The Influence of Bromine Substituent on Optical Properties of Some 1,3-Dithiolium Derivatives

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Mesoionic 2-[2-(dialkylamino)-1,3-dithiol-2-ylium-4-yl]phenolates bearing two bromine substituents on the phenolate moiety have been obtained by the heterocondensation of the corresponding phenacyl carbodithioates. These compounds have been investigated in terms of the influence of bromine substituents on the optical properties of this type of mesoionic phenolates. The bromine substituents were found to induce a negative solvatochromism and a batochromic shift of the long-wavelenght, solvent dependent, absorption band. In polar solvents, 4-(3,5-dibromo-2-hydroxyphenyl)-2-dialkylamino-1,3-dithiol-2-ylium perchlorates have been found to be in equilibrium with the corresponding mesoionic phenolates.

Keywords: intramolecular charge transfer, negative solvatochromism, dithiocarbamates, 1,3-dithiolium salts, mesoionic compounds

The heteroaromatic push–pull chromophores have been investigated as active components of optoelectronic devices, organic light-emitting diodes, photovoltaic cells, semiconductors, switches, data-storage devices [1-3]. In contrast to inorganic materials, the dipolar (hetero)organic materials with readily polarizable structure posses the advantage of their relative ease of synthesis, well-defined structure, chemical and thermal robustness, and possibility for further modification. Heteroatoms may act as auxiliary donors or acceptors and improve the overall polarizability of the chromophore [4-10]. A typical one-component organic D-π-A chromophore consists of a π-conjugated system end-capped with strong electron donors D and strong electron acceptors A. This D-π-A arrangement assures efficient intramolecular charge transfer (ICT) between the donor and acceptor moieties and generates a dipolar push–pull system featuring low-energy and intense CT absorption. A special interest was also given to the systems where the donor moiety is linked through a σ-bonded bridge to the acceptor moiety [11-15].

Recently, we have reported the synthesis of some 4-(hydroxyaryl)-2-(*N,N*-dialkylamino)-1,3-dithiolium salts by heterocyclofunctionalization of the corresponding 1-(2-hydroxyaryl)ethanones and propan-1-ones [16, 17]. In this context, investigations on a series of (1,3-dithiolium-2-yl)phenolates showed that 1,3-dithiolium ions can also serve as an acceptor moiety in intramolecular charge-transfer systems. To extend the scope of our studies, we report here the synthesis of a new class of mesoionic 2-(1,3-dithiolium-2-yl)phenolates and the influence of bromine substituents on the optical properties of these compounds.

Experimental part

Analysis methods

Melting points were obtained on a Mel-Temp II apparatus. IR spectra were recorded on a Bruker Tensor 27 instrument. UV-Vis spectra were recorded on Varian BioCarry 100 spectrophotometer. NMR spectra were recorded on a Bruker DPX-300 spectrometer. Chemical shifts are reported in ppm downfield from TMS. Elemental analyses (C, H, N, S) were conducted using a CE440 Elemental Analyser; the results were found to be in good agreement (±0.35%) with the calculated values.

Synthesis

Phenacyl dithiocarbamates have been synthesized by reacting 2-bromo-1-(3,5-dibromo-2-hydroxyphenyl) ethanone (**1**) [18] with various salts of dithiocarbamic acids (fig. 1).

1-(3,5-Dibromo-2-hydroxyphenyl)-1-oxaethan-2-yl-mopholine-1-carbodithioate(**2e**)

General Procedure

To 3.73g solution of 2-bromo-1-(3,5-dibromo-2-hydroxyphenyl)ethanone (**1**), (10 mmol) in 40mL acetone a 2.5g solution of morpholinium morpholine-1-carbodithioate (10 mmol) in 80mL acetone-water (1:1) was added. A white precipitate was formed. This was filtered, dried and recrystallized from 40mL dioxane to give 3.3 g pure product; yield: 73%. Analytical and spectral data of carbodithioates (**2c-e**) are presented in table 1.

4-(3,5-Dibromo-2-hydroxyphenyl)-2-(morpholin-4-yl)-1,3-dithiol-2-ylium perchlorate(**3e**);

To a mixture of 2mL sulfuric acid (98%) and 6mL glacial acetic acid, 2g 1-(3,5-dibromo-2-hydroxyphenyl)-1-oxaethan-2-yl-morpholine-1-carbodithioate (**2e**) (4.28 mmol) was added in small portions. The reaction mixture was heated at 80°C for 10 min. After cooling, 1mL $HClO_4$ 70%, and 200mL water were added in order to precipitate the corresponding perchlorate. This was filtered and dried off. Recrystallization from 70mL EtOH gave 1.5g colorless

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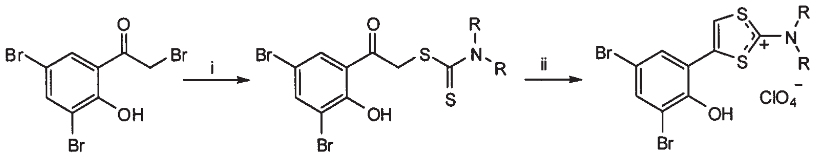


i. $R_2NC(S)S^-$, acetone, reflux; ii. H_2SO_4/AcOH 1:3 (v/v), 80 °C, 70% $HClO_4$

Fig. 1. Synthesis of dithiocarbamates **2** and 1,3-dithiolium perchlorates **3**

2, 3, 4	R	R
a	CH_3	CH_3
b	CH_2CH_3	CH_2CH_3
c	$(CH_2)_4$	
d	$(CH_2)_5$	
e	$(CH_2)_2$-O-$(CH_2)_2$	

Table 1
ANALYTICAL AND SPECTRAL DATA OF DITHIOCARBAMATES (**2**)

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR ($CDCl_3$)
2c	194-195 dec.	71	2949, 1638, 1430, 1313, 1257, 1218, 1149, 856, 790, 691, 555	^1H *NMR* δ : 2.03 (2H, m, CH_2); 2.12 (H, m, CH_2); 3.73 (2H, m, CH_2-N); 3.88 (2H, m, CH_2-N); 4.90 (2H, s, CH_2); 7.89 (1H, d, H-4); 8.12 (1H, d, H-6, J_{H4-H6}=2.4 Hz); 12.34 (1H, s, OH). ^{13}C *NMR* δ : 24.7, 26.2, 43.8, 51.1, 55.7, 111.1, 113.0, 123.0, 132.8, 141.0, 156.5, 194.5, 198.6
2d	183-184 dec.	81	2967, 1642, 1439, 1322, 1251, 1211, 1133, 857, 784, 688, 549	^1H *NMR* δ : 1.73 (6H, m, $3CH_2$); 3.95 (2H, m, CH_2-N); 4.25 (2H, m, CH_2-N); 4.86 (2H, s, CH_2); 7.89 (1H, d, H-4); 8.11 (1H, d, H-6, J_{H4-H6}=2.4 Hz); 12.47 (1H, s, OH). ^{13}C *NMR* δ : 23.4, 25.3, 25.8, 43.5, 51.3, 52.7, 111.0, 112.9, 122.9, 132.7, 140.8, 156.6, 194.8, 198.5
2e	188-189	73	2954, 1640, 1441, 1320, 1249, 1222, 1139, 852, 789, 684, 548	^1H *NMR* δ : 3.77 (4H, m, CH_2-O-CH_2); 4.15 (4H, m, CH_2-N-CH_2); 4.92 (2H, s, CH_2); 7.88 (1H, d, H-4); 8.09 (1H, d, H-6, J_{H4-H6}=2.3 Hz); 12.37 (1H, s, OH). ^{13}C *NMR* δ : 43.9, 51.2, 52.0, 66.0, 110.9, 112.9, 122.8, 132.7, 140.9, 156.7, 195.1, 198.4

Table 2
ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOLIUM PERCHLORATES (**3**)

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR (DMSO-*d*6)
3a	219-220 dec.	85	3043, 1578, 1441, 1299, 1138, 1047, 855, 572	^1H *NMR* δ : 3.58 (6H, s, $2CH_3$); 7.70 (1H,d, H-4); 7.75 (1H, d, H-6, J_{H4-H6}=2.4 Hz); 8.06 (1H, s, H-5); 11.52 (1H, s, OH). ^{13}C *NMR* δ : 47.4, 47.8, 112.6, 114.7, 122.8, 123.0, 130.7, 133.9, 136.6, 150.6, 187.7
3b	183-184	81	3062, 2983, 1567, 1442, 1109, 1020, 867, 783, 576	^1H *NMR* δ : 1.37 (6H, t, $2CH_3$); 3.88 (2H, q, CH_2); 3.91 (2H, q, CH_2); 7.78 (1H, d, H-4); 7.82 (1H, d, H-6, J_{H4-H6}=2.3 Hz); 8.19 (1H, s, H-5); 11.48 (1H, s, OH). ^{13}C *NMR* δ : 17.1, 53.1, 54.5, 112.5, 114.4, 122.9, 123.1, 130.4, 133.5, 136.7, 150.4, 187.9
3c	220-221 dec.	89	3057, 1568, 1439, 1092, 1028, 620, 563	^1H *NMR* δ : 2.29 (4H, m, $2CH_2$); 3.78 (4H, m, $2CH_2$); 7.69 (1H, d, H-4); 7.74 (1H, d, H-6, J_{H4-H6}=2.4 Hz); 8.04 (1H, s, H-5); 11.49 (1H, s, OH). ^{13}C *NMR* δ : 26.1, 26.3, 56.4, 56.8, 112.1, 114.5, 123.0, 123.2, 130.2, 133.9, 136.8, 150.1, 187.7
3d	185-186	79	3086, 2946, 1550, 1439, 1258, 1089, 1046, 854, 619	^1H *NMR* δ : 1.82 (6H, m, $3CH_2$); 3.89 (4H, m, $2CH_2$); 7.68 (1H, d, H-4); 7.72 (1H, d, H-6, J_{H4-H6}=2.3 Hz); 8.00 (1H, s, H-5); 11.58 (1H, s, OH). ^{13}C *NMR* δ : 21.7, 24.9, 25.1, 56.4, 57.7, 111.9, 114.2, 123.0, 123.1, 130.1, 133.7, 136.5, 149.9, 187.5
3e	218-219	64	3061, 1550, 1434, 1261, 1080, 887, 620, 540	^1H *NMR* δ : 3.93 (8H, m, $4CH_2$); 7.72 (1H, d, H-4); 7.76 (1H, d, H-6, J_{H4-H6}=2.3 Hz); 8.12 (1H, s, H-5); 11.56 (1H, s, OH). ^{13}C *NMR* δ : 54.0, 54.6, 64.8, 112.8, 114.6, 122.1, 122.9, 130.8, 132.9, 136.7, 150.6, 188.9

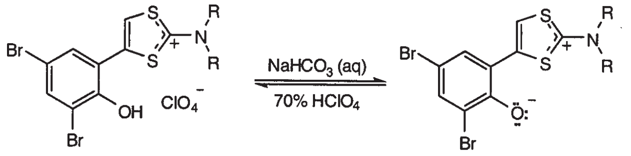


Fig. 2. Synthesis of mesoionic phenolates (**4**)

crystals; yield: 64%. Analytical and spectral data of 1,3-dithiolium perchlorates (**3**) are presented in table 2.

4,6-Dibromo-2-[2-(morpholin-4-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**4e**);

To 20mL saturated sodium hydrogencarbonate solution 1g perchlorate (**3e**) (1.8 mmol) was added. Carbon dioxide evolved and the reaction mixture became yellow. After 2h under vigorous stirring at room temperature, the yellow solid was filtered off, washed with water and dried. Recrystallization from DMF gave 0.81g yellow crystals; yield: 100%. Analytical and spectral data of 1,3-dithiolium phenolates (**4**) are presented in table 3.

Results and discussions

The synthetic strategy for the mesoionic 4,6-dibromo-2-[2-dialkylamino-1,3-dithiol-2-ylium-4-yl]phenolates involves the synthesis of 4-(3,5-dibromo-2-hydroxyphenyl)-2-dialchilamino-1,3-dithiol-2-ylium perchlorates (**3**), following the pathway described in figure 1. Phenacyl dithiocarbamates (**2**) have been synthesized by reacting

Table 3
ANALYTICAL AND SPECTRAL DATA OF MESOIONIC 1,3-DITHIOLIUM PHENOLATES (**4**)

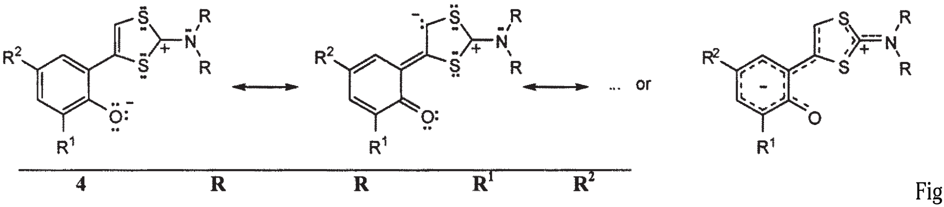
	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR (DMSO-*d6*)
4a	266-267 dec.	100	2986, 1566, 1510, 1465, 1406, 1263, 1133, 867, 806, 717, 661	^{1}*H NMR* δ : 3.50 (6H, s, $2CH_3$); 7.66 (1H, d, H-4); 7,70 (1H, d, H-6, J_{H4-H6}=2.3 Hz); 8.00 (1H, s, H-5). ^{13}*C NMR* δ : 46.8, 47.1, 98.6, 109.4, 116.2, 120.1, 126.7, 134.7, 139.5, 162.6, 190.3
4b	208-209 dec.	100	2975, 1552, 1505, 1457, 1269, 1233, 1130, 857, 762, 715, 663, 560	^{1}*H NMR* δ : 1.35 (6H, t, $2CH_3$); 3.81 (2H, q, CH_2); 3.85 (2H, q, CH_2); 7.70 (1H, d, H-4); 7.76 (1H, d, H-6, J_{H4-H6}=2.2 Hz); 8.09 (1H, s, H-5). ^{13}*C NMR* δ : 10.4, 10.5, 51.7, 52.4, 98.7, 109.5, 116.3, 119.8, 126.4, 134.7, 139.1, 162.8, 190.5
4c	234-235 dec.	100	3007, 1541, 1495, 1461, 1268, 1131, 858, 808, 658, 558	^{1}*H NMR* δ : 2.22 (4H, m, $2CH_2$); 3.74 (4H, m, $2CH_2$); 7.62 (1H, d, H-4); 7.68 (1H, d, H-6, J_{H4-H6}=2.4 Hz); 7.99 (1H, s, H-5). ^{13}*C NMR* δ : 26.4, 26.9, 56.8, 57.1, 98.9, 109.8, 116.0, 120.4, 126.8, 134.9, 139.0, 162.1, 189.9
4d	228-229 dec.	100	3013, 1547, 1497, 1468, 1273, 1133, 862, 801, 661, 570	^{1}*H NMR* δ : 1.77 (6H, m, $3CH_2$); 3.78 (4H, m, $2CH_2$); 7.65 (1H, d, H-4); 7.72 (1H, d, H-6, J_{H4-H6}=2.4 Hz); 7.99 (1H, s, H-5). ^{13}*C NMR* δ : 21.4, 24.9, 25.1, 56.5, 57.9, 98.3, 109.4, 116.0, 120.3, 126.6, 134.9, 139.5, 162.5, 190.4
4e	226-227 dec.	100	2940, 1552, 1505, 1458, 1254, 1131, 852, 714, 667	^{1}*H NMR* δ : 3.85 (8H, m, $4CH_2$); 7.70 (1H, d, H-4); 7.75 (1H, d, H-6, J_{H4-H6}=2.3 Hz); 8.06 (1H, s, H-5). ^{13}*C NMR* δ : 53.1, 53.2, 65.0, 98.4, 109.1, 116.1, 120.0, 126.3, 134.8, 139.2, 162.4, 190.7

2-bromo-1-(3,5-dibromo-2-hydroxyphenyl)ethanone [18] with various salts of dithiocarbamic acids. The synthesis of phenacyldithiocarbamates (**2a**) and (**2b**) has previously been reported by a similar method [19]. The structure of dithiocarbamates (**2**) has been proved by analytical and spectral data (table 1).

1,3-Dithiolium perchlorates (**3**) have been synthesized as colourless crystals by cyclization of dithiocarbamates (**2**), in the presence of a H_2SO_4–CH_3CO_2H (1:3, v/v) mixture, followed by addition of 70% perchloric acid to the reaction medium (fig. 1). The cyclization of dithiocarbamates (**2**) is accompanied by important spectral changes. The IR spectra revealed the disappearance of the absorption band corresponding to the carbonyl group (ca. 1640 cm^{-1}) and the presence of a new, strong and broad, absorption band at ca. 1100 cm^{-1}, corresponding to the perchlorate anion. ^{1}H NMR spectra of 1,3-dithiolium-2-yl perchlorates indicate the absence of the methylene hydrogen from compounds (**2**) (ca. 4.9 ppm) and appearance of a new signal at a low field (ca. 8 ppm) corresponding to the hydrogen atom from the 5-position of the heterocycle (table 2). ^{13}C NMR spectra also support the cyclization of dithiocarbamates (**2**) to the corresponding of 1,3-dithiolium salts by disappearance of the signals of carbonyl and thiocarbonyl atoms from dithiocarbamates spectra and appearance of a new signal at a very low field (ca. 188 ppm) which correspond to the electron deficient C-2 atom. Treatment of these perchlorates with a saturated $NaHCO_3$ solution gives the corresponding phenolates (**4**) as yellow crystalline products, which show mesoionic character [20–22] (fig. 2). The molecular structure of the new compounds was proved by analytical and spectral data (table 3) and by the following chemical transformation: treatment of an acetone suspension of the mesoionic compounds (**4**) with 70% perchloric acid regenerates the 1,3-dithiolium perchlorates (**3**) in quantitative yields (fig. 2).

The presence of the hydroxy substituent induces an extended delocalization of the negative charge up to the C4-C5 bond of the dithiolium ring (fig. 3). In a previous paper [23], the comparative study of UV-Vis absorption spectra of 2-, 3-, and 4-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolates has shown that the yellow color of the above zwitterionic compounds is due to a charge transfer between electron-rich and electron-deficient regions of the molecules and not to the contribution of quinoid structures in the ground states. The intramolecular nature of the charge-transfer band of mesoionic phenolates (**4a-e**) and (**4f, g**) was proved by measurements at different concentrations. The intramolecular charge-transfer UV/Vis absorption of such zwitterionic chromophores results from a charge transfer from the HOMO of the donor part to the LUMO of the acceptor part. For this reason, the position of the charge-transfer band should depend on solvent polarity [24-28] defined here as the overall solvation capability of a solvent (for definitions of the term solvent polarity [27, 28]. The electronic effects of the substituents on the extended delocalization of the negative charge should result on a HOMO orbital of lower energy. Therefore, we decided to investigate the solvatochromism of the mesoionic phenolates (**4a–f**) and the influence of bromine substituents on optical properties of these compounds. By switching from *N*,*N*-dimethylamine to morpholine, we found that the influence of dialkylamino substituents on the LUMO of the acceptor part was found negligible. For this reason the above goals were investigated on compounds bearing a pyrrolidine substituent at the 2 position of 1,3-dithiolium ring.

From the *E*T(30) solvent polarity scale [24, 29-32], methanol was found as the highest polarity solvent, which ensures a sufficient concentration for UV/Vis measurements. Dichloromethane, *N*,*N*-dimethylformamide, and ethanol were also used as solvents for the



4	**R**	**R**	**R^1**	**R^2**
f	(CH$_2$)$_4$		H	H
g	(CH$_2$)$_4$		H	Br

Fig. 3. Extended delocalization charge in mesoionic phenolates (**4**)

Table 4

LONG-WAVELENGTH, SOLVENT-DEPENDENT CHARGE-TRANSFER ABSORPTION MAXIMA, λ_{max} (nm), OF MESOIONIC PHENOLATES **4**

Solvent	**4c**	**4g**	**4f**
CH_2Cl_2	420	403	395
DMF	426	426	416
EtOH	392	386	376
MeOH	389	382	370
$\Delta\lambda$ (nm)	- 37	- 44	- 46

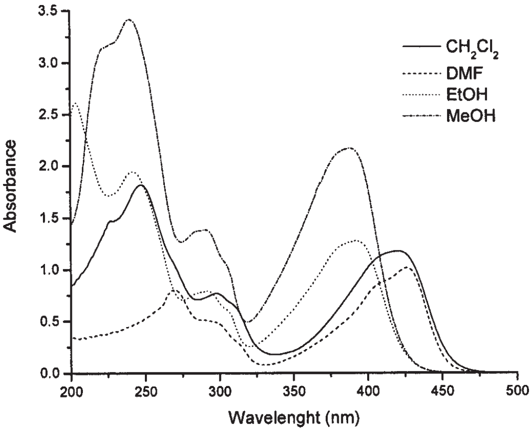


Fig. 4. UV/Vis absorption spectra of 4,6-dibromo-2-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl)phenolate (**4c**) in different solvents

study of optical properties of mesoionic phenolates bearing bromine substituents on the aromatic ring from the 4-position of 1,3-dithiolium ring. The UV/Vis absorption spectra of 4,6-dibromo-2-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl)phenolate (**4c**) recorded in the above mentioned solvents are presented in figure 4. The position of the long-wavelength absorption band was found to be the most solvent dependent one. Thus, with increasing solvent polarity, a hypsochromic band shift of $\Delta\lambda$= -37 nm is observed, corresponding to a negative solvatochromism (table 4).

The UV/Vis absorption spectra of 4-bromo-2-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl)phenolate (**4g**) recorded in the above mentioned solvents are presented in figure 5. The position of the long-wavelength absorption band was again found to be solvent dependent. By switching from methanol to DMF, a hypsochromic band shift of $\Delta\lambda$ = -44 nm was recorded (table 4).

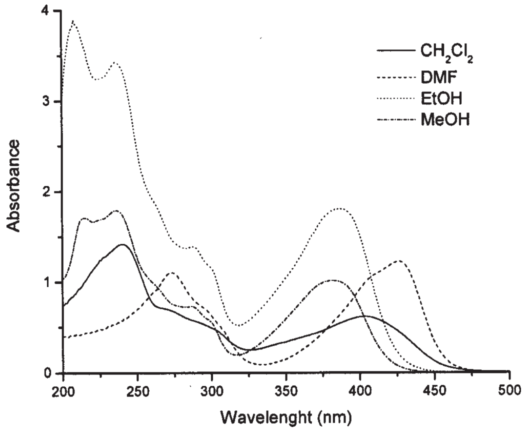


Fig. 5. UV/Vis absorption spectra of 4-bromo-2-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**4g**) in different solvents

A higher negative solvatochromism ($\Delta\lambda$= -46 nm) was recorded for the mesoionic phenolate (**4f**), without bromine substituents on the phenolate moiety. From the data presented in table 4, it might be concluded that the number of bromine substituents is correlated with the hypsochromic shift of the charge-transfer absorption band.

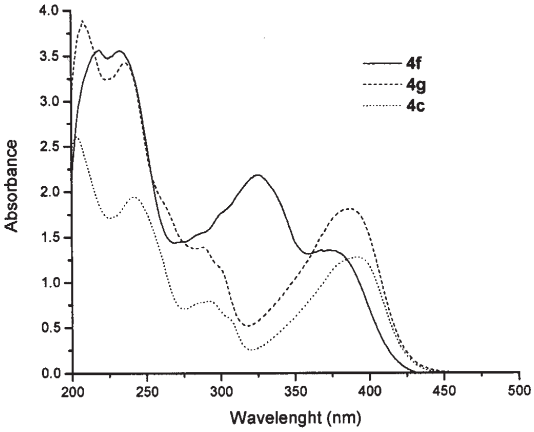


Fig. 6. UV/Vis absorption spectra of mesoionic phenolates **4c**, **4g**, and **4f** in ethanol

Moreover, the presence of bromine substituents also influences the position of other absorption bands. Thus, an important hypsochromic shift was recorded for the n→π* transition; as shown in figure 5 the absorption band was shifted from 325 nm in (**4f**) to 305-310 nm in bromine substituted mesoionic phenolates (**4g**) and (**4c**). The latter compounds also exhibit an absorption band corresponding to the quinoide structure described in figure 6 (ca. 290 nm). This is the result of a bathochromic effect induced by bromine substituents, this band being overlapped by the strong π→π* transition in (**4f**). The presence of bromine substituents also influences the π→π* absorption band, inducing a hypsochromic shift to 204 nm in the case of (**4c**) and 208 nm for (**4g**) (recorded in ethanol).

The position of long-wavelength, solvent-dependent charge-transfer absorption maxima of mesoionic phenolates (**4**) was found to be dependent on the number of bromine substituents; by increasing this number, an important bathochromic effect was recorded (up to 25 nm in dichloromethane). Investigation of UV/Vis absorption spectra of 4-(3,5-dibromo-2-hydroxyphenyl)-2-dialkyl-amino-1,3-dithiol-2-ylium perchlorates revealed new aspects of the influence of bromine substituents. By increasing the polarity of the solvent, a new absorption

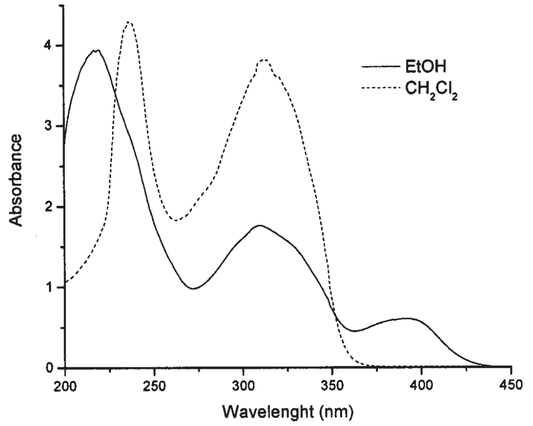


Fig. 7. UV/Vis absorption spectra of 4-(3,5-dibromo-2-hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**3c**) in ethanol and dichloromethane

band, corresponding to the intramolecular charge-transfer, was recorded. As indicated in figure 7, the presence of this peak in ethanol, at the same position as in the corresponding mesoionic phenolate (392 nm) suggests that in this solvent the 4-(3,5-dibromo-2-hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**3c**) exists in equilibrium with the corresponding mesoionic phenolate (**4c**).

Conclusions

A new class of 2-[2-(dialkylamino)-1,3-dithiol-2-ylium-4-yl]phenolates bearing two bromine substituents on the phenolate moiety has been accomplished by the heterocyclization of the corresponding phenacyl carbodithioates. These compounds have been used to investigate the influence of bromine substituents on the optical properties of mesoionic phenolates. The negative solvatochromism of this kind of mesoionic phenolates was found to be smaller as the number of bromine substituents increases. At the same time, an important bathochromic shift of the charge-transfer absorption band was recorded with the increase of the number of bromine substituents. Moreover, in polar solvents, 4-(3,5-dibromo-2-hydroxyphenyl)-2-dialkylamino-1,3-dithiol-2-ylium perchlorates have been found to be in equilibrium with the corresponding mesoionic phenolates.

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References

1. FORREST, S. R., THOMPSON, M. E., Chem. Rev., **107**, 2007, p. 923.
2. HE, G. S., TAN, L.-S., ZHENG, Q., PRASAD, P. N., Chem. Rev., **108**, 2008, p. 1245.
3. MILLER, R. D., CHANDROSS, E. A., Chem. Rev., **110**, 2010, p. 1.
4. KULHANEK, J, BURES, F., Beilstein J. Org. Chem., **8**, 2012, p. 25.
5. BACIU-ATUDOSIE, L., GHINET, A., BELEI, D., GAUTRET, P., RIGO, B., BICU, E., Tetrahedron Lett., **53**, 2012, p. 6127.
6. BELEI, D., BICU, E., JONES, P. G., BIRSA, M. L., Synlett, **2010**, p. 931.
7. BELEI, D., BICU, E., JONES, P. G., BIRSA, M. L., J. Heterocycl. Chem., **48**, 2011, p. 129.
8. BELEI, D., ABUHAIE, C., BICU, E., JONES, P. G., HOPF, H., BIRSA, M. L., Synlett, **2012**, p. 545.
9. BELEI, D., BICU, E., BIRSA, M. L., Acta Chem. Iasi, **17**, 2009, p. 197.
10. DUMITRIU, G., LUCESCU, L., BICU, E., BELEI, D., Acta Chem. Iasi, **18**, 2010, p. 77.
11. BRYCE, M. R., Adv. Mater., **11**, 1999, p. 11.
12. SUNEL, V., CIUGUREANU, C., BUDEANU, C. H., Rev. Chim. (Bucharest), **37**, 1986, p. 855.
13. CIUGUREANU, C., SUNEL, V., Rev. Chim. (Bucharest), **44**, no. 9, 1993, p. 875.
14. MOISE, M., SUNEL, V., DULCESCU, M. M., DOROHOI, D. O., Rev. Chim. (Bucharest), **61**, no. 8, 2010, p. 799.
15. CHEPTEA, C., DASCALU, C. F., SUNEL, V., DOROHOI, D. O., Rev. Chim. (Bucharest), **63**, no. 3, 2012, p. 319.
16. GOANTA, M., CIOBANU, A.S., BIRSA, A., ASAFTEI, I.V., BIRSA, M. L., Acta Chem. Iasi, **17**, 2009, p. 35.
17. SARBU, L. G., BIRSA, M. L., Acta Chem. Iasi, **19**, 2011, p. 125.
18. BUU-HOI, Ng. Ph., LAVIT, D., J. Chem. Soc., **1955**, p. 18.
19. SANDULACHE, A., CASCAVAL, A., TONIUTTI, N., GIUMANINI, A.G., Tetrahedron, **53**, 1997, p. 9813.
20. SIMAS, A. M., MILLER, J., ATHAYDE FILHO, P. F., Can. J. Chem., **76**, 1998, p. 869.
21. ATHAYDE FILHO, P. F., MILLER, J., SIMAS, A. M., Synthesis, **2000**, p. 1565.
22. OLIVEIRA, DE M .B., MILLER, J., PEREIRA A. B., GALEMBECK S.E., MOURA, DE G. L. C., SIMAS, A. M., Phosphorus Sulfur Silicon Relat Elem **108**, 1996, p. 75.
23. BIRSA, M. L., GANJU, D., J. Phys. Org. Chem., **16**, 2003, p. 207.
24. DIMROTH, K., REICHARDT, C., SIEPMANN, T. H., BOHLMANN, F., Justus Liebigs Ann. Chem., **661**, 1963, p. 1.
25. REICHARDT, C., SCHAFER, G., Liebigs Ann. Chem., **1995**, p. 1579.
26. REICHARDT, C., Chem. Soc. Rev., **21**, 1992, p. 147.
27. MULLER, P., Pure Appl. Chem., **66**, 1994, p. 1077.
28. REICHARDT, C., Nachr. Chem. Tech. Lab., **45**, 1997, p. 759.
29. REICHARDT, C., Chem. Rev., **94**, 1994, p. 2319.
30. REICHARDT, C., HARBUSCH-GORNERT, E., Liebigs Ann. Chem., **1983**, p. 751.
31. REICHARDT, C., CHE, D., HECKENKEMPER, G., SCHAFER, G., Eur. J. Org. Chem., **2001**, p. 2343.
32. REICHARDT, C., ESCHNER, M., SCHAFER, G., J. Phys. Org. Chem., **14**, 2001, p. 737

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