Photoemission from Anthracene and Compounds Containing Anthracene-ring Systems

Shojun Hino,† Tomohiko Hirooka,* and Hiroo Inokuchi††
The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106
**Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113*

(Received September 16, 1976)

The Photoemission from the organic compounds containing anthracene rings—anthracene, 9-methylanthracene, 9,10-dichloroanthracene and 9,9′-bianthryl—was measured. The photoelectron energetic responses of all these compounds were nearly the same. The resemblance of the photoelectron energy distribution curves and the spectral dependence of the quantum yield revealed the coincidence of the electronic structures of these compounds in a solid. The comparison between solid- and gas-phase photoelectron spectra showed that the optical excitation process is the most characteristic one in photoemission phenomena.

Anthracene is a typical compound in the research field of molecular crystals, like polycyclic aromatic hydrocarbons and solid rare gases. The various physicochemical properties of anthracene have been reported.[1,2] Among them, photoemission has recently been revealed to be a useful method for the investigation of the electronic structures of the solid state.[3–10]

We have measured the photoelectric response of anthracene and aromatic compounds containing anthracene-ring systems. The photoelectron energy distribution curves (EDCs) were obtained with a high accuracy by means of an electrical differentiation circuit.[7,11]

In this paper, we will compare the photoelectric effect among these compounds, and will also discuss the effect of the anthracene-ring on the photoemission behavior. We will also point out the resemblance of the photoelectron spectra between the gaseous and solid phases.

Experimental

Measurement. Monochromatic light obtained by a half-meter Seya-Namioka-type monochromator[12] was admitted into a chamber through a lithium fluoride window, which limited the measurement to $h\nu < 12$ eV. The energy distribution of the photoemitted electrons was measured by means of a spherical retarding electrode coated with colloidal graphite, Aquadag, on the inside. The small ac voltage (200 mV peak to peak, 4 Hz) was superimposed on the retarding potential in order to differentiate the I—V characteristic curves.[7,11] The spectral width of the monochromatized light was between 0.05 eV at 200 nm and 0.13 eV at 120 nm. In all, the experimental error is estimated to be less than 0.2 eV in measuring the EDCs.

As the total photocurrents were about 10^{-10} A or less, a preamplifier, a Cary 31 vibrating reed electrometer, had to be used to amplify the photocurrent. 4 Hz ac was adopted to differentiate the I—V characteristics, since the time response of the electrometer was not fast enough for a higher frequency to be used.

The spectral dependence of the quantum yield (SDQY) were measured by means of the same electrode, applying enough accelerating voltage between the emitter and the collector. The relative light intensity was also measured by means of a photomultiplier tube RCA 5819 with the aid of a coronene wavelength converter. As the stray light of the monochromator easily affects the photocurrent (this effect could not be neglected in the case of a low incident photon energy), filters, mainly a quartz filter (with a cut-off wavelength of 155 nm), were applied.

Samples. The samples used in this study were anthracene, 9-methylanthracene (9MeA), 9,10-dichloroanthracene (DClA), and 9,9′-bianthryl. Anthracene and 9MeA were deposited onto a cooled emitter (copper disk 12 mm in diameter) as a thin film by the sublimation method in a fairly low vacuum (10^{-3}—10^{-4} Torr) in order to prevent sample evaporation. After the preparation of the specimens, the emitter was introduced into the ionization chamber. During this operation, the specimen absorbed oxygen and water on its surface easily. The effect of this contamination will be discussed later.

DClA and 9,9′-bianthryl, on the other hand, were deposited onto the emitters under a pressure of less than 4×10^{-6} Torr by the sublimation method, this was possible because of their low vapor pressures.

The film thickness is an important factor in the quantitative photoemission measurements of organic crystals; a thinner film is not thick enough to prevent the penetration of light to the substrate, and the photocurrent due to the substrate is often observed, while a thicker film causes a charge-up effect which affects the EDCs. The thickness of the evaporated films in this work was from 40 to 100 nm in the first preparation. As the samples were sublimed successively from the surface of the thin film during the measurements, it was difficult to estimate the film thickness at each measurement.

Results

Energy Distribution Curves. Figures 1—4 show the photoelectron energy distribution curves of anthracene and its derivatives. Each EDC is indicated in arbitrary units, plotted as a function of the retarding potential, V; the numerical value beside each EDC is the incident photon energy. A dominant peak was observed in each EDC at about $V=0$ V. This peak position was independent of the incident photon energy. The kinetic energy of the photoejected electrons which are attributed to this dominant peak was less than 1 eV.

On the left side of the dominant peak (a large retardation voltage was applied) several structures were observed. These structures resemble each other. They come from the valence bands of each material as will be discussed later. On the right side of the peak, most EDCs except those of anthracene were cut sharply by

---

† Present address: Department of Chemistry, Faculty of Science, Josai University, Keyakidai, Sakado, Saitama 350-02.

†† Present address: Institute for Molecular Science, Okazaki 444.

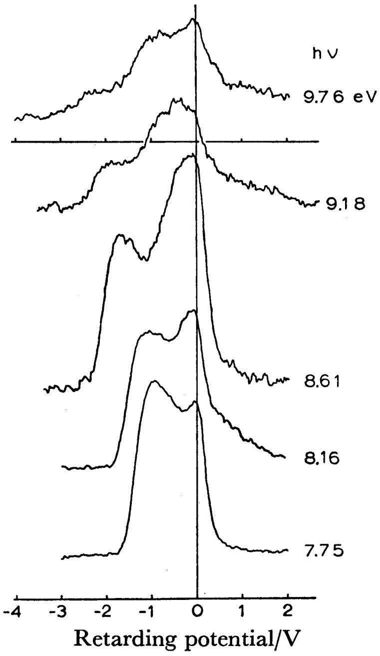


Fig. 1. EDCs of anthracene plotted as a function of retarding potential.

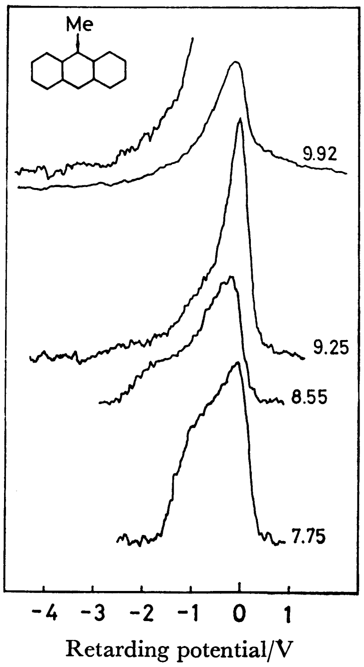


Fig. 2. EDCs of 9MeA plotted as a function of retarding potential.

an effect of the escape function for passing electrons from a solid to a vacuum through the surface. However, long tails were found in some EDCs of anthracene. These long tails were caused by potential drops between the sample surface and the copper disk, since we were sometimes obliged to use thick specimens to avoid quick sample consumption.

The EDCs of 9MeA did not show any distinguishing peaks on the left side of the dominant peak. They showed only shoulders.** These results were perhaps due to the contamination of the specimen surface as

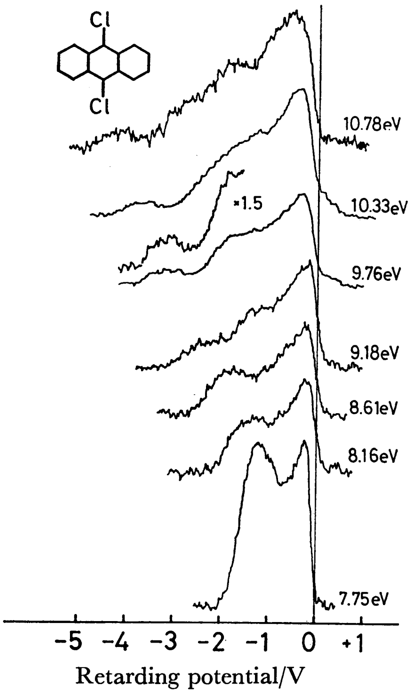


Fig. 3. EDCs of DClA plotted as a function of retarding potential.

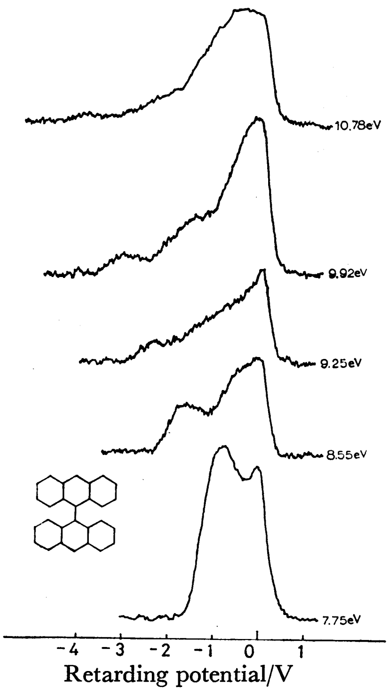


Fig. 4. EDCs of 9,9′-bianthryl plotted as a function of retarding potential.

will be discussed later, because the deposition of 9MeA was not performed under good conditions.

The threshold energy, E_{th}, can be obtained by using the well-known equation:

$$E_{\mathrm{th}} = h\nu - E_{\mathrm{w}}$$

** Moreover, the dominant peaks of 9MeA were much higher than the others.

TABLE 1. THRESHOLD ENERGIES OF THE ORGANIC COMPOUNDS CONTAINING ANTHRACENE-RING SYSTEMS, BOTH OBTAINED FROM THE EDCs AND THE CUBE ROOT PLOT IN eV

	This work		Others	
	E_{th} a)	E_{th} b)		
Anthracene	5.7	5.7_5	5.65 c)	5.95 d)
9-Methylanthracene	5.7_5	5.6_8	5.56 e)	5.95 d)
9,10-Dichloroanthracene	5.8	5.7_5		6.10 d)
9,9′-Bianthryl	5.9	5.9_6	—	

a) Obtained from the EDCs. b) Obtained from the cube root plot. c) Ref. 3. d) Ref. 6. e) Ref. 9.

where *hν* is the energy of the incident photon and E_w is the band width of the EDCs. The threshold energies of these compounds are collected in Table 1.

Quantum Yield. Figure 5 shows the spectral dependence of the quantum yield of anthracene and its derivatives. All the SDQYs showed steep rises at about 6 eV. This is due to the effect of the escape function, which dominates the photoelectron-escape probability at the solid-vacuum interface. In the region between 6.5 and 7.5 eV, all the SDQYs had almost flat slopes. These flat slopes meant a small probability of photoelectron emission in spite of an increase in the light energy. Above 7.5 eV, the quantum yields increased gradually in accordance with the photon energy.

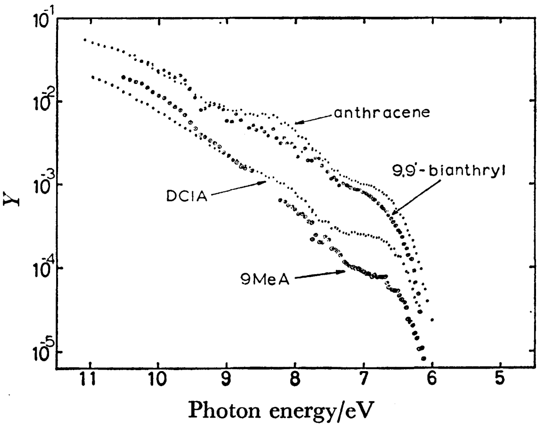
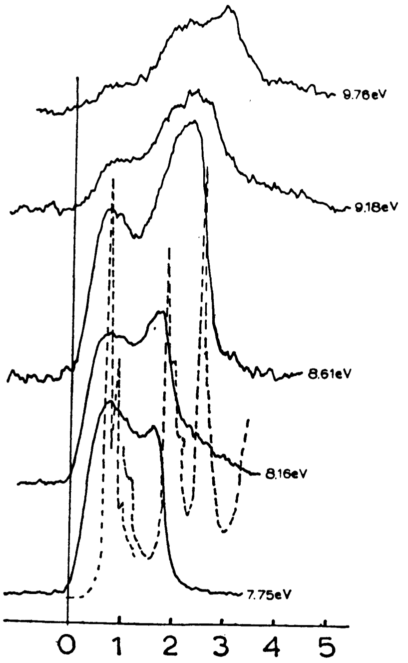


Fig. 5. Spectral dependence of quantum yield of these four compounds.

Anthracene and 9,9′-bianthryl showed the same yields throughout the energy region, while the photoelectric yield of DClA was about a half of that of anthracene. The photoelectric current of 9MeA varied with the exchange of specimens at the same intensity of the exciting light. This phenomenon was probably due to the surface conditions; one specimen was fairly clean and free from the contamination of the surface, while the others were not. As the surface contamination affects the photoelectric quantum yield, the SDQY of 9MeA shown in Fig. 5 is somewhat dubious.

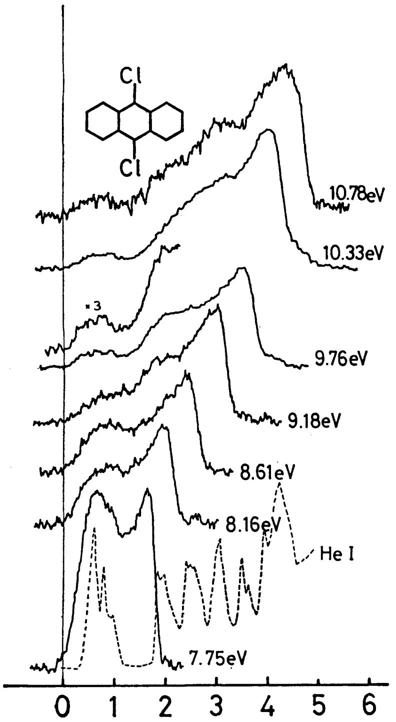
Discussion

Energy Distribution Curves. Figures 6—8 show the replotted EDCs arranged with the first edges of each EDC on the same line. There are fixing peaks in this revised plot which vary the peak position with the incident quanta as shown in Figs. 1—4. These peaks



Energy from threshold energy in eV

Fig. 6. EDCs of anthracene rewritten so that the first edge of each EDC should coincide. Abscissa is energy measured from threshold energy, 5.7 eV. Broken line indicates a molecular photoelectron spectrum of anthracene.[13] See description of text.



Energy from threshold energy in eV

Fig. 7. EDCs (solid line) and molecular photoelectron spectrum (broken line) of DClA.[15] Abscissa is energy measured from threshold energy, 5.8 eV.

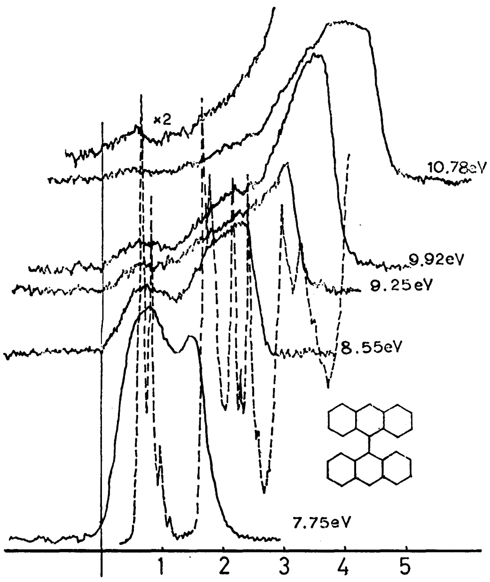


Fig. 8. EDCs (solid line) and molecular photoelectron spectrum (broken line) of 9,9′-binathryl.[16] Abscissa is energy measured from threshold energy, 5.9 eV.

correspond to the valence electrons of each substance. This can be confirmed by a comparison of the broken lines in each figure;[13–16] this line is the molecular photoelectron spectrum, with a slight shift so that the first peaks of both spectra will coincide. The positions of the peaks or shoulders in the EDCs are in good agreement with the photoelectron spectra indicated by the broken lines. This fact indicates that the EDCs obtained by photoemission measurements reflect the state density of the valence band. The ionization potentials obtained by photoemission measurements (peak position) are collected in Table 2, which also lists the I_p's of gaseous anthracene and its derivatives. Table 3 summarizes the energy differences between the first ionization potential and the others.

On the other hand, the dominant peak, which was at the right side of each EDC and had a kinetic energy nearly 0 eV, has no corresponding photoelectron spectrum in the gas phase. This result suggests two possible explanations: The existence of auto-ionization levels in the conduction band, as Zagrubskii and Vilesov proposed,[8] or a scattering mechanism of photoexcited electrons in the transport process, as estimated by Kochi *et al.*[5] and Schechtman.[10]

Table 2. Peak positions of the photoelectron spectra in gaseous and solid phases in eV

	Anthracene		9-Methyl-anthracene		9,10-Dichloro-anthracene		9,9′-Bianthryl	
	Solid	Gas[a]	Solid	Gas[b]	Solid	Gas[c]	Solid	Gas[d]
1 st	6.4	7.47	(6.5)	7.25	6.5	7.58	6.5	7.24 7.42
2 nd	7.6	8.57	(7.8_5)	8.43	7.7	8.88	7.6	8.23 8.34
3 rd	8.2	9.23	—	9.07	8.1	9.42	8.2	8.73 9.00
4 th	—	10.26	—	9.87	8.8	9.91	9.2	9.55 9.87

a) Ref. 13. b) Ref. 14. c) Ref. 15. d) Ref. 16.

Table 3. Energy differences between the first ionization potentials and the others in eV

	Anthracene		9-Methyl-anthracene		9,10-Dichloro-anthracene		9,9′-Bianthryl	
	Solid	Gas	Solid	Gas	Solid	Gas	Solid	Gas[a]
1 st	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
2 nd	1.2	1.10	(1.3_5)	1.18	1.2	1.30	1.1	0.95
3 rd	1.8	1.76	—	1.82	1.6	1.84	1.7	1.53
4 th	—	2.79	—	2.72	2.3	2.33	2.7	2.38

a) Mean values were adopted.

As for the first explanation, it is difficult to consider a characteristic level which uniformly results in the creation of electrons of nearly 0 eV in these compounds. According to Zagrubskii and Vilesov,[8] the vibrational excitation, ΔE_j, of the auto-ionizing state, M_j^*, has a dominant role in making the stationary peaks in the low-kinetic-energy region. The probability of auto-ionizing processes becomes more significant and the EDCs become structureless when ΔE_j is large. Moreover, ΔE_j is considerable in large molecules. It is, however, doubtful whether the ΔE_j of these compounds are the same. Moreover, the resemblance between the obtained results of anthracene and 9,9′-bianthryl (twice as large as anthracene) raises a question about their explanation.

The second explanation is more reasonable. In the solid state, there are various scattering processes, and such processes cause a decrease in the kinetic energy of the photoelectrons over a considerably wide energy range. Moreover, the peak ratio of this dominant peak depends strongly on the photon energy. These facts suggest that the scattering mechanism is the origin of the dominant peak.[17]

The result for 9MeA, which did not show any abrupt large peaks except for the dominant peak, can be understood in terms of the contamination of the solid surface especially with water. The effect of the contamination was checked by the use of DClA evaporated films. The film evaporated at room temperature showed several structures, as is shown in Fig. 4. The films prepared at about −30 °C, however, showed dull shapes, and their EDCs changed with the evacuating time; the structure became sharper. Moreover, the total photoelectric current increased. These facts suggest that the contamination mainly caused by the adsorption of water affects the measurements of the photoemission and that continuous evacuation reduces the contamination of the sample surface. Therefore, if we seek to account for the experimental conditions of 9MeA, low vacuum and a thin sample film which were inadequate to evaporate the contaminated layer of the film, it is probable that the intrinsic EDCs of 9MeA are not just like those of Fig. 2: This figure may be somewhat too vague.

When we consider the exceptional situations in the case of 9MeA, anthracene and its derivatives may be said to show the same EDCs, as may easily be seen in the figures. This finding indicates that the photoelectron energetic responses of these compounds are nearly the same. This fact is useful in considering the mechanism of photoemission from organic crystals. As is well known, photoemission is constituted of three steps: photoelectron generation, electron-transport, and escape from the surface. When electron-transport process is the dominant process in photoemission, the EDCs obtained must be different, unrelated to the photoelectron generation, since the field with which an excited electron is affected differs with the compound. For example, though DClA has a large polarizability and chlorine atoms which have a large electronegativity so as to easily catch the electrons, the EDC patterns of DClA are analogous to those of anthracene. As for the escape process, the resemblance of the EDCs in spite of various experimental conditions may indicate that the electron escape probabilities of these compounds are the same. Therefore, the photoelectron generation process, which is considered to be the same as in the case of gas-phase photoexcitation, plays the dominant role in the photoemission of organic crystals. Electron transport does not affect the shape of the EDCs so much. They are slightly affected by the electron-escape process, mainly by the contamination of the surface, as is 9MeA.

As is shown by the broken lines in Figs. 6 and 8, though the ionization potentials of 9,9′-bianthryl were much more complicated than those of anthracene, the EDCs obtained were almost the same, within the limits of resolution of the analyzer. This result implies an analogy in the electronic states of the two compounds in the solid state. In the gas phase at high temperatures, two anthryl groups may rotate along the C–C axis and may perturb the molecular orbitals of each other. On the other hand, in the solid state the two anthryl groups, mainly π-electron systems, are independent of each other. This phenomenon was also observed in biphenyl derivatives[18] and *p*-terphenyl.[19]

Quantum Yield. The steep rise in SDQYs at about 6 eV is due to the effect of the escape function, which rules the electron transport from the surface into the vacuum. To this region we can apply the following relation in order to obtain the threshold energy;[5]

$$Y \propto (h\nu - E_{\text{th}})^3$$

The cube-root plot of these compounds shows linear relation between the photon energy and the cube root of the quantum yield. The threshold energies of the compounds obtained by this method are collected in Table 1; the threshold energies obtained from the EDCs are also listed in that table.

The values obtained from the cube root plot and from the EDCs show a good accordance. As to the comparison with other works, the threshold energy obtained by Lyons and Morris[3] shows a good agreement with our present results. That of 9MeA reported by Vilesov and Sukhov[9] seems somewhat small, though the method of obtaining the threshold energy reported by Marchetti and Kearns[6] gives a slightly large value because it considers the thermal excitation. Therefore, their values, which were larger than our present results by about 0.2 eV, nevertheless show a good agreement with ours in the trend among these compounds.

In the energy region higher than 7.5 eV, the quantum yield increased in accordance with increase in the photon energy. This is probably due to the photoelectrons from deeper levels. There are some dips in the SDQYs. Seki and his co-workers[17] suggested that these dips might be due to the change in the absorption coefficient. The basis of their conclusion was that the electron-attenuation length, L, is much shorter than the reciprocal of the absorption coefficient α, *i.e.*, $\alpha L \ll 1$; the photoelectrons observed might be produced mainly near the surface. Consequently, the SDQYs of this region depend on the spectral response of the absorption coefficient. However, our recent experiment on electron-attenuation length measurement has shown that the $\alpha L \ll 1$ relation does not always hold good. In some cases αL is nearly equal to unity or slightly larger than unity.[20,21] This fact is not always inconsistent with their postulate that the dips are due to the change in the absorption coefficient. However, particularly when αL is larger than unity, all the photoelectrons excited have a high probability of escaping into the vacuum. Therefore, we should conclude that the dips in the SDQYs are due not only to the spectral response of the absorption coefficient, but also to the beginning of the ionization of deeper levels.

The SDQYs of anthracene and 9,9′-bianthryl resembled each other and showed a larger photoelectron efficiency than that of DClA. The resemblance between them is considered in terms of electronic structures, as has previously been discussed. Though the SDQYs of DClA was about half that of anthracene, their inclination was analogous to that of anthracene. This analogy indicates that the skeletal structure of the molecules (the anthracene ring system) influences the SDQYs as in the EDCs. Moreover, the small quantum yield of DClA is probably due to the effect of the chlorine atom.[22]

The SDQY of 9MeA was not parallel with that of anthracene. The ratio of both SDQYs, 9MeA and anthracene, changed from 0.6 ($h\nu \simeq 10$ eV) to 0.1 ($h\nu \simeq 7$ eV). This fact seems inconsistent with previous discussion. However, the experimental conditions for measuring 9MeA were not good. In this case, as the contamination of the surface reduced the photoelectron-escape probability, we could not obtain the same SDQY. Moreover, the quantum yield of 9MeA changed with the evacuation time and with the conditions at sample preparation. Though we chose the largest photocurrent as the true photoelectron efficiency, there was still some probability of contamination due to the adsorption of water or oxygen.

Therefore, in view of the effect described above, all four SDQYs of anthracene and its derivatives show analogous structures. This fact also indicates that the electronic structures and photoelectric responses of these compounds are almost the same.

Conclusion

The external photoelectric responses of anthracene and its derivatives show the same behavior, and their EDCs correspond with the molecular photoelectron spectra. The coincidence among the EDC of the same skeletal structure (anthracene ring system) implies that the original π-electronic state is the dominant factor in the energy distribution of photoemitted electrons. The resemblance of their SDQYs supports the above conclusion.

The authors wish to thank Professor Werner Schmidt, Institut für Organische Chemie, Universität München, for sending them the photoelectron spectrum of 9,9′-bianthryl.

References

1) F. Gutmann and L. E. Lyons. "Organic Semiconductors," John Wiley and Sons, New York (1967).

2) H. Meier, "Organic Semiconductors," Verlag Chemie, Weinheim (1974).

3) L. E. Lyons and G. C. Morris, *J. Chem. Soc.*, **1960**, 5192.

4) F. I. Vilesov, A. A. Zagrubskii, and D. Z. Garbuzov, *Fiz. Tverd. Tela (Leningrad)*, **5**, 2000, (1963) [*Soviet Physics-Solid State*, **5**, 1460 (1964)].

5) M. Kochi, Y. Harada, T. Hirooka, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **43**, 2690 (1970).

6) A. P. Marchetti and D. R. Kearns, *Mol. Cryst. Liq. Cryst.*, **6**, 299 (1970).

7) T. Hirooka, K. Tanaka, M. Fujihira, H. Inokuchi, Y. Harada, and K. Kuchitsu, *Chem. Phys. Lett.*, **18**, 930 (1973).

8) A. A. Zagrubskii and F. I. Vilesov, *Fiz. Tverd. Tela (Leningrad)*, **13**, 2300 (1971) [*Soviet Physics-Solid State*, **13**, 1927 (1972)].

9) F. I. Vilesov and D. A. Sukhov, *Fiz. Tverd. Tela (Leningrad)*, **14**, 2393 (1972) [*Soviet Physics-Solid State*, **14**, 2069 (1973)].

10) B. H. Schechtman, Ph. D. Thesis, Stanford University, 1968.

11) K. A. Kress and G. L. Lapeyre, *Rev. Sci. Instrum.*, **40**, 74 (1969).

12) Y. Harada and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **39**, 1443 (1960).

13) R. Boschi, J. N. Murrel and W. Schmidt, *Discuss. Faraday Soc.*, **54**, 116 (1972).

14) S. Hino and H. Inokuchi, *Chem. Lett.*, **1974**, 363.

15) D. G. Streets and T. A. Williams, *J. Electron Spectrosc.*, **3**, 71 (1974).

16) W. Schmidt, private communication.

17) K. Seki, T. Hirooka, Y. Kamura, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **49**, 904 (1976).

18) J. Daintith, J. P. Maier, D. A. Sweigart, and D. W. Turner, in "Electron Spectroscopy," ed by D. A. Shirley, North-Holland, Amsterdam (1972), p. 289.

19) S. Hino, K. Seki, and H. Inokuchi, *Chem. Phys. Lett.*, **36**, 335 (1975).

20) S. Hino, N. Sato, and H. Inokuchi, *Chem. Phys. Lett.*, **37**, 494 (1976).

21) S. Hino, to be published.

22) S. Hino, T. Hirooka, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **48**, 1133 (1975).