The Electronic Structure of 1,3-Dithiole-2-thione and Its Selenium Analogues. Photoelectron Spectra and Polarized Electronic Absorption Spectra[1]

Jens Spanget-Larsen,[2] Rolf Gleiter,*[2] Michio Kobayashi,[2] Edward M. Engler,[3] Paul Shu,[4] and Dwaine O. Cowan[4]

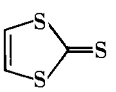
Contribution from the Institut für Organische Chemie der Technischen Hochschule Darmstadt, D-61 Darmstadt, West Germany, IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598, and the Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218. *Received November 1, 1976*

Abstract: The He I photoelectron (PE) spectra of 1,3-dithiole-2-thione (**1**) and its selenium analogues **2–6** have been investigated. The first five bands in the PE spectrum of **1** could be assigned to transitions corresponding to removal of electrons from $5b_2$, $3b_1$, $1a_2$, $2b_1$, $4b_2$, and $7a_1$ orbitals. This assignment is based on a comparison of the PE spectra of **1–6** and on molecular orbital calculations using a ZDO model, and the PPP, EH, and the MINDO/3 methods. The UV polarized absorption spectra of **1**, **3**, **4**, and **6** have been measured by means of the stretched film technique. The measurements were performed in polyethylene sheets at 77 K. Several bands could be assigned to $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions by comparison with model calculations. The results from both types of measurement could be understood in terms of a simple MO diagram.

Recent interest in metallic-like organic charge-transfer complexes between tetrathiafulvalenes (TTF) and tetracyano-*p*-quinodimethane[6] has led to a revival of the interest in 1,3-dithiole-2-thiones, the starting material in the TTF synthesis.[7,8] In connection with our investigations on the electronic structure of TTF and its substitution products by means of photoelectron (PE) spectroscopy and polarized electronic absorption spectroscopy,[9,10] we became interested in the electronic structure of 1,3-dithiole-2-thiones.

The electronic structure of 1,3-dithiole-2-thiones has been discussed several times, mostly in connection with their electronic absorption spectra.[11-13] Recently also the photoelectron spectrum of 1,3-dithiole-2-thione (**1**) has been reported and the first bands have been assigned on the basis of semiempirical calculations.[14,15]

In this paper we try to present a MO picture of these compounds which can explain the electron absorption and photoelectron spectra of **1** and related species. This picture will be based on our investigations of the polarized electronic absorption spectra and PE spectra on **1** and its selenium analogues **2–6** together with some alkyl and benzo derivatives. This series of compounds together with semiempirical calculations allows us to assign the first six bands in the PE spectra of **1–6** and to interpret the first five to six transitions in their electronic absorption spectra. The present study, furthermore, provides new data on organic selenium compounds.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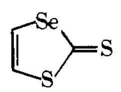
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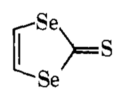
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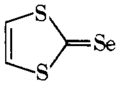
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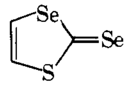
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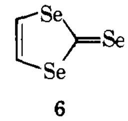
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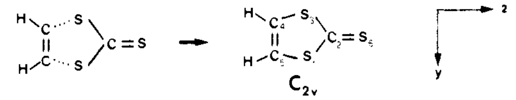
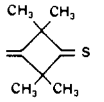
The successive replacement of sulfur by selenium in the above series of compounds can be expected to cause only a minor perturbation of the electronic structure, since the electronegativity of selenium (2.4)[16] is only slightly less than that of sulfur (2.5).[16] This suggests the application of perturbation theoretical arguments in the analysis of the PE and electronic absorption spectra, as a supplement to the standard semiempirical procedures.

Results and Discussion

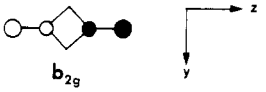
PE Spectra of 1,3-Dithiole-2-thione and Selenium Analogues. The PE spectra of the molecules **1–6** are shown in Figure 1 and the vertical ionization energies $I_{V,J}$ of the first bands are included in Tables I and II. For the interpretation of these spectra we assume the validity of Koopmans' theorem.[17] According to this approximation the orbital energy ϵ_J is set equal to minus the measured vertical ionization potential $I_{V,J}$: $\epsilon_J = -I_{V,J}$.

(a) ZDO Model of 1. In the following we will derive the π MO's of **1** by means of a zero differential overlap (ZDO) model. We will first estimate the basis orbital energies of the trithiocarbonate fragment of **1** and then interact these levels with the π levels of the ethylene fragment to yield the π MO's of **1**. The π orbitals of the trithiocarbonate fragment can be constructed from the 3p π atomic orbitals on the sulfur atoms 1 and 3 and the π and π^* orbitals of the thiocarbonyl group. To determine the energy of the thiocarbonyl π level we have measured the PE spectrum of tetramethylcyclobutane-1,3-dithione (**7**).[21] The observed ionization potentials are given in Table III.





7 (D_{2h})



The ionization potential corresponding to the ejection of an electron out of the b_{2g} orbital is found at 10.75 eV. We assume that the inductive effect of the sulfur atoms at positions 1 and 3 in **1** is about equal to that of a CH_2 group, due to the very similar electronegativities of sulfur and carbon.[16] If we then assume for the inductive effect of the four methyl groups in **7** a value of 0.4 eV,[22] we obtain for the basis orbital energy of the π orbital of the thiocarbonyl group in **1**:[25]

$$\alpha_\pi(\mathrm{C{=}S}) = \alpha_1 = -11.15\ \mathrm{eV}$$

$$\psi_1 \approx 1/\sqrt{2}(p_2 + p_6) \qquad \mathrm{b}_1 \tag{1}$$

The value of the basis orbital energy of the π^* level of the thiocarbonyl group can only be estimated quite approximately.

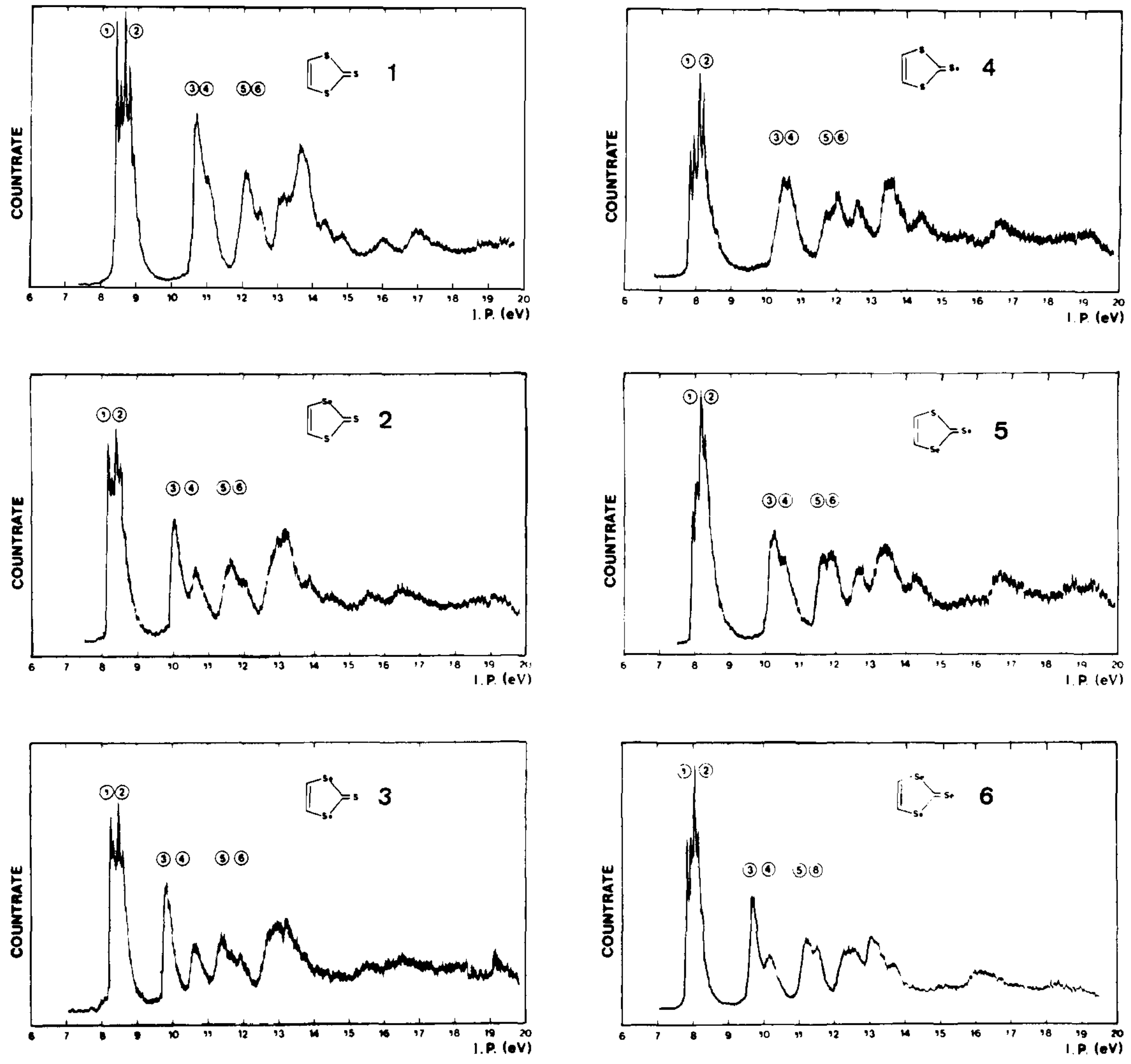


Figure 1. PE spectra of **1**–**6**.

Assuming a $\beta_{C=S}$ value of -2.5 eV[26] we estimate in the ZDO approximation:

$$\alpha_{\pi^*}(C{=}S) = \alpha_2 = -6.1\ \text{eV}$$

$$\psi_2 \approx 1/\sqrt{2}(p_2 - p_6) \qquad b_1 \qquad (2)$$

For the wave functions ψ_1 and ψ_2 of the thiocarbonyl group we assume the same coefficients as those for the π and π^* orbitals of ethylene, due to the small difference in electronegativity between carbon and sulfur.

To obtain the final basis orbitals of the trithiocarbonate fragment, the π and π^* orbitals of the thiocarbonyl group must be interacted with the 3p orbitals on S_1 and S_3. We construct the symmetry adapted combinations ψ_3 and ψ_4:

$$\psi_3 = 1/\sqrt{2}(p_1 + p_3) \qquad b_1 \qquad (3)$$

$$\psi_4 = 1/\sqrt{2}(p_1 - p_3) \qquad a_2 \qquad (4)$$

Both of these wave functions have the energy of a 3p orbital on the ring sulfur atoms:

$$\alpha_3 = \alpha_4 = \alpha_S \qquad (5)$$

We cannot use the value $\alpha_S = -9.4$ eV used previously in the case of TTF,[9] since in **1** we have to correct for the inductive effect of the thiocarbonyl group. We will consider α_S as an empirical parameter to be determined by comparison with experiment. It appears that the value

$$\alpha_S = -10.1\ \text{eV} \qquad (6)$$

leads to a good agreement, as will be shown later.

As in the case of TTF[9] we use for the resonance integral between single-bonded carbon and sulfur:

$$\beta_{C\text{-}S} = -1.8\ \text{eV} \qquad (7)$$

For reasons of symmetry only ψ_3 will interact with the thiocarbonyl orbitals ψ_1 and ψ_2, while ψ_4 will stay unchanged. We thus obtain from eq 1–3 and 5–7 the following secular determinant,

$$\begin{vmatrix} \alpha_1-\epsilon & 0 & \beta_{C\text{-}S} \\ 0 & \alpha-\epsilon & \beta_{C\text{-}S} \\ \beta_{C\text{-}S} & \beta & \alpha_3-\epsilon \end{vmatrix} = \begin{vmatrix} -11.15-\epsilon & 0 & -1.8 \\ 0 & -6.1-\epsilon & -1.8 \\ -1.8 & -1.8 & -10.1-\epsilon \end{vmatrix} = 0 \qquad (8)$$

which yields the following energies and coefficients for the three basis orbitals of b_1 symmetry:

$$\epsilon_1 = -12.69\ \text{eV};\ \Psi_1 = 0.74\psi_1 + 0.17\psi_2 + 0.64\psi_3$$
$$\epsilon_2 = -9.33\ \text{eV};\ \Psi_2 = -0.65\psi_1 + 0.37\psi_2 + 0.66\psi_3 \qquad (9)$$
$$\epsilon_3 = -5.33\ \text{eV};\ \Psi_3 = 0.12\psi_1 + 0.92\psi_2 - 0.39\psi_3$$

Table I. Comparison between Measured Ionization Potentials, $I_{V,J}$, and Calculated Orbital Energies of **1**

Band	$I_{V,J}$[a]	Assignment[27]	$I_{V,J}$[b]	$I_{V,J}$[c]	ZDO	PPP[20]	EH[18]	MINDO/3[19]
1	8.33	$5b_2(n,\sigma)$	8.26 ($3b_1$)	8.3 ($5b_2$)			−12.27 ($5b_2$)	−8.61 ($5b_2$)
2	8.56	$3b_1(\pi)$	8.49 ($5b_2$)	8.5 ($3b_1$)	−8.54 ($3b_1$)	−8.63 ($3b_1$)	−11.94 ($3b_1$)	−8.81 ($3b_1$)
3	10.60	$1a_2(\pi)$	10.48 ($1a_2$)	10.5 ($1a_2$)	−10.64 ($1a_2$)	−10.99 ($1a_2$)	−13.28 ($1a_2$)	−10.26 ($1a_2$)
4	10.90	$2b_1(\pi)$	10.88 ($2b_1$)	10.8	−10.83 ($2b_1$)	−11.00 ($2b_1$)	−13.85 ($2b_1$)	−11.03 ($2b_1$)
5	12.00	$4b_2(\sigma)$	11.87 ($4b_2$)	11.9			−13.12 ($4b_2$)	−9.60 ($4b_2$)
6	12.37	$7a_1(\sigma)$	12.37 ($7a_1$)	12.3			−13.61 ($7a_1$)	−10.32 ($7a_1$)

[a] This work. [b] Reference 15. [c] Reference 14.

Table II. Vertical Ionization Potentials, $I_{V,J}$, of **2–6** (all values in eV)

	2						**3**					
Band	1	2	3	4	5	6	1	2	3	4	5	6
$I_{V,J}$	8.28	8.52	10.17	10.75	11.72	12.12	8.24	8.47	9.80	10.60	11.37	11.89
Assignment	$b_2(\sigma)$	$b_1(\pi)$	$a_2(\pi)$	$b_1(\pi)$	$b_2(\sigma)$	$a_1(\sigma)$	$b_2(\sigma)$	$b_1(\pi)$	$a_2(\pi)$	$b_1(\pi)$	$b_2(\sigma)$	$a_1(\sigma)$
	4						**5**					
Band	1	2	3	4	5	6	1	2	3	4	5	6
$I_{V,J}$	7.81	8.06	10.54	10.54	11.66	11.98	7.83	8.08	10.01	10.40	11.51	11.77
Assignment	$b_2(\sigma)$	$b_1(\pi)$	$a_2(\pi)$	$b_1(\pi)$	$b_2(\sigma)$	$a_1(\sigma)$	$b_2(\sigma)$	$b_1(\pi)$	$a_2(\pi)$	$b_1(\pi)$	$b_2(\sigma)$	$a_1(\sigma)$
	6											
Band	1	2	3	4	5	6						
$I_{V,J}$	7.85	8.08	9.71	10.18	11.26	11.53						
Assignment	$b_2(\sigma)$	$b_1(\pi)$	$a_2(\pi)$	$b_1(\pi)$	$b_2(\sigma)$	$a_1(\sigma)$						

Table III. Comparison between Measured Ionization Potentials $I_{V,J}$ and Calculated Orbital Energies of **7**

Band	$I_{V,J}$	Assignment	MINDO/3[19]
1	8.31	b_{3g}	−8.92
2	8.76	b_{1u}	−9.07
3	10.05	b_{1u}	−9.17
4	10.35	b_{3u}	−10.08
5	10.70	b_{2g}	−10.64

According to eq 4–6, we have for the basis orbital of a_2 symmetry

$$\epsilon_4 = \alpha_S = -10.1 \text{ eV};\ \Psi_4 = \psi_4 \tag{10}$$

The interaction between the π orbitals of the thiocarbonyl group and the 3p orbitals on S_1 and S_3 to yield the basis orbitals of the trithiocarbonate fragment of **1** is illustrated by the diagram in Figure 2.

We are now ready to interact the four orbitals of the trithiocarbonate fragment with the two basis orbitals of the ethylene fragment:

$$\epsilon_5 = \alpha_\pi(\mathrm{C{=}C}) = -10.15 \text{ eV}$$

$$\Psi_5 = 1/\sqrt{2}(p_4 + p_5) \qquad b_1 \tag{11}$$

$$\epsilon_6 = \alpha_{\pi^*}(\mathrm{C{=}C}) = -4.5 \text{ eV}$$

$$\Psi_6 = 1/\sqrt{2}(p_4 - p_5) \qquad a_2 \tag{12}$$

For the basis orbital energies of the ethylene π and π^* levels we have taken the same values as employed in the case of TTF.[9] The two orbitals of a_2 symmetry, Ψ_4 and Ψ_6, will only interact with each other, and we obtain from eq 4, 7, 10, and 12 the following secular determinant:

$$\begin{vmatrix} \epsilon_4 - \epsilon & \beta_{\mathrm{C\text{-}S}} \\ \beta_{\mathrm{C\text{-}S}} & \epsilon_6 - \epsilon \end{vmatrix} = \begin{vmatrix} \alpha_S - \epsilon & -1.8 \\ -1.8 & -4.5 - \epsilon \end{vmatrix} = 0 \tag{13}$$

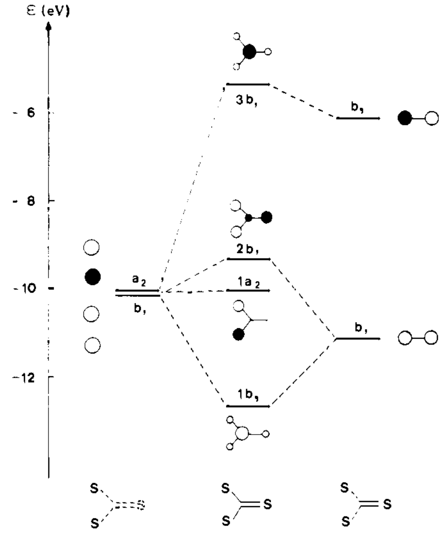


Figure 2. Interaction diagram between the π orbitals of the thiocarbonyl group and two 3p orbitals to yield the basis orbitals of the trithiocarbonate fragment.

The lower eigenvalue obtained by solution of eq 13 must correspond to the level $1a_2$ of **1**.[27] We assign band 3 in the PE spectrum of **1** (10.6 eV) to the ejection of an electron out of this level. This assignment is in line with the results of Wittel et al.,[14] who compared the first three PE bands of five trithiocarbonates. The assignment is furthermore confirmed by the observation that the position of band 3 is only slightly affected by a change of the heteroatom at position 6 (compare the PE spectra of **1** and **4** and of **3** and **6** (Figures 1 and 4); this is expected for a level of a_2 symmetry with a nodal plane through the 2- and 6-positions. Adopting this assignment of band 3 of **1** we derive from eq 13 the value $\alpha_S = -10.1$ eV given in eq 6, and obtain the eigenvalues −10.64 and −3.95 eV for the $1a_2$ and $2a_2$ levels of **1**. Equations 1–3, 7, 9, and 11 yield for the four

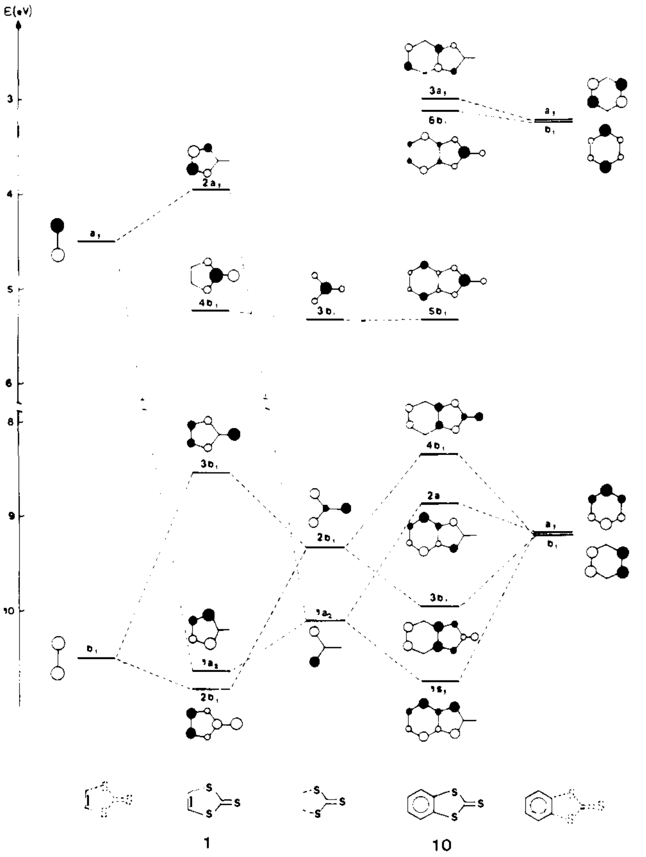


Figure 3. Interaction diagram between the basis orbitals of a trithiocarbonate unit with those of ethylene (left) and benzene (right) to yield the highest occupied and lowest unoccupied MO's of **1** and **11**.

orbitals of b_1 symmetry, Ψ_1, Ψ_2, Ψ_3, and Ψ_5, the following secular problem:

$$\begin{vmatrix} \epsilon_1-\epsilon & 0 & 0 & 0.64\beta_{\text{C-S}} \\ 0 & \epsilon_2-\epsilon & 0 & 0.66\beta_{\text{C-S}} \\ 0 & 0 & \epsilon_3-\epsilon & 0.39\beta_{\text{C-S}} \\ 0.64\beta_{\text{C-S}} & 0.66\beta_{\text{C-S}} & 0.39\beta_{\text{C-S}} & \epsilon_5-\epsilon \end{vmatrix} = \begin{vmatrix} -12.69-\epsilon & 0 & 0 & -1.15 \\ 0 & -9.33-\epsilon & 0 & -1.19 \\ 0 & 0 & -5.33-\epsilon & -0.70 \\ -1.15 & -1.19 & -0.70 & -10.5-\epsilon \end{vmatrix} = 0 \quad (14)$$

Solution of eq 14 gives the eigenvalues −13.26, −10.83, −8.54, and −5.23 eV for the orbitals $1b_1$–$4b_1$ of **1**.

The results are illustrated in the interaction diagram in Figure 3 (left half), where the energies and shape of the most important orbitals are given schematically.

The energies obtained by the ZDO procedure compare very well with experiment (see Table I). It appears reasonable to assign bands 2, 3, and 4 in the PE spectrum of **1** (Figure 1) to ejection of an electron out of the π levels $3b_1$, $1a_2$, and $2b_1$,[27] respectively. The assignment of band 3 to the $1a_2$ level has already been discussed above. Further support for the assignments can be derived from a consideration of the relative shifts of the bands 3 and 4 in the PE spectra of the series **1, 2,** and **3,** and the series **4, 5,** and **6** (see Figure 4).

Application of simple first-order perturbation theory to the orbitals $1a_2$ and $2b_1$ (see Figure 3) predicts that the energy of the $2b_1$ level is much less sensitive to a change of the heteroatom in position 1 or 3 than the energy of the $1a_2$ level. This is consistent with the observed shifts of bands 3 and 4 in our assignment.

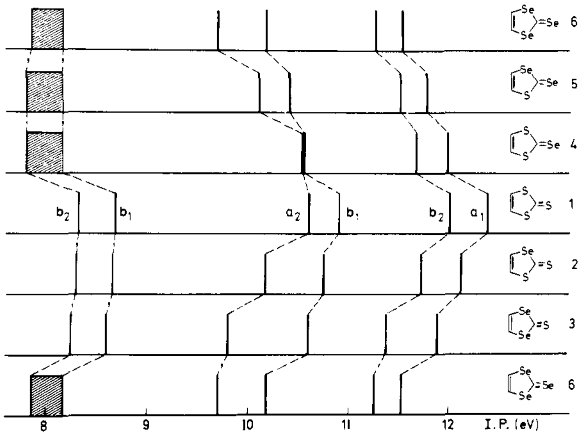
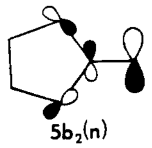


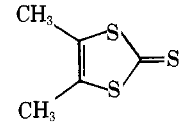
Figure 4. Correlation diagram between the first six bands of the PE spectra of **1–6**.

(b) All-Valence-Electron Calculations on 1. The results of extended Hückel (EH)[18] and MINDO/3[19] calculations on **1** are included in Table I. The ordering of the calculated π levels supports the assignments discussed above. Both methods predict furthermore a high-lying σ level close to the highest occupied π level. This is the "lone pair" level of the thiocarbonyl group.



$5b_2(n)$

This result indicates that the series of peaks in the region 8–9 eV in the PE spectra of **1–6** may be due to two independent ionization processes. This assumption is supported by other criteria: a comparison of the half-height width of the first composite band and the half-height width of the following bands 3 and 4, each of which can be assigned to a single ionization process, renders probable that the ionization in the region 8–9 eV is due to two strongly overlapping transitions. To obtain further information we have measured the PE spectra of the alkyl derivatives **8** and **9**. The PE spectra of **8** and **9** are shown in Figure 5, and the relevant data are given in Tables IV and V.



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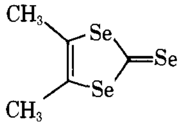


9

The spectrum of **8** clearly shows two separate bands, 1 and 2, between 8 and 9 eV. Moreover, the close correspondence between the vibrational fine structures in the spectra of **1** and **8** makes it possible to determine the positions of bands 1 and 2 in the spectrum of **1** unambigously. Bands 1 and 2 in the spectra of the thiocarbonyl compounds **2** and **3** are very similar to the corresponding bands in **1** and can be identified by analogy. In the spectra of the selenocarbonyl compounds **4, 5,** and **6** it is not possible to determine with absolute safety the positions of the vertical ionization potentials of bands 1 and 2, and the corresponding energies given in Table II are tentative.

The assignment of the first two bands to the $5b_2(n)$ and $4b_1(\pi)$ levels is consistent with the insensitivity to heteroatom change in the ring for the series **1–3** and **4–6** and the large shift

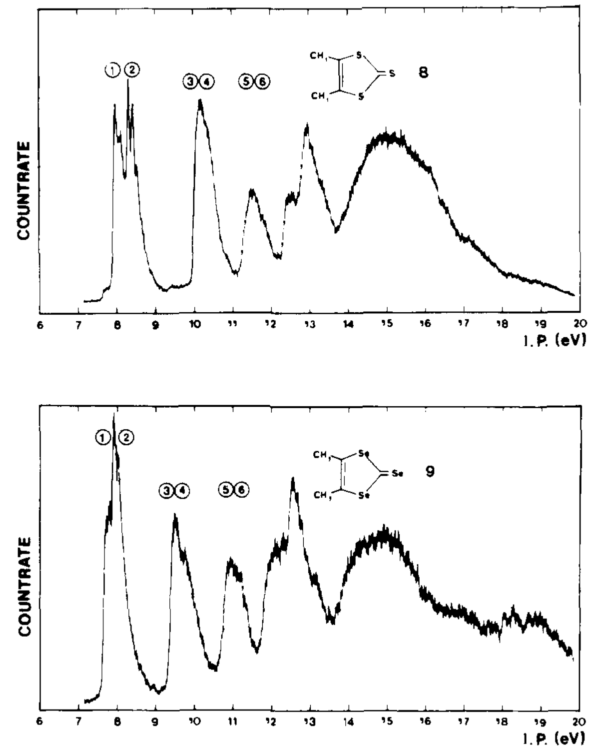


Figure 5. PE spectra of 8 and 9.

Table IV. Comparison between Vertical Ionization Potentials, $I_{V,J}$, and Orbital Energies, ϵ_J, for 8[a]

Band	$I_{V,J}$	Assignment	MINDO/3[19]	ΔI	$\Delta\lvert\epsilon\rvert$
1	7.96	$b_2(\sigma)$	8.41	−0.37	−0.20
2	8.29	$b_1(\pi)$	8.66	−0.27	−0.15
3	10.15	$a_2(\pi)$	10.04	−0.45	−0.22
4	10.33	$b_1(\pi)$	10.45	−0.75	−0.58
5	11.50	$b_2(\sigma)$	9.21	−0.21	−0.39
6		$a_1(\sigma)$	9.90	−0.87	−0.42

[a] All values in electron volts. For the meaning of ΔI and $\Delta\epsilon$ see text.

Table V. Vertical Ionization Potentials, $I_{V,J}$, of 9 (all values in eV)

Band	1	2	3	4	5	6
$I_{V,J}$	7.68	7.90	9.46	9.73	10.90	11.17
Assignment	$b_2(\sigma)$	$b_1(\pi)$	$a_2(\pi)$	$b_1(\pi)$	$b_2(\sigma)$	$a_1(\pi)$

on change of the heteroatom at the 6-position: both orbitals are predominantly localized on the 6-positions. Our preliminary assignment of the ordering of these levels is based on a comparison of the PE spectra of **1** and **8**. As indicated in Table IV, we observe a larger shift of band 1 than of band 2 on methyl substitution; the measured ΔI values are −0.37 and −0.27 eV, respectively. MINDO/3 calculations predict a larger destabilization of the $5b_2(n)$ level than of the $4b_1(\pi)$ level; the calculated $\Delta|\epsilon|$ values are −0.20 and −0.15 eV, respectively (see Table IV). These results suggest an assignment of band 1 to the $b_2(n)$ level and band 2 to the $b_1(\pi)$ level.

Apart from the $b_2(n)$ level the EH and MINDO/3 methods predict two relatively high-lying σ levels $4b_2$ and $7a_1$ with a spacing of 0.5–0.7 eV (see Table I). We put no emphasis on the circumstance that the two methods predict an intermingling of the $1a_2$ and $2b_1$ π levels and the $4b_2$ and $7a_1$ σ levels, but ascribe this to the well-known tendency of many semiempirical all-valence-electron methods to place the σ orbitals too high in energy relative to the π orbitals. The $b_2(\sigma)$ orbital of **1** is similar in structure to the $9b_{1g}$ orbital of TTF[9] (see below).

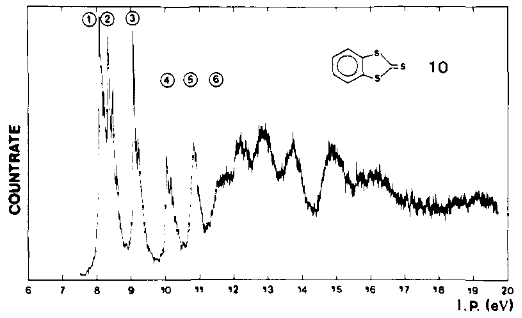
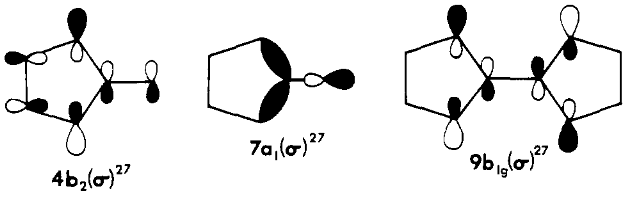


Figure 6. PE spectrum of 10.

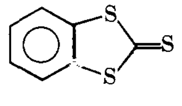


This level was predicted a rather low ionization potential (MINDO/3: 8.53 eV) compared with experiment (10.56 eV).[9] We thus tend to assign bands 5 and 6 at 12.0 and 12.4 eV in the PE spectrum of **1** (see Figure 1) to the second and third highest σ levels $4b_2$ and $7a_1$. It is unlikely that ionization out of the lowest lying π level $1b_1$ occurs in this region, since all the theoretical models applied predict a gap of 2–3 eV between the $1b_1(\pi)$ and $2b_1(\pi)$ levels; according to our assignment of band 4 at 10.9 eV to the $2b_1(\pi)$ level, this places the ionization due to the $1b_1(\pi)$ level above 13 eV. The ZDO model predicts a value of 13.26 eV.

The assignment of the ordering of the $4b_2(\sigma)$ and $7a_1(\sigma)$ levels is less straightforward. Bands 5 and 6 show in most cases very similar shifts in the PE spectra of the series **1–6** (see Figures 1 and 2). Band 5 is shifted more toward lower energies on methyl substitution than band 6, but the MINDO/3 method predicts almost identical shifts of the two levels (see Table IV). An additional complication is the circumstance that the $7a_1(\sigma)$ orbitals obtained by the EH method and the MINDO/3 method have very different shapes. We tentatively assign band 5 to the $4b_2(\sigma)$ level and band 6 to the $7a_1(\sigma)$ level, in accordance with the ordering predicted by the calculations, but a definite assignment must await further investigations.

Our assignment for the first three bands of **1** is supported by Wittel et al.,[14] who based their interpretation on a CNDO/2 calculation and the comparison with oxygen analogues of **1**. Due to the strong change in electronegativity in replacing S (2.5) by O (3.5),[16] their assignment of bands at higher energy is more uncertain. Our assignment furthermore corroborates the one given for **1** by Guimon et al.,[15] who base it only on CNDO/S calculations.

PE Spectrum of Benz-1,3-dithiole-2-thione. The PE spectrum of benz-1,3-dithiole-2-thione (**10**) is shown in Figure 6. The measured vertical ionization potentials $I_{V,J}$ and the results of semiempirical calculations are listed in Table VI. The π MO's of **10** were derived within the ZDO model in the following way. As basis orbitals for the trithiocarbonyl fragment were taken the same as those given in eq 9 and 10. The pa-



10

Table VI. Comparison between Vertical Ionization Potentials, $I_{V,J}$, and Orbital Energies, ϵ_J, of **10** (all values in eV)

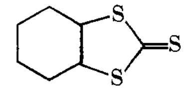
Band	$I_{V,J}$[a]	Assignment[a]	$I_{V,J}$[b]	ZDO	PPP[20]	MINDO/3[19] [c]
1	8.12	$5b_2(\sigma,n)$	8.14 ($4b_1$)			−8.54 ($5b_2$)
2	8.36	$4b_1(\pi)$	8.39 ($5b_2$)	−8.35 ($4b_1$)	−8.82 ($4b_1$)	−8.63 ($4b_1$)
3	9.09	$2a_2(\pi)$	9.12 ($2a_1$)	−8.87 ($2a_2$)	−10.04 ($2a_2$)	−9.21 ($2a_2$)
4	10.04	$3b_1(\pi)$	10.09 ($3b_1$)	−9.96 ($3b_1$)	−10.88 ($3b_1$)	−10.21 ($3b_1$)
5	10.84	$1a_2(\pi)$	10.87 ($1a_2$)	−10.76 ($1a_2$)	−11.67 ($1a_2$)	−10.72 ($1a_2$)
6	11.76	$4b_2(\sigma)$	11.76 ($4b_2$)	−11.91 ($2b_1$)	−12.66 ($2b_1$)	

[a] This work. [b] Reference 15. [c] Some σ levels are placed between the π levels.

Table VII. Measured and Calculated Electronic Absorption Spectra of **11**, **1**, and **10**[h]

		Obsd[a]					Calcd (PPP-CI)[20]			
Compd	Band	ν(0–0)	$\nu(\epsilon_{max})$	ν(vib)	Polarization	log ϵ_{max}[b]	Symmetry	ν	Predominant configurations	f
11	A[b]	2.08	2.16	0.04		1.8				
	B		3.15		z	4.1	$^1A_1$	3.42	$3b_1 \leftarrow 2b_1$ (95%)	0.42
	C		3.40		y	(4.0)	$^1B_2$	3.77	$3b_1 \leftarrow 1a_2$ (100%)	0.19
	D[c]		(3.85)			(2.9)				
	E[b]		4.98			3.9				
1	A[b]	(2.13)	2.32	0.05		1.9				
	B	2.68	2.74	0.06	z	4.2	$^1A_1$	3.11	$4b_1 \leftarrow 3b_1$ (100%)	0.42
	C		3.4		y	3.0	$^1B_2$	3.46	$2a_2 \leftarrow 3b_1$ (92%)	0.07
	D[d]		3.7		d	3.2				
	E		4.32		y	3.9	$^1B_2$	4.52	$4b_1 \leftarrow 1a_2$ (86%)	0.14
	F[e]		(4.36)		z		$^1A_1$	4.66	$2a_2 \leftarrow 1a_2$ (62%), $4b_1 \leftarrow 2b_1$ (38%)	0.16
10	A[b]		2.27			1.8				
	B	2.72	2.78	0.06	z	4.3	^1A	3.04	$5b_1 \leftarrow 4b_1$ (89%)	0.58
	C	3.31	3.42[f]	0.11	z	3.2	$^1A_1$	3.50	$6b_1 \leftarrow 4b_1$ (60%), $3a_2 \leftarrow 2a_2$ (28%)	0.12
	D	3.37	3.45	0.08	y	3.6	$^1B_2$	3.42	$3a_2 \leftarrow 4b_1$ (68%), $5b_1 \leftarrow 2a_2$ (28%)	0.003
	E[g]	3.75	3.75	0.09	y	3.7	$^1B_2$	3.99	$5b_1 \leftarrow 2a_2$ (55%), $3a_2 \leftarrow 4b_1$ (29%)	0.26
	F	4.14	4.14	0.11	z	4.2	$^1A_1$	4.08	$3a_2 \leftarrow 2a_2$ (42%), $6b_1 \leftarrow 4b_1$ (32%)	0.22
	G		~4.4		y		$^1B_2$	4.49	$6b_1 \leftarrow 2a_1$ (86%), $5b_1 \leftarrow 2a_1$ (8%)	0.01
	H		4.44		z	4.2	$^1A_1$	4.80	$5b_1 \leftarrow 3b_1$ (41%), $3a_2 \leftarrow 1a_2$ (26%), $3a_2 \leftarrow 2a_2$ (22%)	0.31

[a] Unless otherwise noted, data measured in stretched polyethylene film at 77 K. [b] Measured in cyclohexane solution at room temperature. [c] Shoulder seen in solution spectrum; further structure is present at 4.1 μm^{-1}. [d] This band shows strongly mixed polarization. [e] The appearance of this band is sensitive to the choice of reduction factor. [f] This peak and the following at 3.53 μm^{-1} (see Figure 7) are tentatively assigned to vibrational components of band C. [g] Band E overlaps a z-polarized peak at 3.9 μm^{-1} (see Figure 7). [h] Wavenumbers are given in μm^{-1} = 10^4 cm^{-1}. C_{2v} symmetry is assumed in all cases. For details of the PPP-CI calculation see the text.



11

rameters for the benzene fragment and the adjoining bonds were taken as those employed in the case of dibenzotetrathiafulvalene.[10] The resulting interaction diagram is given in the right half of Figure 3, and the energies of the five highest occupied π orbitals are included in Table VI. It is seen that an excellent agreement with experiment is obtained. The results suggest the assignment of bands 2, 3, 4, and 5 to the π levels $4b_1$, $2a_2$, $3b_1$, and $1a_2$, respectively. This ordering of the π levels is confirmed by the PPP and MINDO/3 results listed in Table VI. In analogy with the assignment of the first band in the PE spectrum of **1** we assign band 1 in the spectrum of **10** to the "lone pair" orbital of the thiocarbonyl group. These assignments are consistent with the MINDO/3 results in Tables I and VI, and are furthermore in line with the results obtained by Guimon et al.[15] Band 6 can be assigned to the fifth π level $2b_1$, probably overlapping one or more σ levels.

Polarized Absorption Spectra of Some Trithiocarbonate Derivatives. The trithiocarbonate group has long been known as a strongly absorbing chromophore.[13,29,30] To study the effect of conjugation on the characteristic spectrum of the trithiocarbonate group we have compared the polarization spectrum of the alkylated tetrathiocarbonate **11** with the spectra of **1** and **10.** The dichroic absorption curves of the three compounds in the region 2.5–4.5 μm^{-1} are shown in Figure 7. The spectra were measured in stretched polyethylene sheets at 77 K according to the procedure developed by Eggers et al.[31] The absorption in the visible region is too weak to be conveniently studied by the stretched-sheet technique. The measured spectroscopic data are listed in Table VII together with the results of a standard PPP-CI calculation.

The first absorption band of **11** is a weak band A at 2.16 μm^{-1} (cyclohexane), responsible for the yellow color of the compound. The band shows a large blue shift when changing to a more polar solvent, and can safely be assigned to a symmetry forbidden n-π^* transition.[13] The intense band in the UV region with a maximum at 3.15 μm^{-1} is composed of two strongly overlapping transitions B and C.[32] The first transition is polarized parallel and the second perpendicular to the orientation axis[31] (see Figure 7). These transitions can be assigned to π-π^* transitions to excited states of $^1A_1$ and $^1B_2$ symmetry, described by the configurations $3b_1 \leftarrow 2b_1$ and $3b_1 \leftarrow 1a_2$, respectively (see Table VII and Figure 2). The intense absorption band shows a much weaker shoulder starting at 3.8 μm^{-1}. The polarization of this absorption is difficult to estimate due to the overlap with the tails of the much stronger

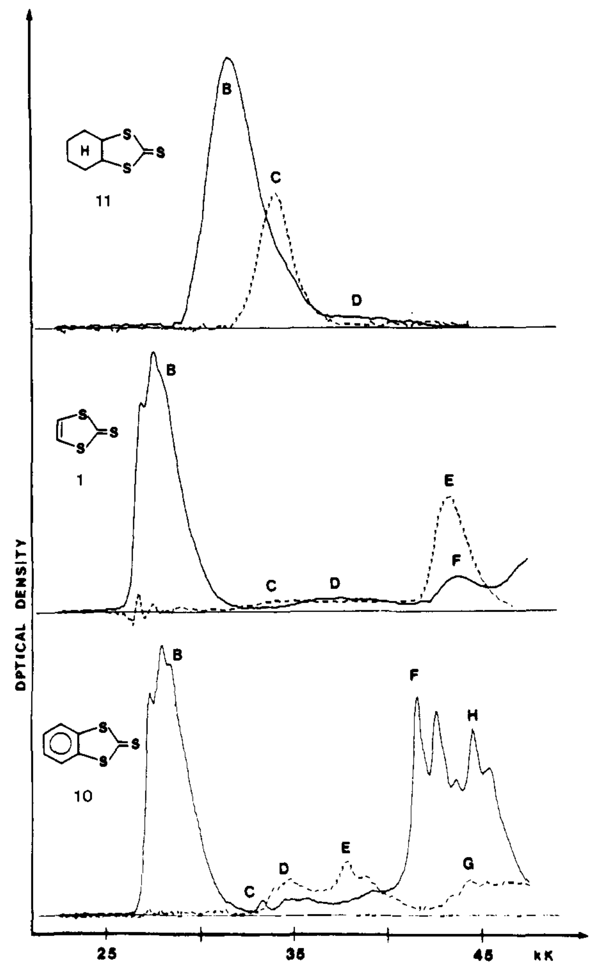


Figure 7. Polarized absorption curves at 77 K of **11**, **1**, and **10** in stretched polyethylene film. The full lines indicate absorption polarized parallel and the dashed lines absorption polarized perpendicular to the orientation axis. The curves were obtained from the measured dichroic spectra by means of the following reduction factors:[31] **11**, $d_{\parallel}^{0}$. = 0.6 and $d_{\perp}^{0} = 0.34$; **1**, $d_{\parallel}^{0} = 0.8$, $d_{\perp}^{0} = 0.61$; **10**, $d_{\parallel}^{0} = 0.60$, $d_{\perp}^{0} = 0.29$. The $d_{\parallel}^{0}$ value in the case of **1** is not well defined due to the apparent absence of a strong purely y-polarized peak, and the details of the curves for **11** may be influenced by the deviation from the assumed C_{2v} symmetry. (1 kK = 0.1 μm^{-1}.)

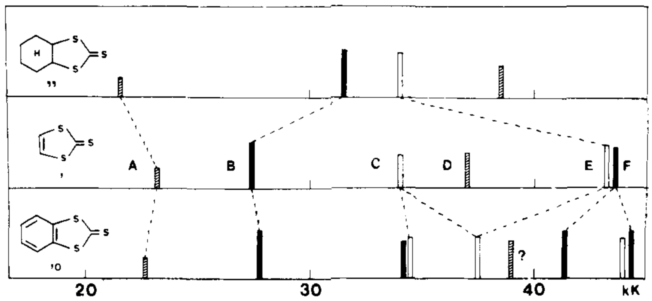


Figure 8. Graphic representation of the observed transitions in the spectra of **11**, **1**, and **10**, see Figure 7 and Table VII. Solid bars represent z-polarized and open bars y-polarized transitions. The weak n–π^* transitions in the visible region and possibly non π–π^* transitions in the UV region are indicated by shaded bars. The length of the bars is proportional to log ϵ_{max} (Table VII). (1 kK = 0.1 μm^{-1}.)

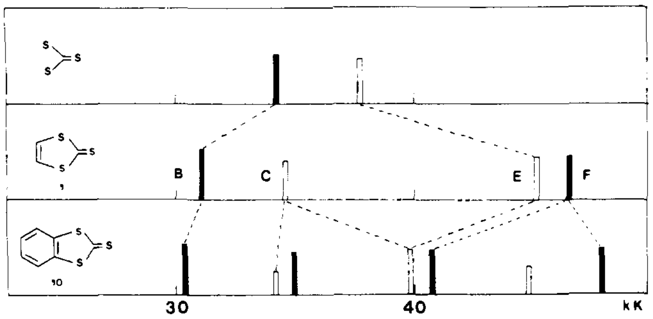


Figure 9. Graphic representation of the π–π^* transitions predicted for **11**, **1**, and **10** by means of a PPP–CI calculation, see Table VII. The symbolism is similar to Figure 8; the length of the bars is proportional to 4.5 + log$f$. (1 kK = 0.1 μm^{-1}.)

transitions. It is unlikely that it can be assigned to a π–π^* transition, since the PPP calculation predicts a gap of more than 3 eV between the second (C) and the third π–π^* transition. It thus possibly involves n or σ levels.

Cyclic conjugation of the trithiocarbonate group has a striking effect on the UV spectrum,[13,30] as evident from a comparison of the spectra of **11** and **1** in Figure 7. In the spectrum of **1** the two principal maxima (B and E) are split by more than 1.5 μm^{-1}, compared with only 0.25 μm^{-1} in the spectrum of **11**. The shifts are illustrated schematically in the diagram in Figure 8. The results of the PPP-CI calculation are visualized in Figure 9, and it is apparent that the shifts of the main bands are well predicted by the calculation. Band B and band E in the spectrum of **1** can be assigned to transitions to states well described by the configurations $4b_1 \leftarrow 3b_1$ and $4b_1 \leftarrow 1a_2$, respectively. The large split of the bands can thus be rationalized by the large separation of the two highest occupied π levels in **1** ($3b_1$ and $1a_2$) relative to the small separation of the corresponding levels in **11**. This in turn is due to the circumstance that the b_1 level in question is destabilized by interaction with the lower lying π orbital of the ethylene fragment, while the a_2 level is stabilized by interaction with the ethylene π^* orbital, as shown by the interaction diagram in Figure 3. The lowest unoccupied π level in **1**, $4b_1$, is slightly destabilized (~0.1 μm^{-1}) relative to the corresponding level in **11**; this is consistent with the observed blue shift of the visible n–π^* band ($4b_1 \leftarrow 5b_2$).

Below the y-polarized band E in the spectrum of **1** the reduced spectrum shows evidence for a "hidden" z-polarized peak F. The appearance of this peak is quite sensitive to the choice of the reduction factor $d_{\parallel}^{0}$, which is not well determined in the case of **1**. Also, possible baseline errors must be considered in this relatively difficult region. The PPP calculation does predict a z-polarized transition at 4.66 μm^{-1}, close to the y-polarized one predicted at 4.52 μm^{-1}. It is thus tempting to assign band F to a separate electronic transition to a state involving the configurations $2a_2 \leftarrow 1a_2$ and $4b_1 \leftarrow 2b_1$, see Table VII.

Between the two main bands in the spectrum of **1** two bands of medium intensity are observed, C and D. The band C is polarized predominantly perpendicular to the orientation axis, while band D shows strongly mixed polarization, see Figure 7. This polarization of bands C and D was confirmed by measuring the stretched-film spectrum of **8**, the dimethyl derivative of **1**. We thus assign band C at 3.4 μm^{-1} to the perpendicularly-polarized transition predicted at 3.46 μm^{-1}, predominantly $2a_2 \leftarrow 3b_1$ (see Table VII). Band D can probably be assigned to either a symmetry-forbidden transition to a state of A_2 symmetry, or a transition polarized perpendicular to the molecular yz plane to a state of B_1 symmetry. According to the orientation model by Eggers et al.,[31] an x-polarized transition will tend to appear with negative absorption in the A_z' curve in the standard reduction procedure. The purely out-of-plane 0–0 component of such a transition is likely to be weak, however, and probably only higher vibronic components which may couple with the neighboring in-plane transitions are observed. This may account for the positive contribution to both A_y' curve and A_z' curve for band D in the spectra of

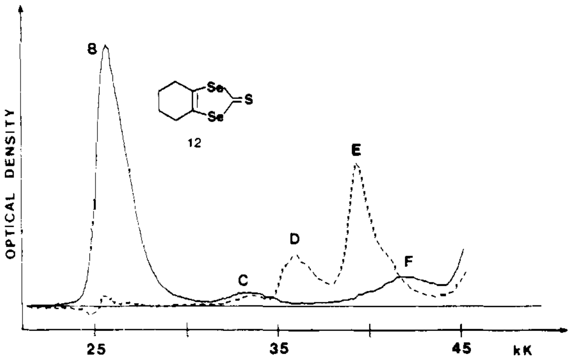


Figure 10. Polarized absorption curves at 77 K of **12** in stretched polyethylene. The full and the dashed curve indicate absorption polarized parallel and perpendicular to the orientation axis, respectively. The reduction factors[31] were $d_{\parallel}{}^0 = 0.91$ and $d_{\perp}{}^0 = 0.41$. The polarization spectrum of the selenone analogue **13** is very similar to the spectrum of **12**, the sequence, polarization, and relative intensity of the bands being the same. (1 kK = 0.1 μm^{-1}.)

1 and **8** (compare band C in Figure 10). The band shows a considerable blue shift when changing to a more polar solvent, which suggests the assignment of n-π^* (such as $2a_2 \leftarrow 5b_2$) or n-σ^* transitions;[13] see also the next section on the selena derivatives of **1**.

The spectrum of the benzo derivative **10** is shown at the bottom of Figure 7. As anticipated from the large extension of the conjugated system the spectrum of **10** is much more complicated than the spectrum of **1**. The spectra show obvious similarities only in the region below 3.2 μm^{-1}. The first intense band B in the spectrum of **10** with a maximum at 2.78 μm^{-1} is thus similar to the corresponding transition in the spectrum of **1**, and can be assigned to transition to a state well described by the configuration $5b_1 \leftarrow 4b_1$. The band shows an interesting blue shift in going from **1** to **10**,[13] which is not reproduced by the PPP-CI calculation, see Figures 8 and 9. The calculated transition energy is sensitive to variation of the β parameter for the bonds between the sulfur atoms and the benzo group, since the $5b_1$ orbital is bonding and the $4b_1$ orbital is antibonding in these positions, see Figure 3. Application of ordinary first-order perturbation theory[33] yields

$$\Delta E(5b_1 \leftarrow 4b_1) = 0.41\Delta\beta_{\text{Ar-S}}$$

This means that a reduction of the numerical value of β for these bonds by 0.3 eV is sufficient to reproduce the observed blue shift of this band relative to the spectrum of **1**. A reduction in this order of magnitude is consistent with the calculated decrease of bond order: 0.32 in **10** compared with 0.37 for the corresponding bonds in **1**. The somewhat unusual blue shift on addition of a fused benzene ring[34] can thus be explained by the assumption that the shift caused by the decrease of double-bond character of the adjoining C-S bonds more than compensates for the tendency toward a red shift on extension of the conjugated system.[34]

The first intense band in the spectrum of **10** is followed by a z-polarized peak C of medium intensity at 3.31 μm^{-1}, with additional somewhat broader peaks at 3.42 and 3.53 μm^{-1}. A further apparently z-polarized peak is observed at 3.90 μm^{-1}. The region above 4.0 μm^{-1} is dominated by an intense band with z-polarized peaks starting at 4.14 μm^{-1}. The broadness of the band and the variation of the intensity of the peaks indicate that the band contains at least two separate electronic transitions, F and H. Two strong bands in this region were also observed in the spectra of related compounds with o-dithiophenyl units.[35] Apart from the first intense transition the PPP-CI calculation predicts z-polarized transitions at 3.50, 4.08, and 4.80 μm^{-1} with oscillator strengths 0.12, 0.22, and 0.31, respectively. We assign bands C, F, and H to these transitions, see Table VII. The z-polarized peaks at 3.42 and 3.53 μm^{-1} can probably be assigned to vibrational components of C, although overlap with the more intense y-polarized band D complicates the assignment. A similar situation applies to the peak at 3.90 μm^{-1}, which may be a nontotally symmetric component of band E, gaining intensity by vibronic coupling between E and the strong bands F and H. It should also be remembered that a band similar to the band D in the spectrum of **1** can be expected in this region.

The spectrum of **10** shows three main absorption bands polarized perpendicularly to the orientation axis with maxima at 3.45, 3.75, and 4.4–4.6 μm^{-1}. We assign these bands, D, E, and G, to the transitions predicted at 3.42, 3.99, and 4.49 μm^{-1}, respectively, see Table VII. The detailed structure of the band G is difficult to determine, because of overlap with the much more intense bands F and H. None of the y-polarized bands D, E, and G (as well as none of the z-polarized bands above 3.2 μm^{-1}) can be compared with bands in the spectrum of **1**. This is due primarily to the extensive configuration interaction in the case of **10**. The correlation lines drawn in Figures 8 and 9 are only tentative. The diagrams illustrate that a number of significant trends are well reproduced by the PPP calculation.

Polarized Absorption Spectra of the Symmetric Selena Derivatives of 1. The results of stretched-sheet measurements on the symmetric selena derivatives of **1**, i.e., **3**, **4**, and **6**, are listed in Table VIII. The measurements were complicated by the reduced solubility of these compounds in polyethylene and by a tendency toward reduced degree of orientation of the molecules in the stretched sheet when sulfur is replaced by selenium (the distribution of the all-selena derivative **6** is thus close to isotropic, see Table IX). The quality of the spectra, however, is in all cases sufficient to determine the polarization of the two main absorption bands B and E as parallel and perpendicular to the orientation axis, respectively (see Table VIII).

The shifts of the main bands can be reproduced by simple perturbation theory.[33] The substitution of sulfur by selenium can be expected to affect the α_x as well as the β_{cx} parameters. Transition to a state described by the configuration r $\leftarrow$ s is thus shifted according to the expression:

$$\Delta E(\mathrm{r} \leftarrow \mathrm{s}) = \sum_{\mu} (c_{\mathrm{r}\mu}{}^2 - c_{\mathrm{s}\mu}{}^2)\Delta\alpha_{\mu} + 2 \sum_{\mu-\nu} (c_{\mathrm{r}\mu}c_{\mathrm{r}\nu} - c_{\mathrm{s}\mu}c_{\mathrm{s}\nu})\Delta\beta_{\mu\nu}$$

Inserting the molecular orbital coefficients obtained by the standard PPP calculation on **1** we obtain for substitution in the 6-position:

$$\Delta E(4b_1 \leftarrow 3b_1) = -0.30\Delta\alpha - 0.82\Delta\beta$$

$$\Delta E(4b_1 \leftarrow 1a_2) = 0.23\Delta\alpha - 0.71\Delta\beta$$

and for substitution in the 1- and 3-positions:

$$\Delta E(4b_1 \leftarrow 3b_1) = -0.10\Delta\alpha - 0.51\Delta\beta$$

$$\Delta E(4b_1 \leftarrow 1a_2) = -0.35\Delta\alpha - 1.68\Delta\beta$$

Band B in the spectrum of **1** ($4b_1 \leftarrow 3b_1$) can thus be expected to be more sensitive to substitution in the 6-position than band E (predominantly $4b_1 \leftarrow 1a_2$), while the trends should be reversed in the case of substitution in the 1- and 3-positions. This is clearly in agreement with experiment, as seen in the correlation diagram in Figure 11. The experimental shifts are well reproduced by adoption of the values $\Delta\alpha = 0.20$ and $\Delta\beta = 0.22$ μm^{-1}. These values yield in the case of substitution of the thione sulfur

$$\Delta E(4b_1 \leftarrow 3b_1) = -0.24\ \mu\mathrm{m}^{-1}$$

$$\Delta E(4b_1 \leftarrow 1a_2) = -0.11\ \mu\mathrm{m}^{-1}$$

Table VIII. Measured and Calculated Electronic Absorption Spectra of **4**, **3**, and **6**[g]

	Obsd[a]				Calcd (PPP-CI)			
Compd	Band	$\nu(\epsilon_{max})$	Polarization	$\log \epsilon_{max}$[b]	Symmetry	ν	Predominant configurations	f
4	A[b]	1.88[c]		2.4				
	B	2.47	z	4.2	$^1A_1$	2.93	$4b_1 \leftarrow 3b_1$ (97%)	0.51
	C	~3.1	(y)	2.8	$^1B_2$	3.75	$2a_2 \leftarrow 3b_1$ (95%)	0.06
	D	3.35	d	3.0				
	E	4.25	y	3.8	$^1B_2$	4.64	$4b_1 \leftarrow 1a_2$ (87%), $2a_2 \leftarrow 3b_1$ (10%)	0.21
	F[b]	4.61		3.8	$^1A_1$	4.50	$4b_1 \leftarrow 2b_1$ (93%)	0.06
3	A[b]	2.21		1.8				
	B	2.63	z	4.2	$^1A_1$	3.07	$4b_1 \leftarrow 3b_1$ (96%)	0.38
	C	3.45	d	3.2				
	D	(3.75)[e]	y	3.5	$^1B_2$	3.84	$2a_2 \leftarrow 3b_1$ (81%), $4b_1 \leftarrow 1a_2$ (18%)	0.03
	E	3.92	y	4.0	$^1B_2$	4.32	$4b_1 \leftarrow 1a_2$ (79%), $2a_2 \leftarrow 3b_1$ (17%)	0.39
	F[b]	4.65		4.2	$^1A_2$	4.66	$4b_1 \leftarrow 2b_1$ (89%)	0.16
6	A[b]	1.79		2.6				
	B	2.40	z	4.2	$^1A_1$	2.85	$4b_1 \leftarrow 3b_1$ (96%)	0.44
	C	~3.3	d	3.1				
	D	(3.60)[e]	y	~3.4	$^1B_2$	3.76	$2a_2 \leftarrow 3b_1$ (78%), $4b_1 \leftarrow 1a_2$ (22%)	0.01
	E	3.76	y	3.8	$^1B_2$	4.18	$4b_1 \leftarrow 1a_2$ (75%), $2a_2 \leftarrow 3b_1$ (21%)	0.39
	F[b]	(4.46)[f]		3.8	$^1A_2$	4.36	$4b_1 \leftarrow 2b_1$ (90%)	0.10

[a] When not otherwise specified, measured in stretched polyethylene film at 77 K. [b] Measured in cyclohexane solution at room temperature. [c] Weakly discernible vibrational spacing of 0.04 μm^{-1}. [d] Strongly mixed polarization. [e] Shoulder seen as a separate peak in the spectra of **12** and **13**, see Figure 10. [f] Prominent shoulder on band with maximum at 4.69 μm^{-1}. [g] Wavenumbers are given in $\mu m^{-1} = 10^4$ cm^{-1}. C_{2v} symmetry is assumed. For details of the PPP-CI calculation see the text.

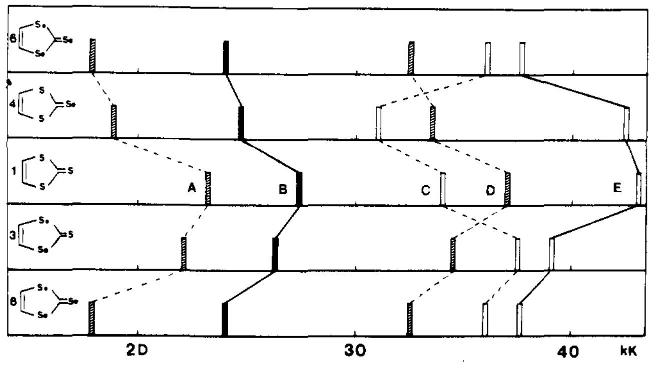


Figure 11. Correlation diagram of the observed transitions in **1**, **3**, **4**, and **6**. The symbolism is similar to Figure 8. The correlation of the two main π-π^* transitions is indicated by heavy lines. (1 kK = 0.1 μm^{-1}.)

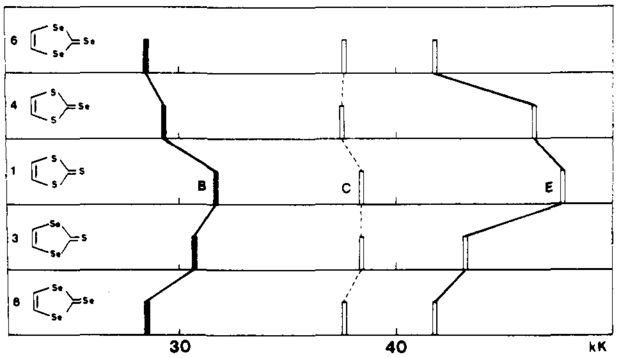


Figure 12. Correlation of the three lowest π-π^* transitions in **1**, **3**, **4**, and **6** predicted by means of a PPP-CI calculation, see Table VIII. The symbolism is similar to Figures 8 and 11. (1 kK = 0.1 μm^{-1}.)

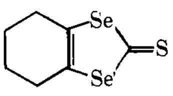
to be compared with the observed shifts of band B and E, −0.27 and −0.07 μm^{-1}, respectively. In the case of substitution of the two thiole sulfurs we obtain

$$\Delta E(4b_1 \leftarrow 3b_1) = -0.13\ \mu m^{-1}$$

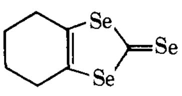
$$\Delta E(4b_1 \leftarrow 1a_2) = -0.44\ \mu m^{-1}$$

to be compared with the experimental shifts −0.11 and −0.40 μm^{-1}, respectively. Substitution of all three sulfur atoms by selenium leads to the predicted shifts −0.37 and −0.55 μm^{-1}, which compare well with the observed ones, −0.34 and −0.56 μm^{-1}, respectively. The experimental shifts are furthermore well reproduced by a PPP-CI calculation (Figure 12, see later). This agreement lends strong support to the assignment of the main bands B and E in the spectra of the series **1**, **3**, **4**, and **6**.

The assignment of the somewhat weaker bands C and D in the region between the two intense transitions is less straightforward. To support the identification of these bands, the spectra of alkyl derivatives such as **12** and **13** were recorded, e.g., Figure 10. The compounds **12** and **13** orient much better than the parent compounds **3** and **6** (see Table IX), and



12



13

are more soluble in polyethylene. The structure of the bands in the intermediate region (3.0–3.8 μm^{-1}) depends strongly on the nature of the heteroatom in the 1- and 3-positions. The spectrum of **4** looks very much like the spectrum of **1** in Figure 7, the sequence and relative intensities of the bands are similar; in the spectra of the 1,3-selena compounds **3** and **6** the situation is quite different. It is clear from Figure 10 that in the spectrum of the alkyl derivative of **3** the band with mixed polarization (C) appears at lower energy than the y-polarized band (D), and it is also apparent that the latter band is by far the stronger of the two; this is contrary to the spectra of **1** and **4**. The spectra of **3** and **6** are similar to the spectrum in Figure 10, except that the peak D is not resolved, but seen only as a shoulder on the onset of band E. The correlation of the first five bands in the spectra of **1**, **3**, **4**, and **6** is shown in Figure 11, which clearly illustrates the crossing discussed above.

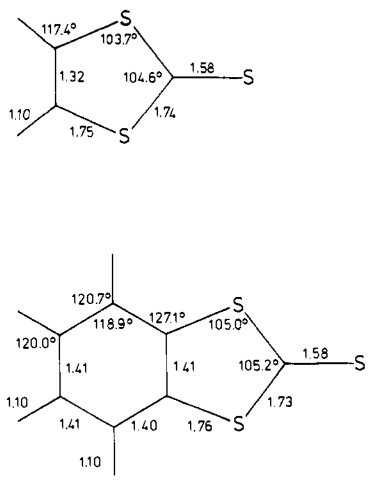


Figure 13. Geometries of 1,3-dithiole-2-thione (**1**) and benz-1,3-dithiole-2-thione (**10**) calculated by the MINDO/3 method under the assumption of C_{2v} symmetry. Bond lengths are in angstroms.

The y-polarized band C in the spectrum of **1** was in the preceding section assigned to transition to a state dominated by the configuration $2a_2 \leftarrow 3b_1$, see Table VII. One might then hope to reproduce the large shifts of this band on replacement of sulfur by selenium in terms of simple perturbation theory as in the case of the bands B and E, see above. The perturbation treatment yields in the case of substitution in the 6-position:

$$\Delta E(2a_2 \leftarrow 3b_1) = -0.54\Delta\alpha + 0.11\Delta\beta$$

and for substitution in the 1- and 3-positions:

$$\Delta E(2a_2 \leftarrow 3b_1) = -0.20\Delta\alpha - 0.07\Delta\beta$$

These expressions are not consistent with a large red shift in the first case and a large blue shift in the second case (see Figure 11) for any reasonable values of $\Delta\alpha$ and $\Delta\beta$. As a second attempt to reproduce the shifts of this band we have carried out full PPP-CI calculations with a carefully adjusted parametrization; in particular, the γ_x values and the bond lengths are chosen according to the nature of the heteroatoms and the bonds (see the section on calculational details). The results are included in Table VIII, and the correlation of the first three transition energies is shown in Figure 12. It is obvious by comparison of Figures 11 and 12 that the shifts of the strong bands B and E are excellently reproduced by the calculation, but the shifts of the intermediate y-polarized band are not well reproduced. In particular, the large blue shift on replacement of the sulfur atoms in the 1- and 3-positions by selenium is not reproduced at all. There may be several reasons why the PPP-CI calculation fails to reproduce these shifts. Assuming that the parameters employed in the calculation are adequate, and that our identification of the observed bands is correct (i.e., that band C in the spectra of **1** and **4** correlates with band D in the spectra of **3** and **6**), one obvious reason would be the influence of n-σ^* or σ-σ^* configurations of B_2 symmetry. The existence of an n-σ^* configuration of B_2 symmetry with low energy would require a low-lying unoccupied totally symmetric orbital.

The shifts of the visible n-π^* transition A ($4b_1 \leftarrow 5b_2$) parallel closely the shifts of the first π-π^* transition B ($4b_1 \leftarrow 3b_1$), see Figure 11. This is consistent with the fact that the first two bands in the PE spectra, assigned to the $5b_2$ and $3b_1$ levels, are shifted almost identically on replacement of sulfur by selenium, see Figure 4. The shifts of the band D in the spectrum of **1** (with mixed polarization) are somewhat similar to the shifts of the visible band. This supports the suggestion that the transition might have n-π^* or n-σ^* character. As argued in the preceding section, this band is probably due to transition to a state of B_1 symmetry, and might thus involve the n-π^* configuration $2a_2 \leftarrow 5b_2$. A low lying unoccupied a_1 orbital (see above) would furthermore introduce a low-energy π-σ^* configuration, $a_1 \leftarrow 3b_1$, with the proper symmetry to interact with this n-π^* configuration. The existence of a similar band in the spectrum of **11** (D) suggests that at least some π-σ^* character might be present. The answer to these and a number of other questions calls for a more quantitative and rigorous theoretical investigation of the excited states of these compounds.

Summary

By means of the powerful combination of PE spectroscopy and polarized electronic absorption spectroscopy we have characterized a number of electronic states of a complete series of 1,3-dithiole-2-thione derivatives and selena analogues and of their positive ions. Many of the spectroscopic properties have been rationalized in terms of simple molecular orbital interaction diagrams, and most of the important transitions could be assigned to transitions predicted by semiempirical calculations; the current methods EH, MINDO/3, and PPP-CI proved reasonably satisfactory in this respect.

The assignment given previously for the PE spectra of **1** and **10** have been confirmed by comparison with the PE spectra of related molecules and on the basis of independent theoretical models. Apart from the first two absorption bands the UV-visible spectrum of **1** does not appear to have been studied theoretically. We have assigned the main bands of the trithiocarbonate derivatives **11, 1,** and **10** to transitions calculated by the PPP-CI method. The two strong bands in the spectra of the series of symmetric selena derivatives could similarly be interpreted in terms of usual π theory. The remaining bands may involve n-π^*, n-σ^*, and π-σ^* transitions, as suggested in the text. A detailed understanding of the excited states of the series **1-6** requires a more sophisticated theoretical treatment with inclusion of all valence orbitals and probably 4s and 3d on sulfur and 5s and 4d on selenium. We feel that the polarization spectra presented in this paper might serve as a useful test of such a treatment.

Experimental Section

With the exception of **7** (Eastman Organics) all compounds have been synthesized. The synthesis of **1-6**[7,8] and **10**[37] have been reported in the literature. The preparation of **8, 9,** and **11** has been carried out analogously to the preparation of the parent compounds.[7,8]

The PE spectra were recorded on a PS 18 instrument of Perkin Elmer Ltd. (Beaconsfield, England) and calibrated with Ar. A resolution of about 20 MeV on the argon line was obtained.

The electronic absorption spectra were measured at 77 K on a Cary 17 spectrometer. A polyethylene sheet was swelled with a chloroform solution of the compound, and after evaporation of the solvent the surface of the sheet was rinsed with methanol. In some cases several sheets were combined to one clear thick sheet through a procedure of heating and pressing. The sheet was then stretched and placed over liquid nitrogen in a quartz Dewar. The dichroic absorption curves and baselines were measured in the way described by Eggers et al.[31] The curves were digitalized and the plots of the reduced spectra[31] were obtained on a Hewlett-Packard 9800-30 computer; C_{2v} symmetry was assumed in all cases. The measured degree of orientation of the molecules in the stretched polyethylene sheet is indicated in Table IX. A remarkable decrease in the degree of orientation is observed when sulfur is replaced by selenium. The observation that alkyl substitution in the 4- and 5-positions improves the orientation is consistent with the assumption that the orientation axis[31] is essentially parallel to an axis through the thione (selenone) bond (the z axis).

Calculations

The extended Hückel (EH),[18,38] Pariser, Parr, and Pople (PPP),[20] and MINDO/3[19] methods have all been described in the literature. In the case of the EH and MINDO/3 calculations the usual parametrizations were employed and the

Table IX. Measured Average Values of $\cos^2 \beta$ According to the Relation $\langle \cos^2 \beta \rangle = 1/(2d_{\perp}^0 + 1)$[a] and Values of the Usual Orientation Function $S = (3 \cos^2 \beta - 1)/2$[b,c]

Compd no.	$\langle \cos^2 \beta \rangle$	$(3 \cos^2 \beta - 1)/2$
10	0.63	0.45
11	0.60	0.40
12	0.55	0.33
8	0.54	0.31
13	0.49	0.24
1	0.45	0.18
4	0.44	0.16
3	0.42	0.13
6	0.39	0.09

[a] β is the angle between the "long" molecular axis and the stretching direction.[31] [b] For perfect alignment, $S = 1$; for isotropic distribution, $S = 0$.[31,36] [c] These values were reproducible at least within ±0.03.

molecular geometries were optimized by the MINDO/3 method, see Figure 13. For the PPP results listed in Tables I, VI, and VII and visualized in Figure 9 the following parameters were used (eV): $U_C = -11.42$, $U_{\text{-S-}} = -20.00$, $U_{=S} = -12.90$, $\gamma_C = \gamma_{\text{-S-}} = 10.84$, $\gamma_{=S} = 9.90$, $\beta_{CC} = -2.318$, and $\beta_{CS} = 1.62$. These parameters are similar to those listed in ref 20 and 32. All bond lengths were taken as 1.4 Å, and the geometries were based on regular polygons. The calculation on **11** was performed on a trithiocarbonate fragment of **1** (with no contribution from the alkyl moiety). All singly excited configurations were included in the CI procedure. For the PPP results listed in Table VIII and visualized in Figure 12 the parameters for carbon and sulfur were taken as those given above, except for $\gamma_{\text{-S-}} = \gamma_{=S} = 9.80$ eV. The parameters for selenium were taken as follows (eV): $U_{Se} = -19.20$, $\gamma_{Se} = 9.30$, and $\beta_{CSe} = -1.39$. These values are similar to those published in ref 39. For the selenone selenium center we used $U_{=Se} = -12.76$ eV. The C–S and C=S bond distances were taken as 1.70 Å and the C–Se and C=Se bond lengths as 1.85 Å; the regular pentagon was correspondingly enlarged at the positions of the heteroatoms.[39]

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$$\beta_{C=S}/\beta_{C=C} = S_{C=S}/S_{C=C}$$

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