

π - π Interactions of Magnesiumphthalocyanine as Evaluated by Energy Partition Analysis

J. Mizuguchi

Department of Applied Physics, Graduate School of Engineering
Yokohama National University, Yokohama, Japan

Abstract

Magnesiumphthalocyanine (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. 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 semi-empirical MO calculations. The Mg-N bond energy along the molecular stack is found to be roughly one-third of the Mg-N bond in the molecular plane and approximately one-half of the Mg-O bond of the MgPc six-coordinate complexes: MgPc/(H₂O)₂(NMP)₂ and MgPc/(2-methoxyethanol)₂. These results indicate the chain formation of five-coordinate MgPc complexes along the stacking axis, showing considerable π - π interactions through the central Mg atom.

Introduction

Metal phthalocyanines are generally known as stable organic pigments due to very strong intermolecular interactions.¹ Among these, copperphthalocyanine (CuPc) is the most stable and is widely used as a blue pigment. However, the central metal is not directly involved in the chromophore of metal phthalocyanines. Metal-free phthalocyanine (H₂Pc) is also a commercial product, but its stability is not so high as that of CuPc. The role of the central metal for the stability is one of the long-standing problems in phthalocyanine chemistry. Quite recently, we have encountered a novel crystal structure of magnesiumphthalocyanine (MgPc) as shown in Fig. 1 (crystal I).^{2,3} 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 intermolecular interaction along the stacking axis through the formation of a five-coordinate Mg-complex. The purpose of the present investigation is to characterize the Mg-N bond by means of energy partition

analysis^{4,5} and to discuss the resulting π - π interactions along the stacking axis. The bond strength is estimated using two kinds of solvated MgPc complex as the reference (Fig. 2): MgPc/(H₂O)₂(NMP)₂ (crystal II) and MgPc/(2-methoxyethanol)₂ (crystal III).^{6,7}

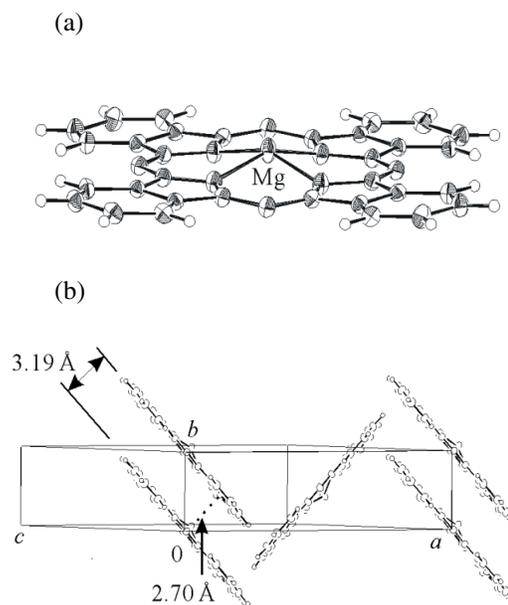


Figure 1. MgPc (crystal I): (a) molecular conformation and (b) molecular stack.

Results and Discussion

1. Energy Partition Analysis for Intermolecular Interactions

The intermolecular interactions can macroscopically be characterized by sublimation or melting point, hardness of the material as well as solubility in solvents. In our attempt to obtain microscopic information on the intermolecular interactions, we noticed that the two-center integral involved in semi-empirical molecular orbital (MO) calculations could be a measure of intermolecular interactions if the crystal structure is known in advance.

In semi-empirical MO calculations, the differential overlap is neglected, so that the total energy of a molecule (E_{total}) can be partitioned into one-center integral (E_i) of the i th atom and two-center integral (E_{ij}) of the bonded i th and j th atoms as shown in Eq. (1).⁴

$$E_{total} = \sum_i E_i + \sum_{i<j} E_{ij} \quad (1)$$

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

$$E_{ij} = E_{res} + E_{exc} + E_{el} \quad (2)$$

It was Hirano and Osawa^{4,5} who applied, for the first time, the two center energy for chemical bonding problems. Since 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.

Based on the pioneer 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 non-bonded atom-pairs between molecules by regarding a pair of molecules as a supermolecule. 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-neighbors. 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.

2. Programs and Calculation Procedure

WinMOPAC Ver.3⁸ was used for energy partition analysis. The Hamiltonians which include parameters for Mg are PM3, MNDO/ d^p and AM1.¹⁰ Among these, MNDO/ d and AM1 were found to be appropriate for reasons described below in Section "Hamiltonians". For crystal I (Fig. 1), 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 (Fig. 2): MgPc/(H₂O)₂(NMP)₂ (crystal II) and MgPc/(2-methoxyethanol)₂ (crystal III).^{6,7}

3. Hamiltonians

As a preliminary test of the Hamiltonians (PM3, MNDO/ d and AM1), we carried out a geometry optimization of the MgPc molecule using the X-ray structure as the initial model in an attempt to examine whether they give a correct geometry that is consistent with experiment. Among three Hamiltonians, MNDO/ d and

AM1 gave an entirely flat molecule (D_{4h} symmetry). Due to 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.^{2,6} This agrees with experiment.^{2,6} 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.

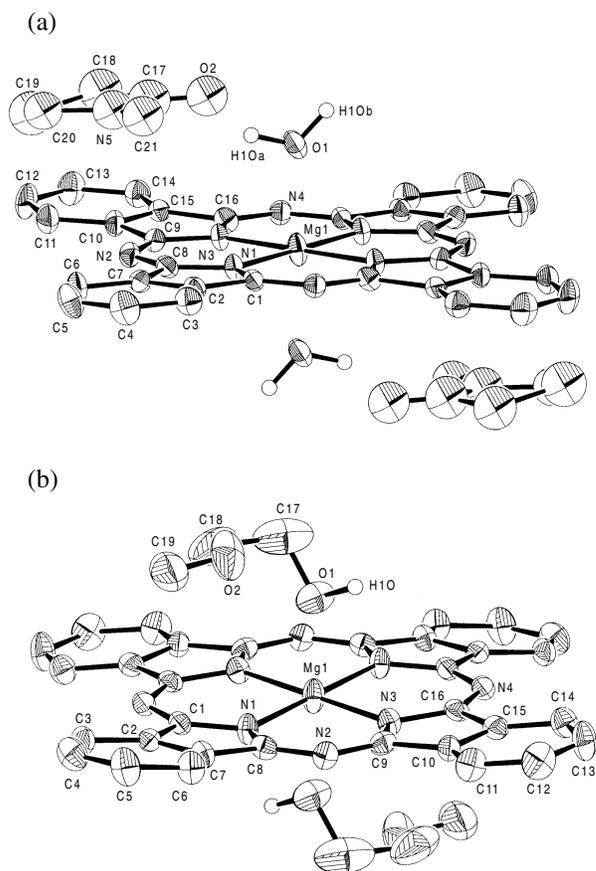


Figure 2. MgPc complexes: (a) MgPc/(H₂O)₂(NMP)₂ (crystal II) and (b) MgPc/(2-methoxyethanol)₂ (crystal III). NMP stands for N-methyl-2-pyrrolidone.

4. Characterization of the Mg-N Bond along the Molecular Stack

Table 1 shows the results of the energy partition analysis for crystals I, II and III on the basis of MNDO/ d Hamiltonian. Table 1 also includes the Mg-N distance along the molecular stack in crystal I (2.70 Å) together with the Mg-O bond in crystal II (2.17 Å) and crystal III (2.24 Å).

As seen from the total energy (EE) in Table 1, the Mg-N bond energy along the molecular stack in crystal I is found to be roughly one-third of the mean Mg-N bond in the molecular plane and approximately one-half 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 1, 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 repulsive in other bonds in all crystals.

The results based on AM1 are quite similar to those of 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 M-O bond energy in crystals II and III is smaller in AM1 than in MNDO/d by 1.3 eV.

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 of about 19 eV (Table 1). This energy is assumed to correspond to the experimental value of 291.6 kJ/mol reported elsewhere.¹¹ Based on the above energy correspondence, the Mg-N bond along the molecular stack is estimated to be about 40 kJ/mol. 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 in crystals II and III is found to be about 62-80 kJ/mol.

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 π - π intermolecular interactions through the central Mg atom in MgPc.

Table 1 Energy partition by means of the MNDO/d Hamiltonian

Crystal	Atom pair	Bond length (Å)	J	K	C	EE
I	Mg-N (molecular stack)	2.70	-1.87	-0.34	-0.42	-2.63
	Mg-N (in molecular plane)	2.03	-6.49	-1.66	0.08	-8.08
	C-N (in macrocycle)	1.38	-19.28	-6.87	7.25	-18.90
	C=N (in macrocycle)	1.33	-21.63	-7.80	8.79	-20.64
II	Mg-O	2.17	-5.35	-0.93	0.55	-5.73
	Mg-N (in molecular plane)	2.02	-6.32	-1.53	0.31	-7.54
	C-N (in macrocycle)	1.36	-19.76	-7.00	7.53	-19.23
	C=N (in macrocycle)	1.34	-21.13	-7.59	8.48	-20.25
III	Mg-O	2.24	-4.67	-0.76	0.40	-5.03
	Mg-N (in molecular plane)	2.01	-6.44	-1.56	0.34	-7.66
	C-N (in macrocycle)	1.39	-18.91	-6.91	6.99	-18.72
	C=N (in macrocycle)	1.34	-21.34	-7.66	8.58	-20.42

J : Resonance energy K : Exchange energy C : Coulomb energy EE : Total energy

Conclusions

The conclusions can be summarized as follows.

1. The Mg-N bond energy along the molecular stack in crystal I is found to be roughly one-third of the mean Mg-N bond in the molecular plane and approximately one-half of the Mg-O bond in crystals II and III. The estimated energy of the Mg-N bond along the molecular stack is about 40 kJ/mol.
2. There are chains of the deformed five-coordinate MgPc complexes along the stacking axis and thus considerable π - π intermolecular interactions are operative through the central Mg atom in MgPc.

References

1. W. Herbst.; K. Hunger "Industrial Organic Pigments"; VCH: 1993.
2. J. Mizuguchi, *J. Phys. Chem. A* 2001, **105**, 1121.
3. J. Mizuguchi, *Z. Krist. NCS 2001*, in press.
4. T. Hirano; E. Osawa, *Croatica Chem. Acta* 1984, **57**, 1633.

5. H. Koinuma; M. Funabashi; K. Kishino; M. Kawasaki; T. Hirano; K. Fueki, *Jpn. J. Appl. Phys.* 1986, **25**, 1811.
6. A. Endo; S. Matsumoto; J. Mizuguchi, *J. Phys. Chem. A* 1999, **103**, 8193.
7. S. Matsumoto; A. Endo; J. Mizuguchi, *Z. Krist.* 2000, 215, 182.
8. WinMOPAC Ver.3, Fujitsu.
9. W. Thiel; A. Voityuk, *A. J. Phys. Chem.* 1996, **100**, 616.
10. M. C. Hutter; J. R. Reimers; N. S. Hush, *J. Phys. Chem. B* 1998, **102**, 8080.
11. L. Pauling, "The Chemical Bond", Cornell Univ. Press, 1967.

Biography

Jin Mizuguchi obtained his B. Sc. in chemistry from Sophia University in 1970, Dr. of Sc. from the University of Tokyo in 1982 and Venia Docendi from the University of Bern in 1994. He worked in the field of organic semiconductors at Sony Corporation Research Center from 1970 to 1985 and at Ciba-Geigy AG (Switzerland) from 1985 to 1995. Since 1995, Prof. Mizuguchi has been at Yokohama National University as professor of materials science.