Electronic Structure of Tetraphenylthieno[3,4-*c*]thiophene. Photoelectron, Electron Spin Resonance, and Electronic Absorption Spectra[1]

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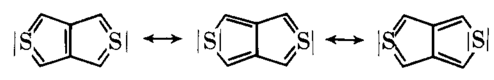
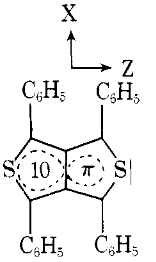
The He I photoelectron (PE) spectrum of tetraphenylthieno[3,4-*c*]thiophene (**2**) has been reassigned by comparison with the PE spectrum of 1-azatriphenylthieno[3,4-*c*]thiophene (**3**) and orbital energies obtained by extended Hückel calculations on **2**. The radical anion and cation of **2** and the radical anion of benzoisothiophene (**4**) have been generated and the hyperfine splitting in their ESR spectra has been completely analyzed. The linear dichroism of the most intense bands in the electronic absorption spectrum of **2** has been measured. An assignment of the first bands in the absorption spectrum of **2** is given based on a comparison with results of PPP–CI calculations. All data measured can be rationalized by a MO model, which generates the "nonclassical" thienothiophene π system by perturbation of the parent pentalene.

The nature of bonding in the "nonclassical" condensed thiophenes still remains a matter of controversy.[6] The parent molecule thieno[3,4-*c*]thiophene (**1**), which has so far escaped isolation, "is expected to be more aromatic than two thiophene molecules",[7] and the photoelectron spectrum of its stable tetraphenyl derivative **2** has been assigned by simply neglecting the phenyl groups.[7] Nevertheless, molecular orbital models proposed[7–9] for the interesting 10 π-electron system of **1** should be useful, if appropriately applied[10] in rationalizing the properties of the individual molecular states of stable derivatives. In the following, photoelectron (PE), electron spin resonance (ESR), and electronic absorption data for **2** and the related compounds 1-azatriphenylthieno[3,4-c]thiophene (**3**) and isobenzothiophene (**4**) or their radical ions, respectively, are reported and discussed.



1a **1b** **1c**



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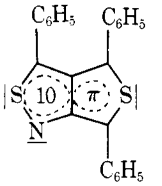

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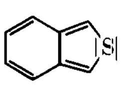

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I. PE Spectra

The PE spectra of **2** and **3** have been reported previously.[7,11] In Figure 1 our assignment for the low-energy region of both spectra is summarized, based on the validity of Koopmans' theorem[12] ($-\epsilon_J = I_{V,J}$).

The two PE spectra display several similarities. A first peak at low ionization energy is separated by a large gap from a second one, which is close to a very intense third one. To label the molecular orbitals of the aryl derivatives **2** and **3** we use the irreducible representations of the D_{2h} group, although X-ray investigations on **2** reveal[13] that its phenyl groups are twisted by 39.6 and 58.4° out of the molecular plane. Also for the aza derivative D_{2h} symmetry is not preserved any more.

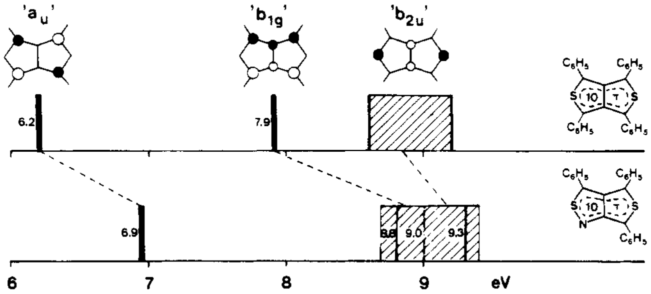

Figure 1. Comparison between the first bands of the PE spectra of **2** and **3**.

Our assignment for the PE bands of **2** is different from that proposed in the literature[7] insofar as our extended Hückel (EH)[14] calculations on **2**, which include the phenyl groups, predict the orbital sequence $a_u < b_{1g} < b_{2u}$ as shown in Figure 1. This reversed sequence with b_{1g} on top of b_{2u} is due to interaction of σ orbitals of the phenyl rings with the b_{1g} orbital of the thieno[3,4-c]thiophene fragment, being strong for a_u and b_{1g} but relatively small for b_{2u}.

The revised assignment is corroborated by the comparison between the PE spectra of **2** and **3** as displayed in Figure 1. Aza substitution causes a strong shift toward higher ionization energy for the first two bands, but not for the one assigned to b_{2u}. This is exactly what one expects from first-order perturbation theory[16] by π-isoelectronic replacement of one $C{-}C_6H_5$ unit by a more electronegative nitrogen atom.

II. ESR Spectra of 2^+ and 2^-

Information on the shape of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) is provided by the ESR spectra of the radical cation 2^+ and the radical anion 2^-. These have been generated by treating a solution of **2** in methylene chloride with $AlCl_3$ or $AgBF_4$ or a solution of **2** in dimethoxyethane with K, respectively. For comparison also **4** has been reduced to 4^-.

The ESR spectra of 2^+, 2^-, and 4^- (Figures 2a–4a) are best reproduced by computer simulation with the assigned coupling constants (Figures 2b–4b). The hyperfine coupling constants obtained by the correlation are listed in Table I, which also contains calculated spin densities according to McLachlan[17] and calculated coupling constants according to Karplus and Fraenkel.[18]

The ESR spectrum of 2^+ comprises 21 lines. It can be re-

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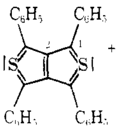
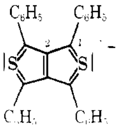
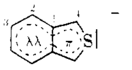
Table I. ESR Data for 2^+, 2^-, and 4^-: Calculated Spin Densities and Coupling Constants

	registry no.	μ	$a_{X,\mu}^{exp}$, mT	ρ_μ^{HMO}	$a_{X,\mu}^{calcd}$, mT	g
	67124-76-9	1	1.146	0.316	1.128[a]	
		2		−0.074		
		S		−0.057		2.0020
		H_o	0.044[b]			
		H_m	0.044			
		H_p	0.132			
	67179-20-8	1		0.231		
		2		−0.062		
		S		0.099		2.0056
		H_o	0.069[b,c]			
		H_m	0.069			
		H_p	0.095			
	35131-96-5	1		−0.060		
		H_2	0.435	0.203	0.508	
		H_3	0.284	0.030	0.075[d]	2.0039
		H_4	0.490	0.276	0.690	
		S		0.114		

[a] According to Karplus–Fraenkel[18] with $Q_C = 3.1$, $Q_{CC} = 1.4$, and $Q_{SC} = -0.8$ mT. [b] Assumed for simulation to be confirmed by ENDOR. [c] Strongly temperature dependent. [d] $Q_{CH} = -2.5$ mT.

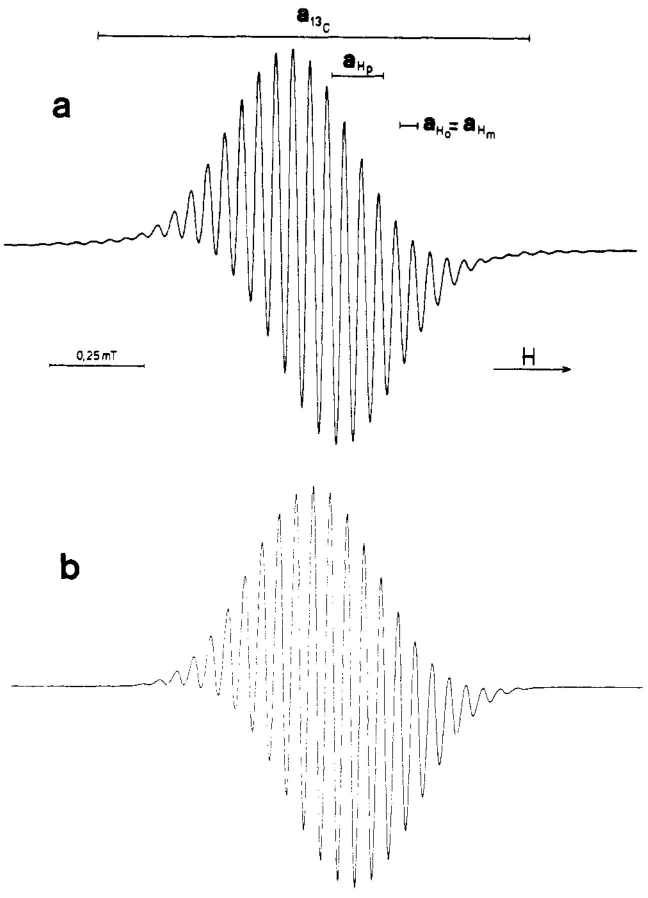


Figure 2. (a) ESR spectrum of 2^+ in CH_2Cl_2 at 200 K. (b) Computer simulation.

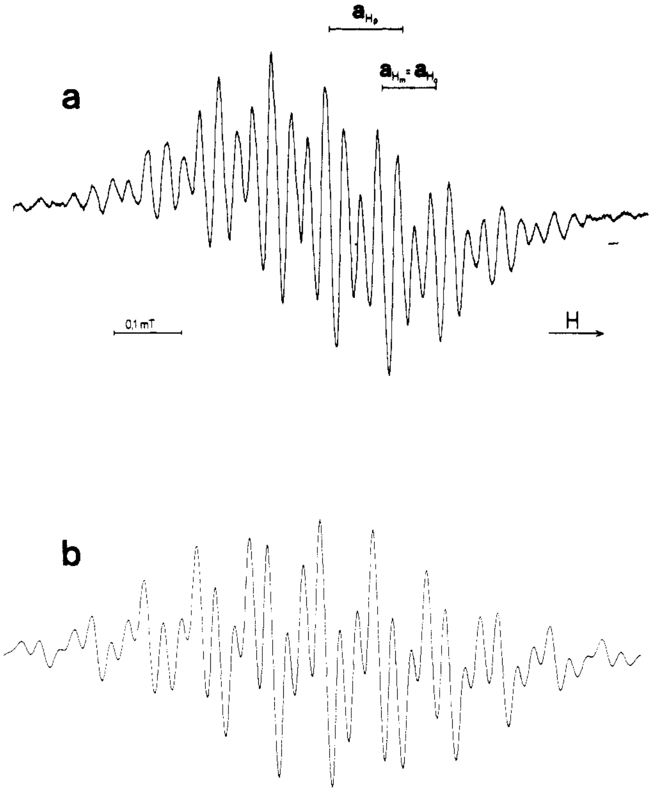


Figure 3. (a) ESR spectrum of 2^- in dimethoxyethane at 270 K. (b) Computer simulation.

produced by simulation only assuming coupling constants for the phenyl protons, e.g., the following set: $a_H^{para} = 0.132$ mT $= 3a_H^{ortho} = 3a_H^{meta} = 3(0.044)$ mT (see Figure 2b). In addition to the 21 lines, at the low- and high-field end of the spectrum a doublet of low intensity appears, which is assigned by its intensity to ^{13}C coupling of the four equivalent carbon atoms of the thieno[3,4-*c*]thiophene fragment. The hyperfine coupling constant amounts to $a_{^{13}C} = 1.146$ mT.

In contrast to the ESR spectrum of the radical cation 2^+, that of the radical anion 2^- is strongly temperature dependent. Whereas below 250 K a spectrum has been recorded (Figure 5) which we were unable to simulate; the spectrum recorded at higher temperature (Figure 3a) can be assigned. It shows a quintet due to the four *p*-phenyl protons which couple with 16 equivalent protons ($a_H^{ortho} \sim a_H^{meta}$). The g factor (2.0056, Table I) obtained for 2^- is higher than the one of a free electron ($g_e = 2.0023$)[19] or for the radical cation 2^+ (2.0020, Table I), indicating considerable spin density at the sulfur centers (cf. discussion of Figure 9).

The ESR spectrum of 4^- is shown in Figure 4a. Its interpretation is straight forward: it consists of three triplets due to the coupling of the ring protons with $a_H = 0.490, 0.435$, and 0.184 mT.

Table II. Observed and Calculated Electronic Absorption Spectrum of 2

obsd				calcd (PPP–CI)			
band	$\tilde{\nu}$, cm^{-1}	polarization	log ϵ_{max}	$\tilde{\nu}$, cm^{-1}	symmetry	predominant configuration (%)	f
A	18 180	x	4.07	17 985	x	$\pi_1^* \leftarrow \pi_1$ (99.3)	1.51
				22 717	y	$\pi_2^* \leftarrow \pi_1$ (96.4)	0.00
				27 278	y	$\pi_1^* \leftarrow \pi_2$ (96.6)	0.00
B	26 320	(z)	3.24	28 032	z	$\pi_3^* \leftarrow \pi_1$ (94.3)	0.21
C	29 400		3.77	30 194	z	$\pi_7^* \leftarrow \pi_1$ (92.2)	0.08
				30 264		$\pi_4^* \leftarrow \pi_1$ (98.8)	0.00
				30 268	x	$\pi_6^* \leftarrow \pi_1$ (98.8)	0.00
				30 323	y	$\pi_5^* \leftarrow \pi_1$ (99.0	0.06
D	34 015	z	4.44	35 268	z	$\pi_1^* \leftarrow \pi_3$ (98.8)	0.21
				37 906	z	$\pi_1^* \leftarrow \pi_4$ (94.1)	0.08
E	39 060	x	4.50	39 271	x	$\pi_2^* \leftarrow \pi_2$ (95.3)	1.56

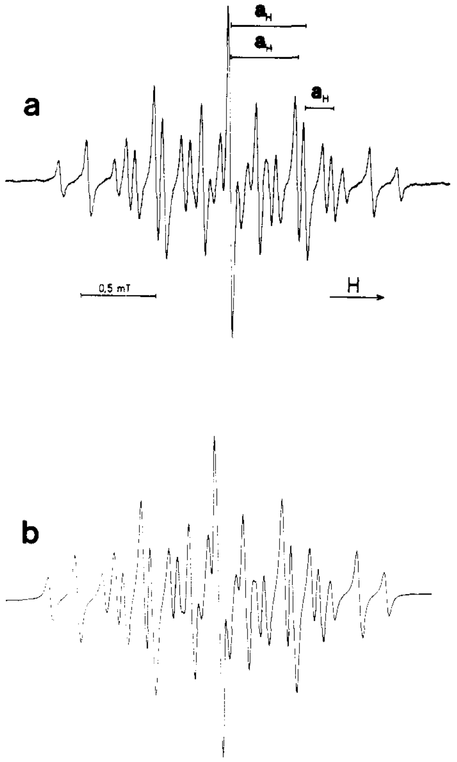


Figure 4. (a) ESR spectrum of 4^- in dimethoxyethane at 220 K. (b) Computer simulation.

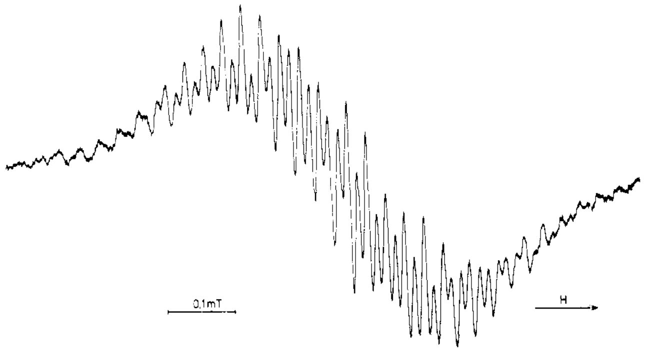


Figure 5. ESR spectrum of 2^- in dimethoxyethane at 210 K.

III. Electronic Absorption Spectrum of 2

The electronic absorption spectrum of 2 in CH_2Cl_2 is shown in Figure 6a. It exhibits five bands in the region between 18 × 10^3 and 40 × 10^3 cm^{-1}. The absorption spectrum of 2 has also been recorded in stretched polyethylene sheets and the polarization direction of bands A, D, and E could be obtained (Table II). An assignment of the observed transitions A–E to the calculated (PPP–CI)[20] ones is indicated in Table II. The calculation predicts several additional weak transitions, which are not observed. They are probably hidden below the intense bands.

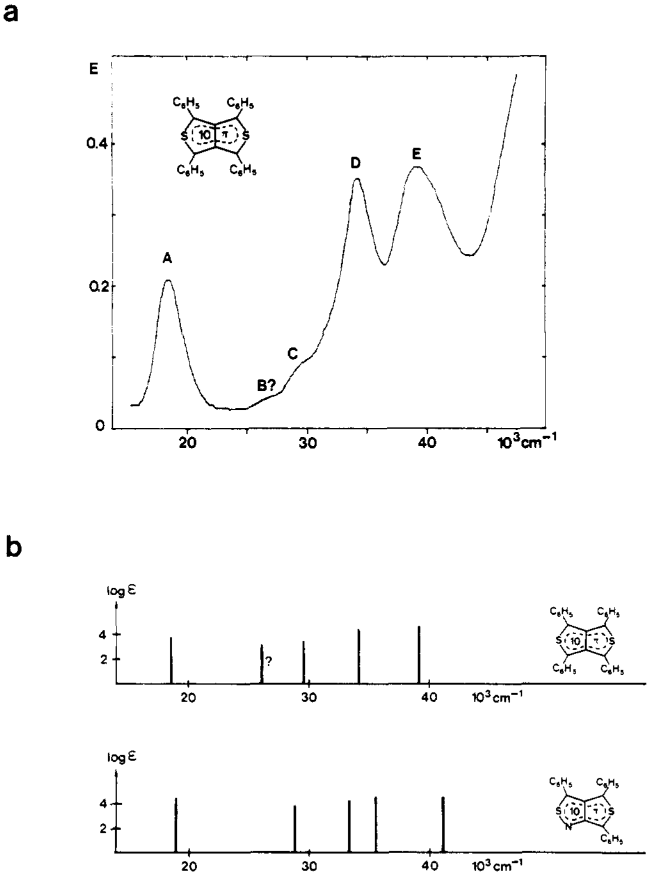


Figure 6. (a) Electronic absorption spectrum of 2 in cyclohexane. (b) Comparison between the first bands of the electronic absorption spectra of 2 and 3.

According to these calculations the first five bands can be described as due to $\pi \rightarrow \pi^*$ electron transitions. Although the interaction between the pentalene system and the phenyl rings is considerable (see Figure 7), we interpret the first three excited states (bands A, B, and C) as due to one-electron transitions with the transition moment localized mainly within the pentalene moiety.

The lowest electronic absorptions of 2 and 3 are compared in Figure 6b. All bands in the spectrum of 3 are shifted toward higher energy as anticipated from simple perturbation theory.

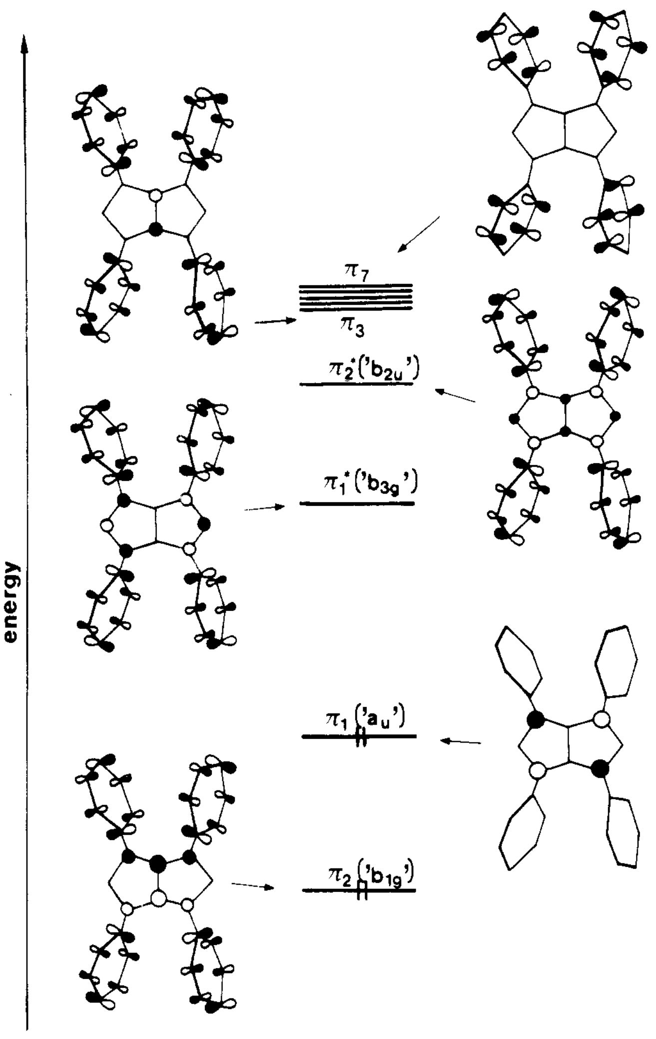


Figure 7. Highest occupied and lowest unoccupied π-MO's of 1 according to a PPP calculation.

The energy difference between the first bands of both absorption spectra, however, is small compared to the difference of the lowest ionizations in both PE spectra. This indicates that in the first ionic state the phenyl participation is less than in the first excited state of **2**.

IV. Discussion

Advantageously, we start by considering the π-MO correlation diagram (Figure 8). At its left are shown the π-MO's of pentalene (**5**) according to an HMO calculation assuming equal bond length. The π-MO's of **1** at the right side were derived from those of **5** by introducing an inductive perturbation at positions 2 and 5, assuming the same resonance integrals as in **5**. The energy levels which are antisymmetric with respect to a vertical plane of symmetry through centers 2 and 5 (b_{1g}, a_u) will remain constant, while the levels which are symmetrical to this plane (b_{2u}, b_{3g}) are lowered due to the higher valence state ionization potential of the sulfur 3p electrons compared with that of the carbon 2p electrons.[22] This perturbation does not affect the LUMO of **5** (a_u), while the next higher orbital, b_{3g}, is lowered considerably.

The MO correlation diagram (Figure 8) implies three corollaries: (i) for the radical cation 1^+ and the radical anion 5^- similar ESR spectra are expected; (ii) analogous to **5**[23] a long wavelength excitation is predicted for **1** due to the small HOMO-LUMO gap; and (iii) the difference between first and second ionization potentials of **1** should be large.

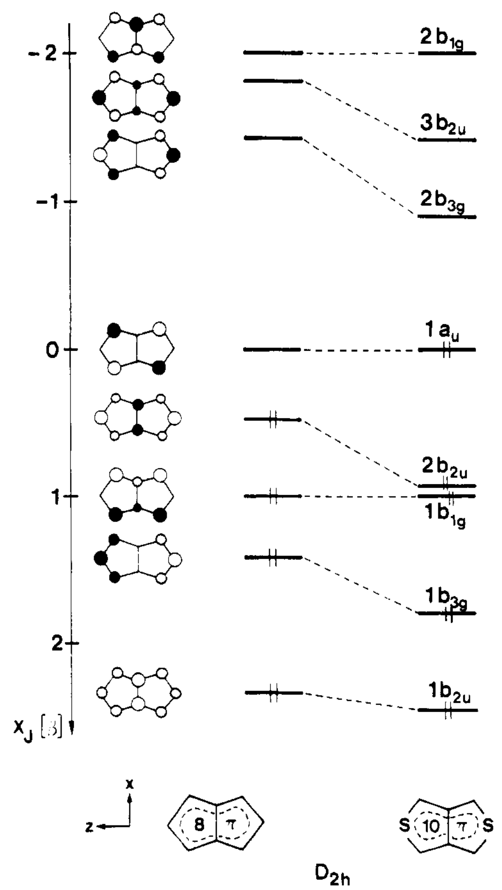


Figure 8. Correlation diagram between the π-MO schemes of pentalene and thieno[3,4-c]thiophene derived from an EH calculation.

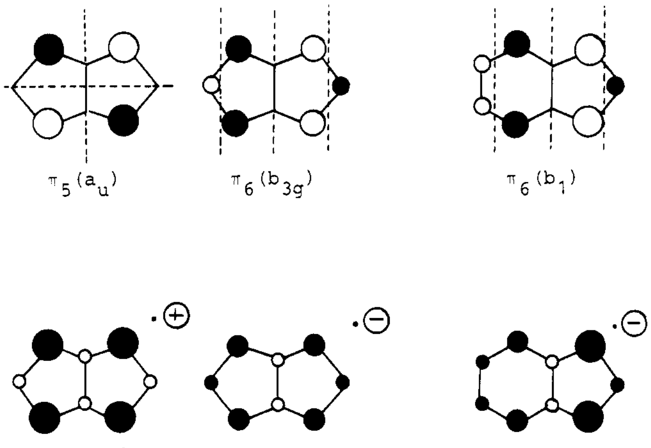
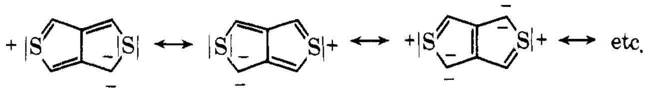


Figure 9. Comparison between the HOMO and LUMO of 2 and LUMO of 4 derived from a HMO calculation (h_s = 1.2, k_{CS} = 0.7) (top) and the calculated positive (●) and negative (○) spin densities according to McLachlan[17] (λ 1.2) (bottom).

Since both parent compounds, **1** and **5**, are unknown, the first deduction can be verified only in part. The ESR spectrum of the radical anion of an alkyl derivative of 5^+, 1,3,5-tri-*tert*-butylpentalene ($5a^+$), has been reported recently.[24] Using the McConnell equation[25] $a_i^H = \rho_i^\pi|Q|$, which relates the calculated spin densities, ρ_i^π, to the observed proton hyperfine coupling constant, a_i^H, the calculated spin densities for 5^- were found to be 0.25 for the equivalent positions 1, 3, 4, and 6, assuming a $|Q|$ value of 2.7 mT.[24] The spin population calculated for the same positions in 2^+ amounts to 0.316 (Table I) with negative spin densities at other centers. The calculated spin densities according to McLachlan[17] for 2^+, 2^-, and 4^- as well as the corresponding HOMO of **2** and the LUMO's of **2** and **4** are displayed in Figure 9. Obviously, the agreement between experiment and model is excellent.

As concerns the electronic absorption spectra of **2** and **5a** the expected long wavelength bands are observed at 18 180 and 16 800 cm^{-1}, respectively. Both transitions are polarized perpendicular to the long axis of the pentalene moiety.[23]

The predicted large gap between the first two radical cation states, according to our perturbation treatment, due to the stabilization of the $2b_{2u}$ orbital by replacing the CH centers in position 2 and 5 of **5** by sulfur, is observed in the PE spectrum of the tetraphenyl derivative (Figure 1). To elaborate whether 3d participation plays a role as suggested by the valence bond formulation **1a** ↔ **1b** ↔ **1c**, semiempirical calculations of the EH and CNDO/2 type with and without 3d orbitals have been performed. The results indicate that the influence of 3d participation on a_u should be much stronger than on b_{1g} and b_{2g}. A large 3d participation on the sulfur centers would lead to a reduction of the gap between $^2\tilde{A}_u$ and $^2\tilde{B}_{1g}$. The large gap of 1.7 eV observed between the corresponding radical cation states does not require 3d participation. This statement is further corroborated by the relatively large ^{13}C coupling constant and the small g factor found in the ESR experiments on 2^+. According to this, the appropriate representation of **1** and its derivatives would be as indicated in **2** or by valence formulas with dipolar structures as shown below.



Among the possible reasons for the relative stability of the tetraphenyl derivative **2** compared to the parent compound **1**, two should be emphasized: the acceptor properties and the bulkiness of the phenyl group.[7] The latter property renders a reaction at the positions 1, 3, 4, and 6 of **1** less likely.

Experimental Section

The compounds **2** and **4** were prepared according to the literature.[26,27] The PE spectrum of **2** was recorded on a PS 18 photoelectron spectrometer (Perkin-Elmer, Ltd., Beaconsfield) equipped with a heated probe. The calibration was done with Ar.

To generate 2^+ a sample of **2** is oxidized with $AgBF_4$ at 200 K in methylene chloride. Also $AlCl_3$ can be used as oxidizing agent. The radical anion, 2^-, can be generated in dimethoxyethane by treating **2** with potassium at 270 K; 4^- is generated similarly.

The electronic absorption spectrum of **2** was recorded in cyclohexane at room temperature with a Cary 17. To measure the linear dichroism of **2** a polyethylene sheet was swelled with a chloroform solution of the compound. The solvent was allowed to evaporate and the sheet was then stretched and placed over liquid nitrogen in a quartz Dewar.

The dichroic absorption curves and base lines were measured in the way described by Eggers et al.[28]

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