometer FACS I with $\lambda(\mathrm{CuK}\bar{\alpha}) =$ 154.178 pm. Reflection width was 1.9°, measuring time for background counts was twice 20 s, for reflections 57 to 68 s. The θ-2θ scan technique with Ni-filtered CuK$\bar{\alpha}$-radiation of 50 kV and 50 mA was used. Three reference reflections, (15, 0, 0), (1, 6, 0) and (0, 0, −8) were measured after every 37th reflection to check electronic and crystal stability. 3300 reflections were recorded within the range of $2\theta = 2°-100°$. Those with intensities less than or equal to $2\sigma(I)$ were considered unobserved. The observed reflections numbered 2719 (90%) out of a scaled total of 3024. - Computer calculations were carried out on a *Hewlett-Packard* 9830 A table computer with 9862 A plotter for HMO-, least square optimization-calculations and electron absorption spectra drawings, and a *Univac*-1108-TSO-system for SCF-CI-computations. - Melting points (m.p.) were observed on a heating table with monocular from *Leitz* (Wetzlar) and were corrected. - Micro-elemental analyses were carried out at *Ciba-Geigy AG* and *Sandoz AG.*

Syntheses. - *3,6-Dibromo-*o*-phenylenediamine* (**2d**). In a mixture of 70 ml acetic acid and 30 ml water, 10 g (34 mmol) 4,7-dibromobenzothiadiazole (**1**) [18] were suspended. At 60°, 20 g (306 mmol) Zn dust was added at once and stirred for 3 h while the temperature was maintained at 70°. After warm filtration the brown solution was poured into 300 ml aqueous NaOH-solution (50%) and cooled. The precipitate was extracted with ether; work-up of the ethereal solution yielded 6.2 g (69%) of crude product m.p. 50-56° which was recrystallized from water to give white needles, m.p. 92-94° ([34], 94.5°).

4,7-Dimethylbenzimidazol-2-one (**3b**). A mixture of 3.47 g (255 mmol) 2,3- and 2,5-diamino-*p*-xylene [14] was mixed with 4.59 g (78.5 mmol) urea and heated to 170° under N_2. After 3 h the black solid was boiled in 200 ml of 2N NaOH with charcoal, filtered, the yellowish filtrate neutralized by acetic acid and the precipitate filtered off. Recrystallization from ethanol/water gave 900 mg (22%) of colourless needles, m.p. 287°.

$C_9H_{10}N_2O$	Calc.	C 66.65	H 6.21	N 17.27	O 9.86%
(162.2)	Found	,, 66.58	,, 6.16	,, 17.51	,, 10.13%

4,7-Dibromobenzimidazol-2-one (**3d**). Using the same procedure as for **3b**, 8 g (30 mmol) **2d** reacted with 5.4 g (90 mmol) urea to yield 5.8 g (66%) of product after recrystallization from amylalcohol, m.p. 302° (contraction from 240°).

$C_7H_4Br_2N_2O$	Calc.	C 28.80	H 1.38	Br 54.74	N 9.60	O 5.48%
(291.9)	Found	,, 28.9	,, 1.4	,, 55.0	,, 9.4	,, 5.6 %

2-Chloro-4,7-dimethylbenzimidazole (**5b**). A suspension of 3 g (18.5 mmol) **3b** in 30 ml of phosphorus oxychloride was heated under reflux for 26 h. The clear yellow solution was poured onto 500 g of ice and stirred until total decomposition of the phosphorus oxychloride. Neutralization with conc. ammonia precipitated a white solid which was filtered off, 3.06 g (91.6%), m.p. 210-213° (contraction) (from ethanol/water).

$C_9H_9ClN_2$	Calc.	C 59.84	H 5.02	Cl 19.63	N 15.51%
(180.6)	Found	„ 59.84	„ 5.00	„ 19.57	„ 15.54%

2-Chloro-4,7-dibrombenzimidazole (**5d**). Treating 7.5 g (25.7 mmol) **3d** in 13 ml phosphorus oxychloride and working up the reaction mixture the same way as for **5b** gave 7.25 g (91%) of crude **5d**, m.p. 243-246° (from ethanol/water) (dec.; [35] 201-203°).

$C_7H_3Br_2ClN_2$	Calc.	C 27.09	H 0.97	Br 51.49	Cl 11.42	N 9.03%
(310.4)	Found	„ 27.34	„ 0.87	„ 51.55	„ 11.08	„ 9.06%

2-Chloro-4,7-dimethyl-1-ethylbenzimidazole (**1b**). A solution of 1.5 g (8.31 mmol) **5b** in 30 ml 1N NaOH at 60°, was treated with 5.76 g (4.8 ml, 37 mmol) diethylsulfate in 0.6 ml portions over 1 h and stirred for a further 15 min. After cooling, the brownish emulsion was extracted with ether, washed twice with 1N NaOH, 3 times with water, and dried ($MgSO_4$). Evaporation of the solvent gave 1.67 g (96.3%) of a pink oil, which solidified slowly, m.p. 70-79° (from benzene/hexane).

$C_{11}H_{13}ClN_2$ (208.7) Calc. C 63.31 H 6.28 N 13.42% Found C 63.47 H 6.39 N 13.30%

2-Chloro-4,7-dimethoxy-1-ethylbenzimidazole (**1c**). A solution of 500 mg (2.35 mmol) 2-chloro-4,7-dimethoxybenzimidazole [15] in 15 ml 1N NaOH reacted at RT. with 1.6 g (1.36 ml, 10.46 mmol) diethylsulfate in 0.2 ml portions over 1 h under vigorous stirring, continuing for another 20 min at 60°. Working up the brown emulsion as with **1b** gave 540 mg of an oil which was chromatographed (silicagel, $CHCl_3$) into 2 fractions. The first fraction was **1c**, m.p. 70-79°.

$C_{11}H_{13}ClN_2O_2$	Calc.	C 54.89	H 5.44	Cl 14.73	N 11.64%
(240.7)	Found	„ 54.58	„ 5.48	„ 14.58	„ 11.43%

The second fraction was 1,3-diethyl-4,7-dimethoxybenzimidazol-1-one, m.p. 113-115°. - IR. (KBr): 1690 cm^{-1} (strong, C=O).

$C_{13}H_{18}O_3N_2$ (250.3) Calc. C 62.38 H 7.25 N 11.19% Found C 62.24 H 7.24 N 11.19%

2-Chloro-4,7-dibromo-1-ethylbenzimidazole (**1d**). A mixture of 2.4 g (7.72 mmol) **5d**, 3.86 g (5.08 ml, 29.8 mmol) diisopropylethylamine and 2.24 g (1.88 ml, 14.4 mmol) diethylsulfate was heated in 16 ml of dimethylformamide (DMF) under reflux for 2.5 h. The reaction mixture was then poured into water and the whitish emulsion extracted with ether. Careful washing of the ether phase with water, drying ($MgSO_4$) and evaporation of the solvent gave, in a quantitative yield, a pale yellow oil which solidified slowly. Recrystallization from hexane produced colourless needles, m.p. 94-95°.

$C_9H_7Br_2ClN_2$	Calc.	C 31.94	H 2.08	Br 47.22	Cl 10.48	N 8.28%
(338.5)	Found	„ 32.06	„ 2.16	„ 47.09	„ 10.51	„ 8.32%

4,7-Disubstituted 2-chloro-1,3-diethylbenzimidazolium tetrafluoroborates (7). - *General procedure:* 4,7-disubstituted 2-chloro-1-ethylbenzimidazole was stirred at RT. in dry ethylene chloride with 1.5 to 2 equiv. of triethyloxonium tetrafluoroborate (washed 4 times with dry ether) for 6 to 22 h. Addition of ether precipitated the crude product which was then recrystallized from ethanol/ether or acetonitrile/ethyl acetate.

7b: 600 mg (2.87 mmol) **1b** and 800 mg (4.2 mmol) of triethyloxonium tetrafluoroborate in 10 ml ethylene chloride gave after 17 h 550 mg (53%) **7b**, m.p. 156-158° (ethanol/ether).

$C_{13}H_{18}BClF_4N_2$	Calc.	C 48.11	H 5.59	Cl 10.92	F 23.42	N 8.63%
(324.6)	Found	„ 48.20	„ 5.61	„ 10.82	„ 23.23	„ 8.69%

7c: 2 g (8.32 mmol) **1c** and 2.8 g (14.7 mmol) triethyloxonium tetrafluoroborate in 10 ml of ethylene chloride after 22 h gave 2.25 g (75%) **7c**, m.p. 156-158° (ethanol/ether).

$C_{13}H_{18}BClF_4N_2O_2$	Calc.	C 43.79	H 5.09	Cl 9.94	F 21.31	N 7.86%
(356.6)	Found	„ 44.07	„ 5.22	„ 9.84	„ 21.49	„ 8.35%

7d: 2 g (5.92 mmol) **1d** reacted with 1.6 g (8.4 mmol) triethyloxonium tetrafluoroborate in 20 ml ethylene chloride for 6.5 h to give 2.13 g (79%) **7d** which, after purification from acetonitrile/ethyl acetate, contracted at 280° without melting.

$C_{11}H_{12}BBr_2ClF_4N_2$	Calc.	C 29.08	H 2.66	Br 35.18	Cl 7.80	F 9.58	N 6.17%
(454.3)	Found	„ 29.21	„ 2.67	„ 35.25	„ 7.74	„ 9.64	„ 6.26%

*4,7-Di-X-2-[3-(4,7-di-X-1,3-diethyl-1,3-dihydro-*2H*-benzimidazol-2-ylidene)-1-triazenyl]-1,3-diethylbenzimidazolium tetrafluoroborates* (**6**). - *General procedure:* a solution of **7** in very little methanol reacted at RT. with exactly 1 equiv. of sodium azide, the white precipitate was filtered off after 5 min at 5° and washed with cold methanol to give crude 4,7-disubstituted 2-azido-1,3-diethylbenzimidazolium tetrafluoroborate **8**. After drying at RT. and without further purification, **8** reacted in a little dry DMF with 0.5 equiv. of sodium azide with ice cooling to keep the solution at RT. After 2 to 2.5 h of stirring, the yellow solution was diluted carefully with water and the yellow precipitated product was filtered off and washed with water.

6b (X = methyl): 500 mg (1.54 mmol) **7b** and 99.6 mg (1.54 mmol) sodium azide in 2 ml methanol gave 450 mg (1.36 mmol, 88.2%) crude **8b**, m.p. 116-120°, which reacted in 2 ml DMF with 4.4 mg (0.68 mmol) sodium azide to yield 200 mg (55.2%) **6b**, m.p. 178-180° (acetone/ether).

$C_{26}H_{36}BF_4N_7$	Calc.	C 58.54	H 6.80	F 14.25	N 18.38%
(533.4)	Found	„ 58.73	„ 6.81	„ 14.20	„ 18.40%

6c (X-methoxy): 356.6 mg (1 mmol) **7c** and 65 mg (1 mmol) sodium azide in 1.5 ml of methanol gave 300 mg (82.6%) of crude **8c**, m.p. 130-133° (dec.). This reacted with 27 mg (0.415 mmol) sodium azide in 1.5 ml DMF to yield 150 mg (61%) **6c**, m.p. 200-201° (acetone/ether).

$C_{26}H_{36}BF_4N_7O_4$	Calc.	C 52.27	H 6.07	F 12.72	N 16.41%
(597.4)	Found	„ 52.20	„ 6.14	„ 12.90	„ 16.47%

6d (X = bromine): 2.13 g (4.68 mmol) **7d** and 304.6 mg (4.68 mmol) sodium azide in 7 ml of methanol gave 1.84 g (85%, 4 mmol) of **8d**, m.p. 170-174°, which reacted in 10 ml DMF with 129 mg (2 mmol) sodium azide to yield 1.4 g (88.3%) **6d**, m.p. 253-256° (red-orange prisms from acetone or ethanol). - ^1H-NMR. (DMF): 1.53 (*t*, $J = 7$ Hz, CH_3); 3.89 (*qa*, $J = 7$, *N*-CH_2); 7.71 (*s*, arom. H). - ^{13}C-NMR. (DMF): 16.25 (C(23), C(27), C(29), C(33), see *Fig. 5*); 42.37 (C(22), C(26), C(28), C(32)); 104.44 (C(3), C(6), C(16), C(19)); 130.83 (C(2), C(7), C(15), C(20)); 132.25 (C(4), C(5), C(17), C(18)); 155.07 (C(9), C(13)).

$C_{22}H_{24}BBr_4F_4N_7$	Calc.	C 33.32	H 3.05	Br 40.31	F 9.58	N 12.37%
(793.0)	Found	„ 33.52	„ 3.07	„ 40.39	„ 9.64	„ 12.42%

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