On the pd Hybridization of the Sulfur Atom in Thiothiophten. I. The Calculations of the Overlap Integrals Involving d Orbitals

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(Received October 6, 1960)

The structure of a molecule named "thiothiophten" was recently clarified through the X-ray analysis study by Bezzi, Mammi and Garbuglio[1], who proposed for this compound a condensed ring system similar to that of thiophten[2] (see Fig. 1), and characterized it by no-bond resonance structure. Giacometti and Rigatti[3], following the deduction to this peculiar structure, have made simple LCAO treatment on the superimposed σ and π systems of non-localized electrons in thiothiophten, by using only p type orbitals for bonding with respect to sulfur atoms. However, since the system involving no-bond resonance structure is somewhat unlikely to occur, an alternative

1) S. Bezzi, M. Mammi and C. Garbuglio, *Nature*, **182**, 247 (1958).
2) H. C. Louguet-Higgins, *Acta. Cryst.*, **3**, 76 (1950).
3) G. Giacometti and G. Rigatti, *J. Chem. Phys.*, **30**, 1633 (1959).

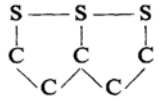

Fig. 1. Molecular structure of thiothiophten.

interpretation on the electronic structure of thiothiophten was given in the previous paper of this series[4], where the explicit participation of d orbitals on the sulfur atoms in bonding was attempted through pd hybridization. Adopting the hybridization for the central sulfur atom, the electronic structure of thiothiophten was treated according to the usual LCAO π approximation without considering the σ skeleton of the molecule. The results obtained there were appropriate in any case, although they were not necessarily the best.

In the present report, further discussions will be conducted on the pd hybridization of the central sulfur atom in thiothiophten, and the possibility of participation of the d orbital will be examined on the standpoint of overlap criterion, giving the values of the overlap integrals.

pd Hybridization.—In considering the valency state of the central sulfur atom in thiothiophten it is convenient to define its coordinates with the sulfur atom as origin so that straight bond S–S–S may go along the coordinate axis and the second axis may be perpendicular to the molecular plane. In this case, the central C–S bond lies on the remaining one, because S–S–C bond with respect to the central sulfur atom has its valency angle of 90°.

It is possible that a 3p electron of the sulfur atom is promoted to a 3d orbital and interacts with other 3p electrons through pd hybridization[5]. The pd configuration of electrons is used in the formation of σ orbitals and the linear arrangement of bonds is obtained from this electron configuration[6]. Then, as pointed out in the previous paper, it may be reasonable to consider that the central sulfur atom in the straight bond S–S–S is not in the normal electron configuration but in a valency state capable of forming a σ skeleton of the bond through the pd hybridization. The central sulfur atom is no longer in the bivalent state, but as the result of the hybridization, is in a tetra-valent state as in the case of the carbon atom. The expected valency state of the central sulfur atom would be in the electron configuration $3s^23p^33d$; two orbitals of 3p's are adopted to form a C–S σ bond with one of the sp^2 orbitals of the neighboring central carbon atom and to participate in the π electron conjugation system of thiothiophten. The remaining 3p orbital would hybridize with a 3d orbital, and would be going to make up the σ bonds of S–S–S in the linear arrangement. These configurations can account for both the right angle of S–S–C with respect to the central sulfur atom and the so-called abnormal length of the bond between two sulfur atoms[5,7,8].

Now a problem still remains, the discussion as to which of the d orbitals of the sulfur atom may hybridize with the 3p orbital to form the σ skeleton of the S–S–S bond. On the sulfur atom there are five d orbitals available for bonding. Of these, two orbitals would be ready to participate in the hybridization, namely $3d_z$ and $3d_{xy}$ orbitals (notation of Pauling and Wilson[9]), both of which have their maximum densities of electron distributions along the respective coordinate axes. In general, the bond-forming power should be a maximum along the direction with maximum electron distributions of the orbitals concerned[10]. The hybrid orbitals may be written as the linear combination of the 3p and the 3d orbitals. The approximate forms of the orbitals after the hybridization are shown in Fig. 2. Either set of the hybrid orbitals may go to form the σ bonds with 3p orbitals of neighboring sulfur atoms.

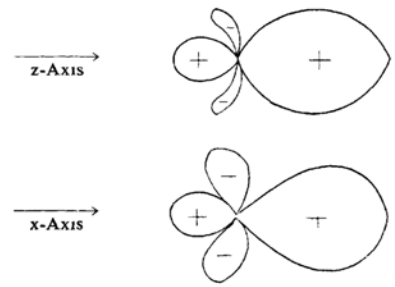

Fig. 2. Approximate forms of hybrid orbitals.

Overlap Integral.—It is, in general, impracticable to calculate accurately the energy of formation of a bond between two atoms. Instead of this, the overlap criterion may be used conveniently in discussing the bond formation[7,8]. The value of the overlap integral may give some measure of the strength of a

4) K. Maeda, This Bulletin, 33, 1466 (1960).
5) K. Maeda, ibid., 33, 303 (1960).
6) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry", John Wiley & Sons, Inc., New York (1944), p. 230.
7) D. P. Craig, A. MacColl, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, **1954**, 332.
8) D. P. Craig and E. A. Magnusson, ibid., **1956**, 4895.
9) L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics", McGraw-Hill, New York (1935), p. 138.
10) C. A. Coulson, "Valence", Oxford University Press, London (1952), p. 195.

TABLE I. OVERLAP INTEGRALS: $S(3p_\sigma - 3d_{xy})$

p/t	−0.5	−0.4	−0.3	−0.2	−0.1	0.0	0.1	0.2	0.3	0.4	0.5
0	0	0	0	0	0	0	0	0	0	0	0
0.5						−0.145	−0.161	−0.163	−0.151	−0.126	−0.093
1.0	−0.028	−0.063	−0.110	−0.165	−0.220	−0.265	−0.293	−0.298	−0.276	−0.232	−0.173
1.5						−0.342	−0.377	−0.383	−0.358	−0.304	−0.229
2.0	−0.055	−0.106	−0.171	−0.242	−0.310	−0.366	−0.402	−0.410	−0.387	−0.334	−0.257
2.5						−0.341	−0.372	−0.382	−0.367	−0.324	−0.258
3.0	−0.063	−0.107	−0.154	−0.200	−0.242	−0.275	−0.301	−0.312	−0.307	−0.283	−0.236
3.5						−0.187	−0.203	−0.217	−0.224	−0.220	−0.197
4.0	−0.052	−0.071	−0.083	−0.087	−0.088	−0.091	−0.099	−0.113	−0.132	−0.147	−0.148
4.5						−0.000	−0.000	−0.015	−0.042	−0.079	−0.096
5.0	−0.029	−0.022	−0.002	0.026	0.055	0.076	0.082	0.069	0.038	−0.004	−0.046
5.5						0.134	0.145	0.135	0.101	0.053	−0.001
6.0	−0.003	0.021	0.057	0.100	0.141	0.172	0.186	0.178	0.148	0.098	0.038
6.5						0.192	0.208	0.204	0.178	0.130	0.069
7.0	0.016	0.047	0.087	0.129	0.168	0.197	0.215	0.214	0.193	0.151	0.092
7.5						0.192	0.208	0.211	0.196	0.161	0.107
8.0	0.027	0.057	0.092	0.125	0.154	0.178	0.194	0.199	0.191	0.163	0.116
8.5						0.160	0.175	0.182	0.178	0.159	0.120
9.0	0.031	0.056	0.081	0.104	0.123	0.139	0.152	0.162	0.163	0.151	0.120
9.5						0.119	0.131	0.140	0.146	0.139	0.117
10.0	0.031	0.049	0.065	0.078	0.089	0.099	0.110	0.120	0.126	0.126	0.111

bond. In practice, it was used successfully in discussing the possibility of participation of d orbital in the π conjugation system with respect to the sulfur atom in thiophene. In this paper, as in the case of thiophene, with the aid of the overlap criterion, the contribution of the d orbital to the hybridization will be examined on the central sulfur atom in thiothiophten. Comparison is made between the values of overlap integral of the 3p and the 3d orbitals with $3p_\sigma$ of the neighboring sulfur atom. A larger amount of the value about the 3d orbital will be associated by a greater extent of the contribution, to the hybridization because the integral of the hybrid orbital may be written as the sum of those of the participating orbitals. The values of the integral of $3p_z - 3d_z$ were already given by Craig et al.[7], while those of $3p_\sigma - 3d_{xy}$ have not been published yet. In this paper, therefore, the values for $3p_\sigma - 3d_{xy}$ were calculated, together with those of $B_n(\alpha)$ necessary to evaluate the overlap integral. In Tables I and II are given the results.

In calculating the integral $S(3p_\sigma - 3d_{xy})$, one must pay some attention to the orientation of the $3d_{xy}$ orbital, because the internuclear axis is usually taken as the z-axis of the coordinate system of integration. The orbital should be rotated by 90° about the y-axis. After the rotation, the angular part of the orbital, $\sin^2\vartheta\cos^2\varphi$, turns into $(\cos^2\vartheta - \sin^2\vartheta\sin^2\varphi)$. The explicit expressions for the overlap integral are as follows:

for $t \neq 0$,

$$S(3p_\sigma - 3d_{xy}) = (1/2^7 \times 3\sqrt{5})(1-t^2)^{7/2} \times p^7 \times \{-A_0(3B_3 - B_5) - A_1(3B_2 - 2B_4 - B_6) + A_2(3B_1 + B_3 + 2B_5) + A_3(3B_0 - B_2 + B_4 - 3B_6) - A_4(2B_1 + B_3 + 3B_5) - A_5(B_0 + 2B_2 - 3B_4) - A_6(B_1 - 3B_3)\}$$

for $t = 0$,

$$S(3p_\sigma - 3d_{xy}) = (1/2^6 \times 315\sqrt{5}) \times p^7 \times (-48A_1 + 256A_3 - 112A_5)$$

for $p = 0$, $\quad S(3p_\sigma - 3d_{xy}) = 0$

where the method of evaluation described by Mulliken et al. and their notations[11] were used. The values of the function $A_n(\alpha)$'s which appear in the above expressions were taken from the table given by Kotani and his collaborators[12]. Those of $B_n(\alpha)$'s were evaluated by them for a wide range of the parameter α and also by Craig et al. for the small values of α [7]. However, some of the values necessary in the calculations of Table I were not available. Therefore, in this paper, a number of $B_n(\alpha)$ were calculated and the results are shown in Table II, together with those obtained by Craig et al.[7] In calculating the values of $B_n(\alpha)$, the recursion formula for $B_n(\alpha)$,

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

12) M. Kotani, A. Amemiya, E. Ishiguro and T. Kimura, "Table of Molecular Integrals", Maruzen Co., Tokyo (1955), p. 146.

TABLE II. $B_n(\alpha)=\int_{-1}^{+1}x^n e^{-\alpha x}dx$

α	$B_0(\alpha)$	$-B_1(\alpha)$	$B_2(\alpha)$	$-B_3(\alpha)$	$B_4(\alpha)$	$-B_5(\alpha)$	$B_6(\alpha)$
0	2	0	0.666667	0	0.400000	0	0.285714
0.05	2.00083	0.033342	0.667167	0.020006	0.400357	0.014290	0.286055
0.10	2.00334	0.066733	0.668668	0.040048	0.401429	0.028609	0.286824
0.15	2.00751	0.100225	0.671173	0.060161	0.403219	0.042982	0.288218
0.20	2.01336	0.133867	0.674686	0.080382	0.405729	0.057440	0.290171
0.25	2.02090	0.167711	0.679213	0.100746	0.408965	0.072009	0.292688
0.30	2.03014	0.201806	0.684763	0.121290	0.412932	0.086718	0.295776
0.35	2.04108	0.236204	0.691346	0.142051	0.417639	0.101596	0.299439
0.40	2.05376	0.270958	0.698973	0.163067	0.423095	0.116672	0.303687
0.45	2.06819	0.306119	0.707657	0.184374	0.429310	0.131975	0.308527
0.50	2.08438	0.341741	0.717416	0.206011	0.436297	0.147534	0.313969
0.55	2.10237	0.377879	0.728265	0.228016	0.444069	0.163382	0.320025
0.60	2.12218	0.414586	0.740224	0.250431	0.452640	0.179547	0.326706
0.65	2.14384	0.451920	0.753315	0.273294	0.462029	0.196063	0.334027
0.70	2.16738	0.489937	0.767562	0.296648	0.472253	0.212961	0.342003
0.75	2.19284	0.528696	0.782989	0.320534	0.483332	0.230274	0.350650
0.80	2.22026	0.568256	0.799625	0.344995	0.495288	0.248037	0.359985
0.85	2.24968	0.608679	0.817499	0.370077	0.508144	0.266285	0.370028
0.90	2.28115	0.650027	0.836643	0.395825	0.521925	0.285052	0.380800
0.95	2.31470	0.692365	0.857093	0.422286	0.536658	0.304377	0.392322
1.00	2.35040	0.735759	0.878885	0.449507	0.552373	0.324297	0.404618
1.05	2.38830	0.780277	0.902057	0.477540	0.569099	0.344852	0.477714
1.10	2.42845	0.825988	0.926653	0.506435	0.586869	0.366083	0.431636
1.20	2.51577	0.921285	0.980294	0.567025	0.625685	0.410739	0.462076
1.25	2.56307	0.971022	1.00944	0.598833	0.646806	0.434253	0.478656
1.30	2.61290	1.02226	1.04019	0.631726	0.669124	0.458620	0.496188
1.35	2.66532	1.07507	1.07263	0.665766	0.692683	0.483888	0.514708
1.40	2.72043	1.12955	1.10679	0.701106	0.717529	0.510108	0.534254
1.50	2.83904	1.24385	1.18057	0.775410	0.771280	0.565613	0.576587
1.60	2.96946	1.36592	1.26206	0.855464	0.830800	0.625579	0.623538
1.65	3.03935	1.43011	1.30589	0.897799	0.862869	0.657384	0.648864
1.70	3.11251	1.49654	1.35187	0.941778	0.896560	0.690487	0.675494
1.75	3.18904	1.56533	1.40009	0.987483	0.931941	0.724956	0.703482
1.80	3.26908	1.63659	1.45065	1.03500	0.971858	0.753143	0.758606
1.90	3.44017	1.78700	1.55912	1.13584	1.04893	0.837261	0.796188
1.95	3.53149	1.86639	1.61724	1.18935	1.09181	0.877915	0.830218
2.00	3.62686	1.94877	1.67809	1.24505	1.13675	0.920311	0.865927
2.20	4.05191	2.31086	1.95113	1.49202	1.33916	1.10910	1.02709
2.25	4.16993	2.41031	2.02743	1.56038	1.39592	1.16158	1.07238
2.30	4.29301	2.51367	2.10721	1.63165	1.45535	1.21638	1.11985
2.50	4.84016	2.96977	2.46435	1.94861	1.72239	1.46106	1.33362
2.55	4.99177	3.09546	2.56396	2.03658	1.79713	1.52923	1.39359
2.60	5.14979	3.22624	2.66807	2.12838	1.87536	1.60047	1.45641
2.70	5.48612	3.50401	2.89056	2.32417	2.04291	1.75274	1.59114
2.80	5.85137	3.80503	3.13349	2.53749	2.22638	1.91913	1.73895
2.85	6.04559	3.96492	3.26319	2.65125	2.32454	2.00804	1.81814
2.90	6.24797	4.13145	3.39870	2.77002	2.42725	2.10101	1.90106
3.00	6.67858	4.48558	3.68820	3.02358	2.64715	2.29987	2.07885
3.20	7.65368	5.28738	4.34907	3.60191	3.15130	2.75525	2.48758
3.40	8.80315	6.23362	5.13632	4.29074	3.75522	3.30040	2.97892
3.50	9.45293	6.76935	5.58473	4.68327	4.10062	3.61216	3.26065
3.60	10.15859	7.35194	6.07418	5.11195	4.47864	3.95343	3.56953
3.80	11.75758	8.67526	7.19166	6.09173	5.34523	4.73615	4.27944
4.00	13.64496	10.24288	8.52352	7.26148	6.38348	5.67476	5.13281

TABLE III. OVERLAP INTEGRALS: $S(3p_z-3d_z)$

p/t	−0.5	−0.4	−0.3	−0.2	−0.1	0.0	0.1	0.2	0.3	0.4	0.5
0	0	0	0	0	0	0	0	0	0	0	0
0.5						−0.167	−0.185	−0.188	−0.174	−0.146	−0.107
1.0	−0.033	−0.072	−0.127	−0.190	−0.254	−0.306	−0.339	−0.344	−0.319	−0.268	−0.199
1.5						−0.395	−0.435	−0.443	−0.413	−0.351	−0.265
2.0	−0.063	−0.122	−0.197	−0.279	−0.358	−0.423	−0.464	−0.473	−0.447	−0.386	−0.297
2.5						−0.393	−0.430	−0.441	−0.423	−0.375	−0.298
3.0	−0.073	−0.123	−0.178	−0.231	−0.279	−0.318	−0.347	−0.360	−0.355	−0.327	−0.272
3.5						−0.216	−0.235	−0.251	−0.259	−0.254	−0.228
4.0	−0.060	−0.082	−0.096	−0.101	−0.102	−0.105	−0.114	−0.131	−0.152	−0.170	−0.171
4.5						−0.000	−0.001	−0.017	−0.048	−0.092	−0.111
5.0	−0.033	−0.025	−0.002	0.030	0.063	0.088	0.095	0.080	0.044	−0.005	−0.053
5.5						0.155	0.167	0.156	0.117	0.061	0.001
6.0	−0.004	0.024	0.066	0.116	0.163	0.199	0.215	0.206	0.171	0.113	0.044
6.5						0.222	0.240	0.236	0.205	0.150	0.079
7.0	0.018	0.054	0.100	0.149	0.194	0.228	0.248	0.247	0.223	0.174	0.106
7.5						0.221	0.241	0.244	0.226	0.186	0.124
8.0	0.031	0.066	0.106	0.144	0.178	0.205	0.224	0.230	0.220	0.188	0.134
8.5						0.184	0.202	0.210	0.206	0.184	0.139
9.0	0.036	0.065	0.094	0.120	0.142	0.161	0.176	0.187	0.188	0.174	0.138
9.5						0.137	0.151	0.162	0.169	0.161	0.135
10.0	0.036	0.057	0.075	0.090	0.103	0.114	0.127	0.138	0.146	0·145	0.128

$$B_n(\alpha)=(1/\alpha)\{(-1)^n e^{\alpha}-e^{-\alpha}+nB_{n-1}(\alpha)\}$$

was used, and the values of e^{α} and $e^{-\alpha}$ were taken from the table published by the Computation Laboratory of NBS[13]. Some of the exponential functions were derived by using the table of hyperboric functions[14]. According to Mulliken's convention concerning the sign of t [11], the values of $S(3p_{\sigma}-3d_{xy})$ for $t<0$ were also evaluated. These are given in Table I. These values can easily be derived by replacing $B_n(\alpha)$ with $B_n(-\alpha)$ of the above expression and $B_n(-\alpha)$ is obtained from $B_n(\alpha)$ through the relation $B_n(-\alpha)=(-1)^n\times B_n(\alpha)$. These integrals are corresponding to the values obtained when $3d_{xy}$ orbital has its greater effective nuclear charge than that of $3p_x$. Further, in Table III, the overlap integrals $S(3p_z-3d_z)$ with the parameter p at intervals of 0.5 and of 1.0 are shown for $t>0$ and $t<0$ respectively. Some of the values were already given, as mentioned above, by Craig et al.[7], who evaluated the values with p at intervals of 1.0.

In order to estimate the values of overlap integrals using the above tables, it is necessary to know the effective nuclear charges of the orbitals concerning the atoms. The respective charges found in accordance with Slater's formula[15] are as follows: 5.80 and 1.00 for 3p and 3d orbitals on the central sulfur atom and 5.45 for 3p orbital on the neighboring sulfur atom. Since the bond distance S-S is 2.36 Å, the values about 3p−3d give 0.7 and 5 for t and p (see Ref. 11) respectively. From Tables I and III it is inferred that negative values of overlap integrals result from these t and p values. With this result, one might not expect any participations of the d orbitals in bonding to occur through the hybridization. This may be due to the straightforward application of Slater's rule to the estimation of the effective nuclear charges of the atoms. As already mentioned[5], since the maximum of the radial function of the d orbital with its effective nuclear charge 1 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 comparable value of the overlap integral to that of 3p orbital. Then it might be expected that the participation of the d orbital in the hybridization would take place to an extent not much smaller than that of 3p orbital. It is necessary, therefore, to examine the influence of the nuclear charges of the neighboring atoms of thiothiophten upon the d orbital of the central sulfur atom. Further discussions, however, will be given in subsequent publications.

It is of interest to notice the following

13) Computation Laboratory, "Tables of the Exponential Function e^x", Natl. Bur. Standards, Washington (1951).
14) Committee for the Calculation of Mathematical Tables, "British Association Mathematical Tables", 1, 30 (1951).
15) J. C. Slater, *Phys. Rev.*, 36, 57 (1930).

points with respect to the values of overlap integral given in Tables I and III; the value $S(3p_z-3d_z)$ is greater than that of $S(3p_\sigma-3d_{xy})$. This may predict a greater possibility of the participation of $3p_z$ orbital than that of $3d_{xy}$. In both tables, the value for $t<0$ is small, as a whole, compared with that for $t>0$. This may imply that it is not easy to form a bond between 3d with a greater effective nuclear charge and 3p with a smaller one.

The author wishes to express his sincere thanks to Dr. S. Nagakura, The University of Tokyo, for his kind advice and helpful discussions.

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