Why Is 1,6,6aλ⁴-Trithiapentalene Colored?

**Jens Spanget-Larsen,***,‡ **Chen Erting,**†,⊥ **and Irene Shim**⊥

*Contribution from the Department of Life Sciences and Chemistry, Roskilde University,
P.O. Box 260, DK-4000 Roskilde, Denmark, and Department of Chemistry and Chemical
Engineering, The Engineering Academy of Denmark, Building 375, DK-2800 Lyngby, Denmark*

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Abstract: Low-energy excited electronic states of the title compound are studied by quantum chemical configuration interaction (CI) calculations, using the semiempirical AM1 model and *ab initio* Hartree−Fock theory. Strong CI is predicted between excited electronic configurations of $\pi-\pi^*$ and $\sigma-\sigma^*$ character, which explains the failure of π-electron calculations to reproduce the observed absorption spectrum. The computed transitions are compared with the measured linear dichroism (LD) absorption spectrum of TTP in stretched polyethylene. The long-axis polarized transition observed at 20 900 cm⁻¹, giving rise to the orange color of the compound, can be explained as the result of strong interaction between the HOMO−LUMO ($\pi-\pi^*$) and the SHOMO−SLUMO ($\sigma-\sigma^*$) configurations. The σ and σ^* orbitals involved in the transition are associated with the unique, electron-rich three-center bonding of the sulfur atoms.

1. Introduction

The electronic and molecular structure of the title compound (TTP) has been investigated for several decades because of the peculiar type of bonding in this heterocyclic ring system.[1−5] It is now well established that TTP can be considered as a naphthalene-like 10π-electron ring system with C_{2v} symmetrical equilibrium structure, incorporating a unique linear arrangement

TTP
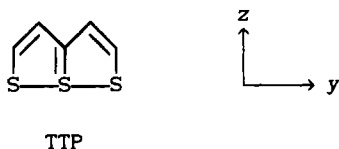
of three sulfur atoms with S−S bond lengths close to 2.35 Å.[6−9] Theoretical investigations of the electronic ground state of TTP have been performed at various levels of sophistication, but the nature of the excited states has not been resolved. In particular, the low-lying singlet state responsible for the electronic transition close to 21 000 cm⁻¹, giving rise to the orange color of the compound, is not well understood. The transition is long-axis (y) polarized[2,10] and is generally believed to be of $\pi-\pi^*$ type, but extensive π-electron calculations fail to reproduce this transition. In fact, Gleiter *et al.*[2,10] concluded that the observed UV−vis polarization spectra were consistent with the results

of PPP calculations only under the assumption of a strongly asymmetric TTP geometry, corresponding to a dithiolylidene-thione structure. Similar conclusions were reached on the basis of CNDO/S-CI calculations.[11]

In this communication, we investigate low-energy electronic transitions in TTP by semiempirical AM1-CI calculations and by *ab initio* Hartree−Fock−CI theory. In addition, for optimal comparison with the computed transitions, we have remeasured the UV−vis linear dichroic (LD) absorption spectrum of TTP.

2. Experimental Section

A sample of TTP was prepared by reacting 1,2-dithiole-3-thione with propynoic acid and thioacetamide as described by Davy and Vialle.[12] The starting material 1,2-dithiole-3-thione was obtained by treatment of 1,1,3,3-tetramethoxypropane with P_4S_{10}.[13] The TTP product was purified by sublimation;[12] the spectroscopic purity of the sample was confirmed by comparison of its absorption spectrum with literature data.[2]

The UV−vis linear dichroism (LD) absorption spectrum of TTP partially oriented in uniaxially stretched polyethylene was measured at room temperature on a Shimadzu MPS-2000 spectrophotometer as previously described.[14] The observed LD spectra were analyzed according to the TEM procedure;[15] the partial absorption curves shown in Figure 1 were obtained with the orientation factors[15] $K_y = 0.53$ and $K_z = 0.3$. The resulting polarization data are in agreement with those published by Gleiter and Gygax.[2] Oscillator strengths f were estimated by comparison with the absorption spectrum observed in cyclohexane solution.[2]

3. Calculations

Excited electronic states of TTP were calculated by limited configuration interaction (CI), using the AM1 model[16] and *ab initio* Hartree−Fock theory.[17] Two calculations were performed

† Permanent address: Shenyang Institute of Chemical Technology, China (PRC).
‡ Roskilde University.
⊥ The Engineering Academy of Denmark.
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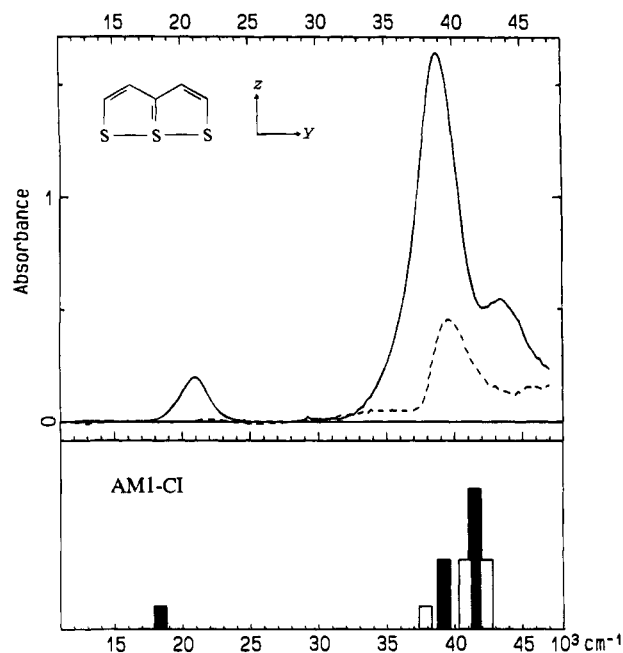
Figure 1. (Top) Partial absorbance curves for $1,6,6a\lambda^4$-trithiapentalene (TTP) in stretched polyethylene. The full curve indicates y-polarized, the dashed curve z-polarized intensity. (Bottom) Graphical representation of calculated transitions with oscillator strength $f > 10^{-2}$. Black and white bars indicate y- and z-polarized transitions, and the height of the bars corresponds to different f values ($f < 0.1$, $0.1 < f < 0.4$, $0.4 < f$).

with each theoretical procedure: One with an optimized molecular geometry, and one with a geometry derived from observed structural data.[6-8]

The AM1 calculations were carried out with the MOPAC[18] and HyperChem[19] software packages. Optimization of all geometrical parameters resulted in a C_{2v} symmetrical ground state structure with predicted heat of formation = 23.78 kcal/mol. The predicted geometry is in fair agreement with the experimental structure[6-8] (the predicted S-S distance is 7% too small, however). The calculated frontier molecular orbital (MO) amplitudes[19] are indicated in Figure 2. Excited electronic states were calculated by CI between the singly excited configurations generated by excitation from the six highest occupied to the six lowest unoccupied MOs.[19] Calculated vertical S_0-S_n transition are shown schematically in Figure 1. Table 1 includes detailed results for the three transitions with lowest energy.

The Hartree-Fock calculations were performed with Gaussian 90[20] and Gaussian 92[21] using the standard basis set 6-31G but with inclusion of $3d$ polarization functions for sulfur, 6-31G-(*). Complete optimization of the geometry of TTP was not attempted;[5] the structure was optimized within the constraints of C_{2v} symmetry, yielding a total energy of $-1384.055\ 280\ 9$ au. The calculated molecular geometry, with an S-S distance

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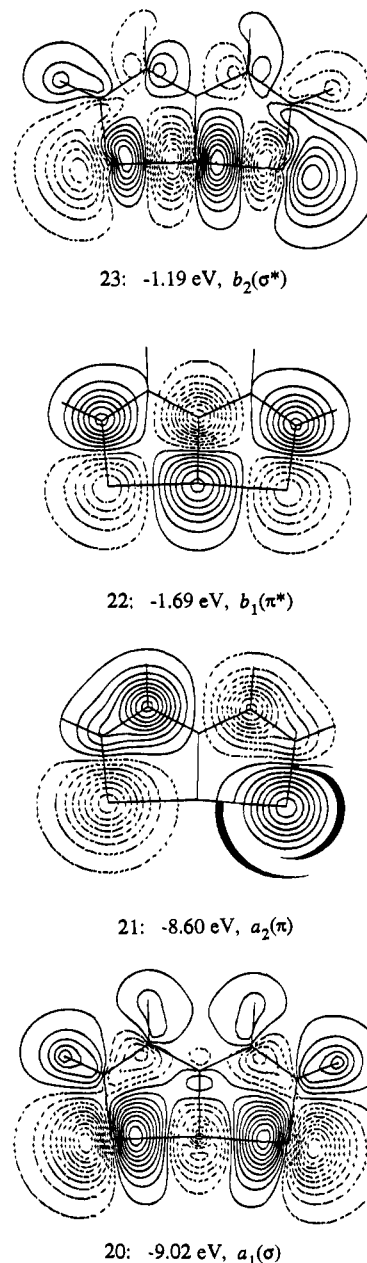

23: -1.19 eV, $b_2(\sigma^*)$

22: -1.69 eV, $b_1(\pi^*)$

21: -8.60 eV, $a_2(\pi)$

20: -9.02 eV, $a_1(\sigma)$

Figure 2. AM1 orbital amplitude contour diagrams of the two highest occupied MOs (SHOMO, HOMO) and the two lowest unoccupied MOs (LUMO, SLUMO) of $1,6,6a\lambda^4$-trithiapentalene (TTP, optimized geometry). The π-type MOs are plotted in a plane 0.7 Å above the molecular plane.

equal to 2.387 Å, is close to the experimental structure. The first three S_0-S_n transitions calculated by the CIS procedure implemented in Gaussian 92[21] are given in Table 1; oscillator strengths were calculated within the dipole length formalism.

4. Results and Discussion

The visible absorption band of TTP has a maximum at 20 900 cm^{-1}, is medium intense ($f \simeq 0.06$), and y-polarized, corresponding to transition to a state of B_2 symmetry. Contrary to earlier calculations, limited CI calculations within the AM1 model successfully predicted this transition (Table 1): The lowest $^1B_2$ state ($1\ ^1B_2$) is predicted at 18 300 cm^{-1}, with an oscillator strength $f = 0.05$. The main contribution (76%) to the CI wave function is the HOMO-LUMO $\pi-\pi^*$ configuration but with a large admixture (21%) of the SHOMO-SLUMO $\sigma-\sigma^*$ configuration.

Table 1. Observed and Calculated Low-Energy $S_0 \rightarrow S_n$ Transitions for 1,6,6aλ⁴-Trithiapentalene (TTP): Wavenumbers $\tilde{\nu}/(10^3$ cm$^{-1})$, Oscillator Strengths f, Polarization Directions, Term Symbols, and Leading Contributions to the Calculated CI Wave Functions[e]

	$\tilde{\nu}$	f	pol	term	leading contributions[a]
obsd	20.9	0.06	y	$^1B_2$	
AM1-CI[b]	18.3	0.0474	y	$1\ ^1B_2$	76%($\pi-\pi^*$), 21%($\sigma-\sigma^*$)
	19.2	0.001	x	$1\ ^1B_1$	62%($\sigma-\pi^*$), 38%($\pi-\sigma^*$)
	21.5	0.0046	x	$2\ ^1B_1$	62%($\pi-\sigma^*$), 38%($\sigma-\pi^*$)
AM1-CI[c]	16.7	0.0463	y	$1\ ^1B_2$	77%($\pi-\pi^*$), 20%($\sigma-\sigma^*$)
	18.1	0.0001	x	$1\ ^1B_1$	82%($\sigma-\pi^*$)
	20.9	0.0022	x	$2\ ^1B_1$	82%($\pi-\sigma^*$)
6-31G(*)-CIS[d]	25.9	0.0268	y	$1\ ^1B_2$	72%($\pi-\pi^*$), 25%($\sigma-\sigma^*$)
	26.4	<10^{-4}	x	$1\ ^1B_1$	98%($\sigma-\pi^*$)
	36.2	0.0009	x	$2\ ^1B_1$	95%($\pi-\sigma^*$)
6-31G(*)-CIS[c]	26.7	0.0336	y	$1\ ^1B_2$	73%($\pi-\pi^*$), 24%($\sigma-\sigma^*$)
	26.9	<10^{-4}	x	$1\ ^1B_1$	98%($\sigma-\pi^*$)
	37.6	0.0009	x	$2\ ^1B_1$	96%($\pi-\sigma^*$)

[a] σ, π, π^*, σ^* indicate the MOs SHOMO, HOMO, LUMO, and SLUMO (e.g., Figure 2). [b] Fully optimized AM1 ground state geometry. [c] Geometrical parameters derived from experimental data.[6-8] [d] Ground state geometry optimized within the constraints of C_{2v} symmetry. [e] For experimental and calculational details, see sections 2 and 3 of this paper.

The four MOs most strongly involved in the low-energy transition are indicated in Figure 2. The $a_2(\pi)$ and $b_1(\pi^*)$ orbitals are similar to the corresponding MOs of naphthalene, but the $a_1(\sigma)$ and $b_2(\sigma^*)$ orbitals are unique for TTP. These MOs are highly localized on the sulfur atoms and are largely composed of $3p_y$ atomic orbitals. Simplified versions of these MOs have been analyzed by Gleiter and Gygax in a detailed discussion of the "electron-rich three-center bond" associated with the three sulfur atoms in TTP.[2]

In the AM1 model, the calculated excitation energies for transitions to SCF states composed of each of the two dominant configurations contributing to the $1\ ^1B_2$ state are equal to 3.14 and 4.96 eV, corresponding to the wavenumbers 25 300 cm^{-1} ($\pi-\pi^*$) and 40 000 cm^{-1} ($\sigma-\sigma^*$). Transitions to both excited configurations are strongly optically allowed; the individual $\pi-\pi^*$ and $\sigma-\sigma^*$ transitions moments M_y are 7.9 and 9.7 D. If the $\pi-\pi^*$ configuration were the only contribution to the $1\ ^1B_2$ state, the predicted oscillator strength for the transition would be $f = 0.74$. But the crossterm corresponding to the interaction between the two configurations amounts to $-11\ 300$ cm^{-1}, leading to a 2 × 2 CI matrix

$$\begin{Bmatrix} 25\ 300 & -11\ 300 \\ -11\ 300 & 40\ 000 \end{Bmatrix}$$

with eigenvalues $\tilde{\nu}$ and eigenfunctions Φ

$$\tilde{\nu}_1 = 19\ 200\ \text{cm}^{-1}, \quad \Phi_1 = 0.88(\pi-\pi^*) - 0.48(\sigma-\sigma^*)$$
$$\tilde{\nu}_2 = 46\ 200\ \text{cm}^{-1}, \quad \Phi_2 = 0.48(\pi-\pi^*) + 0.88(\sigma-\sigma^*)$$

As a result of the interaction with $\sigma-\sigma^*$, the $1\ ^1B_2$ state is

thus lowered by more than 6000 cm^{-1}, from 25 300 to 19 200 cm^{-1}, corresponding to a shift from the near-UV to the Vis region. At the same time, the admixture of $\sigma-\sigma^*$ character leads to a large reduction of the computed transition moment, from 7.9 to 2.3 D, resulting in the prediction of a medium intense transition ($f = 0.05$).

The nature of the predicted $1\ ^1B_2$ state is essentially unaffected by further extension of the CI expansion and by minor variation of the molecular geometry (Table 1). As a result of the occupancy of the S–S antibonding π^* and σ^* orbitals (Figure 2), a significant weakening of the S–S bonds is expected in this state. This is consistent with the observed photochemical reactivity, involving rupture of one S–S linkage and $cis-trans$ isomerization.[1-4]

The above description of the low-energy $1\ ^1B_2$ state responsible for the color of TTP is supported by $ab\ initio$ results, as shown in Table 1. The CIS calculations predict a $1\ ^1B_2$ state around 26 000 cm^{-1} with oscillator strength $f = 0.03$, in qualitative agreement with experiment. The main contributions to the calculated CI wave function are ~72% HOMO–LUMO $\pi-\pi^*$ and ~25% SHOMO–SLUMO $\sigma-\sigma^*$, consistent with the AM1 result.

The present calculations predict low-lying $^1B_2$ states in the vicinity of the $1\ ^1B_2$ state (Table 1). Transitions to these states correspond to $\sigma-\pi^*$ and $\pi-\sigma^*$ and are out-of-plane (x) polarized. These transitions are predicted to be weak, and there is no indication that they have been observed. In the high-energy region between 35 000 and 45 000 cm^{-1} several strong y- and z-polarized transitions to states of B_2 and A_1 symmetry are predicted by AM1-CI, in qualitative agreement with the observed, overlapping band structures (Figure 1). The predicted transitions are all of a composite nature, involving contributions of both $\sigma-\sigma^*$ and $\pi-\pi^*$ character. The $\sigma-\sigma^*$ contributions tend to dominate; the strongest transition ($f = 0.60$) predicted close to 41 000 cm^{-1} has more than 50% $\sigma-\sigma^*$ character (27% SHOMO–SLUMO). The strong y-polarized peak observed close to 39 000 cm^{-1} ($f \simeq 0.7$) could easily be assigned to this transition. However, the calculated results in this region are sensitive to the CI expansion. A detailed assignment of the complex band structures in the high-energy region must await the results of more accurate theoretical procedures, probably with extended basis sets and large CI expansions including multiply excited configurations.