These results seem to discard the previously proposed reaction mechanism, i.e., the "ene" reaction between $^1O_2$ and the hydrazone tautomer.[8] In Schemes II–IV, the process is formulated as involving the electrophilic attack of singlet oxygen onto the position para to the dialkylamino, hydroxy, or methoxy group for azo dyes **1**, **2a**, and **3**, respectively. This is simply an indication that from the initial charge-transfer state a more tightly bound, but still reversible, complex might result and evolve to the final products (possibly with the intervention of the solvent, e.g., by protonation of a zwitterion).

For the methoxy derivative **3**, easy proton transfer is not possible and reaction with $^1O_2$ leads to the endoperoxide **16**, which, in turn, is converted to the 1,2-naphthoquinone **13**. This cycloaddition is similar to the reaction of the parent 1-methoxynaphthalene[43] but occurs at a lower rate, given the higher oxidation potential of **3** with respect to the parent compound. This process also arises from an initial radical ion pair, as shown by the quenching of the process in methanol where, again, cleavage of the aryl–azo bond takes place, leading to the same product as for **2a** (except the bis azo derivatives, since coupling of **3** with PhN_2 is slower). Formation of 1,4-naphthoquinone is less efficient since it requires the cleavage of an O–CH_3 bond. Finally, the only possible process for *N*-methylhydrazone **4**, in aprotic solvents, is N-dealkylation via a mechanism similar to that reported for compound **1**.

Conclusions

Azo dyes are efficient physical quenchers of singlet oxygen as, indeed, it might have been expected since they are good electron donors. Back electron transfer remains by far predominant over chemical reaction, as often observed in photochemical electron transfer reactions,[44] and only a tiny fraction of the charge-transfer complex evolves toward products ($k_r < 10^{-3}k_q$). The rate-determining step of the chemical reaction is a heterolytic cleavage, viz., either proton transfer from the NCH_2, OH, or NH groups or cleavage of the aryl–azo bond. As for the tautomeric dyes, the role of hydrazone tautomers is important both in the generation of singlet oxygen and in its physical quenching, owing to the relatively low E_{ox} of this tautomeric form. Apparently, there is no need to envisage the formation of 1,4-naphthoquinone from these compounds as an "ene" process despite much speculation on this idea.[7b,d,f,8] A concerted process is observed only when there is no acidic proton, viz., in the case of the methoxy derivative **3**, and is a cycloaddition onto the aromatic ring.

Acknowledgment. We are indebted to Prof. Teresa Soldi (Università di Pavia) for the determination of the oxidation potentials of the azo dyes and to Prof. Franco Scandola (Università di Ferrara) for the use of the ruby laser apparatus. The financial support of the Consiglio Nazionale delle Ricerche and of the Ministero della Pubblica Istruzione is gratefully acknowledged.

Registry No. **1a**, 2481-94-9; **1b**, 31464-27-4; **1c**, 3009-51-6; **1d**, 88580-92-1; **1e**, 99566-77-5; **1f**, 3025-57-8; **1g**, 3025-52-3; **1h**, 6373-96-2; **2a**, 3651-02-3; **2b**, 5098-99-7; **3**, 24390-69-0; **4**, 66881-37-6; **5a**, 842-07-9; **5b**, 6756-41-8; **5c**, 13411-91-1; **6a**, 2058-67-5; **6c**, 117919-03-6; **6g**, 31464-32-1; **7a**, 71-43-2; **7c**, 100-66-3; **7g**, 98-95-3; **8a**, 108-95-2; **9**, 103021-63-2; **10**, 130-15-4; **11**, 117940-41-7; **12**, 5290-66-4; **13**, 18916-57-9; **14**, 7473-19-0; O_2, 7782-44-7.

(42) Wilkinson, F.; Brummer, J. G. *J. Phys. Chem. Ref. Data* **1981**, *10*, 809.
(43) Griffiths, J.; Chu, K.-H.; Hawkins, C. *J. Chem. Soc., Chem. Commun.* **1976**, 676.
(44) For a review, see: Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker Inc.: New York, 1983; Vol. 6, Chapter 4.

Penning Ionization Electron Spectroscopy of Diphenyl Chalcogenides: PhOPh, PhSPh, and PhSePh

Warō Nakanishi,* Shigeru Masuda,† Toshimasa Ishida,† Koichi Ohno,† and Yoshiya Harada*,†

Department of Chemistry, Faculty of Education, Wakayama University, Sakaedani, Wakayama 640, Japan, and Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Meguro-ku, Tokyo 153, Japan

Received May 31, 1988

Penning ionization electron spectra (PIES) and ultraviolet photoelectron spectra of PhOPh (**1**), PhSPh (**2**), and PhSePh (**3**) have been measured to explain their reactions with electrophiles such as halogens that produce either trigonal-bipyramidal adducts or molecular complexes. The spectral bands were assigned on the basis of ab initio MO calculations using 4-31G basis sets. The intensities of n and π bands were larger than those of σ bands in PIES. This shows that n and π orbitals in these compounds extend far beyond the repulsive surfaces of these molecules. Especially, the exterior electron distributions of the n orbitals in **2** and **3** were found to be very large. Although the ionization potentials (IP) of the pure π bands show little change among **1–3**, the IP's for the HOMO's having π and n(p_z) characters were found to decrease from 8.30 (**1**) to 7.90 (**2**) and 7.85 (**3**) eV. The IP values of the n(p_z) orbitals were also observed in the order IP(**1**) $\gg$ IP(**2**) > IP(**3**). These results explain the experimental fact that the electron-transfer reaction proceeds much easier in **2** and **3** than in **1**.

Introduction

Photoelectron spectroscopy has recently been extensively applied to organic molecules, since this method can supply basic information required to understand their chemical behaviors.[1] Studies along these lines involve organic molecules containing VIB elements. For example, ethers,[2-6] sulfides,[3-8] selenides,[4-6,8] tellurides,[4-6] their complexes with Lewis acids,[9] and the tri-[10] and tetravalent

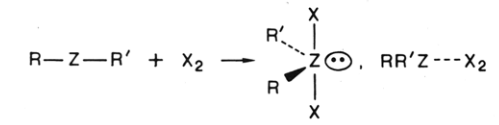
† The University of Tokyo.

(1) (a) Brundle, C. R.; Baker, A. D. *Electron Spectroscopy: Theory, Techniques, and Applications*; Academic: New York, 1977–1984; Vol. 1–5. (b) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules*; Japan Scientific Societies: Tokyo, 1981.
(2) Bock, H.; Mollère, P.; Becker, G.; Fritz, G. *J. Organomet. Chem.* **1973**, *61*, 113.

0022-3263/89/1954-0540$01.50/0

species[11] have been investigated by using ultraviolet photoelectron spectroscopy (UPS).

Much attention has been paid to organic compounds containing VIB elements because they show versatile reactivity and afford many structurally interesting compounds.[12] Ethers, sulfides, selenides, and tellurides react with electrophiles such as halogens and peroxides to give trigonal-bipyramidal adducts (TB) or molecular complexes (MC).[13] The formation of TB supplies an intriguing area both theoretically[14] and experimentally,[15] because it yields compounds containing a hypervalent bond[16] with highly polar apical bonds. TB are formed if the electronegativity[17] of the ligands (χ_X) is larger than that of the VIB elements (χ_Z) in the compounds. The adducts are MC when χ_X is less than χ_Z.[13]



TB ($\chi_X > \chi_Z$) MC ($\chi_Z > \chi_X$)

M (Z or X)	O	S	Se	Te	F	Cl	Br	I
χ_M	3.50,	2.44,	2.48,	2.01,	4.10,	2.83,	2.74,	2.21

This generalization holds well in most of the cases.[13] However, there are some discrepancies. While selenides, in general, react with bromine to give TB, MC **4** is obtained in the reaction of selenoxanthone with bromine, although the chlorine adduct is TB.[18a] The effective electronegativity of selenium in this compound may be modulated by the strongly electron withdrawing carbonyl group. Selenanthrene also reacts with bromine to give MC **5**.[18b] The MC structure (**6**) of thiophane with bromine is another example.[19] Therefore, the reactivities of diorganyl chalcogenides with halogens are primarily governed by the electronegativities of the elements in question. The structures of substrates and the combinations of reactants are also important. Such reactivities with some variations should be attributed to the electronic structures of the substrates, that is, the energies and spatial distributions of electrons in molecular orbitals in the compounds under consideration.

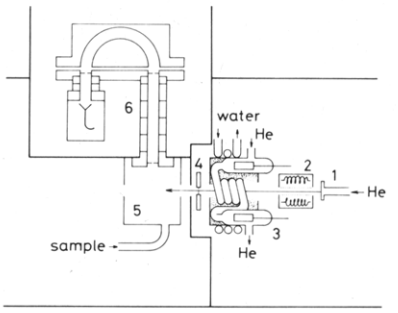
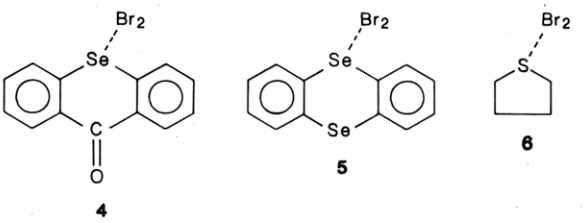


Figure 1. Schematic view of electron spectrometer for PIES: (1) capillary array, (2) electron gun, (3) quench lamp, (4) grid, (5) collision chamber, (6) analyzer.



Recently we have applied Penning ionization electron spectroscopy (PIES) to organic molecules to study their electronic structures.[20] This technique is based on the energy analysis of electrons released in the ionization of an atom or a molecule M by impact of a metastable atom A*: A* electrophilically attacks an orbital of M and extracts an electron, which goes into a vacant orbital of A*, yielding an ionic state of M^+. An electron is ejected simultaneously in this process ($M + A^* \rightarrow M^+ + A + e^-$). The probability of the electron ejection (Γ) from individual molecular orbital $\phi_i(r)$ is essentially proportional to the exterior electron density (EED), which is defined as the integral over the space outside the molecular surface (Ω). $\Gamma \propto \mathrm{EED} = \int_\Omega \phi_i^2(r)dr$. Thus, the spatial distributions of individual molecular orbitals, which are difficult to measure with other methods, can be obtained from the analysis of the band intensities of PIES.[20]

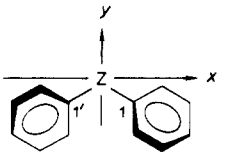
As the first step in the elucidation of the chemical reactivities of diorganyl chalcogenides, the electronic structures of diphenyl chalcogenides, PhOPh (**1**), PhSPh (**2**), and PhSePh (**3**) have been studied with PIES, UPS, and ab initio SCF MO calculations.

Experimental Section

Figure 1 shows a schematic view of a homemade electron spectrometer, which is almost the same as reported previously.[21]

(3) Palmer, M. H.; Kennedy, S. M. F. *J. Chem. Soc., Perkin Trans. 2*, **1974**, 1893.
(4) Colonna, F. P.; Distefano, G.; Galasso, V.; Irgolic, K. J.; King, C. E.; Pappalardo, G. C. *J. Organomet. Chem.* **1978**, *146*, 235.
(5) Distefano, G.; Galasso, V.; Irgolic, K. J.; Pappalardo, G. C. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1109.
(6) Muller, J.-F. *Helv. Chem. Acta* **1975**, *58*, 2646.
(7) (a) Mollère, P.; Bock, H.; Becker, G.; Fritz, G. *J. Organomet. Chem.* **1973**, *61*, 127. (b) Frost, D. C.; Herring, F. G.; Katrib, A.; McDowell, C. A.; McLean, R. A. N. *J. Phys. Chem.* **1972**, *76*, 1030. (c) Clark, P. A.; Gleiter, R.; Heilbronner, E. *Tetrahedron* **1973**, *29*, 3085.
(8) Andreocci, M. V.; Bossa, M.; Furlani, C.; Piancastelli, M. N.; Cauletti, C.; Tarantelli, T. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 105.
(9) Carnovale, F.; Livett, M. K.; Peel, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 5334. Frost, D. C.; Lau, W. M.; McDowell, C. A.; Westwood, N. P. C. *J. Phys. Chem.* **1982**, *86*, 1917.
(10) Bock, H.; Solouki, B. *Chem. Ber.* **1974**, *107*, 2299.
(11) Cowley, A. H.; Lattman, M.; Walker, M. L. *J. Am. Chem. Soc.* **1979**, *101*, 4074.
(12) (a) Patai, S. *The Chemistry of the Ether Linkage*; Interscience: London, 1967. (b) Oae, S. *Organic Chemistry of Sulfur*; Plenum: New York, 1977. (c) Csizmadia, I. G.; Mangini, A.; Bernardi, F. *Organic Sulfur Chemistry: Theoretical and Experimental Advances*; Elsevier Scientific: Amsterdam, 1985. (d) Klayman, D. L.; Günther, W. H. H. *Organic Selenium Compounds: Their Chemistry and Biology*; Wiley: New York, 1973. (e) Irgolic, K. J. *The Organic Chemistry of Tellurium*; Gordon and Breach: New York, 1974. (f) Patai, S.; Rappoport, Z. *The Chemistry of Organic Selenium and Tellurium Compounds*; Wiley: New York, 1986; Vol. 1.
(13) Baenziger, M. C.; Buckles, R. E.; Maner, R. J.; Simpson, T. D. *J. Am. Chem. Soc.* **1969**, *91*, 5749.
(14) (a) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985; Chapter 14. (b) Chen, M. M. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1647. (c) Schwenzer, G. M.; Schaefer, H. F. III *Ibid.* **1975**, *97*, 1393. (d) Hay, P. J. *Ibid.* **1977**, *99*, 1003.
(15) A recent review for sulfuranes: Hayes, R. A.; Martin, J. C. Chapter 8 in ref 12c. See also ref 12d–f.
(16) (a) Pimentel, G. C. *J. Chem. Phys.* **1951**, *19*, 446. (b) Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54.
(17) The values of electronegativity proposed by Allred and Rochow are adopted: Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264 and 269. See also ref 13.
(18) (a) Nakanishi, W.; Yamamoto, Y.; Kusuyama, Y.; Ikeda, Y.; Iwamura, H. *Chem. Lett.* **1983**, 675. (b) Nakanishi, W.; Hayashi, S.; Tsukada, H.; Iwamura, H., unpublished results.
(19) Allegra, G.; Wilson, G. E., Jr.; Benedetti, E.; Pedone, C.; Albert, R. *J. Am. Chem. Soc.* **1970**, *92*, 4002.
(20) Ohno, K.; Mutoh, H.; Harada, Y. *J. Am. Chem. Soc.* **1983**, *105*, 4555. Fujisawa, S.; Ohno, K.; Masuda, S.; Harada, Y. *Ibid.* **1986**, *108*, 6505 and references cited therein.

Table I. Data of the Molecular Structures of 1-3 Used for the MO Calculations



	1	2[a]	3
$r(C_1-Z)$, Å	1.364[b]	1.771	1.925[f]
$\angle C_1ZC_{1'}$, deg	111.7[c]	103.7[e]	106.0[f]
DHA(Ph,Ph), deg	56[d]	56[d]	55[f]
r(C-C), Å	1.399[a]	1.399	1.399[a]
r(C-H), Å	1.089[a]	1.089	1.089[a]
∠CCC, deg	120.0[a]	120.0	120.0[a]

[a] Values in gas phase for **2**.[33a] [b] The value reported for phenol(s).[33b] [c] The value reported for dimethyl ether.[33c] [d] Values reported for ditolyl sulfide in the solid state.[33d] [e] The value of ditolyl sulfide in the solid state is 109°.[33d] [f] Values reported for ditolyl selenide in the solid state.[33d]

The base pressure is about 2×10^{-7} Torr. The helium metastable atoms, 2^3S (19.82 eV) and 2^1S (20.62 eV), were produced by impact of 60-eV electrons with the beams of helium atoms introduced through a glass capillary array. At this impact energy, resonance photons or Rydberg atoms are negligible. A water-cooled helium discharge lamp was used to quench 2^1S atoms (quenching efficiency; more than 95%). A repeller electrode was used to repel stray electrons. Thus highly pure 2^3S atoms were introduced into the ionization chamber and collided with sample molecules. The helium I resonance line (584 Å, 21.22 eV) used for UPS was produced by a differentially pumped discharge lamp (not shown in Figure 1). The electron energy spectra were obtained at an emission angle of 90° with respect to the 2^3S atom beams or the photon beams by means of a hemispherical-type analyzer with electron lens systems. The energy-selected electrons were detected with an electron multiplier (Mullard B419 BL) and a conventional pulse counter combined with a signal averager. Typical time for the data accumulation was about 60 min for UPS and 120 min for PIES. The overall energy resolution was about 40 meV. The relative band intensity of the spectra was calibrated by using the transmission efficiency curve of the electron analyzer.[20]

Sample molecules, PhOPh (**1**) and PhSPh (**2**), were obtained from Tokyo Kasei Co. Ltd., and PhSePh (**3**) from Strem Chemicals Inc. Purity of the samples was checked by ^1H and ^{13}C NMR spectra.

Calculations

Ab initio SCF MO calculations were performed with a library program GFCF2 at the computer center of The University of Tokyo.[22] The 4-31G basis sets were used for H, C, O, and S atoms.[23] Since the 4-31G basis set has not been devised for Se atom, the (33321/3321/3) set derived from the (3333/333/3) set[24] was utilized for Se. C_2 symmetry was assumed for the structures of the molecules, and their geometrical parameters are listed in Table I.

For comparison between the electron distribution and the band intensity in PIES, the exterior electron densities (EED) of MO's were calculated with a lattice sum method.[25] The repulsive molecular surfaces were approximated by compositions of the spheres with the van der Waals radii of the atoms (r_H = 1.20 Å, r_C = 1.70 Å, r_O = 1.40 Å, r_S = 1.85 Å, and r_{Se} = 2.00 Å) in the molecules.

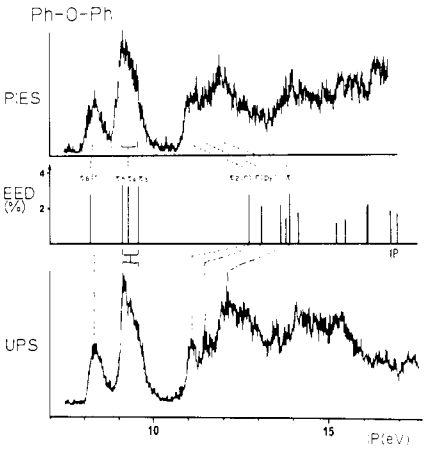


Figure 2. He*(2^3S) PIES, He I UPS, together with calculated IP and EED for PhOPh (**1**).

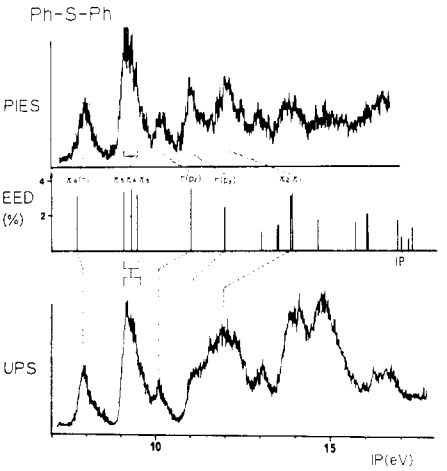


Figure 3. He*(2^3S) PIES, He I UPS, together with calculated IP and EED for PhSPh (**2**).

Table II. Observed and Calculated Ionization Potentials and Exterior Electron Densities (EED) of PhOPh (1)

IP_{obsd},[a] eV	IP_{calcd}, eV	EED, %	assignment
8.30	8.16	2.75	$\pi_6(n)$
9.15	9.09	3.31	π_5
9.3–9.6	9.27	3.20	π_4
	9.55	3.20	π_3
11.15	12.74	2.66	$\pi_2(n)$
11.55	13.09	2.03	$n(p_y)$
12.0	13.66	2.15	σ
	13.82	1.42	σ
12.2	13.90	2.70	π_1

[a] From UPS.

Table III. Observed and Calculated Ionization Potentials and Exterior Electron Densities (EED) of PhSPh (2)

IP_{obsd},[a] eV	IP_{calcd}, eV	EED, %	assignment
7.90	7.72	3.09	$\pi_6(n)$
9.15	9.11	3.34	π_5
9.3–9.6	9.32	3.48	π_4
	9.47	3.17	π_3
10.12	11.04	3.54	$n(p_z)$
11.2	11.99	2.44	$n(p_y)$
11.5–11.8	13.06	1.08	σ
	13.52	1.46	σ
	13.52	1.45	σ
12.0	13.90	3.09	π_2
	13.93	3.22	π_1

[a] From UPS.

(21) Harada, Y.; Ohno, K.; Mutoh, H. *J. Chem. Phys.* **1983**, *79*, 3251.
(22) Kosugi, N. Program GSCF2, Program Library, The Computer Center, The University of Tokyo, Tokyo, Japan, 1981.
(23) The 4-31G set for H, C, and O atoms: Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. For S atom: Hehre, W. J.; Lathan, A. *J. Chem. Phys.* **1972**, *56*, 5255.
(24) Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Netherlands, 1984.
(25) Ohno, K.; Ishida, T. *Int. J. Quant. Chem.* **1986**, *29*, 677.

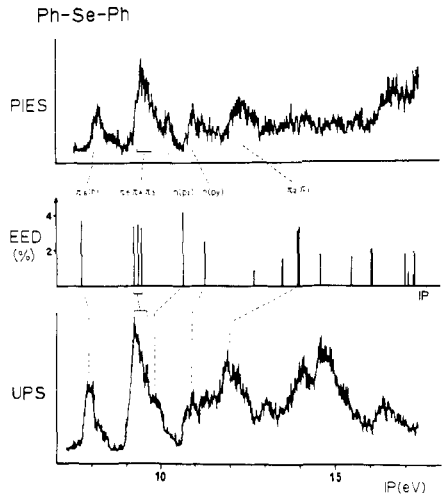


Figure 4. He*(2^3S) PIES, He I UPS, together with calculated IP and EED for PhSePh (**3**).

Table IV. Observed and Calculated Ionization Potentials and Exterior Electron Densities (EED) of PhSePh (3)

IP_{obsd},[a] eV	IP_{calcd}, eV	EED, %	assignment
7.85	7.73	3.72	π_6(n)
9.15	9.23	3.33	π_5
9.3–9.6	9.35	3.41	π_4
	9.46	3.24	π_3
9.80	10.66	4.09	n(p_z)
10.83	11.30	2.49	n(p_y)
11.3–11.7	12.69	0.86	σ
	13.54	1.44	σ
	13.55	1.49	σ
11.9	13.96	3.21	π_2
	14.00	3.35	π_1

[a] From UPS.

Results

Figures 2–4 show the He*(2^3S) PIES and He I UPS for PhOPh (**1**), PhSPh (**2**), and PhSePh (**3**). To facilitate the comparison between the PIES and UPS, the electron energy scales (E_{kin}) for PIES are shifted to those for UPS by the difference in the excitation energy, (21.22 – 19.82) eV = 1.40 eV. Figures 2–4 also show the theoretical PIES on the basis of the EED model for Penning ionization.

Tables II–IV list the observed vertical ionization potentials (IP's) obtained from the UPS and their assignments to respective MO's. The calculated IP's via Koopman's theorem[26] and the EED values are also listed in Tables II–IV.

Discussion

The intensities of the n and π bands are larger than those of σ bands in PIES as shown in Figures 2–4. These results show that the n and π orbitals of these compounds extend far beyond the repulsive molecular surfaces as compared to the σ orbitals. The relative intensities of the n bands for **2** and **3** are larger than those for **1** (n(O) < n(S) ≤ n(Se)). This corresponds to the fact that the electron distributions outside the molecular surfaces of the n orbitals of sulfur and selenium are larger than those of oxygen. Since the repulsive molecular surfaces can be estimated from the van der Waals radii of atoms[27] and the radii become larger in the order r(O) << r(S) < r(Se), the present results exhibit that the n orbitals of sulfur and selenium extend further beyond their enlarged van der Waals radii than those of oxygen.

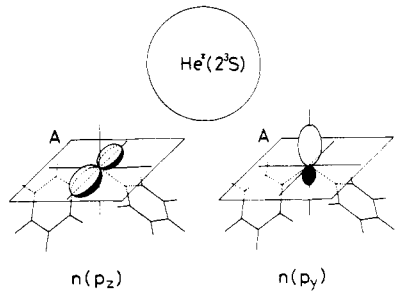


Figure 5. Schematic diagram of the n(p_z) and n(p_y) orbitals of **2**.

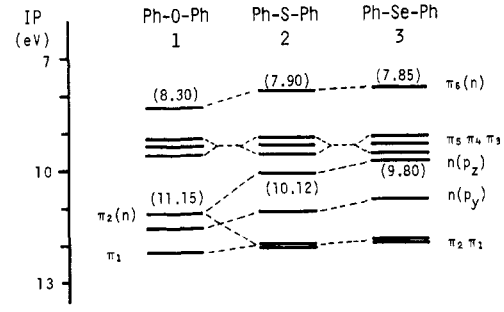


Figure 6. Correlation diagram for the n and π orbitals of **1**, **2**, and **3**.

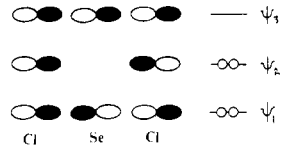


Figure 7. Approximate molecular orbital model for the hypervalent (3c-4e) bond.

The results of the ab initio SCF MO calculations (IP and EED) are useful for assigning the bands, since the relative values of EED are in good agreement with the relative band intensities. However, the band intensity for the n(p_z) orbital in **2** is smaller than that for the n(p_y), which is just the opposite to the expectation based on the calculations (Figure 3, see also Table III). As will be described below, this may arise from the steric hindrance to the n(p_z) orbital by the benzene rings, which are twisted from the $C_{Ph}SC_{Ph}$ plane with a dihedral angle of ca. 56°.

Figure 5 shows the schematic diagram of the n(p_z) and n(p_y) orbitals in **2**. The n(p_y) orbital is an sp hybridized one composed of the sulfur 3s and 3p atomic orbitals and is extended outside above the plane A in Figure 5. As can be seen from the figure, the large He*(2^3S) atom (atomic radius; ca. 3 Å)[28] coming from the lower side of the plane A cannot interact with the n(p_z) and n(p_y) orbitals owing to the steric hindrance by the two phenyl groups. Therefore, about half of the EED of the n(p_z) orbital is ineffective for Penning ionization, while most of the EED is effective for the n(p_y) orbital distributed mainly above the plane A. This explains the discrepancy between the observed and calculated relative intensities of PIES for the n orbitals. A similar trend is also observed in **3**. Such behavior of n orbitals in **1**–**3**, observed by PIES, should be correlated with their chemical properties.

Figure 6 shows a correlation diagram for the n and π orbitals of **1**–**3**. The IP's of the π_5 orbitals of **1**–**3** are around 9.2 eV, which are very close to the first IP (for the doubly degenerate HOMO's) of benzene (9.25 eV[1b]). The

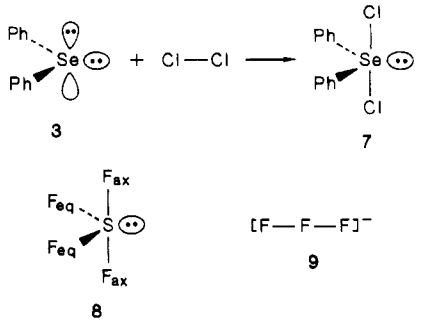
(26) Koopmans, T. *Physica (Utrecht)* **1933**, *1*, 104.
(27) For the discussion in relation to PIES, see ref 20.
(28) Siska, P. E. *J. Chem. Phys.* **1979**, *71*, 3942.

IP's of the π_4 and π_3 orbitals of **1–3** are not much different from those of the π_5 orbitals. Since the interactions of these three π orbitals with the n orbitals of the heteroatoms are negligible, the IP's show little change among the compounds.

On the other hand, the IP's for the HOMO (π_6) in **1–3**, which are the only orbitals that can interact with the n(p_z) orbitals of the heteroatoms, are found to be 8.30, 7.90, and 7.85 eV, respectively. The HOMO's have both π and n(p_z) characters, and, as a result, the corresponding IP's decrease from **1** to **2** and **3** (IP(1) $\gg$ IP(2) $\geq$ IP(3)). The IP values of the n(p_z) orbitals in **1–3** are 11.15, 10.12, and 9.80 eV, respectively (IP(1) $\gg$ IP(2) > IP(3)), and the values of the n(p_y) orbitals are 11.55, 11.15, and 10.83 eV, respectively. The IP values of the HOMO and the n(p_z) orbitals in **1–3** play a very important role in the reaction of these compounds with electrophiles such as halogens:[14d] TB are formed if the electron transfer occurs easily from the p_z orbital of the central atom Z to electrophiles X, as will be described later.

Let us consider, for instance, the reaction of **3** with chlorine to give selenurane **7** to clarify the correlation between the results obtained above and the reactivity. The selenurane **7** is a compound containing a hypervalent bond with a trigonal-bipyramidal structure. The model of the apical bonds in TB is that two chlorine atoms are joined to the central atom Se through its p_z orbital.[29] As shown in Figure 5, the bonds are constructed by three centers with four electrons (3c-4e).[16,30] A pair of electrons are in a bonding orbital (ψ_1) and another pair in a nonbonding one (ψ_2). Since the ψ_2 orbital is distributed only on the ligands, the 3c-4e bond is formed with the electron transfer from the p_z orbital of the central atom Se to the Cl ligands, resulting in the highly polar $Cl^{\delta-}$–$Se^{\delta+}$–$Cl^{\delta-}$ bond. Using photoelectron spectroscopy, such electron transfer has been found in SF_4 (**8**), where the IP's of the 1s and π(2p) orbitals of the axial fluorines are smaller than those of the equatorial ones by 2.4[31] and 2.0[11] eV, respectively. This shows that the amount of the electron transfer to the fluorine atoms in SF_4 is larger in the axial positions than in the equatorial ones. The results of ab initio MO calculations for F_3^- (**9**) also exhibit a similar electron transfer clearly;[30] the negative charge is distributed only on two terminal fluorine atoms, the central fluorine atom being slightly positively charged.

The electron transfer from the central atom to ligands will occur more favorably; the larger the electronegativity of ligands, the smaller that of the central atom is. The values of the IP(n(p_z)) and IP(HOMO), which have both π and n(p_z) characters, are another measure of the ease of the electron transfer.



While sulfides and selenides react with chlorine to give TB,[13] the structure of a chlorine adduct of 1,4-dioxane has been reported to be MC.[32] This can be attributed to the fact that the IP(n(p_z)) and IP(HOMO) are much larger in **1** than those in **2** and **3** (IP(1) $\gg$ IP(2), IP(3)).

Although one might expect that sulfides, as well as selenides, react with bromine to give TB, considering the fact that the electronegetivity of sulfur is almost the same as that of selenium, the bromine adduct of thiophane is reported to be MC.[19] While the values of the IP(HOMO) of **2** and **3** are almost the same, the IP(n(p_z)) of **2** is larger than that of **3** (IP(2) > IP(3)). This may show that the electron-transfer reaction from the n(p_z) orbital of a sulfur atom to bromine is more difficult than in the case of a selenium atom. These results are well correlated with the chemical reactivities of diorganyl chalcogenides.

Conclusion

The intensities of the n and π bands in PIES are larger than those of σ bands for **1–3**, showing the wider distribution of the n and π orbitals. The intensities of the n bands are in the order n(O) < n(S) $\leq$ n(Se). This can be explained from the fact that the n orbitals extend further outside the repulsive molecular surfaces in this order. The EED are useful for assigning the spectral bands since they correlate well with the corresponding band intensities. The effect of the steric hindrance of the phenyl groups is observed in the n(p_z) orbitals in **2** and **3**; the band intensities are smaller than those of the n(p_y), which is just the opposite to the expectation based on the EED. The IP's of the π_3, π_4, and π_5 orbitals show little change among **1–3**, since their interactions with orbitals of the heteroatoms are negligible. The values of the IP(HOMO) are in the order IP(1) $\gg$ IP(2) $\geq$ IP(3) and those of the IP(n(p_z)) are in the order IP(1) $\gg$ IP(2) > IP(3). These results have a close correlation with the chemical reactivities of diorganyl chalcogenides with electrophiles such as halogens.

Registry No. 1, 101-84-8; 2, 139-66-2; 3, 1132-39-4.

(29) Discussed mainly on sulfuranes, see ref 14.
(30) Cahill, P. A.; Dykstra, C. E.; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6359, for 3c-4e bonds, see also references cited therein.
(31) Shaw, R. W., Jr.; Carroll, T. X.; Thomas, T. D. *J. Am. Chem. Soc.* **1973**, *95*, 5870.
(32) Hassel, O.; Stromme, K. O. *Acta Chem. Scand.* **1959**, *13*, 1775.
(33) (a) Bozsondai, B. *Acta Chim. Acad. Sci. Hung.* **1977**, *94*, 321. (b) Gordon, A. J.; Ford, R. A. *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*; Wiley-Interscience: New York, 1972; p 108. (c) Blukis, U.; Kasai, P. H.; Myers, R. J. *J. Chem. Phys.* **1963**, *38*, 2753. (d) Blackmore, W. R.; Abrahams, S. C. *Acta Crystallogr.* **1955**, *8*, 323 and 329.