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Synthesis and characterisation of 3-H-indolo-2-dimethinehemicyanine dyes obtained by the condensation of (1,3,3-trimethylindolin-2-ylidene)acetaldehyde with anilines in acetic acid

Costinela-Laura Gáspár [a], Ioan Panea [b], Ioan Bâldea [c,*]

[a] S.C. Oltchim S.A., Research Centre, 1 Uzinei Street, Râmnicu Vâlcea 240050, Romania
[b] Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, Department of Organic Chemistry, 11 Arany János Street, Cluj Napoca 400028, Romania
[c] Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, Department of Physical Chemistry, 11 Arany János Street, Cluj Napoca 400028, Romania

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Abstract

Twenty, 1,3,3- trimethyl-2-[2-(2-Y-, 3- or 4-X-phenylamino)ethenyl]-3-H-indolium salts **1c**–**1z** were synthesised and characterised by their spectroscopic properties (UV–VIS, IR and NMR), ionisation constants (pK_a), and solvatochromic behaviour. The assigned 3-H-indolo-2-dimethinehemicyanine structure was proven on the basis of NMR data; the strong deshielding of the NH proton from the phenylamino moiety and of the N(1)CH_3 protons from the 3-H-indole moiety (11.5–13.43 and 3.59–3.74 ppm, respectively) indicates partial positive charge at the nitrogen atoms of these groups. Such partial positive charge at both nitrogen atoms from the end of the trimethine chain is compatible with an electron delocalization through the cationic polymethine chain, which is characteristic of hemicyanine dyes. The positive charge at the mentioned NH group is also sustained by the obtained pK_a values (8.05–9.37). The study concerning the solvatochromic behaviour revealed a small hypsochromic shift for all investigated dyes.

Keywords: Hemicyanine dyes; 1,3,3- Trimethyl-2-[2-(2-Y-, 3- or 4-X-phenylamino)ethenyl]-3-H-indolium salts; Structural analysis; Ionisation constants; Solvatochromic properties

1. Introduction

Hemicyanine dyes are widely used in different areas of technology [1–3]. Those containing a 1,3,3-trimethyl-2-methine-3-H-indolium moiety (such as C.I. Basic Yellow 11 (**1a**) and C.I. Basic Yellow 13 (**1b**)) are most often used as textile dyes and are produced on a large scale [1,4]. The usual method to obtain such hemicyanines **1** is the condensation of (1,3,3-trimethylindolin-2-ylidene)acetaldehyde **2** (TIA) with anilines **3** in the presence of acids (Scheme 1) [1,4]. The large-scale employment of some 1,3,3-trimethyl-2-anilinovinyl-3-H-indolium salts **1** as dyes explains the great interest concerning the synthesis and characterisation of these dyes [1,4–21]. However, publications concerning such dyes are most often patents describing only the preparation procedures; they do not give details about their structure or other properties. Indeed, there is only a UV–VIS study of some dyes of type **1** [18] and an ^{1}H NMR analysis of two species of type **4** having a very similar structure to **1** [22, p. 241–242, 349–350]. Moreover, publications concerning dyes of type **1** concern (with few exceptions [1,6,9,10,15,16,19]) derivatives that were obtained from anilines **3** substituted with electron-donating substituents in *para* position [2,4–21].

Therefore, one aim of this work was to synthesise hemicyanine dyes of type **1** by the condensation of TIA **2** with anilines **3** bearing both electron-withdrawing and electron-releasing

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* Corresponding author. Tel.: +40 264 593833; fax: +40 264 590 818.
E-mail address: ibaldea@chem.ubbcluj.ro (I. Bâldea).

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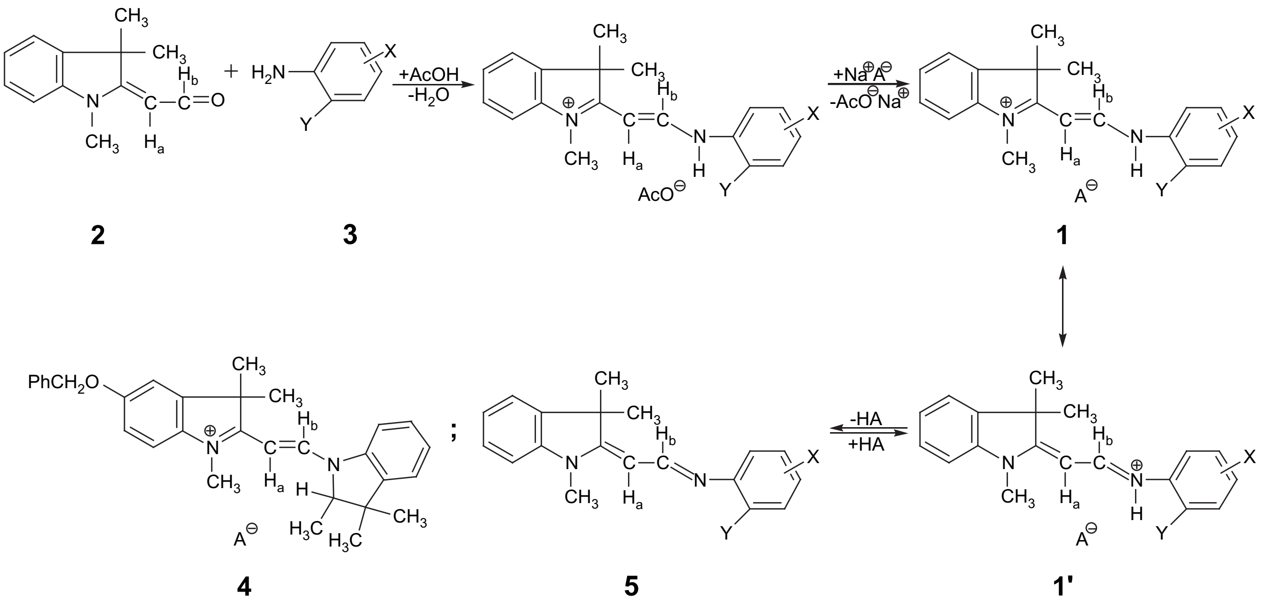

Scheme 1. Synthesis of the 3-H-indolo-2-dimethinehemicyanine dyes by the condensation of (1,3,3-trimethylindolin-2-ylidene)acetaldehyde **2** (TIA) with different anilines **3** in acetic acid. Depending on the used aniline: **1a**: X = 4-OCH$_3$, Y = 2-OCH$_3$; **1b**: X = 4-OCH$_3$, Y = H; **1c**: X = 4-COOH, Y = H; **1d**: X = 4-COOCH$_3$, Y = H; **1e**: X = 4-CN, Y = H; **1f**: X = 4-SO$_3$H, Y = H; **1g**: X = 4-SO$_2$NH$_2$, Y = H; **1h**: X = 4-SH, Y = H; **1i**: X = 4-I, Y = H; **1j**: X = H, Y = 2-OH; **1k**: X = H, Y = 2-NO$_2$; **1l**: X = 3-CH$_2$OH, Y = H; **1m**: X = 3COCH$_3$, Y = H; **1n**: X = 3-COOCH$_3$, Y = H; **1p**: X = 3-CN, Y = H; **1r**: X = 3-OH, Y = H; **1s**: X = 3-OCH$_3$, Y = H; **1t**: X = 3-NO$_2$, Y = H; **1u**: X = 3-F, Y = H; **1v**: X = 3-Cl, Y = H; **1w**: X = 3-Br, Y = H; **1z**: X = 3-I, Y = H. $A^- = Cl^-$, with three exceptions, namely in **1h**, **1k**, **1v** where $A^- = ClO_4^-$.

substituents in *para*, *meta*, or *ortho* position. A protocol described in a previous patent [7] has been slightly modified and used as preparation procedure.

The proposed condensation also allows a systematic study of the applicability of the used protocol as a function of the nature and position of the aniline substituent. However, this paper discusses dyes that were not previously described; their structures are presented in Scheme 1.

This paper presents the spectroscopic characterisation (UV–VIS, IR, and NMR spectra), an investigation of the acid–base equilibria, and study of the solvatochromic behaviour of the described dyes **1c**–**1z**. The detailed characterisation of such dyes is of interest in connection to their application [3, 22 (p. 11–13), 23 (p. 136–137, 290)].

2. Experimental

2.1. Materials

4-Aminobenzonitrile, 3-aminobenzyl alcohol, 3-aminophenol, 2-aminophenol, 3-anisidine, 3-bromoaniline, 3-chloroaniline, 3-iodoaniline, and 4-iodoaniline were purchased from Merck. 3-Aminoacetophenone, 3-aminobenzonitrile, 4-aminothiophenol, 3-fluoroaniline, methyl 3-aminobenzoate, methyl-4-aminobenzoate, 2-nitroaniline, 3-nitroaniline and sulfanilic acid were purchased from Fluka. 4-Aminobenzoic acid was purchased from Kebo AB. Spectroscopic quality acetonitrile, chloroform, ethyl acetate, methanol and 2-propanol were purchased from Riedel-de Haën, whilst the same quality dichloromethane and dimethylsulfoxide were purchased from Fluka; glacial acetic acid, ethyl alcohol, and diethyl ether were purchased from Chimopar. Buffer solutions of various pH values were purchased from Naposenz SRL.

All chemicals were used as received. 4-Aminobenzenesulfonamide and TIA **2** were synthesised as previously described [24–27]. All solutions were prepared by using demineralized and twice-distilled water.

2.2. General procedure for the condensation of (1,3,3-trimethylindolin-2-ylidene)acetaldehyde **2** with anilines **3**

The condensation of TIA **2** and anilines **3** was carried out based on a previously described procedure that was slightly modified [7]. A mixture of TIA **2** (0.01 mol), the corresponding aniline **3** (0.01 mol), and glacial acetic acid (5 ml) was stirred at room temperature for 15–30 h. Then the mixture was diluted with water (25 ml), and salted out with either NaCl or NaClO$_4$. The use of NaClO$_4$ has only been necessary to salt out the condensation products **1h**, **1k**, and **1v**, which did not precipitate with NaCl. The precipitate was filtered, washed first with water, with ethanol and then with ether; the dye was finally recrystallised from methanol.

2.3. Instrumentation and measurements

The melting points were recorded on a Böetius type apparatus (equipped with an HMK05 observation system) and are presented uncorrected. The IR spectra were recorded as KBr pellets on a Nicolet Impact 410 FT-IR spectrometer. The NMR experiments were performed in hexadeuterated dimethylsulfoxide (DMSO-d_6), at room temperature, using a Gemini 300 (300 MHz) spectrometer. The pK_a values were determined spectrophotometrically. The dyes (1.85×10^{-5}–2.52×10^{-5} mol L^{-1}) were dissolved in buffer solution of different pH values in the presence of KCl (0.012 mol L^{-1}). The absorbance of the resulting solutions was measured at λ_{max} observed in acidic medium and represented as a function of pH [28]. All UV–VIS spectra for pK_a determinations were recorded on a Jasco spectrophotometer (Model V-530) at 25 °C. The pH values were measured using a Pracitronic MV-870 digital pH-meter equipped with a SenTix 41-3 pH-electrode (0–14/0–80 °C/3 mol L^{-1} KCl). The UV–VIS spectra for the investigation of the solvatochromic behaviour were recorded on a Cintra 10e GBC spectrophotometer, at room temperature. Spectroscopic quality solvents were used throughout the study to prepare the dye solutions (with concentrations between 2.90 and 2.92×10^{-5} mol L^{-1}). The solvent polarity scale (E_T^N) for these solvents was that derived from negatively solvatochromic pyridinium *N*-phenolate betaine dyes [29]. The absorption spectra of freshly prepared dye solutions were recorded between 200 nm and 550 nm. Plots of the λ_{max} as a function of solvent polarity (E_T^N) were used to evaluate the solvatochromic behaviour of the dyes.

3. Results and discussion

3.1. Spectral characterisation and pK_a determination of the new dyes **1c–1z**

The yields and some properties of the synthesised dyes are presented in Table 1. The fact that the condensation of TIA **2** with all considered anilines **3** has taken place was proved first of all by the formation of coloured products (whilst the starting materials are usually colourless). We have ascribed the hemicyanine structures **1c–1z** to these coloured products (Scheme 1), in a similar manner to authors who have previously studied such condensations with other anilines [1,4–21]. The cationic structures **1c–1z** correspond to the salts of the corresponding Schiff bases [10,18]. Such salts should normally result as last intermediates in the synthesis of these bases by the condensation of the aldehydes with amines in acidic medium [30,31].

The ascribed structures **1c–1z** were confirmed by elemental and spectral analysis, and are also supported by the determined pK_a values. Thus, the elemental analysis data (Table 1) are compatible with the ascribed structures **1c–1z**. In addition, the presence of an intense and relatively sharp absorption band in the visible spectra of the condensation products (Fig. 1) argues also the assigned hemicyanine structures **1c–1z**.

Such a band is characteristic of polymethine dyes (cyanine, hemicyanine, etc.) [1,32–34]. Concerning this visible absorption band, it was observed that the substituents of the benzene ring of the anilines influence only weakly its position (Table 1). A Hammett type correlation between the position of the discussed band, λ_{max}, and the substituent constant, σ, of the corresponding substituent has not been obtained.

The IR spectra of the examined products are also compatible with the ascribed structures **1c–1z**. The recorded IR spectra reveal the presence of the NH group by absorption bands in the range of 3284–3423 cm^{-1} (Table 1), characteristic to NH stretching vibration (ν_{NH}) [35]. They also show the presence of the ethenyl group by the bands in the wave number range 929–944 cm^{-1}. Such bands are considered characteristic for out-of-plane deformation vibrations of the hydrogen atoms in an ethenyl group with a *trans*-configuration [34–36]. In addition, the IR-spectrum of each compound

Table 1
Some chemical and physical–chemical properties of the synthesised compounds

Compound (Scheme 1)	Type of data							
	Elemental analysis N (%)		Melting point (°C)	Yield of synthesis (%)	λ_{max} (nm)[a]; ε_{max} (L mol^{-1} cm^{-1})[a]	ν_{max} (cm^{-1})		pK_a values
	Calc.	Found				ν_{NH}	$\delta_{\mathrm{H}>\mathrm{C=C}<\mathrm{H}}$	
1c	7.85	8.1	231–234	86.5	418; 51.000	3383	937	–
1d	7.55	7.9	209–212	77.5	418; 55.000	3386	931	8.97
1e	12.44	12.1	211–214	85.8	414; 53.000	3393	931	8.83
1f	7.13	6.9	>350	93.3	414; 57.000	3423	929	–
1g	10.72	10.5	184–186	91.3	416; 52.000	3387	932	9.00
1h	6.85	6.5	188–190	94.0	418; 42.000	3375	932	–
1i	6.39	6.1	159–161	86.6	412; 49.000	3330	932	8.07
1j	8.52	8.7	218–220	50.2	412; 42.000	3380	930	–
1k	9.96	10.1	262–265	80.3	414; 29.000	3300	944	–
1l	8.17	8.4	148–150	69.7	410; 45.000	3387	935	9.37
1m	7.89	7.69	232–234	77.0	410; 49.000	3399	933	9.04
1n	7.55	7.72	223–225	73.5	404; 31.000	3383	933	8.98
1p	12.44	12.21	213–215	68.0	402; 40.000	3386	932	8.86
1r	8.52	8.71	243–245	82.0	412; 43.000	3323	929	–
1s	8.17	7.98	215–217	68.3	410; 44.000	3387	933	9.36
1t	11.74	11.69	194–196	90.0	404; 39.000	3393	931	8.45
1u	8.47	8.35	216–218	56.7	410; 45.000	3371	931	9.03
1v	6.81	6.90	235–237	90.6	408; 46.000	3284	930	–
1w	7.15	6.98	146–148	69.0	406; 44.000	3388	932	8.20
1z	6.39	6.2	143–145	63.9	412; 44.000	3381	932	8.05

[a] Data obtained in methanol.

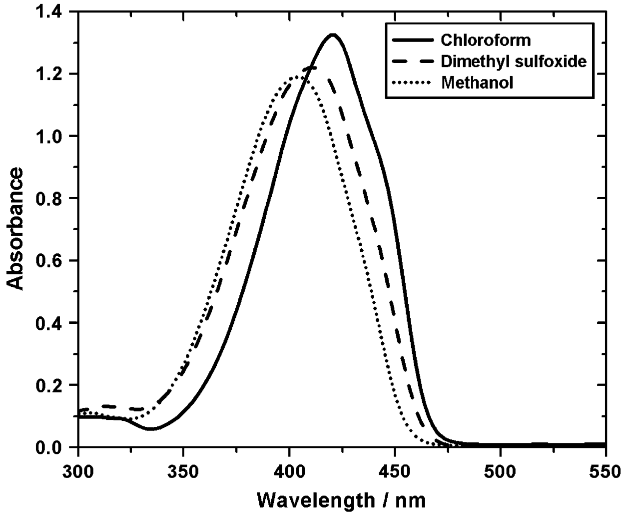

Fig. 1. Visible absorption band of the hemicyanine dye **1p** (obtained by the condensation of TIA **2** with 3-aminobenzonitrile) in different organic solvents.

shows characteristic IR bands for the substituent. For example, the product **1c** exhibits a band at 1702 cm^{-1} specific to $\nu_{C=O}$ in the COOH group. The product **1d** exhibits the corresponding band from the $COOCH_3$ group at 1716 cm^{-1}, and the product **1e** exhibits $\nu_{C\equiv N}$ from the CN group located at 2220 cm^{-1}.

The best evidence of the formation of the expected dyes **1c**–**1z** was obtained from the ^{1}H NMR data, which are summarized in Table 2. There are several features of the ^{1}H NMR spectra, which indicate that the synthesised compounds are indeed hemicyanines (i.e. polymethine dyes where only one of the positive charge-carrying nitrogen atoms at the ends of the polymethine chain is directly bound to the acylic part of this, whilst the other belongs to a heterocycle that includes also a part of the polymethine chain).

The ^{1}H NMR spectra of all synthesised dyes display characteristic signals for the protons of a 1,3,3-trimethyl-2-(2-aminovinyl)-3H-indolium moiety. This moiety is present both in the synthesised dyes **1c**–**1z** and in two 1,3,3-trimethyl-2-[2-(*N*-indolinevinyl)]-3-H-indolinium salts of type **4**. As established previously [22, p. 241–242, 349–350], 1,3,3-trimethyl-2-[2-(*N*-indolinevinyl)]-3-H-indolinium salts of type **4** display characteristic signals for the protons of the N(1)CH_3, C(2)–CH=CH– and C(3)$(CH_3)_2$ groups, in the 3.8–4.3 (singlet, s), 6.0–6.5 (doublet, d) and 8.0–9.0 (d), and 1.6–1.9 (s) ppm regions, respectively. The ^{1}H NMR spectra of the dyes **1c**–**1z** also show these characteristic signals in the 3.59–3.74 (s), 6.09–6.62 (d) and 8.55–8.95 (d), and 1.64–1.7 (s) ppm regions, respectively (Table 2). Different solvents used for the registration of the ^{1}H NMR spectra may cause some small difference between the values of the chemical shifts of the discussed protons in **1c**–**1z** and **4**. It is well known that salts of type **4** are a type of 3-H-indolo-2-dimethinehemicyanines **1** [1, 22 (p. 241–242, 349–350)]. Since the synthesised dyes **1c**–**1z** display all characteristic signals for the 3-H-indolo-2-dimethinehemicyanines of type **4**, the dyes **1c**–**1z** should also belong to this category of dyes.

Concerning the singlet signals for the six equivalent protons of the C(3)$(CH_3)_2$ group, it should be underlined that they have a great diagnosis value due to their nearly constant chemical shift (1.64–1.7 ppm) and their greatest intensity in the spectra (6H). Therefore, they might be used as reference for the determination of the number of protons, which correspond to each signal in the ^{1}H NMR spectra.

The increased chemical shift of the protons of the N(1)CH_3 group in the condensation products **1c**–**1z** (3.59–3.74 ppm), relative to that of the corresponding protons in the starting reactant (1,3,3-trimethylindolin-2-ylidene)acetaldehyde **2** (3.21 ppm), indicates a stronger deshielding effect at the protons of the N(1)CH_3 group in **1c**–**1z** as compared to **2**. Such a deshielding effect has been explained by the fact that the nitrogen atom, to which the CH_3 group is bound, has a partial positive charge for similar compounds [22 (p. 241–242, 349–350), 37]. Therefore, the observed deshielding effect also supports the 1,3,3-trimethyl-2-anilino-vinyl-3H-indolium salt structures for **1c**–**1z** because in such structures the N(1)-atom is positive (see **1**, **1′** in Scheme 1) [1, 4, 22 (p. 241–242, 349–350)]. This charge involves an increased bond order between the two methine groups of the dimethine chain in the dyes of type **1** compared to the situation in TIA **2**. This increased bond order explains the greater coupling constants between the protons of the dimethine chain in **1c**–**1z** ($J = 11$–12.6 Hz, as presented in Table 2) compared to the situation in TIA **2** ($J = 9$ Hz). The observed coupling constants in **1c**–**1z** correspond to a *trans*-configuration of the two vicinal protons (H_a and H_b) of the ethenyl group [22 (p. 241–242, 349–350), 38 (p. 302, 216–217), 39]. The chemical shift of these methine protons of the ethenyl group in **1c**–**1z** obeys the alternating rule established in the case of the cyanines [34,39] and thus supports the ascribed hemicyanine structures. Similar to other systems of type A–CH_a=CH_b–D (where A is an electron-withdrawing moiety while D is an electron-releasing moiety) [22 (p. 241–242, 349–350), 34, 40], the chemical shifts recorded for the H_a protons (6.09–6.62 ppm) of **1c**–**1z** are smaller than those recorded for the H_b protons (8.55–8.95 ppm). That H_b is the proton with the greater chemical shift between the two methine protons of the ethenyl group in the products **1c**, **1d**, **1e**, **1i**, **1n** and **1v** (Table 2) is further argued by the triplet multiplicity of the ^{1}H NMR signal at 8.55–8.95 ppm. Indeed, triplet multiplicity may be expected only for the signal of H_b because this signal may be split by coupling with H_a ($J = 12.5$ Hz) and H–N ($J = 12$ Hz) whilst the signal of H_a may be split only by coupling with H_b ($J = 12.5$ Hz).

Another important and characteristic signal in the ^{1}H NMR spectra appears in the region of 11.5–13.43 ppm, and corresponds to a single proton (Table 2). Such chemical shifts larger than 10 ppm correspond either to an acid hydrogen or to a hydrogen involved in intramolecular bonding [38, p. 302, 216–217]. Since in most of the compounds **1c**–**1z** intramolecular hydrogen bonding is not possible, the ^{1}H NMR signals observed over 10 ppm are due to acid hydrogen atoms. For certain dyes of type **1** (such as **1d**, **1e**, **1g**, **1i**, **1m**–**1p**, **1s**–**1z**) such acidic hydrogen atoms may only be those of the NH

Table 2
^{1}H NMR data (chemical shift, δ [ppm], number of protons and coupling constant J [Hz]) for compounds **1c–1z**

Compound (Scheme 1)	Type of protons and multiplicity[a]					
	$>C(3)(CH_3)_2$ s	$-\overset{\delta^+}{N}(1)CH_3$ s	H_a d	H_b d/t	H_{ar} m	$\overset{\delta^+}{=\!=}NH-$ s/d	Some substituent protons
1c	1.68; 6H	3.69; 3H	6.32; 1H; $J = 12.6$	8.64; 1H; t; $J = 12$; $J = 12.6$	7.3–8.1; 8H	12.47; 1H; d; $J = 12$	–
1d	1.67; 6H	3.69; 3H	6.48; 1H; $J = 12.6$	8.64; 1H; t; $J = 12.6$; $J = 12.5$	7.3–8.1; 8H	12.83; 1H; d; $J = 12.5$	$\delta_{COOCH_3} = 3.83$; s; 3H
1e	1.69; 6H	3.7; 3H	6.6; 1H; $J = 12.4$	8.68; 1H; t; $J = 12$; $J = 12.4$	7.3–8.0; 8H	13.14; 1H; d; $J = 12$	–
1f	1.66; 6H	3.65; 3H	6.11; 1H; $J = 12.4$	8.6; 1H; d; $J = 12.4$	7.2–7.8; 8H	12.05; 1H; s	–
1g	1.65; 6H	3.67; 3H	6.33; 1H; $J = 12.5$	8.58; 1H; d; $J = 12.5$	7.2–8.0; 8H	12.5; 1H; s	–
1h	1.68; 6H	3.68; 3H	6.11; 1H; $J = 12.5$	8.6; 1H; d; $J = 12.5$	7.3–8.77; 8H	11.94; 1H; s	–
1i	1.67; 6H	3.65; 3H	6.41; 1H; $J = 12.6$	8.62; 1H; t; $J = 12$; $J = 12.6$	7.2–7.9; 8H	12.83; 1H; d; $J = 12$	–
1j	1.64; 6H	3.59; 3H	6.42; 1H; $J = 12.6$	8.95; 1H; d; $J = 12.6$	6.8–7.7; 8H	12.05; 1H; s	$\delta_{OH} = 11$; s; 1H
1k	1.67; 6H	3.72; 3H	6.60; 1H; $J = 12.6$	8.55; 1H; d; $J = 12.6$	7.3–8.3; 8H	11.5; 1H; s	–
1l	1.67; 6H	3.74; 3H	6.15; 1H; $J = 12.5$	8.6; 1H; d; $J = 12.5$	7.0–7.7; 8H	12.17; 1H; s	$\delta_{CH_2-O} = 4.55$; s; 2H
1m	1.69; 6H	3.67; 3H	6.52; 1H; $J = 12.4$	8.63; 1H; d; $J = 12.4$	7.3–8.1; 8H	13.13; 1H; s	$\delta_{CH_3CO} = 2.63$; s; 3H
1n	1.69; 6H	3.68; 3H	6.24; 1H; $J = 12.5$	8.74; 1H; t; $J = 12.5$; $J = 12.5$	7.3–8.4; 8H	12.39; 1H; d; $J = 12.5$	$\delta_{COOCH_3} = 3.9$; s; 3H
1p	1.67; 6H	3.66; 3H	6.54; 1H; $J = 12.3$	8.68; 1H; d; $J = 12.3$	7.3–8.2; 8H	13.2; 1H; s	–
1r	1.66; 6H	3.63; 3H	6.25; 1H; $J = 12.4$	8.57; 1H; d; $J = 12.4$	6.6–7.7; 8H	12.66; 1H; s	$\delta_{OH} = 10.02$; s; 1H
1s	1.66; 6H	3.62; 3H	6.27; 1H; $J = 12.5$	8.59; 1H; d; $J = 12.5$	6.8–7.7; 8H	12.42; 1H; s	$\delta_{OCH_3} = 3.8$; s; 3H
1t	1.7; 6H	3.7; 3H	6.62; 1H; $J = 12.4$	8.74; 1H; d; $J = 12.4$	7.3–8.4; 8H	13.43; 1H; s	–
1u	1.67; 6H	3.66; 3H	6.49; 1H; $J = 11.6$	8.63; 1H; d; $J = 11.6$	7.0–7.8; 8H	13.03; 1H; s	–
1v	1.69; 6H	3.69; 3H	6.09; 1H; $J = 12.6$	8.63; 1H; t; $J = 12.4$; $J = 12.6$	7.3–7.7; 8H	11.87; 1H; d; $J = 12.4$	–
1w	1.68; 6H	3.66; 3H	6.51; 1H; $J = 11.0$	8.65; 1H; d; $J = 11$	7.2–8.0; 8H	13.07; 1H; s	–
1z	1.67; 6H	3.65; 3H	6.48; 1H; $J = 12.4$	8.62; 1H; d; $J = 12.4$	7.2–8.0; 8H	13.0; 1H; s	–

[a] s = singlet; d = doublet; t = triplet; m = complex multiplet.

groups. Otherwise, these hydrogen atoms correspond to the proton that is attached to the corresponding Schiff bases **5** in acidic medium [10,18].

The presence of the acidic NH group in the studied dyes might be confirmed by determining the ionisation constants of the dyes. The plots of the maximum absorbance against pH in the range 1–12, exhibited sigmoidal forms (Fig. 2) that is characteristic for acid–base equilibrium [23 (p. 136–137, 290), 28]. This enables us to determine the pK_a values by means of the sigmoidal curve's first derivative. The correlations were fitted using Origin 6.1. v 6.1052 from OriginLab Corporation, Northampton, MA, USA.

The pK_a values, ranging between 8.05 and 9.37 (Table 1), are closer to those of the conjugate acids of the starting anilines (e.g. for $C_6H_5\text{-}NH_3^+$, p$K_a = 4.6$) than to those of the anilines themselves (e.g. for aniline, p$K_a = 26$). This situation is explained by the fact that the examined dyes of type **1** are also conjugated acids of the corresponding Schiff bases **5** [10,18]. However, while in conjugate acids of anilines the whole positive charge is localised at the amine nitrogen, in the hemicyanine dyes of type **1** this charge is delocalised (see **1**, **1′**, in Scheme 1) [1,4]. Consequently, there is only a partial positive charge on the NH group. This is compatible with

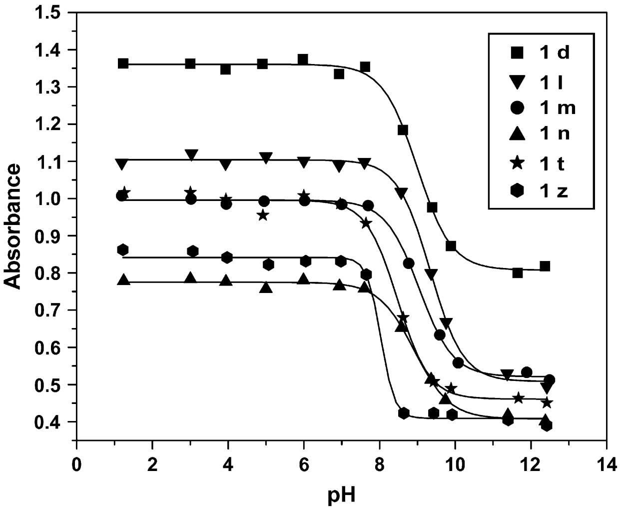

Fig. 2. pH induced absorbance change in the electronic spectra of hemicyanine dyes obtained by the condensation of TIA **2** with 3-aminoacetophenone (●, p$K_a = 9.04$), 3-aminobenzyl alcohol (▼, p$K_a = 9.37$), 3-iodoaniline (⬢, p$K_a = 8.05$), methyl 3-aminobenzoate (▲, p$K_a = 8.98$), methyl-4-aminobenzoate (■, p$K_a = 8.97$), or 3-nitroaniline (★, p$K_a = 8.45$).

Table 3
Position of the maximum absorption band of hemicyanine dyes **1e**, **1p** and **1r** in different solvents

Solvent	**1e**		**1p**		**1r**	
	λ (nm)	$\nu_{\max}$ (cm^{-1})	λ (nm)	$\nu_{\max}$ (cm^{-1})	λ (nm)	$\nu_{\max}$ (cm^{-1})
Ethyl acetate	425	23 529.41	418	23 923.45	insoluble	
Chloroform	429	23 310.02	420	23 809.52	424	23 584.90
Dichloromethane	427	23 419.20	418	23 923.45	insoluble	
Dimethylsulfoxide	422	23 696.68	410	24 390.24	418	23 923.45
Acetonitrile	416	24 038.46	408	24 509.80	412	24 271.84
2-Propanol	420	23 809.52	410	24 390.24	416	24 038.46
Methanol	414	24 154.59	402	24 875.62	412	24 271.84
Water	414	24 154.59	404	24 752.48	408	24 509.80

the diminished acidity of the dyes as compared to the conjugate acids of the corresponding anilines. Such partial positive charge on the NH group, alongside of the expected anisotropic effect of the vicinal polymethine chain, may also explain the strong deshielding of the proton of this group. Therefore, we have assigned the signal from the region 11.5–13.43 ppm to the proton of the NH group. It is noteworthy that the pK_a values determined for several 1,3,3-trimethyl-2-[2-(4-or 3-substituted phenylamino)ethenyl]-3H-indolium salts have failed to correlate with σ values of the corresponding substituent in the phenylamino entity of dyes.

As expected, the ^{1}H NMR spectra of the products **1c**–**1z** also exhibit signals that correspond to the protons of the benzene ring of the 3-H-indole- and phenylamino moieties. These signals could not be assigned to the individual protons since they are present as a complex multiplet for all aromatic protons. In addition, signals which correspond to the protons of the substituents on the aniline moiety appear in some of the examined ^{1}H NMR spectra. Thus, for example, for the condensation product **1d** obtained from TIA **2** and methyl-4-aminobenzoate, there is an additional singlet corresponding to the three protons of the methoxy carbonyl group [38, p. 164, 179, 216–217] at 3.83 ppm, alongside to that of the N(1)CH_3 group (at 3.69 ppm). These signals also indicate that the condensation of TIA **2** with anilines **3** takes place in a 1:1 molar ratio.

A structure of type **1** for the synthesised compounds is also supported by the ^{13}C NMR data. Thus the total number of signals in each ^{13}C NMR spectrum of the condensation products **1c**–**1z** corresponds to the number of carbon atom types in the ascribed formulae. For example, in formula **1i** there are 16 non-equivalent carbon atoms, and the corresponding ^{13}C NMR spectrum shows 16 ^{13}C signals. Moreover, the chemical shifts of three signals ($\delta = 27.3$, 31.6 and 49.5 ppm) indicate that the corresponding carbon atoms are sp^3-hybridized, which is again in accordance with structure **1i**. Similarly, the total number of signals in the ^{13}C NMR spectrum of **1j** and the number of the non-equivalent carbon atoms in structure **1j** is 18. As in the case of compound **1i**, the chemical shifts indicate again only three sp^3-hybridized carbon atoms ($\delta = 27.5$, 31.2 and 49.0 ppm). Similarly, in the case of compound **1m** the total number of signals in the ^{13}C NMR spectrum and the number of non-equivalent carbon atoms is the same (i.e. 20). However, in this case the ^{13}C-chemical shifts have indicated four sp^3-hybridized carbon atoms ($\delta = 26.9$, 27.3, 31.7 and 49.5 ppm), which is in complete agreement with structure **1m**.

The ^{13}C NMR signals at chemical shifts over 90 ppm are due to the sp^2 hybridized carbon atoms from the trimethine chain, the benzene nuclei, or the carbonyl group. As an example, the signal around 90 ppm is characteristic of the carbon atom in position 2 of a trimethine chain of a streptocyanine [41]. Therefore, the presence of this signal in the ^{13}C NMR spectra of the examined compounds also sustains the ascribed hemicyanine structures **1c**–**1z** since the hemicyanines are derived in fact from streptocyanines [1,42].

3.2. Study of the solvatochromic behaviour of 3-H-indolo-2-dimethinehemicyanine dyes

All investigated dyes displayed a small and rather similar negative (hypsochromic) solvatochromism (Table 3 and Fig. 3). The range of the used solvent polarities was somewhat limited by the fact that the synthesised dyes are hardly soluble in non-polar solvents. The effect of the solvent on the absorption bands is

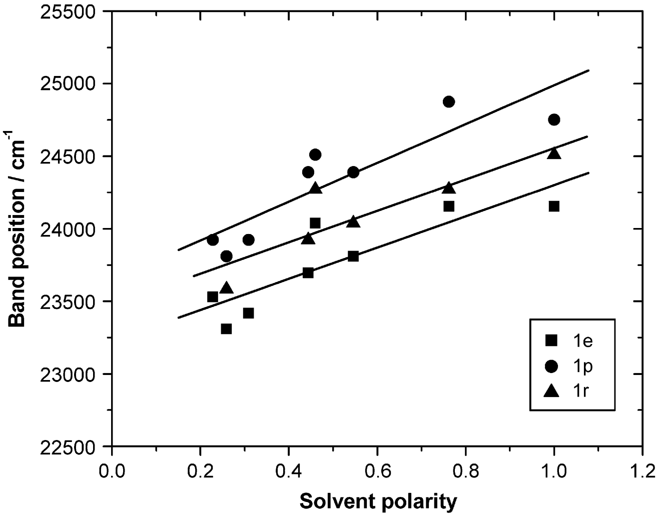

Fig. 3. Solvent induced shift in the absorption spectra of hemicyanine dyes obtained by the condensation of TIA **2** with 4-aminobenzonitrile (■), 3-aminobenzonitrile (●), or 3-aminophenol (▲). The solvent polarity scale was derived from negatively solvatochromic pyridinium *N*-phenolate betaine dyes [29].

due to the differential solvation of dye molecules in the ground and excited states. As the interaction of the solvent with the dye depends on the electron densities of the different states of the dye, the observed small solvatochromism indicates only a small change in the electron densities of the dye by its transition from ground to the excited state. The deprotonation equilibrium $1 \rightleftarrows 5$, characterized by the ionisation constants described above, may also be implicated in the negative solvatochromism of these dyes. As shown in Fig. 3, the effect of the solvent on the position of $\lambda_{\max}$ presented a satisfactory correlation with the polarity parameter E_T^N.

4. Conclusions

The condensation of TIA **2** with anilines in acetic acid was extended to several other *meta*-, *ortho*- or *para*-substituted anilines **3** obtaining 20 new hemicyanine dyes. Thus, it has been demonstrated that the used preparation procedure has a very large applicability.

On the basis of the spectral analysis (UV–VIS, IR, and NMR) and pK_a determinations, the 1,3,3- trimethyl-2-[2-(2-Y-, 3- or 4-X-phenylamino)ethenyl]-3-H-indolium structure **1c**–**1z** was unambiguously assigned to the isolated condensation products.

The investigation of the solvatochromic behaviour of some of the synthesised dyes (**1e**, **1p**, and **1r**) revealed a small hypsochromic shift.

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