

Why Selenoxanthone Gives an MC with Bromine: An Examination of Electronic States of Xanthenes and Xanthenes by Electron Spectroscopy and *ab Initio* MO Calculations

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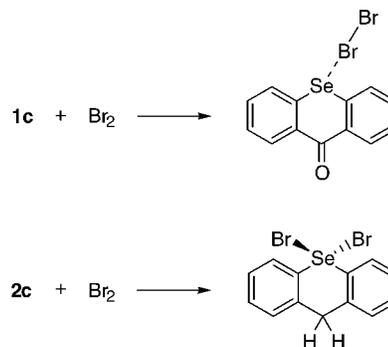
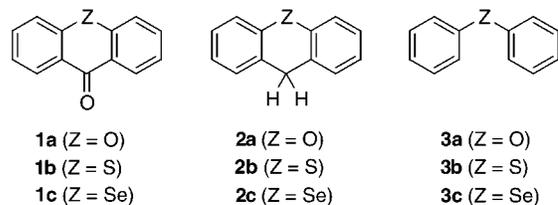
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The PIES and UPS spectra of xanthone (**1a**), thioxanthone (**1b**), and selenoxanthone (**1c**) were measured, together with those of the corresponding xanthene (**2a**), thioxanthene (**2b**), and selenoxanthene (**2c**). *Ab initio* MO calculations were performed with the 6-311+G(d,p) basis sets at the DFT (B3LYP) level on **1a–c** and **2a–c**. The results of the measurements and of the MO calculations explained well the striking difference in the reactivity of the compounds, especially for **1c** versus **2c**. The ionization potentials (IP) of $\pi_6(n)$ (HOMO), $n(p_z)$ ($\pi_2(n)$) for **1a** and **2a**, and $n(p_y)$ were in the order IP(**1a**) > IP(**1b**) > IP(**1c**) and IP(**2a**) > IP(**2b**) > IP(**2c**). The IP of the xanthenes were larger than those of the corresponding xanthenes. The IP of $n(p_z)$ of **1c** was demonstrated to be larger than those of **2b** and PhSPh (**3b**), which showed that **1c** was less reactive than **2b** and **3b** toward electrophiles. These results accounted for the reactivity of **1c** to give a molecular complex (MC) with bromine similar to the case of the MC structure of the sulfide dibromides. The relative intensity of PIES of HOMO in **1c** was smaller than that in **2c**. The electron density outside the molecular surface of the orbital of **1c** must be smaller than that of **2c**, due to the strong electron-withdrawing carbonyl group in **1c**, which was supported by the calculated natural populations at the chalcogen atoms of the compounds.

Introduction

Organic chalcogen compounds are well-known to show versatile reactivities, and they afford many structurally interesting compounds.¹ We have recently reported that the reactivities of some organoselenium compounds could be controlled by chemically modulating the effective electronegativity of the selenium atom in a given selenide and/or by changing the bulkiness around the selenium atom of the compound.² For example, selenoxanthone reacts with bromine to give a molecular complex (MC),^{2b} contrary to the general rule,^{1a,2a} whereas selenoxanthene yields a trigonal bipyramidal adduct (TB) as expected.^{2b} The effective electronegativity of the selenium atom in selenoxanthone would be too large for the compound to give a TB with bromine, due to the strong electron-withdrawing carbonyl group. Such versatile reactivities of organic selenium compounds must come from the variety

of the effective electronegativity of selenium atoms in the selenides. Ionization potentials (IP) of the selenides must be closely related to the effective electronegativity of the selenium atoms in the compounds. It must be noted, however, that the steric effect should also play an important role in the reaction of the selenides.^{1,2}



We have been interested in such versatile reactivities that should be accounted for based on the physical properties of the compounds. Penning ionization electron spectroscopy (PIES)³ has been shown to be a powerful

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(1) (a) Baenziger, M. C.; Buckles, R. E.; Maner, R. J.; Simpson, T. D. *J. Am. Chem. Soc.* **1969**, *91*, 5749. (b) Klayman, D. L., Günther, W. H. H., Eds. *Organic Selenium Compounds: Their Chemistry and Biology*; Wiley: New York, 1973; Chapter XV. (c) Hayes, R. A.; Martin, J. C. Sulfurane Chemistry. In *Organic Sulfur Chemistry: Theoretical and Experimental Advances*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, 1985. See also references cited therein.

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tool to elucidate the chemical reactivities of organic compounds.⁴ It will be more useful if the method is applied with ultraviolet photoelectron spectroscopy (UPS) and ab initio MO calculations. Recently, we reported the electronic structures of diphenyl ether (**3a**), diphenyl sulfide (**3b**), and diphenyl selenide (**3c**) as the first step of our investigation to elucidate the chemical reactivities of diorganyl chalcogenides by their electronic structures.⁵ Indeed, the study revealed general reactivities of diorganyl chalcogenides, but it did not refer to the versatile reactivities of the compounds. Much attention has been paid to such reactivities brought into the compounds by the change of the organyl group(s) in organic chalcogen chemistry thus far.

The electronic states of selenides were investigated by PIES and UPS exemplified by selenoxanthone (**1c**) and selenoxanthone (**2c**). The spectra were also measured for xanthone (**1a**), thioxanthone (**1b**), xanthene (**2a**), and thioxanthene (**2b**) to examine the role of the carbonyl and methylene groups in the compounds, which should shed light on the striking difference in the reactivity of **1c** versus **2c** brought by the groups shown above. Ab initio MO calculations were also performed on the compounds, to assign the spectra, to show how large the positive charge being developed on the selenium atom is in **1c** relative to that in other compounds, and to depict the spatial extension of the molecular orbitals in question. Here, we present the results of the investigations, including those of ab initio MO calculations on the compounds.

Results and Discussion

Figures 1–6 show the He*(2³S) PIES and He I UPS of xanthenes (**1**: **1a–c**) and xanthenes (**2**: **2a–c**), respectively. 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). Table 1 lists the observed vertical ionization potentials (IP) obtained from the UPS and their assignments to respective MO for **1** and **2**, respectively, together with the results for diphenyl chalcogenides (**3**: **3a–c**).⁵ The IP of **1** and **2** were calculated with the 6-311+G(d,p) basis sets of the Gaussian 94 program⁶ at the DFT (B3LYP) level via Koopmans' theorem.⁷ Table 2 shows the collected results. The structure of **1** was optimized to be of C_{2v} symmetry, and that of **2a** was of C_s symmetry and almost planar. The symmetry of **2b** and **2c** was C_1 , which only deviated

(3) This technique is based on the energy analysis of electrons released in the ionization of an atom or a molecule, M, by the 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 an 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 ($\Gamma \propto EED = \int_{\Omega} \phi_i^2(r) dr$). Thus, the spatial distribution of individual molecular orbitals, which is difficult to measure with other methods, can be obtained from the analysis of the band intensities of PIES. The repulsive molecular surfaces are approximated by compositions of the spheres with the van der Waals radii of the atoms ($r_H = 1.20 \text{ \AA}$, $r_C = 1.70 \text{ \AA}$, $r_O = 1.40 \text{ \AA}$, $r_S = 1.85 \text{ \AA}$, $r_{Se} = 2.00 \text{ \AA}$) in the molecules. The EED can be calculated with a lattice sum method.²⁵ The EEDs were calculated for **1a**, **1b**, **2a**, and **2b** with lower basis sets, although not shown. The results were in accordance with the assignments.

(4) Ohno, K.; Mutoh, H.; Harada, Y. *J. Am. Chem. Soc.* **1983**, *105*, 4555. Fujisawa, S.; Ohno, K.; Masuda, S.; Harada, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6505. See also refs cited therein.

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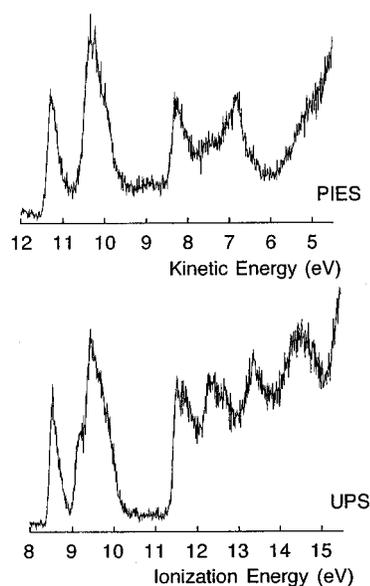


Figure 1. PIES and UPS spectra of xanthone (**1a**).

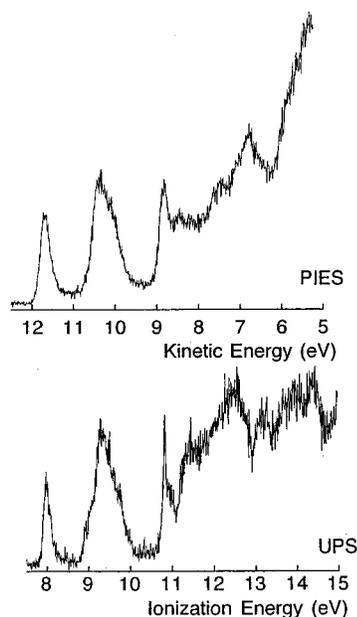
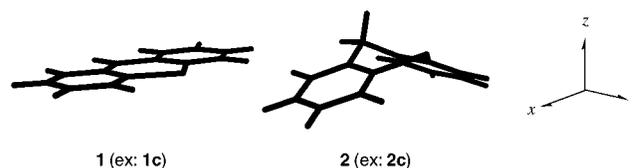


Figure 2. PIES and UPS spectra of thioxanthone (**1b**).

slightly from C_s . The structures are depicted below exemplified by **1c** and **2c**, together with the axes.



The observed IP given in Table 1 were plotted against the calculated IP in Table 2. Figure 7 shows the plot of

(6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.4; Gaussian, Inc.: Pittsburgh, PA, 1995.

(7) Koopmans, T. *Physica (Utrecht)* **1933**, *1*, 104.

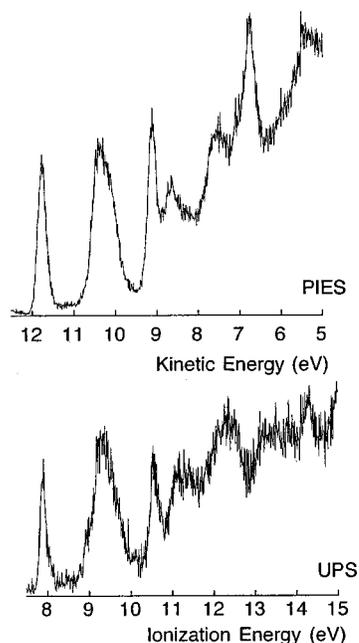


Figure 3. PIES and UPS spectra of selenoxanthone (**1c**).

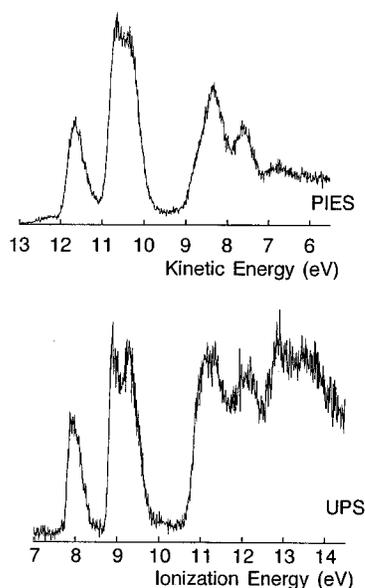


Figure 4. PIES and UPS spectra of xanthene (**2a**).

1c, for example, and the correlations are collected in Table 3. The natural populations at the chalcogen atoms were also calculated based on the natural population analysis.⁸ The results are shown in Table 4. Table 5 exhibits the relative intensities of the first bands ($\pi_6(n)$) of **1** and **2** relative to the total pure π bands ($\pi_3 + \pi_4 + \pi_5$), for which band intensities were taken to be 3.0. The individual orbitals of the compounds were depicted with the 3-21G(*) basis sets of the MacSpartan program⁹ by the single-point calculations on the optimized structures with the 6-311+G(d,p) basis sets at the B3LYP level.

The bands in **1** and **2** were assigned based on the IP calculated with the 6-311+G(d,p) basis sets at the B3LYP level on the compounds shown in Table 2. The band

(8) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO*, version 3.1.

(9) Hehre, H. J. *MacSpartan Plus*, version 1.0; Wavefunction Inc.

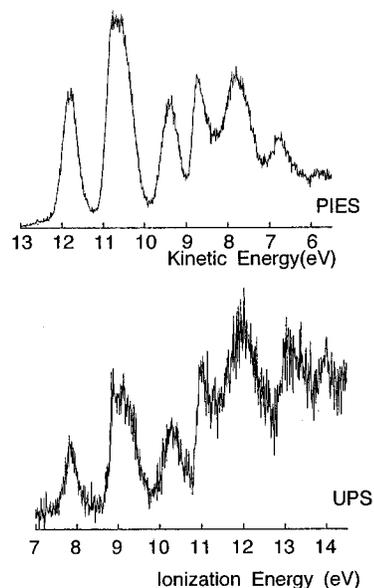


Figure 5. PIES and UPS spectra of thioxanthene (**2b**).

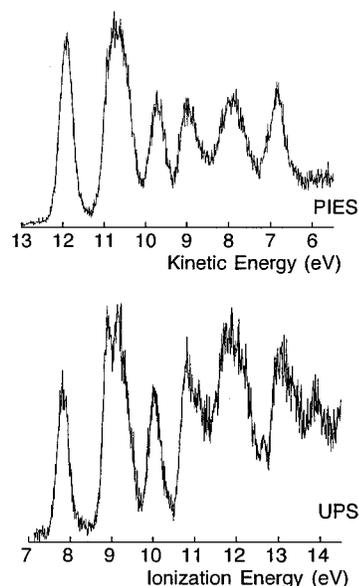


Figure 6. PIES and UPS spectra of selenoxanthene (**2c**).

assignments previously reported for **3**⁵ were also employed to assign those of **1** and **2**; the intensities of the n and π bands were large in PIES relative to those for the σ bands.^{3,5,10} The $n(\text{C}=\text{O})$ bands of the carbonyl compounds were studied by UPS^{11,12} and PIES.¹² The IP of the bands for formaldehyde and acrolein were reported to be 10.88 and 10.10 eV, respectively.^{12a} Since **1** contains the carbonyl group, the $n(\text{C}=\text{O})$ bands are expected to

(10) The protection of the $n(p_z)$ orbitals from the coming metastable helium atom was reported in **3**, due to the phenyl rings being distorted by about 55° with each other.^{5,26} Such protection was not observed in **1** and **2**. It may be due to the structures of **1** and **2**, which are planar and of C_s (or almost C_s) symmetry, respectively. They would not protect the $n(p_z)$ orbitals.

(11) (a) Newton, M. D.; Boer, F. P.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1966**, *88*, 2367. (b) Yonezawa, T.; Katsumata, S.; Kimura, K.; Kobayashi, T. *Vacuum Ultraviolet Photoelectron Spectroscopy of Gaseous Molecules*. In *Electron Spectroscopy*; Kimura, K., Ed.; Gakkai Shuppan Center: Tokyo, 1977.

(12) (a) Ohno, K.; Okamura, K.; Yamakado, H.; Hoshino, S.; Takami, T.; Yamauchi, M. *J. Phys. Chem.* **1995**, *99*, 14247. (b) Ohno, K.; Takano, S.; Mase, K. *J. Phys. Chem.* **1986**, *90*, 2015.

Table 1. Observed IP of Xanthenes (1) and Xanthenes (2), Together with Those of Diphenyl Chalcogenides (3)^a

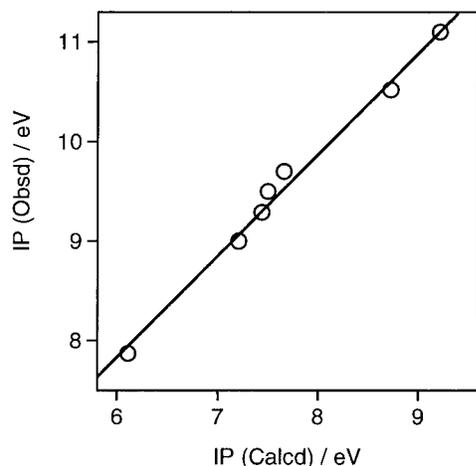
1a	1b	1c	2a	2b	2c	3a ^b	3b ^b	3c ^b	assignment
8.52	7.94	7.87	7.94	7.85	7.78	8.30	7.90	7.85	$\pi_6(n)$
9.1	9.0	9.0							n(C=O)
9.44	9.29	9.29	8.87	8.85	8.85	9.15	9.15	9.15	π_5
9.6–9.8	9.5–9.7	9.5–9.7	9.2–9.4	9.1–9.4	9.1–9.4	9.3–9.6	9.3–9.6	9.3–9.6	π_4, π_3
11.50	10.80	10.52	11.0	10.29	10.02	11.15	10.12	9.80	n(p _z) ^c
11.7	11.4	11.1	11.3	11.00	10.78	11.55	11.2	10.83	n(p _y)

^a In electronvolts. ^b Reference 5. ^c The character of the orbital is $\pi_2(n)$ for **1a**, **2a**, and **3a**.

Table 2. Energies of Xanthenes (1) and Xanthenes (2) Calculated with the 6-311+G(d,p) Basis Sets at the B3LYP Level^a

energy	1a	1b	1c	2a	2b	2c	assignment
total	-650.833	-973.802	-2977.128	-576.780	-899.756	-2903.086	
HOMO	6.65	6.25	6.11	5.96	5.94	5.84	$\pi_6(n)$
HOMO- <i>i</i> ^b	7.17	7.19	7.21				n(C=O)
HOMO- <i>j</i> ^b	7.51	7.47	7.44	6.87	7.02	6.99	π_5
HOMO- <i>k</i> ^b	7.54	7.51	7.50	7.18	7.06	7.06	π_4
HOMO- <i>l</i> ^b	7.70	7.71	7.66	7.27	7.26	7.23	π_3
HOMO- <i>m</i> ^b	9.68 ^c	9.08	8.72	9.12	8.25	7.96	n(p _z) ^d
HOMO- <i>n</i> ^b	9.72 ^c	9.44	9.21	9.36	9.09	8.83	n(p _y)

^a In atomic units for total energies and in electronvolts for each molecular orbital. ^b (*i, j, k, l, m, n*) = (1, 2, 3, 4, 5, 6) for **1** and (null, 1, 2, 3, 4, 5) for **2**. ^c Assignments should be changed. ^d The character of the orbital is $\pi_2(n)$ for **1a** and **2a**.

**Figure 7.** Plot of the observed IP against those calculated at the B3LYP level for **1c**.**Table 3. Correlations of the Observed IP Versus Those Calculated with the 6-311+G(d,p) Basis Sets at the B3LYP Level**

parameter ^a	<i>a</i>	<i>b</i>	<i>r</i>
1a	0.99	2.07	0.997
1b	1.03	1.60	0.994
1c	1.02	1.70	0.995
2a	0.98	2.16	0.999
2b	1.01	1.92	0.995
2c	1.01	1.90	0.994

^a $IP_{\text{obsd}} = aIP_{\text{calcd}} + b$ in electronvolts (*r* = correlation coefficient).

be detected. The n(C=O) bands could be observed in the UPS of **1** at the shoulders of the pure π -bands, π_3 , π_4 , and π_5 , although the bands of **1** were not clearly detected in PIES of **1**,¹³ the shoulders were not observed in UPS of **2**. As shown in Tables 2 and 3, the assignments were

(13) The IP of the n(C=O) bands of formaldehyde, acrolein, and acetophenone were calculated to be 7.67, 7.42, and 7.38 eV, respectively, with the 6-311+G(d,p) basis sets at the B3LYP level, and the IP of the n bands of the C=O groups in **1** were evaluated to be 7.17–7.21 eV with same method. The bands were not observed in PIES as the isolated ones. Since the n(C=O) orbitals lay on the molecular plane, the band would be blocked by the ortho hydrogens, which must result in the decreased intensities for the bands in PIES of **1**.

Table 4. Natural Charges (Q_n) on Some Atoms in 1 and 2 Calculated with the 6-311+G(d,p) Basis Sets at the B3LYP Level

atom ^a	Z	C*=O	C=O*	C*H ₂	CH _e *H _a	CH _e H _a *
1a	-0.4900	0.5219	-0.5815			
1b	0.4056	0.5267	-0.5855			
1c	0.5073	0.5235	-0.5838			
2a	-0.5198			-0.4037	0.2185	0.2185
2b	0.3077			-0.4112	0.2143	0.2297
2c	0.4078			-0.4110	0.2137	0.2315

^a Z stands for the corresponding chalcogen atom, and the atom given the Q_n value is shown with an asterisk. The equatorial and axial hydrogens are shown by H_e and H_a, respectively.

Table 5. Relative Intensities for the π_6 (HOMO) Bands

intensity	1a	1b	1c	2a	2b	2c
π_6	1.1	1.2	1.3	1.0	1.4	1.8
$\pi_3 + \pi_4 + \pi_5^a$	3.0	3.0	3.0	3.0	3.0	3.0

^a The relative intensity is taken to be 3.0.

supported well by the MO calculations performed on **1** and **2** with the 6-311+G(d,p) basis sets at the B3LYP level.^{13,14}

The proportionality constants in the plots of observed IP against those calculated at the B3LYP level were almost unity, and the correlation coefficients were very good, which showed that the results of the calculations at the B3LYP level were reliable, although the observed values were 1.6–2.2 eV larger than the calculated ones (see Figure 7 and Tables 1–3). It may be rationalized that the IP of the n(C=O) bands in **1a–c** could be predicted by the MO calculations with the 6-311+G(d,p) basis sets at the B3LYP level.

As shown in Table 1, the IP of the $\pi_6(n)$, n(p_z) ($\pi_2(n)$) for **1a** and **1b**), and n(p_y) bands in **1** and **2** become smaller in the order $IP(1a) > IP(1b) > IP(1c)$ and $IP(2a) > IP(2b) > IP(2c)$, respectively, whereas those of the pure π -orbitals (π_3 , π_4 , and π_5) were almost constant. The IP of the n and π bands of **1a–c** were larger than those of the corresponding bands of **2a–c**, respectively. The

(14) The IP for the n(C=O) bands in **1** were predicted to be HOMO-4 of about 11.5 eV with the 6-311+G(d,p) basis sets at the HF level, although not shown in the text. The predicted IP did not explain well the observed ones ($IP_{\text{obsd}} = 0.572IP_{\text{calcd}} + 3.61$, $r = 0.816$ for **1c**, and $IP_{\text{obsd}} = 0.726IP_{\text{calcd}} + 2.25$, $r = 0.980$ for **2c**).

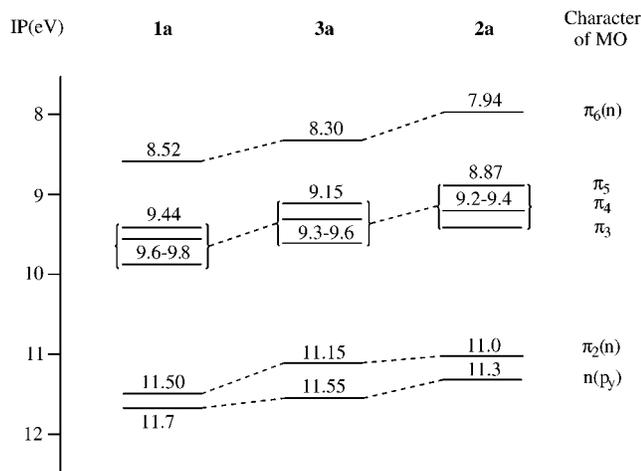


Figure 8. Correlation diagram for **1a**, **2a**, and **3a**.

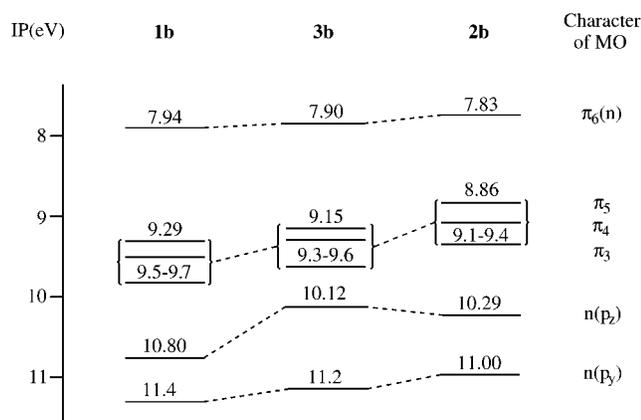


Figure 9. Correlation diagram for **1b**, **2b**, and **3b**.

latter were smaller than those of the corresponding **3a-c**,⁵ respectively, except $IP(n(p_z))$ of **2b** and **2c**.

Next, the IP of the n and π bands of **1x**, **2x**, and **3x**, where $x = a, b,$ and c , were compared to examine the effects of the carbonyl and methylene groups on the electronic states of the compounds. Figure 8 exhibits the correlation diagram for the n and π orbitals of **1a**, **2a**, and **3a**. IP of $\pi_6(n)$, the pure π -orbitals, $\pi_2(n)$, and $n(p_y)$ become smaller in the order $IP(\mathbf{1a}) > IP(\mathbf{3a}) > IP(\mathbf{2a})$. The electron-withdrawing effect of the carbonyl group¹⁵ and the electron-donating effect of the methylene group¹⁵ are effective to increase and decrease the IP of the n and π bands, respectively. The hyperconjugative interaction of the methylene group may also have an important effect on the heteroatoms of the compounds.

Figures 9 and 10 show the correlation diagrams for the n and π orbitals for **1b**, **2b**, and **3b** and **1c**, **2c**, and **3c**, respectively. The two groups of compounds show a very similar trend in IP. The IP of $\pi_6(n)$, the pure π -bands, and $n(p_y)$ become smaller in the order $IP(\mathbf{1x}) > IP(\mathbf{3x}) > IP(\mathbf{2x})$ where $x = a$ and b , although the differences in $\pi_6(n)$ are small. It is worthwhile to comment on the behavior of the IP of $n(p_z)$. The values for **1b** and **2b** are larger than that for **3b** by 0.68 and 0.17 eV, respectively. The larger IP of **1b** must be a reflection of the electron-withdrawing ability of the carbonyl group. The $IP(n(p_z))$

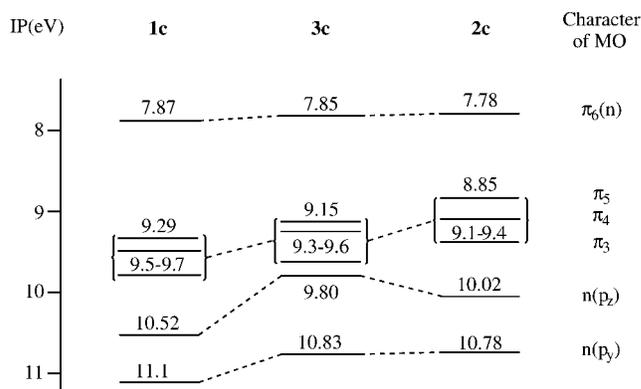


Figure 10. Correlation diagram for **1c**, **2c**, and **3c**.

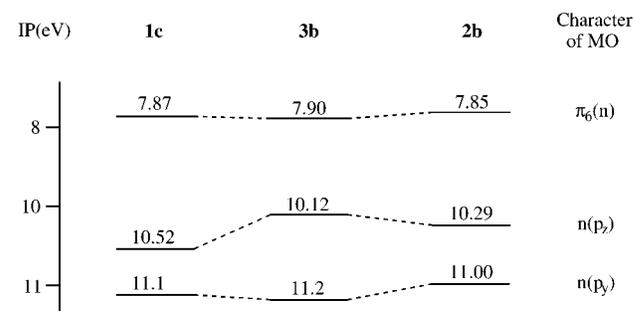


Figure 11. Correlation diagram for **1c**, **2b**, and **3b**.

of **2b** is expected to be smaller than that of **3b** due to the electron-releasing methylene group in the compound. The former was observed to be larger than that of the latter however. The roof structure of **2b** (and **2c**) would be an important factor in determining the IP. The noncyclic structure with the distorted phenyl rings in **3b** might also be the cause of the observation. The trend of IP in **1c**, **2c**, and **3c** was the same as that in **1b**, **2b**, and **3b**. The $IP(n(p_z))$ of **1c** and **2c** were larger than that of **3c** by 0.72 and 0.22 eV, respectively, similar to the case in **1b** and **2b** versus **3b**.

The charge developed on the chalcogen atoms and carbonyl and methylene groups in **1** and **2** was estimated based on the natural population analysis with the 6-311+G(d,p) basis sets at the B3LYP level (Table 4). The negative charges were determined to develop on the O atoms (not in the C=O group) in **1a** and **2a**. The magnitude of the former is smaller than that of the latter by ca. 0.03 ($\Delta Q_n = Q_n(\mathbf{1a}) - Q_n(\mathbf{2a})$). The large positive charge developments were demonstrated at the sulfur and selenium atoms in **1b**, **1c**, **2b**, and **2c**; the magnitudes in **1b** and **1c** were larger than those in **2b** and **2c**, respectively, by about 0.10 ($\Delta Q_n = Q_n(\mathbf{1x}) - Q_n(\mathbf{2x})$, where $x = b$ and c). The differences were substantially larger for the selenium and sulfur compounds relative to the oxygen compounds.

The structure of **2a** was optimized to be almost planar, whereas **2b** and **2c** were found to exhibit the roof structure (close to the C_s symmetry), which must be responsible for the calculated charges discussed above. The developed charges on the carbonyl group in **1** and on the methylene group in **2** were about -0.060 and 0.033 , respectively (cf. Table 4). Each charge developed on the group was almost constant, irrespective of the heteroatoms. The difference in the electronic effects between the two groups in **1** and **2** was estimated to be

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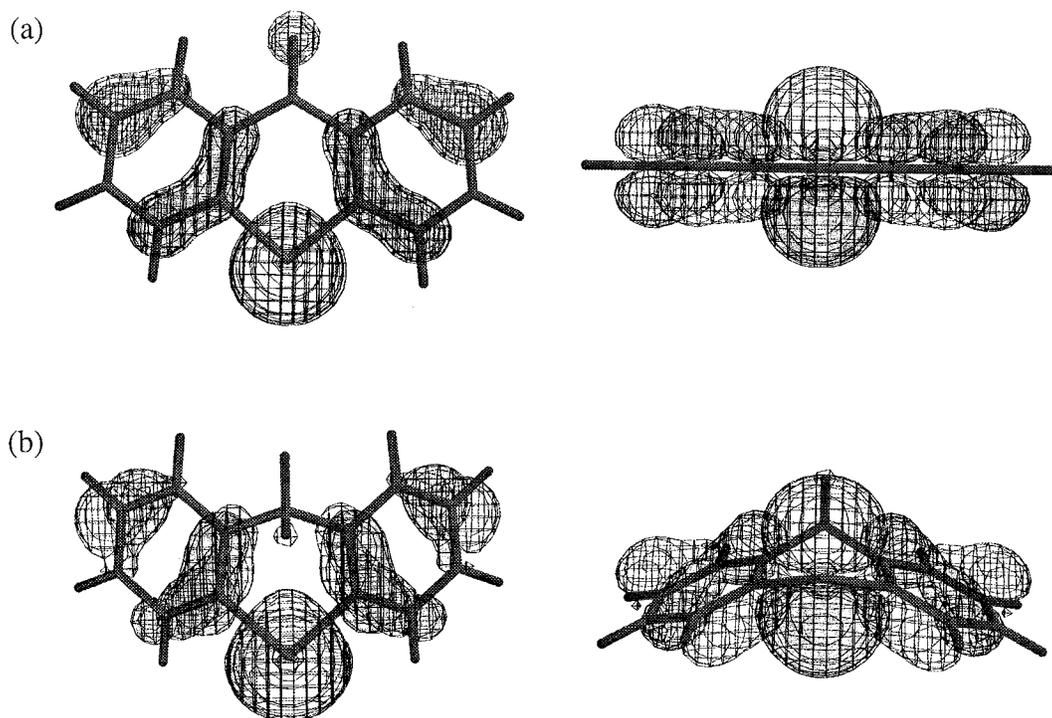


Figure 12. The $\pi_6(n)$ orbitals (HOMO) for (a) **1c** and (b) **2c**.

0.093, which was almost equal to the ΔQ_n values for the sulfur and selenium compounds. The magnitude of the interactions between the π -orbitals of the aryl rings and the $n(p_z)$ -type lone pairs of the heteroatoms must also be considered.¹⁶ It is now established how the IP of **1** and **2** are determined by the electron-withdrawing carbonyl group and by the electron-releasing methylene group, respectively, relative to those of **3**. The next extension of the investigation is to explain the reactivity of the compounds, especially that of **1c** versus that of **2c** and **3c**, based on their physical properties discussed above.

Let us consider the reaction of a diaryl chalcogenide (Ar_2ZAr) with a halogen ($\text{X}-\text{X}$) to give an adduct (Ar_2ZX_2) in order to bring the discussion into focus. When $\text{X}-\text{X}$, an electrophile, comes close to the Z atom of Ar_2ZAr , electrons will move from $n(\text{Z})$ to the $\sigma^*(\text{X}-\text{X})$.¹⁷ The charge transfer may occur from the HOMO of the $\pi_6(n)$ in the early stage of the reaction. As the reaction proceeds, the electrophile will interact more strongly with the $n(p_z)$ orbital of the Z atom, as the total interactions, that is, the charge transfer mainly occurs from the $n(p_z)$ orbital at the final stage of the reaction. The adduct is an MC when the magnitude of the charge transfer is not so large.^{1,2} The halogen cannot exist as a halogen molecule if the magnitude becomes larger. A TB adduct will form with a highly polar $\text{X}^{\delta-}-\text{Z}^{\delta+}-\text{X}^{\delta-}$ bond in this case.¹⁸ The IP($n(p_z)$) must mainly determine the structure of the adducts; the adduct is TB if IP($n(p_z)$) is small

enough, but it will be an MC when IP($n(p_z)$) is not small.⁵ The electron affinity of the halogen must also be considered however.



Figure 11 shows the correlation diagram for the IP of $\pi_6(n)$, $n(p_z)$, and $n(p_y)$ in **1c**, **2b**, and **3b**. Although the IP($\pi_6(n)$) are almost equal among the three compounds, the IP($n(p_z)$) of **1c** is larger than those of **2b** and **3b** by 0.23 and 0.40 eV, respectively. The results clearly show that the $n(p_z)$ orbital of **1c** is substantially less reactive toward electrophiles than those of **2b** and **3b**. Sulfides are well-known to react with bromine to give an MC;^{2a,19,20} that is, the reactivity of the $n(p_z)$ of sulfides is not large enough to give a TB with electrophiles such as bromine. Therefore, the reactivity of **1c** is well-explained; **1c** never gives a TB with bromine. The IP($n(p_y)$) of **1c** is almost equal to those of **2b** and **3b**; the $n(p_y)$ orbitals of chalcogenides are expected not to affect the structure of the adducts. The large positive charge development at the selenium atom of **1c** estimated by the MO calculations also supported the results (Table 4).

The relative intensities of the bands of **1** and **2** are also examined. Table 5 shows those of the first band ($\pi_6(n)$)

(16) The $2p$ π -orbital of the $\text{C}=\text{O}$ group interacts with the π -orbitals of the aryl groups, which, in turn, interact with the p_z -type lone pairs of the heteroatoms. The overlap integral between the π -orbitals of the aryl groups and the $n(2p_z)$ orbital of the oxa group in **1a** is expected to be larger than those with the $n(3p_z)$ or $n(4p_z)$ lone pairs of the sulfanyl or selenanyl group in **1b** or **1c**. The energy differences between the $2p_z$ atomic orbitals of the carbon atoms and the np_z atomic orbitals of sulfur and selenium atoms may also play an important role in this case. See: Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985.

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versus those of the pure π bands (π_3 , π_4 , and π_5), for which the intensities ($I_{\text{rel}}(\pi_3 + \pi_4 + \pi_5)$) are taken to be 3.0. The $I_{\text{rel}}(\pi_6(n))$ values for **1a**, **1b**, and **1c** were 1.1, 1.2, and 1.3, respectively, but those of **2a**, **2b**, and **2c** were 1.0, 1.4, and 1.8, respectively.²¹ The $I_{\text{rel}}(\pi_6(n))$ of **1c** is substantially smaller than that of **2c**, which would be a reflection of the enlargement of the effective electronegativity of the selenium atom in **1c** by the electron-withdrawing carbonyl group, relative to that in **2c** bearing the electron-releasing methylene group. Similar trends are also observed in **1b** relative to **2b**.

Figure 12 shows the HOMO ($\pi_6(n)$) of **1c** and **2c**. The orbital of **1c** extends less widely over the whole molecule relative to that of **2c**, which supports the observation in the $I_{\text{rel}}(\pi_6(n))$ values of the compounds. The calculated natural charges shown in Table 4 also support the effect of the substituents not only on the IP but also on $I_{\text{rel}}(\pi_6(n))$. The chemical reactivity of **1c** toward nucleophiles is now well understood from the physical properties of **1c** and the related compounds, together with the results of ab initio MO calculations performed on the compounds.

Experimental Section

Xanthone (**1a**), xanthene (**2a**), and thioxanthone (**1b**) were commercially available. Thioxanthene (**2b**),²² selenoxanthone (**1c**),²³ and selenoxanthene (**2c**)²⁴ were prepared according to the literature. The compounds were purified by chromatography on silica gel eluted by hexane, and the purities were

confirmed by the melting points, together with the ¹H and ¹³C NMR spectroscopy.

PIES and UPS were measured as reported previously.^{4,5} Highly pure ²³S helium atoms were introduced into the ionization chamber and collided with sample molecules. The helium I resonance line (584 Å, 21.22 eV) was applied for UPS. The electron energy spectra were obtained at an emission angle of 90° with respect to the ²³S atom beams or the photo beams by means of a hemispherical-type analyzer with an electron lens systems. The energy-selected electrons were detected with an electron multiplier and a pulse counter combined with a signal averager. The overall energy resolution was about 40 meV.

Ab initio MO calculations were performed with 6-311+G-(d,p) basis sets of the Gaussian 94⁶ program at HF and DFT (B3LYP) levels using an Origin computer. Natural populations at the atoms were also calculated based on the natural population analysis.⁸ MacSpartan⁹ was also employed to depict the molecular orbitals.

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(21) It is necessary to consider the contributions from the n(C=O) orbitals to the $I_{\text{rel}}(\pi_3(n) + \pi_4(n) + \pi_5(n))$ in **1**, since the bands must coincide with each other. The magnitude of $I_{\text{rel}}(n(\text{C=O}))$ would be negligible, however.

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