On the pd Hybridization of the Sulfur Atom in Thiothiophten.
II. The Contraction of the d Orbital

By Kôgorô MAEDA

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In the previous paper of this series[1], the pd hybridization was proposed on the central sulfur atom in thiothiophten to compose the full σ skeleton of condensed ring system of the molecule. It was shown that the above configuration of electrons on the central sulfur atom is favored in accounting for both the so-called abnormal length of the bond between two sulfur atoms and the right angle of S–S–C, and that the electronic structure of thiothiophten can be treated according to the usual LCAO π approximation without considering the σ skeleton, unlike the procedure proposed by Giacometti and Rigatti[2]. Further, the possibility of participation of the d orbital in the hybridization was examined from the standpoint of overlap criterion, giving the values of the overlap integrals. As the result of the inspection, however, it turned out that one might not except any participation of the d orbitals in bonding to occur through the hybridization. It was pointed out there that this may be due to the straightforward application of Slater's rule[3] to the estimation of the effective nuclear charges for the d orbitals. As already mentioned, since the maximum of the radial function of the d orbital with its effective nuclear charge required by Slater's rule lies at 9 atomic units, the orbital may be regarded as including the full σ skeleton of thiothiophten, so that it would be impossible to avoid the influence of the neighboring atoms in the molecule. The charges of the atoms may contract the d orbital and enlarge its nuclear charge, leading to a value of overlap integral comparable to that of 3p orbital. Contraction of this kind was once examined in the case of the d orbital in thiophene[4], where it might be expected that as the result of the contraction by the perturbation of neighboring carbon atoms, the participation of the d orbitals in bonding would take place to a greater extent than predicted by the direct application of free atom parameter by Slater's rule.

In the present paper, following the treatment about the d orbital of the sulfur atom in thiophene, the influence of neighboring atoms upon the d orbital will be examined on the central sulfur atom in thiothiophten and the possibility of the participation in the hybridization will be inquired into from the standpoint of overlap criterion, comparing the values of overlap integral.

Orbital Contraction.—A model is employed here, in which a single d electron on the central sulfur atom is supposed to move in the field of the nucleus of charge Z_S, and upon this hydrogen-like atom system a perturbation is superposed consisting of three positive charges of the neighboring atoms of thiothiophten. The positive charges come because the field of an atom capable of forming a covalent bond is substantially electron-attracting. The perturbing charges are composed of those of the two sulfur atoms of magnitude $Z_A(=Z_B)$ at the distance of S–S bond, 4.461 atomic units ($\sigma_A(=\sigma_B)$) and of the carbon atom of Z_C at the distance of central C–S, 3.440 atomic units (σ_C). These charges will be treated, not as three hydrogen-like atoms, but just as point charges of respective magnitudes. The actual potential of the perturbation is very intricate because it involves many factors, the attraction of the surrounding nuclei, the coulomb repulsions of their electrons, exchange terms, and others; hence the dependence on distance of the potential will not follow the r^{-1} law at all closely. The system being thus too complicated to be considered, the point charge model is employed as approximation in this paper. The magnitudes of the perturbing charges will be treated rather as parameters, values plausible in a wider range being involved.

Under this point charge approximation, the potential by the outlying charges may be expanded as a sum in the usual $1/r$ series[5] as follows:

For the two charges of sulfur atoms,

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[1] (a) K. Maeda, This Bulletin, 33, 1466 (1960); (b) K. Maeda, ibid., 34, 785 (1961).

[2] G. Giacometti and G. Rigatti, *J. Chem. Phys.*, 30, 1633 (1959).

[3] J. C. Slater, *Phys. Rev.*, 36, 57 (1930).

[4] K. Maeda, This Bulletin, 33, 303 (1960); The idea of orbital contraction was first given by D. P. Craig and E. A. Magnusson, *J. Chem., Soc.*, 1956, 4895.

[5] H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry", John Wiley & Sons Inc., New York (1944), p. 369.

$$V_{A,B}(r>\sigma_A)=-(2Z_A/r)\{1+(1/2)(3\sin^2\vartheta\times\cos^2\varphi-1)(\sigma_A/r)^2+\cdots\cdots\}$$

$$V_{A,B}(r<\sigma_A)=-(2Z_A/\sigma_A)\{1+(1/2)(3\sin^2\vartheta\times\cos^2\varphi-1)(r/\sigma_A)^2+\cdots\cdots\}$$

and for the carbon atom,

$$V_C(r>\sigma_C)=-(Z_C/r)\{1+\sin\vartheta\sin\varphi\,(\sigma_C/r)+(1/2)(3\sin^2\vartheta\sin^2\varphi-1)\times(\sigma_C/r)^2+\cdots\cdots\}$$

$$V_C(r<\sigma_C)=-(Z_C/\sigma_C)\{1+\sin\vartheta\sin\varphi\,(r/\sigma_C)+(1/2)(3\sin^2\vartheta\sin^2\varphi-1)\times(r/\sigma_C)^2+\cdots\cdots\}$$

The perturbation energy due to the outlying potential is given by $\int\psi v\psi\mathrm{d}\tau$, where ψ is the d electron wave function of the usual Slater type. As the wave function, two for the d orbital are taken, $3d_z$ and $3d_{xy}$ (notation of Pauling and Wilson6)), which were discussed in the previous paper2). In integrating the two orbitals, one must pay some attention to the orientation of the $3d_z$ orbital, because in the present consideration the Z-axis is taken to be normal to the molecular plane, and the Y-axis goes along the central C–S bond. The oribital should be rotated by 90° about the Y-axis. After the rotation, the angular part of the orbital, $(3\cos^2\vartheta-1)$, turns into $(3\sin^2\vartheta\times\cos^2\varphi-1)$. Hereafter, the orbital is described as $3d_{x(z)}$ in this paper.

The total perturbation energy is given as the sum of the energies by the above three positive charges, and the terms higher than the 2nd of the potential may be neglected because of their small contributions to the energy. Hence, after the integration, the respective energies of the two orbitals are given as follows:

For $3d_{x(z)}$

$$E=-(2Z_A/\sigma_A)\{\sigma_A R^0_{33}(\alpha\sigma_A)+(2/7)\sigma_A R^2_{33}(\alpha\sigma_A)\}-(Z_C/\sigma_C)\{\sigma_C R^0_{33}(\alpha\sigma_C)-(1/7)\sigma_C R^2_{33}(\alpha\sigma_C)\}$$

and for $3d_{xy}$

$$E=-(2Z_A/\sigma_A)\{\sigma_A R^0_{33}(\alpha\sigma_A)+(1/7)\sigma_A R^2_{33}(\alpha\sigma_A)\}-(Z_C/\sigma_C)\{\sigma_C R^0_{33}(\alpha\sigma_C)+(1/7)\sigma_C R^2_{33}(\alpha\sigma_C)\}$$

where $R^p_{nn}(\alpha\sigma)$ is the auxiliary function which was used in the case of thiophene4), and its explicit form is

$$R^p_{nn}(\alpha\sigma)=(1/\sigma)(2\alpha\sigma/n)^{2n+1}\{1/(2n)!\}\times\{(2n+p)!\times(n/2\alpha\sigma)^{2n+p+1}-A_{2n+p}(2\alpha\sigma/n)+A_{2n-p-1}(2\alpha\sigma/n)\}$$

where

$$A_n(\omega)=\int_1^\infty r^n\exp(-\omega r)\mathrm{d}r$$

In the above expressions, α is a parameter to be determined to minimize the total energy which is the sum of the perturbation energy and the unperturbed given by

$$W=(\alpha/3^2)(\alpha/2-Z_s)$$

for the hydrogen-like orbital of free atom parameter Z_s; that is, the procedure to be performed now is to find the new value of effective nuclear charge for which the total energy is a minimum for given magnitudes of σ_A, σ_C, Z_A and Z_C. The new value of the charge will offer an appropriate basis for the discussion about the d orbital under the perturbation.

In conducting the procedure, it is necessary to set the values of Z_s, Z_A and Z_C. As the value of Z_s, 1 and 2 are chosen, and for Z_c three values are taken, 1, 2 and 3, which were used in the case of thiophene4). With respect to the value of $Z_A(=Z_B)$, four values are assigned, 1, 3, 5 and 6. All the above values are to be treated as tentative parameters. In the real system, it is difficult to determine the straightforward values of the parameters equivalent to the outlying potential, because, as mentioned above, the real field is not truly coulombic but much more complicated. Furthermore, there is, in general, a considerable difference between so-called potential- and field-determined nuclear charge on the same atom7). Hence, in this paper, some attention will be paid rather to a variation in α by adopting the values of the above parameters in wider range. In finding the minimum of the total energy, it is necessary to know the values of $\sigma R^p_{nn}(\alpha\sigma)$, which are taken from the table in the previous paper4).

In Table I are given the results. From this table it is found that the new values of the effective charges under perturbation are considerably greater compared with those of free atom parameters, without exception, and furthermore that there are only small variations between these values despite the adoption of a wider range of the parameters. In the case of thiophene, it was shown that the magnitude of the new value is more sensitive to the bond distance σ than to the parameters for the outlying potential, and that it is little altered

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6) L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics", McGraw-Hill, New York (1935), p. 138.

7) For example, see: F. W. Brown, *Phys. Rev.*, **44**, 214 (1933).

TABLE I. EFFECTIVE NUCLEAR CHARGE α OF 3d ORBITAL UNDER THE PERTURBATION

I. $3d_{xy}$

Z_s	Z_c	$Z_A(=Z_B)$ 1	3	5	6
1	1	2.34	2.66	2.80	2.92
1	2	2.55	2.78	2.90	2.96
1	3	2.73	2.90	3.00	3.04
2	1	2.75	3.05	3.05	3.10
2	2	2.90	3.10	3.15	3.20
2	3	3.05	3.10	3.25	3.30

II. $3d_{x(z)}$

Z_s	Z_c	$Z_A(=Z_B)$ 1	3	5	6
1	1	2.34	2.63	2.75	2.82
1	2	2.50	2.70	2.83	2.88
1	3	2.63	2.80	2.86	2.94
2	1	2.68	2.88	2.96	3.00
2	2	2.90	3.02	3.02	3.05
2	3	3.05	3.12	3.15	3.10

by the charges of neighboring atoms in the range 2$\sim$3 when $\sigma=3$ and 4. In the present consideration, with respect to the bond distance σ, the fixed values are assigned, $\sigma_A(=\sigma_B)$ and σ_C, which are taken from the actual distances in thiothiophten, obtained from the X-ray analysis study by Bezzi, Mammi and Garbuglio[8]. Considering the above situation in thiophene, therefore, the present results may be convincing in regard to making fast the values of σ. This fact is worthy of notice, because to obtain the same results through the different starting points of Z_s might indicate the existence of a self-consistent value of α appropriate for the perturbation in which the geometrical configuration of the outlying potential to the atom in question is settled. In fact, the values given in the Table would serve as the first steps of the procedure to the self-consistent value. The value would probably remain settled near 3$\sim$4. Of course, it must be emphasized that this discussion on the effective value for α is by all means of tentative character under the present point charge approximation. Furthermore, the value of α appropriate to the real system should be determined precisely with respect to the whole energy of the molecule. The values in the Table, however, may be used as useful clues to the studies about the behavior of the d orbital on the central sulfur atom in thiothiophten.

From these discussions, it might be inferred in any case that the effective nuclear charge for the d orbital on the central sulfur atom in thiothiophten would not bear the free atom parameter, but it should bear a greater value considering the influence by the surrounding nuclei, probably near 3$\sim$4. As suggested earlier in this paper, the value for the d orbital will furnish an appropriate basis of the discussion about the orbital.

Overlap Integral. — In the previous section, the influence of the surrounding nuclei upon the d orbital was examined, and the results were given in Table I. Using these results, the overlap integral with the 3p σ orbital of the neighboring sulfur atom were estimated for the corresponding values of Z_s, Z_A and Z_C. These are given in Table II. In calculating these values, the tables of the integrals given in the previous paper[1b] were used, and as the effective nuclear charge for the 3p orbital, the direct value through Slater's rule was assigned, because it was shown that the value for 3p is little affected by the outlying perturbing charges when $\sigma=3$ and 4, and moreover, because, although it was accurate in the case of thiophene[4], in general, the contraction of the orbital is great only when the orbital with high screened and loosely bound electrons lies under the perturbation.

TABLE II. OVERLAP INTEGRALS OF 3d ORBITALS WITH 3p ORBITALS OF NEIGHBORING S ATOM

I. $3d_{xy}$

Z_s	Z_c	$Z_A(=Z_B)$ 1	3	5	6
1	1	0.082	0.129	0.148	0.163
1	2	0.113	0.145	0.161	0.166
1	3	0.138	0.161	0.170	0.172
2	1	0.141	0.173	0.173	0.178
2	2	0.161	0.178	0.181	0.185
2	3	0.173	0.178	0.189	0.192

II. $3d_{x(z)}$

Z_s	Z_c	$Z_A(=Z_B)$ 1	3	5	6
1	1	0.092	0.143	0.162	0.173
1	2	0.121	0.154	0.175	0.181
1	3	0.143	0.170	0.178	0.190
2	1	0.151	0.181	0.192	0.195
2	2	0.183	0.197	0.197	0.200
2	3	0.200	0.206	0.210	0.204

The values in Table II are all positive and of the order of 0.1$\sim$0.2. Craig et al.[9] once proposed that for significantly strong binding a value of the overlap integral of about 0.1 or greater is necessary. According to this proposition, one might expect some significant binding to take place between the 3d and the 3p orbitals. The participation of the d orbital to bonding is performed through the pd hybridization in the present problem, and whether the d orbital is to be used or not depends, amongst other factors, upon whether the overlap integral involving the d orbital is comparable

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[8] S. Bezzi, M. Mammi and G. Garbuglio, *Nature*, **182**, 247 (1958).

[9] D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, **1956**, 4895.

TABLE III. OVERLAP INTEGRALS: $S(3p\sigma-3p\sigma)$

p/t	0.0	0.1	0.2	0.3	0.4	0.5
0.0	−1.000	−0.966	−0.867	−0.719	−0.543	−0.365
0.5	−0.965	−0.933	−0.840	−0.698	−0.531	−0.359
1.0	−0.866	−0.839	−0.761	−0.640	−0.494	−0.342
1.5	−0.715	−0.696	−0.639	−0.549	−0.436	−0.312
2.0	−0.531	−0.520	−0.488	−0.435	−0.361	−0.272
2.5	−0.333	−0.331	−0.324	−0.307	−0.275	−0.224
3.0	−0.140	−0.146	−0.161	−0.178	−0.183	−0.170
3.5	0.031	0.019	−0.013	−0.056	−0.094	−0.114
4.0	0.171	0.155	0.111	0.050	−0.013	−0.060
4.5	0.273	0.256	0.208	0.136	0.055	−0.011
5.0	0.342	0.324	0.275	0.200	0.114	0.033
5.5	0.377	0.361	0.314	0.243	0.155	0.068
6.0	0.385	0.371	0.331	0.266	0.184	0.096
6.5	0.373	0.362	0.328	0.273	0.199	0.116
7.0	0.346	0.338	0.312	0.268	0.205	0.129
7.5	0.311	0.306	0.287	0.253	0.202	0.136
8.0	0.273	0.269	0.257	0.233	0.194	0.138
8.5	0.233	0.231	0.225	0.210	0.181	0.136
9.0	0.195	0.195	0.193	0.185	0.166	0.130
9.5	0.161	0.162	0.163	0.160	0.149	0.123
10.0	0.130	0.132	0.135	0.137	0.132	0.114

to that of 3p in terms of overlap approximation employed here. Therefore, the integral between $3p\sigma$ orbitals of S–S bond in thiothiophten was estimated, for the sake of comparison, using free atom parameters, and it was obtained as 0.243. In estimating this value, Table III given in the present paper was used. The overlap integral $S(3p\sigma-3p\sigma)$ was once given by Mulliken et al. for $t=0$[10], and also by Craig et al., who evaluated the values with parameters p and t in the ranges of 2∼10 and 0∼0.5 at the respective intervals of 1.0 and 0.1[11]. In the present paper, the values with p in the wider range of 0∼10 at the intervals of 0.5 were calculated, and in Table III are given the results obtained.

From the above estimation of the overlap integrals, it is found that almost comarable values are obtained for both the integrals involving the 3p and the 3d orbitals. These values would become more close when the so-called self-consistent value above mentioned may be used as the effective nuclear charge for the d orbital. Then, it may be said that the participation of the d orbital in the hybridization is more favorable than predicted through the direct employment of free atom parameters by Slater's rule, and that the extent to which the d orbital participates in bonding through the hybridization will be of the order nearly the same as, or at least not much less than, that of the 3p orbital. These results may be somewhat deficient in precision under the present point charge and overlap approximations employed in this paper. However, they may be sufficiently valid for discussing semi-quantitatively how the d orbital behaves under the perturbation in the actual molecule.

It is of interest to notice that the values of the overlap integral for the 3d orbital lie very nearly at the corresponding maxima for the respective effective nuclear charges of the orbital (see Tables I and III in Ref. 2). These values approach more nearly to the maxima when the self-consistent values under the present perturbation, 3∼4, may be used, or when a larger value of the distance between the orbitals is adopted. This is because the parameter p in the calculation of overlap integral involves the distance between the orbitals. Hence the so-called abnormal length of S–S bond in thiothiophten may be rather consistent to give the greater possibility of participation of the d orbital in the hybridization.

Hybrid Orbitals. — From the above considerations, it is found that the d orbitals on the central sulfur atom in thiothiophten might be able to participate in the hybridization to the same as, or at least to an extent comparable to that of the 3p orbital. Then the hybrid orbitals may be written with the same mixing coefficient for the two d orbitals in question as follows:

For $3d_{xy}$,

$$(1/\sqrt{2})(\psi_{3d_{xy}}\pm\psi_{3p})$$

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[10] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

[11] D. P. Craig, A. Macoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, **1954**, 332.

and for $3d_{x(z)}$,

$$(1/\sqrt{2})(\psi_{3d_{x(z)}} \pm \psi_{3p})$$

The mixing coefficient is fortunately compatible with the conditions required from the linear bond of S-S-S in thiothiophten and the symmetrical skeleton of the molecule[12]. The approximate forms of the hybrid orbitals were already shown in Fig. 2 of the previous paper[1b].

Of the two sets of hybrid orbitals, those involving the $3d_{x(z)}$ orbital may be more probable for participating in the hybridization to form the S-S-S bond in thiothiophten, because the values of the overlap integral are greater for the $3d_{x(z)}$ than for the $3d_{xy}$ with corresponding p and t values.

All the above discussions are those under the point charge approximation and within the framework of the overlap criterion. Therefore it is more or less inevitable that the results obtained in this paper should not be so readily sufficient for an accurate discussion of the formation of the possibe bond in thiothiophten. Furthermore, in fact, the accurate discussion dealing with the final determining factor in bonding, that is, on balancing of energy should be taken up for consideration with respect to the whole molecule of thiothiophten. Nevertheless, the results obtained above will be valuable enough for approximate and semi-quantitative discussion about the possibility of participation of the d orbital in the central sulfur atom in thiothiophten. Therefore it can now be said that the structure of thiothiophten is not one involving the no-bond resonance structure proposed by Bezzi et al.[8], but rather it may be the condensed ring system of the full σ skeleton involving the hybrid orbitals on the central sulfur atom of the molecule.

Electrotechnical Laboratory
Tanashi, Tokyo

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[12] C. A. Coulson, " Valence ", Oxford University Press, London (1952), p. 195.