# Electronic Structure and Thermal Stability of Thiepins. Photoelectron Spectroscopic Investigations

**Rolf Gleiter,**[*†] **Gerhard Krennrich,**[†] **Dieter Cremer,**[‡] **Kagetoshi Yamamoto,**[§] **and Ichiro Murata**[§]

*Contribution from the Institut für Organische Chemie der Universität Heidelberg, D-6900 Heidelberg, West Germany, Lehrstuhl für Theoretische Chemie der Universität Köln, D-5000 Köln, West Germany, and Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. Received December 11, 1984*
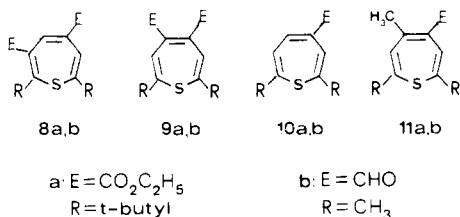
**Abstract:** The He I photoelectron (PE) spectra of 2,7-di-*tert*-butylthiepin (**1a**), as well as its 4-methyl (**2a**) and 4,5-dimethyl (**3a**) derivatives, together with thieno[3,4-*d*]thiepin (**5**) have been investigated. The assignment of the first bands is based on empirical considerations and model calculations (MNDO and ab initio). The first bands in **1a–3a** and **5** are assigned to ionizations from $\pi$-orbitals. Model calculations suggest furthermore that the influence of different substituents (COOR, alkyl) on the thermal stability of thiepin is mainly a steric one, whereas electronic effects are responsible for the thermal stability of **5**.

A comparison of the thermal stability of the three hetero-$8\pi$ systems oxepin, azepine, and thiepin reveals that the latter is the most elusive.[1] The pronounced instability of this system is rationalized as due to the low activation energy for the extrusion of sulfur. With the synthesis of the thermally stable 2,7-di-*tert*-butylthiepin (**1a**)[2] a relatively simple derivative of thiepin is available which allows one to study its chemical and physical properties.

In this paper we report the He I photoelectron spectra of **1a**, two further methyl substitution products **2a** and **3a**,[3] as well as thieno[3,4-*d*]thiepin (**5**).[4] To aid the spectral assignments we also investigated the partially hydrogenated products **4a**[5] and **6**.[4]



1a,b     2a,b     3a,b     4a,b

a: R=t-butyl     b: R=CH₃



5     6     7
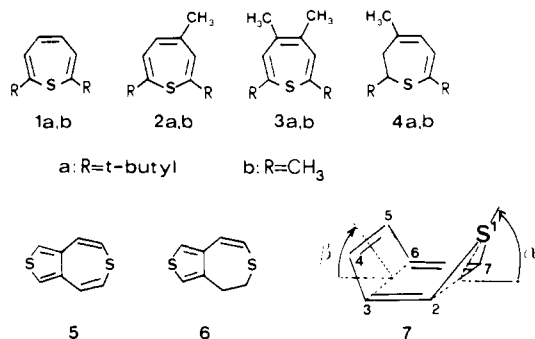
Besides assigning the first ionic states of **1–6** we were interested in a satisfactory description of the ground state of thiepin (**7**) itself. This in turn should uncover the reasons for the differences in thermal stability (expressed in their half lives $\tau_{1/2}$) of the thiepins **1a–3a** and **8a–11a** shown in Table I[1,2,5] as well as the great difference between thiepin and **5**.[4]



8a,b     9a,b     10a,b     11a,b

a: E=CO₂C₂H₅     b: E=CHO
    R=t-butyl         R=CH₃

## PE Spectroscopic Investigations of 1–4

In Figure 1 we show the He I photoelectron spectra of **1a–4a**. The PE spectra of **1a–3a** show one band around 7.5 eV followed by two strongly overlapping bands around 9 eV and a fourth one

**Table I.** Half-Lives of the Thiepins **1a–3a** as well as **8a–11a**. The Half-Lives Were Determined in Toluene-$d_8$ at 130 °C

| compd | $\tau_{1/2}$, h | compd | $\tau_{1/2}$, h |
|-------|-----------------|-------|-----------------|
| 8a | >1000 | 2a | 105 |
| 1a | 365 | 3a | 15 |
| 9a | 254 | 11a | 7 |
| 10a | 157 | | |

close to 10 eV. Neither of these peaks shows any fine structure. A strong effect upon methyl substitution is found in the case of band ② and band ④ in so far as in **2a** and **3a** the separation between bands ② and ③ is enlarged and band ④ is clearly shifted toward lower energy. The most pronounced difference between the PE spectra of **1a–3a** and that of **4a** is the missing of one band around 9 eV (see Figure 1). From our previous experience with the PE spectra of $\pi$-systems containing sulfur[6] we can safely assume that the bands below 10.5 eV are due to ionizations from $\pi$-orbitals. For a more quantitative treatment we assume that the negative orbital energy calculated for the ground state ($-\epsilon_j$) can be set equal to the measured ionization energy ($I_{v,j}$). This approximation[7] seems to hold well for large organic systems[6] like **1–6** if we restrict ourselves to the first ionic states only.

To derive the orbital energies of **1–3** we proceed in two ways: (i) we try empirically to assign the first bands by correlating them with those of related PE spectra or (ii) we compare the spectral data with results of MO calculations.

### Empirical Assignment

X-ray investigations on **1a** show that the thiepin ring is boat shaped,[2] with dihedral angles of $\alpha = 49.6°$ and $\beta = 28°$ between the plane formed by C(2), C(3), C(6), C(7) and the plane S, C(2), C(7) and the plane C(3), C(4), C(5), C(6), respectively. Furthermore, a considerable alternation among the C–C bond lengths is found. These results imply that a simple HMO model with just one or two $\beta$-parameters seems inappropriate to treat the $\pi$-system in **1–3**. A proper starting point to estimate the orbital energies

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(2) Yamamoto, K.; Yamazaki, S.; Kohashi, Y.; Murata, I.; Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N. *Tetrahedron Lett.* **1982**, *23*, 3195.
(3) Yamamoto, K.; Yamazaki, S.; Kohashi, Y.; Matsukawa, A.; Murata, I. *Chem. Lett.* **1982**, 1843.
(4) Schlessinger, R. H.; Ponticello, G. S. *J. Am. Chem. Soc.* **1967**, *89*, 7138.
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[†] Universität Heidelberg.
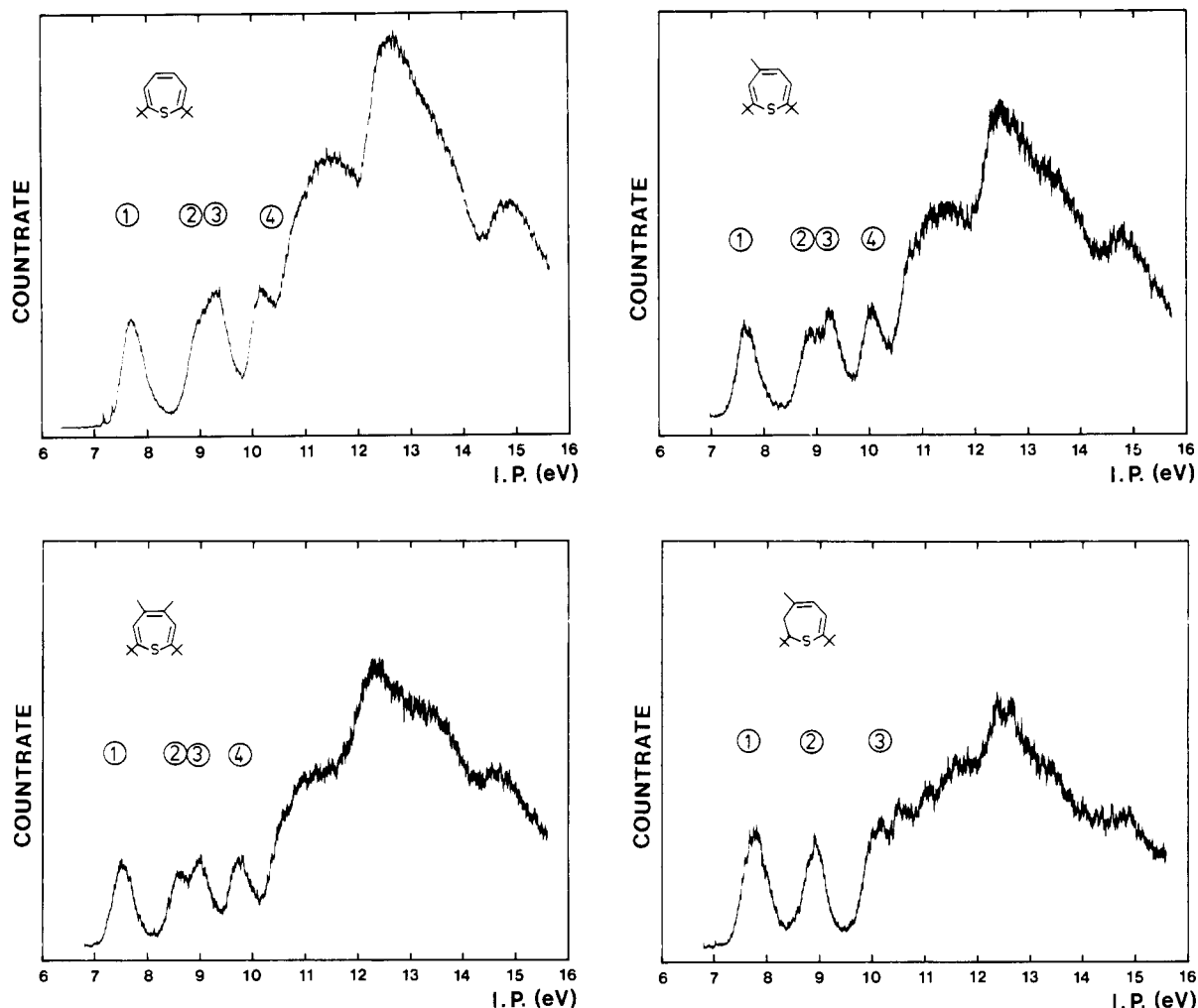[‡] Universität Köln.
[§] Osaka University.

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**Figure 1.** PE spectra of **1a–4a**.

of the π-systems of **1–3** in a qualitative way seems to be that of cycloheptatriene (**12**) which shows a boat conformation with bond alternation in the hexatriene moiety.[8]

To derive the MO's of **1** we replace in the cyclic triene system the $CH_2$ bridge by a sulfur. To estimate the approximate orbital energies for **1a** we have to correct the orbital energies (negative values of the ionization energies) of our triene model for the effect of two *tert*-butyl groups (inductive and hyperconjugative effect) and the hyperconjugative effect of the C–S σ bonds. This latter effect is judged to be considerable especially for the lowest lying π-orbital (a′) since PE studies on simple alkyl sulfides suggest a value of 10.6 eV[6] for the C–S σ-bond which is close to that found for the third band (a′(π₁)) in **12**. This discussion reveals that the energy of all the π-MO's of **12**,[9] especially the lowest one, has to be shifted toward higher energy in **1**. In Figure 2 we have adopted the values –8.0, –9.2, and –10.0 eV, as shown on the right side. To construct an interaction diagram for **1a** we have to assess the basis orbital energy of the sulfur center in **1** which we assume to be –9.4 eV as in previous studies.[10,11] For reasons of symmetry the 3p lone pair on sulfur may interact with the two MO's of the hexatriene system belonging to the irreducible representation A′. This interaction yields the three MO's 14a′, 13a′, and 12a′ as shown in Figure 2. According to this figure we expect two MO's

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(11) Gleiter, R.; Bischof, P.; Böhm, M. C.; Guilard, R.; Yamaguchi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 856.
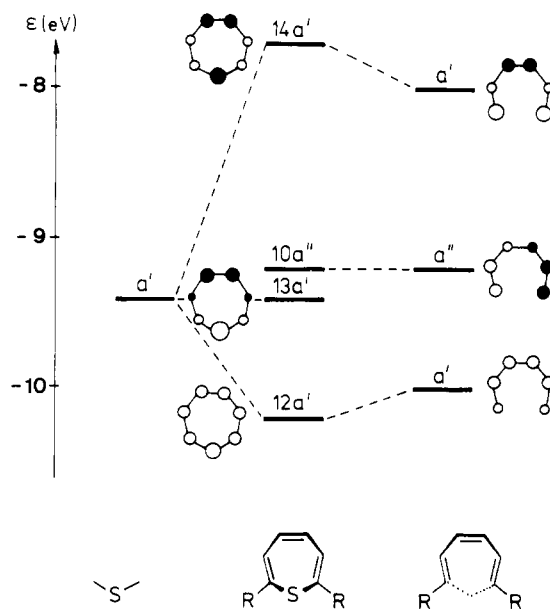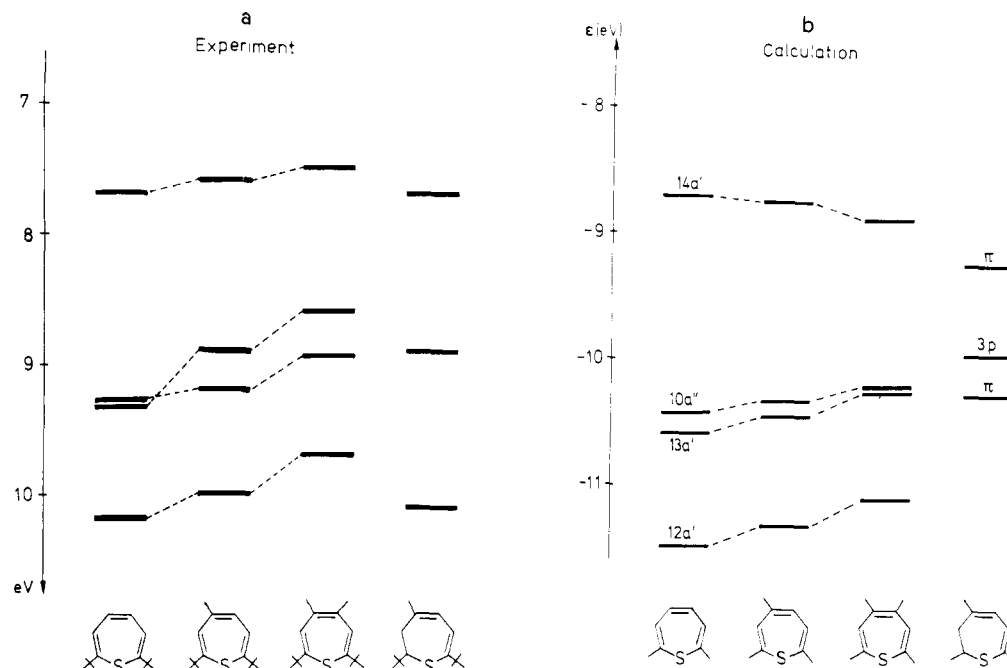
**Figure 2.** Qualitative interaction diagram between the π-MO's of a perturbed hexatriene (right) and a 3p-orbital of S (left) to yield the highest occupied MO's of 2,7-dimethylthiepin (**1b**).

around 9.3 eV close together and well separated from the other ones with strong π-character. The PE spectrum of **1a** is in line with these qualitative arguments. Furthermore, the size of the coefficients at positions 4 and 5 of 13a′ and 10a″ allows us also to rationalize the observed shift when comparing the positions of

**Figure 3.** (a) Correlation between the first PE bands of **1a–4a**. (b) Correlation between the highest occupied MO's of **1b–4b** derived by a MNDO calculation.

the bands in the PE spectrum of **1a** with those of **2a** and **3a**. Using first-order perturbation theory[12] we anticipate a larger shift for 13a' compared to that of 10a''. These arguments favor the assignment of a' to band ② and a'' to band ③ (see also Figure 3a) in the spectra of **1a–3a**.

## Calculations

In addition to the empirical derivation of the highest occupied valence orbitals of **1** we have carried out semiempirical calculations. We restricted ourselves to the MNDO method[14] since MINDO/3[13] did not reproduce the geometrical parameters of **1b–3b** satisfactorily as discussed below. For the parent system (**7**) we also used restricted HF theory employing a STO-3G basis as well as a 44-31G basis for sulfur.[15] Minimizing the heats of formation of the models **1b–3b** with respect to all geometrical parameters we find that MINDO/3 predicts an essentially flat molecule. The MNDO method as well as the HF/STO-3G level on the other hand favor a boat shape which parallels the experimental findings.[2] The ab initio approach predicts for **7** folding angles $\alpha = 35°$ and $\beta = 26°$ while the MNDO method underestimates these values by 6°. The underestimation of ring puckering by MNDO is typical for NDO methods (vide infra) but may also be due to an underestimation of the C–S bond length (1.80 Å in **1a**,[2] 1.78 Å HF/STO-3G in **7**, but 1.72 Å, MINDO/3, and 1.69 Å, MNDO). In view of the pronounced dependence of the folding angles on the bulk of the substituents attached to the thiepin ring, in particular in positions 2 and 7 (see below), and in view of the ab initio results obtained for cycloheptatriene, azepine, and oxepin,[8c] we consider the STO-3G values to represent a fair description of the degree of puckering of **7**. In Table II we have listed the calculated orbital energies of **1b–4b**. A comparison with the measured orbital energies of **1a–4a** is made in Figure 3 and Table II.

As usual the orbital energies calculated by the MNDO method differ from the ionization energies by about 1 eV. The differences

**Table II.** Comparison between the First Vertical Ionization Energies, $I_{v,j}$, of **1a–4a** and Calculated Molecular Orbital Energies, $\epsilon_j$, for **1b–4b** (All Values in eV)

| compd | band | $I_{v,j}$ | assignment | $-\epsilon$(MNDO) |
|---|---|---|---|---|
| **1a** | ① | 7.7 | 14a' ($\pi_4$) | 8.71 |
|  | ② |  | 13a' ($\pi_3$) | 10.41 |
|  | ③ | 9.3 | 10a'' ($\pi_2$) | 10.58 |
|  | ④ | 10.2 | 12a' ($\pi_1$,n) | 11.49 |
| **2a** | ① | 7.6 | $\pi_4$ | 8.76 |
|  | ② | 8.9 | $\pi_3$ | 10.34 |
|  | ③ | 9.2 | $\pi_2$ | 10.44 |
|  | ④ | 10.0 | $\pi_{1,n}$ | 11.31 |
| **3a** | ① | 7.5 | 11a' ($\pi_4$) | 8.88 |
|  | ② | 8.6 | 16a' ($\pi_3$) | 10.23 |
|  | ③ | $8.9_5$ | 13a'' ($\pi_2$) | 10.25 |
|  | ④ | 9.7 | 15a' ($\pi_1$,n) | 11.09 |
| **4a** | ① | 7.7 | $\pi$ | 9.25 |
|  | ② | 8.9 | 3p | 9.98 |
|  | ③ | 10.1 | $\pi$ | 10.28 |

**Table III.** Calculated Orbital Energies for **7** Using the HF/STO-3G, 44-31G, and MNDO Approach (All Values in eV)

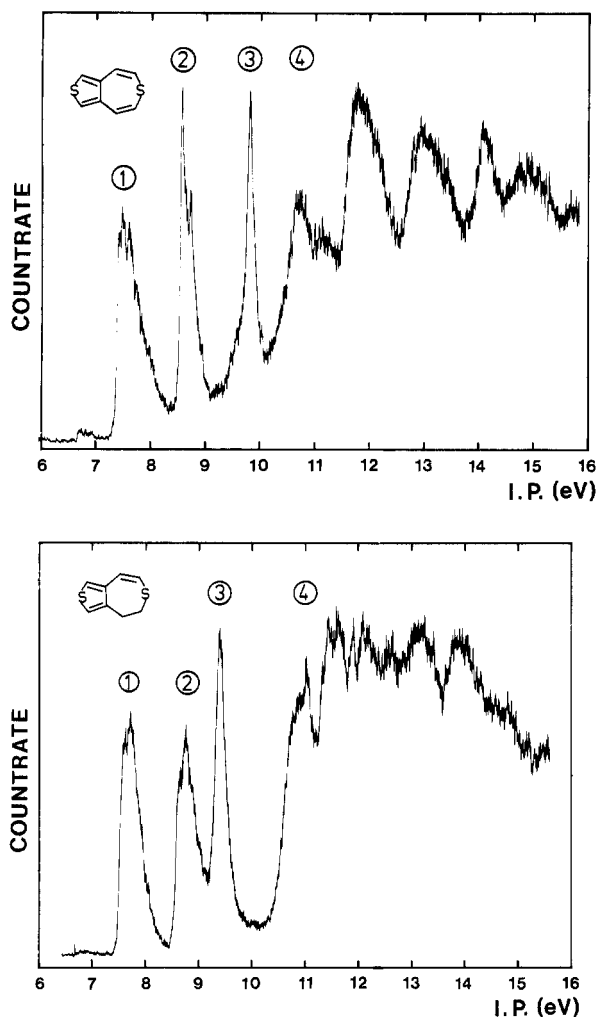| MO | sym-metry | character | $-\epsilon$(STO-3G) | $-\epsilon$(44-31G) | $-\epsilon$(MNDO) uncorr | corr |
|---|---|---|---|---|---|---|
| 29 | 11a' | $\pi_4$ | 5.9 | 8.0 | 8.9 | 8.3 |
| 28 | 10a' | $\pi_3$ | 8.6 | 10.5 | 10.9 | 10.2 |
| 27 | 7a'' | $\pi_2$ | 9.1 | 10.6 | 10.8 | 10.8 |
| 26 | 9a' | $\pi_1$,$n_s$ | 9.5 | 11.6 | 11.9 | 11.3 |
| 25 | 6a'' | $\sigma_{CS}$,$\sigma_{CH}$ | 11.1 | 12.8 | 12.5 | 12.4 |
| 24 | 8a' | $n_s$,$\pi_1$ | 11.8 | 13.6 | 13.2 | 12.8 |

between the energies, however, are reproduced quite well. The sequence predicted empirically differs in the sequence of the two close lying orbitals corresponding to bands ② and ③ (for **1b**: 13a' and 10a''). To clarify this point we have compared the orbital energies obtained for **7** using the different approaches in Table III. The ab initio results are based on those geometrical parameters calculated with the STO-3G basis set. The MNDO values are based on the structure with minimum heat of formation. We also included in Table III a column containing the results of empirically corrected MNDO orbital energies (MNDO correction) according to a formula given by Dewar et al.[16] This correction

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**Figure 5.** Comparison between the first PE bands of azulene and **5**.



**Figure 4.** PE spectra of **5** and **6**.



**Figure 6.** Schematic reaction diagram for the reaction of thiepin to benzene and sulfur with thianorcaradiene as an intermediate.

**Table IV.** Comparison between the First Vertical Ionization Energies, $I_{v,j}$, of **5** and **6** with the Calculated Orbital Energies, $\epsilon_j$ (All Values in eV)

| compd | band | $I_{v,j}$ | assign-ment | $-\epsilon$(MINDO/3) | $-\epsilon$(HMO) | $-\epsilon$(MNDO) |
|-------|------|-----------|-------------|----------------------|------------------|-------------------|
| **5** | 1 | 7.42 | $4b_1(\pi)$ | 7.84 | 7.48 | 8.58 |
|       | 2 | 8.52 | $2a_2(\pi)$ | 8.51 | 8.43 | 9.30 |
|       | 3 | 9.75 | $3b_1(\pi)$ | 9.64 | 10.16 | 10.69 |
|       | 4 | 10.7 | $1a_2(\pi)$ | 11.13 | 11.07 | 11.39 |
| **6** | 1 | 7.67 | $7a''(\pi)$ | 8.03 | 7.92 | 9.05 |
|       | 2 | 8.73 | $6a''(\pi)$ | 8.9 | 9.12 | 9.68 |
|       | 3 | 9.38 | $5a''(\pi)$ | 9.44 | 9.96 | 10.16 |
|       | 4 | 11.0 | $4a''(\pi)$ | 11.19 | 11.22 | 10.84 |

takes care of the fact that MNDO neglects the interactions between inner electrons and valence electrons.

All three results agree in so far as they show $11a'(\pi)$ as the HOMO followed by two close-lying MO's mainly $\pi$ in character. The ab initio approaches as well as the corrected MNDO results predict a' on top of a'' and thus parallel our empirical assignment, while the uncorrected MNDO results favor the reverse order. For MO 24 and 26 all approaches used predict a heavy mixing between $\pi_1$ of the thiepin moiety and the $n_s$ lone pair on sulfur. This mixing has already been anticipated in our empirical derivation of the MO's.

## PE Spectra of 5 and 6

The PE spectra of **5** and **6** are shown in Figure 4. In contrast to the spectra of **1–4** we now observe bands with a relatively steep
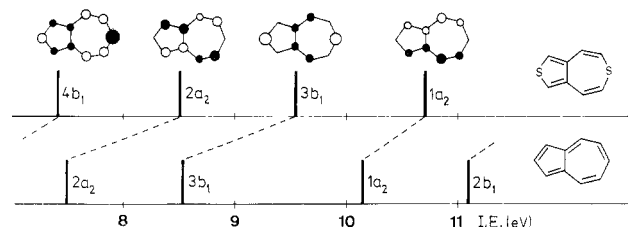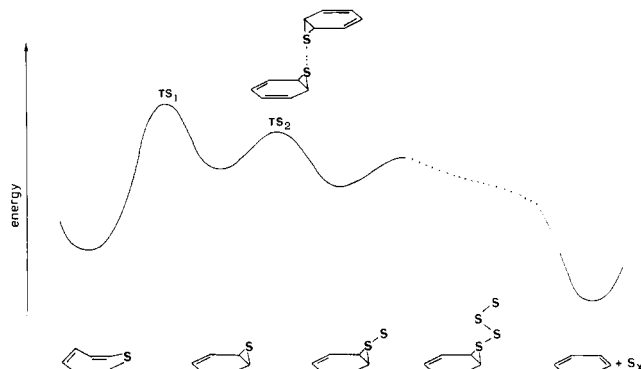
onset, typical for planar $\pi$-systems. From our previous experience on the PE spectra of $\pi$-systems containing sulfur[6] it seems reasonable to assign the bands below 11 eV to ionization events from $\pi$-orbitals. To assign the first PE bands in the spectra of **5** and **6** we compare the measured ionization energies with the calculated orbital energies listed in Table IV. To derive the orbital energies we use a HMO model,[10,11] the MINDO/3 method,[13] and the MNDO[14] method. The parameters chosen for the HMO method have been used for other thiophene systems: $\alpha_s = -9.4$ eV, $\alpha_c = -7.0$ eV, $\beta_{cs} = -1.8$ eV, and $\beta_{cc} = -3.0$ eV.[10,11] The HMO model seems appropriate since the deviation from planarity of **5** seems to be much smaller[17,18] than in the case of **1–3**. A comparison between the values obtained by the HMO method and experiment shows a satisfactory agreement. The MINDO/3 method predicts some $\sigma$ levels between $2a_2$ and $1a_2$ of **5**. If we ignore these levels for the reason stated above we find that both methods reproduce the $\pi$-levels well.

In an earlier investigation a great similarity of the electronic absorption spectrum of **5** with that of azulene (**13**) has been found with respect to the energy and polarization direction of the first four bands.[17] This has been rationalized by assuming that the two highest occupied and the two lowest unoccupied $\pi$-orbitals of both compounds belong to the irreducible representations $B_1$ and $A_2$, respectively, and that the energy separation between them is about the same. To demonstrate this at least for the highest occupied MO's we have compared the first PE bands of **5** with those of **13**[19] in Figure 5. The wave functions schematically drawn for **5** are derived from a MINDO/3 calculation. This correlation confirms that the energy difference between the first MO's of both compounds is about the same. The lower energy of the first band in the electronic spectrum of azulene (14 300 cm$^{-1}$) compared with that of **5** (22 800 cm$^{-1}$)[16] is probably due to a lower $\pi^*$ level in azulene.

## Thermal Stability of Thiepins

All attempts to isolate the parent compound **7** have failed so far,[1] a fact which has been rationalized by postulating for **7** antiaromatic character[19–21] leading to strong bond alternation. An

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(20) Dewar, M. J. S.; Trinajstić, N. *J. Am. Chem. Soc.* **1970,** *92,* 1453.

**Table V.** Most Relevant Geometrical Parameters of **7** and **15-20** as Predicted by MNDOC (Bond Lengths in Å, Bond Angles in deg)

| compd | S-C$_2$ | C$_2$-C$_3$ | C$_3$-C$_4$ | C$_4$-C$_5$ | C$_3$-C$_8$ | C$_4$-C$_8$ | C-O | ∠C$_7$SC$_2$ | ∠SC$_2$C$_3$ | ∠C$_2$C$_3$C$_4$ | ∠C$_3$C$_4$C$_5$ | α$^a$ | β$^a$ | τ$^b$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 7 | 1.692 | 1.344 | 1.462 | 1.352 | | | | 108.3 | 129.3 | 128.6 | 128.5 | 29.4 | 20.5 | |
| 15 | 1.693 | 1.349 | 1.471 | 1.352 | 1.508 | | 1.220 | 107.0 | 128.6 | 126.3 | 128.4 | 34.0 | 25.2 | 83.8 |
| 16 | 1.692 | 1.345 | 1.468 | 1.358 | | 1.510 | 1.220 | 106.5 | 128.7 | 128.1 | 127.4 | 32.8 | 24.3 | 80.9 |
| 17 | 1.694 | 1.350 | 1.471 | 1.352 | 1.509 | | 1.219 | 107.0 | 127.9 | 125.4 | 128.6 | 35.6 | 27.0 | 77.3 |
| 18 | 1.694 | 1.345 | 1.474 | 1.363 | | 1.511 | 1.219 | 104.3 | 127.6 | 127.9 | 125.8 | 35.0 | 27.5 | 81.9 |
| 19 | 1.695 | 1.352 | 1.475 | 1.351 | 1.512 | | | 106.3 | 127.7 | 123.4 | 128.7 | 37.6 | 30.2 | 59.9 |
| 20 | 1.694 | 1.346 | 1.478 | 1.370 | | 1.514 | | 102.7 | 126.9 | 128.3 | 124.1 | 37.7 | 31.3 | 60.4 |

$^a$Folding angles as defined in **7**.  $^b$Torsion angle of the HCO or the CH$_3$ group respectively and the adjacent double bond.

**Table VI.** Heats of Formation ($\Delta H_f°$) of **7** and **15-20** as well as Relative Heats of Formation for **16, 18, 20** ($\Delta\Delta H_f°$), the Thianorcaradiene Form of **7** and **15-20** ($\Delta\Delta H_f°$(NCD)), and the Transition States (TS$_1$ of Figure 6) ($\Delta\Delta H_f°$(TS$_1$)) (SCF Results and Correlation Corrected Results (correl corr) Are Given in kcal/mol)

| compd | $\Delta H_f°$ SCF | $\Delta\Delta H_f°$ SCF | $\Delta\Delta H_f°$ correl corr | $\Delta\Delta H_f°$(NCD) SCF | $\Delta\Delta H_f°$(NCD) correl corr | $\Delta\Delta H_f°$(TS$_1$) SCF | $\Delta\Delta H_f°$(TS$_1$) correl corr |
|---|---|---|---|---|---|---|---|
| 7 | 43.4 | | | -0.3 | 2.1 | 29.0 | 21.7 |
| 15 | 13.8 | | | -1.6 | 0.9 | 27.8 | 21.1 |
| | | 0.1 | 0.8 | | | | |
| 16 | 13.9 | | | -1.4 | 0.4 | 27.6 | 20.3 |
| 17 | -15.6 | | | -2.7 | -1.1 | 26.9 | 18.6 |
| | | 2.0 | 0.6 | | | | |
| 18 | -13.6 | | | -2.8 | -0.8 | 25.9 | 19.1 |
| 19 | 30.8 | | | -3.1 | -0.7 | 27.1 | 20.0 |
| | | 3.8 | 3.2 | | | | |
| 20 | 34.6 | | | -3.3 | -0.8 | 25.1 | 20.1 |

additional reason for its instability might be the low activation energy for the sulfur extrusion reaction which might pass thianorcaradiene (**14**) as an intermediate[22] as shown in (1) followed
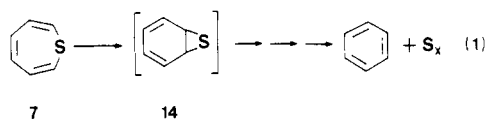


by a sequence of reactions involving several intermediates in which the number of sulfur atoms increases, ending with benzene and stable forms of sulfur. In Figure 6 we have depicted a possible reaction coordinate, analogous to that discussed by Miller et al. for thieno[3.4-c]thiophene.[23] It applies to such thiepin derivatives which are capable of forming thianorcaradiene as an intermediate, e.g., **5** and **7**. For those compounds with bulky substituents in position 2 and 7 like **1a** and **3a** as well as **8a-11a** the norcaradiene form is no longer an intermediate but now a point on the reaction path leading to the transition state which may look similar to TS$_2$ (Figure 6). It should be pointed out, however, that for the kinetic stability of the substituted thiepin discussed in this work, only the highest activation energy is of relevance. This is, according to our studies and those of Miller et al.,[23] definitely TS$_1$ (see Figure 6). According to model calculations on related systems[23] activation energies leading to S$_X$ formation are certainly lower than 5 kcal/mol and of no influence on the kinetic stability.

In order to investigate substituent effects on (1) it is necessary to analyze their effects on the stability of **7, 14**, and the transition state (TS$_1$) of the thianorcaradiene formation (Figure 6). Two possible effects of a substituent have to be considered, its electronic and its steric impact.

### Electronic Effects

To make the discussion of these effects simple we will subdivide the electronic effects into conjugative and inductive effects. To understand both effects on the thermal stabilities of **1a** to **3a** and **8a-11a** as exemplified by their half-lives in toluene (Table I) we have carried out model calculations on **7** and some simple derivatives with one or two formyl groups in order to mimic the effect

(21) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 3907; Gupta, N. K.; Birss, F. W. *Tetrahedron* **1980**, *36*, 2711.

(22) Schönberg, A. *J. Org. Chem.* **1958**, *23*, 104. London, J. D. In "Organic Sulfur Compounds"; Kharash, N., Ed.; Pergamon Press: New York, 1961.

(23) Miller, K. J.; Moschner, K. F.; Potts, K. T. *J. Am. Chem. Soc.* **1983**, *105*, 1705.

**Table VII.** Calculated MNDO Net Charges and Dipole Moments of Thiepin (**7**), Thianorcaradiene (**14**), and the Transition State (TS$_1$) for Reaction 1

| position | 7 | TS$_1$ | 14 |
|---|---|---|---|
| 1 | 0.052 | 0.027 | -0.148 |
| 2,7 | -0.121 | -0.099 | -0.015 |
| 3,6 | -0.048 | -0.064 | -0.073 |
| 4,5 | -0.049 | -0.049 | -0.042 |
| μ[D] | 1.52 | 1.74 | 2.43 |

of ester groups. Furthermore, we also considered the effect of methyl substituents. The most relevant predicted geometrical parameters of **7** and the model compounds **15-20** are listed in Table V. The heats of formation, the differences between the isomers **15-16, 17-18**, and **19-20** as well as the difference between
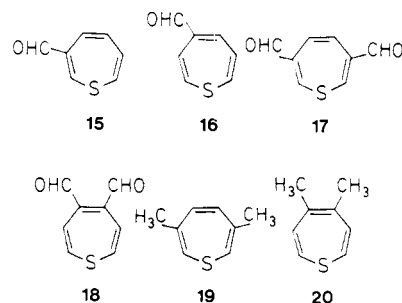


the thiepin and the norcaradiene form are listed in Table VI. For the transition state (TS$_1$ in Figure 6) the MNDO(SCF) results[14] as well as correlation corrections of relative energies are listed. The latter have been obtained by carrying out Brillouin-Wigner second-order perturbation theory with Epstein-Nesbet denominators for the SCF wave functions and correcting empirically for quadruple excitations.[24] The inclusion of correlation has been proven to be important for a proper treatment of ground-state properties of π-systems.[25] The results of our model calculations reveal that the electronic effects of the substituents are generally not very large, leading to changes in the relative energies of less than 3 kcal/mol. In none of the compounds are strong conjugative effects observed. This is corroborated by the results that the plane of the CHO substituent is predicted to be always perpendicular

(24) Thiel, W. *J. Am. Chem. Soc.* **1981**, *103*, 1413, 1420.
(25) Cremer, D.; Kraka, E. to be published.

to the plane of the adjacent thiepin double bond. The calculated OCCC dihedral angles range from 77 to 95°. This suggests that all speculations on the anti- or homoaromatic character of **7** are not relevant when discussing substituent effects on its thermodynamic or kinetic stability. Our findings are in contradiction to HMO results by Hess et al. that electron acceptors should have a significant influence.[26]

For an investigation of the inductive effects of a substituent we use the predicted net charges shown in Table VII. They reveal that negative charge is redistributed from position 2 and 7 to positions 1, 3, and 6 during the valence isomerization of **7** to **14**. Accordingly, electron acceptor substituents at positions 3 and 6 should stabilize **14** while the same substituents at positions 2 and 7 should stabilize **7**. In line with these arguments are the predicted relative stabilities of the norcaradiene (NCD) forms of **15** and **17** (Table V) since **15** and **17** are examples with an electron acceptor in position 3 as well as 3 and 6, respectively. Also, the values for the activation energy of the valence isomerization decrease in the series **7** (21.7 kcal/mol), **15** (21.1 kcal/mol), **17** (18.6 kcal/mol). Since the ease of sulfur extrusion depends on the barrier to valence isomerization (see Figure 6), the consideration of the inductive effects lets us predict that **7** is more stable than **15** or **17**. This, however, provides no explanation of the order of stabilities shown in Table I or the calculated decrease in stability when going from **7** to **16**, **18**, or **20**.

## Steric Effects

The folding angles of the thiepin ring are sensitive to steric effects. These effects increase with the bulk of the substituent (*tert*-butyl > methyl > CHO) and its position. Substituents in positions 2 and 7 show the strongest effect while substituents in positions 3–6 also have a pronounced effect on puckering (see $\alpha,\beta$-values in Table V). Taking these facts into consideration we can rationalize the following:

(1) **1a** is stable due to the steric repulsion of the *tert*-butyl groups. This increases the activation energy for sulfur extrusion considerably (Figure 6).

(2) Additional (acceptor or donor) substituents in positions 3 and 6 enhance the steric effect of substituents in positions 2 and 7 by pressing them together. The formation of the norcaradiene form is even more impeded. Although the electronic effect of an acceptor substituent is working in the opposite direction, electronic changes are far too small compared to the steric effects.

(3) Substituents in positions 3(6) and 4(5) of **1a** will transfer their steric influence in a "domino" effect onto the *tert*-butyl groups (see below). Clearly **8a** has a much lower tendency for S extrusion and, therefore, is much more stable than **1a**.
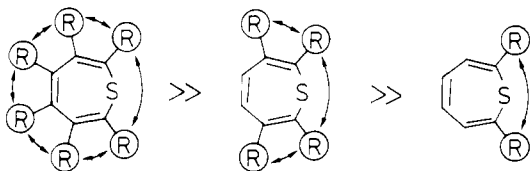


(4) Two substituents in positions 4 and 5 repel each other. Thus steric strain is relieved by conversion to the norcaradiene form since the 4–5 bond is lengthened. This explains why **2a** and **3a** with one or two methyl groups in 4 and 5 position are less stable than **1a**.



(5) Two aldehyde or ester groups in positions 4 and 5 are also destabilizing because of steric and electrostatic repulsion. The repulsive interactions are, however, lowered by an antiparallel

arrangement of the CHO dipoles. This latter effect mitigates the steric repulsion.

Taking together 1–5 allows us to understand the observed order of stabilities shown in Table I.

## Stability of 5

For **5** quantum chemical calculations reveal a small positive resonance energy.[19-21] The great difference in thermal stability between **5** and **7** can be rationalized by writing down the valence structures of the resulting thianorcaradiene (**21**) as shown in (2). The resulting biradical structure is indicative of a rather high activation energy due to electronic effects.
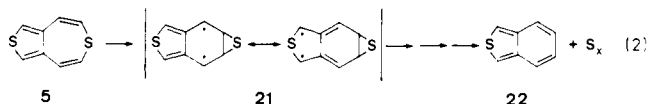


A further corroboration of our arguments can be seen by comparing the thermal stability of **5** with that of benzo[*d*]thiepin (**23**). This latter compound[27] as well as its 2-carbethoxy derivative[28] decompose in less than an hour at room temperature. This can be understood by considering the resulting norcaradiene intermediate for the sulfur extrusion reaction 3. The orthoquinoid structure of the episulfide **24** indicates a considerably smaller activation energy of (3) compared with that of (2). Parallel to
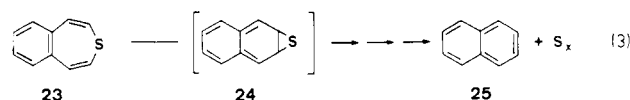


the lower activation energy of (3) is the stabilization of the ground state by resonance. Quantum chemical calculations on **23** indicate about the same resonance energy as for benzene.[19,20]

The thiepin derivatives **26** and **27** owe their thermal stability[1] to electronic and steric effects. In the transition state to a thianorcaradiene the benzene resonance is cancelled and, moreover, the benzene rings behave like bulky groups.



**26**　　　　　　　　　　**27**
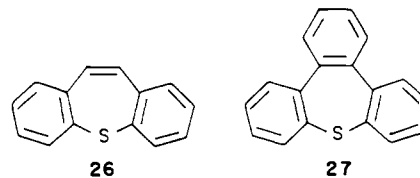
## Experimental Section

The preparation of compounds **1a–4a** has been reported.[2,3] A sample of **5** and **6** has been prepared according to literature procedures.[4] In all cases analytically pure samples were investigated. The He I photoelectron spectra were recorded on a PS 18 spectrometer (Perkin Elmer, Ltd. Beaconsfield, England) and a Leybold-Heraeus UPG 200 spectrometer.

The calibration was done with Ar and Xe. A resolution of 20 meV was achieved with the $^2P_{3/2}$ Ar line. The samples had to be heated to the following temperatures: **1a**, 40 °C; **2a**, 50 °C; **3a**, 70 °C; **4a**, 25 °C; **5**, 70 °C; and **6**, 50 °C.

**Registry No.** **1a**, 83670-21-7; **1b**, 98705-42-1; **2a**, 84477-43-0; **2b**, 98705-43-2; **3a**, 84477-45-2; **3b**, 98705-44-3; **4a**, 98705-35-2; **4b**, 98705-45-4; **5**, 327-25-3; **6**, 92224-19-6; **7**, 291-72-5; **8a**, 98705-33-0; **9a**, 98705-34-1; **10a**, 84435-05-2; **11a**, 71951-58-1; **14**, 87314-35-0; **15**, 98705-36-3; **16**, 98705-37-4; **17**, 98705-38-5; **18**, 98705-39-6; **19**, 98705-40-9; **20**, 98705-41-0.

(26) Hess, B. A., Jr.; Schaad, L. J.; Reinhoudt, D. N. *Tetrahedron* **1977**, *33*, 2685.

(27) Büschken, W. Ph.D. Thesis, Universität Köln, 1972.
(28) Nakasuji, K.; Kawamura, K.; Ishihara, T.; Murata, I. *Angew. Chem.*, **1976**, *88*, 650; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 611.