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Tetrahedron 60 (2004) 195–201
Tetrahedron

New cyanine dyes derived from tetrazolo[5,1-*a*]isoindoles

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Received 6 December 2002; revised 19 September 2003; accepted 20 October 2003

Abstract—The investigation of the acylation reaction of 1-methyltetrazolo[5,1-*a*]isoindole with acyl chlorides gave rise to two series of derivatives. 5-Acyl-1-methyltetrazolo[5,1-*a*]isoindoles and a new type of tetrazoloisoindole based monomethinecyanines were isolated. Their structure was confirmed by X-ray diffraction analysis. A mechanism of the formation of these new dyes is proposed. This reaction permit to introduce easily various alkyl, aryl or heteroaryl substituents on the central methine carbon.

1. Introduction

Reactions of simple isoindoles[1–6] have been well studied, but not those of cyclised isoindole systems with a nodal nitrogen atom, mainly in the tetrazoloisoindole series.[1,7]

The interest in tetrazoloisoindoles is both in fundamental chemistry, due to their ability to lead to formal 14π-electrons aromatic systems[8] (in fact they are 10π-electron aromatic systems, like 1,2-substituted isoindole) and in numerous practical applications. For example, biologically active compounds[9] and dyes with tetrazoloisoindole moieties[10–12] are known and tetrazoloisoindole derivatives are used in the chemical modification of biodegradable natural polymers like cellulose.[13]

In a recent review paper[7] we summarised the few contributions to the chemical properties of the tetrazoloisoindoles: only one example of an alkylation reaction[14] is described and it is the same for the cyanoethylation with isocyanates or isothiocyanates or for acylation.[11] Another recent synthesis and reactivity paper of a closely related tetrazoloisoindole system together with an X-ray structure is worthwhile to refer.[15]

There is more information on the formation of dyes, non-substituted mono- and trimethinecyanine chains and also non-symmetrical.[10–12] We recently synthesised potassium hexacyanoferrate (III) and tetracyanonickelate (II) complexes of the cyanine dyes derived from tetrazolo[5,1-*a*]isoindoles.[16] Some general methods to introduce various substituents on the monomethine chain carbon atom are used.[17–22] Moreover, non-symmetrical cyanine dyes with cyclic quinoline, benzoxazole, [5,6]benzoquinoline and benzothiazole substituents in the methine chain were isolated.[20,23] Finally, methods to introduce halide substituents in the chain were proposed.[24–27]

In this contribution, we want to present a new efficient method to introduce alkyl, aryl and heteroaryl substituents on the methine carbon of monomethine cyanine dyes.

2. Results and discussion

2.1. Synthesis

Following the literature,[7] it is clear that the acylation reactions of the tetrazoloisoindoles were not thoroughly studied. Only two examples are described, the acyl derivatives **Ia**,**b** obtained by the reaction of carboxylic acid anhydrides in DMF[11] with the 1-methyl-5*H*-tetrazolo[5,1-*a*]isoindolium salt (Scheme 1). Moreover no spectroscopic characterisation is given.

The goal of our work was the systematic study of the acylation reactions in the tetrazoloisoindole series. We intended to vary the R substituents between large limits, thus it seemed more convenient to use acyl chlorides because of their greater availability than the acid anhydrides.

In the first stage, we studied the acylation of the 1-methyltetrazolo[5,1-*a*]isoindole **II**. The product was obtained in a previously known way,[14] by the action of a base (KOH or NaOH) on 1-methyl-5*H*-tetrazolo[5,1-*a*]isoindolium **III** perchlorate. In spite of its extreme instability,

Keywords: Tetrazoloisoindole; Cyanine dyes; Acylation reactions; X-ray structure determination.
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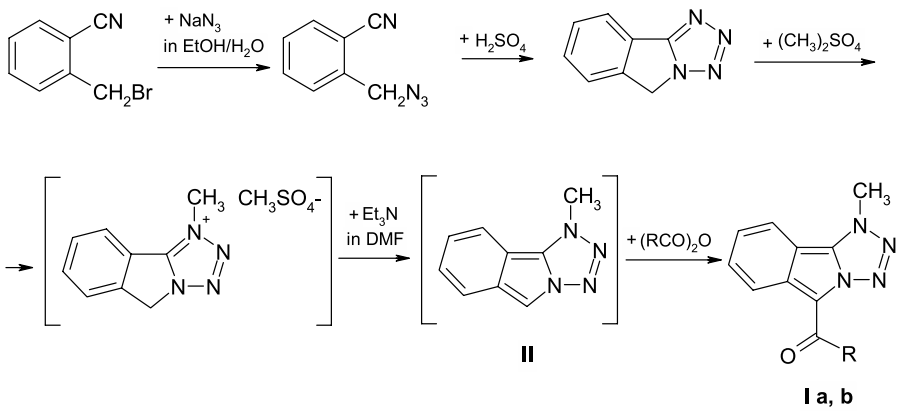
doi:10.1016/j.tet.2003.10.094



Scheme 1. Synthesis of the acylation products **Ia**,**b**.[11,14]

we were able to isolate the tetrazoloisoindole **II** as an analytically pure sample by sublimation under reduced pressure. UV and ^{1}H NMR spectra were recorded. In the UV, the experimental λ_{max} (362 nm) is in good accordance with the PPP calculated one[8] (λ_{max}=364 nm).(see experimental part). In the following step, the acylation of **II** by the benzoyl chloride to give compound **Ib** was nearly quantitative.

In the second stage, we tried to replace the tetrazoloisoindole **II** by the more readily available perchlorate salt **III**. In this case, we obtained an unexpected result: even in varying the reaction conditions [dioxane+K_2CO_3, dioxane+Et_3N, pyridine] we always obtained, together with the acyl product **I**, a new type of compound, the previously unknown cyanine dyes **IV** (Scheme 2).

The yields and the respective ratios between the final products is greatly dependant of the proportion of the starting materials, i.e. **III**, RCOCl and triethylamine. For the optimal formation of product **I** the best ratio is 1/1/1. The easier formation of the cyanines is obtained with the 2/1/1 ratio but in this case, there is a part of the non-reacted perchlorate salt in the residues. Ratios like 1/1/3 or 2/1/3 lead to the formation of oily residues. Thus, for the best yield in cyanine dyes, the 1/1/2 ratio seems preferable.

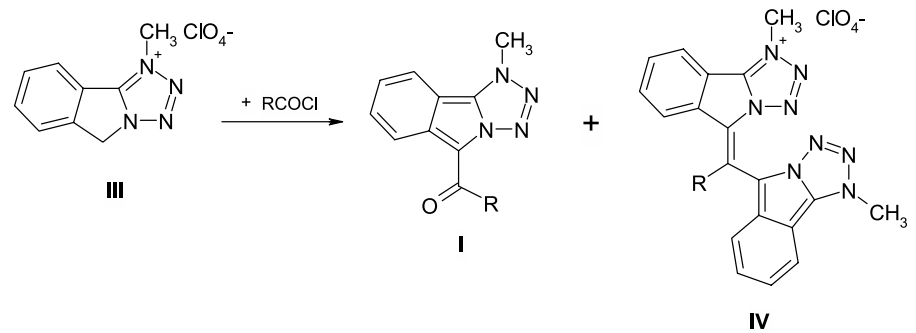
Also, the nature of the R substituent is of great importance. We were unable to isolate the acylated products **I c**,**d**, whereas in this case we obtained the best yields for **IV c**,**d** dyes.

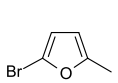
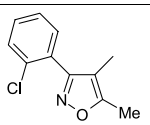
As compared to Scheme 1, we obtained only a small yield of **Ia** with the Scheme 2 type reaction.

On the one hand, the yields of product **I** are high when R is aromatic or heteroaromatic and enhanced by the presence of acceptor substituents on the aromatic site. In this case, the yield of dye are weak, as with **IV e**, **f**, **k**.

On the other hand, the presence of donor groups in the aromatic moieties favour the formation of the dyes in high yield.

The separation and isolation of products **I** and **IV** was always performed by column chromatography, and their



I, IV	**a**	**b**	**c**	**d**	**e**	**f**
R	Me	Ph	$(CH_2)_3Cl$	C_4H_9	2-ClC_6H_4	4-$NO_2C_6H_4$
I, IV	**g**	**h**	**i**	**j**	**k**	
R	4-$CH_3C_6H_4$	2,4-$(MeO)_2C_6H_3$				

Scheme 2. Acylation of the 1-methyl-5*H*-tetrazolo[5,1-*a*]isoindolium **III** perchlorate by acyl chlorides.

structures were confirmed by usual physicochemical methods.

2.2. X-ray structure determination of the dye IVb

Crystal data for **IVb**. $C_{25}H_{19}ClN_8O_4$, M=530.93, monoclinic, $C2/c$, a=22.554(5) Å, b=18.052(4) Å, c=12.349(3) Å, β=101.234(4)°, V=4931.6(19) Å^3, Z=8, ρ_c=1.430 Mg m^{-3}, $F(000)$=2192, λ=0.71073 Å, T=193(2) K, μ (Mo Kα)=0.205 mm^{-1}, crystal size 0.05×0.1×0.5 mm^3, 10898 reflections (3539 independent, R_{int}=0.1531) were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer. The structure was solved by direct methods (SHELXS-97)[28] and 386 parameters were refined using the least-squares method on F^2.[29] Largest electron density residue: 0.458×eÅ^{-3}, R_1(for $I>2\sigma(I)$)=0.0978 and wR_2=0.2754 (all data) with $R_1=\sum||F_o|-|F_c||/\sum|F_o|$ and $wR_2=(\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 197823 for **IVb**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB1 1EZ, UK [Fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk] (Fig. 1).

The crystals were obtained from methylene chloride solution.

The cyanine structure is confirmed by the bond length alternation in the planar methine chain, i.e. C11–C13=1.3669 Å, whereas C13–C10=1.4168 Å. Moreover, C8–C10–C11–C13 lies in the same plane with a maximum deviation of 0.009 Å. The aryl substituent forces the chain to adopt a *cis cis* configuration which was already observed in other cases[31] giving a chiral distorted horseshoe shape. The aryl group makes a near 50° angle with the plane of the methine chain whereas the terminal cyanine nitrogen atoms

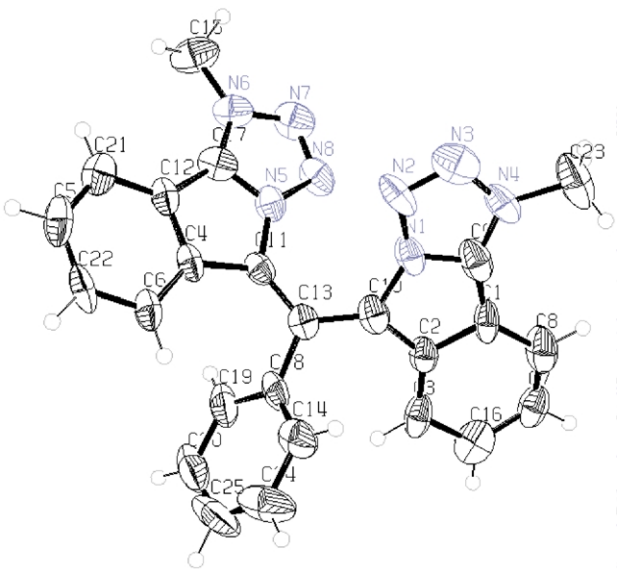


Figure 1. Ortep-3 for Windows[30] Version 1.07 (31st March 2001) drawing of the **IVb** cation with atom numbering.

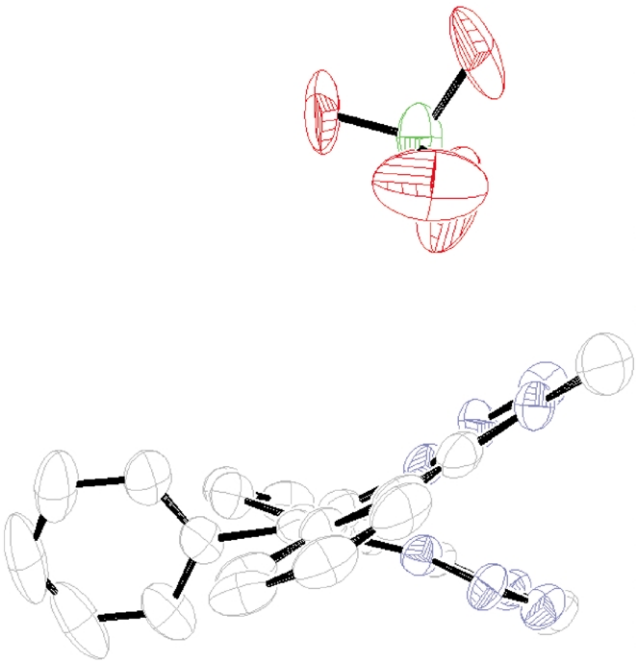


Figure 2. Side view of the **IVb** structure showing the perpendicular R substituent and the angle between the tetrazolo rings.

are respectively 0.916 Å over (N4) and-1.080 Å (N6) under the mean plane. The perchlorate anion is found in two equiprobable rotational conformations centred on the chlorine atom (Fig. 2).

The cartesian coordinates and selected bond length and valence and dihedral angles will be found in Tables 1–4.

2.3. Formation of the cyanine dyes: proposed mechanism

The proposed mechanism for the respective formation of **I** or **IV** is shown in the Scheme 3.

To explain the synthesis of the cyanine **IV**, it is necessary to have at the same time sufficient amounts of compounds **I** and **III**. To confirm this assessment, we have mixed the perchlorate **III** with the acylation product **Ib** and triethylamine in the ratio 1/1/2, respectively. After reaction, by TLC we find only the cyanine **IVb** whose presence is supported by its R_f [R_f=0.42 ($CHCl_3$/MeOH 9/1, 21 °C)]. If we look again to the influence of the ratios of starting products (see Section 2.1) on the respective formation of **I** and **II** it is clear that the lower concentrations of base (1/1/1) are in favour of the direct formation of **I**. On the reverse, excess of triethylamine (1/3/3 or 2/1/3) leads to large quantities of **II** which may be responsible of the great amount of side reactions. In the intermediate case 2/1/1, excess of **III** enhances the formation of **II** due to the le Chatelier principle.

3. Conclusion

We found a new synthetic method for the acylation of the tetrazoloisindoles. In the course of this reaction, we observed the formation of unexpected new monomethine cyanine dyes. Their structure was assessed by an X-ray

Table 1. Fractional coordinates

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
N(1)	0.28802	0.37697	0.31113	C(10)	0.24287	0.43284	0.28143
N(2)	0.30211	0.30932	0.27141	C(11)	0.16724	0.35667	0.16026
N(3)	0.35363	0.28954	0.32882	C(12)	0.11539	0.25693	0.05798
N(4)	0.37120	0.34288	0.40543	C(13)	0.19151	0.42381	0.19590
N(5)	0.17299	0.28903	0.22092	C(14)	0.19371	0.54305	0.09839
N(6)	0.14503	0.17804	0.23950	C(15)	0.11665	0.10572	0.23048
N(7)	0.17746	0.20212	0.33982	C(16)	0.26659	0.60612	0.45900
N(8)	0.19377	0.27029	0.32975	C(17)	0.14210	0.23314	0.16623
C(1)	0.31816	0.46830	0.43139	C(18)	0.16100	0.49168	0.14364
C(2)	0.26336	0.49037	0.35824	C(19)	0.09856	0.49903	0.13381
C(3)	0.23757	0.55939	0.37060	C(20)	0.06851	0.55983	0.07547
C(4)	0.13007	0.33349	0.05376	C(21)	0.08226	0.21860	−0.03406
C(5)	0.06539	0.25934	−0.13021	C(22)	0.07920	0.33497	−0.13442
C(6)	0.11129	0.37246	−0.04603	C(23)	0.43126	0.33537	0.48020
C(7)	0.31994	0.57945	0.53070	C(24)	0.16414	0.60386	0.04038
C(8)	0.34624	0.51476	0.51666	C(25)	0.10306	0.61101	0.03224

Table 2. Selected bond length (Å)

Atom		Distance	Atom		Distance
A	B		A	B	
C1	C9	1.395	C12	C4	1.424
C1	C2	1.438	C13	C18	1.489
C2	C3	1.396	C15	N6	1.449
C2	C10	1.422	C17	N5	1.333
C2	C1	1.438	C17	N6	1.338
C4	C11	1.476	C23	N4	1.489
C9	N4	1.325	N1	N2	1.376
C9	N1	1.346	N2	N3	1.288
C10	C13	1.417	N3	N4	1.354
C10	N1	1.429	N5	N8	1.377
C11	C13	1.367	N6	N7	1.380
C11	N5	1.425	N7	N8	1.297
C12	C17	1.421			

Table 3. selected angles (°)

Atom			Angle	Atom			Angle
A	B	C		A	B	C	
C9	C1	C8	133.39	C11	C13	C10	124.06
C9	C1	C2	105.62	C11	C13	C18	117.88
C3	C2	C10	129.55	C10	C13	C18	118.04
C3	C2	C1	120.27	C14	C18	C13	119.5
C10	C2	C1	110.16	C9	N1	N2	110.04
C2	C3	C16	118.07	C9	N1	C10	112.18
N4	C9	N1	103.55	N2	N1	C10	137.49
N4	C9	C1	147.21	N3	N2	N1	107.22
N1	C9	C1	109.17	N2	N3	N4	107.29
C13	C10	C2	133.93	C9	N4	N3	111.87
C13	C10	N1	123.25	C9	N4	C23	129.55
C2	C10	N1	102.80	N3	N4	C23	118.39

Table 4. Selected dihedral angles (°)

N1	C10	C13	C18	−157.8
N1	C10	C13	C11	24.70
N5	C11	C13	C10	23.55
N5	C11	C13	C18	−154.67

structure determination and we tried to propose a mechanism for this reaction.

4. Experimental

You will find hereafter the numbering scheme of the products **I** and **IV** (Scheme 4).

4.1. General methods

The ^{1}H NMR spectra (400.396 MHz) were recorded with a Varian Mercury 400 with TMS as internal standard. The UV–vis spectra were obtained with a Perkin Elmer Lambda-19 spectrophotometer equipped with a 60 mm integration sphere for solid measurements. Mass spectra were obtained on a Nermag R 10 (in CI with NH_3, the higher peak always correspond to the $[MH]^+$ of the cationic part of the molecule). Elemental analysis were realised with a Carlo Erba analyser. Products **I** and **IV** were purified by column chromatography and possibly crystallised from methylene chloride.

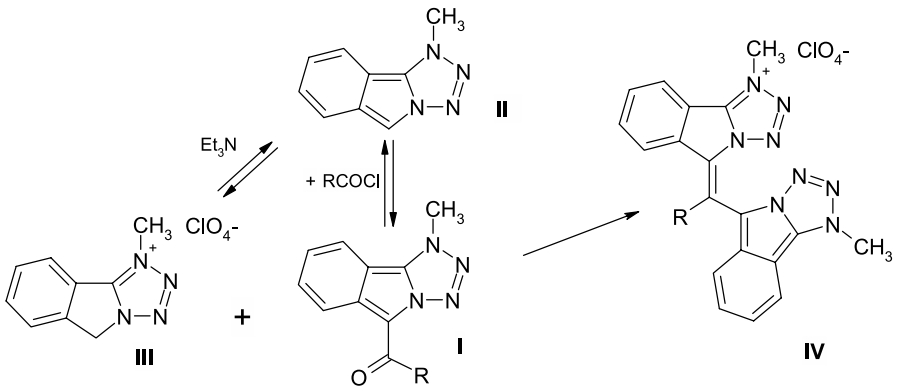
4.1.1. General experimental procedure. The starting products **II** and **III** were obtained by previously described methods.[14] We succeeded in the separation of analytically pure samples of the very unstable 1-methyltetrazoloisoindole by sublimation under reduced pressure (10^{-5} mm Hg). Thus we were able to record for the first time its ^{1}H and UV–vis spectra.

^{1}H NMR δ (CD_3OD) 4.43 (s, 3H, N–CH_3), 6.93 (t, 1H, H_{arom}), 7.26 (t, 1H, H_{arom}), 7.50 (s, 1H, 5-H), 7.55 (d, 1H, H_{arom}), 7.97 (d, 1H, H_{arom}); UV–vis (EtOH) 224 (4.49), 237† (4.23), 248 (4.15), 261† (4.07), 278 (4.09), 330† (3.97), 362 (3.89).

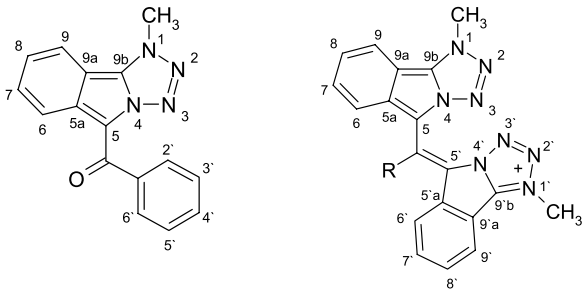
4.2. Synthesis of acylated compounds Ia–b,f–k and of the cyanines IVa–k

Nomenclature for **IVb**. 1-Methyl-5-[(1-methyl-1*H*-tetrazolo[5,1-*a*]isoindol-5-yl)-phenyl-methylene]-5*H*-tetrazolo[5,1-*a*]isoindol-1-ium; perchlorate.

† Shoulder.



Scheme 3. Formation of the cyanine dyes: proposed mechanism.



Scheme 4. Numbering scheme of products **I** and **IV**.

To 0.7 mmol of **III** in 3.5 ml of absolute dioxane were added 0.7 mmol of the corresponding acyl chloride and 1.4 mmol of triethylamine. The mixture was heated at 100 °C for one hour. The resulting mixture was filtered and the precipitate was washed with acetone. The filtrates were combined and dried with a rotatory evaporator. After column chromatography on silicagel (100/250 mesh) with methylene chloride/acetone (3/1) as solvent, the two types of product **I** and **IV** were obtained. Yields of acylation products are between 8.2 (**Ia**) and 78.7 (**Ik**) % whereas the yields of cyanines vary from 0.5 (**IVf**) to 63.8 (**IVc**)%.

Physicochemical constants, melting points, ^{1}H NMR, chromatographic R_f and UV–vis data are given below (structures in Scheme 2).

4.3. Acylated products

4.3.1. Compound Ia. Mp 199 °C; ^{1}H NMR δ (DMSO-d_6) 2.67 (s, 3H, CH_3), 4.55 (s, 3H, N–CH_3), 7.21 (t, 1H, H_{arom}), 7.52 (t, 1H, H_{arom}), 8.11 (d, 1H, H_{arom}), 8.37 (d, 1H, H_{arom}); R_f 0.84 ($CHCl_3$/MeOH 9/1, 21 °C); UV–vis (CH_3CN)[λ, (log ε) 305 (3.78), 336 (3.85), 338 (3.70). $C_{11}H_{10}N_4O$, M is 214.226. Analysis (calcd, found)% C (61.67, 61.65); H (4.70, 4.78); N (26.15, 26.17). Yield: 8.2%.

4.3.2. Compound Ib. Mp 187 °C; ^{1}H NMR δ (DMSO-d_6) 4.54 (s, 3H, N–CH_3), 7.24 (t, 1H, H_{arom}), 7.45 (t, 1H, H_{arom}), 7.52–7.65 (m, 6H, H_{arom}), 8.22 (d, 1H, H_{arom}); ^{13}C NMR δ (DMSO-d_6) 36.69 (N-Me), 102.90 (C-6), 108.63 (C-9a), 119.95 (C-5), 120.98 (C-9, C-9b), 121.32 (C-8),128.38 (C-3′, C-5′), 128.73 (C-2′, C-6′), 129.57 (C-4′), 130.76 (C-7), 136.66 (C-5a), 141.67 (C-1′), 179.49 (C═O); MS *m/z* 277 $(M+1)^+$(calcd 277.10); R_f 0.82 ($CHCl_3$/MeOH 9/1, 21°C); UV–vis (CH_3CN) [λ, (log ε)] 307 (3.54), 342 (3.62), 389 (3.88), 402† (3.80). $C_{16}H_{12}N_4O$, M is 276.297. Analysis (calcd, found)% C (69.55, 69.59); H (4.38, 4.45); N (20.28, 20.27). Yield: 41.7%.

4.3.3. Compound If. Mp 183 °C; ^{1}H NMR δ (DMSO-d_6) 4.56 (s, 3H, N–CH_3), 7.23–7.32 (m, 1H, H_{arom}), 7.44–7.56 (m, 1H, H_{arom}), 7.89 (d, 2H, H_{arom}), 8.11 (d, 1H, H_{arom}), 8.20 (d, 1H, H_{arom}), 8.38 (d, 2H, H_{arom}); R_f 0.79 ($CHCl_3$/MeOH 9/1, 21 °C); UV–vis (CH_3CN) [λ, (log ε)] 256 (4.47), 300 (3.92), 329 (3.80), 397 (398). $C_{16}H_{11}N_5O_3$, M is 321.293. Analysis (calcd, found)% C (59.81, 59.85); H (3.45, 3.51); N (21.80, 21.83). Yield: 81.3%.

4.3.4. Compound Ig. Mp 177 °C; ^{1}H NMR δ (DMSO-d_6) 2.47 (s, 3H, CH_3), 4.55 (s, 3H, N–CH_3), 7.17 (t, 1H, H_{arom}), 7.30 (d, 2H, H_{arom}), 7.37 (t, 1H, H_{arom}), 7.52–7.57 (m, 3H, H_{arom}), 8.14 (d, 1H, H_{arom}); MS *m/z* 291 $(M+1)^+$ (calcd 291.11); R_f 0.81 ($CHCl_3$/MeOH 9/1, 21°C); UV–vis (CH_3CN) [λ, (log ε)] 259† (3.94), 307 (3.45), 389 (3.66), 408† (3.50). $C_{17}H_{14}N_4O$, M is 290.323. Analysis (calcd, found)% C (70.33, 70.32); H (4.86, 4.91); N (19.30, 19.32). Yield: 39.8%.

4.3.5. Compound Ih. Mp 182 °C; ^{1}H NMR δ (DMSO-d_6) 3.60 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 4.53 (s, 3H, N–CH_3), 6.63–6.70 (m, 2H, H_{arom}), 7.16–7.64 (m, 4H, H_{arom}), 8.21 (d, 1H, H_{arom}); R_f 0.79 ($CHCl_3$/MeOH 9/1, 21 °C); UV–vis (CH_3CN) [λ, (log ε)] 263† (4.18), 281 (3.94), 324 (3.93), 389 (3.75). $C_{18}H_{16}N_4O_3$, M is 336.348. Analysis (calcd, found)% C (64.28, 64.31); H (4.79, 4.81); N (16.66, 16.65). Yield: 27.3%.

4.3.6. Compound Ii. Mp 161 °C; ^{1}H NMR δ (DMSO-d_6) 4.58 (s, 3H, N–CH_3), 7.22 (t, 1H, thiophene), 7.26 (d, 1H, H_{arom}), 7.51 (t, 1H, H_{arom}), 7.78 (d, 1H, thiophene), 7.94 (d, 1H thiophene), 8.15 (d, 1H, H_{arom}), 8.18 (d, 1H, H_{arom}); R_f 0.80 ($CHCl_3$/MeOH 9/1, 21 °C); ^{13}C NMR δ (DMSO-d_6) 36.71 (N-Me), 103.27 (C-6), 107.67 (C-9a), 120.42 (C-9b), 121.45 (C-3′), 121.50 (C-9), 128.18 (C-8), 130.21 (C-4′), 130.44 (C-5′), 131.61 (C-7), 134.09 (C-5a), 137.34 (C-5), 145.26 (C-2′),170.83 (C═O); UV–vis (CH_3CN) [λ, (log ε)] 247 (4.27), 262† (4.19), 308 (3.62), 403 (4.14). $C_{14}H_{10}N_4OS$, M is 282.319. Analysis (calcd, found)% C (59.56, 59.61); H (3.57, 3.62); N (19.85, 19.88); S (11.36, 11.39). Yield: 58.9%.

4.3.7. Compound Ij. Mp 156 °C; ^{1}H NMR δ (DMSO-d_6)

4.60 and 4.68 (2s, 3H, N–CH_3), 6.60 and 6.71 (2d, 1H, furan), 7.21–7.28 (m, 1H, H_{arom}), 7.34 and 7.37 (2d, 1H, furan), 7.50–7.57 (m, 1H, H_{arom}), 8.07 and 8.14 (2d, 1H, H_{arom}), 8.20–8.29 (m, 1H, H_{arom}); MS *m/z* 347 $(M+1)^+$ (calcd 344.99); R_f 0.79 ($CHCl_3$/MeOH 9/1, 21 °C); UV–vis (CH_3CN) [λ, (log ε)] 288 (4.29), 402 (4.37), 415† (4.35). $C_{14}H_9BrN_4O_2$, M is 345.154. Analysis (calcd, found)% C (48.72, 48.73); H (2.63, 2.70); Br (23.15, 23.18); N (16.23, 16.26). Yield: 47.2%.

4.3.8. Compound Ik. Mp 172 °C; ^{1}H NMR δ (DMSO-d_6) 2.36 (s, 3H, CH_3), 4.52 (s, 3H, N–CH_3), 7.30 (t, 1H, H_{arom}), 7.37–7.46 (m, 4H, H_{arom}), 7.53 (d, 1H, H_{arom}), 7.60 (t, 1H, H_{arom}), 8.25 (d, 1H, H_{arom}); MS *m/z* 392 $(M+1)^+$ (calcd 392.08); R_f 0.78 ($CHCl_3$/MeOH 9/1, 21 °C); UV–vis (CH_3CN) [λ, (log ε)] 256 (4.49), 263† (4.43), 305 (3.86), 346† (3.96), 384 (4.21), 400 (4.11). $C_{20}H_{14}ClN_5O_2$, M is 391.815. Analysis (calcd, found)% C (61.31, 61.34); H (3.60, 3.68); Cl (9.05, 9.11); N (17.87, 17.91). Yield: 78.7%.

4.4. Cyanine dye

4.4.1. Compound IVa. Mp 166 °C; ^{1}H NMR δ (DMSO-d_6) 3.39, 3.41 and 3.43 (3s, 3H, CH_3), 4.65 and 4.68 (2s, 6H, N–CH_3), 7.22–7.38 (m, 2H, H_{arom}), 7.51–7.68 (m, 4H, H_{arom}), 8.29–8.35 (m, 1H, H_{arom}), 8.43–8.48 (m, 1H, H_{arom}); R_f 0.44 ($CHCl_3$/MeOH 9/1, 21 °C); UV–vis (CH_3CN) [λ, (log ε)] 313 (4.42), 516† (4.86), 552 (5.31). $C_{20}H_{17}ClN_8O_4$, M is 468.857. Analysis (calcd, found)% C (51.24, 51.29); H (3.65, 3.71); N (23.90, 23.93). Yield: 60.9%.

4.4.2. Compound IVb. Mp 197 °C; ^{1}H NMR δ (DMSO-d_6) 4.68 (s, 6H, N–CH_3), 6.56 (d, 2H, H_{arom}), 7.40–7.48 (m, 4H, H_{arom}), 7.65–7.72 (m, 4H, H_{arom}), 7.80–7.83 (m, 1H, H_{arom}), 8.43 (d, 2H, H_{arom}); R_f 0.42 ($CHCl_3$/MeOH 9/1, 21 °C); UV–vis (CH_3CN) [λ, (log ε)] 276 (5.23), 305 (5.10), 326 (5.00), 358 (4.84), 522† (5.28), 561 (5.82). $C_{25}H_{19}ClN_8O_4$, M is 530.928. Analysis (calcd, found)% C (56.56, 56.60); H (3.61, 3.67); N (21.11, 21.13). Yield: 51.3%.

4.4.3. Compound IVc. Mp 158 °C; ^{1}H NMR δ (DMSO-d_6) 3.52–3.56 (m, 4H, H_{alk}), 4.29–4.33 (m, 2H, H_{alk}), 4.55 (s, 6H, N–CH_3), 7.20 (t, 2H, H_{arom}), 7.51 (t, 2H, H_{arom}), 8.11 (d, 2H, H_{arom}), 8.40 (d, 2H, H_{arom}); R_f 0.44 ($CHCl_3$/MeOH 9/1, 21 °C); UV–vis (CH_3CN) [λ, (log ε)] 308 (3.86), 399 (3.20), 527† (4.28), 556 (4.73). $C_{21}H_{18}Cl_2N_8O_4$, M is 517.329. Analysis (calcd, found)% C (48.76, 48.82); H (3.51, 3.56); N (21.66, 21.65). Yield: 63.8%.

4.4.4. Compound IVd. Mp 195 °C; ^{1}H NMR δ (DMSO-d_6) 3.72–4.03 (m, 9H, H_{alk}), 4.65 and 4.70 (2s, 6H, N–CH_3), 7.04–7.11 and 7.17–7.23 (2m, 2H, H_{arom}), 7.49–7.60 (m, 4H, H_{arom}), 8.43–8.47 (m, 2H, H_{arom}); R_f 0.45 ($CHCl_3$/MeOH 9/1, 21 °C); UV–vis (CH_3CN) [λ, (log ε)] 308 (4.06), 406 (3.58), 519† (4.31), 555 (4.80). $C_{23}H_{23}ClN_8O_4$, M is 510.937. Analysis (calcd, found)% C (54.07, 54.12); H (4.54, 4.58); N (21.93, 21.96). Yield: 62.4%.

4.4.5. Compound IVe. Mp 151 °C; UV–vis (CH_3CN) [λ, (log ε)] 301 (4.90), 343 (5.05), 437† (4.01), 531 (4.71), 564 (5.12). Yield: 2.1%.

4.4.6. Compound IVf. UV–vis (CH_3CN) [λ, (log ε)] 310, 362, 508,† 578. Yield: 0.5%.

4.4.7. Compound IVg. Mp 187 °C; ^{1}H NMR δ (DMSO-d_6) 2.60 (s, 3H, CH_3), 4.61 and 4.67 (2s, 6H, N–CH_3), 6.62–6.70 (m, 2H, H_{arom}), 7.19–7.76 (m, 8H, H_{arom}), 8.41 and 8.46 (2d, 2H, H_{arom}); R_f 0.41 ($CHCl_3$/MeOH 9/1, 21 °C); UV–vis (CH_3CN) [λ, (log ε)] 307 (4.74), 366 (4.70), 521† (4.94), 561 (5.46). $C_{26}H_{21}ClN_8O_4$, M is 544.954. Analysis (calcd, found)% C (57.31, 57.34); H (3.88, 3.93); N (20.56, 20.59). Yield: 53.2%.

4.4.8. Compound IVh. Mp 181 °C; ^{1}H NMR δ (DMSO-d_6) 3.51 and 3.65 (2s, 3H, OCH_3), 3.85 and 4.00 (2s, 3H, OCH_3), 4.65 and 4.68 (2s, 6H, N–CH_3), 6.50–6.86 (m, 4H, H_{arom}), 7.16–7.54 (m, 5H, H_{arom}), 8.40 and 8.45 (2d, 2H, H_{arom}); R_f 0.40 ($CHCl_3$/MeOH 9/1, 21 °C); UV–vis (CH_3CN) [λ, (log ε)] 303 (5.12), 361 (5.13), 414† (4.89), 528† (5.22), 564 (5.69). $C_{27}H_{23}ClN_8O_6$, M is 590.979. Analysis (calcd, found)% C (54.87, 54.91); H (3.92, 3.96); N (18.96, 18.97). Yield: 33.7%.

4.4.9. Compound IVi. Mp 185 °C; ^{1}H NMR δ (DMSO-d_6) 4.67 (s, 6H, N–CH_3), 6.80–6.88 (m, 2H, H_{arom}), 7.43–7.62 (m, 6H, H_{arom}), 8.16–8.20 (m, 1H, H_{arom}), 8.43 (d, 2H, H_{arom}); R_f 0.39 ($CHCl_3$/MeOH 9/1, 21 °C);^{13}C NMR δ (DMSO-d_6) 37.25, 104.11, 107.312, 109.44, 121.12, 123.72, 124.99, 127.48, 128.65, 130.32, 132.05, 134.70, 135.34, 135.94, 138.92, 142.29, 145.70; UV–vis (CH_3CN) [λ, (log ε)] 296 (4.91), 388 (4.72), 531† (5.10), 569 (5.57). $C_{23}H_{17}ClN_8O_4S$, M is 536.950. Analysis (calcd, found)% C (51.45, 51.48); H (3.19, 3.23); N (20.87, 20.90). Yield: 29.5%.

4.4.10. Compound IVj. Mp 176 °C; ^{1}H NMR δ (DMSO-d_6) 4.65 (s, 6H, N–CH_3), 6.89–7.08 (m, 2H, H_{arom}), 7.23–7.30 (m, 2H, H_{arom}), 7.51–7.68 (m, 4H, H_{arom}), 8.45 (d, 2H, H_{arom}); R_f 0.39 ($CHCl_3$/MeOH 9/1, 21 °C); ^{13}C NMR δ (DMSO-d_6) 37.29, 105.34, 106.82, 109.63, 112.21, 115.04, 116.70, 120.64, 121.21, 123.03, 123.81, 125.24, 127.36, 128.42, 132.17, 138.61, 142.80;UV–vis (CH_3CN) [λ, (log ε)] 281 (4.77), 307 (4.65), 409 (4.62), 544† (4.87), 582 (5.27). $C_{23}H_{16}BrClN_8O_5$, M is 599.785. Analysis (calcd, found)% C (46.06, 46.11); H (2.69, 2.76); N (18.68, 18.71). Yield: 35.8%.

4.4.11. Compound IVk. R_f 0.39 ($CHCl_3$/MeOH 9/1, 21 °C); UV–vis (CH_3CN) [λ, (log ε)] 309 (3.69), 369 (3.40), 562 (4.26). Yield: 1.7%.

4.5. Synthesis of the acylation product Ib starting from the 1-methyltetrazolo[5,1-*a*]isoindole II

For 0.35 g (0.002 mol) of tetrazoloisoindole II purified by sublimation, we add under inert atmosphere 10 ml of pyridine and 0.24 ml (0.002 mol) of benzoyl chloride. The solution was heathed at 100 °C for 30 min. Pyridine was then evaporated and the residue was crystallized from a mixture of benzene–ethyl acetate to give 0.5 g (89%) of **Ib**.

Acknowledgements

The authors wish to acknowledge Magda Tsapko for the

recording of the ^{1}H NMR spectra and the Paul Sabatier University for financial support under the Toulouse-Kiev co-operation agreement.

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