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A NEW ROUTE TO TRINUCLEAR CARBOCYANINES[1]

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Abstract—Amides or vinylogous amides react with tosyl chloride–pyridine to form activated intermediates which condense with Fischer's base or their vinylogs to give carbocyanine structures. Under the same conditions formylated Fischer's base reacts with vinylogous Fischer's bases to give trinuclear carbocyanines in good yields. Their structure and the limitations of this route are discussed.

In a previous publication,[2] we have shown the possibility of preparing azatrienes **3**, by condensing heterocyclic dienamines **1** with the isonitrosomalonic derivative **2** (Scheme 1).

The heterocyclic dienamines **1a–c** have been obtained by condensing the Fischer's base **4** with the corresponding aldehydes (propionaldehyde for **1a**; butyraldehyde for **1b**; phenylacetaldehyde for **1c**). The non-substituted dienamine **5a** and its vinylogous **5b** are not accessible by this method since they condense with Fischer's base **4** present in the reaction mixture to form the dienamines **6**[2] and **7**[3] (Scheme 2). This reaction may be compared with the dimerisation of the methylene-anhydrobases of benzothiazoles or quinolines.[4]

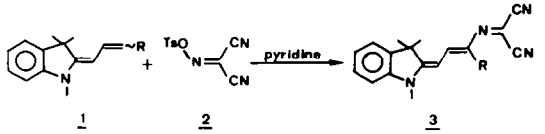
In the present paper we describe the preparation of the polyenamines **5a** and **5b** from the formylated Fischer's base **8** and Grignard reagents. Indeed the preliminary attempts at synthesis led to the mixtures of formylated Fischer's base **8** and trienamine **5b** which give, with the isonitroso-derivative **2**, coloured products with carbocyanine characteristics and not analogous of **3**. This statement may be explained if the isonitroso-derivative **2** acts as tosylating agent and consequently as an activating agent of the formylated Fischer's base **8**.

On this basis the synthesis of trinuclear or dinuclear cyanines by condensation of polyenamines **5** with the formylated Fischer's base **8** in the presence of tosyl chloride and pyridine was carried out (Scheme 3).

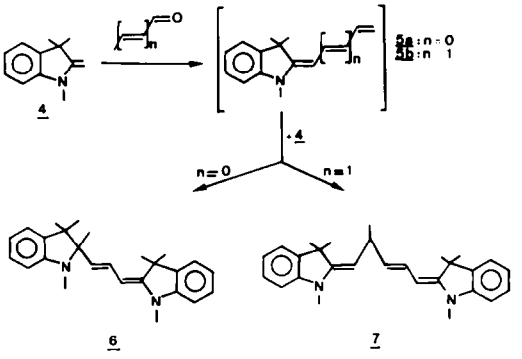
Synthesis of the polyenamines **5** *and the trinuclear cyanines* **9** *and* **10**

The reaction of the formylated Fischer's base **8**, readily accessible by Vilsmeier's reaction,[5] and methylmagnesium iodide or allylmagnesium bromide allows ethereal solutions of the polyenamines **5** to be obtained.

Thus, by addition of an ethereal solution of the formylated Fischer's base **8** (1 equiv.) to an ethereal solution of the allylmagnesium bromide (3 equivs of allylbromide and magnesium), we obtain, after



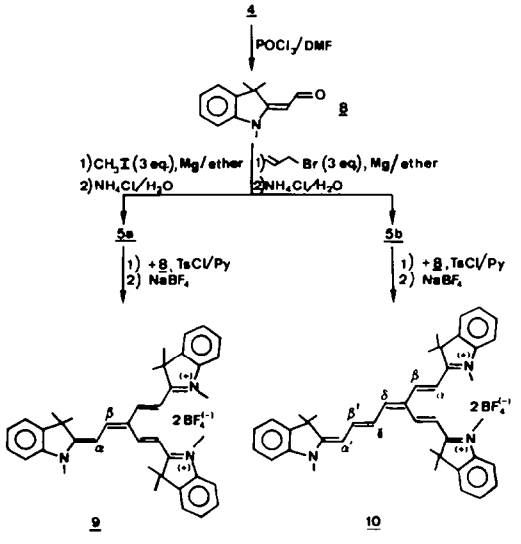
Scheme 1. **1a**, **3a**: R = CH_3; **1b**, **3b**: R = C_2H_5; **1c**, **3c**: R = C_6H_5.



Scheme 2.

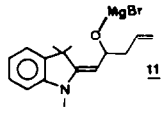
treatment with aqueous ammonium chloride, a solution of the heterocyclic trienamine **5b**, free from the original formylated base **8**. Due to its instability, this trienamine **5b** could be characterized only through its ^{1}H-NMR spectrum.

The use of 3 equivalents of allylbromide to 1 equivalent of formylated base **8** may be justified thus: it is well known[6] that during the reaction of Mg on allylbromide 1,4-hexadiene is formed (~20–30% of the



Scheme 3.

allylbromide used, depending on the reaction conditions). If two equivalents of allylbromide (i.e. about a stoichiometric quantity of allylmagnesium bromide) are reacted with the base **8**, one observes the formation of a yellow precipitate which on treatment with aqueous ammonium chloride provides a mixture of trienamine **5b** and of the formylated derivative **8**. It is reasonable therefore, to assume that in the absence of an excess of allylmagnesium bromide the reaction stops, at least partly at an intermediate of type **11**. Aqueous treatment of this intermediate results in the reformation of the formylated Fischer's base **8**. The phenomenon of reversible Grignard reactions has been documented previously.[7]



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The utilization of an excess of allylmagnesium bromide apparently decomposes this intermediate into **5b** and thus prevents the reformation of the formylated base.

In a similar way the dienamine **5a** can be obtained by reacting an excess of methylmagnesium iodide with the formylated Fischer's base **8**.

The addition of formylated base **8** to these ethereal solutions of polyenamines **5** in the presence of tosyl chloride and pyridine, almost instantaneously yields a colouring that becomes more accentuated in the course of time. By the end of the reaction, the cyanines **9** and **10** precipitate. These are purified and recrystallized as tetrafluoroborate.

Structure of the cyanines **9** *and* **10**

The cyanine **9** has been prepared by Reichardt and Mormann[8] from triformylmethane and 1,2,3,3-tetramethylindolenine salt. Its spectroscopic properties, which have been reported by these authors and by Grahn[9] (^{13}C-NMR) are identical to those of our own sample.

The spectroscopic data of the cyanine **10** have been summarized in Table 1. Using ^{1}H-NMR we found two vinyl protons with a coupling constant of 15 Hz corresponding to the two equivalent methinic chains. The vinyl protons of the branch with four methines can be clearly assigned, except perhaps the γ-proton which disappears under the massif of the aromatic protons. A distinction may also be observed between the two types of $C(CH_3)_2$ groups in each type of branch and the two types of methyl attached to the nitrogen. ^{13}C-NMR also allows identification of every carbon in the system (except the γ- and ε-carbons). The chemical shifts both in ^{1}H- and ^{13}C-NMR correspond perfectly to the

Table 1. Spectroscopic data of pentamethine cyanine **16** and trinuclear cyanines **9** and **10**

		Cyanine					
		9		**10**		**16**	
UV/VIS	solvent	MeOH	MeOH + traces of Et_3N	MeOH	MeOH + traces of Et_3N	MeOH	
	λ_{max} (nm)	635	635	635–687	635–737	637	
	log ε	5.20	—	4.96	—	5.26	
NMR (δ ppm/TMS; multip.; intensit.)	position	^{1}H[8] $(CD_3)_2CO$	^{13}C[9] DMSO-d_6	^{1}H $(CD_3)_2CO$	^{13}C $CDCl_3$	^{1}H $(CD_3)_2CO$	^{13}C[9] DMSO-d_6
	α	7.11; d; 1	106.5; d	6.90; d; 2	102.7; d	6.25; d; 2	103.3
	β	8.51; d; 1	149.5; d	8.38; d; 2	149.6; d	8.15; t; 1	154.0
	α'	—	—	7.25; d; 1	112.5; d	6.72; t; 1	—
	β'	—	—	8.53; t; 1	145.7; d	—	—
	γ	—	121.8; s	~7.5; m; 1	—	—	125.2
	δ	—	—	8.25; d; 1	157.5; d	—	—
	Arom.	~7.6; m; 4	—	~7.5; m; 12	—	~7.6; m; 8	
	$C(CH_3)$	1.86; s; 6	26.4; q	1.82; s; 12 1.83; s; 6	26.3; q 27.8; q	1.72; s; 12	26.9
	$N—CH_3$	4.05; s; 3	32.8; q	3.93; s; 6 4.05; s; 3	33.0; q 32.2; q	3.68; s; 6	30.9
	^{1}H-NMR ^{3}J	(α,β) = 15 Hz		$(\alpha,\beta) = (\alpha',\beta') = (\beta,\gamma) = (\gamma,\delta) =$ 15 Hz		$(\alpha,\beta) = (\beta,\gamma) =$ 14 Hz	

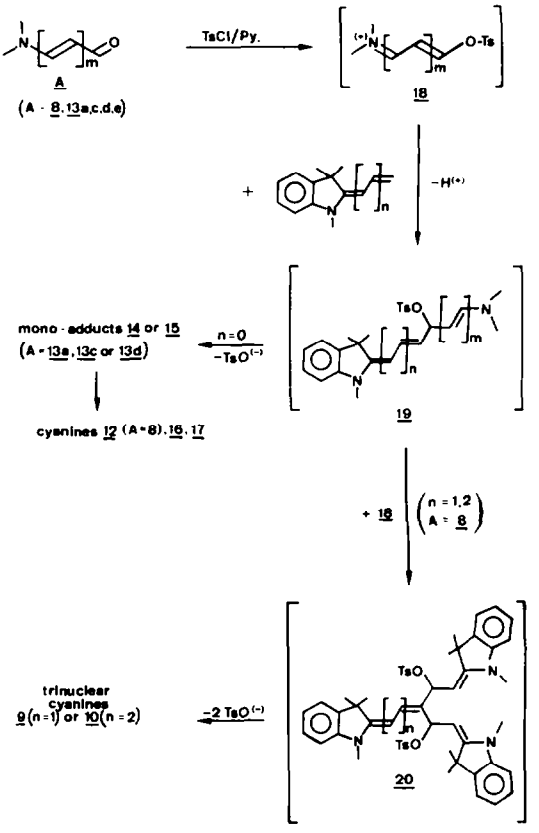
proposed structure. For a comparison NMR data for the dinuclear pentamethine cyanine **16** are included in Table 1.

In the case of the symmetrical trinuclear cyanine **9** UV/VIS spectroscopy reveals the existence of various conformers, as proposed by Reichardt and Mormann.[8] The maxima occurring at 635 nm and 737 nm (in the case of **10**) therefore may correspond to a penta- or heptamethine cyanine conformer substituted in the γ-position by a lateral chain oriented perpendicularly; the latter peak is observed on the addition of small quantities of triethylamine to the methanol medium. The maximum at 687 nm is most likely due to the presence of a third conformer disfavoured in polar medium.

Extension of the reaction mechanism

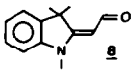
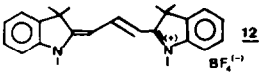
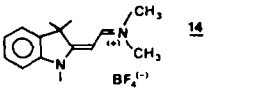
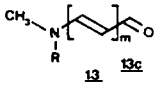
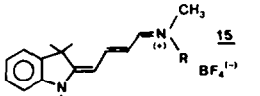
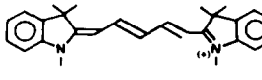
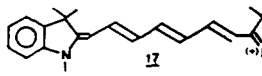
A parallel may be drawn between the reaction of the formylated Fischer's base **8** in the presence of tosyl chloride and pyridine, and the Vilsmeier's reaction. We have examined therefore whether this type of reaction can be applied to the Fischer's base **4** itself and whether other amide derivatives are suitable for such condensations. Table 2 summarizes the attempted reactions.

With the Fischer's base **4**, the absence of a structure with branched chains of the type **9** or **10**, results in all cases. Hence, the trimethine cyanine **12** is the condensation product which is observed with the formylated base **8**. With DMF or vinylogous amides of type **13** the reaction stops at either a monoadduct of type **14**, or a mixture of monoadduct **15** and dinuclear pentamethine cyanine **16** or else at the heptamethine cyanine **17**. As has already been observed[10] **16** and **17** may form simultaneously. It is also noteworthy that the



Scheme 4.

Table 2. Reaction of the Fischer's base **4** with amides or vinylogous amides in the presence of tosyl chloride and pyridine

Amides	Reactions product
 **8**	 **12**
m R	
13a 0 CH_3	 **14**
13b 0 C_6H_5	No reaction
 **13** **13c** 1 CH_3	 **15**
13d 1 C_6H_5	 **16**
13e 2 C_6H_5	 **17** + **16**

N-methyl-N-phenyl-formamide **13b** does not react under the same conditions.

All these observations enable us to rationalize the formation of the trinuclear cyanines **9** and **10**. The tosyl chloride/pyridine obviously activate the amides A (formamide **13a**, their vinylogous **13c–d** or the cyclic analogue **8**, Scheme 4) by forming very reactive tosylated derivatives of type **18**. These tosylated amides react with the methylene-anhydrobases and lead to intermediates of type **19** which themselves possess an enamine character. For n = 0 (in the case of Fischer's base **4**) the nucleophilic carbon in position α in the chain is likely to be hindered and the system evolves to the monoadducts **14** and **15** or the cyanine **16**. Cyanines may be synthesised from the monoadducts via well-established routes.[11] For n = 1 respectively 2, the terminal nucleophilic carbon is more easily accessible to the electrophilic reagent **18** and can therefore lead to the formation of an intermediate of type **20** bearing a branched chain; compound **20** is a precursor of trinuclear cyanines. The existence of the intermediates **18** can be established by ^{1}H-NMR spectroscopy (Experimental) and they may represent a mean by which 1, 3 or 5 carbons can be introduced into a nucleophilic system under mild conditions. Research is at present orientated in this direction.

EXPERIMENTAL

M.ps were taken on a Büchi m.p. apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a Varian T-60, Bruker WP-80-CW and Bruker WP-80. The ^{13}C-NMR spectrum was recorded on a Brucker WP-80 operating at 20.1

MHz. Chemical shifts are given as δ-values in ppm relative to TMS and J-values are in hertz. UV/VIS spectra were recorded on a Perkin–Elmer 550-SE UV/VIS-spectrophotometer. Elemental analyses were performed by Service Central d'Analyses, C.N.R.S., Vernaison.

The following compounds were prepared according to the published procedures: **8**, yield 81%/**4**, m.p. = 115–116°;[5b] **13c**, yield 82%/propargylalcohol, b.p.$_{0.5}$ = 110°;[12] **13d**, yield 55%/pyridine, m.p. = 78–80°.[13]

Activation of formylated Fischer's base **8** *by tosyl chloride and pyridine*

To a soln of formylated **8** (35 mg, 0.17 mmol) in about 250 μl $CDCl_3$ in an NMR-tube, was added 18 mg (0.09 mmol) tosyl chloride and 1 μl pyridine-d_5. Initially a signal arising from the N—CH_3 group of **8** was observed (δ3.3), but after a few minutes a second N—CH_3 signal (δ4.3) appeared; this may be attributed to the activated species **18** (integration δ3.3/4.3 = 1.3 after 2 hr).

Synthesis of 2-*pentadienylidene*-1,3,3-*trimethylindoline* **5b**

A 250 ml two necked round-bottomed flask fitted with a reflux condenser (protected with a $CaCl_2$ drying tube) and a pressure-equalizing dropping funnel was charged with Mg turnings (0.98 g, 41 mg atom) and flame dried. After the flask was cooled to room temp 30 ml of anhyd ether was introduced, followed by the dropwise addition of allylbromide soln (1.4 g, 11.6 mmol of allylbromide in 12 ml of anhyd ether). The mixture was stirred magnetically at room temp. After a few min an exothermic reaction started and the mixture turned grey. After completion of the addition (~40 min) the mixture was stirred for a further 3 hr at room temp.

A soln of formylated **8** (0.8 g, 4 mmol) in 60 ml anhyd ether was now added dropwise to the mixture at room temp. The formation of a yellow ppt on the addition of each drop was observed; this ppt dissolved with stirring. Upon completion of the addition, the mixture was stirred for 15 min at room temp and the Mg suspension left to settle down.

The clear soln was decanted into a separating funnel containing ~80 g of ice. Again a yellow ppt formed which dissolved on shaking with 60 ml of ice-cooled NH_4Cl aq (5%). The ethereal phase was separated, washed with 3 × 20 ml of ice-cooled water and filtered through hydrophobic Whatman paper 1PS.

TLC-analysis of the filtrate gave only a single spot of **5b** (R_f = 0.7, eluent: $CHCl_3$–n-heptane–EtOAc, 1:1:1 volume ratio). ^{1}H-NMR (after removal of ether) ($CDCl_3$): δ1.6 (s, 6H, $C(CH_3)_2$); 3.0 (s, 3H, N—CH_3); 4.6–5.5 (m, 4H, $H_\alpha + H_\gamma + 2H_\varepsilon$); 6.4–7.4 (m, 5H, $H_{ar} + H_\beta$); 5.7–6.3 (m, 1H, H_δ).

1,7,9 - *Tris*[1,3,3 - *trimethyl* - *indoline* - 2 - *yl*] - [4,2,2]*nonamethindium bisterafluoroborate* **10**

To a fresh ethereal soln of **5b** was added 1.2 g (6 mmol) of formylated **8** followed by 1.5 g (19 mmol) of dry pyridine and 1.9 g (10 mmol) of tosyl chloride, the latter added in small portions. After a few min a coloured mixture (dark blue) was obtained which was stirred at 32° for a further 16 hr.

Upon cooling to room temp the solvent was removed by decantation and the solid product dissolved in 30 ml of hot aqueous MeOH (MeOH–H_2O, 2:1 by volume). A hot soln of sodium tetrafluoroborate (1.2 g in 10 ml H_2O) was subsequently added; the mixture was kept at 60° for 30 min. Upon cooling to room temp **10** was obtained in crystalline form, filtered off, washed with ether and cold water and dried in a desiccator (1.98 g, 65% yield/formylated base **8**).

Analytical sample was prepared by recrystallization from aqueous MeOH (MeOH–H_2O, 4:1 by volume). M.p.: 195° (dec). (Found: C, 65.49; H, 6.11; N, 5.33. Calc for ($C_{42}H_{47}B_2F_8N_3$, 767.47): C, 65.73; H, 6.17; N, 5.48%.)

UV/VIS spectrum (MeOH): λ_{max} = 687 nm (log ε = 4.76); 635 nm (log ε = 4.96). Addition of traces of triethylamine give rise to peaks at λ_{max} = 737 and 635 nm (Fig. 1).

^{1}*H-NMR*: See Table 1.

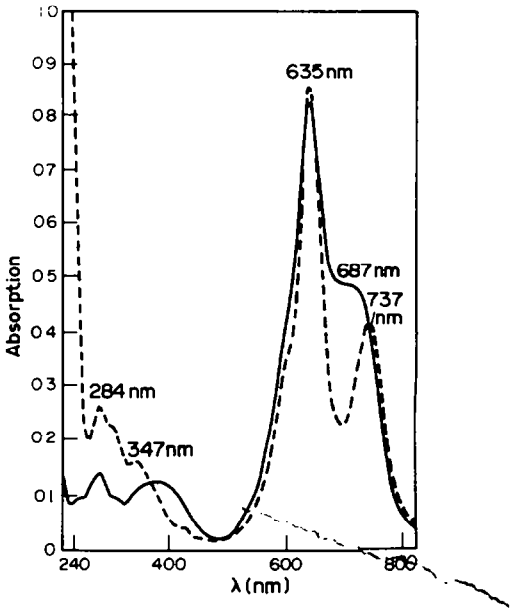


Fig. 1. UV/VIS-absorption spectrum of **10** in MeOH (——) and in MeOH–triethylamine 8×10^2:1 by volume (——).

Synthesis of 2-*propenylidene*-1,3,3-*trimethylindoline* **5a**

The synthesis of **5a** was carried out as described for the synthesis of **5b**. Thus the Grignard's reagent was prepared by the addition of 15 ml of MeI soln (2.13 g, 15 mmol in 15 cm^3 anhyd ether) to an ethereal suspension of Mg in anhyd ether (0.98 g, 41 mg atom of Mg in 30 cm^3 of ether); a soln of formylated **8** (1.1 g, 5.5 mmol of **8** in 60 cm^3 of anhyd ether) was added to the soln of Grignard reagent. Upon completion of the addition the mixture was stirred for 30 min at room temp.

The mixture was worked up as described previously. TLC-analysis gave a single spot (R_f 0.8, eluent: $CHCl_3$–n-heptane–EtOAc, 1:1:1 volume ratio).

The ^{1}H-NMR spectrum of the oil obtained after evaporation of solvent is complex (multiple $C(CH_3)_2$ and N—CH_3 signals), corresponding probably to a dimer.

For the synthesis of **9** a fresh ethereal soln of **5a** was reacted directly with formylated **8** (1.4 g, 7 mmol) in presence of pyridine (1.6 g, 20 mmol) and tosyl chloride (1.9 g, 10 mmol). The mixture was stirred for about 16 hr at room temp and the solid product obtained was treated with an aqueous soln of sodium tetrafluoroborate (1.5 g of $NaBF_4$, 15 ml H_2O) as described previously. Yield: 2.23 g, 55%/formylated base **8**.

For spectroscopic analysis 1.8 g of the product was recrystallized from hot aqueous MeOH (17 ml MeOH + 13 ml H_2O) yielding 1.3 g of fine crystals which displayed a green metallic lustre. Spectroscopic data are summarized in Table 1.

Synthesis of the trimethine cyanine **12**

To a soln of 0.8 g (4 mmol) of formylated **8** in 40 ml anhyd ether, was added 0.7 g (4 mmol) of **4** (fresh distl.) and 0.5 g (6.3 mmol) of dry pyridine. Tosyl chloride (0.8 g, 4.2 mmol in 10 ml anhydrous ether) was added dropwise and the resulting coloured mixture refluxed with stirring for 2 hr.

After cooling to room temp, the solvent was removed by decantation and the solid residue treated with an aqueous soln of sodium tetrafluoroborate (1.8 g in 20 cm^3 H_2O). A viscous product was obtained and was taken up in 35 ml $CHCl_3$, washed with 3 × 40 ml cold water and filtered through Whatman-paper (1PS). The filtrate was concentrated to half its volume and cooled to −5° where upon a solid crystalline product was obtained (1.5 g, 85%/**8**); it was recrystallized from aqueous MeOH (MeOH–H_2O, 4:1 by volume ratio).

UV/VIS spectrum (96% EtOH): λ_{max} = 547 nm (log ε

– 4.87); λ_{max} – 548 nm.[14] ^1H-*NMR* ($CDCl_3$ TMS) δ1.73 (s, 12H, 2 × $C(CH_3)_2$); 3.73 (s, 6H, 2 × N—CH_3); 6.77 (d, 2H, 2H_γ, $J_{\gamma,\beta}$ – 14 Hz); 7.0–7.57 (m, 8H, H_{ar}); 8.40 (t, 1H, H_β).

Synthesis of the monoadduct **14**

To an ethereal mixture (45 cm^3 anhyd ether) of **4** (1.7 g, 10 mmol, fresh distl.), N,N-dimethylformamide (2.2 g, ~ 30 mmol) and dry pyridine (1.5 g, 19 mmol), was added in small portions and with magnetic stirring, tosyl chloride (1.9 g, 10 mmol). After stirring for a further 16 hr, at 45° (bath temp) the condensation product precipitated.

On cooling to room temp and subsequent removal of solvent by decantation, the residue was treated with an aqueous sodium tetrafluoroborate solution as described for **10**. A dark-grey crystalline product was obtained which was filtered, washed with cold water and dried (2.1 g, 67%, **4**). The following spectroscopic data for the salt **14** was obtained without further purification.

UV/VIS spectrum (96% EtOH) λ_{max} – 370 nm.

^1H-*NMR* ($CDCl_3$ TMS): δ1.60 (s, 6H, $C(CH_3)_2$), 3.30 (s, 3H, N—CH_3); 3.52 (s, 3H, N—CH_3); 3.60 (s, 3H, N—CH_3); 5.53 (d, 1H, H_α, $J_{\alpha,\beta}$ – 13 Hz); 7.0–7.5 (m, 4H, H_{ar}); 8.2 (d, 1H, H_β).

Synthesis of the pentamethine cyanine **16**

Ethereal solns of **13c** (2.0 g, 20 mmol in 25 ml anhyd ether) and **4** (1.7 g, 10 mmol in 30 ml anhyd ether) were mixed together and treated with 2.5 g (31.6 mmol) dry pyridine. Tosyl chloride (3.8 g, 20 mmol) was added to stirred soln in small portions. A blue mixture formed which was stirred for 26 hr at room temp.

The cyanine **16** precipitated in crystalline form. After removal of solvent by decantation, the solid product was treated as described above with aqueous sodium tetrafluoroborate soln (2.1 g $NaBF_4$ in 15 ml H_2O).

On cooling to room temp the crystalline product precipitated and was filtered off. Concentration of the filtrate produced a second crop of product (total yield: 3.8 g of **16**, 80%, of **4**). For spectroscopic purposes a portion of **16** was recrystallized from hot aqueous MeOH (spectroscopic data: see Table 1).

Isolation of the monoadduct **15** (R = CH_3)

As described above, the reaction of 1.5 g (15 mmol) of **13c** and 0.85 g (5 mmol) of **4** in the presence of 1.5 g (19 mmol) pyridine and 2.9 g (15 mmol) of tosyl chloride, resulted in a mixture of **16** and **15**. By successive recrystallizations from hot aqueous MeOH (MeOH : H_2O, 3:1) **15** was separated from the mixture and characterized by UV/VIS and ^{1}H-NMR spectroscopy (signals arising from **16** were present as impurities).

UV/VIS (96% EtOH): λ_{max} – 471 nm.

^1H-*NMR* ($CDCl_3$/TMS): δ1.67 (s, 6H, $C(CH_3)_2$); 3.23 (s, 3H, N—CH_3); 3.47 (s, 3H, N—CH_3); 3.55 (s, 3H, N—CH_3); 5.77–6.30 (m, 2H, H_α, H_γ); 6.80–7.53 (m, 5H, H_{ar}, H_β), 8.10 (d, 1H, H_δ, $J_{\gamma,\delta}$ – 15 Hz).

Similarly the reaction of **4** with **13d** gave **16**. Although the formation of the corresponding **15** was observed by UV/VIS spectroscopy no attempt was made to isolate it.

Synthesis of the dinuclear heptamethine cyanine **17**

To a soln of **13e** (1.87 g, 10 mmol in 40 ml anhyd ether) was added a soln of **4** (fresh distl., 2.5 g, 20 mmol in 20 ml anhyd ether). Dry pyridine (2 g, 25 mmol) was added followed by tosyl chloride (1.9 g, 10 mmol) in small portions; the coloured mixture was stirred for 24 hr at room temp.

The solvent was removed from the solid crystalline product by decantation and the product treated with aqueous sodium tetrafluoroborate soln (2 g of $NaBF_4$ in 15 ml H_2O). The resultant crystalline product (2.7 g) was analyzed by UV/VIS spectroscopy. Besides the expected λ_{max} at 740 nm[15] due to **18**, an absorption peak at λ_{max} 640 nm was observed; this may be attributed to **16**, present at less than 16%. The crude product was recrystallized from aqueous MeOH resulting in a decrease in the amount of **16** to < 9%.

Condensation of the Fischer's base **4** *with crotonaldehyde*

Freshly distilled Fischer's base (5 g, 30 mmol) and crotonaldehyde (1.1 g, 16 mmol) were dissolved in 60 ml ether and refluxed for 48 hr. After washing with water the ether phase was dried on Drierite and evaporated. The residue was recrystallized from MeOH. The solid dimer **7** (m.p., 50°) oxidized rapidly.

^1H-*NMR* ($CDCl_3$): 1.19 (d, 3H, CH_3—CH, J – 6.5 Hz), 1.5 (s, 12H, $C(CH_3)_2$), 2.93 (s, 3H, N—CH_3); 2.97 (s, 3H, N—CH_3), 3.35 (m, 1H, CH_3—CH); 4.12 (d, 1H, H_α, J = 11 Hz); 5.19 (d, 1H, H_α, J – 11 Hz); 5.42 (dd, 1H, H_γ, J – 5 and 15 Hz); 6.3–7.2 (m, 9H, H_{ar} and H_β).

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