

THE CHEMICAL STUDY OF PSEUDOAROMATIC COMPOUNDS. IV<sup>1)</sup>

## THE ELECTRONIC STRUCTURE OF TROPOTHIONE

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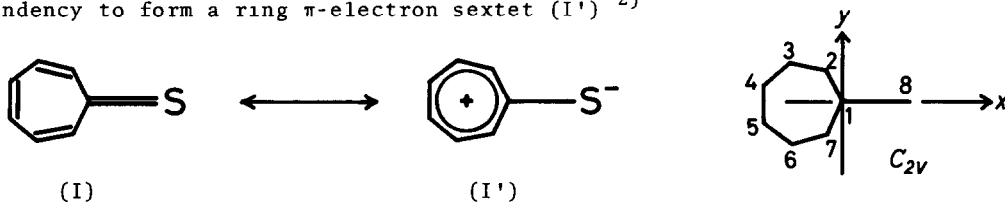
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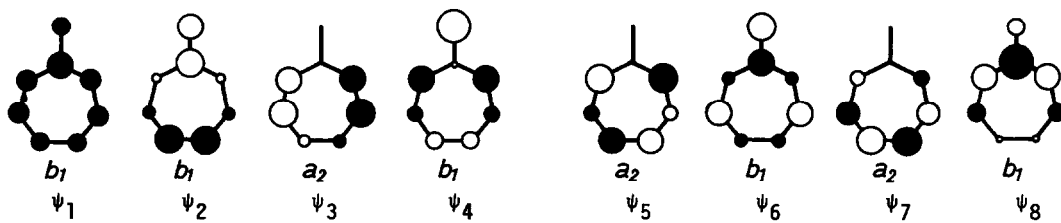
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Tropothione (cycloheptatrienethione) (I) is  $8\pi$ -electron system iso-electronic with and a sulfur-analog of parent tropone, and seems to have the same tendency to form a ring  $\pi$ -electron sextet (I')<sup>2)</sup>



We have recently described the preparation,<sup>3)</sup> structural characterization, and unusual chemical reaction behaviors on cycloadditions of this new troponoid compound.<sup>4)</sup> Although (I) assumes a deep red color, the color fades easily at room temperature because of its thermal instability. This is in contrast with tolerable stability of tropone. In this communication, we wish to discuss the electronic structure and chemical nature of (I) from the view-point of an MO

Fig 1 Relative signs and magnitudes of the SCF MO wave functions of (I).



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Fig. 2 Orbital energies of HMO's and SCF MO's of tropothione (I)

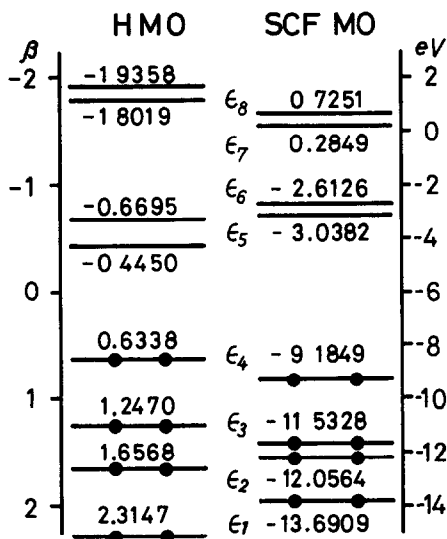
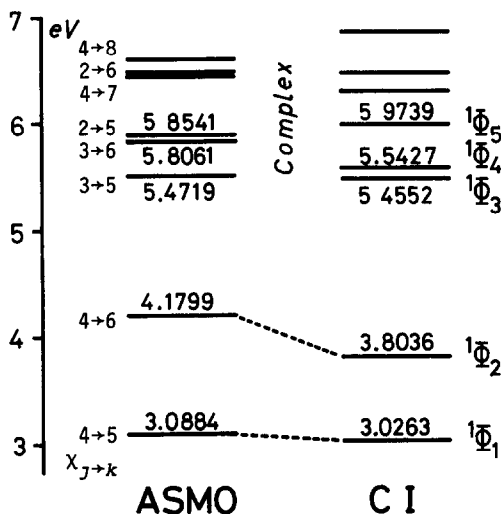
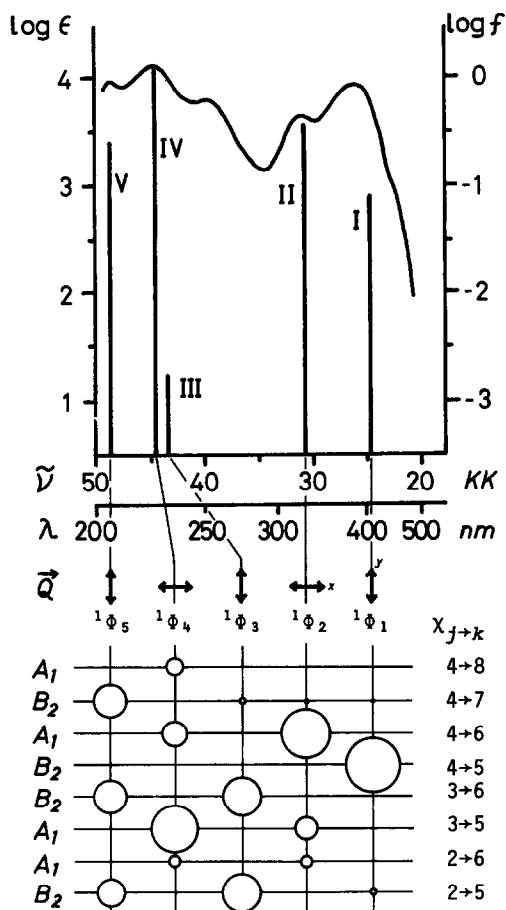


Fig. 3 Excitation energies of (I) with and without taking CI into account



theory In the present HMO and SCF calculations, the following empirical parameters were used  $h=0.9$ ,  $k=1.2$ , and  $\gamma=0.1$ ,<sup>5)</sup>  $r_C=11.42$ ,  $r_S=13.31$ ,<sup>6)</sup>  $a_C=0.58$ ,  $a_S=2.70$ <sup>6)</sup> eV<sup>7)</sup> The geometry of (I) is assumed to be planar, in which  $d_{CC}=1.395$  and  $d_{CS}=1.540$  Å,<sup>8)</sup> because the precise molecular configuration of this compound has been unknown. Therefore we adopted here the variable- $\beta$  approximation<sup>9)</sup> which is not required to specify a precise molecular geometry The orbital energies  $\epsilon_1$ , and graphical representation of the SCF MO wave functions  $\psi_1$  for (I) are shown in Fig. 1 and 2 The electronic absorption spectrum of (I) is shown in Fig. 4. The spectrum was obtained at  $-30^\circ\text{C}$ , immediately after the isolation in a thermostated room ( $-10^\circ\text{C}$ ). In this figure we used an empirical relationship<sup>10)</sup> assuming that  $\log \epsilon = 4 + \log f$ , and the calculated polarization directions  $\vec{Q}$  are also given The calculated transition energies described in Fig. 3 and 4 are in good agreement with the observed band maxima That is, the calculated first, second, third, and fourth electronic transitions may correspond to the observed  $\lambda_{\text{max}}$  (MeOH) 382, 316, 255, and 225 nm bands, respectively. The main contributor in the first excited state CI wave function is  $\chi_{4-5}$ . The electronic transition from  $\psi_4$  to  $\psi_5$  results in a charge migration from the sulfur atom to the seven membered ring (Fig. 1) Hence, this transition is regarded as intramolecular charge-

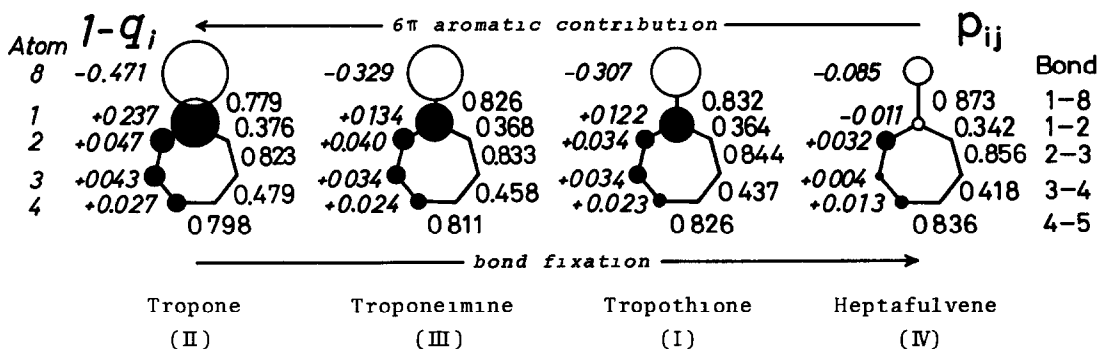
Fig 4 11) Comparison of calculated transition energies and observed absorption spectrum for (I).



transfer type. On the other hand, the main contributors in the second and fourth excited states are respectively  $\chi_{4-6}$  and  $\chi_{3-5}$ , and these two transitions are localized in the seven membered ring. Because, the transition  $\psi_4 \rightarrow \psi_6$  does not result in an appreciable charge migration from the sulfur to the seven membered ring, and in the  $\psi_3 \rightarrow \psi_5$  transition the charge migration is strictly restricted within the ring (Fig. 1)

The calculated charge densities  $q_i$  and bond orders  $p_{ij}$  are compared with those of analogs tropone (II), troponeimine (III), and heptafulvene (IV),<sup>12)</sup> in Fig. 5. The magnitudes of the negative charge reside on the exo-ring atoms increase in order of (II) > (III) > (I) > (IV), that is to say, the magnitudes of positive charge reside in the seven membered ring increase in the same order, while, the bond fixations decrease in order of (II) < (III) < (I) < (IV). This means

Fig. 5 Comparison of charge densities and bond orders of (I) with its analogs.



that the contribution of  $6\pi$  dipolar structure (I') in tropothione is considerably small compared with that in tropone. Consequently, we may conclude that tropothione (I) shows polyolefinic characters rather than aromatic, and behaves unusually in chemical reactions compared with the parent tropone.

Detailed discussions will be shown in our full paper.

#### REFERENCES AND FOOTNOTES

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- 11) Lower part of this figure is given by a graphical representation of the contributions of the individual configurations which are shown as circles of diameter  $c_{1m}$ , to the CI wave functions  ${}^1\Phi_1 = \sum_m c_{1m} (\chi_{j \rightarrow k})_m$ , since the  $\Phi_1$ 's are normalized.
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