metal–metal transitions then Figure 9 indicates that it would be obscured by intense charge-transfer transitions for all other compounds of this study.[26]

Comparisons to Related Systems

While no single-crystal absorption experiments have been undertaken for other quadruply bonded dimers possessing mixed halide/phosphine coordination spheres, a circular dichroism study of the torsionally distorted β-$Mo_2X_4(PP)_2$ complexes (X = Cl, Br; PP = chiral bridging diphosphine) has been reported.[28] Although direct comparisons of band positions among the spectra of the β-$Mo_2X_4(PP)_2$ and $Mo_2X_4(PMe_3)_4$ compounds are difficult due to the fact that the former series has a greater number of absorption features, the spectra of the chiral compounds display an intense ($\epsilon > 3000$) feature at 370–380 nm that has been assigned[28] to $\pi_{yz} \rightarrow \delta^*$.[29] Since this absorption band also appears in the spectrum of D_2 β-$Mo_2Cl_4(dmpe)_2$[13c] at nearly the same position, and with equal intensity, as band II of the latter compound's D_{2d} rotamer, $Mo_2Cl_4(PMe_3)_4$, we conclude that these bands instead correspond to P → Mo excitations.

Relevant to our findings for $M_2X_4(PMe_3)_4$ systems are the results of spectroscopic studies on the $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$ ions. The low-temperature single-crystal spectra of $K_4[Mo_2Cl_8]\cdot 2H_2O$[9] show an exceedingly weak feature near 450 nm that might be $^1(\pi \rightarrow \delta^*)$, which is dipole-forbidden in D_{4h} symmetry. A moderately intense ($\epsilon \sim 200$) feature of mixed polarization at 345 nm was attributed to a ^3E_u excited state, with the corresponding ^1E_u state being assigned to the strong x,y-polarized absorption whose maximum ($\lambda < 330$ nm) was far too intense to be recorded. The triplet assignment seems reasonable, but we suggest that an $e_g(\pi(Cl)) \rightarrow \delta^*$ assignment for the intense band is far more likely to be correct than the proposed[9] $\pi \rightarrow d_{x^2-y^2}$ assignment. The crystal spectrum of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ has been extensively studied,[4,7,8] and several weak ($\epsilon < 100$) features are found in the 400–600-nm region. While two of them are highly vibronically structured in $\nu(Re_2)$, and therefore quite certain to be metal–metal-localized transitions, their interpretation is complicated by crystal disorder, so experimental assignments are not very secure. A band near 570 nm has been assigned to $^1(\pi \rightarrow \delta^*)$, perhaps overlapping with $^1(\delta \rightarrow \pi^*)$. A similarly highly vibronically structured band has been reported[4] at a similar wavelength for $[(n\text{-}C_4H_9)_4N]_2[Re_2Br_8]$. Since $^1(\pi \rightarrow \delta^*)$ is dipole-forbidden in D_{4h} symmetry, the very low intensity is reasonable, but additional work needs to be done on these systems. In particular, the possibility of a $\sigma \rightarrow \delta^*$ assignment should be considered for the 570-nm band.

Acknowledgment. We thank Bill Schaefer for assistance with the X-ray photography. M.D.H. acknowledges the Sun Co. and Standard Oil Co. (Ohio) for graduate fellowships. This work was supported by National Science Foundation Grant CHE84-19828. Part of the research included in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

Registry No. $Mo_2Cl_4(PMe_3)_4$, 67619-17-4; $Mo_2Br_4(PMe_3)_4$, 89707-70-0; $Mo_2I_4(PMe_3)_4$, 89637-15-0; $W_2Cl_4(PMe_3)_4$, 73133-20-7.

Supplementary Material Available: $\perp z$-polarized single-crystal absorption spectra of $Mo_2Cl_4(PMe_3)_4$ and $Mo_2Br_4(PMe_3)_4$ in the region of their $^1(\delta \rightarrow \delta^*)$ transition at ca. 5 K (2 pages). Ordering information is given on any current masthead page.

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[29] The designation of this transition arises because the degenerate $\pi_{xz,yz}$ level in molecules of the parent D_{2d} symmetry may be split in the D_2 symmetry of the diphosphine-bridged species. Judging by the high d-orbital character of the π level calculated by Ziegler[16] (Figure 1), a large splitting would not be expected, since a pure metal-dπ level is invariant to rotation about the metal–metal bond.

Electronic Structure of Tetrakis(isopropylthio)thieno[3,4-*c*]thiophene Studied by Photoelectron and Electronic Absorption Spectroscopies Combined with MO Calculations

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Abstract: Photoelectron and electronic absorption spectra of tetrakis(isopropylthio)thieno[3,4-*c*]thiophene (I) were measured. On the basis of these data combined with MO calculations the ground- and excited-state electronic structures of this compound containing two thiophene rings uniquely fused with each other were studied in detail. The He I photoelectron spectrum of I shows the bands at 6.72, 7.89–8.71, and 9.14 eV in the ionization energy scale. On the basis of the photoelectron spectrum it was concluded that the CSC planes relevant to the isopropylthio groups are twisted out by about 60° from the parent ring plane. The first band, the energy of which is as low as that of tetrathiafulvalene, corresponds to the ionization from the HO-π-MO almost completely localized on the 1-, 3-, 4-, and 6-carbon atoms of the parent framework. The electronic absorption spectrum of I in hexane shows the first band at 2.46 eV, this band being assigned to the $^1B_{3u} \leftarrow {}^1Ag$-like (mainly LU-$\pi$-MO ← HO-$\pi$-MO) transition almost localized on the parent ring system. It is concluded that compound I is as effective as tetrathiafulvalene for the electron-donating ability and reflects strongly the electronic character of the unknown parent compound, thieno[3,4-*c*]thiophene, for the relatively low energy phenomena such as chemical reactions relevant to HOMO and/or LUMO. Combination of photoelectron and electronic absorption spectroscopies assisted by MO calculations is effective in elucidating electronic structure of molecules as demonstrated in this work.

Among various types of spectroscopies photoelectron spectroscopy is the most powerful tool for studying occupied molecular orbitals for it gives almost directly orbital energy diagrams if we follow Koopmans' theorem.[2] In this paper electronic structure

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Table I. Molecular Orbital and Vertical Ionization Energies (ϵ and E_{iv})

	thieno[3,4-*c*]thiophene			tetrakis(isopropylthio)thieno[3,4-*c*]thiophene							
				planar			twisted (60°)				
		ϵ/eV			ϵ/eV			ϵ/eV		obsd	
level	sym	PPP	HMO	sym[a]	PPP	HMO	sym[a]	PPP	HMO	band	E_{iv}/eV
3L	b_{1g}	2.07	-1.80	b_{1g}	2.62	-1.67	b_{1g}	2.26	-1.76		
2L	b_{2u}	0.21	-3.59	b_{2u}	0.83	-3.26	b_{2u}	0.42	-3.49		
1L	b_{3g}	-2.13	-5.31	b_{3g}	-1.36	-4.79	b_{3g}	-1.87	-5.15		
1H	a_u	-7.24	-7.20	a_u	-5.78	-6.03	a_u	-6.65	-6.72	(1)	6.72
2H	b_{2u}	-9.79	-9.37	b_{1g}	-7.94	-7.63	b_{1g}	-8.54	-8.01	(2)	7.89
3H	b_{1g}	-10.13	-9.90	b_{2u}	-9.07	-8.36	b_{2u}	-8.98	-8.27	(3)	8.2
4H	b_{3g}	-11.65	-11.02	b_{3g}	-9.19	-8.45	b_{3g}	-9.03	-8.30	(4)	8.5
5H	b_{2u}	-13.44	-13.27	b_{2u}	-9.37	-9.38	a_u	-9.40	-8.71	(5)	8.71
6H				a_u	-10.12	-9.40	b_{2u}	-9.63	-9.38	(6)	9.14
7H				b_{1g}	-10.96	-10.64	b_{1g}	-10.43	-10.15	(7)	10.3
8H				b_{3g}	-11.58	-11.32	b_{3g}	-11.57	-11.11		
9H				b_{2u}	-13.26	-13.46	b_{2u}	-13.34	-13.32		

[a] Symmetry notations are for the D_{2h} point group for the sake of convenience.

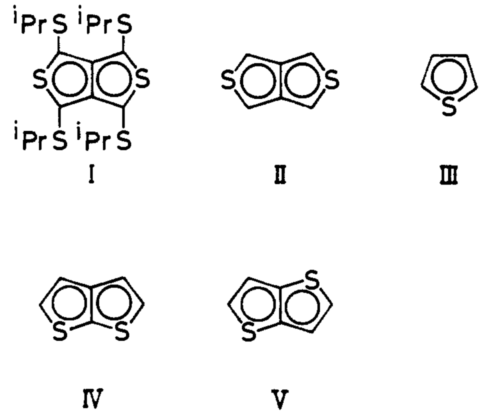

Figure 1. Molecular structural formulae.

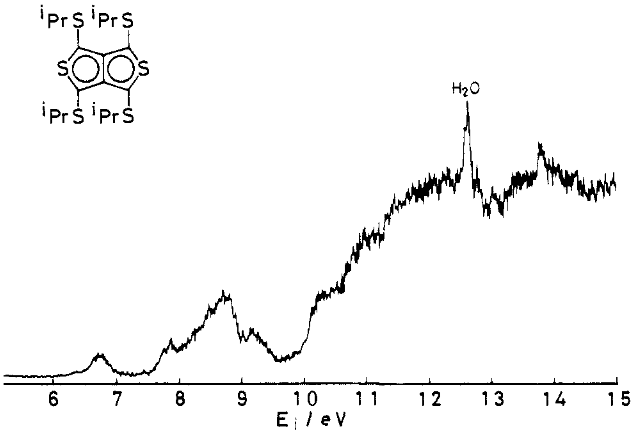

Figure 2. Gas-phase He I photoelectron spectrum of I.

of recently synthesized tetrakis(isopropylthio)thieno[3,4-*c*]thiophene (I)[3] (see Figure 1) is studied in detail by photoelectron spectroscopy in combination with electronic absorption spectroscopy and MO calculations.

Originally planar unsaturated systems containing two heteroaromatic rings fused with each other have been quite attractive both for organic and theoretical chemists.[4] At present these systems are important even from the standpoint of materials science because of their being promissing candidates as efficient electron-donor-type components of molecular complexes with high electrical conductivity or as effective monomers for electrical conducting polymers, for example.

Thienothiophenes belong to such condensed heteroaromatic systems and contain two thiophene units fused with each other in each molecule. Among the thienothiophene isomers, thieno[3,4-*c*]thiophene (II) is the most fascinating for it is a kind of "nonclassical" condensed aromatic system,[5a] and II and its related compounds have been receiving much attention from synthetic, spectroscopic, and theoretical standpoints.[5] To our regret II itself has not successfully been synthesized as yet, and the tetraphenyl derivative of II[5d] has been the only isolable derivative of II for a long time. However, recently synthesized I[3] is quite stable and is now one of the most simply structured stable derivatives of II. Therefore, studying I will simultaneously be very helpful in getting insight into the electronic structure of the unknown parent compound II also. Spectroscopic studies on the II series[5h-j] have inevitably been confined solely to the tetraphenyl derivative of II so far.

Experimental and Computational Section

Material. Compound I was prepared as described formerly.[3]

Measurements. The gas-phase He I photoelectron spectrum of I was measured with the instrument described formerly.[6,7] The sample inlet and target chamber systems were heated up to 145 °C during the measurement. The electronic absorption spectrum of I in hexane was measured on a Hitachi EPS-3T recording spectrophotometer.

Computational. Pariser-Parr-Pople-type SCF-MO-CI calculations of I and II were carried out on a FACOM M 380 computer at the Institute of Physical and Chemical Research adopting the atomic integral set suggested by Fabian et al.[8] The molecular dimensions of I and II were properly assumed on the basis of the X-ray diffraction data for bis(*tert*-butylthio)bis(ethylthio)thieno[3,4-*c*]thiophene.[3a] All the singly excited valence $\pi^*-\pi$ configurations were taken into account in the configuration interaction (CI) calculations.

Results and Discussion

Photoelectron Spectrum. The gas-phase He I photoelectron spectrum of I is shown in Figure 2. The vertical ionization energy values of I obtained from this spectrum are given in Table I. The

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Table II. Calculated and Observed Vertical Ionization Energies (E_{iv})

compd		E_{iv}/eV			
III	obsd[a,b]	8.90	9.50	12.10	
	calcd	8.87	9.49	12.37	
		a_2	b_1	b_1	
IV	obsd[b]	8.32	8.41	10.08	11.27
	calcd	8.39	8.52	10.19	11.02
		a_2	b_1	b_1	a_2
V	obsd[b]	8.10	8.61	10.04	11.5
	calcd	8.25	8.74	10.15	11.02
		a_u	a_u	b_g	b_g

[a] Reference 9. [b] Reference 11.

spectrum shows the first band at 6.72 eV well separated from the following highly overlapping band region.

In order to assign the photoelectron spectral bands, at first we analyze from the standpoint of empirically parametrized HMO model. The CC resonance integral (β_{CC}) value was assumed to be −2.70 eV according to Eland[9] and the ring β_{CS} value −1.90 eV according to our former result for tetrathiafulvalene and bis(dithiafulvenyl).[10] The one-center Coulomb integral for a carbon atom (α_C) and ring α_S were evaluated as −7.20 and −9.13 eV, respectively, to reproduce the first and second ionization energies of thiophene.[9,11] In order to check the validities of this set of parameter values thiophene (III), thieno[2,3-*b*]thiophene (IV), and thieno[3,2-*b*]thiophene (V) were treated and the calculated ionization energies according to Koopmans' theorem[2] are summarized in Table II with the observed ones.[9,11] The overall agreement between theory and experiment is satisfactory if we take experimental errors into account (for the assignments, see also ref 12), and the parameter set adopted here seems reasonable. Now let us apply this method to I and II in question.

The calculated orbital energies of I and II are given in Table I. In the case of the planar model of I the α_S and β_{CS} relevant to the substituents (these will be designated as α_S' and β_{CS}' hereafter) were assumed to be −8.23 and −1.60 eV, respectively, following the results for methylthioethylenes studied by Bock et al.[13] The MOs of II are schematically drawn in Figure 3. On the basis of this computational result for II let us try to interpret the observed photoelectron spectrum of I.

The π-MOs of I can roughly be regarded to be formed by the combination of the eight π-MOs of II with the four symmetry-adapted group orbitals constructed by the combination of the four sulfur lone-pair (n) orbitals of the substituents. These four symmetry-adapted orbitals are b_{1g}, b_{2u}, b_{3g}, and a_u type orbitals (symmetry notations for the D_{2h} point group are used hereafter for the sake of convenience in the case of I), and their energies before the conjugation with the parent ring system are expected around −8.23 eV according to the result for the methylthioethylenes.[13] The calculation suggests the first and second photoelectron spectral bands of II should be observed around 7.20 and 9.37 eV, and these values are rather close to the vertical ionization energy of the first band of I observed at 6.72 eV and that of the sixth one at 9.14 eV. In addition I shows strong highly overlapping bands just in the window region between the first and second predicted bands of II. Therefore, the strong overlapping bands between 7.89 and 8.71 eV bands of I are expected to correspond to the ionizations from the four MOs mainly contributed from the alkylthio group n orbitals.

If we assume I is nearly planar the MO energies are calculated by using the above parameter values as shown in Table I. The result is qualitatively consistent with the above discussion for the low-energy region. But the HOMO is predicted to be rather high in energy compared to the observed first vertical ionization energy. The HOMO of I is a_u MO formed by the out-of-phase-type (antibonding-type) combination of the a_u HO-π-O of the parent ring system and the a_u group orbital constructed by the combination of the substituent sulfur n orbitals. Therefore, the MO energy should be sensitive to the overlapping between these component group orbitals at the SC bonds. So the β_{CS}' values were optimized to reproduce the overall pattern of the photoelectron spectral bands in the low-energy region up to around 10 eV. The best result is shown in Table I. The optimized β_{CS}' value was −0.85 eV, that is, around a half of the parameter value adopted at first. This is ascribed to the twisting-out of the CSC planes relevant to the substituents from the parent ring plane. Let us denote the twist angles as θ hereafter. If we assume cos θ dependence of the resonance integral, β_{CS}', the θ value can now be estimated around 60°. Because of this large twisting the HOMO of I corresponding to the first photoelectron spectral band is almost completely localized on the parent ring, that is, the HOMO of I is close to that of II itself in orbital shape. The photoelectron spectral bands and molecular orbital energy levels are now correlated as shown in Figure 3 and assigned as in Table I.

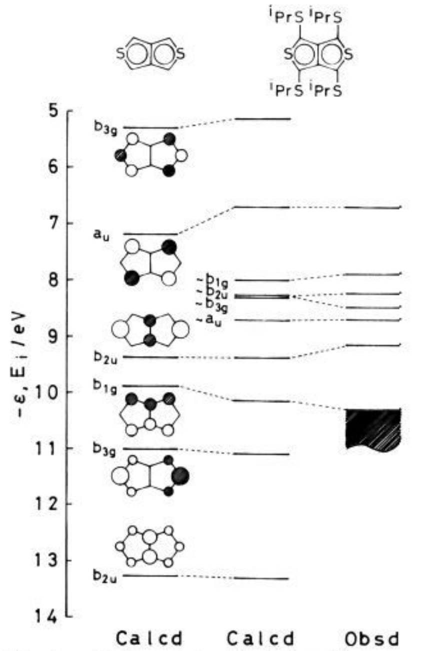

Figure 3. Molecular orbital energy level and photoelectron spectral band correlation diagram.

For comparison the Pariser–Parr–Pople (PPP)-type SCF–MO calculations were also carried out for I and II by using the parameter set suggested by Fabian et al.[8] In the case of I the PPP calculations were carried out both for the planar and the 60° twisted models as seen in Table I. By the PPP calculations also, the twisted model is adequate in the case of II. Also in the PPP calculation of the twisted model the β_{CS}' values were evaluated on the assumption of cos θ dependence.

From the above result the first ionization energy of the parent compound II is predicted to be around 7.2 eV. The first ionization energy of I, 6.72 eV, coincides accidentally with that of tetrathiafulvalene (TTF),[10] and I is expected to be as effective as TTF for the electron-donating ability. The first photoelectron spectral band of the tetraphenyl derivative of II observed at 6.19 eV has also been assigned as a_u and mainly contributed from the parent ring π system[5h] just as in the case of I.

Electronic Spectrum. Now let us examine the electronic structure of I from the standpoint of electronic spectrum. The electronic absorption spectrum of I was measured in hexane and is shown in Figure 4. The spectrum shows strong bands in the low-energy region around 2.46, 4.12, and 4.81 eV. In order to

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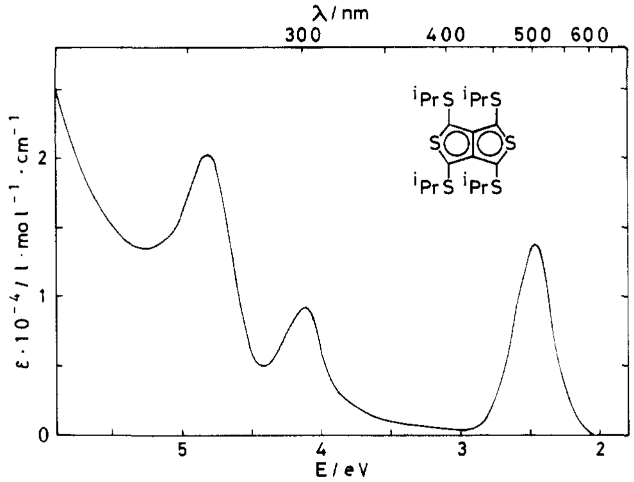

Figure 4. Electronic absorption spectrum of I in hexane.

interpret the observed absorption bands of I CI calculations were carried out for the 60° twisted model of I and II by using the MOs calculated by the PPP method, the results being summarized in Table III.

According to the calculation the observed first band of I is safely assigned as the $^1B_{3u}$ transition and almost completely contributed from LUMO–HOMO excitation configuration. Both of the observed 4.12- and 4.81-eV bands are ascribed to the $^1B_{1u}$ transitions according to the calculation. The tailing region between the 2.46- and 4.12-eV bands may correspond to the $^1B_{2g}$ forbidden band. In the above discussion all the symmetry notations are for the D_{2h} point group for the sake of convenience. It became evident from the discussion on the photoelectron spectrum that the HOMO of I is very close to the HOMO of II in the orbital shape because of the large twisting of the substituents, and as predicted by the MO calculation the contribution from the sulfur n orbitals to the LUMO of I is small because of the large energy difference between the component group basis orbitals. Therefore, the first band of I should be very close to the LUMO ← HOMO transition of II itself in nature. The calculation predicts the first $^1B_{3u}$ band of II should be observed around 2.98 eV only slightly higher in energy than that of I. The first $^1B_{3u}$ transition energy of II has formerly been predicted to be 2.79 eV by Müller et al.[5h] using the CNDO/S–CI method. This value is close to the present one. The calculated 4.02-eV transition of I is a kind of charge-transfer transition associated with electron migration from substituent sulfur n orbitals to the parent ring system, and, therefore, the corresponding 4.12-eV observed band is characteristic of I and not of II.

Table III. Electronic Transitions in I (60° Twisted Model) and II Calculated by the PPP Method and the Observed Ones

	calcd					obsd	
compd	sym	E/eV	f	main CI component[a]		E/eV	log (ε·M·cm)
I	$^1B_{3u}$	2.67	0.567	1L-1H	0.985	2.46	4.02
	$^1B_{2g}$	3.59	0	1L-2H	0.934		
				2L-1H	-0.315		
	$^1B_{1u}$	4.02	0.097	1L-3H	0.967	4.12	3.96
	$^1B_{2g}$	4.06	0	1L-2H	0.325		
				2L-1H	0.898		
	^1A_g	4.19	0	1L-4H	0.984		
	$^1B_{3u}$	4.49	0.027	1L-5H	0.954		
	$^1B_{1u}$	4.52	0.175	1L-6H	0.841	4.81	4.31
				3L-1H	-0.482		
	$^1B_{2g}$	5.58	0	1L-7H	0.950		
				2L-1H	-0.303		
	$^1B_{1u}$	5.66	1.125	1L-6H	0.496		
				3L-1H	0.831		
	$^1B_{3u}$	5.91	0.403	2L-2H	0.939		
II	$^1B_{3u}$	2.98	0.467	1L-1H	0.984		
	$^1B_{2g}$	4.14	0	1L-3H	0.578		
				2L-1H	0.816		
	$^1B_{1u}$	4.46	0.370	1L-2H	0.904		
				3L-1H	-0.398		
	$^1B_{2g}$	5.21	0	1L-3H	0.814		
				2L-1H	-0.577		
	$^1B_{1u}$	5.95	1.243	1L-2H	0.414		
				3L-1H	0.899		
	^1A_g	6.52	0	1L-4H	-0.509		
				2L-2H	0.837		

[a] Transition, indicated as j–i, refers to a one-electron excitation from orbital i to virtual orbital j. The second column gives the CI coefficient of the configuration j–i, nH means the nth HOMO, and nL the nth LUMO.

Conclusion

From the photoelectron spectrum the isopropylthio groups in I were found to be twisted out by ca. 60° from the parent ring plane. The first ionization energy of II is expected to be ca. 7.2 eV on the basis of the MO analysis. Compound I shows the first vertical ionization energy very close to that of TTF and is expected to become an electron donor as efficient as TTF. As the HOMO and LUMO of I can be said to be very close to those of II in nature according to the above analysis, compound I is expected to reflect strongly the electronic character of II for the relatively low energy phenomena such as chemical reactions mainly relevant to HOMO and/or LUMO. Combination of photoelectron and electronic spectroscopies assisted by MO calculations is effective for studying the electronic structure of molecules as demonstrated in this work.