the electron pair of R^- if the second step of the Markovnikov addition adds R^- to bridged $C_2H_5^+$.

Open Structure. The lowest unoccupied orbital is symmetric in the plane of open $C_2H_5^+$ (type 1), has a negative eigenvalue (Table IX), and is almost entirely p_z of C_1 (its normalized coefficient is 0.98). This nearly vacant orbital would be an ideal receptor for a lone pair upon addition of R^- to open $C_2H_5^+$ in the Markovnikov addition. Although both the bridge and open structures of $C_2H_5^+$ have favorable orbitals and eigenvalues for addition of R^-, the open structure seems more favorable from these results. Hence, if the bridge structure of $C_2H_5^+$ is more stable than the open form, we suggest that a transformation from the bridge to the open form may occur during the addition of R^-. However, a detailed study is required. Hence, we are presently examining theoretically the addition of H^- to $C_2H_5^+$.

Transferability. The use of localization procedures for obtaining transferable bonds[22] leads us to compare our localized bonds with one another and with those on hydrocarbons. It is most appropriate to compare the C_1H bonds of the CH_2 group in open $C_2H_5^+$ with the CH bonds of the bridge structure (Tables VII and VIII). Even though C_1 (open) is positive (0.21 e), while C (bridge) is negative (−0.05 e), the CH bonds are remarkably alike, having the same hybridization ($sp^{1.8}$) and differing only slightly in 1s (of H) and p_y (of C) character. A survey of all of our results shows variations of electron populations of 0.01 e in p_y and of 0.08 e in p_x and 2s of C. Populations of 1s of H vary by 0.16 e in the opposite direction from that of the changes in p_x and 2s of C. The CH bonds in ethylene are $sp^{2.0}$ hybrids and have atomic orbital coefficients close to those in the bridge and open structures even though the charge distribution is quite different. These results suggest that CH bonds, in approximately the same geometry with respect to a CC bond, may be transferable. However, CC bonds which are more reactive are not transferable.

Acknowledgment. We wish to thank the Office of Naval Research for support of this research, and we are grateful to D. S. Marynick and J. H. Hall, Jr., for helpful advice. We also thank R. M. Stevens for the use of his SCF program.

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[22] (a) C. Trindle and O. Sinanoglu, *J. Chem. Phys.*, **49**, 65 (1968); (b) C. Trindle and O. Sinanoglu, *J. Amer. Chem. Soc.*, **91**, 853 (1969).

Electronic Structure of Thieno[3,4-*d*]thiepin

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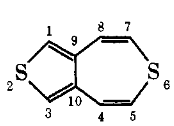
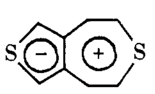
Contribution from Physikalisch-Chemisches Institut der Universität Basel, Basel, Switzerland, and the Chemistry Department, The Johns Hopkins University, Baltimore, Maryland 21218. *Received May 15, 1972*

Abstract: CNDO/2 and extended Hückel calculations of thieno[3,4-*d*]thiepin (**1**) reveal a small difference in energy between a planar and a nonplanar structure, both with bond alternation. The electronic spectrum of **1** was measured with polarized light using the stretched-film technique. The first four bands are assigned to $\pi^* \leftarrow \pi$ transitions on the basis of PPP–CI calculations. These bands are correlated with the first four bands of azulene. For the first transition a hypsochromic shift is predicted upon methyl substitution in all positions.

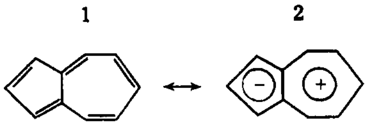
Schlessinger[3a–c] has recently reported the synthesis of the novel 4*n*-π-electron heterocycle, thieno[3,4-*d*]thiepin (**1**). The relative stability of **1** was attributed to an extensive delocalization in the π system, and it has been proposed that this delocalization may be due to charge-separated resonance structures summed up by **2**. In order to ascertain the nature of the π-electron delocalization in **1**, an X-ray structure analysis has been carried out.[3b] A disordered structure similar to that of azulene was found, and this hampered a complete analysis. It was reported that the molecule is almost planar in the crystal and that the length of the transannular bond is 1.46 Å.



1



2



4a **4b**

In an attempt to learn more about the electronic structure of this 12π-electron heterocycle,[4] the electronic spectra of **1** in cyclohexane and ethanol, the polarization spectra (uv) in stretched polymer sheets, and the fluorescence spectrum in cyclohexane were measured.

In addition, CNDO/2,[5] EH,[6] and PPP[7] calculations

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[1] Physikalisch-Chemisches Institut der Universität Basel.

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[3] (a) R. H. Schlessinger and G. S. Ponticello, *J. Amer. Chem. Soc.*, **89**, 7138 (1967); (b) T. D. Sakore, R. H. Schlessinger, and M. H. Sobell, *ibid.*, **91**, 3995 (1969); (c) R. H. Schlessinger and G. S. Ponticello, *Tetrahedron Lett.*, **25**, 3017 (1968).

[4] For a recent review on 4*n*-π-electron heterocycles, see L. A. Paquette in "Nonbenzenoid Aromatics," Vol. I, J. P. Snyder, Ed., Academic Press, New York and London, 1969, p 249.

[5] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, and references therein.

[6] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962). The Slater exponent for hydrogen used was 1.3.

[7] R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York, N. Y., 1964, and references therein.

Table I. Calculated Total Energies (eV) of **1** with Different Geometric Parameters

	I		II		III	
	CNDO/2[5,14]	EH[6,14]	CNDO/2[5,14]	EH[6,14]	CNDO/2[5,14]	EH[6,14]
Planar	2239.06[a]	862.04[a]	2242.66[a]	863.88[a]		
	2259.05[b]	863.63[b]	2259.68[b]	865.01[b]		
					2243.05[a]	864.14[a]
					2259.89[b]	865.23[b]
S_6 10° out of plane	2239.00[a]	862.04[a]	2242.52[a]	863.88[a]		
	2259.09[b]	863.62[b]	2259.64[b]	865.01[b]		

[a] Without the inclusion of the 3d orbitals on sulfur. [b] With the inclusion of the 3d orbitals on sulfur.

have been used to help understand the ground- and excited-state properties of **1**. Moreover, comparison between the measured spectrum and the calculated transitions yields an additional test for the validity of the sets of parameters proposed in the literature.

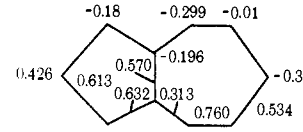
Experimental Procedure

Preparation of 1. 4,9-Dithiabicyclo[5.3.0]deca-1(10),2,7-triene, the 4,5-dihydro derivative of **1** (**3**), was prepared according to the method of Eglinton, *et al.*[8] This compound (**3**) was converted to **1** using the procedure described by Schlessinger and Ponticello.[3a] The yellow thieno[3,4-*d*]thiepin (**1**) was sublimed and then recrystallized from CCl_4: mp 152-153° (lit.[3a] 149-151°).

Spectroscopic Measurements. The electronic spectra were measured on a Cary 14 spectrometer using spectrograde solvents. The stretched-film technique described by Eggers[9] was applied using unplasticized polyethylene sheets. The fluorescence spectrum in cyclohexane was recorded at room temperature on a Zeiss PMQ II spectrometer using a Zeiss M365 filter.

Ground-State Properties of 1

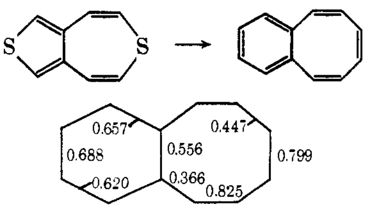
We can derive qualitatively some of the properties of **1** from isoelectronic models. One such model with the same topology as **1** is the dianion of azulene (4^{2-}). The bond orders and charge densities derived for 4^{2-} from an HMO model are shown below. These numbers clearly indicate that there should be a pronounced



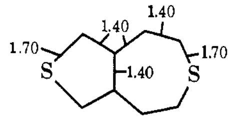
bond alternation and a charge distribution opposite to the one indicated in the resonance formula **2**. This is mostly due to the occupation of χ_{-1} of **4** (see Figure 3).

The esr results of the radical anion of **4** support this conclusion.[10] The spin population derived from these measurements is much larger in the seven-membered ring than in the five-membered ring.

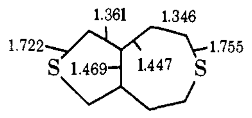
Substituting an ethylene moiety for each of the two sulfur atoms in **1** provides a second isoelectronic model, benzcyclooctatetraene. The HMO bond orders of this alternant hydrocarbon also clearly indicate bond alternation.



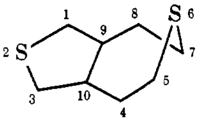
Carrying out SCF-MO calculations on the π system of **1**, Dewar and Trinajstić[11] found bond alternation and a charge distribution opposite to the one indicated in **2**. The predicted bond lengths for an assumed planar molecule are given in II. The calculated resonance energy (3.8 kcal/mol) is of the same order of magnitude as the nonbonded interactions and angle strain in the planar seven-membered ring. Therefore a nonplanar conformation is likely. To test this we have carried out molecular orbital calculations using the CNDO/2[5] and the extended Hückel (EH)[6] model for the three different geometries I, II, and III. In I (no bond alternation) and II (bond alternation), the carbon skeleton was kept planar, with only the sulfur atom of the seven-membered ring bent out of the molecular plane by 10°. In III, the conformation of the seven-membered ring was made similar to that of known 1*H*-azepin derivatives.[12] For the dihedral angle between the plane $C_4–C_5–C_7–C_8$ and the five-membered ring we assumed 30°, while the dihedral angle between the planes $C_4–C_5–C_7–C_8$ and $C_5–C_6–C_7$ was assumed to be 60°.



I



II



III

As can be seen from the total energies listed in Table I, bond alternation is preferred in the 12π system. Additionally, in both geometries I and II, the potential curve for the movement of the sulfur atom out of the molecular plane is very flat.[13] Another interesting fact which should be pointed out is

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[8] G. Eglinton, I. A. Lardy, R. A. Raphael, and G. A. Sims, *J. Chem. Soc.*, 1154 (1964).

[9] J. Michl, E. W. Thulstrup, and J. H. Eggers, *J. Phys. Chem.*, **74**, 3878 (1970), and references therein.

[10] I. Bernal, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 1489 (1962).

[11] M. J. S. Dewar and N. Trinajstić, *J. Amer. Chem. Soc.*, **92**, 1453 (1970).

[12] I. C. Paul, S. M. Johnson, L. A. Paquette, J. H. Barrett, and J. Haluska, *ibid.*, **90**, 5023 (1968).

[13] If C_6 of **4** is bent 5° out of the molecular plane, one finds a raising of the total energy by 3 kcal (EHT) and 4 kcal (CNDO/2).[14]

[14] The parameters used for sulfur in the CNDO/2 calculations were the basis sets sp and spd referred to by Santry and Segal.[15] For the EH calculations, the Slater exponents of sulfur are from Clementi and Raimondi,[16] except for the sulfur 3d orbitals. This exponent was estimated to be 1.6. The valence state ionization potentials were estimated as $H_{ii}(3s) = -20.0$ eV, $H_{ii}(3p) = -13.30$ eV, and $H_{ii}(3d) = -6.00$ eV.

[15] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

[16] E. Clementi and D. L. Raimondi, *ibid.*, **38**, 2686 (1963).

Table II. Comparison between the Electronic Transition Energies of Thieno[3,4-*d*]thiepin and Azulene

Thieno[3,4-*d*]thiepin							Azulene	
Experiment			Calculation				Experiment[c]	
Band	ν, kK[a]	Direction of polarization along axis[b]	ν, kK	Symmetry	f	Confign (%)	ν, kK[a]	Direction of polarization along axis[b]
1	22.1	y	22.8	B_1	0.003	$\pi_{-1} \leftarrow \pi_1$ (99)	14.3	y
2	28.0	x	28.9	A_1	0.199	$\pi_{-2} \leftarrow \pi_1$ (75), $\pi_{-1} \leftarrow \pi_2$ (23)	28.1	x
3	36.5	y	39.0	B_1	0.103	$\pi_{-2} \leftarrow \pi_2$ (98)	33.6	y
4	38.0	x	39.7	A_1	1.551	$\pi_{-1} \leftarrow \pi_2$ (74), $\pi_{-2} \leftarrow \pi_1$ (23)	35.0	x

[a] The values given pertain to the onset of a band and not to the maximum. [b] For definition of x and y, see Figure 2a. [c] D. Schmidt, Ph.D. Thesis, ETH, Zürich, 1970, No. 4517.

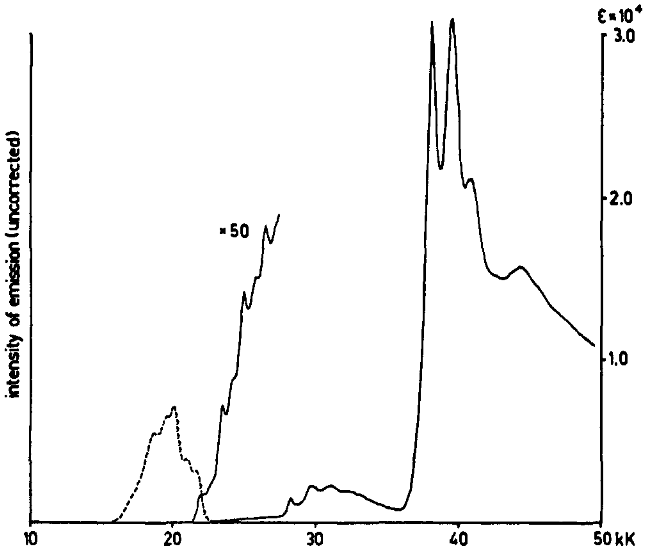

Figure 1. Absorption and fluorescence spectra of thieno[3,4-*d*]-thiepin in cyclohexane at room temperature.

the small difference in energy between II and III. If the listed numbers are significant, then the shape of the molecule in the gaseous state is nonplanar.

The inclusion of charge-separated resonance structures summed up by **2** is sound only if the participation of 3d orbitals in the bonding of compounds with divalent sulfur is important. We would like to adopt a pragmatic point of view with regard to this often-discussed topic. Initially, the bonding scheme is developed without the 3d orbitals on the sulfur atom. Then the calculations are repeated including the 3d orbitals with a Slater exponent and an ionization potential which allows a moderate interaction.

The all-valence electron calculations furthermore reveal the following. (1) The character of the orbitals π^*, π, or σ is retained in going from II to III. Therefore the electronic spectrum of either species in the visible or near uv region should not change appreciably. (2) The 3d participation has a minor effect on the energy of the MO's. This is in accord with recent *ab initio* calculations on compounds with divalent sulfur atoms.[17]

The Electronic Spectrum of 1

The absorption and fluorescence spectra of **1** are shown in Figure 1. Both spectra exhibit a pronounced vibrational fine structure. In contrast to the reported spectrum in the literature,[3a] we find an additional band at 22.1 kK. The numbers pertaining to the absorption maxima measured in cyclohexane are collected in Table II. To obtain an assignment of individual electronic transitions to the absorption bands we have measured the dichroism of **1**. For this purpose **1** was dissolved in a polyethylene film stretched by 600%. The absorption spectra obtained with light polarized parallel and perpendicular to the stretching direction of the film [$E_{\parallel}(\lambda)$ and $E_{\perp}(\lambda)$, respectively] are shown in Figure 2a. To correct for the fact of partial molecular orientation we used the following equations

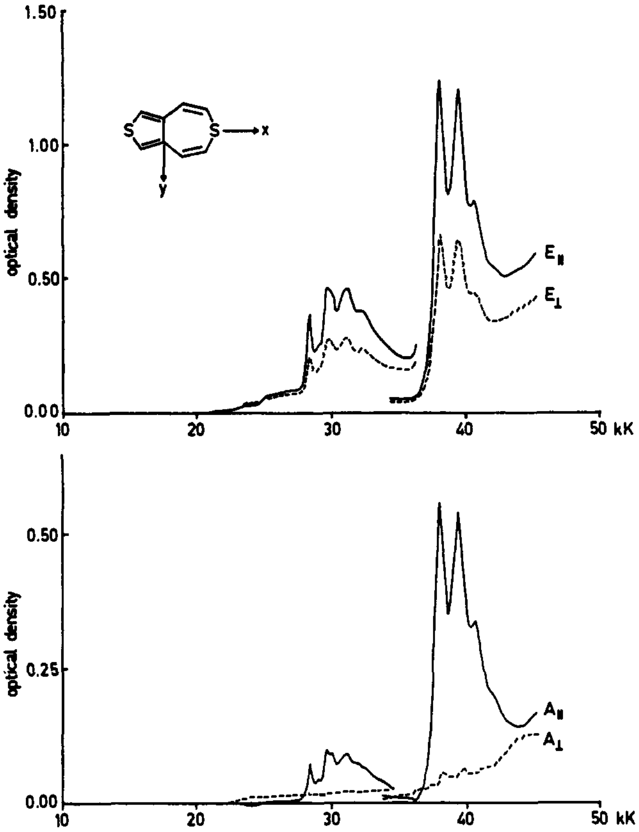

Figure 2. (a) (top) Dichroic spectra of thieno[3,4-*d*]thiepin in polyethylene at room temperature. $E_{\parallel}$ and $E_{\perp}$ are the optical densities for absorption of light polarized parallel and perpendicular to the stretching direction. For the spectral region 35–45 kK, the concentration was reduced by a factor of 4. (b) (bottom) Computer corrected dichroic spectra of thieno[3,4-*d*]thiepin. For the meaning of $A_{\parallel}$ and $A_{\perp}$ see text.

$$A_{\parallel}(\lambda) = E_{\parallel}(\lambda) - d_{\parallel}E_{\perp}(\lambda)$$

$$A_{\perp}(\lambda) = E_{\perp}(\lambda) - d_{\perp}E_{\parallel}(\lambda)$$

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(17) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **21**, 368 (1971); I. H. Hillier and V. R. Saunders, *Chem. Phys. Lett.*, **4**, 471 (1970); D. T. Clark and D. R. Armstrong, *Chem. Commun.*, 319 (1970).

where $A_{\parallel}(\lambda)$ and $A_{\perp}(\lambda)$ are the absorbances of **1** parallel and perpendicular to the long molecular axis. Figure 2b shows the "reduced" spectra,[9] $A_{\parallel}(\lambda)$ and $A_{\perp}(\lambda)$, with values of $d_{\parallel} = 1.0$ and $d_{\perp} = 0.5$. The parameter $d_{\parallel}$ was chosen so that $A_{\parallel}$ did not show any absorption in the region of the first transition of the electronic spectrum (22–28 kK). In addition, the fine structure of the first band vanished completely.

The detection of a transition polarized perpendicular to the long axis of the molecule in the region 36–42 kK, which is hidden under the intense parallel polarized absorption band, depends on the choice of the parameter $d_{\perp}$. We used a value of 0.50 since an increase to 0.52 is sufficient to cause a reversion of the fine structure of the fourth band (see Table II) in the sense that the maxima of the $A_{\parallel}$ spectrum at 37.9 and 39.3 kK are converted into minima of the $A_{\perp}$ spectrum. As can be seen, the first band (22.1 kK) consists of a transition polarized perpendicular to the long molecular axis. The second band arises from a transition polarized parallel to the twofold axis (28.0 kK). The third band consists of two transitions: an intense transition (38.0 kK) polarized parallel and a weak transition (36.5 kK) polarized perpendicular to the long axis of the molecule.

In this assignment we have attempted to postulate as few independent electronic transitions as possible. In addition to the regularities in the fine structure, we considered approximate mirror image symmetry between the fluorescence spectrum and the first electronic absorption band.

The experimental results are summarized in Table II.

Discussion of the Electronic Spectrum of 1

We start by considering the HMO scheme of Figure 3. At the left are shown the π molecular orbitals of **4** derived from an EH calculation[6,13] assuming a bond length of 1.4 Å for the C–C bonds and a C–H bond distance of 1.1 Å. The π levels of a planar **1** can be derived from those of **4** by introducing a perturbation at positions 2 and 6. The energies of levels which are antisymmetric (a_2) with respect to a plane of symmetry through atoms 2 and 6 will stay approximately constant, while the levels which are symmetric (b_2) will be lowered due to the higher ionization potential of the sulfur 3p orbitals compared with the carbon 2p orbitals. Due to this perturbation, the energy of the antibonding orbital χ_{-1} of **4** is lowered and lies relatively close to the highest occupied orbital (χ_1) of **4**. The resulting scheme suggests that four transitions of low energy should involve the following excited configurations with increasing energy: $\pi_{-1} \leftarrow \pi_1(B_1)$; $\pi_{-2} \leftarrow \pi_1$, $\pi_{-1} \leftarrow \pi_2(A_1)$; and $\pi_{-2} \leftarrow \pi_2(B_1)$. Including configuration interaction, the small energy separation between the configurations with A_1 symmetry should yield two states with contributions of both configurations. However, the relatively large energy difference between the configurations of B_1 symmetry (compare Figure 3) should result in two states described by the almost pure configurations $\pi_{-1} \leftarrow \pi_1$ and $\pi_{-2} \leftarrow \pi_2$, respectively.

For a comparison of theoretical predictions with experiment, we have carried out SCF–CI calculations using a PPP model with parameters similar to those suggested by Zahradnik, *et al.*[18]

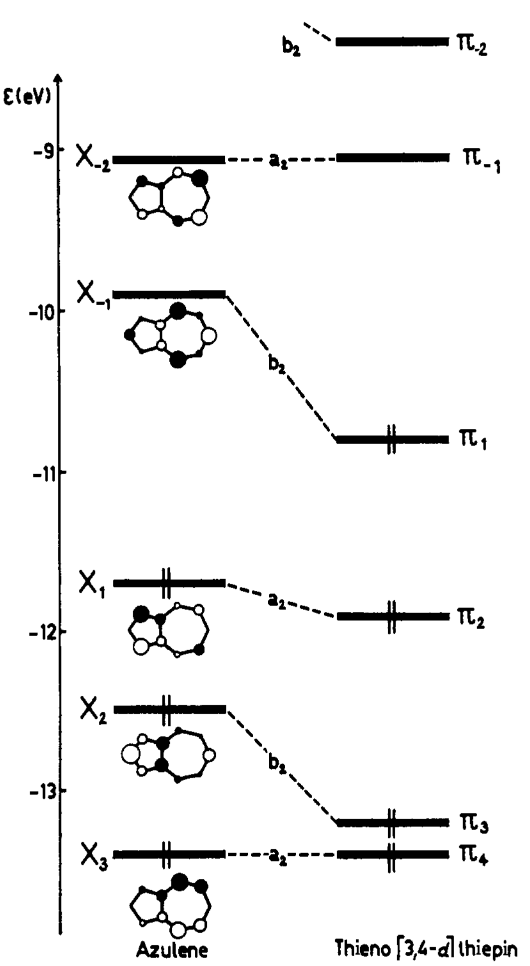

Figure 3. Correlation diagram between the π MO schemes of thieno[3,4-*d*]thiepin and azulene derived from an EH calculation. Only the highest occupied and lowest empty MO's were included.

The appropriate nature of a π model for the calculation of the electronic transitions is justified by the EH and CNDO/2 results. Both methods show that the two highest occupied orbitals of **1** are of π type.

The assumed geometry for the PPP calculations was I. The parameters used were $\Delta U_S = -9$ eV, $\gamma_{SS} = 10.84$ eV, $\beta_{CS} = -1.62$ eV, $U_C = -11.42$ eV, $\gamma_{CC} = 10.84$ eV, and $\beta_{CC} = -2.318$ eV. The two-center integrals were calculated according to the Mataga–Nishimoto[19] approximation. All singly excited configurations were used for the CI treatment. The results of the model calculation are listed in Table II. As can be seen by comparing the experimental and calculated values, the agreement between model and experiment is excellent and confirms our qualitative considerations.

Below is shown the difference $\delta q_\mu = q_\mu^* - q_\mu$ between the net charges[7] of the first excited state q_μ^* and those of the ground state q_μ. The result shows that a transfer of charge from the sulfur atoms to the carbon atoms is associated with the first transition. The bond order[7] changes $\delta p_{\mu\nu} = p_{\mu\nu}^* - p_{\mu\nu}$ between the bond order of the first excited state $p_{\mu\nu}^*$ and the ground state $p_{\mu\nu}$ are indicated in parentheses. The calculated numbers reveal that the bond alternation

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(18) J. Fabian, A. Mehlhorn, and R. Zahradnik, *J. Phys. Chem.*, **72**, 3975 (1968).

(19) N. Mataga and K. Nishimoto, *Z. Phys. Chem.* (*Frankfurt am Main*), **13**, 140 (1957).

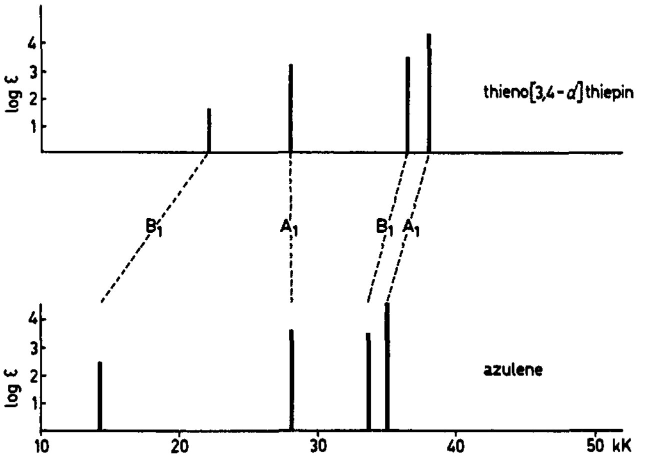
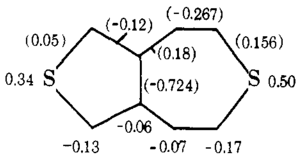


Figure 4. Correlation between the first four $\pi^* \leftarrow \pi$ transitions of thieno[3,4-*d*]thiepin and azulene.



in the first excited state is decreased as compared to the ground state.

Concluding Remarks

The electronic spectrum of **1** can be interpreted with a PPP-CI model. All the models used to calculate the ground-state properties show that although there is a considerable delocalization in **1** the molecule prefers bond alternation. The MO results can be translated into the valence bond structure shown in **1** corresponding to a cyclic thioether. The reactions known so far for thieno[3,4-*d*]thiepin are in agreement with this interpretation.[3,4] For the reasons given previously, it is not valid to compare the ground-state properties of **1** with those of **4**. On the other hand, one is tempted to compare the electronic spectrum of both compounds. The reason for this can be seen from Figure 3. The MO schemes of **1** and **4** are similar insofar as they show two high-lying occupied MO's of a_2 and b_2 symmetry and two low-lying unoccupied MO's of a_2 and b_2 symmetry with approximately the same energy separation. The four transitions due to these four orbitals are compared in Table II and correlated in Figure 4.

In compounds in which the charge distribution in the excited state differs from that in the ground state, an inductive perturbation causes a band shift. In the case of azulene, the shift of the long-wave transition follows a simple pattern, known as Plattners rules,[20] which were explained using first-order perturbation theory.[20-22]

Since there is a formal similarity between the electronic spectra of **1** and **4**, we can predict the shift of the long-wave transition upon methyl substitution.

Inasmuch as a methyl substitution product of **1** is not known, we assumed the same parameters as for azulene ($\Delta c_1^2 = c_1(\chi_{-1})^2 - c_1(\chi_1)^2 = 812$ cm^{-1}.[20] With these results we obtain the following values: position 1 or 3, +137 cm^{-1}; position 4 or 8, +32 cm^{-1}; and position 5 or 7, +400 cm^{-1}. The substitution by a methyl group yields a hypsochromic shift in all positions.

Acknowledgment. The measurements were performed with the skillful technical assistance of Miss E. Rommel. This work was supported by the Schweizerischer Nationalfonds Project No. SR 2.477.71 and in part by a grant from the National Science Foundation (D. O. C.). In addition we wish to thank Sandoz AG (Basel) for computer time, and D. O. C. wishes to acknowledge a 1970–1971 Guggenheim Fellowship for work at the University of Basel.

(20) E. Heilbronner, in "Non Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience, New York, N. Y., 1959, p 171 ff.

(21) H. C. Longuet-Higgins and R. G. Sowden, *J. Chem. Soc.*, 1404 (1952).

(22) C. A. Coulson, *Proc. Phys. Soc. London, Sect. A*, **65**, 933 (1952).