79. The He(Iα) Photoelectron Spectra of Substituted 1,2-Dithietes

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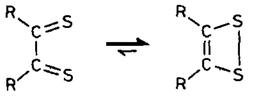
Summary

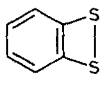
The He(Iα) photoelectron (PE.) spectra of a series of substituted 1,2-dithietes have been recorded and assigned with respect to the orbital sequence derived from an STO-3G model calculation and by correlation with the PE. spectra of related compounds. The results provide additional support for the presence of a closed, four-membered ring moiety in all the 1,2-dithietes investigated. In all cases the two highest occupied molecular orbitals are $b_2(\pi)$ = HOMO, $a_2(\pi)$, with exception of 3,4-bis(trifluoromethyl)-1,2-dithiete where the sequence $b_2(\pi)$, $a_2(\pi)$ or $a_2(\pi)$, $b_2(\pi)$ is uncertain.

The position of the equilibrium between 1,2-dithiones (**1**) and 1,2-dithietes (**2**) depends on the substituents R. The conjugated open-chain system **1** is isolated, if at least one of the substituents is a strongly electron-donating group, such as a dimethylamino [1–3], methoxy [4] or methylthio [5] substituent. The four-membered cycle **2** is obtained, if the substituents R are either *1)* strongly electron-withdrawing (*e.g.* trifluoromethyl, [6] [7]), or *2)* bulky alkyl groups (*e.g.* *t*-butyl [8] or structurally related groups [9] [10]), or *3)* an annellated benzene ring [11] [13]. If R = *p*-dimethylaminophenyl, both **1** and **2** are observed in equilibrium in solution, whereas only **2** exists in the solid state [12].

Recently, *Breitenstein, Schulz & Schweig* [13] have recorded and interpreted the He(Iα) PE. spectrum of thermolytically generated benzodithiete **3**, belonging



1 **2**



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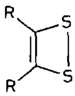
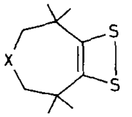
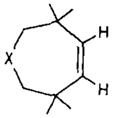


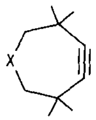
4 R = CF_3
5 R = *t*-Bu



6 X = CH_2
7 X = S
8 X = SO_2



9 X = S
10 X = SO_2



11 X = S
12 X = SO_2

to type 3, mentioned above. Since annellated benzene rings must have a profound influence on the electronic structure of the 1,2-dithiete system, putting them in a class apart, we present here PE. spectroscopic data for the following isolable 1,2-dithietes belonging to types *1* and *2:* 3,4-bis(trifluoromethyl)-1,2-dithiete (**4**) [6], 3,4-di-*t*-butyl-1,2-dithiete (**5**) [8], 3′,3′,7′,7′-tetramethylcyclohepteno[1′,2′-*c*]-1,2-dithiete (**6**) [10], 3′,3′,6′,6′-tetramethyl-1′-thia-cyclohepteno[4′,5′-*c*]-1,2-dithiete (**7**) [9] and 3′,3′,6′,6′-tetramethyl-1′-thia-cyclohepteno[4′,5′-*c*]-1,2-dithiete-1′,1′-dioxide (**8**) [9].

For comparison, we have recorded the PE. spectra of (*Z*)-3,3,6,6-tetramethyl-1-thia-4-cycloheptene (**9**) [14] and its *S,S*-dioxide (**10**) [15], and for self consistency, the PE. spectrum of 3,3,6,6-tetramethyl-1-thiacycloheptyne (**11**) [14], which has previously been described by *Schmidt, Schweig & Krebs* [16], and that of its *S,S*-dioxide (**12**) [15] [17].

The He(I*a*) PE. spectra of the dithietes **4–8** are presented in *Figures 1* and *2*. The orbital energies, *i.e.* the negative positions of the band maxima I_j^m, assuming the validity of *Koopmans'* theorem in reverse, are correlated in *Figures 3* and *4*, which are almost self-explanatory. However, a few remarks seem indicated.

Both the PE. spectra and the corresponding orbital description of disulfides RSSR' have been extensively investigated before (*cf.* the review article by *Gleiter & Spanget-Larsen* [18]). Although theoretical calculations on 1,2-dithietes and related systems are available [19] [20] they do not provide a consistent set of the data needed. Therefore it seemed of advantage to perform an *ab initio* STO-3G calculation [21] for the parent compound **2** (R = H) in the *syn-* and *anti*-conformation.

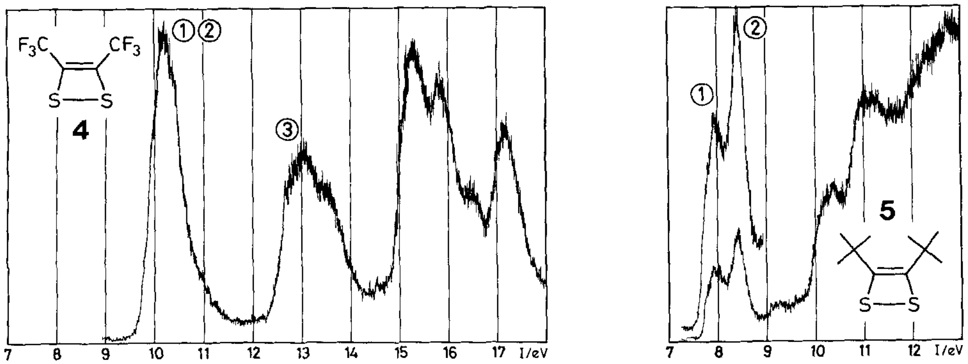


Fig. 1. *He(Ia) PE. spectra of the dithietes* **4** *and* **5**. Positions I_j^m of the band maxima: **4**: ① ② 10.2$_0$ eV, ③ ~ 12.7$_0$ eV; **5**: ① 7.9$_5$ eV, ② 8.4$_5$ eV.

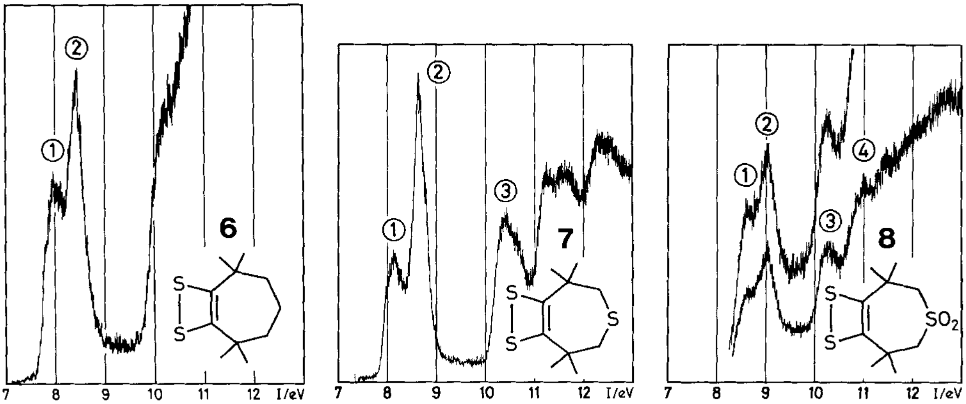
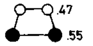
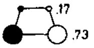
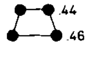
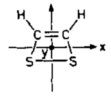


Fig. 2. *He(Ia) PE. spectra of the dithietes* **6**–**8**. Positions I_j^m of the band maxima: **6**: ① 7.9_5 eV, ② 8.4_5 eV, ③ 10.2_5 eV; **7**: ① 8.1_5 eV, ② 8.6_0 eV, ③ 10.4_0 eV; **8**: ① 8.5_5 eV, ② 9.0_5 eV, ③ 10.2_5 eV, ④ 11.0 eV.

Experimental structure determinations of 1,2-dithietes [7] [11] and 1,2-dithiones [2] [3] have been carried out, which suggest the following parameters for the parent compounds: **1** (R=H), r(C=S) = 165 pm, r(C–C) = 147 pm; **2** (R=H), r(S–S) = 210 to 212 pm, r(C=C) = 134 to 135 pm, r(C–S) = 178 to 179 pm. However, for the sake of consistency it was judged preferable to use the geometries obtained by *Haddon et al.* [20] through energy minimization of the structures of **1** (*syn*) and **2** (R = H) within the same theoretical procedure (STO-3G [21]) used for the present orbital energy calculations. These are the following: **1** (R=H, *syn*), C_{2v}-symmetry, r(C–C) = 148.9 pm, r(C=S) = 159.1 pm, r(C–H) = 109.2 pm, ∢C–C–H = 112.4°, ∢C–C–S = 126.4°; **2** (R=H), C_{2v}-symmetry, r(C–C) = 131.9 pm, r(C–S) = 176.9 pm, r(S–S) = 209.9 pm, r(C–H) = 108.0 pm, ∢C–C–H = 131.1°. For the *anti*-conformer of **1** (R=H, *anti*) (symmetry C_{2h}) we have assumed the same structure parameters as those given above for **1** (R=H, *syn*).

The results for the dithiete **2** (R=H) are as follows:

Orbital energy ε/eV	Orbital	π-Orbital diagrams
−6.78	HOMO $b_2(\pi)$	
−6.78	$a_2(\pi)$	
−9.13	$a_1(\sigma_{SS})$	
−9.76	$b_1(\sigma)$	
−12.05	$b_2(\pi)$	
−12.83	$a_1(\sigma)$	



(I)

It should be noted that due to the use of a minimal basis set, the absolute ε-values are not of significance, but the relative spacings presumably are. Thus the model predicts that the first two coincident bands in the PE. spectrum of **2** (R=H) should be of π^{-1}-type ($b_2(\pi)^{-1}$, $a_2(\pi)^{-1}$) separated by about 2 eV from a

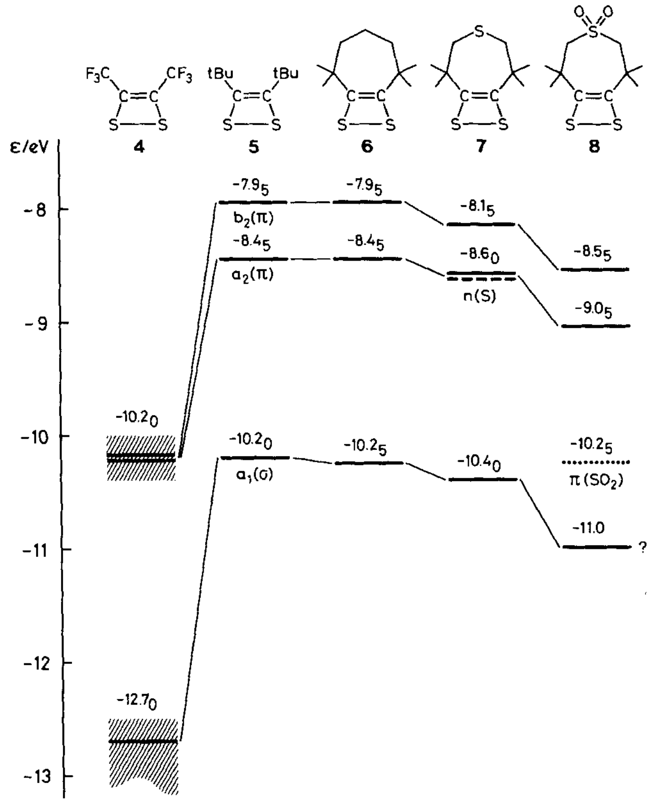


Fig. 3. *Orbital correlation diagram for the PE. spectra of the 1,2-dithietes* **4**–**8**. The orbital energies given are the negative ionization energies – I_j^m in eV.

third band ($a_1(\sigma_{S,S})^{-1}$), due to electron ejection from an orbital which is essentially that of the S,S σ-bond. The fourth band ($b_1(\sigma)^{-1}$) corresponds to the removal of an electron from an orbital of dominant C,S character and the fifth ($b_2(\pi)^{-1}$) to the lowest π-orbital of **2** (R=H). These results are in excellent agreement with the observed data collected in *Figure 3*, if the influence of the substituting groups is taken into account. As can be deduced from the π-orbital diagrams of **2** (R=H) shown in *Scheme 1*, alkylsubstitution will have a much larger destabilizing effect on the HOMO $b_2(\pi)$ than on $a_2(\pi)$ which is concentrated on the S-3p-orbitals. Assuming that the orbital destabilizing effect of alkyl moieties in positions 3 and 4 of **2** can be estimated by using the μ^H_R-parameters derived previously [22], one finds for **5** (and thus in a first approximation for **6** to **8**) that $I_1(b_2(\pi)^{-1})$ and $I_2(a_2(\pi)^{-1})$ should be shifted at least by $2(0.47)^2\mu^H_{t\text{-Bu}} = -0.60$ eV and $2(0.17)^2\mu^H_{t\text{-Bu}} = -0.08$ eV, respectively ($\mu^H_{t\text{-Bu}} = -1.36$ eV). The expected gap of 0.5 eV between bands ① and ② of **5** to **8** is in excellent agreement with observation. However, the true shift induced by the *t*-butyl groups could well be up to ~1 eV for $b_2(\pi)$ and ~0.5 eV for $a_2(\pi)$. The resulting assignment, corresponding to $b_2(\pi)$ above $a_2(\pi)$ is further supported by the fact that band ② is more intense and sharper, as expected for electron ejection from an orbital of dominant *S*-character (*cf.* orbital coefficients shown in (1) and discussion below).

For comparison with *Scheme 1,* the orbital energies calculated for **1**(R=H) in the *syn*- and *anti*-conformation are as follows (axes for **1**(R=H, *syn*) as for **2**(R=H) given in *Scheme 1*):

1(R=H, *syn*) C_{2v}		**1**(R=H, *anti*) C_{2h}		
ε/eV	Orbital	ε/eV	Orbital	
−6.53	a_1(nS)	−6.43	a_g(nS)	
−6.91	b_1(nS)	−7.15	$b_g(\pi)$	
−7.13	$a_2(\pi)$	−7.16	b_u(nS)	(2)
−10.51	$b_2(\pi)$	−10.57	$a_u(\pi)$	
−11.30	$b_1(\sigma)$	−11.09	$a_g(\sigma)$	
−12.04	$a_1(\sigma)$	−12.98	$b_u(\sigma)$	

In the *syn*-conformation of **1**(R=H), which would be close to the local ones of **6** to **8** if these molecules had the open 1,2-dithione structure, the two highest occupied orbitals are (essentially) the in-phase a_1(nS)- and out-of-phase b_1(nS)-combinations of the sulfur lone pair orbitals nS. Note that the 'inverse' sequence of a_1(nS) above b_1(nS) indicates the domination of 'through bond' interaction of the lone pair orbitals *via* the σ (C, C) relay orbital. Of the two π-orbitals $a_2(\pi)$, $b_2(\pi)$ the former would presumably be shifted at least by ~0.4 eV, the latter by ~0.7 eV in the open-chain valence isomers of **5** to **8**, assuming that a local *syn*-conformation is roughly conserved. This is of course impossible for s-*cis*-di-*t*-butyldithion (**1**: R=*t*-Bu) due to steric interference of the *t*-butyl groups. In view of the orbital correlation indicated in *Scheme 2* it is obvious that even in the case of a significant departure from the strict C_{2v}- towards the C_{2h}-conformation, the predicted spectra, *i.e.* three bands within a rather small interval, followed by a fourth at a distance of ~3 eV, would not agree with the observed ones. This rules out the 1,2-dithione structure for our compounds and completely confirms the results by *Schweig* [13] and his conclusion concerning the ring-closed structure of the dithietes, *e.g.* of **3**. As a corollary there is hardly any doubt that the orbital sequence given for **5** in *Figure 3* is the correct one and that it is conserved in the series **5**→**6**→**7**→**8**.

This is also supported by the observed band shapes for the first two bands ① ② in the PE. spectra of **5**–**8**. Previous experience has shown that PE. bands stemming from the ejection of sulfur lone pair electrons are rather slim and thus of relatively high intensity at the position I_j^m of their maximum [18]. This behaviour is shown by the second band in the PE. spectra of *Figures 1* and *2*, which is in agreement with the prediction that it is due to the $a_2(\pi)^{-1}$-process involving the out-of-phase combination of the sulfur 3 p(π)-orbitals.

Replacement of the *t*-butyl groups in **5** by trifluoromethyl groups to yield **4**, leads to a significant lowering of all the orbital energies under the influence of the electron attracting substituents. This is in agreement with previous observations [23], both qualitatively and quantitatively [24].

Comparing the band positions in the PE. spectra of **7** and **8** with those of **6** one notes that all π-orbitals are shifted towards more negative values in **7** and especially in **8**. This is what one expects if a methylene group of the seven-membered ring is replaced by a stronger electron acceptor [25] such as $-S-$ or $-SO_2-$. In the spectrum of **7** as well as that of **8** there is an additional band present at $I_3^m \approx -8.6$ eV and $I_3^m \approx -10.2_5$ eV, respectively. Comparison with other cyclic sulfides (*e.g.* **9**, **11**) or sulfones (*e.g.* **10**, **12**) as shown in *Figure 4*, identifies these bands with semi-localized orbitals pertaining to the $-S-$ or $-SO_2-$ moieties. The positions of these bands are in excellent agreement with those given in the literature for acyclic and cyclic sulfides [18] [26] and for the orbitals of alkyl sulfones [27].

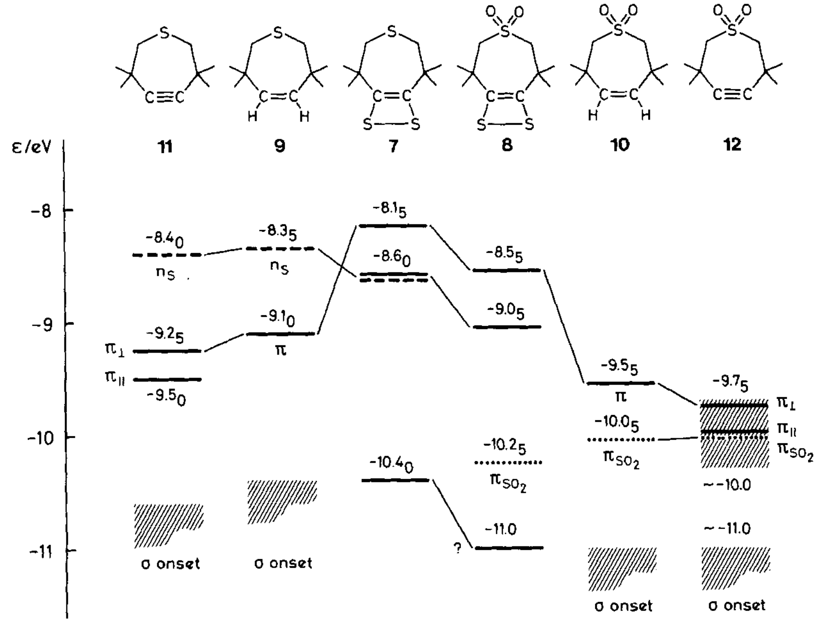


Fig. 4. *Correlation diagram for the formal genesis of the orbitals of* **7** *and* **8**

In *Figure 4* is shown a correlation diagram for the genesis of the orbital sequences in **7** and **8**, based on the observed PE. band positions. It shows in a rather clear fashion how these sequences come about. In **9** (see also [16]) the sulfur lone pair orbital nS is the HOMO followed by the local π-orbital of the $-HC{=}CH-$ group. The energy difference of the C,C π-orbital energies in **9** and **10** is about 0.4$_5$ eV, a difference which is also reflected in that of the π-orbitals $b_2(\pi)$ formed by the out-of-phase interaction with the sulfur $3p(\pi)$ combination. The in-phase combination *(cf. Scheme 1)* leads to an ionization energy higher by ~5 eV, *i.e.* to a band buried in the large σ-band system due to the alkyl moieties of **7** and **8**.

To summarize: There is hardly any doubt that the electronic doublet ground state of the radical cations of the 1,2-dithietes investigated in this work is $^2B_2$ and that the first excited state is $^2A_2$. The state of **7**, corresponding to the removal of an electron from the sulfide lone pair orbital is very close to $^2A_2$, and may well be the second excited, *Koopmans*-allowed state of **7**. All this is consistent with the dithiete structure of the compounds **4** to **8**, in agreement with the conclusions derived by other means.

Notes added in proof:

1) Prof. *A. Schweig* has kindly provided the preprint of an important investigation [29] in which the PE. spectra of the thermolytically generated parent compounds **2** (R = H) and **2** (R = Me) are described. It is found that the corresponding radical cations have again a $^2B_2$ ground state and a $^2A_2$ first excited state (coordinate system as defined in *Scheme 1*). Their respective separation is 0.31 eV and 0.41 eV. Thus the destabilizing alkyl group effect implied above is about the same for the $b_2(\pi)$- and $a_2(\pi)$-orbital, which shows that the postulated discrimination has to be taken with a grain of salt [30].

2) In the meantime an x-ray structure analysis of **7** has become available [31]. The following structure parameters are obtained: r(S–S) = 207.9 pm, r(C=C) = 134.6 pm, r(C–S) = 177.5 pm, symmetry C_{2v}.

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