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Ultraviolet Photoelectron Spectra of α- and β-Polymorphs of Copper Phthalocyanine

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The ultraviolet photoelectron spectra have been measured for α- and β-forms of copper phthalocyanine at 183 °C, to investigate the correlation of photoemissive behavior with crystal structure. Their threshold ionization potentials were 4.8_8 and 4.6_2 eV,[**] with polarization energy of 1.2_7 and 1.5_3 eV, respectively. This difference could not be explained by calculation with point charge-point dipole approximation, but calculation with distributed charge on the cation and distributed induced dipoles on the nearest neighbor two molecules gave semi-quantitative agreement with the experimental findings.

The phthalocyanines are used as pigments or photoreceptors, and their structures are similar to those of porphyrins such as chlorophyll and hemoglobin; accordingly they have been extensively studied.[1–5] Copper phthalocyanine (CuPc) is representative. In 1963, Vilesov *et al.*[6] measured its photoelectron spectrum. In 1968, Schechtman and Spicer[7] reexamined this and compared the density of the occupied states of CuPc from experimental results with that derived from theoretical calculations. This revealed a good agreement between them. In 1978, Berkowitz[8] measured the photoelectron spectra of various phthalocyanine compounds in the gas phase.

As is well known,[9–10] CuPc exists in different crystal structures as α-, β-, and x-forms. The β-form is the most stable and the others are metastable at room temperature. It is interesting to study the dependence of photoemissive behaviors on their polymorphism. From these measurements we could establish a correlation between the molecular packing and the electronic structure.

In this paper, we report the threshold ionization potential of α- and β-CuPc by means of ultraviolet photoelectron spectroscopy (UPS). There is 0.2_6 eV difference in the threshold ionization potentials between them. We believe this to be the first UPS study of polymorphs of organic crystal with known structures, which permit a detailed analysis of the origin of the difference between the two forms.

Experimental

Two samples of CuPc were used and gave the same results. One of them was prepared and purified as described previously.[11] The other was supplied by Dainihon Ink Co. Ltd., and was used without further purification. The sample film was prepared on a Cu-substrate by evaporation and measured *in situ* in vacuum of 10^{-5} to 10^{-6} Pa; the film thickness was controlled around 50 nm and measured with a quartz thickness monitor. The α- and β-polymorphs were prepared by evaporation on the substrate at room temperature and 250 °C, respectively. The resultant structures were examined by X-ray diffraction, and the data agreed with those in the literature.[9,10]

The light source of the photoemission machine was a Hinteregger-type hydrogen-discharge lamp used in conjunction with a 0.5 m Seya-Namioka-type monochromator. The energy of the photoelectron was analyzed with a retarding-potential-type energy analyzer as reported previously.[12] The energy resolution was about 0.2 eV. All the observed values were reproducible within ±0.05 eV.

Results and Discussion

Initially, we tried to measure the photoelectron spectra of α- and β-CuPc at room temperature. The measurement of the α-form was not difficult, but for the β-form there was a severe charging of the sample. This is probably due to the low conductivity of the β-form at room temperature. As reported by Wihksne, dark conductivity of β-metal free phthalocyanine is 10^5 times lower than that of α-form at 180 °C, and further, this difference is expected to increase at room temperature.[11] It is reasonable to assume similar relations for the α- and β-CuPc. This experimental difficulty was revolved by elevating the temperature to increase the conductivity of the β-form. We found that the α-form does not change to β-form below 200 °C, then both forms could be measured at the same temperature (183±2 °C).

The photoeletron spectra of the β- and α-forms at this temperature, 183±2 °C, and that of α-form at room temperature using a photon energy of 7.8 eV are shown in Fig. 1 as curve a, b, and c, respectively. Table 1 lists the photoemission threshold values I_s^{th} obtained from these curves using the Einstein relation $I_s^{th}=h\nu-E_k^{max}$, where E_k^{max} is the maximum kinetic energy of the photoeletrons.

From Table 1, we see that I_s^{th} of the α-form at 183 °C is a little lower than that at room temperature. Most of this we can ascribe to the coupling of ionizing electronic excitation with low-energy modes of lattice phonon which satisfy $\hbar\omega \ll kT$, where $\hbar\omega$ is the phonon energy quantum, k the Boltzmann factor, and T the temperature. Using the theory of Duke,[13] a lowering of I_s^{th} proportional to $T^{1/2}$ is expected. With a theoretical value of proportional constant for benzene with all lattice phonon modes taken into account,[13] we can estimate a lowering of ≈0.18 eV, which is comparable with the observed value for α-CuPc. Since all the lattice phonon modes of phthalocyanines

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[**] 1 eV≅0.1602 aJ.

TABLE 1. THE THRESHOLD IONIZATION POTENTIALS AND POLARIZATION ENERGIES OF α- AND β-COPPER PHTHALOCYANINE

Crystal form	Threshold ionization potential eV			Polarization energy eV	
	Crystal at RT	Crystal at 183 °C	Gas	Crystal at RT	Crystal at 183 °C
α	$5.0_9 \pm 0.05$	$4.8_8 \pm 0.05$	6.15[a)]	1.0_6	1.2_7
β	—	$4.6_2 \pm 0.05$	6.15[a)]	—	1.5_3

a) Estimated from Berkowitz's data (Ref. 8).

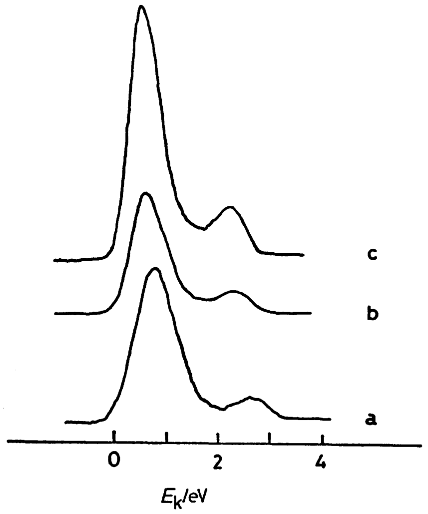

Fig. 1. Photoelectron spectra of copper phthalocyanine at $h\nu = 7.8$ eV in kinetic energy (E_K) scale. a: β-form at 183 °C, b: α-form at 183 °C, and c: α-form at room temperature.

will appear in the region $\hbar\omega \ll 100\ \mathrm{cm}^{-1}$,[14)] all modes will contribute to the temperature dependence in both the α- and β-forms. Therefore we can expect that the temperature dependence of I_s^{th} is almost common in the two phases, and its difference will not play an important role in discussing the I_s^{th} difference of α- and β-forms at the same temperature.

From Table 1, it can be seen that there is a small but distinct difference 0.2_6 eV in threshold ionization potentials between the two crystal forms. According to Lyons,[15)] the ionization potential of solid is determined by gas phase ionization potential and its lowering due to the electric polarization of the molecules surrounding the cation, which is called polarization energy. In Table 1, the polarization energies obtained by using gas phase threshold ionization potential of 6.15 eV[8)] are also listed.

The present results indicate that the polarization energies of the two crystalline forms are different. Our work offers the first experimental evidence for the dependence of photoelectron spectra on polymorphs of known strucure. In 1978, Nielsen[16)] reported the substrate dependent ionization and polarization energies of dibenzotetrathiafulvalene and explained the experimental results as due to the formation of different structure or orientations. However, he did not show the direct evidence to demonstrate the existence of different crystalline forms.[17)]

The polarization energy of molecular solid constructed with nonpolar molecules can be considered as the interaction energy of the charge of the cation and electric multipoles induced on surrounding molecules.[15)] For simplicty, we will neglect multipoles higher than dipole and the interaction among dipoles.

In general, the charge on the cation and the dipole for the neutral molecules are distributed over each molecule. If we represent them by a point charge and a point dipole at the center of the molecule, the polarization energy can be expressed as[15)]

$$P_s = \sum_i \frac{e^2}{2r_i^6} \boldsymbol{r}_i \alpha \boldsymbol{r}_i, \tag{1}$$

where $\boldsymbol{r}_i$ is the distance vector of i-th molecule from the cation, r_i, its absolute value, e, electronic charge, α, the molecular polarizability tensor, and summation is taken over all the molecules in the crystal except the ionized molecule.

To obtain a roughly correct order of P_s, calculations with more simplified forms[18,19)]

$$P_s = ke^2\bar{\alpha}d^{-4/3}, \tag{2a}$$

or

$$P_s = (e^2/2\rho)(1-1/\varepsilon), \tag{2b}$$

are known to be useful, where k is a constant, $\bar{\alpha}$, the averaged molecular polarizability, d, the density, ρ, half of r_i of the nearest neighbor molecule, ε, the optical permissivity which can be estimated from $\bar{\alpha}$ and k. In the present case of CuPc, $\bar{\alpha}$ is common to the α- and β-forms, and d is also almost the same (1.62 and 1.61) for α- and β-forms, respectively.[20–22)] Therefore, such simple formulae cannot be used to explain the difference in P_s in these forms.

We calculated P_s of both forms using Eq. 1. Since there seems to be no experimental data of α, we expressed the polarizability perpendicular and parallel to the molecular plane as α_0 and $b\alpha_0$, respectively. The data for other molecules suggest that $\alpha_0 \approx 30 \times 10^{-27}\ \mathrm{m}^3$ [23)] and b is between 2 and 3.[23,24)] The crystal structures of α- and β-forms[4)] are shown in Fig. 2. The summation in Eq. 1 was taken for molecules within cubes of edge length of l=60, 80, 120, and 200 Å. They showed good linear relationships with $1/l$, and the extrapolation to $l=\infty$ gave the values P_1 in Table 2. The values for the α-form are larger than those of the β-form, which does not agree with the observed results. Further, the calculated values are too large.

In order to improve this situation, we took account of the distribution of charges and dipoles on the cation

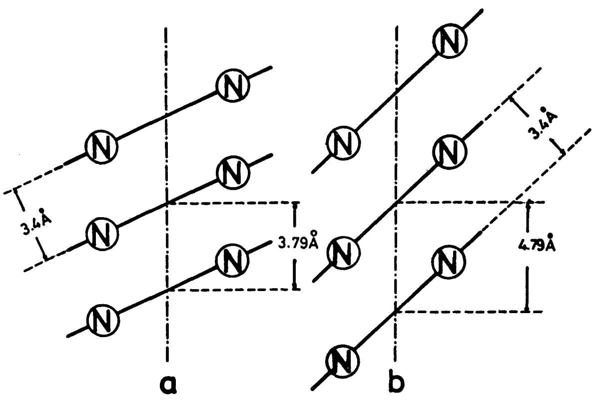

Fig. 2. Molecular arrangements in copper phthalocyanine crystals of (a) α- and (b) β-forms.[18) —·—·—· : b-Axis, N-N: Molecular plan. The angle between the b-axis and the molecular plane for the α- and β-forms are 65.2° and 45.7°, respectively.

Table 2. Calculated polariztion energies

Anisotropy parameter b	Form	P_1/eV	B/eV	P_2/eV
2	α	3.35	0.85	1.45
	β	2.24	1.01	1.53
3	α	4.06	1.15	1.86
	β	3.05	1.41	2.05

and the nearest neighboring two molecules. As seen in Fig. 2, the overlap of the cation and nearest neighbors is large in both forms of CuPc, and the validity of the point-charge and point-dipole is dubious for the interaction among these molecules. When we divide P_1 into the contribution from the nearest neighbors A_1 and that from the other molecules B ($P_1=A_1+B$), A_1 is overwhelmingly large as shown in Table 3. Thus the examination of A_1 is important.

The highest occupied orbital of CuPc is known to be the π-orbital shown by the bold line in Fig. 3.[7,8,25) We approximated this with a dotted square in Fig.3, and assumed a uniform charge distribution of total amount of e. As for the dipole distribution, we adopted the "submolecular concept," [26,27) where we regard a large aromatic molecule as an aggregate of independently polarizable aromatic rings. This treatment is known to give reasonable dielectric properties for large molecules.[26,27) We treated CuPc as 12 aggregated rings in Fig. 3, with each ring represented by a dipole at its center. The polarizability of each ring was assumed to be 1/12 of α_0 and $b\alpha_0$.

Initially, we calculated the electric field at the center of each ring by the distribution charge on the cation, and calculated the induced dipole and the dipole-electric field interaction energy. These were summed for the twelve rings to give the total contribution A_4 from the nearest neighboring two molecules. For comparison, we also calculated the values for point charge-distributed dipole(A_2) and distributed charge-point dipole (A_3) approximations. Table 3 lists these values. We see that the values of both forms decrease by the consideration of distributions, but the change of α-form is much more than that of β-form. As a result, the difference between the two forms becomes very small, in particular for the distribution of the positive charge in the cation.

Table 3. Contributions of Nearest neighbor two molecules to polarization energy calculated with various approximation for $b=2$.

Form	A_1/eV[a)	A_2/eV[b)	A_3/eV[c)	A_4/eV[d)
α	2.50	1.28	0.75	0.60
β	1.23	0.96	0.72	0.52

a) Point charge-point dipole, b) Point charge-distributed dipole, c) Distributed charge-point dipole, d) Distributed charge-distributed dipole.

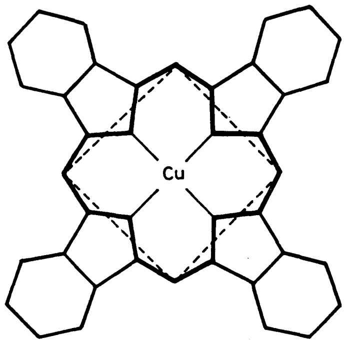

Fig. 3. Molecular structure and the highest occupied π-orbital (bold line) of copper phthalocyanine. The dotted line indicates the approximated charge arrangement.

The values of P_s reevaluated as $P_2=A_4+B$ is shown in Table 2. The values of α-form become larger than those of β-form, in agreement with the experimental findings. Further, the absolute magnitude of P_2 is comparable with the observed values, although the estimation of α_0 may include considerable error. We should note that the ratio of P_2 values of α- and β-forms does not depend on α_0 but only on b.

Although the above estimation of P_s is very approximate, we may safely say that the extended distrubution of charges on the cation(and maybe the distribution of dipoles on neutral molecules and the anisotropy of polarizability) results in a very small difference for the contribution of the nearest neighbor. This made the total P_s difference to be determined by a larger difference of B. This is instructive about the role of the charge distribution, since at first glance of Fig. 2 we may expect a larger P_s of α-form because of the smaller center-to-center distance and a larger overlap of molecules than in the β-form. Studies of the P_s of aromatic hydrocarbon crystals using a similar formulation will be interesting, since those molecules are not stacked as in CuPc, and the effect of charge distribution may be not so important as in the present case. The validity of simplified formulae Eq. 2a and 2b can be also examined.

Finally we wish to stress the usefulness of studying polymorphs for a detailed examination of the theory of polarization energy. If the theory is satisfactory, it should explain the data of two or more polymorphs using the same molecular parameter α, and this will restrict the degree of freedom in adjusting the theoretical parameters much more than in studying different compounds. Further future studies of various polymorphs with known structures are therefore desired.

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References

1) K. Wihksne and A. E. Newkirk, *J. Chem. Phys.*, **34,** 2184 (1961).

2) C. Y. Liang and E. G. Scalco, *J. Electrochem. Soc.*, **110**, 779 (1963).

3) F. W. Karasek and J. C. Decius, *J. Am. Chem. Soc.*, **74**, 4716 (1952).

4) M. Ashida, N. Uyeda, and E. Suito, *J. Cryst. Growth*, **8**, 45 (1971).

5) J. H. Sharp and R. L. Miller, *J. Phys. Chem.*, **72**, 3335 (1968).

6) F. I. Vilesov, A. A. Zagrubskii, and D. Garbuzov, *Sov. Phys.-Solid State*, **5**, 1460 (1964).

7) B. H. Schechtman and W. E. Spicer, *Chem. Phys. Lett.*, **2**, 207 (1968).

8) J. Berkowitz, *J. Chem. Phys.*, **70**, 2819 (1979).

9) J. H. Sharp and M. Abkowitz, *J. Phys. Chem.*, **77**, 477 (1973).

10) F. A. Hamm and E. Van Norman, *J. Appl. Phys.*, **19**, 1097 (1948).

11) 1st group, 4th Lab., Inst. Chem., Acad. Sinica, *Huaxue Xuebao*, **34**, 262 (1976).

12) T. Hirooka, K. Tanaka, K. Kuchitsu, M. Fujihira, H. Inokuchi, and Y. Harada, *Chem. Phys. Lett.*, **18**, 390 (1973).

13) C. B. Duke, J. S. Miller, "Extended Linear Chain Compounds," Plenum, New York (1982), Chap. 2.

14) T. Kobayashi, *Spectrochim. Acta, Part A*, **26**, 1313 (1970).

15) F. Gutmann and L. E. Lyons, "Organic Semiconductors," John Wiley and Sons, New York (1967); M. Batley, L. J. Johnstone, and L. E. Lyons, *Aust. J. Chem.*, **23**, 2397 (1970).

16) P. Nielsen, *Solid Siate Commun.*, **26**, 835 (1978).

17) Recently Sato found that the UPS and also the X-ray diffraction patterns of this compound evaporated on Cu and In substrates are different (N. Sato, private communication).

18) N. Sato, K. Seki, and H. Inokuchi, *J. Chem. Soc., Faraday, Trans. 2*, **77**, 1621 (1981).

19) M. Born, *Z. Phys.*, **1**, 45 (1920).

20) M. Ashida, N. Uyeda, and E. Suito, *Bull. Chem. Soc. Jpn.*, **39**, 2616 (1966).

21) C. Hamann, *Phys. Status Solidi*, **20**, 481 (1967).

22) C. J. Brown, *J. Chem. Soc., A*, **1968**, 2488.

23) R. J. W. Le Fevre and K. M. S. Sundaram, *J. Chem. Soc.*, **1963**, 4442.

24) W. Liptay and H.-J. Schlosser, *Z. Naturforsch., A*, **27**, 1336 (1972).

25) M. Iwan, E. E. Koch, T, C. Chiang, D. E. Eastman, and F.-J. Himpsel, *Solid State Commun.*, **34**, 57 (1980).

26) T. Lüty, *Chem. Phys. Lett.*, **44**, 335 (1976).

27) P. J. Bounds and R. W. Munn, *Chem. Phys.*, **24**, 343 (1977).