176. The He 584 Å Photoelectron Spectra of Analoga of Thiathiophthene

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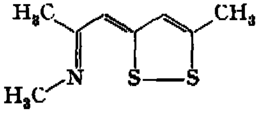
(30. V. 75)

Summary. The photoelectron spectra of the four oxygen and nitrogen analogs of thiathiophthene **1** to **4** are reported and discussed. The first two bands are assigned to ionization from the π- and n-molecular orbitals on the basis of CNDO/2 calculations. The assignment of bands ③ and ④ to ionization from π-molecular orbitals is suggested.

The structure of thiathiophthene and its analoga is still a question of considerable interest [1]. To draw any conclusions based on quantum chemical arguments, a detailed investigation on the physico-chemical properties is necessary. In this communication we wish to present our photoelectron (PE) spectroscopic measurements of the following derivatives: 3-(2-methyl-3-aza-but-2-en-1-ylidene)-5-methyl-3*H*-1,2-dithiole (**1**) [2], 1,2,5,6-tetramethyl-6a-thia-1,6-diazapentalene (**2**) [3], 3-acetonylidene-5-methyl-3*H*-1,2-dithiole (**3**) [4] and 1,6-dioxa-6a-thiapentalene (**4**) [5].



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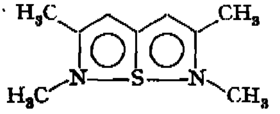

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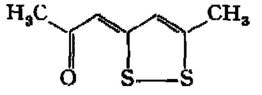

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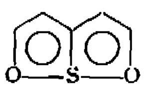

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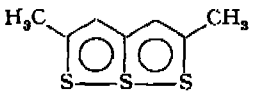

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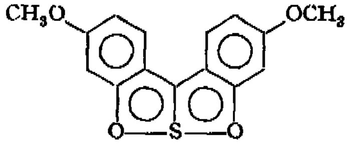

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The He 584 Å PE-spectra of **1**–**4** were measured with a PS-16 spectrometer (*Perkin Elmer Ltd.*, Beaconsfield, England) which was equipped with a heated probe. The vibrational fine structure of the bands could not be resolved. In Fig. 1 the PE-spectra of **1**–**4** are shown and the data are collected in the Table. In Fig. 2 we have correlated the PE data of **1** to **4** with those of 2,5-dimethyl-6a-thiathiophthene (**5**) [6][2]).

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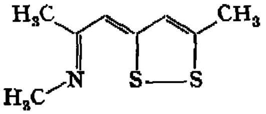
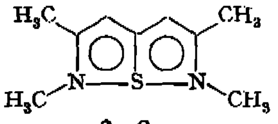
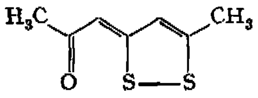
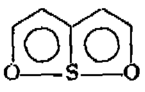
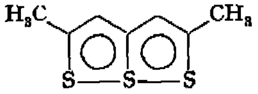
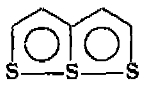
[2]) The unsubstituted species of **1**-**3** and **5** are called here **1a**, **2a**, **3a** and **5a**.

Table 1. *First four Ionization Potentials of* **1** *to* **5** (All values in eV)

Compound	Band	Orbital	$I_{v,j}$
 **1** C_s	①	π	7.17
	②	σ, n	7.97
	③	π	8.83
	④	π	9.17
 **2** C_{2v}	①	$a_2(\pi)$	6.44
	②	$a_1(\sigma, n)$	8.10
	③	$b_1(\pi)$	8.44
	④	$b_1(\pi)$	8.95
 **3** C_s	①	π	7.68
	②	σ, n	8.88
	③	π	9.60
	④	π	9.94
 **4** C_{2v}	①	$a_2(\pi)$	8.58
	②	$a_1(\sigma, n)$	9.76
	③	$b_1(\pi)$	10.28
	④	$b_1(\pi)$	10.98
 **5** C_{2v}	①	$a_1(\sigma, n)$	7.73
	②	$a_2(\pi)$	7.9
	③	$b_1(\pi)$	9.08
	④	$b_1(\pi)$	9.53
 **6** C_{2v}	①	$a_1(\sigma, n)$	8.11
	②	$a_2(\pi)$	8.27
	③	$b_1(\pi)$	9.58
	④	$b_1(\pi)$	10.11

Since the shapes of all the bands in the PE-spectra of **1**–**4** look very similar our interpretation must rely mainly on calculations and perturbational arguments under the assumption that *Koopmans'* theorem [7] ($-\varepsilon_j = I_{v,j}$) holds.

The π-molecular orbitals of **1**–**5** can be derived from those of the more familiar π-orbitals of pentalene dianion **7** [8]. The three highest occupied MO's of **7** are shown in the correlation diagram of Fig. 3. By replacing the centers 1,6 and 7 by heteroatoms, *e.g.* S, we have to take into account that the symmetry is reduced from D_{2h}- to C_{2v}- or C_s-symmetry and that the distances 1–7 and 6–7 are elongated due to the formation of an electron rich three center bond [9]. This perturbation causes a

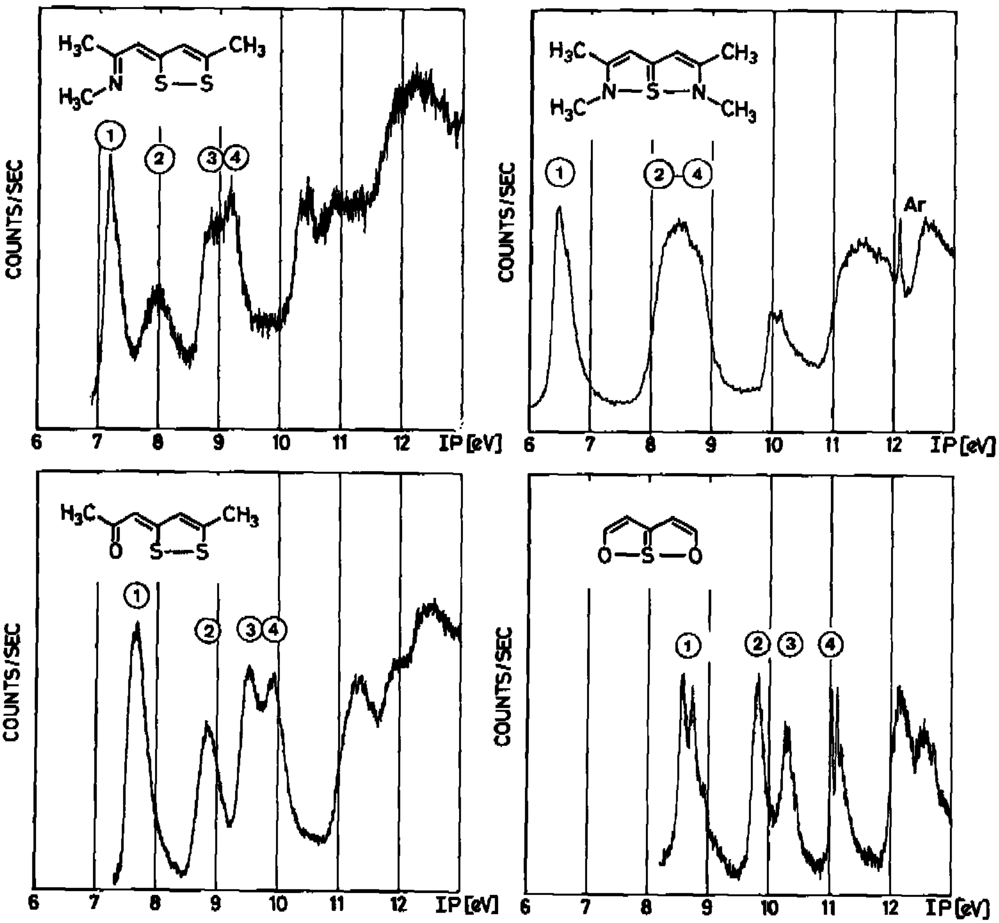


Fig. 1. *Photoelectron spectra of* **1**, **2**, **3** *and* **4** *between* 6 *and* 13 *eV*

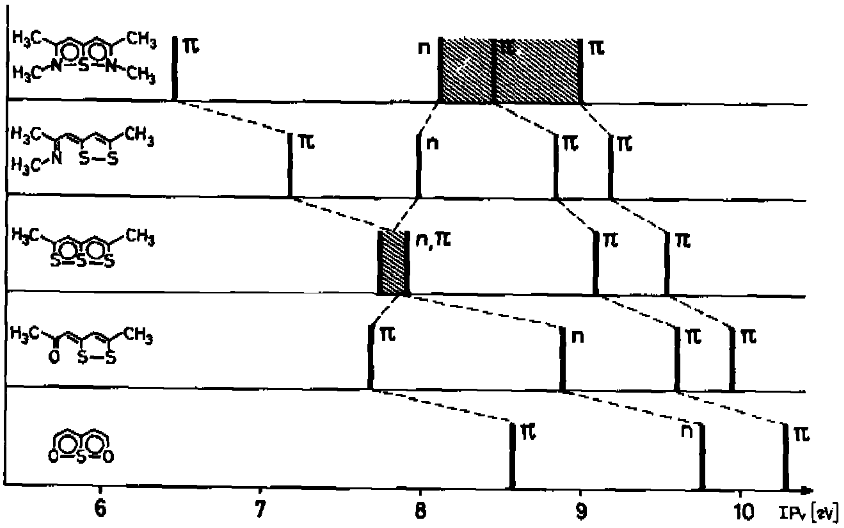


Fig. 2. *Correlation between the first bands of the photoelectron spectra of* **1** *to* **5**

change in the energy levels of the pentalene dianion and due to the only slightly bonding character of the electron rich three center bond, a high lying n-orbital appears as shown in Fig. 3.

In Fig. 4 the orbital energies for **1a** to **3a**, **4** and **5a** are shown for the highest occupied orbitals as obtained by a CNDO/2 [10] calculation[3]).

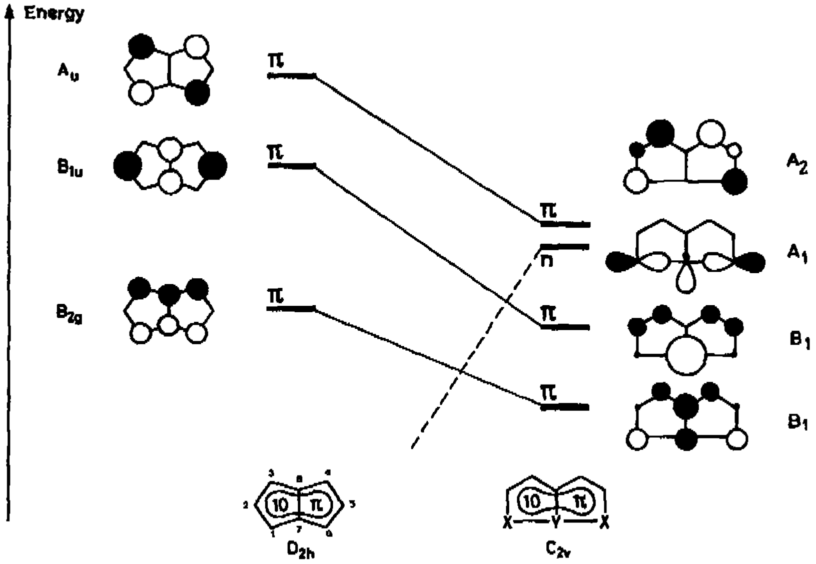


Fig. 3. *Qualitative correlation diagram between the highest occupied molecular orbitals of pentalene-dianion and an isosteric 1, 6, 7-heteropentalene*

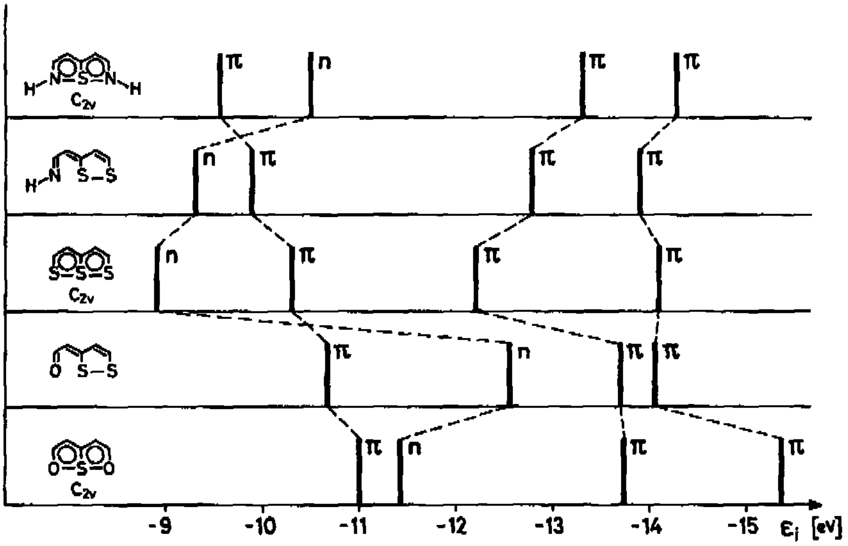


Fig. 4. *Correlation between the highest occupied molecular orbitals of* **1a**, **2a**, **3a**, **4** *and* **5a** *according to a CNDO/2 calculation*

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[3]) The geometrical parameters adopted for the calculations were taken from similar compounds whose X-ray structures are reported [1] [11–14].

We shall discuss the calculated three highest occupied π-orbitals and the highest occupied n-orbital separately. Although according to our experience semiempirical methods give the correct sequence among the π-, the n- and the σ-orbitals considered independently, the relative positions among these groups collectively is often reproduced incorrectly within *Koopmans'* assumption [7].

π-Orbitals. – As a starting point we assume the assignment for thiathiophthene [6] to be correct (see table 1) since it is supported by semiempirical [6] and *ab initio* calculations [15].

Comparing the ionization potentials for **5**, **3** and **4** as shown in Fig. 2 with the orbital energies given in Fig. 4, the assignment for **3** and **4** given in the Table (π, n, π, π) seems straight forward. Due to the inductive effect the three π-orbitals are lowered in energy in going from **5** to **3** to **4**.

The correlation between **5**, **1** and **2** given in Fig. 2 based on a comparison with the CNDO/2-orbital energies (Fig. 4) is not quite as straight forward. The most striking observation in the sequence **5**, **1** and **2** is the strong rise of the first band in Fig. 2. A simple electronegativity consideration, as used for the sequence **5**, **3** and **4**, should give a marked opposite behaviour because the coefficients at centers 1 and 6 in **5** are very large both for the first π- and the first n-orbital as shown in Fig. 3.

Two factors, however, account for the observation that the ionisation potential of the highest occupied π-orbital in the sequence **5**, **1** and **2** should be lowered on substituting a sulfur center by a N–CH$_3$ group:

1) According to a SCF calculation the one electron orbital energy ε_j is given by the sum of the one electron core hamiltonian (H_{jj}), the coulomb (J_{jk}) and the exchange (K_{jk}) integrals.

$$\varepsilon_j = H_{jj} + \sum_{k}^{n} (2\,J_{jk} - K_{jk}). \qquad (1)$$

This sum can be rewritten as

$$\varepsilon_j = H_{jj} + G_{jj}. \qquad (2)$$

Here the term G_{jj} comprises the sum of the two electron terms J and K.

From (2) it is seen that the orbital energy ε_j is a function of two terms, namely H_{jj} and G_{jj}. In Fig. 5 it is shown that the CNDO/2 method predicts for the highest occupied π-orbital a domination of the two electron term, G, over the core electron energy, H, in contrast to the highest occupied n-orbital (Fig. 5). Thus for ε_j one obtains smaller values by substituting NH for S although the one electron term, H, increases due to the higher electronegativity of N compared with S [16].

2) A second factor which contributes to a destabilization of the first π-orbital is the methyl group attached to the N-atom. We expect a destabilization effect in the order of 0.4 eV. For a comparison we mention the ionization potential corresponding to b_1 (π) of pyrrole (9.22 eV) and the corresponding one in N-methylpyrrole (8.80 eV) [17]. The value predicted by the CNDO/2 method is in the order of 0.1–0.3 eV.

The assignment of the band which is due to the ejection of an electron out of the n-orbital (see below) to band ② leaves the bands ③ and ④ to be assigned in the PE spectra of **1** and **2**.

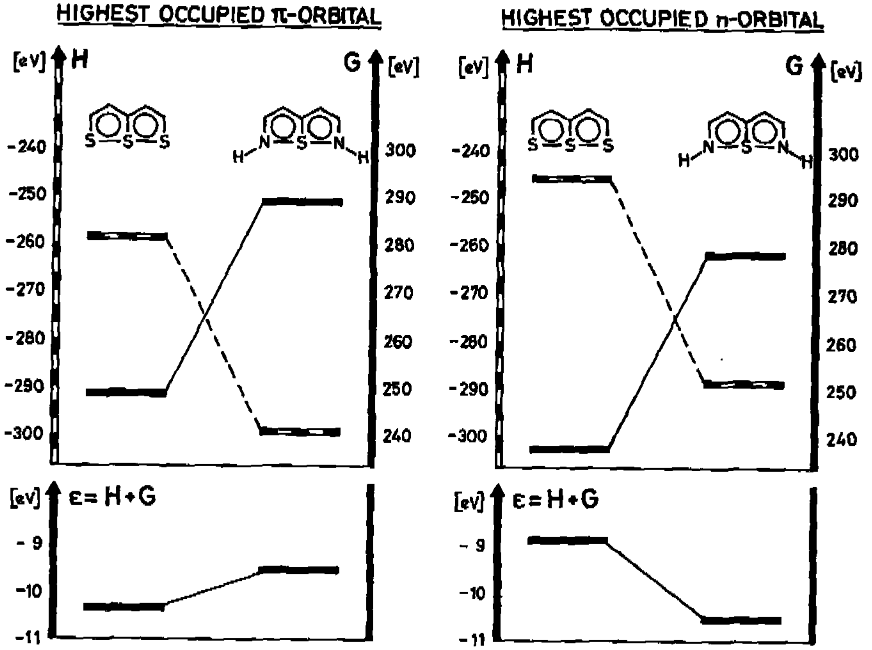

Fig. 5. *Comparison between the one and two-electron terms H and G of the highest occupied π- and n-orbitals for* **2a** *and* **5a** *according to a CNDO/2 calculation*

From Fig. 2 we see that bands ③ and ④ in the PE spectrum of **1** are lower in energy than in the PE spectrum of **5**. In the latter compound bands ③ and ④ were assigned to π-orbitals which belong to the irreducible representation B_1 (see Fig. 3) if we accept a C_{2v} symmetry for **5**. From the similarity of the PE spectra of **1** and **5** it seems reasonable that bands ③ and ④ correspond to the ejection of an electron from a π-orbital.

If a continuous lowering of the ionization potential is assumed for substituting the second S-atom in **1** by N-CH_3 we can estimate that the broad peak in the PE spectrum of **2** between 8.1 and 9.0 eV is due to three bands as indicated in Fig. 2. The assumption that this peak is composed of three strongly overlapping bands is also in line with a comparison of its half width with that of the first peak (see Fig. 1).

The assignment of bands ③ and ④ to the two $b_1(\pi)$-orbitals is only in agreement with the CNDO/2-results shown in Fig. 4 in so far that the third and fourth highest occupied orbital is predicted to be a $b_1(\pi)$-orbital. The CNDO/2 method predicts in the series **5**, **1** and **2** a rising in energy of these two π-orbitals. This discrepancy between calculation and experiment might be due to the non validity of *Koopmans'* theorem. As can be seen from the orbitals shown in Fig. 3 the orbital density on the heteroatoms is rather high and the ejection of an electron should initiate a migration of electron density from the other centers as in the case of fulvene [18]. The methyl groups on the nitrogens are especially good donors therefore this effect should be rather large in the series **5**, **1** and **3**. The nonvalidity of *Koopmans'* theorem might also play a role in the strong rise of $A_2(\pi)$ in the series **5**, **1** and **3**.

n-Orbital. – The orbital energy of the n-orbital in the sequence **5a**, **3a** and **4** is predicted by the CNDO/2 calculation to be higher in energy for **3a** than for **4**. This can be rationalized by the assumed O–S distance. The O–S distance in **3** (2.41 Å) [13] is considerably larger than in **6**, a derivative of **4** (1.879 Å) [14]. This CNDO/2 result for **4** is in contrast to a recent *ab initio* calculation [19] which predicts a gap of 2.62 eV between $a_2(\pi)$ and $a_1(\sigma, n)$. These as well as our CNDO/2 results are based on assumed geometries for **4**. For the sequence **5**, **1** and **2** a continuous rise of the ionization potential corresponding to the n-orbital is predicted by a CNDO/2 calculation (see Fig. 3). This is anticipated since in this series the N–S distance remains approximately constant.

Conclusions. – In substituting N–CH_3 and O for S in thiathiophthene at positions 1 and 6 successively does not yield a simple pattern in the PE spectra as anticipated from the electronegativity of S, N–CH_3 and O. Besides the electronegativity of the centers other factors play an important role:

1) The orbital energy is a function of one and two electron terms and 2) the high orbital density on the heteroatoms may invalidate *Koopmans'* assumption. Despite these points and a different geometry in the series **1** to **5**, the first four orbitals are assigned to π, n, π and π. However, it must be emphasized that we do not claim the assignment and explanation offered is necessarily the truth. One of the purposes of this communication is to point out the problems which have to be considered in assigning PE spectra in these series.

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177. Low Temperature Photochemistry of the Acetone/2-Propanol System

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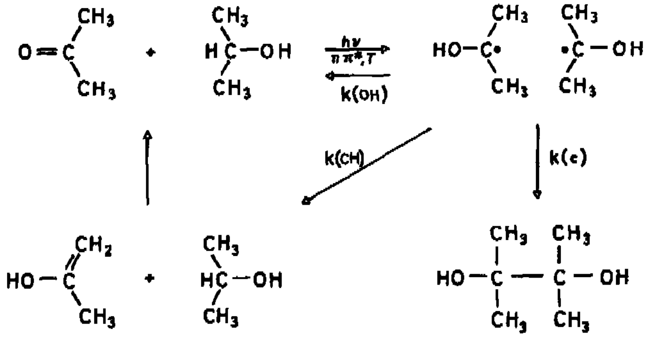
(26. VI. 75)

Summary. During UV.-irradiation of acetone/2-propanol mixtures at –70° products of photoaddition of acetone to intermediate enols are formed. The yields of those products exceed the yield of pinacol, the major room temperature product. At –70° the photoadditions are favoured by the long lifetime of acetone enol (≥ 5000 s).

The photoreactions of acetone and 2-propanol have been studied by many authors [1–6]. At room temperature, the only isolated photoproduct is pinacol (**PIN**) [1]. Additional minor unidentified products have been mentioned by *Gorzny* [2]. Observation of free radicals $(CH_3)_2\dot{C}OH$ by ESR. [3] and UV. [4], and detection of acetone enol by CIDNP. [5] as intermediates lead to the formulation of the reactions of *Scheme 1* as the dominant processes [5] [6]. At room temperature, the enol lifetime is ≈ 14 s [5a]. We recently determined the ratios of rate constants for the reactions of *Scheme 1* (26°, acetonitrile solution) as $k(\mathrm{CH})/k(\mathrm{c}) = 3.4 \pm 0.2$ and $k(\mathrm{OH})/k(\mathrm{CH}) = 0.3 \pm 0.1$ [6], *i.e.* disproportionation of the radicals to enol and 2-propanol is more important than the other radical terminations.

Scheme 1



The temperature dependence of product yields of the acetone/2-propanol system has been studied by *Gorzny* [2]. He found that the yields of the products which are