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Gas and Solid Phase Photoelectron Spectra of 5,6,11,12-Tetraphenylnaphthacene (Rubrene)

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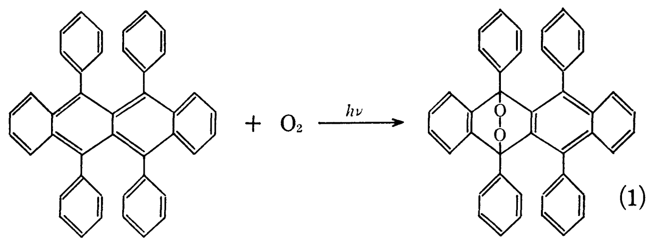
The gas and solid phase UV photoelectron spectra of rubrene were measured. In the molecule there is little conjugation of π-electrons between four substituent phenyl groups and the naphthacene skeleton owing to the effect of the steric hindrance of the phenyl groups. Therefore, the lower IP bands in the gas phase spectrum could be correlated to the π-bands in the photoelectron spectra of benzene and naphthacene. The features of the solid phase spectrum are similar to those of the gas phase one except for a large peak due to inelastically scattered electrons. The polarization energy due to the molecular ion in the solid, the peak to peak difference between the gas and solid phase spectra, was observed to be 0.6 eV, which is about half the polarization energy for naphthacene. This means that rubrene molecules are loosely packed in the solid as a result of the steric hindrance of four phenyl groups.

The compound 5,6,11,12-tetraphenylnaphthacene (rubrene) has aroused considerable chemical interest, since Moureu *et al.*[1] observed that its solution became colourless when irradiated in the presence of air. Subsequently, it was established that the change in colour is due to the formation of a transannular compound:[2]



(1)

rubrene rubrene peroxide

Recently we have studied the photooxidation process (1) in solid phase by ultraviolet photoelectron spectroscopy.[3] In the course of the study, it was necessary to assign the bands in the photoelectron (PE) spectrum of rubrene.

We therefore present the PE spectra of rubrene for gas and solid phases, and a subsequent analysis of the electronic structure in comparison with that of the unsubstituted compound, naphthacene.

Experimental

Rubrene was purified by vacuum sublimation. The gas phase He I spectrum was recorded on a Perkin-Elmer PS-18 photoelectron spectrometer. The temperature of the sample was kept at 280 °C during the experiment.

The He I spectrum of solid rubrene was measured using an ultra high vacuum spectrometer constructed at our laboratory (the University of Tokyo), the details of which will be described elsewhere.[3] A 180° hemispherical analyzer of 5 cm mean radius was used for electron energy analysis. The solid phase photoelectron spectrum was also obtained with 7.75 eV† monochromatic light which was provided by a 0.5 m Seya-Namioka type monochromator fitted with a hydrogen discharge lamp. In this case a spherical retarding type analyzer was used with an ac-modulation method. Rubrene films were prepared by vacuum sublimation *in situ* onto copper substrates. The thickness of the films was controlled by means of a quartz osicillator monitor and was about 15 nm.

Results and Discussion

Gas Phase Spectrum. Figure 1 shows the gas phase spectrum of rubrene. The observed lower ionization potentials (*IP*'s) are listed in the first column of Table 1. Since four substituent phenyl groups in the rubrene molecule are considered to be rotated out of the molecular plane owing to the effect of steric hindrance,†† little conjugation of π-electrons between the phenyl groups and the naphthacene skeleton is expected. Therefore, bands in the lower *IP* region of the rubrene spectrum can be correlated to the π-bands in the photoelectron spectra of benzene[4,6] and naphthacene.[5] The correlation is listed in Table 1 for the bands 1 to

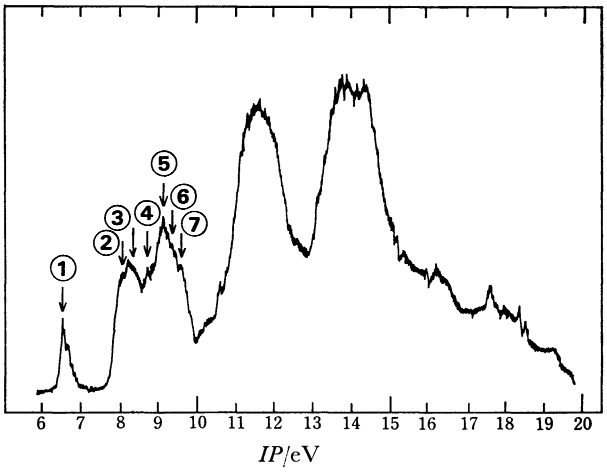


Fig. 1. Gas phase He I photoelectron spectrum of rubrene.

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† Throughtout this paper 1 eV$=1.62\times10^{-19}$ J.

†† The conformation of rubrene has not been determined experimentally.

Table 1. Vertical ionization potentials of rubrene and related compounds with assignment

Vertical IP/eV			ΔIP/eV[a)]	Partial electron density[b)]
Rubrene	Benzene[c)]	Naphthacene[d)]		
① 6.52		$6.97(2a_u\pi)$	0.45	0.148
② 8.0_5		$8.41(3b_{1u}\pi)$	0.3_6	0.048
③ 8.3_0		$8.41(2b_{2g}\pi)$	0.1_1	0.000
④ 8.7_5	$9.24\ (1e_{1g}\pi_3)$			
⑤ 9.15	$9.24\ (1e_{1g}\pi_2)$	$9.56(1a_u\pi)$	0.41	0.044
⑥ 9.4		$9.70(2b_{3g}\pi)$	0.3	0.034
⑦ 9.6		$10.25(1b_{2g}\pi)$	0.6_5	0.112

a) The difference between the IP value of naphthacene and that of rubrene b) partial π-electron density due to the orbital of naphthacene at one of the substituted positions (5-, 6-, 11-, and 12-positions). c) Refs. 4 and 6. d) Ref. 5.

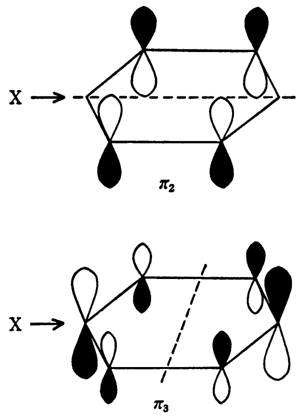

Fig. 2. The $1e_{1g}$ π-orbitals of benzene. X represents a substituent.

7 in Fig. 1. The 9.24 eV band of benzene has been assigned to the degenerate π_2 and π_3 orbitals.[6)] At the point of substitution, the π_2 orbital has a node, while the π_3 has its maximum electron density (Fig. 2). Accordingly, on substitution, the π_2 orbital may be relatively unaffected, whereas the π_3 may have its energy lowered relative to the π_2. Thus, in Table 1 we assign the bands at 8.7_5 and 9.15 eV of rubrene to the π_3 and π_2 orbitals, respectively. This assignment is supported by the fact that the bands ascribable to the π_2 and π_3 orbitals are also found in the IP region 8.8—9.3 eV of the photoelectron spectrum of 5,10-diphenylanthracene.[7)] Moreover, it has been observed that the bands corresponding to the 8.7_5 and 9.15 eV bands of rubrene remain in the photoelectron spectrum of a rubrene peroxide film (*cf.* Eq. 1).[3)] Although the intensities of the bands ④ and ⑤ involving the ionization of four benzene rings are much stronger than those of the bands ⑥ and ⑦, they are not strong enough in comparison with the intensities of the bands ① to ③. The transmission coefficient ($\propto \Delta E/E$; E, the energy of photoelectrons) of the energy analyzer used may partly account for this effect.

When the naphthacene molecule is substituted by phenyl groups, similar effect as above can be expected; the shift of the π-orbital energy may become greater, the larger the partial π-electron density due to the orbital at the position of substitution.[†††] In Table 1 the differences between the IP values of naphthacene and those of rubrene (π-orbital energy shifts) are shown in comparison with the π-electron densities of naphthacene at one of the substituted positions (5-, 6-, 11-, and 12-positions). The electron densities were calculated on the basis of the Pariser-Parr-Pople method. It can be seen from Table 1 that the correlation of the IP shift with the π-electron density is satisfactory. This supports the present assignment of the bands in the lower IP region of the rubrene spectrum.

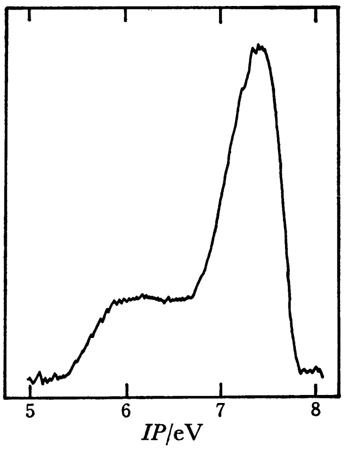

Fig. 3. Solid phase photoelectron spectrum of rubrene for $h\nu = 7.75$ eV.

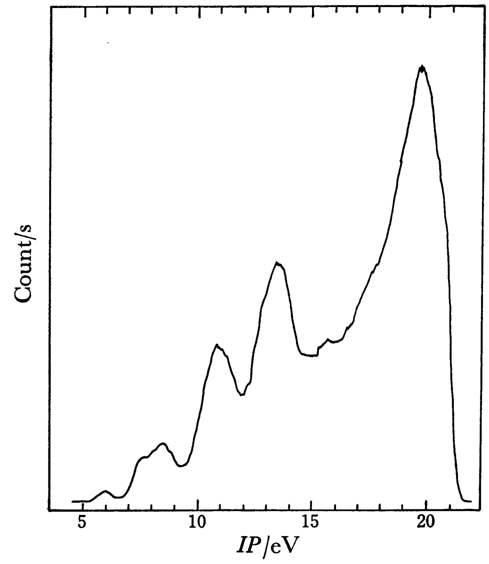

Fig. 4. Solid phase photoelectron spectrum of rubrene for $h\nu = 21.22$ eV.

[†††] When a π LCAO MO, $\psi_i = \sum_k C_{ik}\chi_k$, is perturbed by a substituent X, the first-order perturbation energy of the MO is expressed by $\Delta E_i = \int \psi_i^* \hat{H}' \psi_i \mathrm{dv} = \sum_{k,l} C_{ik}^* C_{il} H'_{kl}$, where $\hat{H}'$ is the perturbation operator and $H'_{kl} = \int \chi_k^* \hat{H}' \chi_l \mathrm{d}v$. Let s be the number of the carbon atom substituted by X, H'_{ss} is considered to be much larger than the other H'_{kl}'s. Neglecting them, we have $\Delta E_i \doteqdot |C_{is}|^2 H'_{ss}$; the MO energy shift is proportional to the partial π-electron density $|C_{is}|^2$ due to ψ_i at the position of substitution.

Solid Phase Spectrum. Figures 3 and 4 show the photoelectron spectra of solid rubrene for photon energies of 7.75 and 21.22 eV, respectively. The numbers on the abscissas indicate the ionization potential, which could be obtained by a spherical retarding type analyzer for $h\nu = 7.75$ eV. In Fig. 3 only the first band located at 6.0 eV appears in the spectrum because of the small photon energy. The value of its adiabatic *IP* (threshold energy) is 5.3 eV. As can be seen from Figs. 1 and 4, the appearance of the solid phase spectrum for 21.22 eV is similar to that of the gas phase one except for a large peak due to inelastically scattered electrons. This behaviour means that the features of the solid phase spectrum are mostly associated with the valence bands. Further, it is found from Figs. 1 and 4 that the peak positions of the solid phase spectrum are lowered by *ca.* 0.6 eV relative to those of the gas. The shift corresponds to the polarization energy due to the molecular ion left in solid after a photoelectron is removed. In the case of naphthacene the polarization energy is observed to be around 1.1 eV,⁸⁾ which is about twice as large as that for rubrene. Being non-planar as a result of the steric hindrance of four phenyl groups, rubrene molecules are considered to be loosely packed in solid. This seems to be the reason for the small polarization energy for rubrene.[‡]

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[‡] The values of the polarization energy for benzene, naphthalene and anthracene are 1.15, 1.1, and 1.2 eV, respectively (W. D. Grobman and E. E. Koch, "Photoemission in Solids I," ed by M. Cardona and L. Ley, Springer, Berlin (1978)). Thus the polarization energy is fairly constant for the aromatic molecules, benzene to naphthacene, which suggests that its value depends on the molecular packing in the crystal, irrespective of the size of the molecule.