Evaluation of Intermolecular Forces in Thioindigo Derivatives by Energy Partition Analysis

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Abstract

4,4’,7,7’-tetrachlorothioindigo (TCTI) and 4,4’,5,5’,7,7’-hexachlorothioindigo (HCTI) are thionated derivatives of indigo and are known as reddish purple pigments and photoconductors. Although the molecular structures of these compounds are quite similar, TCTI is less soluble in organic solvents and more photoconductive than HCTI by about one order of magnitude. Obviously, intermolecular interactions are responsible for these phenomena. Therefore, the intermolecular forces in TCTI and HCTI have been investigated in terms of an energy partition analysis based on semi-empirical molecular orbital calculations. The results indicate that there are intermolecular CH···O hydrogen bonds in both TCTI and HCTI. Especially, the H-bond network of TCTI is found to be quite significant and is correlated with its high insolubility in solvents.

Introduction

4,4’,7,7’-tetrachlorothioindigo (TCTI) and 4,4’,5,5’,7,7’-hexachlorothioindigo (HCTI) are thionated derivatives of indigo and are known as reddish purple pigments$^{1)}$ and photoconductors$^{2)}$ for electrophotographic photoreceptors. As is well known, in indigo, there are strong NH···O intermolecular hydrogen bonds that assure high light-stability and low solubility in solvents. Although there is no corresponding NH···O hydrogen-bond network in TCTI and HCTI, these are more stable and less soluble than indigo. Furthermore, TCTI is significantly less soluble than HCTI and more photoconductive than HCTI by one order of magnitude.$^{2)}$ Obviously, intermolecular interactions are responsible for the difference of physical properties.

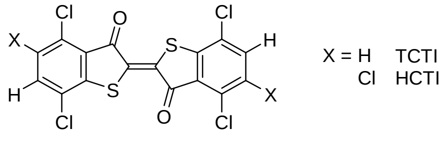


Fig.1 Thioindigo derivatives

The present investigation aims at clarifying how the intermolecular forces are different in TCTI and HCTI on the basis of energy partition method based on semi- empirical molecular orbital (MO) calculations.

Energy partition method as a tool for the evaluation of intermolecular forces

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 energy (E_i) of the component atoms and two-center energy (E_{ij}) of the bonded atoms as shown in Eq. (1).$^{3)}$

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

Where the two-center energy is composed of resonance energy (E_{res}), exchange energy (E_{exc}) and coulomb energy (E_{el}):

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

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.$^{3)}$ 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.

The idea of using the energy partition method as a tool for the evaluation of intermolecular forces stems from the extension of the two center integral *within a molecule* to non-bonded atom-pairs *between molecules* by regarding a pair of molecules as a supermolecule.$^{4)}$ The present method has been, for the first time, proposed by one of us for modification III of dithioketopyrrolopyrrole.$^{4)}$

As for the reliability of the present method, we say that this method is as much reliable as that of MO calculations for geometry optimization and spectroscopic calculations, because the energy partition is just to break down the total electronic energy into one and two-center components. In other words, if one finds the MO calculations meaningful, one must believe that the energy partition calculations also make sense with no further assumption.

Energy partition calculations

1. Calculation procedure

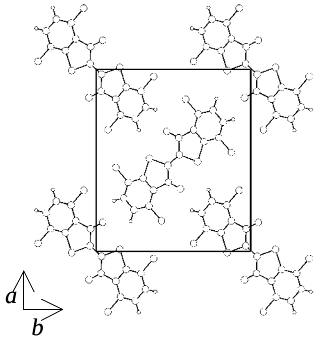
On the basis of the crystal structures of TCTI and HCTI, we focused on a given molecule in the lattice and extracted the nearest-neighbors that surround the central molecule. The calculations were carried out for each molecule-pair using the AM1 Hamiltonian of MOPAC 6. The X-ray coordinate sets were used for the non-H atoms for TCTI and HCTI$^{3)}$, while geometry was optimized for the H-atoms.

2. Crystal structure and typical molecule-pairs

Figs.2 (a) and 2 (b) show the projection of the crystal structure onto the (*a*,*b*) plane for TCTI and HCTI, respectively. The molecules are stacked in a herringborn fashion along the *c* axis in both TCTI and HCTI.

There are five molecule-pairs in both TCTI and HCTI. Among these, the two typical pairs which show strong intermolecular interactions are designated by dotted ellipses as shown in Figs.3: pair 1 and pair 2.

(a) TCTI



(b) HCTI

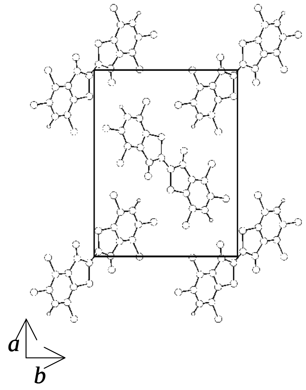
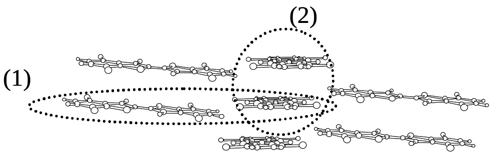


Fig.2 Projection of the crystal structure onto the (a,b) plane: (a) TCTI and (b) HCTI.

(a) TCTI



(b) HCTI

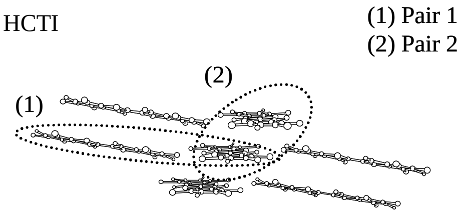
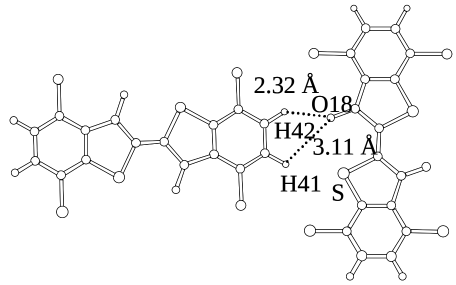


Fig.3 Molecular arrangement along the stacking axis: (a) TCTI and (b) HCTI.

(a) TCTI



(b) HCTI

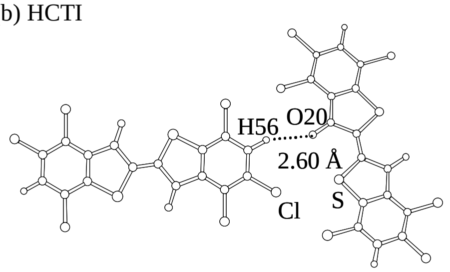


Fig.4 H-bond pair: (a) TCTI and (b) HCTI.

Results and discussion

1. Pair 1 (H-bond pair)

Figs.4 (a) and 4 (b) show the molecule-pairs for TCTI and HCTI, respectively. The strong attractive interactions are designated by dotted lines: H42/O18 and H41/O18 in TCTI and H56/O20 in HCTI. The distances and the two-center energies (*J*, *K* and *C*) are also listed in Table 1 for TCTI and HCTI together with those of as well as indigo, where the minus sign in energy denotes the attractive force. The H42/O18 and H41/O18 distances in TCTI are 2.32 Å and 3.11 Å, respectively. The former is extremely short and the total energy amounts to –0.377 eV, in which the electrostatic component (–0.304 eV) is predominant.

Judging from the CH/O distance and their angles, it is reasonable to assume that the CH···O hydrogen bond is operative in TCTI.[5)] Similarly, the H41/O18 pairs in TCTI and the H56/O20 pairs in HCTI form CH···O hydrogen bonds, although their total energy is appreciably smaller than that of the H42/O18 pair in TCTI. In addition, the CH···O bond is roughly one-third of the H-bond energy calculated for indigo (Table 1). It should be also noted that there are two H-bonds at the corner of the molecule-pair in TCTI while only one in HCTI.

The H-bond energy based on NH···O falls generally in the range between 8 and 10 kcal/mol.[6)] So the 8-10 kcal/mol energy is assumed to correspond to the value of about 1 eV obtained for indigo (Table 1).

Table 1. Energy partition of the total energy (eV) for H-bond in TCTI, HCTI, and indigo

Atom-pair	Distance	*J*	*K*	*C*	*EE*
TCTI					
H42/ O18	2.32 Å	–0.067	–0.007	–0.304	–0.377
H41/ O18	3.12 Å	–0.002	0.000	–0.221	–0.223
HCTI					
H56/ O20	2.60 Å	–0.021	–0.002	–0.279	–0.302
Indigo					
NH···O	2.11 Å	–0.280	–0.040	–0.586	–0.906

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

Figs.5 (a) and 5 (b) show the H-bond network for TCTI and HCTI, respectively. It is important to note that there are eight H-bonds per molecule in TCTI and four H-bonds in HCTI. Roughly speaking, the intermolecular force on the molecular plane is twice stronger in TCTI than in HCTI. This would qualitatively explain why TCTI is less soluble in solvents than HCTI.

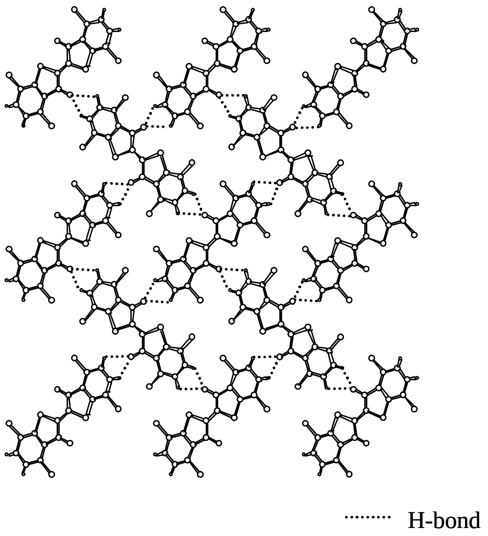
2. Pair 2 (Stack pair)

There are significant atomic contacts along the stacking axis in TCTI and HCTI. There are two characteristic points to be noted: one is that the interactions are purely electrostatic in nature. The other point is that the sulfur atom is predominantly involved in the interactions along the stacking axis.

Fig.6 shows the stack pair for TCTI, where the strong interactions are designated by circles. The sulfur atom is positively charged while the central olefinic carbon bears a small negative charge, so that the attractive force is operative in the S31/C5 and C43/S16 contacts (3.53 Å; –0.422 eV). Another attractive force is also found between the carbonyl carbon and the O atom: C34/O4 and C17/O46 contacts (3.51 Å; –0.280 eV). The close atomic contacts are therefore characterized by attractive forces in TCTI.

Also recognized are the electrostatic interactions between non-overlapping atomic pairs. Significant repulsive forces are found between the S atoms (0.504 - 0.727 eV) and less significant interactions are also observed between the positively charged carbonyl carbon and the S atoms. On the other hand, appreciable attractive forces are recognized between the central olefinic carbon and S atoms (about –0.4 eV). These are again purely electrostatic in nature.

(a) TCTI



(b) HCTI

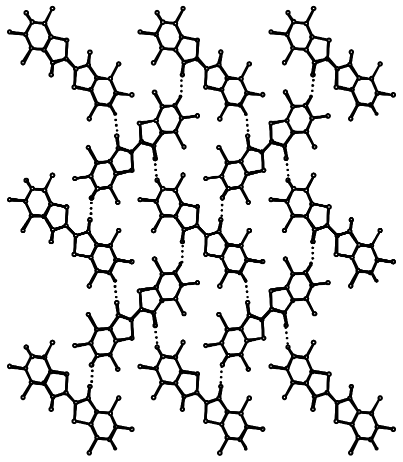


Fig.5 Schematic diagram of two-dimensional H-bond network: (a) TCTI and (b) HCTI.

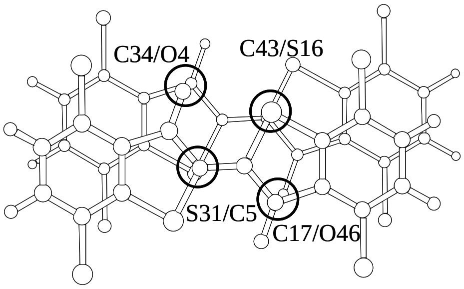
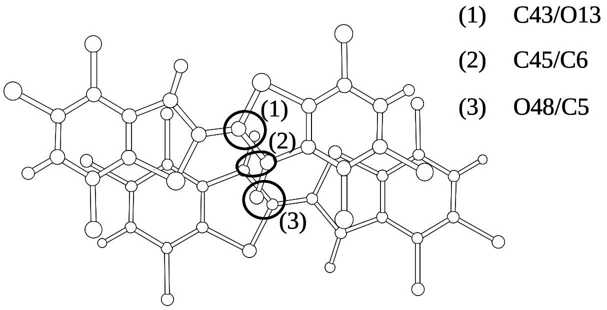


Fig.6 TCTI stack pair

The situation is quite different in HCTI. There are five atomic contacts along the stacking axis as shown in Figs.7, three of which are repulsive (Fig.7 (a)) and two of which are attractive (Fig.7 (b)). Large repulsive forces are found in the C43/O13 (1) and O48/C5 (3) contacts (in both cases 3.38 Å; 0.296 eV) and C45/C6 ((2), 3.45 Å; 0.388 eV). On the contrary, the attractive interactions are found in the C45/O13 (4) and the O48/C6 (5) contacts (3.42 Å; –0.264 eV). In total, the repulsive interactions prevail in close atomic contacts in HCTI, quite contrary to the situation in TCTI.

(a) Repulsive pair



(b) Attractive pair

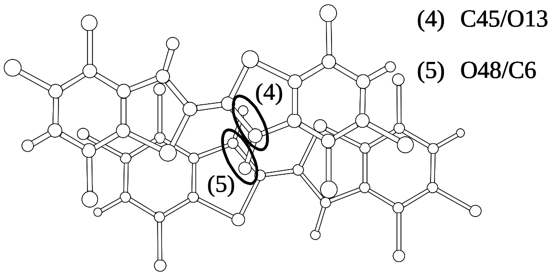


Fig.7 HCTI stack pair: (a) repulsive and (b) attractive pair.

Conclusions

1. On the molecular plane, there are CH···O hydrogen-bond network both in TCTI and HCTI. The CH···O hydrogen bond energy is approximately one-third of the NH···O energy in indigo. There are eight CH···O bonds per molecule in TCTI while only four in HCTI. This qualitatively explains why TCTI is less soluble than HCTI.
2. Along the stacking axis, there are close atomic contacts in both TCTI and HCTI. The former contacts are characterized by attractive forces, while the latter are repulsive.
3. The S atoms are predominantly involved in strong intermolecular interactions in the stack pairs.
4. The energy partition method is found to be a simple but very powerful means for the evaluation of intermolecular forces.

References

1. W. Herbst, K. Hunger, *Industrial Organic Pigments*, VCH, 1993.
2. K. Fukushima, K. Nakatsu, R. Takahashi, H. Yamamoto, K. Gohda, S. Homma, *J. Phys. Chem., B* **102**, 5985–5990 (1998).
3. T. Hirano, E. Osawa, *Croatica Chem. Acta,* **57**, 1633–1642 (1984).
4. J. Mizuguch, Denshi Shashin, **37**, 67–73 (1998).
5. Desiraju, G R., *Acc. Chem. Res.,* **24**, 290–296 (1991).
6. L. Pauling, *The Nature of the Chemical bond*, Cornell Univ. Press, 1960, ch.12.

Biography

Misato Mochizuki received her Bachelor of Education from Yokohama National University in 2000. She is currently in the graduate course for materials science at Yokohama National University. Her research interest includes electronic characterization of organic pigments together with their electronic applications. E-mail: m00db146@ynu.ac.jp