Azomethine Chromogens Derived of 4-(β-sulphato-ethylsulphonyl)-Phenylamine

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The article presents experimental data regarding some chromogenes obtained either by condensation of 4-(β-sulphato-ethylsulphonyl)-phenylamine, with different aromatic aldehydes or by sulphatation reaction of corresponding azomethine dyes bearing β-hydroxy-ethylsulphonyl group grafted on the structure. Reaction products were purified and characterized by means of elemental analysis, UV-VIS, IR, ^{1}H-NMR spectroscopy. Structure-property relationship in the azomethine derivatives are discussed with respect to the structure and nature of the substituents.

Keywords: 4-(β-sulphato-ethylsulphonyl)-phenylamine, vinylsulphone, azomethines

The chromogen materials usage in sol-gel processes has determined a remarkable interest due to their possible industrial applications for obtaining of solid lasers, sensors and light concentrators in solar cells or materials with NLO properties [1].

Among the intense studied dyes are Schiff bases due to their special properties in connection with biological activity on the one side, but more recently they were investigated for their NLO applications or as sensor type devices [2-4].

The photochromic keto-enol tautomerism characteristic of Schiff bases derived of 2-hydroxy-aldehydes, having a hydrogen intramolecular bond in cis-enol form [5] leads to posible applications in optical switch devices having as advantages rapid transfer reaction [6] and high photochemical fastness [7,8].

The pursued objective consists of synthesis of some chromogens with potential luminescent properties, but as a function of structural characteristics, having complexing properties of cations or for non linear optical applications (NLO) [9].

Starting to followed goal in synthesis of some azomethine chromogens derived of 4-(β-sulfatoethyl-sulphonyl)-phenylamine, it was to keep in mind the selection of some aromatic aldehydes with structural characteristics, for each type of aimed application.

Thus, the aldehyde component must have grafted groups able for complexation of cations or ion exchange (for selected structures to obtaining ion sensors) or branched electronodonating groups for nonlinear optical applications while the amino component is intended to create the anchoring point by the β-vinylsulphone group.

Experimental part

This paper illustrates experimental data concerning synthesis and characterization of six new organic compounds (fig.1) having azomethine structure synthesized either by condensation of 4-(β-sulfato-ethyl-sulphonyl)-phenylamine with different aromatic aldehydes, such as: 1-formyl-2-hydroxy-benzene, 1-formyl-3-methoxy-4-hydroxy-benzene, 1-formyl-2-hydroxy-naphtalene, 4-formyl-3-hydroxy-naphtalene-2-carboxylic acid, 4-acetamido-benzaldehyde,N,N-diethylamino-benzaldehyde,or by sulphatation of corresponding azomethine dyes with β-hydroxy-ethylsulphone group grafted on the structure, compounds presented previously [9].

General method for obtaining azomethine derivatives

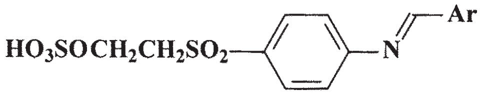

Fig. 1 General formula of azomethine derivatives

It is dissolved by heating at 90-95^{0}C and under stirring in 10-20 mL acetic acid 96%, 0.0015 mol aromatic amine (4.22 g 4-(β-sulfato-ethylsulphonyl)-phenylamine). Over the solution thus formed is added for 20 min and under stirring at a temperature of 40-50^{0}C, a solution obtained by dissolving a quantity of 0.015 mol aromatic aldehyde (1-formyl-2-hydroxy-benzene, 1-formyl-3-methoxy-4-hydroxy-benzene, 1-formyl-2-hydroxy-naphtalene, 4-formyl-3-hydroxy-naphtalene-2-carboxylic acid, 4-acetamido-benzaldehyde, N,N-diethylamino-benzaldehyde) in 30-40 mL acetic acid 96%.

After adding the aldehyde solution, reaction mass is heated to 100-108^{0}C, maintaining at this temperature for 8 to 15 h, when monoazomethine compound precipitates. Reaction mass is cooled to room temperature and the resulting suspension is filtered and washed with 40 mL acetic acid, followed by washing with 150 mL of water in portions to *p*H 6.5. Isolated product is dried at 50-70^{0}C. The rough product is purified by recristallization from a mixture of acetone and ethyl alcohol (1:1 vol). Yields for the synthesized compounds, and specifical work conditions are presented in table 1.

General method for obtaining monoazomethines by esterification of Schiff bases having β-hydroxy-ethylsulphonyl group

It is suspended under stirring, in 38 mL sulfuric acid 96% 0.02 mol azomethine component $\mathbf{A}_n$ (according to table 2) during 30 min at 20-25^{0}C. After adding the azomethine component, reaction mass as solution is maintained at this temperature under stirring for 24 h. Reaction mass is added during 15-20 min over a mixture of : 100 mL water and 200 g finely grinding ice. So that the temperature does not exceed 10-15^{0}C, then *p*H is adjusting to 4.5 – 5 by adding 110 g sodium acetate. The resulting suspension is filtered and washed with 200 mL of water in portions to *p*H 6.5. Isolated product is dried at 50-70^{0}C and are grinding correspondingly.

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Table 1
WORKING CONDITIONS FOR AZOMETHINE DERIVATIVES

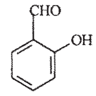
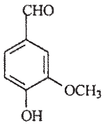
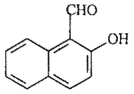
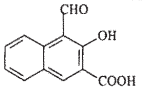
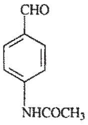
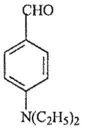
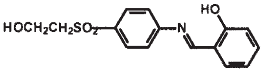
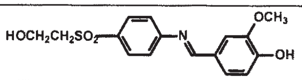
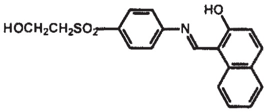
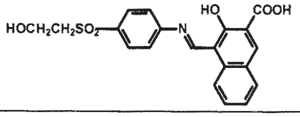
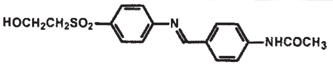
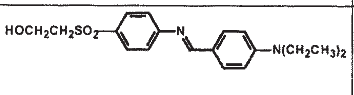
Compound	Carbonyl component (ArCHO)	ArCHO Quantity (g)	Acetic acid Quantity (g)	Reaction temperature (⁰C)	Reaction time (hours)	Yield (%)
1		1.83	40	100	8	94
2		2.28	50	107	11	95
3		2.58	60	105	10	92
4		3.24	60	108	15	90
5		2.45	50	106	11	87
6		2.66	40	108	10	95

Table 2
WORKING CONDITIONS FOR AZOMETHINE DERIVATIVES

Compound	Azomethine component (A_n)	A_n Quantity (g)	Yield (%)
1		6.1	80
2		6.7	78
3		7.1	82
4		8	85
5		6.9	81
6		7.2	84

Yields for the synthesized compounds and specifical work conditions are presented in table 2.

Purified substances were subject to elemental analysis. Determinations were made with a Carlo Erba M 1106 apparatus and sulfur content through Schoniger combustion. Results obtained are presented in table 4 and are in good agreement with those theoretically calculated. UV-Vis absorbtion spectra were made in ethanolic solutions at 10^{-4} molar concentrations, at 25± 0.5⁰C, in rectangular quartz cuvettes with a thickness of 1 cm, on a UV-VIS-NIR Jasco V 570 spectrometer (results and work conditions being those from table 5), IR spectra were recorded in KBr disks on a FT-IR BRUKER TENSOR 37 spectrometer (results and work conditions being those from table 6). ^{1}H-NMR spectra were recorder on a BRUKER AVANCE 400 MHz spectrometer at 25⁰C (results and work conditions being those from table 7).

The experimental study for obtaining the azomethine compounds through direct synthesis has aimed at the establishment of optimal reaction parameters which assure a relative entire transformation of the reactants to azomethine derivative, with maximum speed.

The concentration of two components (aromatic amine and aromatic aldehyde) in reaction mass established from experiments ranged within 1-10 and 4-8%, respectively limits. The best results were obtained at a weigth concentration of amine in the reaction mass of 9 to 9.23%.

For aromatic aldehydes, their optimal concentration in the reaction mass was 4-7%. At higher concentrations, the rate of condensation is slowed down due to premature precipitation of azomethine derivatives, leading to impurified products and lasting the condensation time.

The choice of solvent type regards that reaction is catalyzed by acids, from the reaction results water, and the *p*H to reach maximum speed is a function of amine basicity constant. When using N,N-dimethylformamide as solvent, the products obtained are soluble in the reaction mass and must be precipitated by mixing with water,

Table 3

R_f VALUES FOR AZOMETHINE DERIVATIVES

Compound number	1	2	3	4	5	6
R_f	0.74	0.80	0.89	0.83	0.82	0.81
Spot color (UV)	yellowish fluorescence	yellowish fluorescence	bluish fluorescence	green-yellowish fluorescence	yellowish fluorescence	yellowish fluorescence

Table 4

RESULTS FOR ELEMENTAL ANALYSIS

Compound	Molecular formula	Molecular mass	Elemental analysis (%)							
			C		H		N		S	
			Calculated	Founded	Calculated	Founded	Calculated	Founded	Calculated	Founded
1	$C_{15}H_{15}NO_7S_2$	385.41	46.75	46.65	3.92	3.82	3.63	3.58	16.64	16.84
2	$C_{16}H_{17}NO_8S_2$	415.43	46.26	46.18	4.12	4.02	3.37	3.30	15.44	15.54
3	$C_{19}H_{17}NO_7S_2$	435.47	52.40	52.25	3.93	3.89	3.22	3.13	14.73	14.85
4	$C_{20}H_{17}NO_9S_2$	479.48	50.1	49.98	3.57	3.49	2.92	2.84	13.37	13.45
5	$C_{17}H_{18}N_2O_7S_2$	426.46	47.88	47.72	4.25	4.15	6.57	6.49	15.03	15.16
6	$C_{19}H_{24}N_2O_6S_2$	440.53	51.8	51.69	5.49	5.42	6.36	6.29	14.56	14.71

method leading to impurification of finished products with exceeding raw materials or secundary reaction products.

Reactions carried out in lower aliphatic alcohols (methanol, ethanol), which allows a convenient degree of solubility of raw materials and easy isolation of the obtained products, requires an acid catalyst and reaching maximum temperatures of 68-78^{0}C which do not allow reaching optimal conditions (conversions and reaction time) for the evolution of condensation reaction. Using acetic acid as solvent, allows to reach an adequate temperature for achieving optimal conditions of condensation reaction and also catalyses addition reaction.

Molar ratio amine : aldehyde established as convenient for reaction evolution was 1:1 in terms of using acetic acid as solvent and achieving high conversions (99%). The manner of adding the of reactants influences decisive reaction evolution. It is prefered to introduce firstly the amine in the solvent chosen, justified by its solubility and only after dissolving it, to add aromatic aldehyde previously dissolved in the same solvent.

The time for reaction concluding was established at 8-15 h depending on aldehyde used, so that finaly, the quantity of unreacted aldehyde or amine, respectively, was about 0.1-0.2% up to reaction mass (chromatography check) correspondingly to a 99% conversion.

For the achievement of esterification (sulphatation) reaction of azomethine components $\mathbf{A}_n$ having hydroxy-ethylsulphone groups, compounds presented in a privious paper [9], it was used sulfuric acid 96% at a molar ratio which was varied between the limits 1:5 to 1:40, correlated with $\mathbf{A}_n$ reactivity solvent and especially taking into account that sulfuric acid is reagent, water binding agent and solvent. For both limit cases the reaction took place in good conditions with remark that reaction mass has a very viscous consistency to 1 : 5 ratio, it was hard to stirr and dificult to handle while at 1 : 40 ratio the reaction mass is solution, was easy to stirr, but reaction nedeed large excess of sulfuric acid, which requires increased quantities of water and ice to perform the dilution. Optimum molar ratio was established at 1 : 35. The time for esterification at 20-25^{0}C was varied between 10 and 30 h. It was established an optimal time of 24 h.

Regarding water : ice ratio needed to dilution, this was varied between 1:10 to 1:25, optimum ratio established was 1:20, which assured good stirring conditions and a volume of reaction mass kept at minimum while the quality of azomethine compound was maintained. During the experimental study have been synthesized 6 monoazomethine derivatives having reactive groups, the global yields beeing located between 78-85% while for direct synthesis of the same products the yields were 90-95%. Differences were recorded because of the products solubility in aqueous-sulphuric acid resulted after processing the esterification mass.

Purity of azomethine compounds synthesized through both variants and testing during synthesis were done by thin layer chromatography. Thus, for each compound were established stationary and mobile phases and were determined the specific developing methods.

It was established as optimal separation method, the ascending method on glass plates having Silicagel 60G Merck as a stationary phase and using as a mobile phase the mixture n-propanol : n butanol : ethyl acetate : water in a 2:4:1:3 (v/v) ratio. Samples dissolution was made in ethyl alcohol at a 0.2% concentration and application of the analyzed solutions was made at a 3µL level. After elution, chromatographic plate was dried on air 15 min and separated spots were identified after exposure to UV light. R_f values for all compounds studied are presented in table 3.

The obtaining of pure compounds requires the separation by column chromatography synthesis mixtures using as stationary phase Silicagel 60 G Merck or Cellulose Merck and the same mobile phase used thin layer chromatography.

After for elemental analysis on purified products, it was founded a good agreement between experimental obtained values and those theoretical calculated (table 4).

The compounds 1-6 are azomethine with electron donating group (phenole or amine) on the aldehydic residue and electron accepting group (sulfone) in the aminic residue, so that the molecules are polarized, belonging to chromogens category of donor-acceptor type.

In the visible absorption spectra of Schiff bases were not observed distinct bands corresponding to n-π^* transitions, which are overlapped with bands corresponding to π-π^* transitions.

It is noted that the presence of several absoption maxima in visible domain is due to tautomerism.

Compound C= 1 x 10^{-4} (mol/l)	λ(nm)	ε	lgε
1	274.5	13877	4.142
	351	1682	3.226
2	274.5	20472	4.311
	316.5	5698	3.756
	360	1787	3.252
	435.5	299	2.476
3	271.5	20933	4.320
	341	3253	3.512
	368	2176	3.337
	388.5	1871	3.272
	438.5	832	2.92
4	261.5	14802	4.170
	368	6136	3.788
	436	963	2.893
5	260	13740	4.138
	327.5	15849	4.200
	435.5	293	2.467
6	272.5	8472	3.928
	344	8758	3.942
	401	1740	3.241
	408	4175	3.621

Table 5
RESULTS FOR UV-VIS ABSORPTION SPECTROSCOPY (ETHANOL)

Compound	Typical frequencies (cm^{-1}) and intensities
1	3432vs, 3000vs, 2605s, 1601s, 1539s, 1496m, 1418m, 1310vs, 1294s, 1233s, 1149vs, 1084vs, 1057vs, 886m, 833m, 758s, 726m, 651s, 615s, 553s, 534s
2	3466vs, 3044vs, 2660s, 1657vs, 1605vs, 1578vs, 1519vs, 1459s, 1434s, 1392s, 1337vs, 1313m, 1220s, 1177vs, 1139s, 1066m, 1021m, 968w, 859m, 819m, 733m, 703w, 606w, 573s, 571s
3	3441vs, 3000vs, 2620s, 1618s, 1571s, 1521s, 1454m, 1309s, 1200vs, 1142vs,1085vs, 892m, 707m, 621s, 580s, 533s
4	3379vs, 3050vs, 2750s, 1652vs, 1564m, 1504vs, 1455vs, 1431vs, 1333s, 1293s, 1207s, 1094s, 1012m, 940m, 897m, 798m, 740s, 651m, 603m, 477s, 431m
5	3485vs, 3310s, 3000s, 2670s, 1717s, 1649s, 1596vs, 1553vs, 1539vs, 1508vs, 1454m, 1319vs, 1226vs, 1177vs, 1138s, 1047vs, 878s, 840s, 762w, 615w, 578vs, 561w
6	3487vs, 3050vs, 2654s, 1650vs, 1612vs, 1577vs, 1542vs, 1454s, 1327s, 1228m, 1194m, 1146vs, 1049s, 912m, 829m, 795m,634m,575w, 513w, 475w

Table 6
RESULTS FOR FT-IR ABSORPTION SPECTROSCOPY

As it was seen for compound 1 which has salicylaldehyde as carbonyl component, in UV-VIS absorption spectrum is remarked the presence of one absoption maximum situated at a short wavelength $\lambda_{max.}$=351 nm, while for compound 3 which has 2-hydroxy-1-naphtaldehyde as carbonyl component, in spectrum were found two absorption maxima situated at $\lambda_{max.}$=388.5 nm and $\lambda_{max.}$=438.5 nm, respectively.

Against the compound 1 was remarked the bathochromic shift of the absorption maxima due to the presence of the naphtalene ring on the structure. The two absorption maxima suggest the existence of a enolimino-ketoenamino tautomeric equilibrium in solution.

In case of compounds 5 and 6 derived from aromatic aldehides having substituted amino residues, it was seen that bathochromic shift of the absorption maximum is about of the same magnitude with that obtained by extension of lateral conjugation through naphthalene nucleus as in compound 3 having $\lambda_{max.}$=438.5 nm.

Infrared absorption spectra of the synthesized compounds recorded on kalium bromide disks showed characteristic bands of basic structural elements of these compounds.

Presence of the amino and hydroxy groups simultaneously, lead to large bands corresponding to stretching vibration of the hydroxyl group (ν_{OH}) which are overlapped with the stretching vibrations of amino group and valence vibration bands of aromatic hydrogen atoms, situated at 3487-3379 cm^{-1}. It is noted for compound 5 the presence of very intense characteristic valence vibration of acetylamino carbonyl group, situated at 1717 cm^{-1}.

For compound 4 the large and very intense band situated at 1652 cm^{-1} corresponds to vibration bands of izolated and condensed aromatic ring skeletons overlapping with stretching vibration of azomethine group and vibration of carbonyl group from carboxylic residue, confirming its involvement in an intramolecular hydrogen bond with adjoining hydroxyl group.

The very intense band situated at 1094-1146 cm^{-1} and founded in IR spectra of compounds, resulted through overlapping of more vibrations, the major contribution beeing attributed to symmetrical valence vibrations of the sulphone groups, while at 1319 -1337 cm^{-1} were situated asymmetrical vibrations.

The characteristic out of plane deformation vibration bands (γ_{CH}) were situated at 740 cm^{-1} and depend on the substitution type. Vibration of phenolic bond (ν_{C-OH}) for all the compounds 1-4 was identified at aproximatively 1200 cm^{-1}.

According to provided information of COSY spectrum (Homonuclear Correlation) it was established the protons position, confirming the influence of different substituents on the shift values.

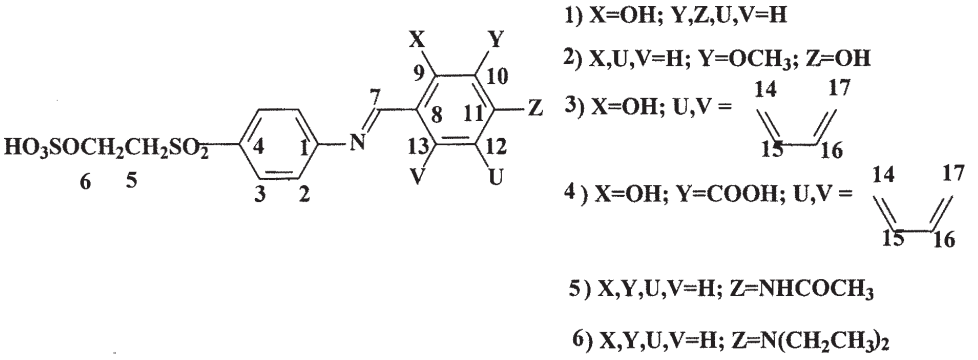


Fig. 2 Localization of the atoms for NMR spectra

Table 7
RESULTS FOR ¹H-NMR SPECTROMETRY

Compound	^{1}H-NMR((CD_3)$_2$SO) – (ppm)
1	H-2 = 7.44; H-3 = 6.65; H-5 = 3.23; H-6 = 3.50; H-7 = 7.78; OH=4.83; H-10=6.76; H-11 = 7.10; H-12 = 6.97; H-13 = 7.23
2	H-2 = 7.46; H-3 = 6.67; H-5 = 3.47; H-6 = 4.21; H-7 = 7.83; OH=5.53; OCH_3=3.84; H-9=7.39; H-12 = 6.95; H-13 = 7.42
3	H-2 = 7.44; H-3 = 6.65; H-5 = 3.23; H-6 = 3.60; H-7 = 6.08; OH=4.43; H-10 = 7.00; H-11 = 7.90; H-17 = 7.83; H-16 = 7.13; H-15 = 7.23; H14=7.57
4	H-2 = 7.39; H-3 = 7.22; H-5 = 3.25; H-6 = 3.62; H-7 = 7.80; OH=4.81; H-11 = 8.49; H-17 = 8.13; H-16 = 7.88; H-15 = 7.90; H-14 = 8.11
5	H-2 = 7.34; H-3 = 76.66; H-5 = 3.24; H-6 = 3.64; H-7 = 8.01; OH=4.65; $COCH_3$=1.91; H-9 = 7.48; H-10 = 7.56
6	H-2 = 7.45; H-3 = 6.63; H-5 = 3.24; H-6 = 3.62; H-7 = 7.81; H-19 = 7.64; H-10 = 7.65

The corresponding protons of the carbon atoms from amino component were situated at a shift value δ=7.34-7.46 ppm and δ=6.63-7.22 ppm, respectively, as doublets well defined and intense. For ethylsulfone residue hydrogen H-5 was found at a shift value δ= 3.23-3.47 ppm and H-6 at δ=6.63-7.22 ppm, as characteristic triplets.

Azomethine proton is situated at a chemical shift value of δ=7.78-8.08 ppm as a singlet. All the values obtained for the chemical shifts confirm the structures proposed for all the compounds studied.

Conclusions

Six new azomethine dyes with β-sulphato-ethylsulphonyl reactive groups were synthesized, by condensation of 4-(β-sulfato-ethylsulphonyl)-phenylamine with various aromatic aldehydes or by subsquent esterification with sulfuric acid of Schiff bases previously obtained from 4-(β-hydroxy-ethylsulphonyl)-phenylamine.

The azomethine compounds have functional groups able to form complexes with tranzitional metals or alkylated amino groups for nonlinear optical devices.

Structural analysis of the studied compounds confirm synthesized structures.

The synthesis method established as convenient was condensation of 4-(β-sulfato-ethylsulphonyl)-phenylamine with aromatic aldehydes, due to purity of the products and the higher yield obtained.

Compounds will be tested in addition processes to nucleophilic groups grafted on alkoxysilanes used in practice as anchoring agents for obtaining organic-inorganic hybrids.

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