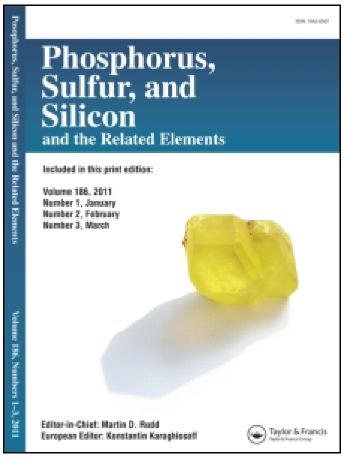

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Flash Vacuum Thermolysis of 4*H*-3,1-Benzodithiin-4-thione: UV-Photoelectron Spectroscopy Characterization of Benzothiet-2-thione and Quantum Chemistry Studies

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To cite this Article Drewnowski, Tomasz , Leśniak, Stanisław , Chrostowska, Anna , Dargelos, Alain and Khayar, Saïd(2009) 'Flash Vacuum Thermolysis of 4*H*-3,1-Benzodithiin-4-thione: UV-Photoelectron Spectroscopy Characterization of Benzothiet-2-thione and Quantum Chemistry Studies', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 5, 1269 — 1284

To link to this Article: DOI: 10.1080/10426500902856362

URL: http://dx.doi.org/10.1080/10426500902856362

Phosphorus, Sulfur, and Silicon, 184:1269–1284, 2009
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902856362

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Flash Vacuum Thermolysis of 4*H*-3,1-Benzodithiin-4-thione: UV-Photoelectron Spectroscopy Characterization of Benzothiet-2-thione and Quantum Chemistry Studies

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*Flash vacuum thermolysis of 4*H*-1,3-benzodithiin-4-thione (**2**) resulted in the formation of phenanthro[9,10-*c*]-1,2-dithiete (**3**) and 3*H*-1,2-benzodithiole-3-thione (**4**). The mechanism of this reaction, including the formation of benzothiet-2-thione (**5′**) as an intermediate, has been postulated. UV photoelectron spectra of **2** at variable temperature flash vacuum thermolysis have been recorded and analyzed considering the theoretical evaluation of ionisation potentials.*

Keywords Benzothiet-2-thione; flash vacuum thermolysis; ionization potentials; UV-photoelectron spectra

Received 9 January 2008; accepted 11 February 2008.

Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

TD and AC are grateful to the French Ministry of Foreign and European Affairs for its Eiffel Doctorate Scholarship, the French Ministry of High Education and Research for financial support, and they acknowledge Mr. Patrick Baylère for very efficient technical assistance. The authors thank the Rector of the University of Łódź for financial support (Grant 505/740).

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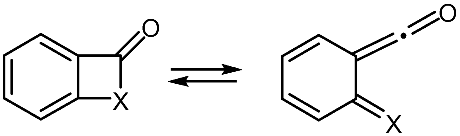
INTRODUCTION

Benzopropiolactone **1a** and benzopropiothiolactone (benzothiet-2-one) **1b** have been the subject of chemical studies due to their interesting features, high reactivity, and synthetic utility.[1–9] Thiet-2-ones are usually delicate compounds, isolable as crystalline solids in naphtho-annelated cases,[6] but oligomerize in the benzo cases.[6,7] They are susceptible to nucleophilic attack at the carbonyl group with ensuing ring opening. Theoretically, both, benzopropiolactone **1a** and benzopropiothiolactone **1b** could exist in equilibrium with their ring-opened isomers, i.e., 6-oxocyclohexa-2,4-dienylideneketene and 6-thioxocyclohexa-2,4-dienylideneketene, respectively (Scheme 1).



1a X=O
1b X=S

SCHEME 1

It is noteworthy that benzopropiothiolactones were characterized by IR, ^{1}H, and ^{13}C NMR spectroscopy,[6] and in addition, the UV photoelectron spectra of benzothiet-2-one (**1b**) were recorded.[5] Although, benzopropiothiolactone could exist in equilibrium with its ring-opened valence tautomer, the UV-PES characterization of the latter has been postulated.[10] In contrast, especially the opened keto-ketene form of the dioxygen analogue was characterized by IR[3] and photoelectron spectroscopy[5] 30 years ago. However, the photochemical equilibrium between the ketoketene and the isomeric lactone has been detected using IR (Ar matrix) spectroscopy.[4]

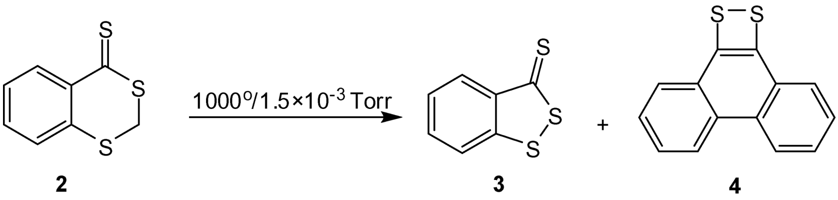
α-Thiocarbonylthioketenes have hitherto been a poorly known class of compounds. Only a few noncyclic examples of such compounds have been described.[7,12–14] On the other hand, the formation of the disulfur analogue of **1**, i.e., benzothiet-2-thione, has been postulated for the first time in our recent work.[11] Phenanthro[9,10-*c*]-1,2-dithiete and 3*H*-1,2-benzodithiole-3-thione were formed as secondary products of the flash vacuum thermolysis of 4*H*-1,3-benzothiazine-4-thione. The formation of 6-thioxocyclohexa-2,4-dienylidenethioketene (benzothiet-2-thione) as transient species in this reaction has been suggested; however no spectral data indicating its formation were given.[11]

The present article is dedicated mainly to the synthesis of benzothiet-2-thione under preparative FVT conditions using 4*H*-3, 1-benzodithiin-4-thione as a precursor. UV-PES technique in tandem with variable temperature FVT has been applied to characterize the unstable benzothiet-2-thione.

RESULTS AND DISCUSSION

We have shown previously that FVT of 4*H*-1,3-benzothiazine-4-thione proceeds mainly with elimination of acetonimine, although it was not the only course of the reaction.[11] For our study, we have selected 4*H*-1,3-benzodithiin-4-thione **2**, which is supposed to be more selective than 4*H*-1,3-benzothiazine-4-thione. Thermal reactions have been carried out on preparative FVT scale, as well as in FVT apparatus, in conjunction with variable temperature UV photoelectron spectral detection.

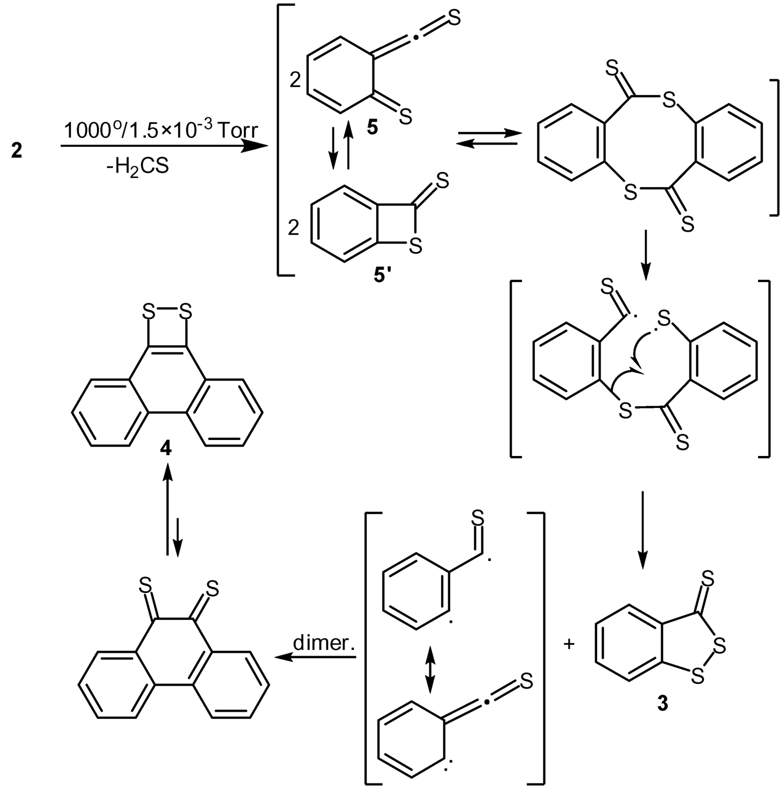
The preparative FVT experiment of 4*H*-1,3-benzodithiin-4-thione was performed at 1000°C under 1.5×10^{-3} Torr. Products of the reaction were separated using prep. TLC and were identified as 3*H*-1,2-benzodithiole-3-thione (**3**) and phenanthro[9,10-*c*]-1,2-dithiete (**4**) (Scheme 2), compounds identical with those obtained starting from 4*H*-1,3-benzothiazine-4-thione.[11]



SCHEME 2

Therefore, the mechanisms of both reactions should be similar, and the relevant transformation for 4*H*-1,3-benzodithiin-4-thione is suggested in Scheme 3. In the initial step of the reaction, the elimination of thioformaldehyde takes place leading to the thioacylthioketenes **5** (or equiv. benzothiet-2-thion **5**′). The next step of the conversion proceeds with initial dimerization of **5** (**5**′) and subsequent unsymmetrical fragmentation (the symmetrical cleavage would lead to the starting **5**) to give **3** and **4** as a result of the dimerization of the biradical or carbene (Scheme 3).

In order to shed some light on the mechanism of this reaction, flash vacuum thermolysis of **2**, in conjunction with variable temperature UV photoelectron spectral detection, have been applied. Considering the lesser vacuum applied in preparative FVT (10^{-3} Torr), different intermolecular reactions could not be excluded, whereas in the case of FVT–UV-PES tandem, due to the high vacuum (10^{-8} Torr),



SCHEME 3

dimerization of **5** should be avoided. The UV photoelectron spectrum of 4*H*-1,3-benzodithiin-4-thione **2** has been recorded and is displayed in Figure 1.

The first five PE bands are clearly distinguished at 8.25, 8.45, 8.9, 9.45, and 10.2 eV. The interpretation of these experimental data has been supported by three different levels of IP theoretical evaluation (TD-DFT, "corrected" IP, OVGF) after full geometrical parameters optimization [B3LYP/6–311G(d,p)]. Table I displays selected geometrical parameters of **2**.

As can be seen from Table I, calculated single (C5–S7, C8–S7, C8–S13, and C11–S13) carbon-sulfur bond lengths correspond to the nearly typical range for such bonds (Csp^3-S = 1.82 Å).[15] The double C=S bond is slightly shorter (1.656 Å) than in unsaturated six-membered thioketone.[16] The aromatic ring part and S7 atom are in the same plane, whereas C11 and C8 are out of this plane (5.7° and 26.5°), respectively.

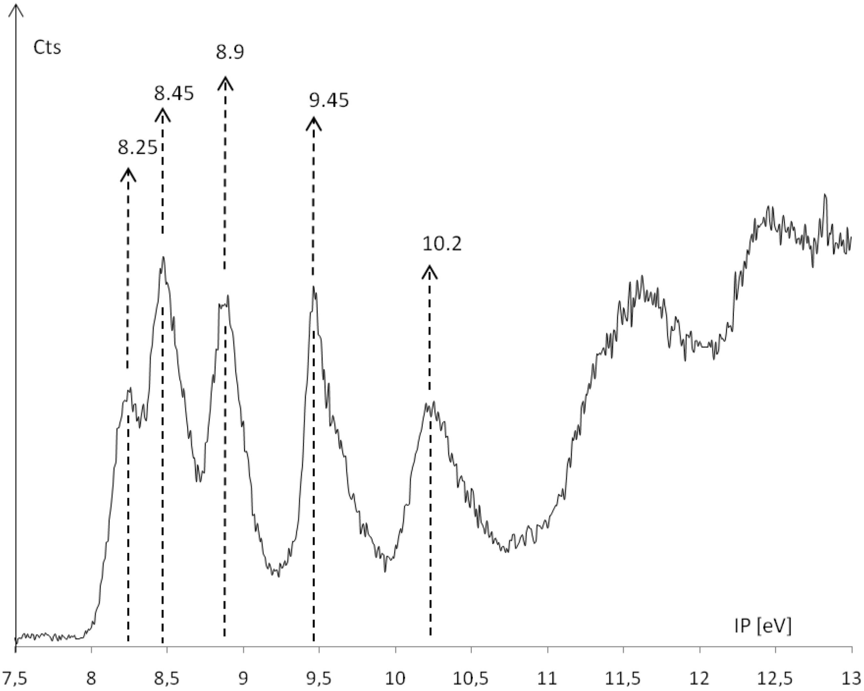
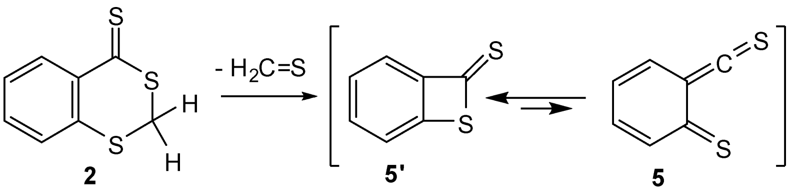


FIGURE 1 Photoelectron spectrum of 4*H*-1,3-benzodithiin-4-thione **2**.

Corresponding to this geometry of **2**, calculated and experimental values of IP are presented in Table II.

The attribution of observed PE bands has been done considering theoretical evaluation of IPs. The first value of 8.25 eV, which appears as a shoulder, corresponds to the ejection of one electron from the sulfur S12 lone pair in the sigma plane (n^{σ}_{S12}). The very intense band at 8.45 eV is attributed to the bonding sulfur S12 and S7 lone pairs interaction, but antibonding with respect to the S13 lone pair. The third IP at 8.9 eV describes the antibonding interaction of thiocarbonyl group with bonding S13–S7 lone pairs combination. Two following PE bands correspond to the ejection of one electron from the orbitals of the interacting aromatic ring with S13 abd S7 lone pairs, respectively.

The PE spectrum remained practically unchanged until 700°C, but at 770°C (Figure 2), the intensity of several bands changed clearly and a very sharp and intense band at 9.4 eV, corresponding to the ionization of σ-sulfur lone pair of $H_2C{=}S$,[17] appeared. Thus the retro-Diels–Alder cleavage shown in Scheme 4 was confirmed.



SCHEME 4

Thus, the most interesting question rose on this step of FVT-PES experiment. Which form—the “cyclic” **5**′ or the “opened” one **5**—of transient isomer corresponds to the photoelectron spectrum at 770°C? The quantum chemistry approach has been applied, and first a full optimization of the geometry parameters for **5**′ and **5** has been done to answer this question (Tables V and VI). The comparison of the calculated geometrical parameters of **5**′ and **5** (Tables III and IV) shows that the two molecules are planar, the shortest carbon–sulfur double bond is observed for thioketene **5** (C9–S9 1.539 Å), and the longest

TABLE I Calculated [B3LYP/6–311G(d,p)] Geometrical Parameters of 4*H*-1,3-Benzodithiin-4-thione 2

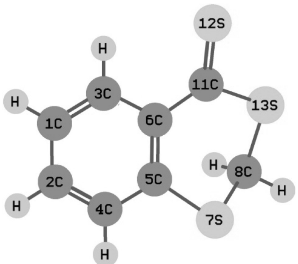
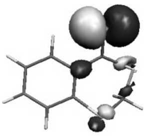
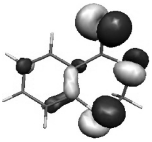
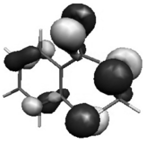
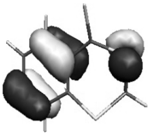
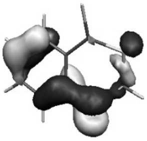
Bond length (Å)	Angle (Degrees)	Dihedral angle (Degrees)
C1–C2 = 1.395	C4–C5–S7 = 116.1	C2–C4–C5–S7 = –179.8
C1–C3 = 1.384	C5–S7–C8 = 97.1	C4–C5–S7–C8 = 143.3
C1–H15 = 1.083	S7–C8–H9 = 107.6	C5–S7–C8–H9 = –179.4
C2–C4 = 1.387	S7–C8–H10 = 110.3	C5–S7–C8–S13 = 64.2
C2–H16 = 1.084	S7–C8–S13 = 112.4	S7–C8–S13–C11 = –50.3
C3–C6 = 1.410	C8–S13–C11 = 103.9	C8–S13–C11–C6 = 3.2
C3–H14 = 1.082	S13–C11–S12 = 114.7	C8–S13–C11–S12 = –178.1
C4–C5 = 1.399	S13–C11–C6 = 121.8	S13–C11–C6–C5 = 26.5
C4–H17 = 1.084	S12–C11–C6 = 123.5	C3–C6–C11–S13 = –157.3
C5–S7 = 1.782	C11–C6–C3 = 117.5	C1–C3–C6–C11 = –174.3
C5–C6 = 1.418	C6–C5–S7 = 123.9	
C6–C11 = 1.483	C11–C6–C5 = 124.9	
S7–C8 = 1.813	C3–C6–C5 = 117.5	
C8–H9 = 1.090	C4–C5–C6 = 120.00	
C8–S13 = 1.828	H9–C8–S13 = 106.0	
C8–H10 = 1.090		
C11–S13 = 1.754		
C11–S12 = 1.656		

TABLE II Comparison of Calculated and Experimental Ionization Potentials of 4*H*-1,3-Benzodithiin-4-thione 2

Nature of molecular orbitals	$-\varepsilon^{KS}$	TD-DFT	"Corrected" x = 2.03	OVGF	Exp.
	6.22	8.02*	8.25**	8.04	8.25
	6.54	8.37	8.57	8.37	8.45
	6.85	8.60	8.88	8.38	8.9
	7.56	9.18	9.59	9.11	9.45
	8.23	9.88	10.26	9.97	10.2

All values in eV, *ΔSCF, **Exp. IP.

one has been found in the thiocarbonyl group of the same molecule **5** (C5–S7 1.683 Å), while the benzothiet-2-thione **5′** C=S bond length has an intermediate value **5** (C8–S9 1.611 Å). All three values are in good agreement with the data in the literature.[18] The single C—S bonds of **5′** feature (C8–S7 = 1.855 Å, C5–S7 = 1.811 Å) nearly typical Csp^3-S values (1.82 Å).[15] The C5–S7–C8 bond angle in **5′** is very small (73.1°), but despite that, the cyclic isomer **5′** is more stable than the open one **5** by 11.25 kcal/mol.

Considering IP's evaluation for **5′**, the first PE band should appear at 8.2–8.4 eV and corresponds to the ejection of one electron from the

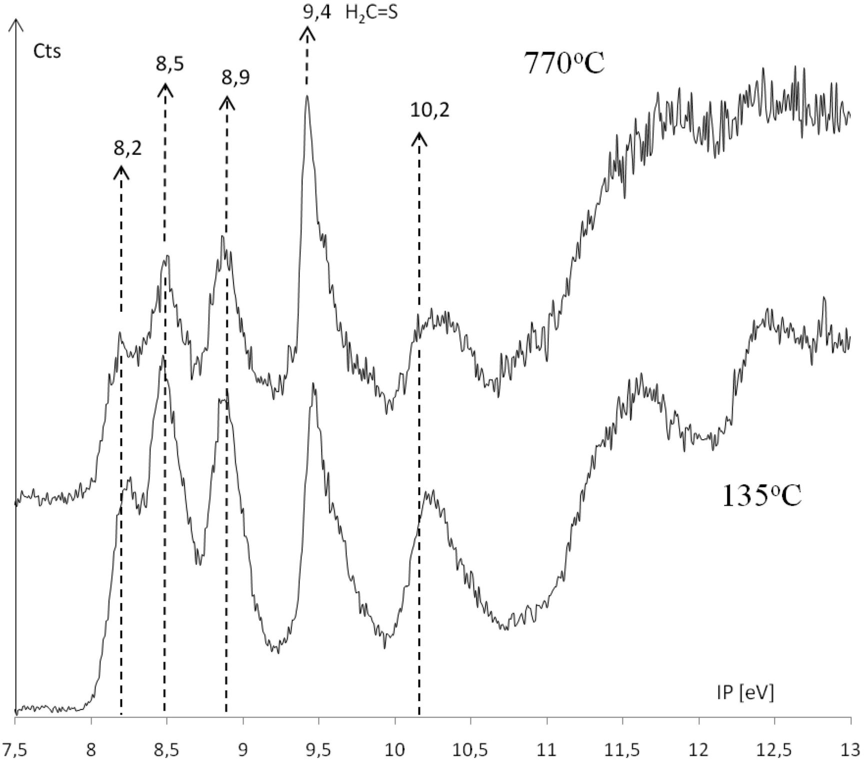


FIGURE 2 Photoelectron spectrum of 4*H*-1,3-benzodithiin-4-thione **2** at 770°C.

molecular orbital of sulfur S7 lone pair in antibonding interaction with π-electrons of aromatic ring (n_S^π–π_2). The second IP should be expected at 8.4–8.6 eV reflecting the ionisation of the sulfur S9 lone pair (n_S^σ). Then, the thiocarbonyl antibonding interaction with the π-electrons of aromatic ring ($\pi_{C=S}$–π_3) should be observed at 9.0–9.3 eV.

The same analysis for **5** shows that the first IP corresponding to the totally antibonding interaction of π-system is expected at 7.2–7.6 eV. The second one, close to the latter, at 7.6–7.7 eV should be due to the S7 σ-lone pair ionisation (n_{S7}^σ). Then, nearly 2 eV farther, at 9.4–9.6 eV, S9 π-sulfur lone pair antibonding interaction with π-electrons of aromatic ring is expected (n_{S9}^π–π_3).

The main difference between the expected IPs for these two molecular structures are the very low values, which have to appear before 8 eV in the spectrum corresponding to the 6-thioxocyclohexa-2,4-dienylidenethioketene **5**. Unfortunately, this is not the case, because the

TABLE III Calculated [B3LYP/6–311G(d,p)] Geometrical Parameters of Benzothiet-2-thione 5′

Bond length (Å)	Angle (Degrees)	Dihedral angle (Degrees)
C1–C2 = 1.396	H13–C4–C5 = 123.3	H13–C4–C5–S7 = 0.0
C1–C3 = 1.403	C4–C5–S7 = 141.3	C4–C5–S7–C8 = 180.0
C1–H11 = 1.083	C5–S7–C8 = 73.1	C5–S7–C8–C6 = 0.0
C2–C4 = 1.410	S7–C8–C6 = 91.8	C5–S7–C8–S9 = 180.0
C2–H12 = 1.084	S7–C8–S9 = 131.8	S7–C8–C6–C5 = 0.0
C3–C6 = 1.384	S9–C8–C6 = 136.4	S7–C8–C6–C3 = 180.0
C3–H10 = 1.083	C8–C6–C5 = 99.0	C3–C6–C8–S9 = 0.0
C4–H13 = 1.083	C6–C5–S7 = 96.0	C3–C6–C5–S7 = 180.0
C4–C5 = 1.374	C8–C6–C3 = 139.0	C5–C6–C8–S9 = 180.0
C5–S7 = 1.811	C3–C6–C5 = 121.9	
C5–C6 = 1.401	C6–C5–C4 = 122.6	
C6–C8 = 1.470		
S7–C8 = 1.855		
C8–S9 = 1.611		

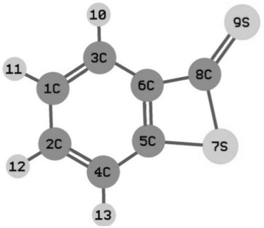


TABLE IV Calculated [B3LYP/6–311G(d,p)] Geometrical Parameters of 6-Thioxocyclohexa-2,4-dienylidenethioketene 5

Bond length (Å)	Angle (Degrees)	Dihedral angle (Degrees)
C1–C2 = 1.432	H13–C4–C5 = 116.8	C2–C4–C5–S7 = 180.0
C1–C3 = 1.357	C4–C5–S7 = 122.7	C4–C5–C6–C8 = 180.0
C1–H11 = 1.083	S7–C5–C6 = 122.2	C4–C5–C6–C3 = 0.0
C2–C4 = 1.364	C5–C6–C8 = 119.0	S7–C5–C6–C8 = 0.0
C2–H12 = 1.085	S9–C8–C6 = 176.5	S9–C8–C6–C5 = 180.0
C3–C6 = 1.447	C8–C6–C3 = 119.5	S9–C8–C6–C3 = 0.0
C3–H10 = 1.083	C6–C3–C1 = 119.5	C1–C3–C6–C8 = 180.0
C4–H13 = 1.083	C3–C6–C5 = 121.5	
C4–C5 = 1.435	C6–C5–C4 = 115.1	
C5–S7 = 1.683		
C5–C6 = 1.463		
C6–C8 = 1.349		
C8–S9 = 1.539		

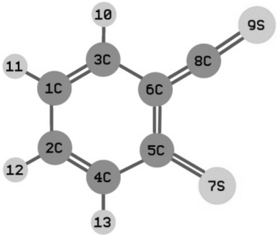
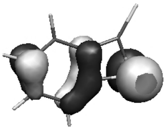
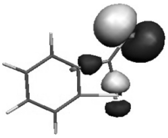
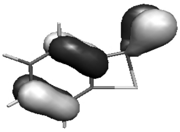
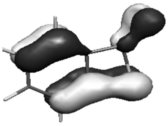
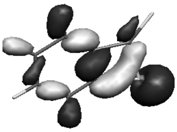
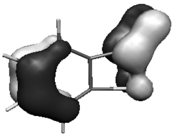


TABLE V Calculated Ionization Potentials of Benzothiet-2-thione 5′

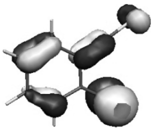
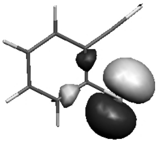
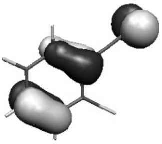
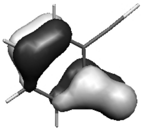
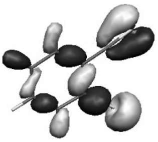
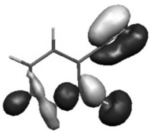
Nature of molecular orbitals	$-\varepsilon^{KS}$	TD-DFT	"Corrected" x = 1.66	OVGF
	6.54	8.41	8.2	8.16
	6.69	8.48	8.35	8.57
	7.48	9.27	9.14	9.21
	8.31	10.23	9.97	10.06
	9.33	11.24	10.99	11.25
	9.66	11.46	11.32	11.54

All values in eV, *ΔSCF.

first PE band is observed at 8.2 eV. Therefore, the formation of this less stable isomer **5** in our FVT-PES conditions of 4*H*-1,3-benzodithiin-4-thione **2** at 770°C should be ruled out.

Thus, the assignement of PE bands corresponding to the FVT of 4*H*-1,3-benzodithiin-4-thione **2** at 770°C has been done on the basis of theoretical IP evaluation for benzothiet-2-thione **5**′ as follows:

TABLE VI Calculated Ionization Potentials of 6-Thioxocyclohexa-2,4-dienylidenethioketene 5

Nature of molecular orbitals	$-\varepsilon^{\mathrm{KS}}$	TD-DFT	"Corrected" x = 1.73	OVGF
	5.83	7.56	7.56	7.23
	5.86	7.68	7.59	7.63
	7.86	9.62	9.59	9.36
	8.44	10.62	10.17	10.00
	9.47	11.32	11.20	11.43
	10.05	11.78	11.78	11.89

All values in eV, *ΔSCF.

- The PE band at 8.2 eV is attributed to the n_{S7}^{π}–π_2 ionisation.
- The second signal at 8.5 eV is due to the ejection of one electron from the sulfur S9 lone pair in the sigma plane.
- 8.9 eV IP describes the thiocarbonyl group antibonding interaction with π-electrons of aromatic ring.

- The fourth PE band at 10.2 eV reflects the ionization of thiocarbonyl group in interaction with π-sulfur (S7) lone pair and π-electrons of aromatic ring $[(\pi_3 + n^{\pi}_{S7}) - \pi_{C=S}]$.

Increasing of the FVT temperature provoked only the growth of intensity of $H_2C{=}S$ band (9.4 eV) without any significant changes.

CONCLUSION

The preparative FVT of 4*H*-1,3-benzodithiin-4-thione (**2**) at 1000°C has allowed the formation of phenanthro[9,10-*c*]-1,2-dithiete (**3**) and 3*H*-1,2-benzodithiole-3-thione (**4**). Variable temperature UV photoelectron spectral detection has been successfully applied to direct follow-up of the FVT of **2** and has allowed first benzothiet-2-thione characterization. Compared to the 4*H*-3,1-benzooxathiin-4-thione, which undergoes the Schönberg–Newman–Kwart rearrangement at 400°C, followed by thioformaldehyde elimination at 650°C and the formation of benzothiet-2-one, rather high thermal resistance of 4*H*-1,3-benzodithiin-4-thione must be noted. The replacement of the oxygen atom in the 4*H*-3,1-benzooxathiin-4-thione by the sulfur atom (formation of 4*H*-1,3-benzodithiin-4-thione) provokes only a slight destabilization (0.15 eV) of the second IP. However, all the benzothiet-2-thione IPs are shifted to the lower energy in respect to those of benzothiet-2-one[5,10] (8.56, 9.94, 10.87 and 11.76 eV), which corresponds to the important electronic structure modification. In two cases, the calculated cyclic isomer structures are more stables than the α-thiokarbonyloketene (9.9 kcal/mol) and α-thiocarbonylothioketene (11.25 kcal/mol), respectively. Very good agreement between calculated and experimental ionization potentials should be underlined.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded with a Varian Gemini 200 BB VT instrument, operating at 200.11 and 50.33 MHz for ^1H and ^{13}C nuclei, respectively. $CDCl_3$ was used as solvent; chemical shifts are given in ppm (TMS). IR spectra were recorded in KBr with a Thermo-Nicolet Nexus FT-IR spectrophotometer. Melting points (mp) (uncorrected) were determined with a Boëtius apparatus. Thin layer chromatography (TLC) was performed on Merck 5554 aluminium-backed SiO_2 plates; products were visualized by UV light.

Starting Materials

Compound **2** was prepared following the procedure in the literature.[19]

Preparative Flash Vacuum Thermolysis

The flash vacuum thermolysis of was carried out in a 30 × 2.5 cm^2 electrically heated at horizontal quartz tube packed with quartz rings at 1.5 × 10^{-3} Torr. The starting compound **2** (1 mmol) was slowly sublimed from a flask held at 50–60°C into the thermolysis tube preheated to 1000°C. The products were collected in a CO_2-aceton trap. After thermolysis, the system was brought to atmospheric pressure allowing a slow warming up to r.t., and the products were dissolved in $CHCl_3$. The solvent was removed under reduced pressure, and the products were purified chromatographically on prep. TLC (SiO_2 hexane:CH_2Cl_2 4:1).

3H-1,2-Benzodithiole-3-thione (3)

(60 mg, 65%). Yellow solid, mp 95–97°C.

Phenanthro[9,10-c]-1,2-dithiete (4)

(40 mg, 67%). Orange solid, mp 213–215°C.

Both compounds **3** and **4** have identical spectroscopic data with authentical samples.[11]

Flash Vacuum Thermolysis in Tandem with UV-Photoelectron Spectroscopy

The PE spectra were recorded on a home-built, three-part spectrometer equipped with a spherical analyzer (Omicron), main body device (Meca2000), He I radiation source (Focus), and monitored by a microcomputer supplemented with a digital–analog converter. The spectra were calibrated against the auto-ionization of xenon at 12.13 and 13.45 eV, and nitrogen at 15.59 and 16.98 eV. They contain 2000 points and are accurate to 0.1 eV. Sample manipulations were carried out in a thermolysis oven attached directly to the inlet probe; the distance between the oven exit and the ionization head does not exceed 1 cm. Compound **2** was slowly vaporized under low pressure (10^{-7} Torr in the ionization chamber) directly in the oven, and the gaseous thermolysate was continuously analyzed.

Computational Details

The calculations were performed using the Gaussian 98[20] program packages. The 6–311G(d,p) basis set was used for all calculations, since the inclusion of polarization functions is necessary for the accurate description of the neutral molecules containing third-row atom and their cations. Geometry optimizations were carried out at the density functional theory (DFT)[21,22] level of theory with the B3LYP[23–25] functional and confirmed as true minima via frequency analysis. Ionization energies were calculated with ΔSCF-DFT, which means that separate SCF calculations are performed to optimize the orbitals of the ground state and the appropriate ionic state ($IE = E_{cation} - E_{neut.mol.}$). The TDDFT[26,27] approach provides a first principles method for the calculation of excitation energies within a density functional context taking into account the low lying ion calculated by ΔSCF method. The vertical ionization potentials were also calculated at the ab initio level according to the outer valence Green's function (OVGF)[28,29] method. In this case, the effects of electron correlation and reorganization are included beyond the Hartree–Fock approximation, and the self-energy part was expanded up to third order. To compare the ionization potentials resulting from these rigorous methods of calculation, we proceeded also to the currently used estimation of ionization potentials. Indeed, recent works[30–34] have shown that ε_i^{KS} could be linked up to experimental vertical ionization potentials (IP_v) by uniform shift $x = | -\varepsilon_i \text{ (HOMO)} - IP_v^{exp}|$. This approach gives a remarkable agreement with experimental values and is justified by the fact that the first calculated vertical ionization potential lies very close to experimental values. Stowasser and Hoffman[35] have shown that the localization of KS orbitals is very similar to those obtained after HF calculations.

DFT has been shown to predict various molecular properties successfully.[23–25] The advantages of the most employed method of calculations of the first ionization energies (ΔSCF – DFT calculations) have been thoroughly demonstrated.[36–39] On the other hand, the frequently used estimation of IPs by "shifting" of calculated Kohn–Sham energies (a not very rigorous process, but nicely working) has also proved its efficacy. Nevertheless, we have to consider that each theoretical method of approaching ionization potentials is limited by the calculation procedure. In the ΔSCF method, we have to take into account that the single-configuration approximation is not valid when several ions of the same symmetry are near in energy. For TDDFT approach, the configuration interaction processes is based on the quality of the evaluation of the low-lying ion described by ΔSCF method. In the OVGF calculation, the quality of the theoretical results depends on the validity of the Hartree–Fock approximation.

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