On the Electronic Structure of Thiothiophten

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Recently the structure of a thiothiophten molecule was clarified through the X-ray analysis by Bezzi, Mammi and Garbuglio[1], who proposed a condensed ring system characterized by no-bond resonance structure. On the basis of this peculiar structure, Giacometti and Rigatti[2] have made simple LCAO treatment on the superimposed σ and π systems of nonlocalized electrons in thiothiophten, by using only p type orbitals for valence states of sulfur atoms. However, since the system involving no-bond resonance structure is somewhat unlikely to occur, an alternative interpretation on the electronic structure of thiothiophten will be given in the present report.

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[3]. Then it may be reasonable to consider that the central sulfur atom in the straight bond S-S-S of thiothiophten is in a valency state capable of forming the σ skeleton of bonds through the pd hybridization. The expected valency state of the central sulfur atom would be in the electron configuration $3s^2 3p^3 3d$; one of $3p$'s, $3p_x$, hybridizes with a $3d$ orbital, going to make up the σ bonds of S-S-S in the linear arrangement, and $3p_y$ is adopted to form a C-S σ bond with one of sp^2 orbitals of the neighboring central carbon atom. These configurations can account for both the so-called abnormal length of the bond between two sulfur atoms[3-5] and the right angle of S-S-C with respect to the central sulfur atom. Thus it might be said that the full σ skeleton of the condensed ring system of thiothiophten is composed of the bonds obtained above through the hybridization and other C-S and C-C bonds without introducing the no-bond resonance structure. Over this σ ring system covers the π electron conjugation system, in which the remaining $3p$ orbital, namely the $3p_z$ orbital participates. The electronic structure of thiothiophten can now be treated according to the usual LCAO approximation without considering the σ skeleton.

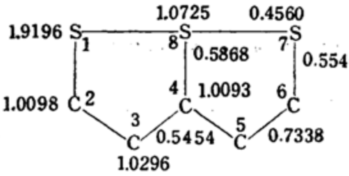

Fig. 1. Molecular diagram of thiothiophten.

In Fig. 1 are given the results obtained by the simple LCAO π approximation on thiothiophten. In calculating the molecular diagram, the following assumptions were adopted: All the Coulomb intengrals were taken to be equal to the common value (so-called α_c) except for two sulfur atoms S_1 and S_7 (see Fig. 1), for which a value less by 0.2β was applied, because the equivalent conjugation systems of thiothiophten in terms of valence bond method are liable to make the atoms positively charged[6]. Furthermore Longuet-Higgins' idea was employed for the two atoms[7]. With respect to the exchange integrals, the standard of the value, β was used for all C-C bonds. For S-S and central C-S bonds were given the values 0.3β and 0.6β, respectively, which are both found in the report of Giacometti and Rigatti[2]. The results given in Fig. 1 are those obtained when the exchange integral of C-S involving S_1 or S_7 bears the same value as that of C-C. The employment of the value is due to nonsymmetrical character between the two bonds on the sulfur atom.

The results obtained in this paper are almost the same as those of Giacometti and Rigatti[2], but they are not necessarily the best. It must be noticed, however, that the results obtained without the help of no-bond resonance idea are appropriate at any rate, although many approximations were necessary in the calculation. The insufficient character of the results may be due to the inadequate values of parameters, which should be determined to predict correctly the values of the dipole moment and resonance energy[6]. Details will be further discussed in subsequent publications.

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