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Intramolecular Charge-transfer Absorption Spectra of Tetracyanotetrathiafulvalene

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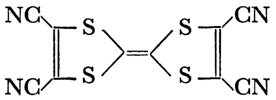
The electronic spectrum and structure of tetracyanotetrathiafulvalene have been investigated by the ASMO-SCF-CI method, in which the 3d orbitals of sulfur atoms are taken into account. The calculated results showed that the absorption band at the longest wavelength can be interpreted in terms of intramolecular charge-transfer.

In preceding papers,[1,2] we reported the syntheses of several electronegative substituted tetrathiafulvalenes such as tetracyanotetrathiafulvalene (**1**).



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The compound **1** is composed of two parts, that is, the electron-donating part (the central electron-rich olefin moiety) and the electron-accepting part (the dicyanoethylene moiety). It seems reasonable to expect the appearance of an intramolecular charge-transfer[3] band in the electronic spectrum of **1**. In the present work, experimental and theoretical investigations of the electronic spectrum of **1** were carried out, and the absorption band at the longest wavelength (502 nm in benzene) was shown to be due to an intramolecular charge-transfer transition.

In addition, the electronic structure of **1** in the ground state will be discussed and compared with that of the parent tetrathiafulvalene (TTF).

Experimental

The compound, **1**, was prepared from 4,5-dicyano-1,3-dithiole-2-thione in the presence of triphenyl phosphite; mp 264—265 °C (dec.).[2] The ultraviolet and visible absorption spectra of **1** were recorded on a Hitachi EPS-3T spectrophotometer in benzene, dichloromethane, acetonitrile, and methanol. The observed spectra were analyzed by assuming Gaussian curves for the absorption bands. Three absorption bands thus obtained and their molecular extiction coefficients are presented in Table 1.

Calculation

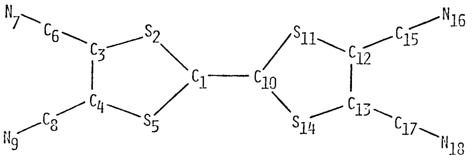
The calculations were carried out by the use of the semiempirical ASMO-SCF-CI method involving all valence electrons.[4] The sulfur atom has not only 3s and 3p, but also 3d orbitals in the valence shell. As regards unsubstituted TTF, it was pointed out that the inclusion of sulfur 3d orbitals is necessary to explain the relative bond lengths of the two carbon-carbon double bonds obtained from the X-ray analysis of TTF.[5] Accordingly, in this calculation the 3d orbitals of the sulfur atom were taken into account.

The overlap integrals were calculated using Slater-type atomic orbitals, where the orbital exponents are taken from Clementi and Raimondi.[6] The one-center exchange integrals were estimated from the Slater-Condon parameters evaluated by Hinze and Jaffé.[7] The Slater exponents (ζ_r), valence-state ionization potentials (I_r) of atomic orbitals, one-center Coulomb integrals $(rr|rr)$, and one-center exchange integrals $(rr'|rr')$ used in the present calculations are listed in Table 2.

The structural model for **1** is shown in Fig. 1. The molecule is assumed to have D_{2h} symmetry; the interatomic distances are taken from the X-ray data of TTF[5] and the book by Pople and Beveridge.[8]

The MO energies for each of the six occupied and vacant levels, and their approximate descriptions are shown in Table 3, although the LCAO coefficients of the MO's are not given.

In calculating the electronic transition energies, the 36 lowest singly-excited configurations were considered. The calculated singlet transition energies



$\angle S_5C_1S_2 = 114.5°$ $C_1\text{-}C_{10} = 1.349$ Å
$\angle C_1S_2C_3 = 94.4°$ $C_1\text{-}S_2 = 1.757$ Å
$\angle S_2C_3C_4 = 118.3°$ $S_2\text{-}C_3 = 1.731$ Å
$\angle C_6C_3C_4 = 120.0°$ $C_3\text{-}C_4 = 1.314$ Å
$C_3\text{-}C_6 = 1.450$ Å
$C_6\text{-}N_7 = 1.160$ Å

Fig. 1. Geometries and bond lengths of tetracyanotetrathiafulvalene.

TABLE 1. ELECTRONIC SPECTRA OF TETRACYANOTETRATHIAFULVALENE

Solvent	A-band		B-band		C-band	
	λ_{max} (nm)	($\log \varepsilon_{max}$)	λ_{max} (nm)	($\log \varepsilon_{max}$)	λ_{max} (nm)	($\log \varepsilon_{max}$)
Benzene	502	(3.30)	328	(4.18)		
Dichloromethane	500	(3.36)	326	(4.20)	262	(4.41)
Acetonitrile	492	(3.30)	323	(4.16)	261	(4.33)
Methanol	480	(3.30)	320	(4.04)	261	(4.20)

TABLE 2. SLATER EXPONENTS (ζ_r) AND VALENCE STATE IONIZATION POTENTIALS (I_r)[a] OF ATOMIC ORBITALS AND ELECTRON REPULSION INTEGRALS[a]

		ζ_r	I_r	(rr|rr)[b]	(rr'|rr')[c]
C	2s	1.6083	−20.01	12.10	(2s2p|2s2p) =2.30
	2p	1.5679	−11.27	10.93	(2p2p'|2p2p')=0.54
N	2s	1.9237	−26.92	12.87	(2s2p|2s2p) =2.99
	2p	1.9170	−14.42	11.88	(2p2p'|2p2p')=0.77
S	3s	2.1223	−20.08	8.54	(3s3p|3s3p) =1.02
	3p	1.8273	−13.32	9.82	(3p3p'|3p3p')=0.55
	3d	0.8400	−3.67	5.90	

a) Energy in eV. b) $(rr|rr)=I_r-E_r$. c) Ref. 7.

TABLE 3. ENERGIES AND APPROXIMATE DESCRIPTION OF THE MOLECULAR ORBITALS OF TETRACYANOTETRATHIAFULVALENE

MO No.	Energy / eV	Symbol	Description	D_{2h} Symmetry label
12	−3.13	σ		B_{3u}
11	−3.14	π	Delocalized over bridge carbons and sulfur atoms	B_{1g}
10	−3.19	σ		A_g
9	−3.42	σ		A_g
8	−3.53	π	Node at bridge carbons (delocalized over DCNE)[a]	B_{1g}
7	−3.54	π	Node at bridge carbons (delocalized over DCNE)[a]	B_{2u}
6	−10.47	π	Delocalized over TTE[b]	A_g
5	−12.65	π	Delocalized over whole molecule (TTF)	B_{3u}
4	−13.78	π	Node at bridge carbons (delocalized over DTE)[c]	B_{1g}
3	−13.84	π	Node at bridge carbons (delocalized over DTE)[c]	B_{2u}
2	−13.88	σ		B_{2u}
1	−13.98	σ		B_{2u}

a) DCNE: Dicyanoethylene moiety. b) TTE: Tetrathioethylene moiety. c) DTE: Dithioethylene moiety.

and oscillator strengths are presented in Table 4. For comparison, the results calculated both including and neglecting 3d orbitals of sulfur atoms are listed in Table 4.

The electron densities and overlap populations of **1** are also shown, together with those of parent TTF, in Fig. 2.

Discussion

In the calculations of transition energies of organic compounds with a bivalent sulfur atom, the contribution of sulfur 3d orbitals is usually not evaluated and often neglected. However, as seen in Table 4, the transition energies calculated with 3d orbitals were in better agreement with the observed ones than those calculated without 3d orbitals. This evidently suggests that the 3d orbitals of the sulfur atom are essential for the explanation of the electronic structure of the system **1**.

Intramolecular Charge-transfer Absorption Band. According to the calculated results, since the wave function for the excitation at 2.48 eV was composed of V_{6-7} (95%), V_{5-8} (4%), and V_{4-11} (1%), where V_{m-n} represents the singly excited configuration from the m-th level to the n-th (Table 3), the absorption band at 2.48 eV can be assigned to the excitation from the 6th orbital (HOMO) to the 7th (LUMO):

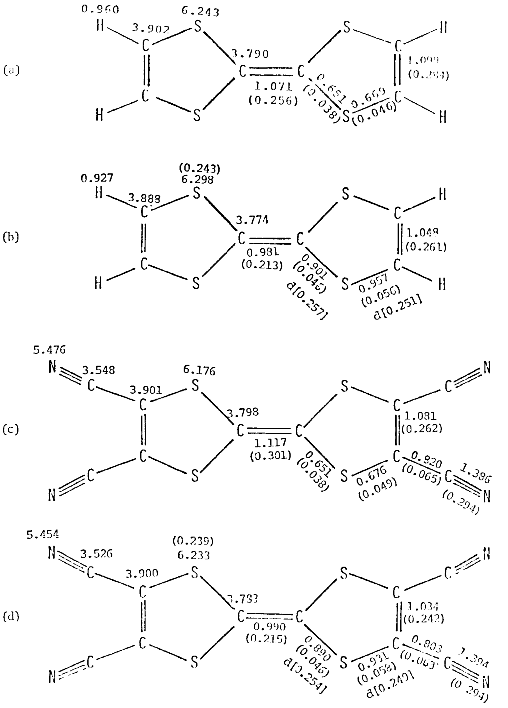


Fig. 2. Electron densities and overlap populations of tetrathiafulvalene (TTF) and tetracyanotetrathiafulvalene. (a): The results of TTF in the case of neglecting d orbitals, (b) the results of TTF in the case of including d orbitals, (c) the results of tetracyanotetrathiafulvalene in the case of neglecting d orbitals, (d) the results of tetracyanotetrathiafulvalene in the case of including d orbitals. The numbers in the parentheses, ( ) and [ ], indicate π- and d-overlap populations, respectively.

$$\begin{aligned}\Phi_6 = &-0.332(\chi_1+\chi_{10})_{2pz} + 0.383(\chi_2+\chi_5+\chi_{11}+\chi_{14})_{3pz}\\ &+0.007(\chi_2+\chi_5-\chi_{11}-\chi_{14})_{3dxz}\\ &+0.113(\chi_2-\chi_5+\chi_{11}-\chi_{14})_{3dyz}\\ &-0.177(\chi_3+\chi_4+\chi_{12}+\chi_{13})_{2pz}\\ &-0.002(\chi_6+\chi_8+\chi_{15}+\chi_{18})_{2pz}\\ &+0.087(\chi_7+\chi_9+\chi_{16}+\chi_{18})_{2pz}\end{aligned} \tag{1}$$

$$\begin{aligned}\Phi_7 = &-0.147(\chi_2+\chi_5+\chi_{11}+\chi_{14})_{3pz}\\ &+0.172(\chi_2-\chi_5+\chi_{11}+\chi_{14})_{3dxz}\\ &-0.091(\chi_2+\chi_5+\chi_{11}+\chi_{14})_{3dyz}\\ &+0.360(\chi_3-\chi_4+\chi_{12}-\chi_{13})_{2pz}\\ &+0.148(\chi_6-\chi_8+\chi_{15}-\chi_{17})_{2pz}\\ &-0.216(\chi_7-\chi_9+\chi_{16}-\chi_{18})_{2pz},\end{aligned} \tag{2}$$

where the m of χ_m corresponds to the number of atoms in Fig. 1.

As can be seen from Eqs. 1 and 2, the large contribution of the tetrathioethylene part ($S_2C{=}CS_2$) to the highest occupied π-MO and that of the dicyanoethylene part (NC–C=C–CN) to the lowest vacant

Table 4. Calculated transition energies[a] and oscillator strengths

ΔE_{obsd}	ASMO-SCF-CI (with d)		ASMO-SCF-CI (without d)		Assignment[b]
	ΔE_{calcd}	f	ΔE_{calcd}	f	
2.48 (3.30)[c]	3.22	0.357	4.07	0.527	$\pi_{\text{TTE}} \to \pi^*_{\text{DCNE}}$
3.54 (4.18)[c]	3.36	0.656	5.80	0.506	$\pi_{\text{TTF}} \to \pi^*_{\text{TTE}}$
4.77	5.41	0.519	8.12	0.347	$\pi_{\text{TTF}} \to \pi^*_{\text{DCNE}}$
	5.75	0.130			$\pi_{\text{DTE}} \to \pi^*_{\text{DCNE}}$
	6.21	0.585			$\pi_{\text{DTE}} \to \pi^*_{\text{TTE}}$

a) Energy in eV. b) TTE: Tetrathioethylene component. DCNE: Dicyanoethylene component. TTF: Tetrathiafulvalene component. DTE: Dithioethylene component. c) The numbers in parentheses indicate $\log \varepsilon_{\max}$, obtained from measurements.

π^*-MO are clearly represented. Thus, this $\pi_{\text{TTE}} \to \pi^*_{\text{DCNE}}$ transition is reasonably understood as the transition from the electron-rich moiety ($S_2C{=}CS_2$) to the electron-deficient moiety (NC–C=C–CN). Consequently, the absorption band at the longest wave length is well interpreted in terms of intramolecular charge-transfer.

A similar result was obtained in the calculations of **1** by the CNDO/2-CI method. If 3d orbitals of the sulfur atom are considered, the longest wave length absorption band can also be reasonably assigned to the $\pi_{\text{TTE}} \to \pi^*_{\text{DCNE}}$ transition.

This interpretation is also supported by the results that the absorption band at the longest wave length exhibits blue shifts upon changing the polarity of solvents from benzene (502 nm) to methanol (480 nm); these results are listed in Table 1.

The strong absorption band at 3.54 eV can be assigned to the excitation from the tetrathiafulvalene moiety to the tetrathioethylene moiety, since the molecular orbitals of the ground and excited states for this transition correspond to π_{TTF} and π^*_{TTE}, respectively (Table 4). Similarly, the absorption band at 4.77 eV is assigned to the excitation from the tetrathiafulvalene moiety to the dicyanoethylene moiety.

In the case of the TTF's substituted with electron-donating groups (such as methyl, hydroxyl and amino groups), the transition from the highest occupied MO to the lowest vacant MO could not be assigned to the $\pi \to \pi^*$ one; this is obviously a different result from that of the calculation for **1**. Therefore, it is reasonably concluded that the phenomenon of the intramolecular charge-transfer is characteristic of electronegatively substituted tetrathiafulvalenes.

Electron Population Analysis. As seen in Fig. 2(b), the total electron densities on the carbons, C_1 and C_3, in TTF are smaller than 4.0, but those of the 2pz orbitals are 1.058 and 1.027, respectively, indicating that TTF can be considered to be an electron-rich olefin so far as π-electron system is concerned. The formal charge of the sulfur atom in TTF, in spite of a rather large positive charge (+0.17) in the $3p_\pi$ net charge, is negative (−0.30) as a result of the back donation of the σ electrons. This back donation of electrons is mainly caused by the 3d orbitals of the sulfur atom, to which indeed considerable charge densities (about 0.24) are attributed.

With regard to the overlap populations of TTF, in comparing the values calculated by including 3d orbitals with those found by neglecting 3d orbitals, the values for C_1–C_3 and C_3–C_4 bonds are smaller. Those for C_1–S_2 and S_2–C_3 bonds reveal the most significant difference, in amount 0.25—0.29, between the case of including 3d orbitals and the case of neglecting them. This prominent difference of overlap populations can be explained by the concept of the partial overlap populations between 3d orbitals of sulfur and 2pz orbitals of carbon atoms, whcih distributes to the C–S bonds in the amount of 0.25. Such participations of 3d orbitals should strengthen the C–S bonds up to those comparable to the double bond. These results indicate that the 3d orbitals of sulfur atoms are quite important in tetrathiafulvalene systems.

Similar aspects in the electronic structure of **1** were obtained by comparing the results calculated by including and neglecting 3d orbitals with each other.

It may be expected that the charge density of the central ethylene carbon atom would be decreased by the substitution of an electron-withdrawing group (CN). However, the calculated result shows that the charge density of the central carbon atom increases and that of the sulfur atom decreases, which indicates a transfer of electrons from the sulfur atoms of the central tetrathioethylene part to the dicyanoethylene part. This suggests that **1** is composed of two separable components, namely, a dicyanoethylene part and a tetrathioethylene part, which is coincident with the result obtained from the study of the electronic absorption spectra of **1**.

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