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Electronic Structure of Lone Pairs. V.[*1] Thiothiophthene and 2,5-Dimethyl-dithiofurophthene

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The electronic structure and the electronic transition of thiothiophthene(I) and 2,5-dimethyl-dithiofurophthene(II) are calculated by the semi-empirical ASMO SCF method. The E_{AB} value, used instead of the bond order of the S···S bond of Compound I, and those of the S···S bond and the S···O interaction of Compound II are found to be −6.125 eV, −12.957 eV, and −0.740 eV respectively. These E_{AB} values are compared with that of the previously-obtained transannular interaction and the hydrogen bond of water dimers calculated by the same method. The properties of the electronic transition of these compounds are discussed. No separability of the π-$\pi^*(B_2)$-type and σ-$\sigma^*(B_2)$-type transitions of the Compound I is indicated. The orbital energy of the highest occupied MO of the Compound I is remarkably high, which corresponds well with the very small I_p value.

Once the structures of thiothiophthene (I of Fig. 1) and 2,5-dimethyl-dithiofurophthene (II of Fig. 1) had been determined correctly, using X-ray diffraction, and once the concept of the 'no-bond' resonance of thiothiophthene had been presented by Bezzi *et al.*[1-3] in 1958, various investigations of their properties were performed. Thiothiophthene has been prepared by different routes, and many derivatives[*3] have been prepared, employing

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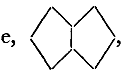
1) S. Bezzi, M. Mammi and C. Garbuglio, *Nature*, **182**, 247 (1958); M. Mammi, R. Bardi, C. Garbuglio and S. Bezzi, *Acta Cryst.*, **13**, 1048 (1960).

2) M. Mammi, R. Bardi, G. Traverso and S. Bezzi, *Nature*, **182**, 247 (1958).

3) A. A. Bothner-By and G. Traverso, *Chem. Ber.*, **90**, 453 (1957).

[*3] The non-benzonoid aromatic hydrocarbon pentalene, , has not been prepared, in spite of the large resonance energies predicted (D. P. Craig and A. Maccoll, *J. Chem. Soc.*, **1949**, 964.

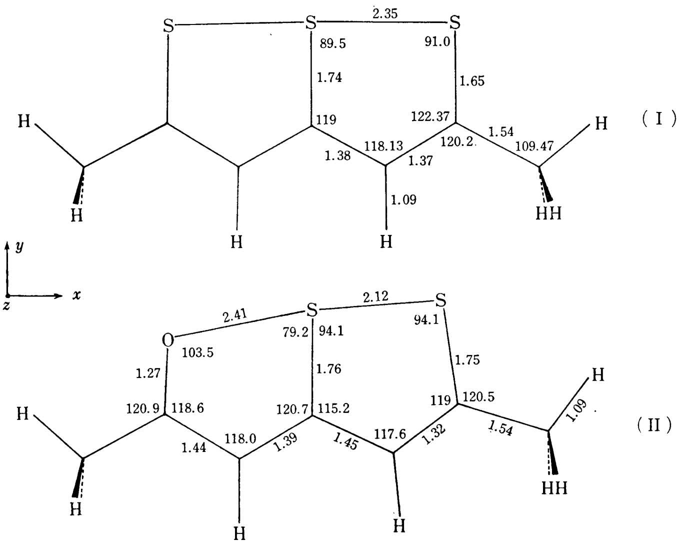


Fig. 1. Bond angles (in degree), bond lengths (in Å) employed and coordinate axis of Thiothiophthene (I) and 2,5-dimethyl-dithiofurophthene (II).

the UV, IR, and NMR techniques.4–12) Some reviews13) of these compounds have been presented. According to Bezzi *et al.*1–3) the two end sulfur atoms of thiothiophthene are equivalent, judging from the results of X-ray analysis.*4 The S–S bond length is 2.36 Å, greater than that of 2.00—2.10 Å in disulfides, but less than the sum of the van der Waals radii of 3.07 Å between two sulfur atoms.13) The C–C bonds are all in the 1.37—1.38 Å range, the bond length of aromatic double bonds. This compound was considered to exhibit a 'no-bond' resonance,1) which confers an aromatic character on the rings, this is in agreement with the properties of the substance3) (see Fig. 2).

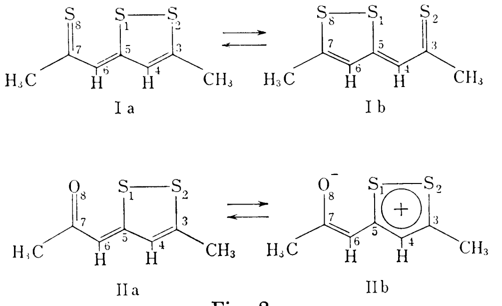


Fig. 2

In Compound II2,13), the S–S distance of 2.12 Å is the normal bond length, suggesting a contribution by structure IIa of Fig. 2. However, the S–O distance*5 of 2.41 Å is halfway between the normal S–O single bond length and the sum of the van der Waals radii of the sulfur and oxygen atoms.13) This compound shows no lines of anormal shift for CO-CH_3 protons in its NMR4,5) spectrum, and it lacks infrared carbonyl absorption.6,12) The absence of a ketonic character can be accounted for by the polarized structure of IIb. Bezzi *et al.* established that the essential features characterizing thiothiophthene were present in Compound II, but to a small extent; therefore, the actual electronic distribution is best represented by the formula IIa in Fig. 2.

As for the theoretical investigation of these molecules, a simple LCAO MO calculation of the electronic structure, including only the *p* orbitals, was carried out by Giacometti;14) they mentioned that

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4) H. G. Hertz, G. Traverso and W. Walter, *Ann. Chem.*, **625**, 43 (1959).

5) G. Pfisfer-Gillouso and N. Lozach, *Bull. Soc. Chim. Fr.* **1964**, 3254.

6) E. Klingsberg, *J. Org. Chem.*, **31**, 3489 (1966).

7) H. Behringer, M. Ruff and R. Wiedenmenn, *Chem. Ber.*, **97**, 1732 (1964).

8) H. Behringer and D. Weber, *ibid.*, **97**, 2567 (1964).

9) H. Behringer and R. Wiedenmann, *Tetrahedron Lett.*, **1965**, 3705.

10) E. Klingsberg, *J. Org. Chem.*, **31**, 3489 (1966).

11) R. J. S. Beer, D. Cartwright and D. Harris, *Tetrahedron Lett.*, **1967**, 953.

12) G. Claeson and J. Pedersen, *ibid.*, **1967**, 3283.

13) a) W. G. Salmond, *Quart. Rev.*, **22**, 253 (1968); b) H. A. Bent, *Chem. Rev.*, **68**, 587 (1968); c) E. Klingsberg, *Quart. Rev.*, **23**, 537 (1969).

*4 Recently there have been several discussions of the question of whether or not the S–S spacing is equal (Ref. 13(c)).

*5 A heterocycle with a very short (2.034 Å) S...O intermolecular distance has been reported (P. L. Johnson and I. C. Paul, *J. Amer. Chem. Soc.*, **91**, 781 (1969)).

14) G. Giacometti and G. Rigatti, *J. Chem. Phys.*, **30**, 1633 (1959).

the abnormal bond lengths can be interpreted. Later Maeda[13,15] reported that the S–S–C bond angles and the S–S bond lengths of Compound I can be understood by considering the system to be bicyclic and the central sulfur atom to be quadrivalent, judging from the *p–d* hybridization. Gleiter and Hoffmann[16] regarded the bonding in Compound I as an electron-rich, three-centered bond.[6] Very recently theoretical work on Compound I and its analogues has been reported by Johnstone *et al.*[17] They observed the I_p and UV spectra and made a semi-empirical SCF LCAO calculation of the π electron system. However, no MO calculation including all the valence σ and π electrons has yet been made, as far as we know.

Previously we investigated the electronic structure and the interaction of the lone pair of the sulfur atom of trimethylene disulfide, $(CH_2)_3S_2$,[18] which is a five-membered cyclic disulfide. It seemed that it would be interesting to know the interaction of the lone pair of the S···S···S system of Compound I and to compare it with the S–S system of trimethylene disulfide. Futhermore, compound I has a fused form of five-membered cyclic disulfides, and its electronic structure has been calculated before.[18] On the other hand, the S···S interaction of compound I and the S···O interaction of Compound II have the character of a transannular interaction. It seemed that there would be some value in obtaining the amount of such an interaction in terms of the bond order and in comparing it with the value obtained previously in our MO calculation of the transannular interaction.[19] This S···S···S interaction of Compound I is also interesting as a form of reaction intermediate.[20] Though the UV spectra of Compound I[7] and its analogues[8,9] have been observed, an interpretation of them based on MO calculations has been tried for only an electron system.[17]

Under these circumstances, we calculated the electronic structures of Compounds I and II by the semi-empirical ASMO SCF method,[21],*6 taking into account all the valence and electrons, but excluding the contribution of the *d* orbitals of the sulfur. The bond lengths and bond angles exployed here are shown in Fig. 1; they were taken from the work by Bezzi *et al.*,[1] but slightly modified.

Results and Discussion

Population Analysis of Thiothiophthene. In the present treatment, the following E_{AB} value[21] is used instead of the bond order:

$$E_{AB}=\sum_{r}^{\mathrm{on A}}\sum_{s}^{\mathrm{on B}}P_{rs}(H_{rs}+F_{rs})$$

where H_{rs} is the core resonance integral,[21] where F_{rs} is the Fock's operator, and where $\sum_{r}^{\mathrm{on A}}$ denotes

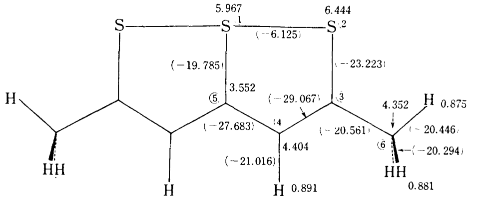

Fig. 3. Atomic density and E_{AB} value (eV) of thiothiophthene (I).

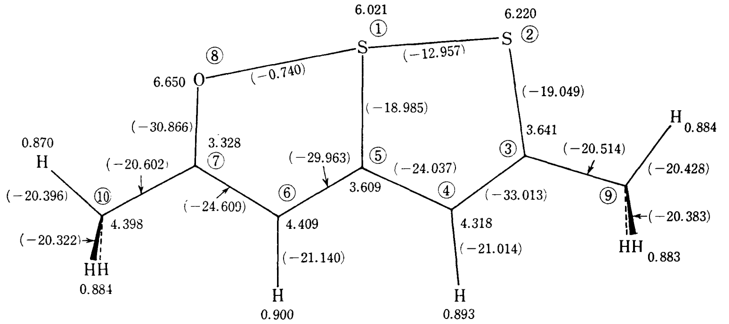

Fig. 4. Atomic density and E_{AB} value (eV) of 2,5-dimethyl-dithiofurophthene (II).

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15) K. Maeda, This Bulletin, **33**, 1466 (1960).

16) R. Gleiter and R. Hoffmann, *Tetrahedron*, **24**, 5899 (1968).

17) A. W. Johnstone and S. D. Ward, *Theor. Chim. Acta* (Berl), **14**, 420 (1969).

18) H. Yamabe, H. Kato and T. Yonezawa, "Electronic Structure of Lone Pairs. II. Disulfides and Acylthiol" (to be published in This Bulletin).

19) H. Yamabe, H. Kato and T. Yonezawa, "Electronic Structure of Lone Pairs. IV. Transannular interaction of Some Mesocycles" (to be published in This Bulletin).

20) A. Fava, A. Iliceto and E. Camera, *J. Amer. Chem. Soc.*, **79**, 833 (1956).

21) T. Yonezawa, H. Konishi and H. Kato, This Bulletin, **42**, 933 (1969); Symposium on the electronic structure of molecules, Hokkaido, October, 1967.

*6 In the previous calculation of the cyclic disulfides (Ref. 18), the value of the orbital exponents was evaluated by Slater's rule. In the present work, the exponents by Clementi *et al.* are adopted (Ref. 21).

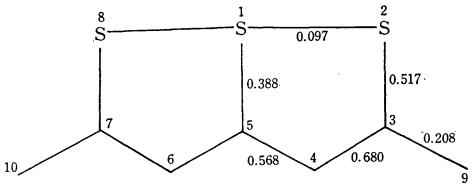


Fig. 5. π Bond orders of thiothiophthene (I).

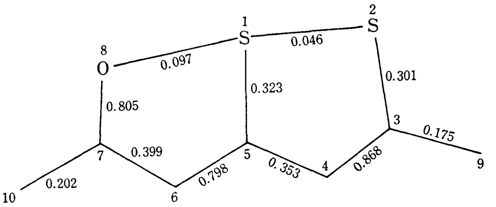


Fig. 6. π Bond orders of 2,5-dimethyl-dithiofurophthene (II).

TABLE 1. ATOMIC ORBITAL DENSITY OF THIOTHIOPHTHENE

S_1s	1.838	C_3s	1.116	C_5s	1.109
x	0.914	x	0.900	x	0.942
y	1.350	y	0.838	y	0.785
z	1.866	z	0.659	z	0.716
S_2s	1.773	C_4s	1.091	C_6s	1.008
x	1.588	x	0.968	x	1.074
y	1.295	y	1.035	y	1.136
z	1.789	z	1.310	z	1.135

TABLE 2. ATOMIC ORBITAL DENSITY OF 2,5-DIMETHYL-DITHIOFUROPHTHENE

S_1s	1.771	C_5s	1.125	C_8s	1.814
x	1.022	x	0.915	x	1.928
y	1.322	y	0.782	y	1.423
z	1.905	z	0.787	z	1.484
S_2s	1.755	C_6s	1.108	C_9s	1.001
x	1.190	x	0.994	x	1.052
y	1.355	y	1.030	y	1.131
z	1.920	z	1.276	z	1.140
C_3s	1.123	C_7s	1.106	$C_{10}s$	1.008
x	0.916	x	0.837	x	1.119
y	0.787	y	0.710	y	1.141
z	0.815	z	0.675	z	1.131
C_4s	1.095				
x	0.979				
y	1.026				
z	1.218				

the summation over all the valence AO's belonging to the A atom. The atomic density and the E_{AB} value of Compound I are shown in Fig. 3, and those of Compound II, in Fig. 4. The π bond orders of Compounds I and II are shown in Figs. 5 and 6 respectively. The atomic orbital (AO) density of Compound I is given in Table 1, and that of Compound II, in Table 2.

First we will discuss the electron density of thiothiophthene. From the value of the atomic density of Fig. 3, three sulfur atoms of Compound I polarize $\overset{-}{S}-\overset{-}{S}-\overset{+}{S}$. The AO densities of the p_z orbital of the S_1 and S_2 atoms, which constitute a MO of the π type with the p_z orbitals of the carbon atoms, are 1.866 and 1.789.*[7] In the limiting structure of Ia in Fig. 2, 5 electrons are offered formally to the π orbital from three sulfur atoms, namely, two lone pairs from the central sulfur S_1 atom and the S_2 atom, and a p_z electron from the S_8 atom. If this contribution of the S_2 and S_8 atoms is replaced mutually, a similar relation is seen in the structure I_b. The summation of the AO densities of the p_z AO of the three sulfur atoms, 5.444, nearly equals the above-mentioned value of 5. The excess electrons of 0.444 are drawn mainly from the electron of the carbon (see Table 1). Four electrons from the three sulfuratoms contribute formally to the S···S···S p_σ bond of I_a, namely two p_x electrons from the S_1 and S_2 atoms, and a lone pair (p_x) from the S_8 atom. The summation of the AO densities of the p_x AO's is 4.090; it agrees with the above value, 4.0. The AO densities of the p_x AO of the S_2 and S_8 atoms are both 1.588. This value is reasonable, because the offered electrons from the S_2 atom and S_8 atoms are formally 3.0. As the electron density of the p_y AO of the S_1 and S_2 atoms is considerably larger than 1.0, and as that of the C_3 or C_5 atom is smaller than 1.0, the electrons of the S–C p_σ bond can be said to depend much on the sulfur atom. Judging from the E_{AB} value between the S_1 and the S_2 atoms (−6.125 eV), the S···S bond is considerably weaker than the other bonds, while it should be much stronger than the usual transannular interaction.*[7] However, this interaction may be considered to be a sort of transannular interaction, in an extended sense, between the p_x orbital (a pseudo lone-pair orbital) of the S_2 atom and the central atom S_1. Otherwise, it can be regarded as a sort of intramolecular nucleophilic interaction of the p_x orbital of the S_2 to the S_1–S_8 bond. As will be shown later, in Table 5, the MO coefficient of $S_2(x)$ in HO and those of $S_1(x)$ and $S_8(x)$ in LV are large. On the other hand, in our previous calculation of trimethylene disulfide(five-membered ring), we found that the nucleophilic interaction takes place in the direction of the S–S bond. This type of interaction should play an important role in the formation of a nucleophilic intermediate,[20] such as $\mathrm{RS{-}\underset{\underset{R}{|}}{S}{-}SR}$. The symmetric property of a molecule, such as compound I and $\mathrm{RS{-}\underset{\underset{R}{|}}{S}{-}SR}$ about the central S–C bond will stabilize this interaction to a great extent.

Population Analysis of 2,5-Dimethyl-dithiofurophthene. Next let us discuss the electron density of compound II, in which the symmetry of the S···S···S bond of the compound I is disturbed. Some electronic properties of the compound II which are different from those of I are observed in our calculation, but there are similarities as well. In view of the atomic density shown in Fig. 4, the O_8, S_1 and S_2 atoms can all be said to be electronegative, but the central sulfuratom, S_1 is most electron-poor, much like compound I. The AO densities of the p_z AO of the S_1 and the S_2 atoms are 1.905 and 1.920, which form a lone pair of the p type and which constitute a π MO with the other

TABLE 3. TRANSITION ENERGIES (eV) AND TRANSITION MOMENTS OF THIOTHIOPHTHENE

Transition	Type of transition	Transition energies			Transition moment M and its components			
		Calcd	Obsd[8]	Obsd (der)[8]	m	$m(x)$	$m(y)$	$m(z)$
2→2*	π-$\pi^*(B_2)$[a]	3.84	~2.38	~2.92	1.483	1.483	0.000	0.000
1→1*	σ-$\sigma^*(B_2)$[a]	4.26	~4.55	~6.02	2.069	2.069	0.000	0.000
3→2*	π-$\pi^*(A_1)$	5.40	—	—	0.936	0.000	0.936	0.000

Obsd(der): The observed value of phenyl derivative, which is estimated from the absorption spectra of Fig. 7 (Ref. 8).

a) The matrix element between these two transitions, π-$\pi^*(B_2)$ and σ-$\sigma^*(B_2)$, is large(−1.197 eV). This indicates a possibility of large mixing and no separability of the transitions of the two types. Including 2 excitations for B_2, 4 excitations for A_1 and 3 excitations for B_1, the CI calculation does not give better results. The exctitations with higher energies being included, the better results will be expected.

TABLE 4. TRANSITION ENERGIES (eV) AND TRANSITION MOMENTS OF 2,5-DIMETHYL-DITHIOFUROPHTHENE

Transition	Type of transition	Transition energies		Transition moment M and its components			
		Calcd	Obsd(der)[8]	m	$m(x)$	$m(y)$	$m(z)$
1→2*	π-$\pi^*(A')$[a]	4.15	~3.27	1.305	1.223	0.456	0.000
2→1*	σ-$\sigma^*(A')$[a]	4.88	~5.04	0.759	0.726	0.222	0.000
3→2*	π-$\pi^*(A')$	5.77	—	0.794	0.457	−0.649	0.000

Obsd(der): The observed value of phenyl derivative, which is estimated from the absorption spectra of Fig. 7 (Ref. 8).

a) The matrix element between these two transition, π-π^*(A′) and σ-σ^*(A′) is not so large (0.476 eV). After the CI calculations including seven (A′) excitations, the transition energies and transition moments of π-π^*(A′) and σ-σ^*(A′) transitions become as follows:

π-π^*	σ-σ^*
3.83 eV	5.02 eV
$m=0.778$	$m=1.123$
$m(x)=0.74782$	$m(x)=0.93344$
$m(y)=0.21326$	$m(y)=0.44116$
$m(z)=0.00000$	$m(z)=0.00000$

Transition energies considerably approach to the observed values, but the relative intensity become inverse to the observation in Fig. 7.

TABLE 5. ENERGY LEVELS (eV) CONCERNING TO THE TRANSITIONS OF TABLE 3 AND ORBITAL COEFFICIENTS[a] OF THIOTHIOPHTHENE

No of level	$3(b_1)$	$2(a_2)$	$1(a_1)$	$1^*(b_2)$	$2^*(b_1)$
Energy (eV)	−11.178	−9.727	−8.926	−1.576	−1.418
Type	π	π	σ	σ^*	π^*
MO Coefficient	$S_1(z)$ 0.647		$S_1(s)$ −0.265	$S_1(x)$ 0.731	$S_1(z)$ 0.238
			$S_1(y)$ −0.157		
	$S_2(z)$ −0.434	$S_2(z)$ −0.442	$S_2(x)$ −0.626	$S_2(s)$ −0.123	$S_2(z)$ −0.245
				$S_2(x)$ 0.440	
	$C_3(z)$ −0.230	$C_3(z)$ 0.174			$C_3(z)$ 0.482
		$C_4(z)$ 0.516		$C_4(x)$ 0.100	
	$C_5(z)$ 0.172				$C_5(z)$ −0.572

a) The orbital coefficients larger than 0.1 are shown in this table.

Table 6. Energy levels (eV) concerning to the transitions of table 4 and main orbital coefficients[a] of 2,5-dimethyl-dithiofurophthene

No of level	$3(a'')$	$2(a')$	$1(a'')$	$1^*(a')$	$2^*(a'')$
Energy (eV)	−11.140	−9.692	−9.460	−0.915	−0.786
Type	π	σ	π	σ^*	π^*
MO Coefficient	$S_1(z)$ −0.625	$S_1(s)$ 0.111	$S_1(z)$ 0.375	$S_1(s)$ 0.192	$S_1(z)$ 0.192
				$S_1(x)$ 0.692	
	$S_2(z)$ 0.347	$S_2(x)$ 0.217	$S_2(z)$ −0.403	$S_2(s)$ −0.206	$S_2(z)$ −0.168
				$S_2(x)$ 0.621	
	$C_3(z)$ 0.259		$C_3(z)$ 0.222		$C_3(z)$ 0.541
	$C_4(z)$ 0.170	$C_4(x)$ 0.126	$C_4(z)$ 0.349		$C_4(z)$ −0.216
	$C_5(z)$ −0.204		$C_5(z)$ −0.203		$C_5(z)$ −0.546
		$C_6(x)$ −0.294	$C_6(z)$ −0.571		$C_6(z)$ 0.347
		$C_6(y)$ 0.111			
	$C_7(z)$ 0.257	$C_7(x)$ 0.240			$C_7(z)$ 0.289
	$O_8(z)$ 0.474	$O_8(x)$ −0.752	$O_8(z)$ 0.384		$O_8(z)$ −0.270
	$C_9(z)$ −0.123				
	$C_{10}(z)$ −0.121	$C_{10}(s)$ −0.111			
		$C_{10}(x)$ −0.312			
		$C_{10}(y)$ −0.155			

a) The orbital coefficients larger than 0.1 are shown in this table.

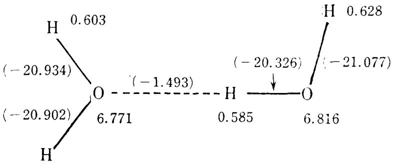
p_z AO's of the C atom and the O atom. From the value of the AO density, the p_x AO of the O atom can be considered to be a lone-pair orbital. The AO densities of the p_x AO's of the S_1 and S_2 atoms are approximately 1.0. This is different from the case of compound I (see Table 1). That is, the resonance between five-membered rings, as in compound I, can not be expected; rather, a nucleophilic interaction (a transannular interaction) between the lone pair of the O_8 atom and the S_1–S_2 bond of the five-membered cyclic disulfide is observed. The E_{AB} value between the S_1 and O_8 atoms in Fig. 4 confirms this. That is, the E_{AB} values of the $O_8 \cdots S_1$ and $S_1 \cdots S_2$ bonds are −0.740 eV and −12.957 eV respectively. The order of the $O_8 \cdots S_1$ interaction seems to be that of a usual transannular interaction[*8,19]; it is ten times as small as the S···S interaction of compound I (Fig. 3). The S–S bond of Compound II is about two times as strong as the S···S interaction of Compound I and about one half as weak as a usual σ bond.

For comparison, an example of the hydrogen bond has been calculated by the same semi-empirical ASMO SCF method,[21] though only the relative value of the E_{AB} value will be discussed. The E_{AB} value corresponding to the hydrogen bond between the oxygen atom, O_I and the hydrogen atom, H_{II}, of the water dimer is found to be −1.493 eV.[*8] From these calculations, the S···O interaction of compound II seems to be weaker than, or approximately equal to, the hydrogen bond.[*9,*10] This type and this order of interaction will be important in a catalytic interaction of a biochemical substance, as has been discussed in a previous paper.[19] Some examples may be seen in the literature.[22]

[*7] In the calculation of $(CH_2)_3S_2$, the atomic density of the lone-pair AO of the sulfur atom was almost 2.00 at the various dihedral angles (Ref. 18).

[*8] In our previous calculation of the electronic structure of several mesocycles with transannular interactions, this interaction was found to be −0.5 eV— −1.2 eV in terms of the E_{AB} value. In the extreme conformation, its value was −7.6 eV. However, this value is too large, for the conformation has been revealed as too extreme (Ref. 19).

[*9] The ∠HOH angle is taken as 105°, and a planar configuration of the dimers is adopted. The O–H bond length and the O···O distance are taken to be 0.96 Å and 2.76 Å respectively. The atomic densities and the E_{AB} values, denoted by the parentheses, are calculated to be as follows:



The E_{AB} value, −1.493 eV, of the hydrogen bond is slightly larger than that of the transannular interaction (*7); this is in accordance with the experimental trend. That is, the frequenncy shift of IR caused by the hydrogen bond is about 10 cm^{-1} several hundred cm^{-1}, while that of the transannular interaction reported is about 10 cm^{-1}~20 cm^{-1} (Ref. 19).

[*10] The E_{AB} value of the hydrogen bond varies over some range of values, depending on the kind of hydrogen bond, although only are example of a water dimer is calculated in the present work.

22) "Organic Sulfur Compounds," ed. by N. Kharasch, Pergamon Press (1961), Chap., 9 35, *etc.*; T. C. Bruice, *J. Amer. Chem. Soc.*, **81**, 5444 (1959); T. C. Bruice and B. Holmquist, *ibid.*, **89**, 4028 (1967).

π-Bond Orders. The main bond densities among the p_z orbitals (the π-bond orders) of compounds I and II are shown in Fig. 5 and 6. The π-bond order of the S···S bond of the compound I and those of the S–S bond and the S···O bond of the compound II are not very different. The π character of the C–O bond of Compound II, and conjugation with a π electron system from the C_7 atom to the C_9 atom, hexene, are seen. The S–C bond of the compound I has something of the nature of the single bond. The alternating π-bond order of the hexene is more flattened in the compound I, and the π-bond orders in the ring are averaged out, compared to the compound II.

Electronic Transitions. The calculated transition energies and transition moments are listed in Tables 3 and 4. The energy levels connected with these transitions and the main orbital coefficients are shown in Tables 5 and 6. The levels are numbered from the highest occupied level to the lower levels, and from the lowest unoccupied level, denoted by *, to the higher levels. In Table 6, the highest occupied MO and the next highest occupied MO of the compound II are, approximately, degenerated π and σ orbitals. The contribution of the p_x AO of the oxygen atom (denoted by O(x)), which is a lone-pair AO of the oxygen atom to this σ orbital is large. That is, this σ MO has the character of the lone-pair MO. In the π MO's and the π MO's of Table 5 and 6, the coefficients of the S(z) AO's, which are lone-pair-type AO's of the sulfur atom, are comparatively large.

The highest occupied σ orbital of the compound I has a remarkably high energy (-8.926 eV).*[11] Though there is a possibility that the inclusion of the $3d$ orbital of the sulfur atom stabilizes the S···S···S interaction, more or less, and lowers the enregy of this σ MO, the highest occupied MO of this compound seems to be higher than that of an ordinary molecule with lone pairs. This may correspond to the very small I_p (7.47 eV) of the Compound I.[17)] In Table 5, the main contributions to this σ orbital of the Compound I are shown to be made by $S_1(s)$ AO and $S_2(s)$ AO, which is a pseudo lone-pair AO of the S_2 atom. That is, this orbital has the character of a lone-pair MO and of a S···S···S p_σ bond. Perhaps the reaction in termediate,[20)] $\underset{\text{R}}{\text{RS–}\overset{}{\text{S}}\text{–SR}}$, also has such a high energy and becomes very reactive.

The UV spectrum of the Compound I (in cyclohexane and/or dioxane) has been reported,[7)] but there is no data on the Compound II in the same solvent. In these calculations, there is an unexpected agreement of the absolute values of the calculated and the observed transition energies, as may be seen in Table 3. Therefore, as the experimental values of the UV spectrum, those of the phenyl derivatives in the same solvent (in acetic acid.[8)]) are adopted in making a comparison of the electronic transitions of the Compounds I and II.

The spectra of these derivatives are shown in Fig. 7(Ic[8)] and IIc),[8)] together with that of the Compound I.[7)] In Fig. 7, the spectra of I and Ic show typical electronic absorptions, with a strong peak in the ultraviolet region and a weaker peak in the visual region. That is, the strong peak of the Compound Ic at ~210 mμ[8)] and that of Compound I at 273 mμ[7)] are characteristic of the S···S···S bond of the series[10)] and are shifted, more or less, among them. Another property of these spectra[7,8,10)] is that the oxygen compound, IIc, absorbs much more weakly in the ultraviolet region about 250 mμ, and more strongly in the visual region, but at a lower wave length than I and Ic. This feature is also seen in the UV spectra of other derivatives.[10)] That is, the spectra of Fig. 7 conform closely to the pattern that is evidently characteristic of the series.[7,8,10)]

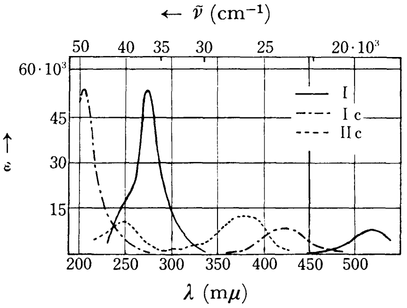
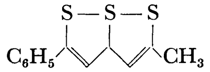
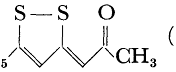


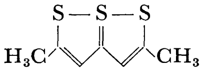
Fig. 7. UV spectra of



(Ic) (Ref. 8),



(IIc) (Ref. 8) and



(I) (Ref. 7).

In view of the calculated transition moment, the observed longer wavelength absorption of the Compound I (C_{2v}) may be said to correspond to π–π* (B_2, 2→2*)-type transition, and the shorter one may be said to be a σ–σ*(B_2, 1→1*)-type transition, as primary results. However, the matrix element between these π–π* and σ–σ* excitations is calculated to be large, -1.197 eV. This indicates the possibility of a large mixing and no separability of the transitions of the two types after the configuration interaction is calculated. Furthermore, the longer wavelength absorption of Compound II (C_{1h}) may correspond to the π–π*(A', 1→2*)-type transition, and the shorter one may correspond to the σ–σ*(A', 2→1*) type.*[12] The agreement between

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*[11] No such high energy, higher than -9 eV, of the highest occupied level has ever before been found in our ASMO SCF calculations.

*[12] Johnston *et al.* ascribed the absorption to the π–π* transition only in their semi-empirical SCF LCAO calculation of the π electron system (Ref. 17).

the observed⁸⁾ and the calculated transition energies is not very good, but a relatively high intensity of the absorption in the 270(210)mμ region of the Compound I can be obtained in our calculations. This high intensity is caused mainly by the delocalized S···S···S interaction (σ bond character) of the Compound I, as has previously been mentioned. The relative position of the absorption in the visual region of I (Ic) and IIc (that is the fact that IIc absorbs at a lower wavelength), is correctly predicted in these calculations.

The previous semi-empirical ASMO SCF calculation²¹⁾ of the electron structure of the cyclic disulfides,¹⁸⁾ neglecting the contribution of *d* orbitals, predicted the main absorption maximum in the UV spectra well. In the present case, however, for quantitative discussions a consideration of the *d* orbitals and of the configuration interaction seems to be necessary.

The calculations were carried out on an HITAC 5020 computer at the Computation Center of the University of Tokyo.