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Intramolecular Orbital Interactions in 6,6′-Bi(1,4-dithiafulvenyl) Studied by Photoelectron Spectroscopy

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Photoelectron spectra of tetrathiafulvalene (TTF) and 6,6′-bi(1,4-dithiafulvenyl) (BDTF) were measured and compared with each other. The first photoelectron spectral band of BDTF is only slightly shifted relative to that of TTF, though the BDTF molecule is lengthened compared with the TTF molecule by two sp^2 carbon atoms. From the LCGO model orbital interaction analysis, this apparent anomaly is ascribed to the near cancellation of the effects of two main factors, the energy and the terminal atomic orbital coefficient differences between the central olefinic group π orbitals. Orbital interaction analysis as demonstrated in this work may be useful for molecular design, especially for orbital energy control.

In 1973 a charge transfer complex between tetrathiafulvalene (TTF) and tetracyano-*p*-quinodimethane was found to show high electrical conductivity.[1] This finding triggered off present-day active researches on organic metals. Especially several cation radical salts of tetramethyltetraselenafulvalene closely related to TTF was recently found to show superconductivity at low temperature.[2]

During the course of the study to develop good electron donors, 6,6′-bi(1,4-dithiafulvenyl) (BDTF, 2,2′-ethanediylidenebis[1,3-dithiole]) structurally closely related to TTF was recently synthesized.[3] In this paper the photoelectron (PE) spectra of TTF and BDTF are measured and compared with each other in order to get informations useful for molecular design.

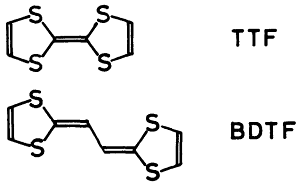

Fig. 1. Structural formulae of TTF and BDTF.

Experimental

Materials. Tetrathiafulvalene (TTF) purchased from the Aldrich Chemical Co. was recrystallized twice from hexane just before use. 6,6′-Bi(1,4-dithiafulvenyl) (BDTF) was synthesized as reported formerly[3] and purified by column chromatography (neutral alumina, benzene) and subsequent recrystallization from benzene.

Measurements. Vapor phase HeI PE spectra of TTF and BDTF were measured with the PE spectrometer described in Refs. 4 and 5. The sample inlet and target chamber systems were kept at 120 °C during the measurements. Xe gas was used as the internal reference standard for the calibrations of the energy scale.

Computational

Pariser-Parr-Pople (PPP) type SCF MO calculations of TTF and BDTF were carried out on a FACOM M-380 computer at the Institute of Physical and Chemical Research. The parameter set necessary in the calculations was taken from Ref. 6. The geometrical structural data for TTF were taken from Ref. 7. The bond angles and bond lengths of the central olefinic moiety of BDTF were assumed to be the same as those of *s-trans*-1,3-butadiene[8] and the dimensions of the two five-membered rings of BDTF were assumed to be the same as those in TTF.[7]

Results and Discussion

Photoelectron Spectral Band Assignments. The vapor phase HeI PE spectra of TTF and BDTF are shown in Fig. 2. The vertical ionization energies, E_{iv}, of TTF and BDTF obtained from the PE spectra are summarized in Table 1. The PE spectra of TTF were formerly reported,[9–11] but was remeasured this time for the sake of consistency. Our PE spectrum of TTF is consistent with those reported formerly.[9–11]

The first four PE spectral bands of TTF have already been assigned as $4b_{1u}\pi$, $3b_{3g}\pi$, $2a_u\pi$, and $2b_{2g}\pi$ from the top, respectively.[9b] Here in this paper the *z*-axes are taken perpendicular to the molecular planes for TTF and BDTF, and the *x*-axis is taken along the short molecular axis for TTF. The $2a_u$ and $2b_{2g}$ orbitals of TTF are completely localized on the two SCCS groups and are predicted degenerate within the simple zero-

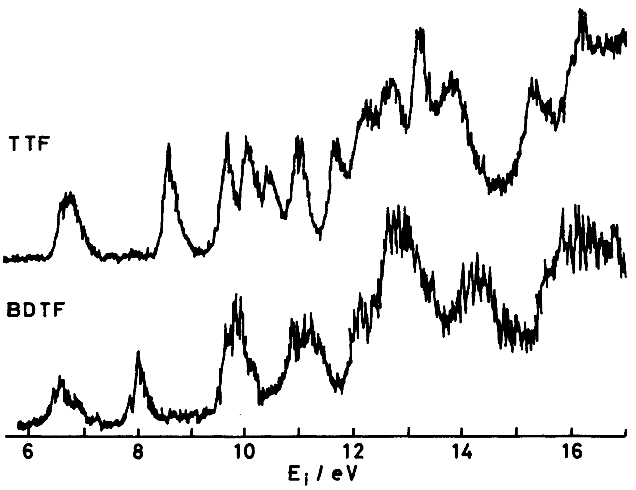

Fig. 2. Vapor phase HeI photoelectron spectra of TTF and BDTF.

TABLE 1. OBSERVED AND CALCULATED VERTICAL IONIZATION ENERGIES, E_{iv}, OF TTF AND BDTF WITH ORBITAL ASSIGNMENTS

Compd			E_{iv}/eV						
TTF	Obsd		6.72	8.56	9.71	10.04	10.50	11.0	
			$4b_{1u}$[a)]	$3b_{3g}$[a)]	$2a_u$[a)]	$2b_{2g}$[a)]	$3b_{1u}$[b)]	$9b_{1g}$[b)]	
	Calcd	PPP[c)]	6.80	8.96	10.01	10.01	10.61		
			$4b_{1u}$	$3b_{3g}$	$2a_u$	$2b_{2g}$	$3b_{1u}$		
		LCGO[d)]	6.72	8.49	9.88	9.88	10.51		
			$4b_{1u}$	$3b_{3g}$	$2a_u$	$2b_{2g}$	$3b_{1u}$		
BDTF	Obsd		6.61	8.02		9.70		10.82	11.3
			$6b_g$	$6a_u$	$5b_g$	$5a_u$	$4b_g$		
	Calcd	PPP[c)]	6.87	8.63	10.11	10.12	10.20		11.35
			$6b_g$	$6a_u$	$5b_g$	$5a_u$	$4b_g$		$4a_u$
		LCGO[d)]	6.77	7.93	9.86	9.88	9.88	11.02	
			$6b_g$	$6a_u$	$5b_g$	$5a_u$	$4b_g$	$4a_u$	

a) Ref. 9b. b) Ref. 11. c) The Pariser-Parr-Pople type calculation, see the text. d) The linear combination of group orbitals calculation, see the text.

differential overlap approximation, but in reality, are split slightly because of the long range through-space interactions with the $2a_u$ orbital above the $2b_{2g}$ orbital.[9b)] As for the fifth and sixth bands of TTF, Gleiter *et al.*[9b)] suggested that these bands should be ascribed to $9b_{1g}n$ and $3b_{1u}\pi$ bands, respectively, based on the MINDO/3 calculations. However, afterwards, Schweig *et al.*[11)] assigned those bands as the $3b_{1u}$ and $9b_{1g}$ bands, respectively, from the comparison among the PE spectra of TTF, diselenadithiafulvalene, and tetraselenafulvalene.

For the PE spectral band assignments of BDTF, we use two types of computational methods. One is the linear combination of group orbitals (LCGO) method and the other one is the PPP type method. As the PPP type calculation with Fabian *et al.*'s parameter set[6)] reproduces well the observed E_{iv}'s for the first five bands of TTF[9b)] (see Table 1 also) on the assumption of the Koopmans theorem,[12)] let us apply this method to the case of BDTF. The calculated results are given in Table 1.

The calculated ionization energies reproduce rather well the observed E_{iv}'s for the first three bands of BDTF. The calculation suggests that the observed third band corresponds to the three ionizations, and this is reasonable from the band intensity relative to those of the first two bands. The $5b_g$ and $5a_u$ orbitals of BDTF calculated by the PPP method correspond almost to the $2b_{2g}$ and $2a_u$ orbitals of TTF which are completely localized on the two SCCS groups. The $5b_g$ and $5a_u$ bands of BDTF, therefore, are expected to appear in the same energy region as the $2b_{2g}$ and $2a_u$ bands of TTF, that is, around 9.7—10.0 eV. This is consistent with the assignment suggested above for the 9.70 eV band of BDTF. It is uncertain from the PPP calculation if the fourth 10.82 eV band should be assigned as the $4a_u$ band.

Now we use the LCGO model to make the band assignments more definite. This model has been used by Gleiter *et al.*[9b)] in the PE spectral band assignments of TTF formerly. In the LCGO model calculations the TTF molecule is regarded to be composed of three CC double bond groups and four sulfur atoms. The BDTF molecule is regarded to be composed of two CC double bond groups, four sulfur atoms, and a *trans*-butadiene-like group. The interactions among the π and π^* orbitals of the CC double bond groups and the n orbitals of the sulfur atoms are considered in the case of TTF. As for BDTF the contributions from the $1a_u\pi_1$, $1b_g\pi_2$, $2a_u\pi_3^*$, and $2b_g\pi_4^*$ orbitals of the central *trans*-butadiene type group are also taken into account.

At first we reestimate the parameter values necessary in the LCGO model calculations. The newly reevaluated basis group orbital energy values are summarized in Table 2. Of the values in Table 2 the occupied π orbital energies of the CC double bond groups and the *trans*-butadiene-like group were estimated by using the E_{iv} values of ethylene[13)] and *trans*-butadiene[14)] obtained by PE spectroscopy. The vacant π basis orbital energies of those component groups were estimated by using the electron affinities of ethylene[15)] and *trans*-butadiene[16)] obtained by electron transmission spectroscopy. The resonance integral values for the CS π bonds, β_{CS}, and the basis orbital energy values of the sulfur atoms, A_S, were readjusted as −1.90 eV and −9.57 eV, respectively, to reproduce the first, third, and fourth E_{iv} values of TTF. The β_{CS} and A_S values suggested by Gleiter *et al.*[9b)] formerly were −1.80 eV and −9.4 eV, respectively, and these values are close to those readjusted here. The

TABLE 2. BASIS GROUP ORBITAL ENERGIES, A

Basis group orbital	A/eV[a)]
Ethylene type group	
$(b_{1u})\pi_1$	−10.51
$(b_{3g})\pi_2^*$	1.78
trans-Butadiene type group	
$a_u\pi_1$	−11.46
$b_g\pi_2$	−9.03
$a_u\pi_3^*$	0.76
$b_g\pi_4^*$	2.8
Sulfur atom	
n	−9.57

a) For the evaluations of the A values, see the text.

calculated results for the first five bands of TTF with the new parameter set are given in Table 1, and the overall agreement between theory and experiment is satisfactory with the band ordering assigned formerly.[11]

Now let us apply the simple LCGO method with our new parameter set to BDTF in question. The calculated results are shown in Table 1. The calculated band ordering by the simple LCGO model is the same as that suggested by the PPP method. The predicted E_{iv} values for BDTF by the LCGO method are closer to the observed ones as for the first three bands than those by the PPP method. Now the first two bands are unambiguously assigned as the $6b_g$ and $6a_u$ bands, respectively, and the apparent third band is ascribed to the three bands, $5b_g$, $5a_u$, and $4b_g$ bands highly overlapping with one another. The assignment of the 10.82 eV band is left unsettled for further detailed examinations.

Orbital Interaction Analysis. It is quite natural to expect that the first E_{iv} of BDTF is far smaller than that of TTF because the BDTF molecule is extended longer than the TTF molecule just by almost the same length as in the case of *trans*-butadiene compared with ethylene, the first E_{iv} values of these compounds being 9.03 eV[14] and 10.51 eV,[13] respectively. In reality, however, the first band of BDTF is only slightly (by 0.11 eV) shifted to the lower energy side compared with that of TTF, while the second band of BDTF is reasonably shifted to the lower energy side by 0.54 eV compared with that of TTF. This small shift of the first band of BDTF relative to that of TTF is interesting because of its contradiction to natural expectation. Theoretically both LCGO and PPP type methods predict well the point that the first E_{iv} value of BDTF is very close to that of TTF. For the second bands of these molecules, the LCGO model predicts quantitatively the reasonably large E_{iv} difference, 0.5 eV, and the PPP method predicts semiquantitatively this tendency.

Now let us analyze the PE spectral band shifts of BDTF relative to TTF by the LCGO model. At first we examine the case of the first bands. The highest occupied molecular orbital (HOMO) of TTF is of b_{1u} symmetry and is regarded to be formed mainly by the interaction among the following occupied π group orbitals: One is the central ethylene type group π orbital, and other two ones are those formed by the in-phase (b_{1u}) type combinations of the occupied π orbitals of the two SCCS groups of the TTF molecule. On the other hand the HOMO of BDTF is of b_g symmetry and is regarded to be formed mainly by the interactions among the following orbitals: One is the b_g symmetry π_2 orbital of the *trans*-butadiene type group and other two ones are the orbitals formed by the out-of-phase combinations of the occupied π orbitals of the two SCCS groups. It is noticed that the $4b_g$ MO in the LCGO model of BDTF is completely localized on the two SCCS groups just as the $2b_{2g}$ MO of TTF and is not taken into account in the above consideration. The energies of those out-of-phase type group orbitals described above are almost equal to those of the corresponding in-phase type group orbitals. In addition to those the π_4^* orbital of the *trans*-butadiene type group is also expected to contribute to the b_g HOMO of BDTF from the symmetry reason.

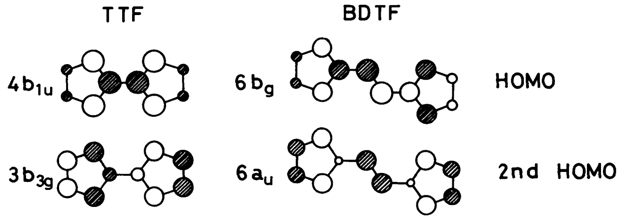

Fig. 3. Schematic representations of the first and second HOMO's of TTF and BDTF calculated by the PPP type method.

On the first stage we estimate the effect of the central olefinic group occupied π orbital energy change. In the case of TTF the central olefinic group π orbital energy is −10.51 eV, and the π_2 basis orbital energy of the *trans*-butadiene-like group is −9.03 eV. If we change the central olefinic group occupied π basis orbital energy from −10.51 eV to −9.03 eV, the effect of this change on the HOMO energy of TTF is evaluated to be −0.525 eV. Only 35% of the central olefinic group π orbital energy change is reflected on the HOMO energy change toward the destabilization.

In addition to the above effect, in the process of replacing the central ethylenic group of TTF by a *trans*-butadiene type group we must take into account the effect of the resonance integral change between the olefinic occupied π orbital and the group π orbital of the appropriate symmetry composed of the four sulfur atom 3p lone pair orbitals. The absolute values of the atomic orbital (AO) coefficients of the terminal carbon atoms of the central olefinic group HO-π-MO are 0.7071 in the case of the ethylene type group and 0.5727 in the case of the *trans*-butadiene type group. The latter values have been calculated by a modified CNDO method[17] for *trans*-butadiene. By using the latter values we can estimate the resonance integral value for the case of BDTF in question as −2.176 eV, that is, decrease in the absolute value by 0.5 eV from the corresponding one for TTF (−2.687 eV). By using this resonance integral value thus estimated we can estimate the additional HOMO energy change as −0.456 eV or stabilization of the HOMO by 0.456 eV. In this case the resonance integral value change influences almost directly on the HOMO energy change.

In order to estimate the effect of the π^* level on the HOMO energy, let us now introduce the π_4^* orbital of the *trans*-butadiene-like group into the above model with the appropriate symmetry. Thus, the effect is estimated to be 0.122 eV, or stabilization of the HOMO by 0.122 eV. From the above stepwise model calculations it is said that in replacing the central CC double bond in TTF by a longer *trans*-butadiene-like group, the central olefinic group HOMO energy change contributes considerably toward the stabilization of the HOMO by around 0.5 eV, while this effect is almost completely compensated by the decreases in the absolute values of the terminal AO coefficients of the central olefinic group HOMO. The HOMO stabilization effect of the π_4^* level of the central *trans*-butadiene-like group of BDTF is not so large (*ca.* 0.1 eV).

From the above model consideration it is concluded that the anomalously small shift of the first band of BDTF compared with that of TTF can be explained by the almost perfect cancellation of the two main effects, the energy and the terminal AO coefficient changes of the central olefinic group π orbital.

Next let us compare the second E_{iv}'s of TTF and BDTF. The second E_{iv} of BDTF is smaller than that of TTF by *ca.* 0.5 eV, and this seems to be reasonable as stated before. Now we analyze the situation with the LCGO model. In the case of TTF the second HOMO is of b_{3g} symmetry and is contributed by the π^* orbital of the central ethylenic group toward stabilization. If we change only the energy of the central olefinic group vacant π basis orbital from 1.78 eV to 0.76 eV, the π_3^* basis orbital energy of the *trans*-butadiene type group, in TTF, the second HOMO stabilization by this change is only 0.04 eV and this effect is negligibly small.

Further let us change the absolute values of the terminal AO coefficients of the central olefinic group vacant π orbital from 0.7071 for the ethylene type group to 0.5595 for the *trans*-butadiene type π_3^* orbital. So the second HOMO of TTF is destabilized on this second step by 0.15 eV.

Introduction of the π_1 basis orbital of the *trans*-butadiene type group into this last model with the appropriate symmetry causes large destabilization of the second HOMO by 0.45 eV. From the above model calculations, it is concluded that the apparently reasonable decrease in the second E_{iv} energy of BDTF compared with that of TTF is ascribed mostly to the second HOMO destabilization caused by the contribution of the π_1 basis group orbital of the central *trans*-butadiene type group.

In the discussion so far we have been concerned with the apparent relative energy shifts of the first (second) bands of TTF and BDTF. However, from the standpoint of MO symmetry the HOMO and the second HOMO of TTF are to be correlated with the second HOMO and the HOMO of BDTF, respectively, that is, if we take the orbital symmetry into account, the original first band of TTF should be regarded to be shifted to the higher ionization energy side by 1.30 eV, while the second band of TTF is shifted to the lower ionization energy side by 1.95 eV, the ordering of the first and second bands being reversed, when the TTF molecule is stretched to BDTF.

Let us examine the HOMO energy shift of TTF in the above sence. The HOMO of TTF is of b_{1u} symmetry and contributed from the occupied group π orbital of the central CC double bond. In the LCGO model, if we change the basis orbital energy of this central CC double bond from -10.51 eV to -11.46 eV for the *trans*-butadiene type group π_1 orbital, the HOMO energy is only slightly stabilized by 0.24 eV. In this model if we change the terminal AO coefficients from 0.7071 for the ethylene π orbital to 0.4324 for the *trans*-butadiene π_1 orbital, the HOMO is additionally stabilized by 0.67 eV. In this model, if we introduce the π_3^* orbital of the *trans*-butadiene type group, the HOMO is further stabilized by 0.31 eV. The stabilization of the HOMO of TTF by the extension of TTF to BDTF is ascribed to the cumulative effect of the above three factors.

Next we discuss the second HOMO energy shift of TTF caused by the molecular lengthening to BDTF taking the orbital symmetries into account. The second HOMO of TTF is contributed from the π^* orbitals of the central olefinic group. If we change the π^* orbital energy of the central olefinic group in TTF from 1.78 eV for the ethylene type group to 2.8 eV for the *trans*-butadiene type group π_4^* orbital, the second HOMO of TTF is destabilized only by 0.03 eV. If we change in this model the absolute values of the terminal AO coefficients from 0.7071 for the ethylene π^* orbital to 0.4147 for the *trans*-butadiene π_4^* orbital, the second HOMO is further destabilized by 0.24 eV. If we introduce the π_2 basis orbital of the *trans*-butadiene type group into this model, the second HOMO is further considerably destabilized by 1.45 eV. The large destabilization of the second HOMO of TTF by the molecular lengthening to BDTF is mostly ascribed to the contribution of the π_2 orbital of the *trans*-butadiene type group.

Conclusion

Lengthening of a molecule toward its long molecular axis does not necessarily lead to the apparent efficient destabilization of the HOMO as seen in the case of TTF and BDTF treated in this paper. Anomalously small shift of the first PE spectral band of BDTF compared with that of TTF is ascribed to the near cancellation of the effects of two main factors, the energy and the terminal AO coefficient changes of the basis orbital of the central olefinic part. Orbital interaction analysis as demonstrated in this paper is expected to be useful for molecular design, especially for orbital energy control.

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