

Electron-spectroscopic Evidence for an Unsymmetrical Structure for 2,5-Dimethylthiathiophthen¹

By ROLF GLEITER* and DIETER SCHMIDT

(Physikalisch-Chemisches Institut der Universität, Basel, Switzerland)

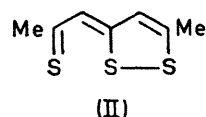
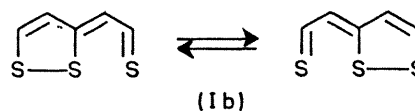
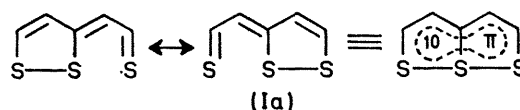
and HANS BEHRINGER

(Organisch-Chemisches Institut der Universität München)

Summary The electronic polarization spectrum of 2,5-dimethylthiathiophthen (II) suggests an unsymmetrical structure of the molecule in its electronic ground state.

INVESTIGATIONS so far have not allowed an unequivocal decision to be made between structures (Ia) and (Ib) for thiathiophthen (I).^{2,3} (Ia) describes a situation where the molecule has C_{2v} symmetry in its equilibrium conformation, while (Ib) corresponds to a double minimum situation[†] where the molecules at their energy minimum have only C_s symmetry. To obtain additional information concerning the structure of (I) and related molecules, the band polarizations of their electronic spectra have been compared with the results of model calculations.

Figure 1 shows the electronic spectrum of 2,5-dimethylthiathiophthen (II) measured by the stretched film technique.⁴ The curves correspond to the absorption spectrum measured with polarized light parallel and perpendicular to the y axis of the molecule. (If the molecule had C_{2v}



symmetry the x axis would be parallel to the C_2 axis). In constructing the curves in Figure 1 we have assumed that

[†] The equilibrium (Ib) is also consistent with the n.m.r. results obtained for symmetrically substituted thiathiophthens (II) if the n.m.r. time scale is large compared with the rate constant for the interconversion of the two forms.

the first band, which is polarized parallel to the long axis (y) of the oriented molecules, does not contain a perpendicular component. Since we believe that the molecule (II)

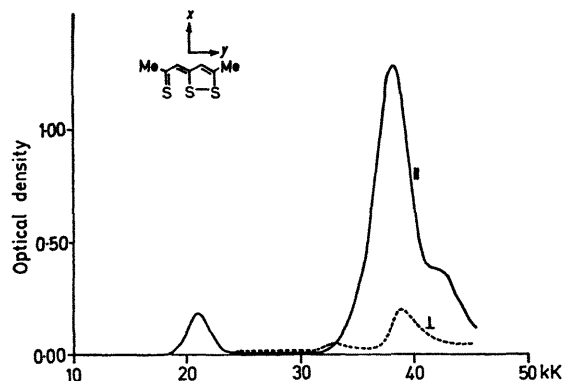


FIGURE 1. Electronic spectrum of 2,5-dimethylthiathiophthen (II) in a polyethylene film measured with light parallel (||) (—) and perpendicular (⊥) (---) to the y axis. The spectrum is computer corrected for the non-ideal orientation of the molecules in the stretched film.

has C_s symmetry this assumption is only approximately true.

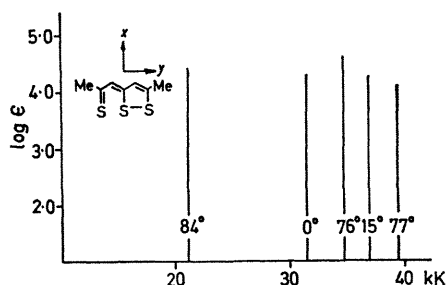
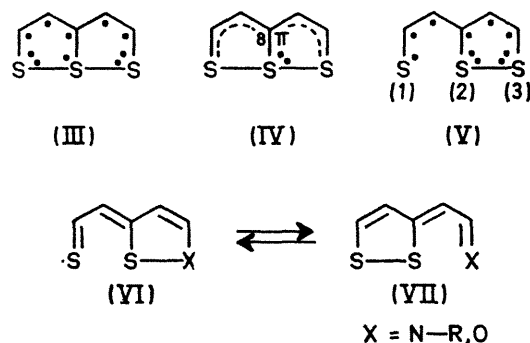


FIGURE 2. Calculated electronic spectrum of 2,5-dimethylthiathiophthen (II) assuming model (V). The numbers in degrees indicate the angle between the x axis and the calculated direction of the transition moment.

In addition to the polarization of each band our measurements also reveal that the spectrum in the interval 30–45 kK is composed of four overlapping bands. Theory predicts that all these are $\pi^* \leftarrow \pi$ in character.

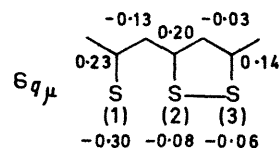
To interpret these results we have carried out SCF-CI calculations of the PPP-type for the models (III),⁵ (IV), and (V) using only p orbitals as a basis. We have varied the parameters for the hetero-atoms independently starting with parameters suggested for similar sulphur compounds by other authors.⁶ The assumed geometry for (III) and

(IV) was that reported in the literature.⁷ For (V) we used the same geometry as for (III) and (IV) except for a S(2)–S(3) bond length of 2.05 Å. The parameters of the



sulphur atoms have been varied within the following range: $\Delta\alpha(\ddot{S}) = 0$ to -2 , $\Delta\alpha(\ddot{S}) = -5$ to -10 , $\beta(S-S) = -0.5$ to -2 , $\beta(C-S) = 1.1$ to 2.4 , and $\gamma(SS) = 9$ to 11 eV. In the framework of this approximation, our experimental results can only be explained if the equilibrium structure corresponds to the unsymmetrical model (V). The parameters used for the results shown in Figure 2 were essentially those suggested by the Prague group.⁶ As can be seen from Figure 2 the sequence of polarization and the positions of the bands correspond reasonably well with experiment.

The experimentally determined sequence of the polarization of the individual π -bands demands an asymmetrical



model which in turn leads to the following prediction. The first $\pi_{-1}^* \leftarrow \pi_1$ transition (band at 20.7 kK) must be accompanied by the redistribution of charge $\delta q = q_{\mu}^* - q_{\mu}$, where q_{μ}^* and q_{μ} are the charge densities in the first excited and the ground-state, respectively. This explains the shift towards higher energy ($\bar{\nu}$ ca. 2.5 kK) when the sulphur atom S(1) is substituted by an arylimino-group or an oxygen atom.⁸ This shift can be used as a criterion for the deduction of the structure of different tautomers such as (VI) [$\bar{\nu}_{\max}(\pi_{-1}^* \leftarrow \pi_1)$ ca. 19.6–21.3 kK] or (VII) [$\bar{\nu}_{\max}(\pi_{-1}^* \leftarrow \pi_1)$ ca. 22.2–23.3 kK].

We thank Sandoz AG (Basel) for computer time and Ciba-Geigy AG (Basel) for their support.

(Received, December 29th, 1970; Com. 2249.)

¹ For previous paper in the series see F. Gerson, R. Gleiter, J. Heinzer, and H. Behringer, *Angew. Chem.*, 1970, **82**, 294; *Angew. Chem. Internat. Edn.*, 1970, **9**, 306.

² Recent reviews: E. Klingsberg, *Quart. Rev.*, 1970, **23**, 537; N. Lozac'h *Adv. Heterocyclic Chem.*, in the press.

³ R. Gleiter and R. Hoffmann, *Tetrahedron*, 1968, **24**, 5899; D. Leaver and D. M. McKinnon, *Chem. and Ind.*, 1964, 461; J. H. van den Hende and E. Klingsberg, *J. Amer. Chem. Soc.*, 1966, **88**, 5045.

⁴ E. W. Thulstrup and J. H. Eggers, *Chem. Phys. Letters*, 1968, **1**, 690.

⁵ R. A. W. Johnstone and S. D. Ward, *Theor. Chim. Acta*, 1961, **14**, 420.

⁶ R. Zahradnik, *Fortschr. Chem. Forsch.*, 1968, **10**, 1; J. Fabian, A. Mehlhorn, and R. Zahradnik, *J. Phys. Chem.*, 1968, **72**, 3975; J. Fabian, K. Fabian, and H. Hartmann, *Theor. Chim. Acta*, 1968, **12**, 319.

⁷ F. Leung and S. C. Nyburg, *Chem. Comm.*, 1969, 137.

⁸ H. Behringer and J. Falkenberg, *Chem. Ber.*, 1969, **102**, 1580.