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Newly substituted pentamethine merocyanines. Part 1: Synthesis, physical properties, and synthetic applications

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Abstract—New 1,5-substituted pentamethine merocyanine dyes were synthesised in high yields. Their reaction towards acid chlorides or anhydrides leads to new hemicarboxonium salts with enhanced reactivity due to their better leaving groups. They are able to combine with soft nucleophiles to obtain a new cyanine dyes series. Thus, these merocyanines may be used as stable intermediate reagents in cyanine synthesis. Moreover, from a theoretical point of view, the synthesis of substituted derivatives of the well-known polyenic donor acceptor models for non-linear optics, opens the route to physicochemical determinations of their effects on the polarisation of the chain and the bond length alternation (Part 2 of study in progress).

1. Introduction

Methods for the synthesis of new 1,5-substituted pentamethine cyanine dyes have been developed.

Mainly, the reactivity of carboxonium salts with nucleophiles was explored to obtain symmetrical, unsymmetrical or chiral dyes from amines, amino alcohols, or 'imino' compounds like phosphaimines, amidines, or guanidines.[1,2,3] More recently, hydrazino and hydrazido dyes have been synthesised.[4] Nevertheless, in the course of this work, the necessity to replace the ethoxy leaving groups on the carboxonium or hemicarboxonium starting salts were studied in order to enhance their reactivity against soft nucleophilic reagents. One way to achieve this goal was to first obtain the merocyanines derived from our substituted dyes. Numerous examples of merocyanines are well documented,[5] and this research area has received much attention due to their large application, mainly in physics (non-linear optics,[6] optical memories[7]), chemistry (photosensitisers,[8] photochromic devices,[9] solvatochromic dyes[10]) and biology (cell membrane probes,[11] photo treatment of malignant cells[12]).

Nevertheless, there are only a few substituted derivatives of these model molecules for the theoretical calculations of push–pull polyenic molecules for non-linear optics.[13] As they are easily obtainable by our method, their vibrational study by IR, Raman, correlation with electronic spectra and solid state structure is in progress (Part 2).

Presented here is the improved synthesis of new 1,5-aryl-substituted pentamethine merocyanines, their physicochemical determinations, and their reactivity with acid chlorides and anhydrides. Which gives new hemicarboxonium salts with enhanced reactivity against soft nucleophiles. The first examples of these reactions are described here.

2. Results and discussion

In the literature,[3] among the numerous methods used to synthesise merocyanines (mainly chain-forming synthons with nucleofugal capabilities against activated methyl or methylene groups offering CH acidic groups) we chose to utilise cyanines as starting materials and then to hydrolyse them in a basic medium. Thus, the formed product contains the required odd-numbered carbon chain and substitution pattern. Examples of such reactions with unsubstituted compounds are described[3] and the nucleophilic base attacks always at the end carbons. For substituted systems the question is somewhat different, with nucleophilic metallates it was demonstrated that the regioselectivity depends on the acid–base fit in the Pearson theory.[14] Moreover with heterocyclic end groups the action of HO^- leads to the hydrolytic breakdown of the cycle.[15]

Scheme 1 presents the synthesis of cyanines **II**–**III** and their hydrolysis giving **IV**–**V** in quantitative yields. The progress of the reactions are followed by TLC on silica gel with solvent mixtures (C_6H_6/CH_3CN 9/1) or ($CHCl_3$/EtOH

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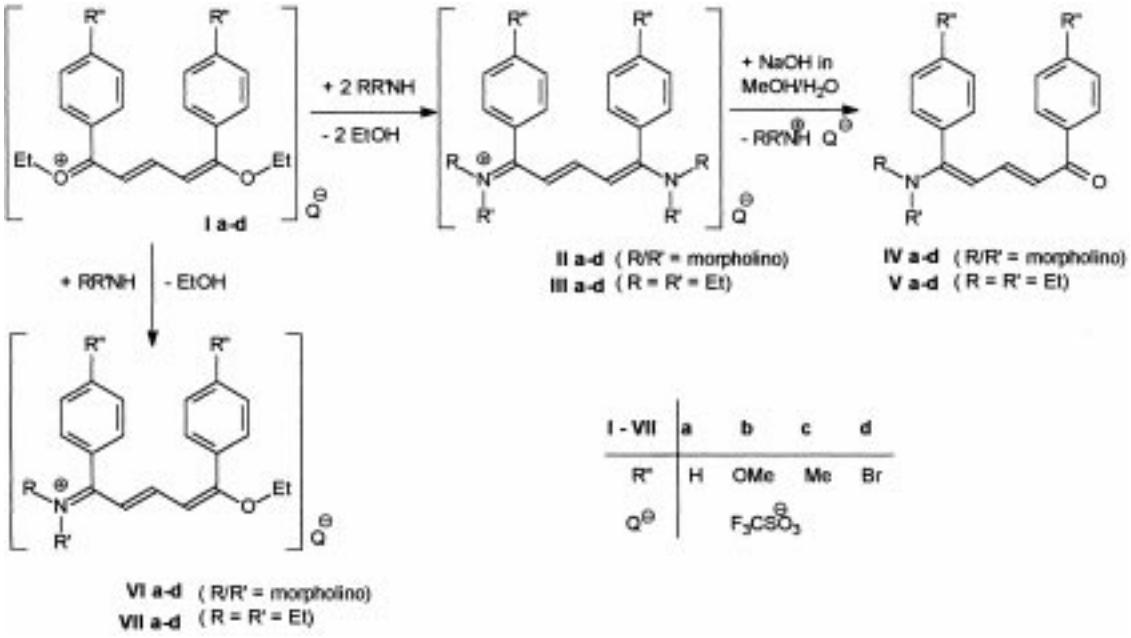


Scheme 1. Reaction pathway to the merocyanines **IV** and **V**, and the hemicarboxonium salts **VI** and **VII**.

24/1) as eluting systems. Under these conditions, the cyanine and the formed merocyanine are separated easily (see Experimental). After completion of the reaction, the product is extracted, washed with water, and then dried. All compounds were fully characterised by physical methods, mainly mass spectroscopy.

By chemical ionisation they all present the expected MH^+ peak in their mass spectra. Moreover, for **Vd**, we observed a good fit between the calculated isotopic repartition for M and the experimental one for MH^+ (Table 1).

Table 1. Mass spectra experimental and calculated isotopic repartition for **Vd**

Exp. $[MH]^+$ Peak	%	Calcd $[M^+]$ Peak	%
462	49.74	461	50.63
463	17.54	462	12.14
464	100.00	463	100.00
465	26.47	464	23.72
466	55.57	465	50.81
467	12.88	466	11.68
468	3.87	467	1.41
469	—	468	0.09

By ^1H NMR, to attribute unambiguously the chain H-atom shifts, additional COSY {H–H} experiments were performed, and it was noticed that the chemical shifts of compounds **IV**–**V** are solvent sensitive (see Experimental). In the ^{13}C NMR spectra, one signal for each carbon atom is observed, thus, indicating that only one conformation is present in solution, most probably the *trans–trans–cis* one as calculated for **IVa** by molecular modelling (this assumption is confirmed by the X-ray structure of **Vd** to be published in Part 2). [Semi-empirical geometry optimisation with AM1 Hamiltonian, Hyperchem 5.01 (1997); Fig. 1.]

To ensure our chain carbon attributions, a COSY {C–H} spectrum was recorded for **IVd** (Fig. 2).

The merocyanines are coloured systems and their properties arise from their electronic delocalisation. Thus, their UV–visible spectra were studied either in solution or in the solid state.

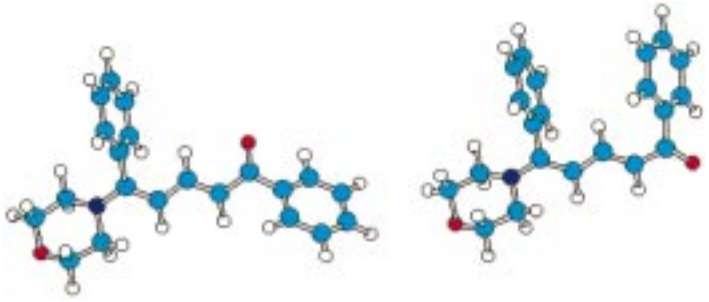


Figure 1. Calculated conformations for **IVa**: '*trans–trans–cis*' (left) versus 'all-*trans*' conformer (AM1; energy difference: 1.666 kcal mol^{-1} in favour of the former).

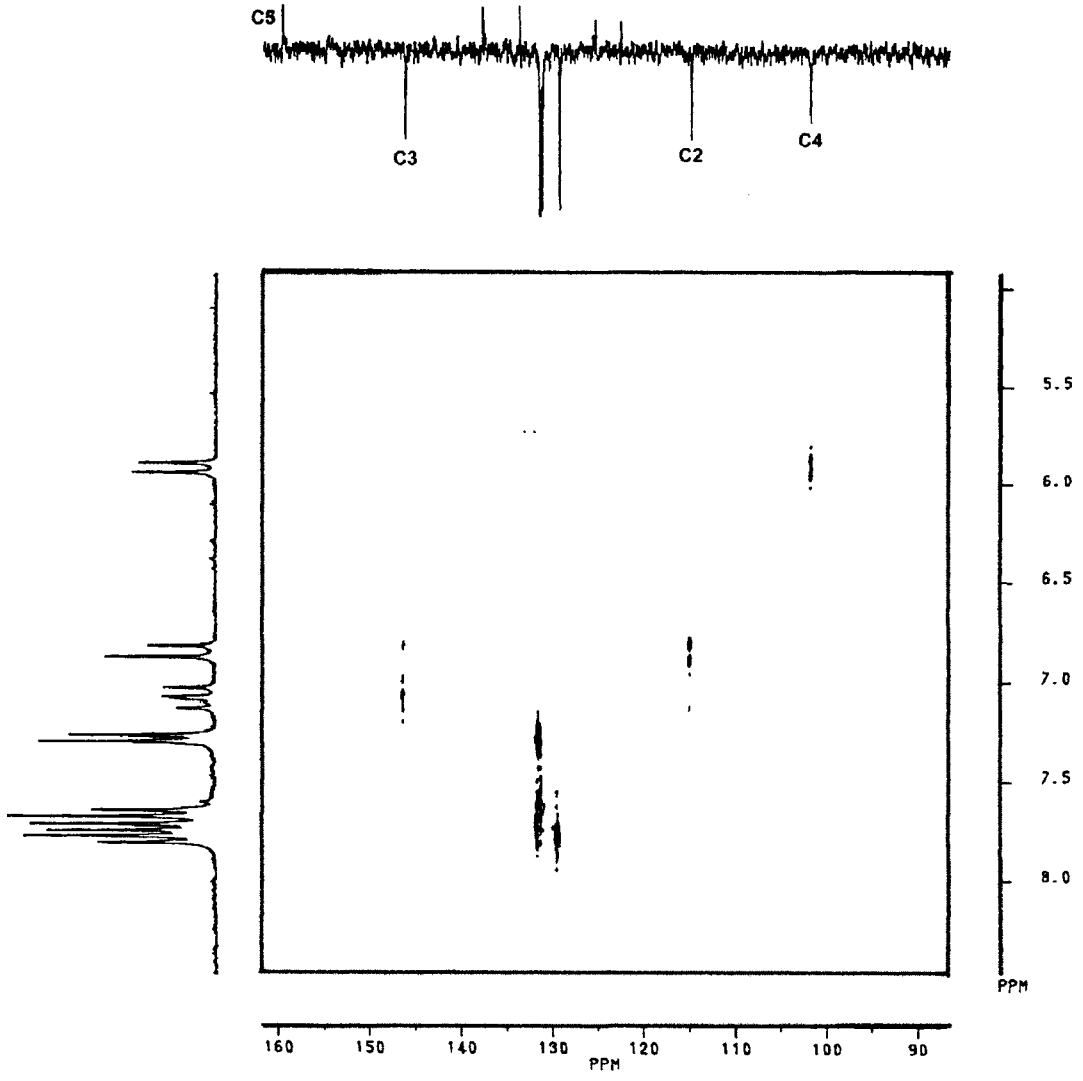


Figure 2. Proton carbon correlation NMR spectra for compound **IVd** (see δ ^{13}C in Experimental).

In solution products, **IV–V** showed two main absorption bands, one between λ_{1max} of 261 and 290 nm corresponding to the aromatic cycles, and the $\pi-\pi^*$ absorption giving a λ_{2max} from 405 to 434 nm. In two cases, for compounds **IVb** and **Vd**, a small additional charge-transfer band was observed, at 488 and 514 nm, respectively, which may be due to the possible conjugation pathway to quinoid forms only accessible with methoxy and bromine *para*-substituents.

As expected,[10] the merocyanine dyes present a neat but moderately positive solvatochromism, i.e. a bathochromic shift of the λ_{max} band with increasing solvent polarity. Table 2 gives the results obtained with compound **Va** in a solvent range of 1,4-dioxane to water where we measured a $\Delta\lambda = 29.5$ nm. It was noticed that only the long wavelength λ_{2max} band is solvent-dependent whereas the band in the UV region remains unchanged.

Table 2. Solvatochromic properties of **Va**

Solvent	Dielectric constant	λ_{1max} nm (log ε)	λ_{2max} nm (log ε)
Water	78.5	261 (3.50)	442 (4.01)
Acetonitrile	37.5	259 (4.04)	427 (4.60)
Chloroform	4.7	263 (4.35)	428 (4.84)
1,4-Dioxane	2.2	260 (4.12)	412.5 (4.60)
		$\Delta\lambda = 1$ nm	$\Delta\lambda = 29.5$ nm

Some solid state spectra (**IVb–d** in KBr pellets) were recorded in a total reflectance mode with a 60mm integration sphere. All visible λ_{max} bands are red-shifted by $\Delta\lambda$ of 27–54 nm. Moreover, for **IVb**, the small charge-transfer band is also observable at 553 nm ($\Delta\lambda = +65$ nm).

The reactivity of the new merocyanines must be close to the reactivity described in the literature[16] for unsubstituted systems, with the noticeable difference of a terminal keto group instead of an aldehyde. To take this change into account, we calculated the charge repartition in the case of **Va** (Fig. 3). Following this result, it seems that the keto carbon is the most favourable site for a nucleophilic attack.

To prepare equivalent hemicarboxonium salts with an enhanced reactivity against nucleophiles, firstly anhydrides and acid chlorides were used. Scheme 2 presents our results.

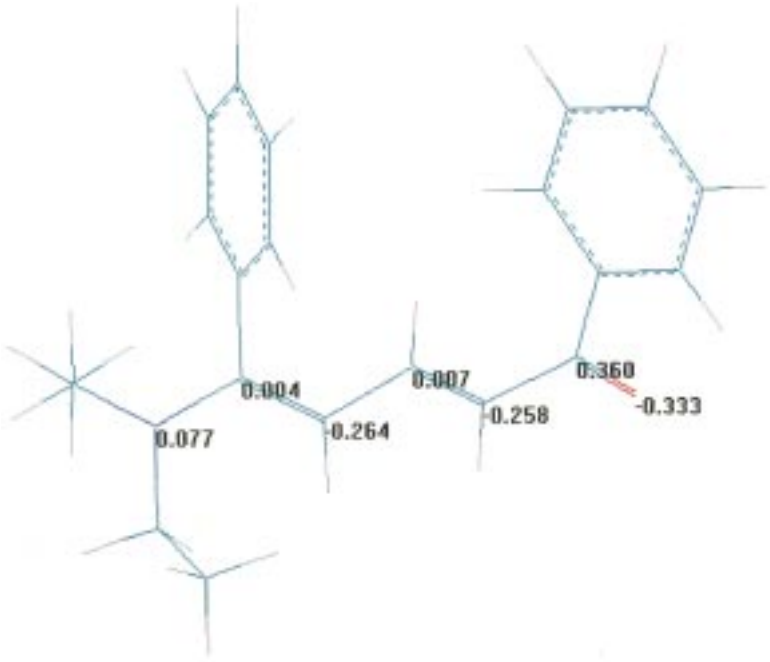
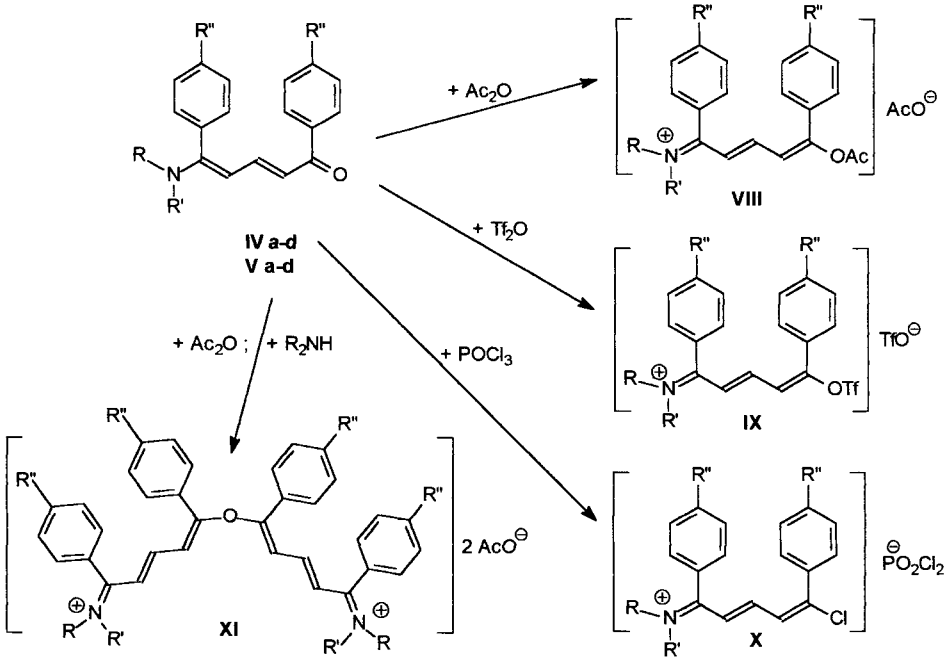


Figure 3. Calculated charges on the pentamethine merocyanine chain of compound **Va** (PM3).

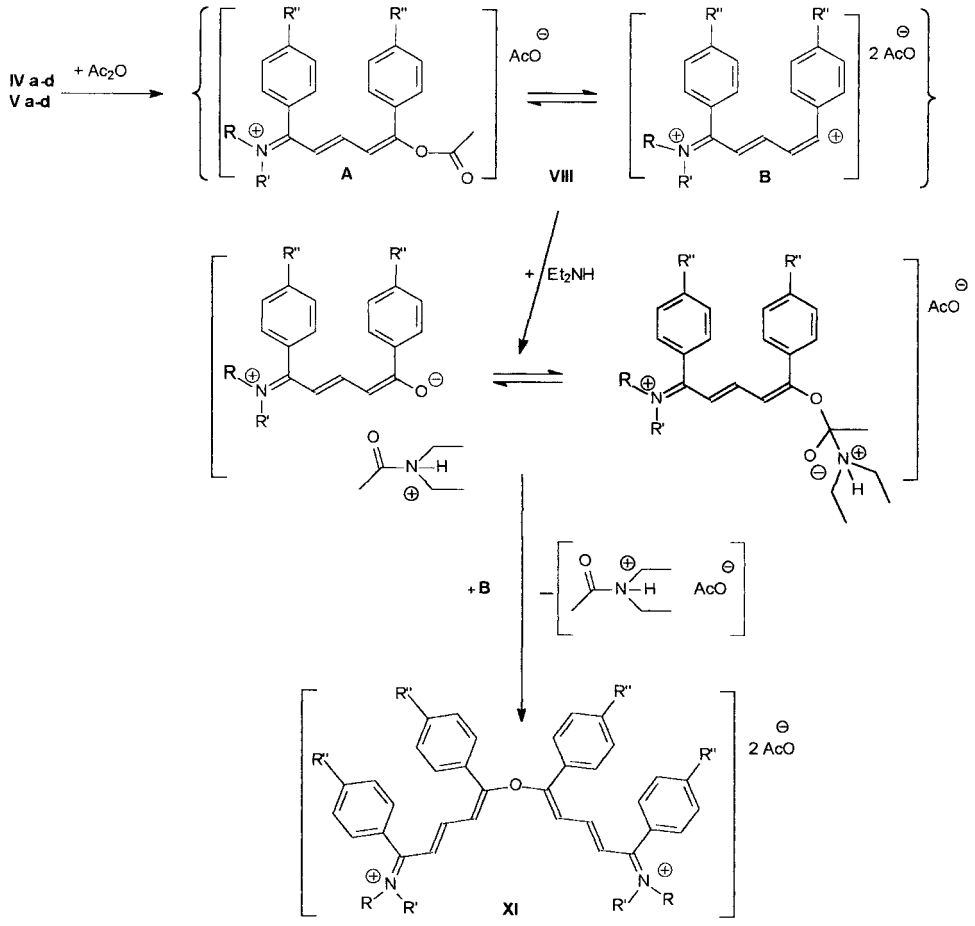
The reactions of **IV**–**V** under dry atmosphere with acid anhydrides lead to the formation of the O acyl or O triflic (triflic=Tf=trifluoromethane sulfonyl) hemicarboxonium equivalent **VIII** and **IX**, characterised by NMR (see Experimental) and an additional mass spectra for **IX**. Attempts to make further reactions with secondary amines, afforded in both cases the "dimeric" salt **XI** or its "ditriflic" equivalent, which were fully analysed. A possible mechanism for this reaction is proposed in Scheme 3.

The formal acyl acetate salt **A** may be in equilibrium with its disalt carbocation **B**. (One indication in favour of this hypothesis is the fact that we observe only one acetate signal by ^{1}H NMR.) The addition of a highly nucleophilic secondary amine may occur on the acyl carbon to leave a diethylacetamide acetic salt and an oxaanion, which can react with the carbocation **B** to form **XI**.

Nevertheless, with fewer nucleophilic systems, reactions



Scheme 2. Reaction pathways to derivatives **VIII**–**XIa–d** of the hemicarboxonium salts **VIa–d** and **VIIa–d**.



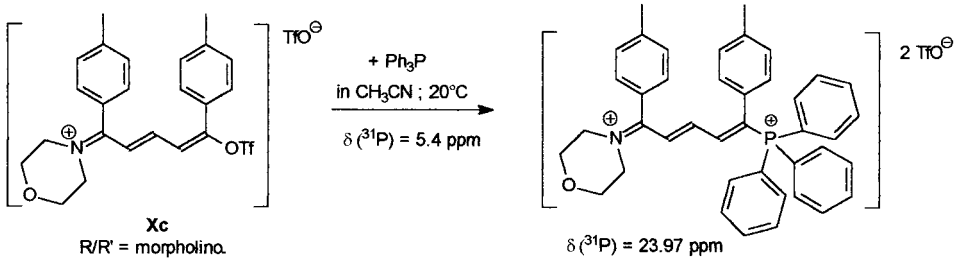
Scheme 3. Proposed mechanism for the formation of compounds **XIa–d**.

can occur in the expected way, i.e. in the case of the triphenyl phosphane addition (Scheme 4).

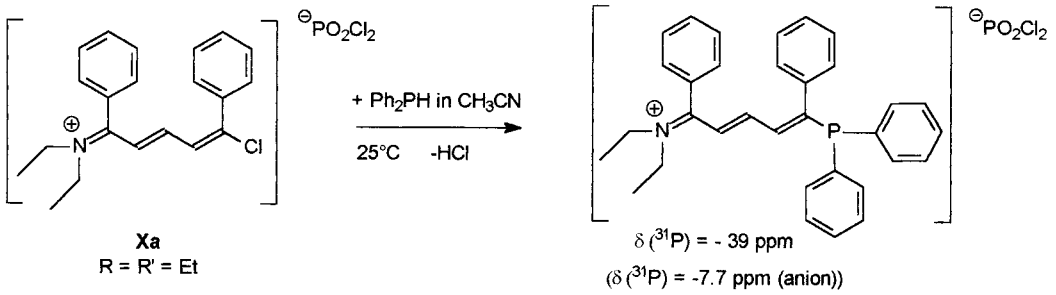
Finally, the action of an acid chloride ($Cl_3P{=}O$ in our case) leads to the most promising chloro reagents. These compounds are substituted pentamethine equivalents of the Vilsmeier–Haack–Arnold reagents recently reviewed by Reichardt,[17] and to the best of our knowledge only the trimethine vinamidinium salts were studied. Their reactivity was also described in two older but more exhaustive papers.[18,19]

The use of $Cl_3P{=}O$ is interesting in that it offers an internal probe for the synthesis of the chloro hemicarboxonium. The formed anion has a characteristic shift in ^{31}P NMR at $\delta = -7.4 \pm 2$ ppm. All other physical constants are in accordance with this result (see Experimental), i.e. for **Xd** an M^+ peak in the mass spectrum at *m/z* of 482, representing the expected isotopic repartition for two Br and one Cl atoms. The mechanism of the formation of the chloro salts must be close to the one proposed by Arnold and Holý[20] for $Cl_3P{=}O$, Alt and Speziale[21] for PCl_5, or trichloroacetic chloride.

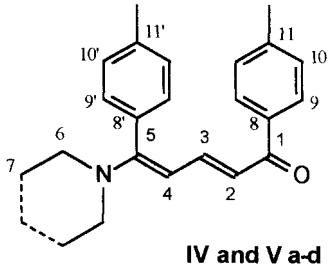
The reactivity of the new salts was then explored, the aim of this work being to extend the panel of the nucleophilic substitutions available. Reactions were attempted with nucleophiles that proved to be unreactive with our standard hemicarboxonium salts, i.e. diphenyl phosphane. Nevertheless, in the set-up process of the experiments aliphatic amine derivatives were also used to compare with previously obtained compounds. The reactivity was first checked by the action of the trimethylsilyl derivative of



Scheme 4. Reaction of **Xc** with triphenyl phosphane.



Scheme 5. Reaction of **Xa** with diphenyl phosphane.



Scheme 6. NMR spectra numbering scheme.

dimethylamine on the chlorocyanines **Xa** (R=R′=Et) and **Xc** (R/R′=morpholino). By NMR, we controlled the formation of the expected disymmetric dyes either in ^{1}H or in ^{13}C. Moreover in ^{31}P the signal of the anion was observed at a δ of −8.23 ppm. Thus we tried to carry out the reaction between **Xa** and the diphenyl phosphane (Scheme 5). The reaction proceeds at room temperature and is followed by ^{31}P NMR. After 4 h, Ph_2PH had completely disappeared (no peak at δ=−41 ppm). One other signal appeared at δ=−39 ppm, the anion signal remaining at δ=−7.7 ppm. We checked that the former has no J_{P-H} coupling constants, and that the chemical shift observed is in the Ph_2PC vinyl region.[22] The green solid glass obtained after removal of the solvent is stable under inert atmosphere but is unstable in solution.

3. Conclusion

The synthesis of new pentamethine merocyanines with enhanced substitution patterns was achieved in good yields. The physical properties of these new products should be studied from a non-linear optics application point of view. Moreover they are stable starting materials for the synthesis of highly reactive intermediates, new hemicarboxonium salts, with extended reactivity towards weak nucleophiles. Thus, it seems possible to use these new reagents to obtain previously unreachable compounds and further work is in progress (Scheme 6).

4. Experimental

4.1. General methods

NMR spectra were recorded on a multinuclear Bruker AC 250 spectrometer operating at 250.133 and 62.896 MHz for ^{1}H and ^{13}C, ^{31}P (101.375 Mhz), and ^{19}F (235.194 Mhz), respectively. Chemical shifts are expressed in ppm downfield from an internal TMS standard for ^{1}H and ^{13}C, and external 85% H_3PO_4 for ^{31}P.

UV–visible spectra were recorded on a Perkin–Elmer Lambda-19 spectrophotometer equipped with a 60 mm integration sphere for solid measurements. Mass spectra were obtained on a Nermag R10. (Surprisingly, in CI with NH_3, the higher peak always corresponded to the $[MH]^+$ of the cationic part of the molecule.)

Elemental analyses were realised in the 'Service commun de microanalyses' at the ENSC Toulouse.

4.2. General experimental procedure

The synthesis of compounds **I–III** and **VI–VII** have been previously described in preceding papers.[1,2,3]

4.3. Synthesis of the merocyanines IV and Va–d (1,5-diaryl, 5-(dialkylamino) penta-2,4-dien-1-one)

The cyanines **II–III** (2 mmol) were dissolved in 15 ml of ethanol or methanol. To this solution was added 3 mmol of KOH or NaOH (1.5 equivalent) dissolved in a mixture ethanol/water (1/2). The solution was stirred for 3–5 h in a temperature range of 25–40°C. The end of the hydrolysis is reached when no more starting material is observable by TLC. On obtaining compounds **IV** or **V**, if there is a precipitation, the solids are filtered, washed with distilled water, and recrystallised from ethanol/hexane mixtures. If the final product remains in solution, it is extracted with chloroform. The organic phase is washed with water, dried with $CaCl_2$. The solvent is removed at reduced pressure. Recrystallisation of the crude product gives small crystals from ethanol/hexane and powder from diethylether. Yields: 90–96%. Physical constants: melting points, mp, ^{1}H and ^{13}C NMR, mass spectra (ppm), chromatographic R_f, and UV–vis (cm^{-1}) data are given hereafter.

4.3.1. Merocyanine IVa. Mp 93°C; ^{1}H NMR δ($CDCl_3$) 3.11 (t, 4H, H_6), 3.73 (t, 4H, H_7), 5.74 (d, 1H, H_4), 7.33 (dd, 1H, H_3 COSY), 6.77 (d, 1H, H_2), 7.26–7.46 (m, 10H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 48.75 C(6), 66.59 C(7), 103.18 C(4), 117.56 C(2), 128.02 C(11′), 128.24 C(10′), 128.75 C(10), 129.47 C(9′), 129.88 C(11), 131.61 C (9), 135.03 C(8′), 139.43 C(8), 146.42 C(3), 160.91 C (5), 189.88 C(1); MS *m/z* 320 $(M+1)^+$; R_f 0.48 (C_6H_6/CH_3CN 9/1, 26°C), 0.92 ($CHCl_3$/EtOH 24/1, 21°C); UV–vis ($CHCl_3$) 261 (4.01), 405 (4.31).

4.3.2. Merocyanine IVb. Mp 119°C; ^{1}H NMR δ($CDCl_3$) 3.09 (t, 4H, H_6) 3.70 (t, 4H, H_7) 3.83 (s, 6H, OCH_3), 5.69 (d, 1H, H_4), 6.79 (d, 1H, H_2),7.41 (dd, ^{1}H, H_3), 6.80 (d, 2H, H_{arom}), 6.90 (d, 2H, H_{arom}), 7.20 (d, 2H, H_{arom}), 7.80 (d, 2H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 55.36, 55.39 (OCH_3), 48.94 C(6), 66.66 C(7), 103.28 C(4), 113.46 C(10), 114.15 C(10′), 117.0 C(2), 127.24 C(8′), 131.31 C(9), 132.26 C(8)C(9′), 145.84 C(3), 160.51 C(11′), 160.60 C(5), 162.52 C(11), 188.24 C(1);MS *m/z* 380 $(M+1)^+$; R_f 0.36 (C_6H_6/CH_3CN 9/1, 26°C), 0.89 ($CHCl_3$/EtOH 24/1, 21°C); UV–vis ($CHCl_3$) 290 (3.95), 406 (4.33), 488 (3.05).

4.3.3. Merocyanine IVc. Mp 114°C; ^{1}H NMR δ(C_6D_6) 2.02 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.61 (t, 4H, H_7), 3.32 (t, 4H, H_6), 5.58 (d, 1H, H_4), 6.87–7.15 (m, 7H, H_2, H_3, H_{arom}), 7.91–8.11 (m, 3H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 21.35 (CH_3), 21.57 (CH_3), 48.79 C(6), 66.63 C(7), 103.10 C(4), 117.20 C(2),128.13 C(10′), 128.95 C(10), 129.43 C(9′), 129.82 C(9), 132.09 C(11), 137.61 C(11′), 139.48 C(8′), 142.16 C(8), 146.17 C(3), 160.98 C(5), 188.50 C(1); MS *m/z* 348 $(M+1)^+$; R_f 0.50 (C_6H_6/CH_3CN 9/1, 26°C), 0.92 ($CHCl_3$/EtOH 24/1, 21°C); UV–vis ($CHCl_3$) 272 (4.26), 408 (4.61).

4.3.4. Merocyanine IVd. Mp 165°C; ^{1}H NMR δ($CDCl_3$) 3.09 (t, 4H, H_6), 3.72 (t, 4H, H_7), 5.72 (d, 1H, H_4), 6.73 (dd, 1H, H_3), 7.10–7.77 (m, 9H, H_2, H_{arom});($DMSOd_6$) 3.13 (t, 4H, H_6), 3.65 (t, 4H, H_7), 5.90 (d, 1H, H_4), 7.06 (dd, 1H, H_3),6.83 (d, 1H, H_2), 7.28 (d, 2H, H_{arom}), 7.63–7.80 (m, 6H, H_{arom}); ^{13}C NMR (DMSO-d_6/acetone-d_6) δ 48.20 C(6), 65.57 C(7), 101.98 C(4), 115.04 C(2), 122.70 C(11),125.47 C(11′), 129.43 C(10), 131.31 C(10′), 131.54 C(9), 131.62 C(9′), 133.84 C(8), 137.85 C(8′), 146.22 C(3), 159.67 C(5), 186.50 C(1); MS *m/z* 478 $(M+1)^+$; R_f 0.58 (C_6H_6/CH_3CN 9/1, 26°C), 0.94 ($CHCl_3$/EtOH 24/1, 21°C); UV–vis (CH_3CN) 270 (4.35), 420 (4.64).

4.3.5. Merocyanine Va. Mp 96°C; ^{1}H NMR δ (acetone-d_6) 1.15 (t, 6H, CH_3), 3.22 (q, 4H, CH_2), 5.78 (d, 1H, H_4), 6.68 (d, 1H, H_2), 7.12 (dd, 1H, H_3), 7.07–7.52 (m, 8H, H_{arom}), 7.84 (dd, 2H, H_{arom}); ^{13}C NMR (acetone-d_6) δ 13.40 CH_3, 45.04 CH_2, 100.53 C(4), 113.54 C(2), 128.28 C(9), 128.86 C(9′), 129.23 C(10), 129.55 C(11′), 130.10 C(10′), 136.79 C(8), 137.66 C(11), 141.11 C(8′), 148.41 C(3), 160.80 C(5), 188.10 C(1); MS *m/z* 306 $(M+1)^+$; R_f 0.43 (C_6H_6/CH_3CN 9/1, 26°C), 0.90 ($CHCl_3$/EtOH 24/1, 21°C); UV–vis ($CHCl_3$) 263 (4.35), 428 (4.84).

4.3.6. Merocyanine Vb. Mp 81°C; ^{1}H NMR δ (acetone-d_6) 1.13 (t, 6H, CH_3), 3.26 (q, 4H, CH_2), 3.83 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 5.73 (d, 1H, H_4), 6.70 (d, 1H, H_2), 7.12 (dd, 1H, H_3), 6.92–7.23 (m, 7H, H_{arom}), 7.87 (d, 2H, H_{arom}); ^{13}C NMR (acetone-d_6) δ 13.31 CH_3, 44.84 CH_2, 55.53 OCH_3, 55.62 OCH_3, 100.81 C(4), 113.30 C(2), 114.05 C(10), 114.53 C(10′), 128.79 C(8′), 130.31 C(9), 131.47 C(9′), 133.71 C(8), 147.69 C(3), 160.27 C(5), 186.75 C(1); MS *m/z* 366 $(M+1)^+$; R_f 0.32 (C_6H_6/CH_3CN 9/1, 26°C), 0.90 ($CHCl_3$/EtOH 24/1, 21°C); UV–vis ($CHCl_3$) 286 (4.02), 427 (4.55).

4.3.7. Merocyanine Vc. Mp 88°C; ^{1}H NMR δ($CDCl_3$) 1.16 (t, 6H, CH_3), 2.36 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 3.21 (q, 4H, CH_2), 5.63 (d, 1H, H_4), 6.60 (d, 1H, H_2), 7.08–7.27 (m, 7H, H_{arom}), 7.77 (d, 2H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 13.21 CH_3, 21.34 CH_3, 21.50 CH_3, 44.38 CH_2, 100.04 C(4), 113.01 C(2), 127.94 C(10′), 128.75 C(10), 129.15 C(9′), 129.20 C(9), 132.44 C(11′), 137.51 C(11), 138.74 C(8′), 141.37 C(8), 148.27 C(3), 160.57 C(5), 188.78 C(1); MS *m/z* 333 $(M)^+$; R_f 0.51 (C_6H_6/CH_3CN 9/1, 26°C), 0.94 ($CHCl_3$/EtOH 24/1, 21°C); UV–vis ($CHCl_3$) 272 (4.13), 426 (4.62).

4.3.8. Merocyanine Vd. Mp 102°C; ^{1}H NMR δ(C_6D_6), 0.70 (t, 6H, CH_3), 2.60 (q, 4H, CH_2), 5.64 (d, 1H, H_4), 6.62–7.76 (m, 10H, H_{arom}); ($CDCl_3$) 1.13 (t, 6H, CH_3), 3.21 (q, 4H, CH_2), 5.64 (d, 1H, H_4), 6.67 (d, 1H, H_2), 7.07–7.59 (m, 9H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 13.21 CH_3, 44.59 CH_2, 100.29 C(4), 112.93 C(2), 123.43 C(11′), 125.90 C(11), 129.45 C(9), 130.86 C(10), 131.34 C(9′), 131.91 C(10′), 134.13 C(8′), 136.75 C(8), 148.20 C(3), 159.40 C(5), 187.73 C(1); MS *m/z* 464 $(M+1)^+$; R_f 0.71 (C_6H_6/CH_3CN 9/1, 26°C), 0.95 ($CHCl_3$/EtOH 24/1, 21°C); UV–vis (CH_3CN) 265 (4.83), 434 (4.38), 514 (2.75).

4.4. Synthesis of the merocyanine derivatives

4.4.1. Acetates VIII. Merocyanines **IVa–d**–**Va–d** are dissolved in an excess of acetic anhydride under argon at room temperature. The solution is stirred for 1 h. The colour of the solution changes from orange to red. The progress of the reaction is followed by TLC with the disappearance of the starting materials **IV**–**V**. Excess anhydride is removed by distillation under reduced pressure to give a red powder. For **VIIIb** ^{1}H NMR (CD_3CN) 2.19 (6H) acyl CH_3; 3.09 (4H) and 3.66 (4H) morpholino group; 3.81(s, 3H) and 3.83 (s, 3H) anisyl; 5.76 (d, 1H) H_2; 6.76–7.23 (m, $6H_{arom}+H_3$); 6.79 (d, 1H) H_4; 7.84 (d, $2H_{arom}$).

4.4.2. Triflates IX. To a dichloromethane solution of **IV**–**V** in a Schlenck tube under argon atmosphere was added one equivalent of trifluoromethane sulfonate anhydride (in slight excess 5%) at −30°C. After 1 h, the temperature was raised to 20°C, and the solution stirred for 12 h. Then the solvent and the excess anhydride was distilled off under vacuum to give a bordeaux red powder. For **IXc** ^{1}H NMR (CD_3CN) 2.41 (3H) and 2.46 (3H) tolyl CH_3; 3.80 (4H), 4.05 (m, 2H) and 4.25 (m, 2H) morpholino group; 6.65 (m, 1H), 6.88 (2H) and 7.21–7.58 (8H) aromatic+chain protons. MS electrospray: $[C_{25}H_{25}NF_3O_4S]^+$ 480.

4.5. Chloropentamethinium salts X

4.5.1. Xd. To 0.317g (1.03 mmol) of the merocyanine **Vd**, 5 ml of acetonitrile was added, at room temperature and 0.158 g (1.03 mmol) of $POCl_3$. After 5 h, a control by ^{31}P NMR shows a characteristic singlet at $\delta = -7.5$ ppm for the anion $PO_2Cl_2^-$. The solvent is removed under reduced pressure to leave the expected chloro salt as a green hygroscopic powder. Yield is 72%. ^{1}H NMR (80 MHz; $CDCl_3$) δ (ppm): 1.32 (t, 3H, J=7.1 Hz, N—CH_2—CH_3); 1.59 (t, 3H, J=7.3 Hz, N—CH_2—CH_3); 3.6 (q, 2H, N—CH_2—CH_3); 4.31 (q, 2H, N—CH_2—CH_3); 6.95 (dd, 1H, H_3); 7.2 and 7.6 (m, 8H phenyl group, H_4, H_2). ^{31}P NMR: δ (ppm): −7.3 (CH_3CN). ^{13}C NMR: ($CDCl_3$) δ (ppm): 125.0 C(4); 125.8 C(2); 147.2 C(5); 154.1 C(3); 176.2 C(1). MS: (DCI/NH_3) $[M^+]$ 482.

4.5.2. Xa. To 0.359g (0.775 mmol) of merocyanine **Va** in 5 ml acetonitrile is added, at room temperature, 0.118g (0.775 mmol) of $POCl_3$. ^{31}P NMR control after 5 h reveals the presence of a singlet at $\delta = -7.5$ ppm ($PO_2Cl_2^-$ anion). After distillation of the solvent the residue is recovered as a green powder. Yield: 71%. ^1H NMR (80 MHz; $CDCl_3$) δ (ppm): 1.20 (t, 3H, J=7.1 Hz, N—CH_2—CH_3); 1.52 (t, 3H, J=4.3 Hz, N—CH_2—CH_3); 3.6 (q, 2H, N—CH_2—CH_3); 4.21 (q, 2H, N—CH_2—CH_3); 6.52 (dd, 1H, H_3); 7.0 and 7.8 (m, 8H phenyl group, H_4, H_2). ^{31}P NMR: −7.5 (CH_3CN). ^{13}C NMR: ($CDCl_3$) δ (ppm): 124.5 C(4); 125.4 C(2); 148.3 C(5); 154.4 C(3); 177.1 C(1). MS: (DCI/NH_3) [M^+] 324.

4.5.3. 'Dimers' XI. To the compounds **VIII** obtained as described above, one molar equivalent of diethylamine was added in carefully dried CH_3CN. The mixture is left stirring overnight at 20°C. After removal of the solvent, the crude solid is crystallised from dry diethylether to give a yellow-green powder characterised by NMR and elemental analysis. For **XIb** $C_{50}H_{56}N_2O_4$ M is 860.38. Analysis calcd, found)% C (69.75, 69.73); H (6.56, 6.43); N (3.25, 3.40). ^1H NMR (CD_3CN): 2.20 (s, 6H) acyl anion CH_3; 3.80 (4H), 3.84 (4H), 4.03 (4H), 4.24 (4H) morpholino group; 3.85 (s, 6H) and 3.89 (s, 6H) anisyl group; 6.90–7.75 (m, 22H) aromatic+chain protons.

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