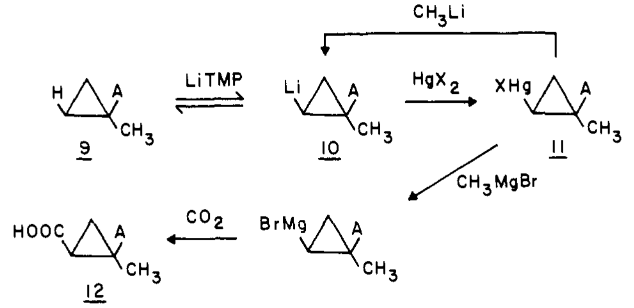
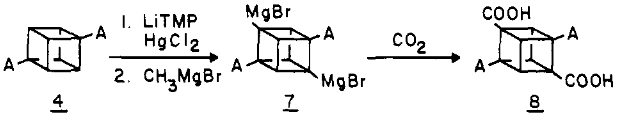
J. Am. Chem. Soc. 1987, 109, 949-950

Scheme II



of **5** with CH_3Li in THF at -78 °C gives **6** cleanly, as demonstrated by high-yield formation of dideuteriated **4** on quenching the reaction mixture with CH_3OD. Following a similar path (eq 4), and particularly usefully, conversion of **4** to **5** (not isolated),



(4)

its reaction with CH_3MgBr in THF at -20 °C to form the di-Grignard **7**, and subsequent carboxylation gives the cubane tetraacid derivative **8** in 60% yield *overall*.

Use of the reverse-transmetalation procedure is not limited to the cubane system. It should in principle pertain to other systems of relatively high C–H acidity. We have not yet pursued this extensively, but we can give two examples now, one using cyclopropane C–H and the other, aromatic C–H. On treatment with LiTMP/$HgCl_2$ the cyclopropyl amide **9** is converted, by way of ortho-lithiated amide **10**, to the ortho-mercuriated derivative **11**,[8] isolable pure as its chloride in 85% yield (Scheme II). Upon reverse transmetalation with a stoichiometric amount (2 equiv) of CH_3Li, conversion to **10** is essentially quantitative, as shown by high-yield formation of monodeuteriated **9** on quenching with CH_3OD. In this particular case, the amide group is susceptible to attack by excess CH_3Li, and it is better to use CH_3MgBr instead. This modification of reverse-transmetalation methodology gives the corresponding cyclopropyl Grignard, which upon carboxylation yields the *cis*-1,2-dicarboxycyclopropane **12** in 90% isolated yield from **11**.

2,6-Dilithio-*N*,*N*-diethylbenzamide is also readily available by the double transmetalation approach.[9] Treatment of *N*,*N*-diethylbenzamide with LiTMP/$HgCl_2$ gives in 60% isolated yield the *o*,*o*′-dimercuriated compound by iterative lithiation/mercuriation. Reverse transmetalation with *n*-BuLi followed by addition of CH_3OD produces the *o*,*o*′-dideuteriated benzamide. If CH_3I is added, 2,6-dimethyl-*N*,*N*-diethylbenzamide is formed in good yield.

We are extending this work to include the preparation of yet more highly metalated cubanes, to the use of these compounds in synthesis, and to application of these techniques to other saturated, strained systems.

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Supplementary Material Available: Experimental details for dimercuriation and dicarboxylation of cubane diamide and the associated characterizations (2 pages). Ordering information is given on any current masthead page.

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Local Electron Distribution of Individual Molecular Orbitals Studied by Penning Ionization Electron Spectroscopy: Iron Phthalocyanine

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Recently we have shown that Penning ionization electron spectroscopy, which utilizes metastable rare gas atoms as the excitation source, is a unique technique to provide direct information on the outer spatial electron distribution of individual molecular orbitals.[1] In this paper, we demonstrate that the local distribution of π, σ, and $3d_\perp$-like MO's of iron phthalocyanine (FePc) at different parts of the molecule can be probed by applying this technique to a monolayer film and a crystalline one.

When Penning spectroscopy is applied to a gas-phase sample, in which molecules are randomly oriented, it is its "averaged" orbital distribution that is reflected in the Penning ionization electron spectrum (PIES). If we wish to probe the "local" distribution of an MO at a definite part of a molecule, we should control the orientation of target molecules with respect to the metastable beam. Experimentally, this can be effectuated by introducing the beam onto ordered molecules in solid phase. Unlike photons or electrons used for photoelectron, Auger electron, or electron impact spectroscopy, metastables do not penetrate into the solid and hence interact with the outermost surface layer selectively.[2,3] If we expose various parts of molecules to metastables, controlling their arrangement on a substrate, we can probe the distribution of MO's from various directions. Thus, the whole picture or the "shape" of each MO can be obtained. As the first approach from this standpoint, the local distribution of MO's of FePc is investigated here by PIES.

We prepared two kinds of vapor-deposited FePc films. Film I was prepared on a graphite substrate (cleavage plane) held at 213 K and was a monolayer, in which molecules lie flat on the substrate.[3] Film II was formed on a stainless steel substrate at room temperature and was crystalline with tilted molecular orientation.[4] Since FePc molecules are held together by weak van der Waals forces, the electronic structure of molecules in each film is essentially unchanged from that in gas phase. When surface molecules lie flat on the substrate (see the bottom of Figure 1a), π-type MO's spreading normal to the molecular plane (xy plane) exclusively interact with metastables, whereas σ MO's distributed within the plane and shielded by π-type MO's are hardly attacked by metastables. Among π-type MO's, those mainly originated from the iron $3d_{xz}$, $3d_{yz}$, or $3d_{z^2}$ AO (the $3d_\perp$-like MO) should interact with metastables more effectively than those derived from the carbon and nitrogen $2p_z$ AO's because the former orbitals protrude outside the molecular (van der Waals) surface more prominently than the latter ones. On the other hand, in the tilted molecular orientation (see the top of Figure 1a), the σ MO's as well as the π are effectively attacked by metastables, but the $3d_\perp$-like MO's with little distribution outside the film surface can be scarcely attacked.

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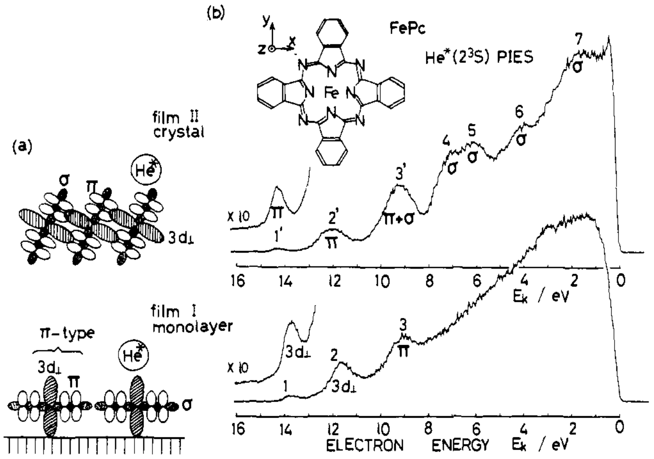

Figure 1. (a) Orientations of surface molecules in monolayer film I and crystalline film II interacting with metastables. (b) He* ($2\,^3S$, 19.82 eV) Penning ionization electron spectra of films I and II. Each band is labeled with the character of MO's mainly responsible for it.

The PIES of the FePc films are shown in Figure 1b. He* ($2\,^3S$, 19.82 eV) metastable beams were used to obtain the spectra. Bands 4–7, which are clearly observed in the tilted orientation (film II), are absent in the flat one (film I). Therefore, these bands are assigned to σ MO's. The π-type bands, which are selectively observed in the film I (bands 1–3), are also found in the film II (bands 1′–3′). However, the origins of these three bands in the both films are different. Bands 1′ and 2′ correspond to the first and second bands in the UPS of the both films.[5] In the UPS of FePc, the first band is due to π MO's distributed on the inner porphine-like ring,[6,7] and the second one is mainly ascribable to π MO's with a large contribution from the benzene ring.[6,8,9] Accordingly, π MO's are selectively probed to form bands 1′ and 2′ in film II. On the other hand, bands 1 and 2 correspond to the 3d-like bands observed in the XPS of an FePc film.[10] Hence, the $3d_\perp$-like MO's are predominantly detected to form these bands in film I. Thus it is confirmed experimentally that the $3d_\perp$-like MO's have a more diffuse distribution to the direction normal to the molecular plane than the π MO's. It is worthwhile to note that the $3d_\perp$-like MO's are detected only when metastables can approach the center of FePc molecules (compare the two orientations in Figure 1a), which is achieved by arranging molecules flat on the substrate. Though both bands 3 and 3′ correspond to the third band in the UPS,[5] which is related to the second UPS band (σ and π) of solid benzene,[8,11] band 3′ is more enhanced than band 3. In this case the π MO's are selectively probed in film I, but the σ MO's as well as the π are detected in film II.

In conclusion, the wave function tails of the $3d_\perp$-like, π, and σ MO's at two different parts of FePc molecules have been probed by PIES. In general, the selections among various substrates, film preparation methods (vacuum deposition, adsorption, Langmuir–Blodgett technique[12] etc.), deposition conditions (depending on the substrate temperature and deposition speed), and film treatments (e.g., annealing) enable us to obtain various films exposing different parts of molecules outside. Studying the PIES of such films, we can probe the local distributions of individual MO's in more detail and approach their whole picture.

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(11) For assignments of benzene, see: Jonsson, B. Ö.; Lindholm, E. *Ark. Fys.* **1969**, *39*, 65–76.

(12) See, for example: Gaines, G. L., Jr. *Insoluble Monolayers at Liquid–Gas Interfaces*; Wiley-Interscience: New York, 1966.

Selective Observation of Molecular Ends Exposed outside Langmuir–Blodgett Monolayer Films by Penning Ionization Electron Spectroscopy

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Langmuir–Blodgett (LB) films[1] have attracted recently particular interest as ultrathin films, because the thickness together with the ordered structure can be controlled at the molecular level and, therefore, unique functions are anticipated to be developed.[2] For such studies, it is of fundamental importance to elucidate the molecular arrangement in the films. However, we have no means for obtaining direct evidence as to which end of the molecule (either head or tail) is exposed to the film surface; it has only been presumed by such an indirect method as contact angle observation.[3] The knowledge of the molecular end exposed outside is not only useful to determine the types (X, Y, or Z) of LB film[4] but is also indispensable in designing LB films containing functional parts at the film surface. We demonstrate here that the molecular end exposed to the outside of an LB film can be selectively probed by Penning ionization electron spectroscopy.

In Penning ionization electron spectroscopy, the kinetic energy of electrons ejected by collisions between targets T and metastable atoms A* is analyzed:[5]

$$T + A^* \rightarrow T^+ + A + e^-, \quad e^- \text{ for energy analysis}$$

Since metastables do not penetrate into the solid, this technique provides information on the outermost surface layer selectively.[6–11] Furthermore, an orbital of T spreading outside the surface interacts with a metastable atom more effectively than an inner orbital and hence gives a stronger band in the Penning ionization electron spectrum (PIES).[7,9–11] These characteristics of PIES enable us

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