

## 118. Isomerization of the Radical Anions of 6a-Thiathiophthenes<sup>1)</sup>

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### Summary

The radical anions of 6a-thiathiophthenes ([1,2]dithiolo[1,5-*b*][1,2]dithioles), I(R), convert into those of 4*H*-thiapyran-4-thiones, III(R), via *cis-trans* isomerization. The reaction is slowed down when the size of the substituent R in the 2,5-positions of 6a-thiathiophthene increases, and it is prevented by the introduction of a 3,4-polymethylene bridge. The primary and the secondary radical anions, I(R)<sup>⊖</sup> and III(R)<sup>⊖</sup>, respectively, exhibit very similar hyperfine splitting patterns. *E.g.*, in the case of the unsubstituted 6a-thiathiophthene, I(H), and 4*H*-thiapyran-4-thione, III(H), the proton coupling constants are  $a_{\text{H}2,5} = 6.72$  and  $a_{\text{H}3,4} = 1.73$  Gauss for I(H)<sup>⊖</sup>, and  $a_{\text{H}2,6} = 6.35$  and  $a_{\text{H}3,5} = 2.07$  Gauss for III(H)<sup>⊖</sup>. In contrast to I(H)<sup>⊖</sup>, *cis-trans* isomerization could not thus far be proved to occur with its 1,6-dioxa-analogue, IV(H)<sup>⊖</sup>, since no ESR. spectrum of the radical anion of 4*H*-pyran-4-thione, V(H), was detected upon reduction of IV(H).

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**Introduction.** - The first excited state of 6a-thiathiophthene, I(H), can closely be approximated by the configuration  $a_2(\pi)^1 b_1(\pi^*)^1$  if the  $C_{2h}$  symmetry is assumed [1] [2]. Thus, the excitation implies an electron transfer from a HOMO  $a_2(\pi)$ , which is nonbonding between the sulfur centres, to a LUMO  $b_1(\pi^*)$  the contribution of which to the S-S linkages is strongly antibonding. The resulting decrease in the pertinent bond orders nicely accounts for the *cis-trans* isomerization which occurs upon irradiation in the long-wave band of I(H) [1] [3]. The MO model also suggests that an analogous process should take place upon reduction of I(H), since the additional electron enters the LUMO  $b_1(\pi^*)$ . Although radical anions have previously been produced from I(H) [4] and from several substituted derivatives, such as I(Me), I(Ph), II(Me) and II(Et) [5], in none of these

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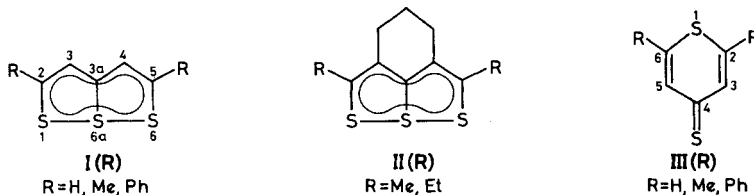
1) In the IUPAC notation, 6a-thiathiophthene, I(H), is [1,2]dithiolo[1,5-*b*][1,2]dithiole. An alternative trivial name for I(H) is 1,6,6a-trithiapentalene.

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experiments evidence of isomerization was obtained. The recent availability of a modified cell [6] has induced us to perform an electrolytic reduction of the aforementioned 6a-thiathiophthenes under more controllable conditions. This investigation not only revealed that the radical anions of I(H) and some of its derivatives indeed undergo *cis-trans* isomerization, but also brought about new ESR. spectroscopic aspects which are briefly reported in the present paper.



**Results.** - 6a-Thiathiophthene, I(H), and its derivatives I(Me), I(Ph), II(Me) and II(Et) were reduced electrolytically in a cylindrical cell containing a helical cathode of amalgamated gold and an anode of platinum wire placed along the axis [6]. *N,N*-Dimethylformamide (DMF) and tetraethylammonium ( $\text{Et}_4\text{N}^\oplus$ ) perchlorate served as the solvent and supporting salt, respectively. If use was made of the lowest temperature ( $-60^\circ$ ) and the least negative voltage possible, the ESR. spectra of the primary radical anions could be observed for all five 6a-thiathiophthenes under study. The stability of these radical anions decreased in the sequence  $\text{II}(\text{Me})^\ominus \approx \text{II}(\text{Et})^\ominus > \text{I}(\text{Ph})^\ominus > \text{I}(\text{Me})^\ominus > \text{I}(\text{H})^\ominus$ , their respective half-lives being *ca.* 60, 60, 30, 10 and 5 min. The reverse order holds for the case of conversion of the primary into secondary radical anions. Such a conversion proceeded for I(R) $^\ominus$  in the sequence  $\text{I}(\text{Ph})^\ominus < \text{I}(\text{Me})^\ominus < \text{I}(\text{H})^\ominus$  of increasing facility, whereas no subsequently formed paramagnetic products were found in the case of II(R) $^\ominus$ . It is evident from the *Table* listing the hyperfine data that the corresponding primary and secondary radical anions obtained from the three compounds I(R) exhibit closely similar splitting patterns, *i. e.*, not only have the sets of equivalent protons the same multiplicities, but also are the coupling constants  $a_{\text{H}\mu}$  of comparable magnitude in the two series. Noteworthy is the difference in the *g* factors which lie in the ranges of 2.0074 to 2.0080 and of 2.0066 to 2.0068 for the primary and secondary radical anions, respectively (*Table*).

The secondary paramagnetic species formed from I(H) was identified as the radical anion of 4*H*-thiopyran-4-thione, III(H), through comparison of its ESR. spectrum with that of III(H) $^\ominus$  observed upon direct reduction of III(H) under the same experimental conditions. By analogy, the ESR. spectra of the secondary species from I(Me) and I(Ph) could be attributed to the radical anions of the substituted 4*H*-thiopyran-4-thiones, III(Me) and III(Ph), respectively. (For the positions of the methyl and phenyl groups in III(Me) and III(Ph) see Discussion.) Such an obvious conclusion is in full accord with the *g* factor of these species which equals that of III(H) $^\ominus$  within the limits of experimental error.

A raise in the temperature and/or application of a more negative voltage led in the case of I(H) to formation of a third paramagnetic product which, due to its

Table. ESR. data for the primary and secondary radical anions from 6a-thiathiophthenes. Solvent: DMF; counterion:  $\text{Et}_4\text{N}^\oplus$ ; temp.:  $-60^\circ$ . Numbers of protons giving rise to the coupling constants,  $a_{\text{H}\mu}$  in Gauss, are indicated in parentheses. Experimental error:  $\pm 0.02$  Gauss for  $a_{\text{H}\mu}$  and  $\pm 0.0001$  for  $g$ .

Primary radical anion			Secondary radical anion			
	$a_{\text{H}\mu}$	Assignment $\mu$		$a_{\text{H}\mu}$	Assignment $\mu$	
$\text{I(H)}^\ominus$ $g=2.0080$	6.72 (two)	2,5	$\text{III(H)}^\ominus$ $g=2.0068$	6.35 (two)	2,6	
	1.73 (two)	3,4		2.07 (two)	3,5	
$\text{I(Me)}^\ominus$ $g=2.0076$	6.75 (six)	2,5- $\text{CH}_3$	$\text{III(Me)}^\ominus$ $g=2.0066$	6.35 (six)	2,6- $\text{CH}_3$	
	1.65 (two)	3,4		2.11 (two)	3,5	
$\text{I(Ph)}^\ominus$ $g=2.0074$	1.59 (two)	3,4	$\text{III(Ph)}^\ominus$ $g=2.0067$	1.81 (two)	3,5	
	1.59 (two)	$p$ -		} 2,6- Phenyl	1.53 (two)	$p$ -
	1.38 (four)	$o$ -			1.36 (four)	$o$ -
	0.45 (four)	$m$ -			0.46 (four)	$m$ -
$\text{II(Me)}^\ominus$ $g=2.0075$	6.60 (six)	2,5- $\text{CH}_3$				
	3.02 (two)	} 3,4- $\text{CH}_2$ ( $\beta$ )				
	1.24 (two)					
	0.52 (one)	} 3,4- $\text{CH}_2$ ( $\gamma$ )				
0.13 (one)						
$\text{II(Et)}^\ominus$ $g=2.0075$	4.08 (two)	} 2,5- $\text{CH}_2$				
	3.55 (two)					
	2.95 (two)	} 3,4- $\text{CH}_2$ ( $\beta$ )				
	1.19 (two)					
	0.51 (one)	} 3,4- $\text{CH}_2$ ( $\gamma$ )				
0.12 (one)						

high stability, rapidly prevailed over the secondary radical anion,  $\text{III(H)}^\ominus$ . The ESR. spectrum of this product displays unusually broad components and - like those of  $\text{I(H)}^\ominus$  and  $\text{III(H)}^\ominus$  - is consistent with hyperfine splittings from two pairs of equivalent protons. The pertinent coupling constants are:  $7.4 \pm 0.1$  and  $2.6 \pm 0.1$  Gauss<sup>5)</sup> ( $g=2.0068 \pm 0.0001$ ). The origin and structure of the long-lived paramagnetic species in question is still unknown. Since its ESR. spectrum was not observed upon direct reduction of  $\text{III(H)}$ , it cannot be formed from  $\text{III(H)}^\ominus$ , but must arise in some way from the primary radical anion  $\text{I(H)}^\ominus$ .

**Discussion.** - *MO models.* The lowest unoccupied HMO's (LUMO's) calculated with the use of the conventional heteroatom parameters<sup>6)</sup> for 6a-thiathiophthene,  $\text{I(H)}$ , and 4*H*-thiapyran-4-thione,  $\text{III(H)}$ , are depicted in the *Figure*, whereby the LUMO of  $\text{I(H)}$  is the one denoted as  $b_1(\pi^*)$  in the Introduction. It is evident that

<sup>5)</sup> 1 Gauss =  $10^{-4}$  Tesla.

<sup>6)</sup>  $a_s = a + 0.5\beta$ ;  $a_s = a + \beta$ ;  $\beta_{C-S} = \beta$ ;  $\beta_{C-S} = 0.7\beta$ ;  $\beta_{S-S} = 0.4\beta$ .

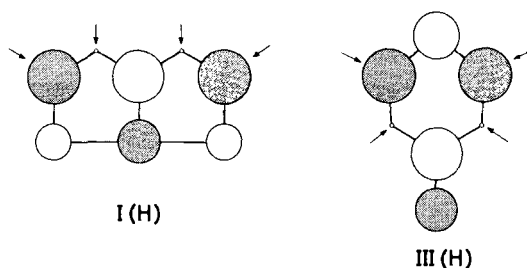


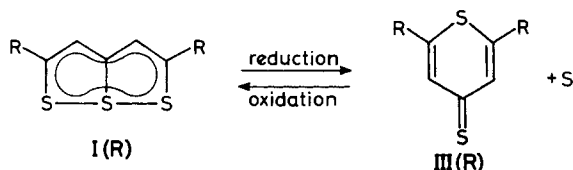
Fig. Lowest unoccupied HMO's of 6a-thiathiophthene, I(H), and 4H-thiapyran-4-thione, III(H)<sup>6</sup>). The areas of the circles are proportional to the squares of LCAO coefficients. Dotted and blank circles symbolize different signs of these coefficients. The proton bearing centres are marked by arrows.

- apart from being strongly antibonding between the sulfur atoms - this LUMO exhibits at the four proton bearing centres ( $\mu = 2,5$  and  $3,4$ ) almost the same LCAO coefficients as the LUMO of III(H) at the analogous positions ( $\mu = 2,6$  and  $3,5$ ). The HMO model thus rationalizes the striking similarity in the coupling constants  $a_{H\mu}$  observed for I(H)<sup>⊖</sup> and III(H)<sup>⊖</sup>. Moreover, since in the LUMO of III(H) the absolute values of the coefficients at the centres 2,6 vastly exceed those at 3,5, the assignment of the larger coupling constant (6.35 Gauss) to the pair of equivalent protons in the 2,6-positions of III(H)<sup>⊖</sup> is fully justified. An extension of the HMO model to the substituted derivatives I(R) and III(R), where R=Me or Ph, also accounts for the similar hyperfine data found in the ESR. spectra of I(R)<sup>⊖</sup> and their subsequently obtained counterparts III(R)<sup>⊖</sup>. Such a treatment leaves no doubt that the substituent R in the secondary radical anions III(R)<sup>⊖</sup> must be placed in the 2,6-positions, as specified in advance by the formulas given in the Introduction.

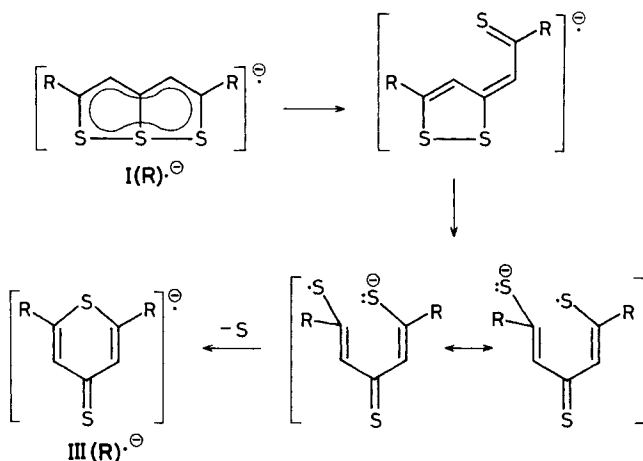
*Comparison with previously published data.* The great similarity in the hyperfine patterns of I(R)<sup>⊖</sup> and III(R)<sup>⊖</sup>, renders the ESR. spectra prone to misinterpretation. This is particularly the case for R=H and Me where the primary radical anions, I(H)<sup>⊖</sup> and I(Me)<sup>⊖</sup>, are rather short-lived and their occurrence can easily be overlooked. It is therefore not surprising that the coupling constants  $a_{H\mu}$  reported previously for I(Me)<sup>⊖</sup> [5] are actually those of the protons in the secondary radical anion III(Me)<sup>⊖</sup>. As for the parent 6a-thiathiophthene, I(H), the experimental conditions applied to its reduction several years ago, precluded the observation not only of the primary radical anion, I(H)<sup>⊖</sup>, but also of the subsequently formed III(H)<sup>⊖</sup>. The  $a_{H\mu}$  values cited in a recent review [1] are therefore those for the long-lived species the ESR. spectrum of which has been described in the Results. On the other hand, because of the substantially higher stability of I(Ph)<sup>⊖</sup>, II(Me)<sup>⊖</sup> and II(Et)<sup>⊖</sup>, the previously observed ESR. spectra [5] were correctly ascribed to the primary radical anions<sup>7</sup>).

<sup>7</sup>) This statement should also apply to the structurally related thiathiophthenes the radical anions of which were studied previously [5], but have not been reexamined in the present work. By the arguments put forward in the following Section, it will be shown that the radical anions in question ought to exhibit a stability comparable to that of I(Ph)<sup>⊖</sup> and II(R)<sup>⊖</sup>, since they either bear phenyl substituents in 2,5-positions or are bridged by a 3,4-polymethylene chain.

Conversion of  $I(R)^{\ominus}$  into  $III(R)^{\ominus}$ . It is known that 6a-thiathiophthene,  $I(H)$ , can be synthesized from 4*H*-thiapyran-4-thione,  $III(H)$ , by making use of  $K_3[Fe(CN)_6]$  as an oxidizing agent [1] [7]. A reversal of this process takes place when  $I(H)$  is

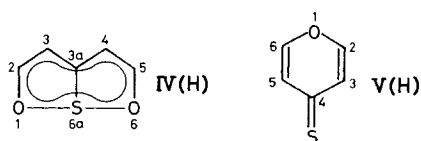


reduced with hydrogen sulfide or sulfide [1] [8]. Both reactions may be represented by the scheme ( $R=H$ ) which also readily accommodates the conversion of the radical anions  $I(R)^{\ominus}$  into  $III(R)^{\ominus}$ . If this conversion proceeds *via* the mechanism suggested below, the formation of  $III(R)^{\ominus}$  from  $I(R)^{\ominus}$  must involve a *cis-trans* isomerization of the thiathiophthenes to open chain compounds, by analogy with a photochemically induced process [1] [3].



The isomerization is expected to take place less easily when the size of the 2,5-substituent  $R$  increases, *i. e.*, on going from  $I(H)$  to  $I(Me)$  and  $I(Ph)$ . It should be prevented by a 3,4-trimethylene bridge, such as the one contained in  $II(Me)$  and  $II(Et)$ . The finding that the conversion of  $I(R)^{\ominus}$  into  $III(R)^{\ominus}$  is slowed down in the sequence  $R=H > Me > Ph$  and that formation of a secondary radical anion from  $II(R)^{\ominus}$  does not occur (see Results) can thus be considered as an experimental support for the proposed reaction mechanism.

**Appendix.** - In order to test whether a reaction analogous to the conversion of  $I(R)^{\ominus}$  into  $III(R)^{\ominus}$  takes place also in the case of the 1,6-dioxa derivatives, we carried out the electrolytic reduction of  $IV(H)$  under the same experimental conditions ( $-60^{\circ}C$ ;  $DMF/Et_4N^{\oplus}$  as the solvent/counterion).



No ESR. spectra were observed of either the primary or the secondary radical anion, IV(H)<sup>⊖</sup> and V(H)<sup>⊖</sup> respectively. Lowering of the temperature to  $-90^{\circ}$  (with the use of 1,2-dimethoxyethane/tetrabutylammonium cation as the solvent/counterion) also failed to produce signals which might be attributed to these radical anions. Undoubtedly, IV(H)<sup>⊖</sup> is even shorter-lived than its thia-analogue I(H)<sup>⊖</sup>. That such a statement also holds for V(H)<sup>⊖</sup> with respect to III(H)<sup>⊖</sup> was confirmed by a direct electrolytic reduction of pyran-4-thione, V(H), where an ESR. spectrum of very weak intensity could be detected only at  $-90^{\circ}$ . The coupling constants determined therefrom for two pairs of equivalent protons in V(H)<sup>⊖</sup> are  $a_{H_{2,6}} = 6.3 \pm 0.1$  and  $a_{H_{3,5}} = 2.0 \pm 0.1$  Gauss ( $g = 2.0067 \pm 0.0001$ ).

Thus, in view of the instability of V(H)<sup>⊖</sup>, our experiments do not provide a clear-cut answer to the question whether this radical anion is formed from IV(H)<sup>⊖</sup> or not. It is possible that the latter alternative is true, i.e., IV(H)<sup>⊖</sup> differs in the reaction path from its thia-analogue I(H)<sup>⊖</sup>. This possibility is also suggested by the finding that IV(H) and I(H) exhibit different photochemical behaviour [2] [9].

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