

## The Reaction of 5-Aryl-3-chloro-1,2-dithiolylium Ions with Phenols and Phenolic Ethers

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The reaction between 5-aryl-1,2-dithiolylium perchlorates in boiling acetic acid and a phenol or phenol ether has been shown to give only one isomer in the following cases: naphthols and their methyl ethers, resorcinol and its dimethyl ether, and 3-methoxycatechol.

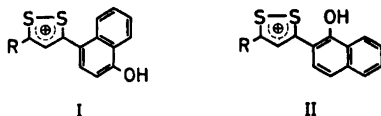
Two isomers have been obtained in the case of 3-methoxyphenol and of 3,5-dimethoxyphenol.

Similar results have been obtained with 5-aryl-3-bromo-1,2-dithiolylium perchlorates.

As has been shown by Reynolds<sup>1</sup> the reaction of 5-aryl-3-chloro-1,2-dithiolylium ions with reactive phenols and phenol ethers leads to the formation of 3,5-diaryl-1,2-dithiolylium ions.

When a phenol is used in this reaction the resulting cation can be deprotonated by a base, giving a compound which may be considered either as a dithiolylium ketone or as a dithiolyliophenolate ion.<sup>2</sup>

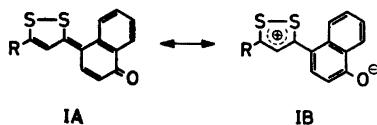
For instance, two structures, I and II, can be considered for the cations obtained from 1-naphthol.



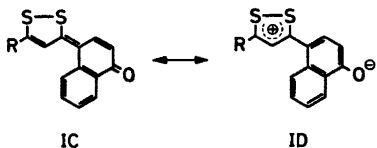

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The deprotonated forms may be represented by mesomeric formulae such as IA and IB:



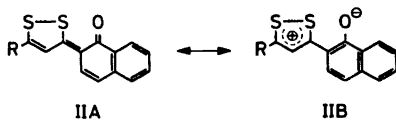
It has been shown<sup>3</sup> in similar cases, that the experimental dipole moment is intermediate between those that can be calculated for IA and IB, a fact which indicates the necessity of considering a mesomeric representation. However, the conditions under which *cis-trans* isomerism (corresponding, in the case of I, to the configurations IC and ID) may be observed, cannot be predicted.



It should be noted here that, neither with the cation I nor with the zwitterions IB (or ID) can a *cis-trans* isomerism be predicted, the bond between the dithiolylium ring and the naphthalene nucleus being a single bond.

The existence of *cis-trans* isomers depends upon the contribution of the unionized forms IA or IC. When NMR measurements are made in deuteriotrifluoroacetic acid, the spectra of the cations, such as I, are obtained. In moderately polar solvents, such as deuteriochloroform, deprotonated forms (such as IA  $\leftrightarrow$  IB) are too sparingly soluble. More polar solvents such as hexadeuteriodimethyl sulfoxide may be used but will certainly facilitate isomerization *via* the ionized forms.

When the dithiole ring is fixed in a position *ortho* to the phenol hydroxy group as in II, it has been shown that, in the deprotonated form, the configuration in which the oxygen is nearer to the sulfur atoms is preferred (*i.e.* IIA  $\leftrightarrow$  IIB).



Structures such as IA or IC are called dithiolyliidene ketones, while structures such as IB are termed dithiolyliphenolates (or naphtholates). For the sake of consistency and brevity, however, we shall refer to all compounds only by the dithiolyliidene ketone names without prejudice of the contribution of structures such as IB.

Often, different isomers are obtained because the initial 5-aryl-3-chloro-1,2-dithiolylium ions may attack either *ortho* or *para* to the phenolic hydroxyl group; for example Reynolds<sup>1</sup> has reported that 1-naphthol and 3-methoxyphenol are attacked in the 4-position exclusively, whereas 2-naphthol is attacked in the 1-position exclusively.

On the other hand, it has been shown that if 5-aryl-3-methylthio-1,2-dithiolylium ions are reacted with phenolate ions instead of a phenol, *para* condensation takes place only if the *ortho* position is blocked.<sup>3</sup>

The reaction with phenolate ions may differ from the preceding case by two main features. Firstly, the negative oxygen atom could have a stronger attracting effect than the unionized hydroxy group on the attacking cation, and, secondly, the leaving group (chloro or methylthio) of the attacking cation could influence the steric course of the reaction.

For these reasons it seemed that some further studies of these reactions were necessary in order to ascertain the orientation of the reaction of 5-aryl-3-halogeno-1,2-dithiolylium cations with phenols and phenol ethers.

#### Reactions of 3-chloro-5-aryl-1,2-dithiolylium- and 3-methylthio-5-aryl-1,2-dithiolylium salts with naphthols and naphthol ethers

We have reacted 5-phenyl- and 5-(4-methoxyphenyl)-3-chloro-1,2-dithiolylium perchlorate with 1-naphthol in glacial acetic acid, using the method described by Reynolds.<sup>1</sup> Two structures, I and II, are possible for the resulting cation. However, the fact that the product of this reaction is different from that obtained by the action of sulfur on 2-cinnamylidene-1-tetralone,<sup>4</sup> which yields a compound of structure II (R=phenyl) exclusively, confirms the conclusions, made by Reynolds, that the isomer derived from the 3-chloro-1,2-dithiolylium salt has structure I. From the NMR spectrum of the crude perchlorate obtained from the reaction of 1-naphthol, it can be seen that the isomer I is formed exclusively as only one dithiole proton signal is present.

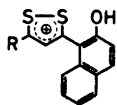
We have found, however, that if 5-(4-methoxyphenyl)-3-methylthio-1,2-dithiolylium iodide is reacted with 1-naphthol in propanol, using pyridine as a catalyst, structure II (R=4-methoxyphenyl) is obtained.

For Ia (R=phenyl), Ib and IIb (R=4-methoxyphenyl) the NMR spectra, in deuteriotrifluoroacetic acid, show only one singlet for the dithiole proton, a fact consistent with free rotation between the dithiole ring and the naphthalene nucleus. The following chemical shifts have been found:

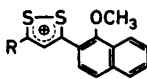
for Ib:  $\delta = 8.72$  ppm; for IIb:  $\delta = 8.57$  ppm.

The difference between these results may be accounted for by the fact that, in some conformations of I, the unsubstituted ring of the naphthalene moiety can be near enough to the dithiole proton to have a deshielding effect, something which cannot occur with structure II.

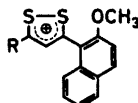
The reaction of 3-chloro-dithiolylium salts with 2-naphthol was found to give exclusively compounds of type III, which have been prepared in an unambiguous way both by Stavaux and Lozac'h,<sup>5</sup> and by Poirier and Lozac'h.<sup>6</sup>

IIIa R = C<sub>6</sub>H<sub>5</sub>IIIb R = (4)CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>

A similar cation (IV) has been obtained with 2,6-naphthalenediol.  
The reaction with methyl ethers of 1- and 2-naphthol gave rise to the cations V and VI, respectively.



V



VI

It was not possible to detect any isomer in the crude perchlorates of V and VI.

The structure of V was confirmed by its 100 Mc/s NMR spectrum shown in Fig. 1. The doublet found at high field is the signal from the one  $\beta$ -proton which is coupled with only one  $\alpha$ -proton. Had the condensation occurred in the 4-position, we would have found two  $\beta$ -protons coupled only with each other.

The 100 Mc/s NMR spectrum of VI, shown in Fig. 2, is not as clearly resolved as that of V, but the spectrum is in accordance with structure VI. At low field in this spectrum, two sharp signals are found with a splitting of 9.5 cps. By comparison with the 60 Mc/s spectrum, it can be seen that this splitting is the result of a coupling. The proton which causes this signal can only be the 4-proton of the naphthalene moiety, since this is the only  $\alpha$ -proton which is coupled only to one proton with an *ortho* coupling. If the condensation had occurred in the 4-position, one  $\alpha$ -proton would couple with one  $\beta$ -proton with a *meta* coupling. It can be seen from Fig. 1 that the  $\beta$ -proton neighbouring the positively charged dithiolylium moiety, occurs at much higher field than the other  $\beta$ -protons. In Fig. 2 no signals resulting from  $\beta$ -protons are found at high field, which is in accordance with the structure assigned.

The structural relationship between IIIb and VIb, and between IIB and Vb is consistent with the position of the signal of the dithiole proton which has been found at:

$$\begin{array}{ll} \delta = 8.78 \text{ ppm in IIIb,} & \delta = 8.57 \text{ ppm in IIB,} \\ \delta = 8.83 \text{ ppm in VIb,} & \delta = 8.54 \text{ ppm in Vb.} \end{array}$$

#### Reactions of 3-chloro-5-aryl-1,2-dithiolylium salts with resorcinol and resorcinol ethers

The NMR spectrum of the condensation product with 1,3-dimethoxybenzene showed three methoxy signals at  $\delta$  4.30, 4.05, and 4.00 with identical integrals, *i.e.* the isolated compound has the structure VII, and not VIII,

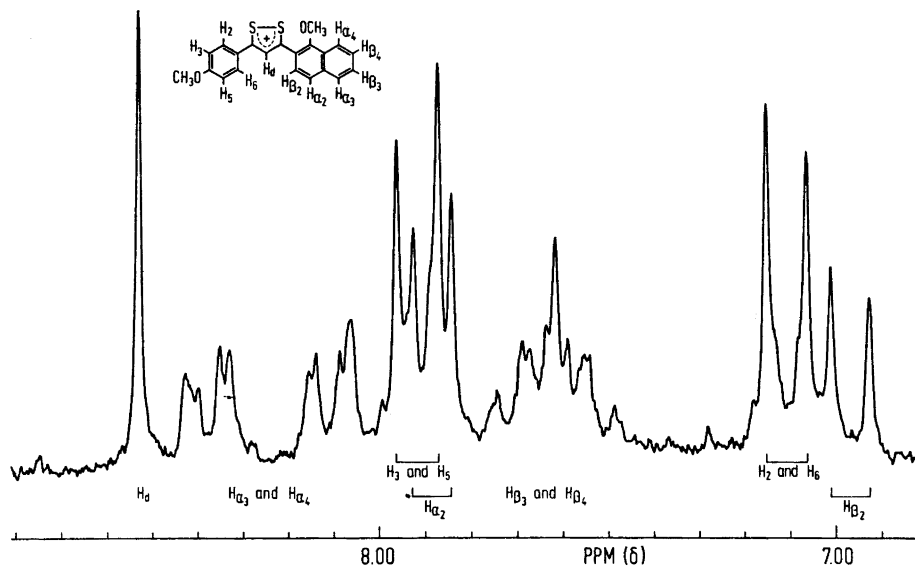


Fig. 1. The aromatic part of the 100 Mc/s NMR spectrum of 3-(1-methoxy-2-naphthyl)-5-(4-methoxyphenyl)-1,2-dithiolium perchlorate (Vb) in deuteriotrifluoroacetic acid.

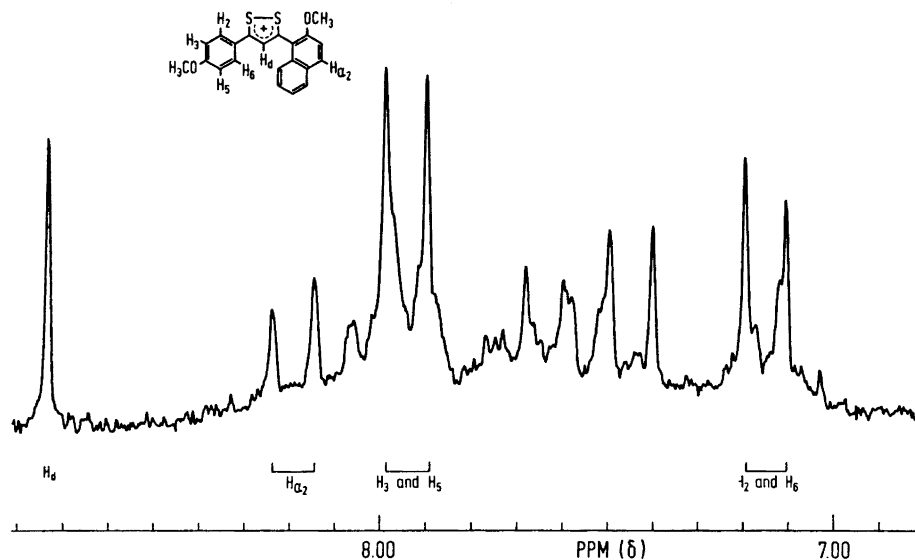
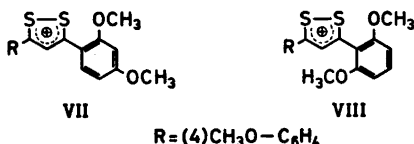
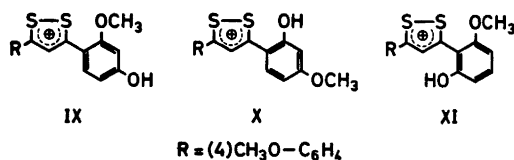


Fig. 2. The aromatic part of the 100 Mc/s NMR spectrum of 3-(2-methoxy-1-naphthyl)-5-(4-methoxyphenyl)-1,2-dithiolium perchlorate (VIb) in deuteriotrifluoroacetic acid.

since the two methoxy groups of the resorcinol moiety of the latter are equivalent.



The condensation of 3-chloro-5-aryl-1,2-dithiolylium salts with 3-methoxyphenol may result in the three isomers IX, X, and XI.



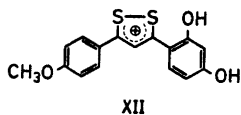
The crude perchlorate was found to give three different methoxy signals at  $\delta$  4.29, 4.05, and 4.03. From the integral values it can be seen that the signal at  $\delta$  4.05 is caused by the methoxy group in the 4-methoxyphenyl radical.

The deprotonated products were separated by fractionated recrystallization in pyridine. The less soluble fraction, having a paraquinoid structure, is IX A; the NMR spectrum of the corresponding cation, IX, shows two singlets, one at  $\delta$  4.05 (CH<sub>3</sub> of the 4-methoxyphenyl), and one at  $\delta$  4.29 (CH<sub>3</sub>O *ortho* to the dithiole, in the resorcinol moiety).

The more soluble fraction was expected to contain X A and/or XI A. Purified by chromatography, in order to eliminate IX A, this fraction proved to contain only X A, because the NMR spectrum of the corresponding cation has only two methoxy signals at  $\delta$  4.03 and 4.05 with the same integral. A CH<sub>3</sub>O group *ortho* to the dithiole as in XI would appear near,  $\delta$  4.20–4.30 ppm.

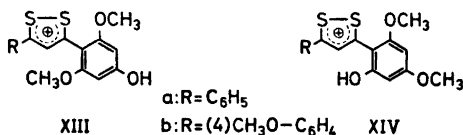
Moreover, the integrated spectrum of the crude product shows that IX and X are obtained in equivalent quantities.

The crude product obtained from resorcinol gives only one dithiole proton signal and, according to the preceding results, the cation probably has the structure XII.



Reactions of 3-chloro-5-aryl-1,2-dithiolylium salts with 3,5-dimethoxyphenol and 3-methoxycatechol

There are only two possibilities, XIII and XIV, for the structure of the condensation product of 3-chloro-1,2-dithiolylium salts with 3,5-dimethoxyphenol.



In the NMR spectrum of the crude perchlorate of the compound with  $\text{R} = 4\text{-CH}_3\text{OC}_6\text{H}_4$ , four different methoxy signals were found; one strong signal at  $\delta$  4.20, and three signals, which were not fully resolved, at  $\delta$  4.03,

Comparison of  $\text{CH}_3\text{O}$  NMR signals of resorcinol derivatives: 3-aryl-5-(4-methoxyphenyl)-1,2-dithiolium cations.

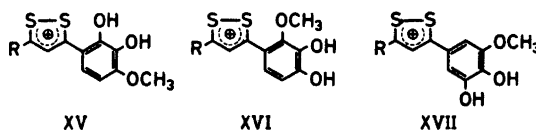
Ref.	Nature of the aryl	$\text{CH}_3\text{O}$ of the aryl		$\text{CH}_3\text{O}$ of 4-methoxyphenyl
		2-methoxy	4-methoxy	
VII	2,4-Dimethoxyphenyl	4.30	4.00	4.05
IX	4-Hydroxy-2-methoxyphenyl	4.28	—	4.05
X	2-Hydroxy-4-methoxyphenyl	—	4.03	4.05
XII	2,4-Dihydroxyphenyl	—	—	4.05

4.00, and 3.97. The ratio between the integral value of the signal at  $\delta$  4.20 and the sum of the integral values of the other methoxy signals was 1:1. The ratio between the integral values of the two signals at  $\delta$  9.62 and 9.56, corresponding to dithiole protons and of the signals of methoxy protons, was 1:9. No signal corresponding to the aromatic protons of the phenolic moiety was detectable in trifluoroacetic acid-*d*, as they are rapidly exchanged with deuterium. The same was found to be the case with the NMR spectrum of 3,5-dimethoxyphenol.

On the basis of these NMR data, one can conclude that the crude perchlorate is a 1:1 mixture of the isomers corresponding to XIII and XIV. If the crude deprotonated product is recrystallized from pyridine, a compound which only shows two methoxy signals at  $\delta$  4.22 and 4.04 can be isolated. The signal at  $\delta$  4.04 arises from the 4-methoxyphenyl groups, while that at  $\delta$  4.22 is due to the methoxy groups of the phenolic moiety. The compound must, therefore, be XIII, since this is the only isomer which possesses two equivalent methoxy groups.

If the crude product is chromatographed on alumina, isomer XIII does not move, but another compound is eluted with petroleum ether. The isolated compound gives an NMR spectrum which shows three different methoxy signals at  $\delta$  4.24, 4.03, and 4.00. This must be the isomer XIV, in which the three methoxy groups are non-equivalent.

The reaction of 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolium perchlorate with 3-methoxycatechol may, *a priori*, give three different cations: XV, XVI, and XVII.



In the NMR spectrum of the crude perchlorate only two methoxy signals at  $\delta$  4.00 and 4.15 are found, *i.e.* only one of the possible isomers is present. This is also in agreement with the fact that only one signal corresponding to the dithiole proton is found, at  $\delta$  = 8.87. Further, two AB systems are present in the spectrum. One is due to four protons and occurs at  $\delta$  8.14, 8.00, 7.37, and 7.23 ( $J$  = 8.4 cps), and is caused by the aromatic protons of the methoxyphenyl group. The other, corresponding to 2 protons, is found at  $\delta$  7.96, 7.80, 7.06, and 6.90 ( $J$  = 9.6 cps), and is the signal of the aromatic protons of the phenolic moiety. The fact that these aromatic protons appear as an AB system, with a typical *ortho* coupling constant, rules out XVII. We cannot establish with certainty from the NMR data whether the isolated compound has structure XV or XVI. However, the methoxy signals at  $\delta$  4.00 and 4.15 seem in favour of one methoxy group in *para*, and one in *ortho* relative to the dithiole ring, as in XV.

Moreover, we have found that deprotonated compounds with the *ortho*-quinoid structure are generally red and soluble in non-polar solvents, whereas compounds of the *para*-quinoid type are normally reddish violet or bluish red and sparingly soluble in non-polar solvents. As the compound isolated from the reaction between 3-chloro-1,2-dithiolylium salts and 3-methoxy-catechol is dark brownish red and sparingly soluble in non-polar solvents, we believe that the compound has structure XV.

#### Role of the anion, of the solvent and of the leaving group

In order to elucidate the role of the anion, we have reacted 1-naphthol, 3-methoxyphenol, and 3,5-dimethoxyphenol with 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium dichlorophosphate; in all cases we found the reaction products to be identical to those obtained from the perchlorate.

To see whether the size of the leaving group has any influence on the orientation of the substitution, 1-naphthol, 3-methoxyphenol, and 3,5-dimethoxyphenol were reacted in acetic acid with 3-bromo-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate; it was found that reaction products were identical to those obtained from the corresponding chloro compound. Under the same conditions 3-methylthio-5-(4-methoxyphenyl)-1,2-dithiolylium iodide failed to yield a condensation product with 1-naphthol; the only reaction observed was partial demethylation to the corresponding 1,2-dithiole-3-thione.

We have found that in propanol containing some pyridine, 5-(4-methoxyphenyl)-3-methylthio-1,2-dithiolylium iodide attacks 1-naphthol at carbon 2. Under the same conditions 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium chloride was found to react at carbon 4, with relatively low yields.

From these facts we can infer that the orientation of the attack on 1-naphthol is determined by the leaving group. However, the solvent, and perhaps the anion, may influence the yields.



*ortho*- and *para*-Diphenols and their ethers

The compounds hitherto discussed have been *meta* diphenols and their ethers. As examples of the reaction with *ortho* and *para* diphenols and their ethers we have investigated the reaction of catechol, hydroquinone, and ethers of these two compounds with 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate.

In the case of catechol and hydroquinone and their monomethyl ethers the reaction resulted in black tars, which were not further investigated. It is likely that the phenols are oxidized by the dithiolylium ion. In the case of dimethyl ethers of catechol and hydroquinone, no reaction had taken place after 3 h. The 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate was recovered after 3 h of reflux in glacial acetic acid, which indicates that the 5-(4-methoxyphenyl) compound is more stable towards hydrolysis than the 5-phenyl compound described by Faust and Mayer.<sup>7</sup>

## EXPERIMENTAL

UV spectra were obtained on a Unicam SP 700 A spectrophotometer from approximately  $10^{-4}$  M solutions in acetonitrile or  $10^{-4}$  M solutions in acetonitrile containing 1 % of 70 % perchloric acid.

The 60 Mc/s NMR spectra were recorded on a Varian A 60 or a Varian A 60 D spectrometer, and the 100 Mc/s NMR spectra on a Varian HA 100 spectrometer. The spectra were obtained from approximately 5 % solutions in deuteriotrifluoroacetic acid with TMS as internal standard. The chemical shifts are given in  $\delta$ -values.

The ratios of isomers formed were always estimated from the NMR spectra of their crude perchlorates.

*3-Chloro-5-phenyl-1,2-dithiolylium perchlorate.* The dichlorophosphate was prepared according to Reynolds from 5-phenyl-1,2-dithiol-3-one and  $\text{POCl}_3$ .<sup>1</sup> The isolated dichlorophosphate could be stored for months in a desiccator.

The dichlorophosphate was transformed into the perchlorate by the addition of 0.5 ml of 70 % perchloric acid to a suspension of 500 mg dichlorophosphate in 5 ml of acetic anhydride, as described by Faust and Mayer.<sup>7</sup>

*3-Chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate.* The dichlorophosphate prepared from  $\text{POCl}_3$  and 5-(4-methoxyphenyl)-1,2-dithiol-3-one crystallized during the reaction and was found to be much less hygroscopic than the phenyl compound. The perchlorate formed as above was recrystallized from acetone, m.p. 197–198°. (Found: C 35.24; H 2.43; S 18.75. Calc. for  $\text{C}_{10}\text{H}_8\text{Cl}_2\text{O}_6\text{S}_2$ : C 35.95; H 2.35; S 18.66.) NMR spectrum: 4.07 s ( $\text{OCH}_3$ ); 7.18, 7.33, 8.02, 8.17 (4 H),  $J=9.0$  cps; 8.50 s (dithiole).

*3-Bromo-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate.* Prepared as the 3-chloro compound from  $\text{POBr}_3$  and 5-(4-methoxyphenyl)-1,2-dithiol-3-one.  $\text{POBr}_3$  was melted, and the dithiolone was added. The perchlorate was recrystallized from acetone, m.p. 190–191°. (Found: C 30.99; H 2.19; S 16.29. Calc. for  $\text{C}_{10}\text{H}_8\text{BrClO}_6\text{S}_2$ : C 30.98; H 2.08; S 16.54.) NMR spectrum: 4.06 s ( $\text{OCH}_3$ ); 7.16, 7.32, 8.00, 8.16 q,  $J=9.6$  cps (4H); 8.57 s (dithiole).

*Preparation of condensation products.* Dithiolylium salts (2 mmol) and phenol or phenol ether (4 mmol) were refluxed for 3 h in 4 ml of glacial acetic acid. On cooling, the perchlorate crystallized. Triethylamine (0.5 ml) was added to the crude perchlorate suspended on 30 ml of acetonitrile. The mixture was stirred for 1 h, after which it was evaporated to dryness, washed with water to remove triethylammonium perchlorate and dried in a desiccator over  $\text{P}_2\text{O}_5$ .

*4-(5-Phenyl-1,2-dithiol-3-ylidene) (4H)1-naphthalenone (I Aa).* From 1-naphthol and 3-chloro-5-phenyl-1,2-dithiolylium perchlorate and the subsequent action of triethyl-

amine. Yield 55 %. Recrystallized from acetonitrile, m.p. 194–195°.\* (Found: C 71.41; H 3.70; S 19.79. Calc. for  $C_{19}H_{13}OS_2$ : C 71.22; H 3.77; S 20.02.) NMR spectrum of Ia, in  $CF_3CO_2D$ : 7.0–8.6 m (11H) 8.84 s (dithiole).

3-(4-Hydroxy-1-naphthyl)-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate (Ib). From 1-naphthol and 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate. Purified by dissolution in acetonitrile and subsequent precipitation with dry ether, m.p. 204–206°. (Found: C 53.23; H 3.58; S 14.16. Calc. for  $C_{20}H_{15}ClO_4S_2$ : C 53.27; H 3.35; S 14.22.)

4-(5-(4-Methoxyphenyl)-1,2-dithiol-3-ylidene)(4H)1-naphthalenone (I Ab). From the perchlorate prepared above; yield 70 %. Recrystallized from acetonitrile, m.p. 185–186°. (Found: C 68.21; H 4.01; S 17.93. Calc. for  $C_{20}H_{14}O_4S_2$ : C 68.55; H 4.03; S 18.30.) (UV and VIS:  $\lambda_{max}(MeCN)$ , 349, 383, 532  $m\mu$  ( $\epsilon$ : 12 400, 8200, 15 460)  $\lambda_{max}(MeCN+HClO_4)$  270, 298, 416, 483  $m\mu$  ( $\epsilon$ : 9660, 11 590, 14 490, 14 490).) NMR spectrum of Ib, in  $CF_3CO_2D$ : 4.09 s ( $OCH_3$ ); 7.1–8.2 m (10H); 8.72 s (dithiole).

2-(5-(4-Methoxyphenyl)-1,2-dithiol-3-ylidene)(2H)1-naphthalenone (II Ab). A mixture of 1 g of 3-methylthio-5-(4-methoxyphenyl)-1,2-dithiolylium iodide, 1.3 g of 1-naphthol, and 0.5 ml of pyridine were refluxed in 60 ml of propanol for 4 h. On cooling, a red compound crystallized, m.p. 220–221°. (UV and VIS:  $\lambda_{max}(MeCN)$  300, 354, 525  $m\mu$  ( $\epsilon$ : 10 890, 12 020, 12 270),  $\lambda_{max}(MeCN+HClO_4)$  303, 368, 420, 467  $m\mu$  ( $\epsilon$ : 11 260, 11 510, 12 140, 12 450).) NMR spectrum of IIb, in  $CF_3CO_2D$ : 4.02 s ( $OCH_3$ ), 7.0–7.9 m (10H), 8.57 s (dithiole).

1-(5-Phenyl-1,2-dithiol-3-ylidene)(1H)2-naphthalenone (III Aa). From 2-naphthol and 3-chloro-5-phenyl-1,2-dithiolylium perchlorate and the subsequent action of triethylamine. Yield 35 %. Recrystallized from cyclohexane, m.p. 144–145°. (UV and VIS:  $\lambda_{max}(MeCN)$  324, 496  $m\mu$  ( $\epsilon$ : 10 570, 11 790),  $\lambda_{max}(MeCN+HClO_4)$  292, 362, 479  $m\mu$  ( $\epsilon$ : 9090, 11 670, 10 690).) NMR spectrum of IIIa, in  $CF_3CO_2D$ : 7.3–8.3 m (11H); 8.94 s (dithiole).

1-(5-(4-Methoxyphenyl)-1,2-dithiol-3-ylidene)(1H)2-naphthalenone (III Ab). From 2-naphthol and 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate and subsequent action of triethylamine. Yield 82 %. Recrystallized from cyclohexane, m.p. 158–159°. (UV and VIS:  $\lambda_{max}(MeCN)$  346, 499  $m\mu$  ( $\epsilon$ : 10 000, 11 520),  $\lambda_{max}(MeCN+HClO_4)$  275, 419, 468  $m\mu$  ( $\epsilon$ : 8480, 11 520, 10 630).) NMR spectrum of IIIb, in  $CF_3CO_2D$ : 4.05 s ( $OCH_3$ ) 7.1–8.2 m (10H), 8.78 (dithiole).

3-(2,6-Dihydroxy-1-naphthyl)-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate (IV b). From 2,6-naphthalenediol and 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate. Yield 81%, m.p. > 300°. (Found: C 51.54; H 3.11; S 13.34. Calc. for  $C_{20}H_{16}ClO_4S_2$ : C 51.44; H 3.24; S 13.79.)

6-Hydroxy-1-(5-(4-methoxyphenyl)-1,2-dithiol-3-ylidene)(1H)2-naphthalenone (IV Ab). From the perchlorate prepared above. Yield 87 %. Recrystallized from acetone, m.p. 255–257°. (Found: C 65.24; H 3.96; S 17.19. Calc. for  $C_{20}H_{14}O_5S_2$ : C 65.55; H 3.85; S 17.50.) NMR spectrum in  $DMSO-d_6$ : 3.86 s ( $OCH_3$ ); 7.0–7.5 m, 7.8–8.1 m (9H); 8.97 s (dithiole).

3-(1-Methoxy-2-naphthyl)-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate (Vb). From 1-methoxynaphthalene and 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate. Yield 80 %. Recrystallized from acetonitrile, m.p. 218–220° d. (Found: C 54.35; H 3.89; S 13.46. Calc. for  $C_{21}H_{17}ClO_4S_2$ : C 54.25; H 3.69; S 13.79.) NMR spectrum: 4.04 s ( $OCH_3$ ); 4.15 s ( $OCH_3$ ); 7.0–8.2 m (10H); 8.54 s (dithiole).

3-(2-Methoxy-1-naphthyl)-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate (VIb). From 2-methoxynaphthalene and 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate. Yield 31 %. Purified by dissolution in glacial acetic acid and subsequent precipitation with dry ether, m.p. 240–241°. (Found: C 54.25; H 3.93; S 13.20. Calc. for  $C_{21}H_{17}ClO_4S_2$ : C 54.25; H 3.69; S 13.79.) NMR spectrum: 4.06 s ( $OCH_3$ ); 4.25 s ( $OCH_3$ ); 7.0–8.2 m (10H); 8.83 s (dithiole).

3-(2,4-Dimethoxyphenyl)-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate (VII). From 1,2-dimethoxybenzene and 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate. Yield 76 %. Recrystallized from acetonitrile, m.p. 275° d. (Found: C 48.79; H 3.91; S 14.19. Calc. for  $C_{18}H_{17}ClO_5S_2$ : C 48.63; H 3.85; S 14.19.) NMR spectrum: 4.00 s ( $OCH_3$ ),

\* In Ref. 1 the melting point is given as 145–146°, but we have not succeeded in isolating a compound with this melting point. Reynolds<sup>8</sup> has recently found a compound with m.p. 194–195°. The infrared spectra of the high and low melting compound are identical, so the two compounds are probably polymorphic.

4.05 s (OCH<sub>3</sub>), 4.30 s (OCH<sub>3</sub>); 7.10, 7.24, 7.91, 8.05 q (4H),  $J=8.4$  cps; 6.75–7.10, 8.18, 8.32 (3H); 8.74 s (dithiole).

*3-Methoxy-4-(5-(4-methoxyphenyl)-1,2-dithiol-3-ylidene)-2,5-cyclohexadienone (IX A)*. The crude product from the reaction of 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate on 3-methoxyphenol and subsequent reaction with triethylamine was dissolved in the minimum volume of hot pyridine. On cooling, a red-brown compound separated. NMR spectrum of IX, in CF<sub>3</sub>CO<sub>2</sub>D: 4.29 s (OCH<sub>3</sub>); 4.05 s (OCH<sub>3</sub>); 7.13, 7.27, 7.90, 8.04 q (4H),  $J=8.4$  cps; 6.7–7.0, 8.10, 8.26 (3H), 8.74 s (dithiole).

*5-Methoxy-2-(5-(4-methoxyphenyl)-1,2-dithiol-3-ylidene)-3,5-cyclohexadienone (X A)*. The pyridine mother liquor from the isolation of IX was concentrated and chromatographed on alumina. A bright red compound was eluted with petroleum ether (b.p. 60–90°)/ethyl acetate (9:1); recrystallized from cyclohexane, m.p. 240–242°. (Found: C 61.74; H 4.33; S 19.29. Calc. for C<sub>17</sub>H<sub>14</sub>O<sub>3</sub>S<sub>2</sub>: C 61.79; H 4.27; S 19.40.) NMR spectrum of X, in CF<sub>3</sub>CO<sub>2</sub>D: 4.03 s (OCH<sub>3</sub>); 4.05 s (OCH<sub>3</sub>); 7.20, 7.34, 7.96, 8.10 q (4H),  $J=8.4$  cps; 6.8–7.1, 8.11, 8.25 (3H); 8.80 s (dithiole).

*5-Hydroxy-2-(5-(4-methoxyphenyl)-1,2-dithiol-3-ylidene)-3,5-cyclohexadienone (XII A)*. From resorcinol and 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate and subsequent reaction with triethylamine. Yield 56%. Recrystallized from acetonitrile, m.p. > 300°. (Found: C 60.78; H 3.87; S 20.16. Calc. for C<sub>16</sub>H<sub>12</sub>O<sub>3</sub>S<sub>2</sub>: C 60.75; H 3.82; S 20.27.) NMR spectrum of XII, in CF<sub>3</sub>CO<sub>2</sub>D: 4.05 s (OCH<sub>3</sub>); 7.16; 7.32, 7.92, 8.08 q (4H),  $J=8.4$  cps; 6.7–7.0, 8.00, 8.18 (3H); 8.74 s (dithiole).

*Reaction of 3,5-dimethoxyphenol with 3-chloro-5-phenyl-1,2-dithiolylium perchlorate*. Yield of crude product 80%. NMR spectrum: 3.97 s (OCH<sub>3</sub>); 4.22 s (OCH<sub>3</sub>); 7.5–8.1 m (5H); 9.62 s (dithiole), 9.58 s (dithiole). The two isomers were not separated.

*3,5-Dimethoxy-4-(5-(4-methoxyphenyl)-1,2-dithiol-3-ylidene)-2,5-cyclohexadienone (XIII A)*. Isolated from the crude product in the same manner as described for IX, but with 3,5-dimethoxyphenol instead of 3-methoxyphenol. NMR spectrum of XIII, in CF<sub>3</sub>CO<sub>2</sub>D: 4.04 s (OCH<sub>3</sub>); 4.22 s (OCH<sub>3</sub>); 7.13, 7.28, 7.85, 8.00 q (4H),  $J=9.0$  cps; 9.60 s (dithiole).

*3,5-Dimethoxy-2-(5-(4-methoxyphenyl)-1,2-dithiol-3-ylidene)-3,5-cyclohexadienone (XIV A)*. Isolated from the mother liquor of XIII, as described for X. Bright red crystals, recrystallized from cyclohexane, m.p. 209–210°. (Found: C 59.88; H 4.50; S 17.57. Calc. for C<sub>18</sub>H<sub>16</sub>O<sub>4</sub>S<sub>2</sub>: C 59.98; H 4.47; S 17.29.) NMR spectrum of XIV A, in CDCl<sub>3</sub>: 3.82 s (OCH<sub>3</sub>); 3.87 s (OCH<sub>3</sub>); 3.98 s (OCH<sub>3</sub>); 5.85, 5.87, 6.16, 6.18 q (2H),  $J=1.2$  cps; 6.87, 7.01, 7.66, 7.80 q (4H),  $J=8.4$  cps; 9.04 s (dithiole). NMR spectrum of XIV A, in CF<sub>3</sub>CO<sub>2</sub>D: 4.00 s (OCH<sub>3</sub>); 4.03 s (OCH<sub>3</sub>); 4.24 s (OCH<sub>3</sub>); 7.11, 7.25, 7.86, 8.00 q (4H),  $J=8.4$  cps; 9.73 s (dithiole).

*Reaction product of 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate with 3-methoxycatechol*. Yield 33%. NMR spectrum: 4.08 s (OCH<sub>3</sub>); 4.15 s (OCH<sub>3</sub>); 6.90, 7.06, 7.80, 7.96 q (2H),  $J=9.6$  cps; 7.23, 7.37, 8.00, 8.14 q (4H),  $J=8.4$  cps; 8.87 s (dithiole).

*Reaction of 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate with catechol, catechol monomethyl ether, hydroquinone, and hydroquinone monomethyl ether*. After a few minutes the solution turned dark brown and not as usually dark red. On cooling, no compound separated, and on addition of ether a dark black tar deposited. It was not possible to obtain any crystalline compound.

*Reaction of 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate with catechol dimethyl ether and hydroquinone dimethyl ether*. Only slow evolution of HCl; on cooling, bronze-green crystals separated which were found to be the starting perchlorate. 50% of the perchlorate was recovered.

*Reaction of 3-bromo-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate with 1-naphthol, resorcinol monomethyl ether, and phloroglucinol dimethyl ether*. The reaction was carried out in the same manner as the reaction with 3-chloro-5-(4-methoxyphenyl)-1,2-dithiolylium perchlorate.

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