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$\pi-\pi$ Interactions of Magnesium Phthalocyanine as Evaluated by Energy Partition Analysis

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Magnesium phthalocyanine (MgPc) is a near-IR-active photoconductor used for laser printers. Our recent structure analysis revealed that the MgPc molecule is not flat in the solid state, but the central Mg atom is projected upward, forming a pyramidal structure. On top of the Mg atom along the stacking axis, the aza-methine nitrogen atom is located with a distance of only 2.70 Å. The present arrangement is quite indicative of an appreciable interaction along the stacking axis through the formation of a five-coordinate Mg complex. Therefore, the Mg−N interaction along the molecular stack has been investigated by energy partition analysis based on semiempirical molecular orbital calculations. The Mg−N bond energy along the molecular stack is found to be roughly one-third that of the Mg−N bond in the molecular plane and approximately one-half that of the Mg−O bond of the six-coordinate MgPc complexes, MgPc/$(H_2O)_2(NMP)_2$ and MgPc/(2-methoxyethanol)$_2$. These results indicate the formation of five-coordinate MgPc complexes along the stacking axis, showing considerable $\pi-\pi$ interactions through the central Mg atom.

1. Introduction

Metal phthalocyanines are generally known as very stable organic pigments because of very strong intermolecular interactions.[1] Among these, copper phthalocyanine (CuPc) is the most stable and is widely used as a blue pigment. However, the central metal is not directly involved in the chromophore composed of the conjugated C−N and C═N macrocycle around the central metal.[1] Metal-free phthalocyanine (H_2Pc) is also a commercial product, but its stability is not as high as that of CuPc. The role of the central metal for the stability is one of the long-standing problems in phthalocyanine chemistry. As early as 1968, Brown made a stimulating and suggestive comment on the polymorph of CuPc.[2] He proposed that the essential difference between α and β forms is that the copper coordinates to different nitrogen atoms located in the upper and lower layers along the stacking axis (Figure 1). If these Cu−N contacts are regarded as genuine interactions, then the copper coordination to nitrogen is distorted octahedral. Copper generally coordinates with four atoms in a square-planar system, with two other atoms at right angles to the plane at a greater distance, thus forming a distorted octahedron.[3,4] In other words, the central metal bridges the upper and lower layers to enhance the $\pi-\pi$ interactions. To date, however, no direct experimental evidence has been presented to support the formation of the intermolecular Cu−N bond along the stacking axis.

Quite recently, we have encountered a novel crystal structure of magnesium phthalocyanine (MgPc) as shown in Figure 2 (crystal I).[5,6] The MgPc molecule is not flat, but the central Mg atom is projected upward, forming a pyramidal structure. On top of the Mg atom along the molecular stack, the aza-methine nitrogen atom is located with a distance of only 2.70 Å. The present atomic arrangement is, at first sight, quite indicative of an appreciable interaction along the stacking axis through formation of a five-coordinate Mg complex (sp^3d hybrid structure). The purpose of the present investigation is to characterize the Mg−N bond by means of energy partition analysis[7−9] and to discuss the resulting $\pi-\pi$ interactions along the stacking axis. The Mg−N bond is evaluated in the present report using two kinds of six-coordinate MgPc complexes as the reference (Figure 3, sp^3d^2 hybrid structure), MgPc/$(H_2O)_2$-$(NMP)_2$ (crystal II) and MgPc/(2-methoxyethanol)$_2$ (crystal III).[10,11]

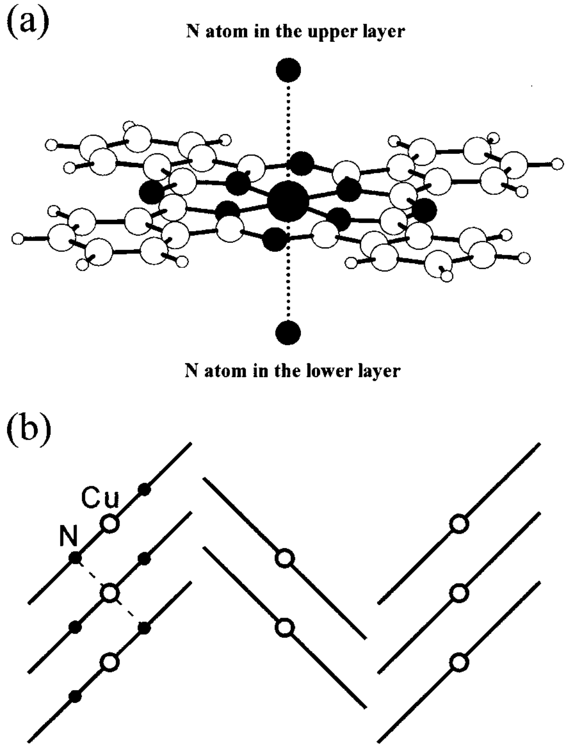

Figure 1. β-CuPc: (a) molecular conformation; (b) molecular stack.

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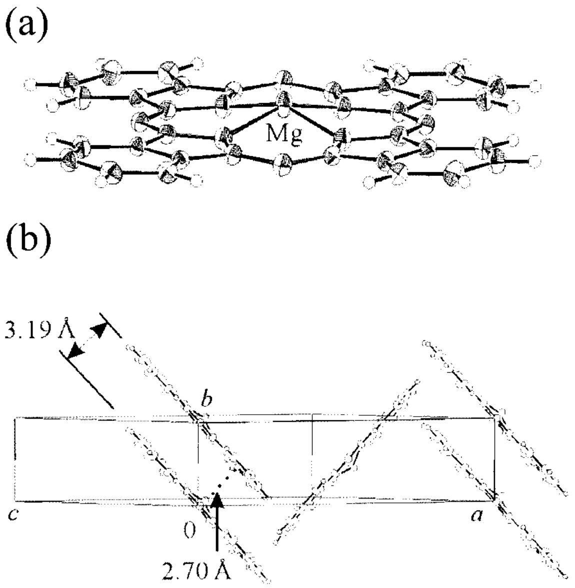

Figure 2. MgPc (crystal I): (a) molecular conformation; (b) molecular stack.

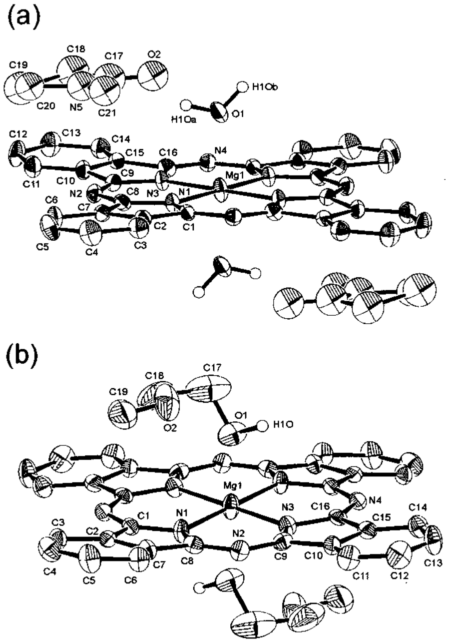

Figure 3. MgPc complexes: (a) MgPc/$(H_2O)_2$(NMP)$_2$ (crystal II); (b) MgPc/(2-methoxyethanol)$_2$ (crystal III). NMP stands for *N*-methyl-2-pyrrolidone.

2. Energy Partition Analysis for Intermolecular Interactions

The intermolecular interactions can macroscopically be characterized by sublimation or melting point, hardness of the material, and solubility in solvents. In our attempt to obtain microscopic information on the intermolecular interactions, we noticed that the two-center integral involved in semiempirical molecular orbital (MO) calculations could be a measure of intermolecular interactions if the crystal structure is known in advance. We have variously examined the validity of the present method for diketopyrrolopyrroles,[7] thioindigos,[8] and tetrathiobenzoquinones.[9]

In semiempirical MO calculations, the differential overlap is neglected, so the total energy of a molecule (E_{total}) can be partitioned into the one-center integral (E_i) of the *i*th atom and the two-center integral (E_{ij}) of the bonded *i*th and *j*th atoms as shown in eq 1.[12]

$$E_{\text{total}} = \sum_i E_i + \sum_{i<j} E_{ij} \tag{1}$$

where the two-center energy is further divided into the resonance energy (E_{res}), exchange energy (E_{exc}) and coulomb energy (E_{el}).

$$E_{ij} = E_{\text{res}} + E_{\text{exc}} + E_{\text{el}} \tag{2}$$

It was Hirano and Osawa[12,13] who proposed, for the first time, an application of the two-center energy for chemical-bonding problems. Because the two-center integral concerns the energy between bonded atom-pairs, it is directly correlated with the bond energy, although it is not exactly the same. This means that the energy term due to orbital overlap approximately corresponds to the covalent bond while the electrostatic term is related to the ionic bond.

On the basis of the pioneering work of Hirano and Osawa, we believed that the present two-center integral could also provide us with information on intermolecular interactions if we applied it for nonbonded atom pairs between molecules by regarding a pair of molecules as a supermolecule.[7] In the evaluation procedure, we specify a given molecule in the lattice and extract typical molecule pairs composed of the specified molecule and its nearest neighbor. For each pair, we carry out the energy partition analysis and then list up all atom pairs with significant interactions. In this way, we can characterize the intermolecular bonding state. However, it should be remembered that the present method is solely powerful for intermolecular bonds that are covalent or ionic in nature and is obviously powerless for “van der Waals” interactions due to instantaneous dipole moments in a statistical sense.

As for the reliability of the present method, we say that this method is as reliable as that of MO calculations for geometry optimization and spectroscopic calculations, because the energy partition is just the breakdown of the total electronic energy into one- and two-center components. In other words, if one finds the MO calculations meaningful for a given system, one must believe that the energy partition analysis also makes sense with no further assumption. It should additionally be noted that the present method is specific to semiempirical MO calculations and is intractable with ab initio calculations, because the total energy cannot be partitioned into one-center and two-center integrals in ab initio calculations (eq 1).

3. Programs and Calculation Procedure

WinMOPAC version 3[14] was used for energy partition analysis. The Hamiltonians, which include parameters for Mg, are PM3, MNDO/*d*[15] and AM1.[16] Among these, MNDO/*d* and AM1 were found to be appropriate for reasons described in section 4. For crystal I (Figure 2), two MgPc molecules along the molecular stack were taken out of the crystal lattice. The X-ray coordinates were used for non-H atoms, while geometry was optimized for the H atoms. The calculations were carried out for the molecule pair by specifying the keywords “1SCF” and “ENPART”. The same calculations were also made for two kinds of MgPc complexes (Figure 3), MgPc/$(H_2O)_2$(NMP)$_2$ (crystal II) and MgPc/(2-methoxyethanol)$_2$ (crystal III).[10,11]

The ab initio calculations for the atomic charges of Mg, N, and O in crystals I, II, and III were also made at Hartree−Fock level by means of natural population analysis (NPA)[17] using Gaussian 98[18] (basis function, 6-31-G(d,p)).

TABLE 1: Atomic Charges for Mg, N, and O Atoms Calculated by MNDO/*d*, AM1 and ab Initio/NPA[a]

crystal	atom	MNDO/*d*	AM1	ab initio/NPA
I	Mg	0.77	0.36	1.78
	N^b	−0.38	−0.18	−0.84
	N^c	−0.25	−0.13	−0.65
II	Mg	0.69	0.30	1.74
	N^b	−0.38	−0.17	−0.80
	O	−0.30	−0.35	−1.02
III	Mg	0.70	0.31	1.74
	N^b	−0.38	−0.17	−0.81
	O	−0.27	−0.26	−0.84

[a] The values are averaged. [b] N atoms which surround the Mg atom in the molecular plane. [c] Aza-methine N atom.

4. Results and Discussion

4.1. Hamiltonians. As a preliminary test of the Hamiltonians (PM3, MNDO/*d*, and AM1), we carried out geometry optimization of the MgPc molecule using the X-ray molecular structure as the initial model in an attempt to examine whether they give a correct geometry that is consistent with experiment. Among the three Hamiltonians, MNDO/*d*, and AM1 gave an entirely flat molecule (D_{4h} symmetry). Because of the D_{4h} symmetry, the excited state is doubly degenerate as characterized by E. In consequence, one single absorption band is expected to appear in solution on the basis of the $A_2 \rightarrow E$ transition.[10] This agrees with experiment.[5,10] In contrast, PM3 gave an optimized structure of C_1 symmetry. Because of the lowered symmetry, the degeneracy of the excited state is removed to give two absorption bands. This is not compatible with experiment. For this reason, PM3 was ruled out.

4.2. Atomic Charges for Mg, N, and O Atoms. The atomic charges in MgPc have been evaluated for Mg, N, and O atoms to examine the consistency between MNDO/*d*, AM1, and ab initio calculations. The results are shown in Table 1. One can see that the atomic charges calculated from MNDO/*d* are roughly one-half (or one-third in the case of oxygen) of those calculated by ab initio/NPA and that the atomic charges based on AM1 are approximately one-fifth (or one-third in the case of oxygen) of the ab initio values. Nevertheless, the tendency of the atomic charges accords in these calculations. Judging from the results for the present atomic charges together with geometry optimization, the energy partition analysis by means of MNDO/*d* and AM1 Hamiltonians appears reasonable for the present investigation.

4.3. Characterization of the Mg−N Bond along the Molecular Stack. Table 2 shows the results of the energy partition analysis for crystals I, II, and III on the basis of MNDO/*d* and AM1 Hamiltonians. Table 2 also includes the Mg−N distance along the molecular stack in crystal I (2.70 Å) together with that of the Mg−O bond in crystal II (2.17 Å) and crystal III (2.24 Å).

We look first at the result based on MNDO/*d*. As seen from the total energy (*EE*), the Mg−N bond energy along the molecular stack in crystal I is found to be roughly one-third that of the mean Mg−N bond in the molecular plane and approximately one-half that of the Mg−O bond in crystals II and III. The present Mg−N bond energy is significant and can be regarded as a genuine chemical bond. As evident from Table 2, most of the bond energy is due to resonance energy (*J*), indicating that the bonds are covalent in nature. This agrees with the consideration that the Mg atom coordinates to nitrogen or oxygen atoms to form five- or six-coordinate complexes. The exchange energies (*K*) are approximately $^1/_4$ to $^1/_6$ of the resonance energy in all crystals; whereas the contribution of the coulomb energy (*C*) is quite small. It is also to be noted that only the coulomb energy in Mg−N bond along the molecular stack in crystal I is attractive, while all the rest are repulsive.

TABLE 2: Energy Partition by Means of the MNDO/*d* and AM1 Hamiltonian (eV)[a]

crystal	Hamiltonian	atom pair	bond length (Å)	*J*	*K*	*C*	*EE*
I	MNDO/*d*	Mg−N^b	2.70	−1.87	−0.34	−0.42	−2.63
		Mg−N^c	2.03	−6.49	−1.66	0.08	−8.08
		C−N^d	1.38	−19.28	−6.87	7.25	−18.90
		C=N^d	1.33	−21.63	−7.80	8.79	−20.64
	AM1	Mg−N^a	2.70	−1.86	−0.42	−0.20	−2.08
		Mg−N^c	2.03	−6.79	−2.06	1.51	−7.34
		C−N^d	1.38	−18.69	−6.91	7.28	−18.33
		C=N^d	1.33	−20.85	−7.82	8.43	−20.25
II	MNDO/*d*	Mg−O	2.17	−5.35	−0.93	0.55	−5.73
		Mg−N^c	2.02	−6.32	−1.53	0.31	−7.54
		C−N^d	1.36	−19.76	−7.00	7.53	−19.23
		C=N^d	1.32	−21.79	−7.79	8.92	−20.66
	AM1	Mg−O	2.17	−4.44	−0.92	0.92	−4.43
		Mg−N^c	2.02	−6.62	−1.90	1.65	−6.87
		C−N^d	1.36	−19.14	−7.04	7.54	−18.64
		C=N^d	1.32	−20.98	−7.81	8.55	−20.24
III	MNDO/*d*	Mg−O	2.24	−4.67	−0.76	0.40	−5.03
		Mg−N^c	2.01	−6.44	−1.56	0.34	−7.66
		C−N^d	1.39	−18.91	−6.91	6.99	−18.72
		C=N^d	1.34	−21.34	−7.66	8.58	−20.42
	AM1	Mg−O	2.24	−3.81	−0.73	0.84	−3.70
		Mg−N^c	2.01	−6.59	−1.90	1.63	−6.85
		C−N^d	1.39	−18.34	−6.85	7.06	−18.12
		C=N^d	1.34	−20.57	−7.69	8.25	−20.00

[a] *J* = resonance energy; *K* = exchange energy; *C* = coulomb energy; *EE* = total energy. The minus or plus sign denotes the attractive or repulsive energy, respectively. The values for bond lengths and energies are averaged. [b] In molecular stack. [c] In molecular plane. [d] In macrocycle.

The results based on AM1 are quite similar to those based on MNDO/*d*. However, the energy values are estimated generally smaller than those of MNDO/*d* by about 0.4−0.7 eV. In particular, the Mg−O bond energy in crystals II and III is smaller in AM1 than in MNDO/*d* by 1.3 eV.

We have then roughly estimated the intermolecular Mg−N bond energy using the C−N bond in the molecule as the reference. The C−N bond energy in the macrocycle in MgPc (composed of alternating C−N and C=N bonds around the Mg atom) falls in the range between 18.90 and 18.33 eV for the MNDO/*d* and AM1 Hamiltonians, respectively (Table 2). This energy is considered to correspond to the experimental value of 291.6 kJ/mol reported elsewhere.[19] On the basis of the above energy correspondence, the Mg−N bond along the molecular stack is estimated to be about 41 and 33 kJ/mol for the MNDO/*d* and AM1 Hamiltonians. The present value of 33−41 kJ/mol is nearly equivalent to the hydrogen-bond energy. This energy is significant enough to insist that the five-coordinate Mg complex is formed in the solid state along the stacking axis. Similarly, the Mg−O bond energies in crystals II and III are estimated to be 69−87 and 60−78 kJ/mol, respectively.

On the basis of the above results, it is safe to say that there are chains of the five-coordinate MgPc complexes along the stacking axis, showing considerable $\pi-\pi$ intermolecular interactions through the central Mg atom in MgPc.

5. Conclusions

The $\pi-\pi$ interactions in MgPc have been investigated in terms of energy partition analysis with special attention to the role of the central Mg atom. The conclusions can be summarized as follows.

(i) The Mg−N bond energy along the molecular stack in crystal I is found to be roughly one-third that of the mean Mg−N bond in the molecular plane and approximately one-half that of the Mg−O bond in crystals II and III. The estimated energy of the Mg−N bond along the molecular stack is about 33−41 kJ/mol, which is equivalent to the hydrogen-bond energy.

(ii) There are chains of the deformed five-coordinate MgPc complexes along the stacking axis, and thus, considerable $\pi-\pi$ intermolecular interactions are operative through the central Mg atom in MgPc.

(iii) The question originally raised by Brown on CuPc can basically be answered in the same way as in the present case. However, the treatment for CuPc is obviously more difficult, because CuPc does not represent a completely saturated entity (closed shell) like MgPc because of an unpaired d electron.

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