PERKIN 2

Assessment of the substituent constants of the 3-thioxo-1,2-dithiol-4- and -5-yl groups through pK_a values measurements of 4 and 5-(hydroxy- or amino-phenyl)-1,2-dithiole-3-thiones in water at 298 K

Marylène Chollet, Béatrice Legouin and Jean-Louis Burgot *

Laboratoire de Chimie Analytique, UFR des Sciences Pharmaceutiques et Biologiques,
Université de Rennes I, 35043 Rennes cedex, France

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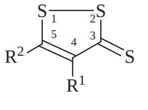
The UV–VIS spectrophotometric assessment of the electronic substituent constants of the 3-thioxo-1,2-dithiol-4- and -5-yl and 3-oxo-1,2-dithiol-4- and -5-yl groups through pK_a measurements in water of 4 and 5-(hydroxy or amino-phenyl)-1,2-dithiole-3-thiones and corresponding dithiolones has been performed. Linear free-enthalpy relationships based on pK_a values of phenols and anilinium ions indicated a strong withdrawing effect for the 3-thioxo-1,2-dithiol-5-yl group by both an inductive and a resonance effect [$\sigma_{p-} = 0.76$, $\sigma_m = 0.44$ (anilinium ions relationship) and $\sigma_{p-} = 0.97$, $\sigma_m = 0.45$ (phenols relationship)]. The corresponding 3-oxo group was slightly less attractive than the 3-thioxo one [$\sigma_{p-} = 0.64$ (anilinium ions) and $\sigma_{p-} = 0.78$ (phenols)]. The 3-thioxo-1,2-dithiol-4-yl group and also its oxo analogue had only a weak withdrawing effect by an inductive effect ($\sigma_p \cong \sigma_{p-} \cong 0.2$) indicating a lack of conjugation between the dithiole and phenyl nuclei in 4-phenyldithiolethiones. The original 1,2-dithiole-3-thiones and 1,2-dithiol-3-ones used in correlations are described.

Introduction

1,2-Dithiole-3-thiones **1** are promising compounds in the field of pharmacology and especially for the prevention of carcinogenesis.[1,2] Many recent publications have shown that, among other properties, some dithiolethiones **1** enhance the production of phase II detoxifying enzymes.[3,4] The interaction between compounds **1** and phase I detoxifying enzymes is still under investigation.[5]



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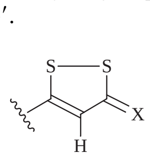
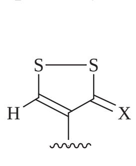
In the course of our studies devoted to the synthesis of new dithiolethiones[6] and to their physico-chemical properties,[7] we have taken an interest in the quantitative assessment of the electronic effect of the 3-thioxo-1,2-dithiol-5-yl **2** and 3-thioxo-1,2-dithiol-4-yl **3** groups and of the corresponding oxo groups **2′** and **3′**.

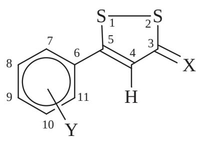


2 X = S
2′ X = O

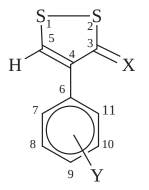


3 X = S
3′ X = O

In addition to the intrinsic physico-chemical interest of such an assessment, there exists a need for firm grounds for the rational design of new pharmacologically active dithiolethiones **1** and for quantitative data which can help to forecast the reactivity of these compounds. To determine quantitatively the electronic effects of groups **2**, **2′**, **3** and **3′**, we turned to linear Gibbs energy relationships based on the pK_a values in water of some 5-[*m*- or *p*-amino(or hydroxy)phenyl]dithiolethiones and dithiolones **4** and **4′**, and of some 4-[*m*- or *p*-amino(or hydroxy)phenyl]dithiolethiones and dithiolones **5** and **5′**. Most of these derivatives were new compounds.



4a X = S; Y = *p*-NH$_3^+$
4b X = S; Y = *m*-NH$_3^+$
4c X = S; Y = *p*-OH
4d X = S; Y = *m*-OH
4′a X = O; Y = *p*-NH$_3^+$
4′c X = O; Y = *p*-OH
4′d X = O; Y = *m*-OH

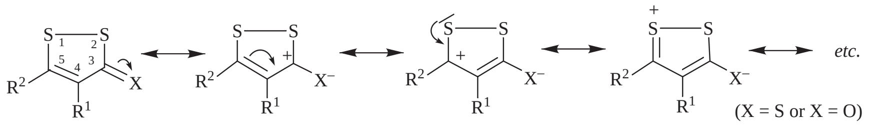


5a X = S; Y = *p*-NH$_3^+$
5b X = S; Y = *m*-NH$_3^+$
5c X = S; Y = *p*-OH
5d X = S; Y = *m*-OH
5′a X = O; Y = *p*-NH$_3^+$
5′c X = O; Y = *p*-OH

An incomplete set of values of the substituent constants of groups **2**, **2′** and **3** had been found by some of us in a preliminary work.[8,9] They are $\sigma_{p-} = 1.14$ and $\sigma_{p-} = 0.86$ for groups **2** and **2′** and $\sigma_p = 0.07$ for the **3** group.

Results and discussion

The 5-(hydroxyphenyl)dithiolethiones **4c** and **4d** and the dithiolone **4′c** exhibited pK_a values (Table 1) much weaker than phenol (pK_a = 10.0)[10] and so did the conjugated acids of the 5-(aminophenyl)dithiolethiones **4a** and **4b** and the dithiolone **4′a** compared to the anilinium ion (pK_a = 4.60).[10] This is in good agreement with the pK_a values found in a previous work concerning 3-thioxo-1,2-dithiole-5-carboxylic acids which fell in the range 1.10–1.60.[11] We explained these results by the occurrence of both a withdrawing inductive effect and a withdrawing resonance effect of groups **2**, well rationalized by a strong



Scheme 1

Table 1 pK_a values[a] of dithiolethiones **4** and **5** and dithiolones **4′** and **5′**

Compound	pK_a (spectrophotometry[b])
4a	2.31 ± 0.08
4′a	2.66 ± 0.03
4b	3.25 ± 0.12
4c	7.86 ± 0.02
4′c	8.27 ± 0.04
4d	8.96 ± 0.06
4′d	8.91 ± 0.02
5a	3.95 ± 0.08
5′a	4.08 ± 0.21
5b	3.95 ± 0.13
5c	9.28 ± 0.03
5′c	9.39 ± 0.02
5d	9.58 ± 0.20

[a] The 95% confidence limits on the average value are given by −log ($K_a \pm 2.447\ \sigma_{n-1}/n^{\frac{1}{2}}$) according to Student's table. [b] pK_a determined in methanol–water 2:100 (v/v) at 298 K.

Table 2 Substituent constants for groups **2** and **2′** from regressions I and II

Group	Correlation used	σ_{p-}	σ_m
2	I	0.76	0.44
	II	0.97	0.45
2′	I	0.64	—
	II	0.78	0.47

participation of several dithiolylium sulfide polar forms to the true structure of 1,2-dithiole-3-thiones and also of dithiolones (Scheme 1).[12]

All these pK_a values prompted us to test derivatives **4** and **4′** in linear free-enthalpy relationships on the σ_{p-} scale since the strong donor groups, hydroxy and phenate on the one hand and amino on the other, can enter into very strong conjugation with the dithiole groups **2**, **2′** endowed with a −R effect. The substituent constants mentioned in Table 2 were obtained from regressions I and II (see Experimental section).

These values are in reasonable agreement with those found in our pioneering work where we found $\sigma_{p-} = 1.14$ (group **2**) and $\sigma_{p-} = 0.86$ (group **2′**). These values were obtained after studying by electrochemical means 5-(*p*-nitrophenyl)-dithiolethione and -dithiolone in DMF.[8,9]

With mean values of $\sigma_{p-} = 0.86$ and $\sigma_m = 0.45$ (Table 2), the 3-thioxo-1,2-dithiol-5-yl group **2** is as strong a withdrawing group as the formyl ($\sigma_{p-} = 1.04$, $\sigma_m = 0.41$) or acetyl ($\sigma_{p-} = 0.82$, $\sigma_m = 0.36$) groups.[13] Hence, the 3-thioxo-1,2-dithiol-5-yl group **2** is a very strong withdrawing heterocyclic group, perhaps the strongest one.[14] Of course, as is usually the case, σ_m can be considered at first glance as representing only the inductive effect which is equal to that of the trifluoromethyl group. Hence, it can be qualified as being a strong one. The 3-oxo-1,2-dithiol-5-yl group **2′** is a weaker withdrawing group than group **2**. This fact has been recognized in the literature and explained on the basis of a greater resonance effect in dithiolethiones than in dithiolones.[15] The result obtained with dithiolone **4′d** gives experimental confirmation of this assertion. Dithiolethione **4d** and dithiolone **4′d** exhibit, indeed, the same pK_a value while dithiolethione **4c** and dithiolone **4′c** exhibit a pK_a difference of around 0.4 units. This is a strong argument for the occurrence of a similar inductive effect exhibited by groups **2** and **2′** on the one hand, the lower value of pK_a of dithiolethione **4c** arising, hence, from a resonance effect.

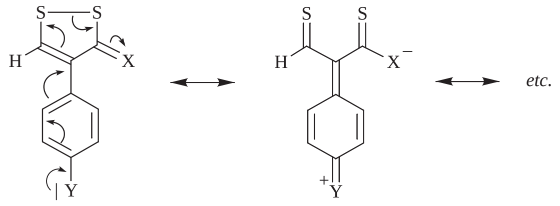
Table 3 Substituent constants for groups **3** and **3′** from regressions I, II, I′ and II′

Group	Correlation used	σ_{p-}	σ_p	σ_m
3	I	0.19		0.19
	II	0.28		0.16
	I′		0.17	—
	II′		0.21	—
3′	I	0.15		—
	II	0.25		—
	I′		0.13	—
	II′		0.18	—

Like their isomers, dithiolethiones **5** and dithiolones **5′** exhibited weaker pK_a values than the phenol and anilinium ions, but the differences of the pK_a values between them and the two parent compounds are far less marked than with derivatives **4** and **4′** (Table 1). The introduction of pK_a values found in regressions I, II, I′, and II′ gives the values of the substituent constants mentioned in Table 3.

Firstly, it appears that the values obtained through regressions I and II are in good mutual agreement.

An interesting result is that the substituent constant values found through regressions I and II, which make allowance for the fact that a strong conjugation of the dithiole nucleus with the substituents may exist, and those found through regressions I′ and II′, which do not take into account this extraconjugation, are equal. Such a result shows that a resonance of the type shown in Scheme 2 is negligible. This does not necessarily mean that such a conjugation could not exist in any dithiolethione. It means however that such a conjugation cannot exist in 4-phenyldithiolethiones and dithiolones. This may be, for instance, for steric reasons, since the phenyl and dithiole nuclei may be twisted sufficiently to preclude the conjugation. This point deserves further investigation.



Scheme 2

Whatever the reason, it is ascertained that groups **3** and **3′** still exert a withdrawing inductive effect as is indicated both by σ_m and σ_p values which are nearly identical. This withdrawing inductive effect is markedly weaker than that exerted by groups **2** and **2′**. This is well explained by the several dithiolylium sulfide polar forms of dithiolethiones and dithiolones that can be written (see above) and which all indicate that the carbon 4 is the atom of the dithiole frame which is the less depleted in electrons. It is interesting to note that the values obtained with the dithiolone group **3′** are nearly identical to those found with the dithiolethione group **3**. This reinforces the hypothesis of the occurrence of a resonance effect to explain

Table 4 pK_a values of *meta*- and *para*-substituted anilines and phenols (see ref. 10) and their substituent constants σ_x (see ref. 13) retained for establishing linear free-enthalpy relationships

	pK_a						
	Aniline substituted		Phenol substituted				
Substituent X	*-meta*	*-para*	*-meta*	*-para*	σ_m	σ_p	σ_{p-}
$-CH_3$	4.69	5.10	10.09	10.26	−0.06	−0.14	—
$-OCH_3$	4.20	5.31	9.65	10.21	0.12	−0.27	—
$-SCH_3$	4.00	4.35	9.53	9.53	0.14	0.06	—
-H	4.60	4.60	10.00	10.00	0	0	0
-Cl	3.46	3.98	9.02	9.38	0.37	0.24	—
$-CO_2CH_3$	3.55	2.47	—	8.47	0.35	0.44	0.74
-CN	2.75	1.74	8.61	7.95	0.62	0.71	0.99
$-NO_2$	2.47	1.02	8.40	7.15	0.71	0.78	1.23
$-SO_2CH_3$	2.58	1.35	8.40	7.83	0.64	0.73	1.05

the difference of behavior between groups **2** and **2′**.[15] The substituent constants of group **3** obtained in this work are in modest agreement with those obtained in our previous study which gave a value of $\sigma_p = 0.07$ for group **3** through a study of the electrooxidation of 4-ferrocenyl-1,2-dithiole-3-thione.[8,9]

Experimental

Materials

All commercially available chemicals were of analytical grade. The water used throughout this work was deionized on a set of ion exchanging columns (Bioblock Scientific, Illkirch, France) to $\rho > 2$ MΩ cm^{-1}. The buffer solutions were those of Britton and Robinson.

Instrumentation

For analysis, the following instruments were used: FTIR spectra with a Perkin-Elmer FTIR 16PC instrument, mass spectra with a VARIAN MAT 311 spectrometer, ^{1}H and ^{13}C NMR spectra with a Bruker AM 360 spectrometer.

Absorbances were measured using a UV–VIS spectrophotometer (Uvikon Model 930) with 1 cm silica cells.

Spectrophotometric UV–VIS pK_a determinations

For UV–VIS studies, two different working wavelengths corresponding to the maxima of molar absorptivities were selected for each compound. The strategy followed was to select the wavelengths endowed with the larger differences of molar absorptivities between the conjugated acid and base under study (working wavelengths are mentioned with the description of dithiolethiones and dithiolones). For each compound, 50 buffer solutions (the pH values of which were below and above the pK_a value) were used. pK_a values were extracted from the pH and absorbance data by using a non-linear least-squares procedure.[16,17] To obtain meaningful statistical parameters, six independent determinations were performed for each derivative. The molar absorptivity ε of each one was systematically considered as unknown. This strategy allowed a comparison of the molar absorptivity determined through the fitting process with the experimental one. Consistence of both the results provided an indirect proof of accuracy of the experiments and of the calculations. The upper limit of the difference between the experimental and determined molar absorptivities ε was 150 dm^3 mol^{-1} cm^{-1}.

The solutions ($c = 5.10^{-4}$ mol l^{-1}) were prepared by dissolving weighed amounts of compounds in a minimum of methanol and then by diluting the methanolic solution in the appropriate buffer. The amount of methanol in the working solutions never exceeded 2% (v/v). In every case, one or several isobestic points were found.

Linear free-enthalpy relationships

In Table 4 are recalled the pK_a values of some *meta*- and *para*-substituted anilines and phenols used to establish free-enthalpy relationships.

The linear regressions obtained were:

$$\mathrm{p}K_a = 4.52 - 2.89\,\sigma_{p-}\ (\text{or } \sigma_m) \qquad r = 0.998 \quad \text{I (anilines)}$$
$$\mathrm{p}K_a = 9.91 - 2.11\,\sigma_{p-}\ (\text{or } \sigma_m) \qquad r = 0.993 \quad \text{II (phenols)}$$
$$\mathrm{p}K_a = 4.58 - 3.71\,\sigma_{p}\ (\text{or } \sigma_m) \qquad r = 0.964 \quad \text{I}' \text{ (anilines)}$$
$$\mathrm{p}K_a = 9.85 - 2.58\,\sigma_{p}\ (\text{or } \sigma_m) \qquad r = 0.958 \quad \text{II}' \text{ (phenols)}$$

Synthesis

Dithiolethiones **4a**, **4b**, **4c** and **5a** are described below. Dithiolethiones and dithiolones **4d**, **4′a**, **4′c**, **4′d**, **5b**, **5c**, **5d**, **5′a** and **5′c** are novel compounds.

5-(*p*-Ammoniophenyl)-1,2-dithiole-3-thione 4a. This compound was obtained by a selective indirect electroreduction of 5-(*p*-nitrophenyl)-1,2-dithiole-3-thione (56%).[18] The nitro compound is described in the literature.[19] λ(pH = 0.0)/nm = 311 (ε/dm^3 mol^{-1} cm^{-1} 15190), λ(pH = 3.8)/nm = 425 (22049).

5-(*m*-Ammoniophenyl)-1,2-dithiole-3-thione 4b. This compound was also obtained by a selective indirect electroreduction of 5-(*m*-nitrophenyl)-1,2-dithiole-3-thione (45%).[18] The nitro compound is described in the literature.[8] λ(pH = 1.2)/nm = 280 (ε/dm^3 mol^{-1} cm^{-1} 14574), λ(pH = 5.0)/nm = 340 (21055).

5-(*p*-Hydroxyphenyl)-1,2-dithiole-3-thione 4c. This compound was provided by Solvay-pharma Industry. λ(pH = 6.0)/nm = 358 (ε/dm^3 mol^{-1} cm^{-1} 16779), λ(pH = 10.1)/nm = 455 (39655).

5-(*m*-Hydroxyphenyl)-1,2-dithiole-3-thione 4d. This compound was prepared from 5-(*m*-acetoxyphenyl)dithiolethione by hydrolysis with a sulfuric acid solution 50% (v/v) at 100 °C. The acetoxy compound was obtained by sulfuration of α-[bis(methylthiomethylene)]propenone with P_4S_{10} in refluxing xylene according to the procedure describe by Thuillier and Vialle.[20] The α-[bis(methylthiomethylene)]propenone was prepared from *m*-hydroxyacetophenone (commercial product) by action of acetyl chloride in pyridine followed by condensation of carbon disulfide with sodium *tert*-amylate followed, in turn, by methylation. Thus 5-(*m*-acetoxyphenyl)dithiolethione [(15%) from the α-[bis(methylthiomethylene)]propenone], red crystals, mp 107 °C (toluene); ν_{max}/cm^{-1} 1756 (C=O ester) gave **4d** (38%), orange crystals, mp 159 °C (toluene); ν_{max}/cm^{-1} 3226 (OH); *m*/*z* (EI): 225.9580 (calc. for $C_9H_6OS_3$: 225.9581) (Calc.: C, 47.80; H, 2.68; S, 42.45. Found: C, 47.99; H, 2.52; S, 42.39 %); λ(pH = 5.2)/nm = 282 (ε/dm^3 mol^{-1} cm^{-1} 5836), λ(pH = 10.6)/nm = 417 (13868).

5-(*p*-Ammoniophenyl)-1,2-dithiol-3-one 4′a. This compound was obtained by action of benzonitrile oxide on the corresponding dithiolethione **4a**[21] (65%), yellow crystals, mp 154 °C

Table 5 ^{1}H NMR data of dithiolethiones **4** and **5** and dithiolones **4′** and **5′** (δ; 300 MHz)

Compound correlation	**4d**^{a}	**4′a**^{b}	**4′c**^{a}	**4′d**^{a}	**5b**^{b}	**5c**^{b}	**5d**^{a}	**5′a**^{b}	**5′c**^{a}
(1H; s; C4-H)	7.6	6.7	7.0	7.0	—	—	—	—	—
(1H; s; C5-H)	—	—	—	—	8.4	8.4	8.9	8.2	8.8
(4H; AB; C7-H, C8-H, C10-H, C11-H)	—	6.7–7.4	7.0–7.7	—	—	6.9–7.5	—	6.7–7.4	6.9–7.5
(2H; s; C9-NH_2)	—	4.1	—	—	—	—	—	3.8	—
(1H; s; C9-OH)	—	—	9.3	—	—	5.0	—	—	8.7
(1H; s; C7-H)	7.4	—	—	7.3	6.9	—	7.0	—	—
(1H; s; C8-H)	7.4	—	—	7.4	7.2	—	7.3	—	—
(1H; s; C9-H)	7.1	—	—	7.1	6.7	—	6.9	—	—
(2H; s; C10-NH_2)	—	—	—	—	3.8	—	—	—	—
(1H; s; C10-OH)	9.0	—	—	9.0	—	—	8.6	—	—
(1H; s; C11-H)	7.3	—	—	7.2	6.9	—	7.1	—	—

^{a} Measurement in [$^2H_6$]acetone. ^{b} Measurement in $CDCl_3$.

Table 6 ^{13}C NMR data of dithiolethiones **4** and **5** and dithiolones **4′** and **5′** (δ; 75 MHz)

Compound correlation	**4d**^{a}	**4′a**^{b}	**4′c**^{a}	**4′d**^{a}	**5b**^{b}	**5c**^{b}	**5d**^{a}	**5′a**^{b}	**5′c**^{a}
C3	216.9	194.3	193.9	194.0	214.0	214.2	215.1	193.7	194.1
C4	136.5	114.8	116.1	118.3	149.6	149.4	149.4	134.1	133.8
C5	174.3	170.7	171.4	171.3	153.7	153.1	157.9	147.2	151.1
C6	133.8	122.4	124.8	134.6	134.2	124.1	135.8	122.0	124.4
C7	119.1	128.1	129.2	118.6	119.3	130.2	121.1	128.7	129.7
C8	131.8	114.8	117.2	131.7	129.5	115.5	130.2	115.0	116.2
C9	120.2	150.1	162.0	119.9	115.5	158.1	116.5	147.0	158.8
C10	159.2	114.8	117.2	159.1	146.5	115.5	158.1	115.0	116.2
C11	114.4	128.1	129.2	114.0	115.7	130.2	116.8	128.7	129.7

^{a} Measurement in [$^2H_6$]acetone. ^{b} Measurement in $CDCl_3$.

(toluene); ν_{max}/cm^{-1} 3466 and 3358 (NH), 1654 (C=O); *m*/*z* (EI): 208.9976 (calc. for $C_9H_7NOS_2$: 208.9969) (Calc.: C, 51.68; H, 3.38; N, 6.70; O, 7.65; S, 30.60. Found: C, 51.58; H, 3.35; N, 6.58; O, 7.52; S, 30.33%); λ(pH = 1.2)/nm = 280 (ε/dm^3 mol^{-1} cm^{-1} 14574), λ(pH = 5.0)/nm = 340 (21055).

5-(p-Hydroxyphenyl)-1,2-dithiol-3-one 4′c. This compound was prepared by the same procedure as **4′a** (79%), white crystals, mp 165 °C (chloroform); ν_{max}/cm^{-1} 3334 (OH), 1646 (C=O); *m*/*z* (EI): 209.9816 (calc. for $C_9H_6O_2S_2$: 209.9809) (Calc.: C, 51.43; H, 2.88; S, 30.45. Found: C, 51.45; H, 2.75; S, 30.53%); λ(pH = 5.9)/nm = 319 (ε/dm^3 mol^{-1} cm^{-1} 18061), λ(pH = 9.6)/nm = 379 (20252).

5-(*m*-Hydroxyphenyl)-1,2-dithiol-3-one 4′d. This compound was prepared by the same procedure as **4′a** (47%), white crystals, mp 155 °C (toluene); ν_{max}/cm^{-1} 3220 (OH), 1608 (C=O); *m*/*z* (EI): 209.9816 (calc. for $C_9H_6O_2S_2$: 209.9809); λ(pH = 6.2)/nm = 264 (ε/dm^3 mol^{-1} cm^{-1} 7105), λ(pH = 11.7)/nm = 264 (12718).

4-(*p*-Ammoniophenyl)-1,2-dithiole-3-thione 5a. This preparation has already been described but compound **5a** was obtained as a minor product.[8] We preferred to use a different procedure: action of sulfur on 4-isopropylaniline (commercial product) in refluxing ethyl benzoate according to Teste and Lozac'h (5%).[22] λ(pH = 5.5)/nm = 280 (ε/dm^3 mol^{-1} cm^{-1} 10950), λ(pH = 2.3)/nm = 410 (10136).

4-(*m*-Ammoniophenyl)-1,2-dithiole-3-thione 5b. This compound was prepared using the same procedure as for **5a** by sulfuration of 3-isopropylaniline with sulfur in refluxing ethyl benzoate for 2 h. 3-Isopropylaniline was, in turn, obtained by amination of isopropylbenzene with trichloroamine and aluminium chloride.[23] **5b** (5%), orange crystals, mp 114 °C (toluene); ν_{max}/cm^{-1} 3422 and 3344 (NH); *m*/*z* (EI): 224.9743 (calc. for $C_9H_7NS_3$: 224.9740) (Calc.: C, 48.01; H, 3.14; N, 6.22; S, 42.63. Found: C, 48.10; H, 3.24; N, 6.16; S, 41.53%); λ(pH = 7.0)/nm = 300 (ε/dm^3 mol^{-1} cm^{-1} 6150), λ(pH = 1.0)/nm = 410 (9080).

4-(*p*-Hydroxyphenyl)-1,2-dithiole-3-thione 5c. This compound was prepared using the same method as for **5a** by sulfuration of 4-isopropylphenol (commercial product) with sulfur in refluxing ethyl benzoate for 12 h. **5c** (15%), orange crystals, mp 194 °C (toluene); ν_{max}/cm^{-1} 3450 (OH); *m*/*z* (EI): 225.9603 (calc. for $C_9H_6OS_3$: 225.9581) (Calc.: C, 47.80; H, 2.68; O, 7.08. Found: C, 49.30; H, 2.78; O, 6.66%); λ(pH = 11.6)/nm = 285 (ε/dm^3 mol^{-1} cm^{-1} 14045), λ(pH = 7.1)/nm = 412 (9195).

4-(*m*-Hydroxyphenyl)-1,2-dithiole-3-thione 5d. This compound was obtained using the same procedure as for **5a** by sulfuration of 3-isopropylphenol (commercial product) with sulfur in boiling ethyl benzoate for 3 h. **5d** (15%), orange crystals, mp 130 °C (chloroform); ν_{max}/cm^{-1} 3292 (OH); *m*/*z* (EI): 225.9581 (calc. for $C_9H_6OS_3$: 225.9581) (Calc.: C, 47.80; H, 2.68; S, 42.45. Found: C, 47.33; H, 2.48; S, 41.30%); λ(pH = 7.1)/nm = 282 (ε/dm^3 mol^{-1} cm^{-1} 6052), λ(pH = 11.1)/nm = 302 (6211).

4-(*p*-Ammoniophenyl)-1,2-dithiol-3-one 5′a. This compound was prepared by the same procedure as **4′a**. **5′a** (42%), yellow crystals, mp 148 °C (toluene); ν_{max}/cm^{-1} 3466 and 3358 (NH), 1632 (C=O); *m*/*z* (EI): 208.9976 (calc. for $C_9H_7NOS_2$: 208.9969) (Calc.: C, 51.68; H, 3.38; N, 6.70; O, 7.65; S, 30.60. Found: C, 52.14; H, 3.34; N, 6.64; O, 7.54; S, 29.95%); λ(pH = 6.0)/nm = 250 (ε/dm^3 mol^{-1} cm^{-1} 15561), λ(pH = 2.4)/nm = 325 (8438).

4-(*p*-Hydroxyphenyl)-1,2-dithiol-3-one 5′c. This compound was obtained using the same procedure as for **4′a**. **5′c** (46%), yellow crystals, mp 134 °C (chloroform); ν_{max}/cm^{-1} 3254 (OH), 1636 (C=O); *m*/*z* (EI): 209.9816 (calc. for $C_9H_6O_2S_2$: 209.9809) (Calc.: C, 51.43; H, 2.88; S, 30.45. Found: C, 51.15; H, 2.65; S, 30.68%); λ(pH = 11.7)/nm = 259 (ε/dm^3 mol^{-1} cm^{-1} 14359), λ(pH = 7.1)/nm = 332 (6541).

^{1}H and ^{13}C NMR data of compounds **4d**, **4′a**, **4′c**, **4′d**, **5b**, **5c**, **5d**, **5′a** and **5′c** are given in Tables 5 and 6.

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