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Classification of Phenothiazine Complexes by Structure and Electronic Properties

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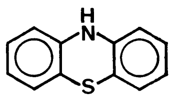
Donor-acceptor complexes were prepared, and their structures and electronic properties were observed. Donors were phenothiazine and its four derivatives, and acceptors were metallic chlorides (Lewis acids), iodine, and two π-type acceptors. By the absorption edge of diffuse reflection spectra (λ_E) and crystal structure, the complexes were classified into four groups. Groups I, II, and III correspond to the complexes with Lewis acids or iodine, and group IV consists of complexes with π-type acceptors. The summarized characteristics of each group are as follows. Group I: $\lambda_E \leqslant 950$ nm, complete charge transfer, insulator, and alternate arrangement of cations and anions. Group II: 1200 nm$\leqslant \lambda_E \leqslant$1700 nm, complete charge transfer, semiconductive behavior, and oligomeric or columnar arrangement of cation radicals. Group III: $\lambda_E > 2500$ nm, partial charge transfer, metallic conductor or semiconductor with small activation energy, and columnar arrangement. Group IV: $\lambda_E \geqslant 1700$ nm, and semiconductive behavior. Based on these classifications, we have proposed a mechanism for controlling the aggregate manner of cation radicals.

Recently, functional organic solid materials have attracted attention due to their potential for practical applications. These materials include organic conductors (or superconductors), photosensitive materials used for information recording, and substances having nonlinear optical properties. In designing these organic functional materials, it should be noted that not only their molecular structure but also their aggregate manner (i.e., crystal structure) plays a very important role, since the interactions (such as electron transfer or energy transfer) between neighboring molecules closely depend on their arrangements in the crystal. For instance, the magnitude of the electrical conductivity of organic conductors is greatly affected by the arrangement of the molecules in the crystal.[1] However, it has not been elucidated what rules determine the arrangement of molecules in the solid state, especially the formation of segregated stacks of molecules, though several authors have tried to define these rules.[2]



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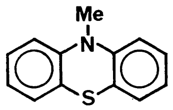

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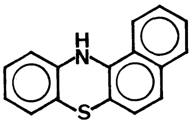

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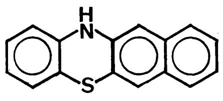

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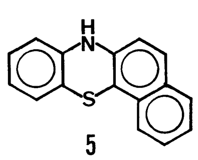

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We have been studying solid complexes of the electron donor–acceptor type, relating their electronic properties to their crystal structures. This report describes the results of our studies of phenothiazine (hereafter PT) and its derivatives (hereafter PT derivatives) as electron donors.

PT derivatives used in this study were the following five substances: phenothiazine (PT, **1**), 10-methylphenothiazine (MPT, **2**), benzo[*a*]phenothiazine (B[*a*]PT, **3**), benzo[*b*]phenothiazine (B[*b*]PT, **4**), and benzo[*c*]phenothiazine (B[*c*]PT, **5**). Acceptors used in this study were various metal chlorides (Lewis acids): $SbCl_3$ (**6**), $SbCl_5$ (**7**), $SnCl_4$ (**8**), $TeCl_4$ (**9**), and $CuCl_2$ (**10**), iodine (**11**) and two typical π-acceptors: 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, **12**) and 7,7,8,8-tetracyanoquinodimethane (TCNQ, **13**). Many complexes, possessing a variety of both structures and electronic properties, were prepared by the combination of these donors and acceptors. The purpose of this research was to describe the determining factor of molecular arrangements in the solid state through the classification of the complexes obtained, and to search for a method to control the molecular arrangement.

Experimental

Materials. PT (Wako Junyaku Co.) was purified by sublimation in vacuo after repeated recrystallization from benzene. MPT was prepared by the method described in the literature,[3] and purified by recrystallization from hexane. B[*a*]PT, B[*b*]PT, and B[*c*]PT were also synthesized according to the literature[4] and purified by sublimation in vacuo. $SbCl_3$ and $TeCl_4$ were purified by sublimation in vacuo and I_2 was sublimed by the usual method.

Each complex was prepared by slow evaporation of solvent from a solution of a suitable donor and an acceptor. Single

Table 1. Numbering and Preparative Conditions of Complexes with Some Characteristics

No.a)	Donor	Acceptor	Mole ratiob)	Solventc)	Features
1-6a	PT	$SbCl_3$	1 : 2	DCE	$PT^{+\cdot}$–$SbCl_4^-$, triclinic
1-6b		$SbCl_3$	1 : 2	DCE	$PT^{+\cdot}$–$SbCl_4^-$, monoclinic
1-7a		$SbCl_5$	1 : 1	DCE	$PT^{+\cdot}$–$SbCl_6^-$
1-7b		$SbCl_5$	1 : 3	DCE	$PT^{+\cdot}$–$SbCl_6^-\cdot H_2O$
1-7c		$SbCl_5$	1 : 5	DCE	$DCPT^{+\cdot}$–$SbCl_6^-$ d)
1-9		$TeCl_4$	1 : 1	DCE	
1-11		I_2	2 : 3	BZ	
1-12		DDQ	1 : 1	BZ	
1-13		TCNQ	1 : 1	DCM	
2-6	MPT	$SbCl_3$, $SbCl_5$	2 : 6 : 1	DCE	
2-7		$SbCl_5$	1 : 1	DCE	$MPT^{+\cdot}$–$SbCl_6^-$
2-9		$TeCl_4$	1 : 1	DCE	
2-11		I_2	2 : 3	ETH	
2-12		DDQ	1 : 1	BZ	
2-13		TCNQ	1 : 1	AN	
3-6	B[*a*]PT	$SbCl_3$	1 : 5	DCE	
3-7		$SbCl_5$	1 : 20	DCE	
3-9		$TeCl_4$	1 : 1	DCE	$(B[a]PT^{+\cdot})_2$–Te_2Cl_{10} e)
3-10		$CuCl_2$	1 : 1	AN	
3-11		I_2	2 : 3	BZ	
3-12		DDQ	1 : 1	BZ	
3-13		TCNQ	1 : 1	AN	
4-7	B[*b*]PT	$SbCl_5$	1 : 1	DCE	
4-8		$SnCl_4$	1 : 2	DCE	
4-11		I_2	1 : 2—6	BZ	$B[b]PT^{+\cdot}$–$I_{2.5}$
4-13		TCNQ	1 : 1	AN	
5-6a	B[*c*]PT	$SbCl_3$	1 : 4	DCE	$B[c]PT^{+\cdot}$–$SbCl_4^-\cdot$0.5DCE
5-6b		$SbCl_3$	1 : 1	DCE	
5-7		$SbCl_5$	1 : 1	DCE	
5-9		$TeCl_4$	1 : 1	DCE	
5-10		$CuCl_2$	1 : 1	AN	
5-11		I_2	2 : 3	BZ	
5-12		DDQ	1 : 1	BZ	
5-13		TCNQ	1 : 1	DCE	

a) Complexes are presented by their numbering hereafter. The first and second numbers indicate the donor and acceptor, respectively. A letter represents a different crystal from the same combination of donor and acceptor. b) Mole ratio of a solution. c) DCE: 1,2-dichloroethane; BZ: benzene; DCM: dichloromethane; ETH: diethyl ether; AN: acetonitrile. d) DCPT: 3,7-dichlorophenothiazine (PT was substituted). e) Ref. 18.

crystals were also obtained by a similar method. Table 1 shows the preparative conditions of the complexes along with their numbering.

Electrical Resistivity. For a single crystal of **4-11**, resistivity was measured along its three axes by direct current with the four probe method from −170 °C to room temperature.[5] Resistivities of other single crystals of **1-6b**, **5-6a**, and **2-7** were measured by direct current with the two probe method from room temperature to 100 °C, from −65 °C to room temperature, and only at room temperature, respectively. For other complexes, direct current with the two probe method was applied to a compressed polycrystalline pellet of 3 mm diameter. The electric potential generator used was a Takedariken (Advantest) TR6142 or a Yokogawa Electric Co. 2853, 2861. A Takedariken TR8651 was used for current measurements. Probes were 100 μmϕ Pt wires. Specimens and probes were connected with Dotite XC-12 paint (Fujikurakasei carbon series). Measurements were carried out in a dry nitrogen atmosphere.

Diffuse reflectance spectra of powder crystalline complexes were measured with a Hitachi 330 spectrometer with a 60 mmϕ integral sphere and an Al_2O_3 plate as a reference. Although the nominal measurable ranges of this sphere were 250—800 nm and 900—1500 nm, absorption was observed in the ranges 800—900 nm and 1500—2500 nm. Hence, measurements were carried out in the range 250—2500 nm.

In order to determine the oxidation state of the PT derivatives in the solid state, solution spectra of the complexes, dissolved in 1,2-dichloroethane, were measured with a Hitachi 330 spectrometer. Although the donors do not always remain in the same oxidation state when dissolved, a stable oxidized state might be confirmable by this procedure.

The X-ray structure determinations were carried out for several complexes, of which appropriate single crystals were obtained.

Results and Discussion

Classification of the PT Complexes. PT is readily oxidized to a cation radical which is fairly stable in solution and in the solid state.[6,7] Figure 1 shows a typical solution spectra of neutral PT and $PT^{+\cdot}$. The characteristic λ maxima of each cation radical are presented in Table 2.

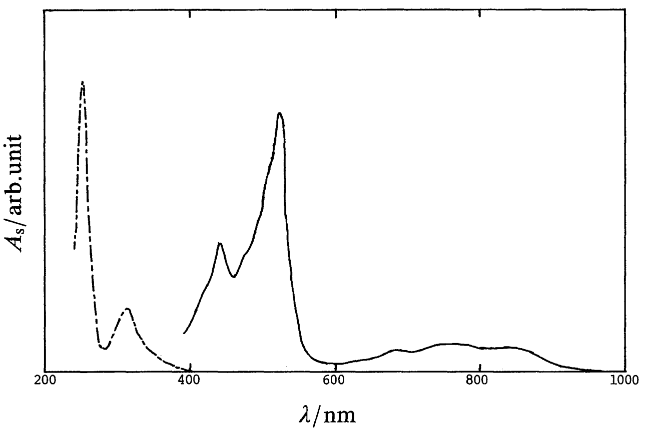

Fig. 1. Absorption spectra of PT (– – – –) and PT-SbCl$_6$ (**1-7a**) (———), in 1,2-dichloroethane solution.

Table 2. Characteristic Absorption Maxima of the Cation Radical of Phenothiazine Derivatives

Cation radical	Absorption maximum λ/nm						
$PT^{+\cdot a)}$		271,	435,	480,	500,	515,	
$MPT^{+\cdot b)}$		271,	450,			518	
B[*a*]$PT^{+\cdot c)}$	230,	299,					597
B[*b*]$PT^{+\cdot c)}$		305,	425,			540	
B[*c*]$PT^{+\cdot c)}$	234,	302,					608

a) Ref. 6. b) This work. c) Ref. 19.

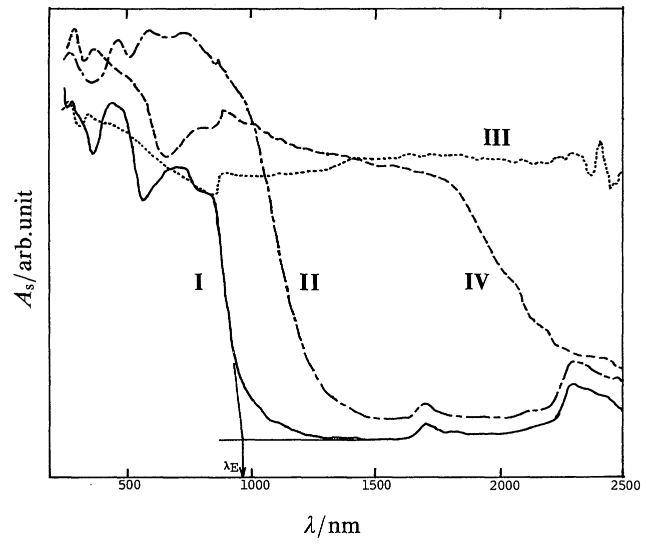

Fig. 2. Diffuse reflection spectra of **2-7**(I), **5-6a**(II). **4-11**(III), and **1-13**(IV). The manner for evaluation of λ_E is shown in the curve of **2-7**.

Figure 2 shows four typical diffuse reflectance spectra, in which reflectance is converted to absorbance by Kubelka-Munk's equation. The wavelengths of the absorption edge (λ_E) are defined by the intersection of tangent lines of the absorption edge and the baseline, as shown in Fig. 2.

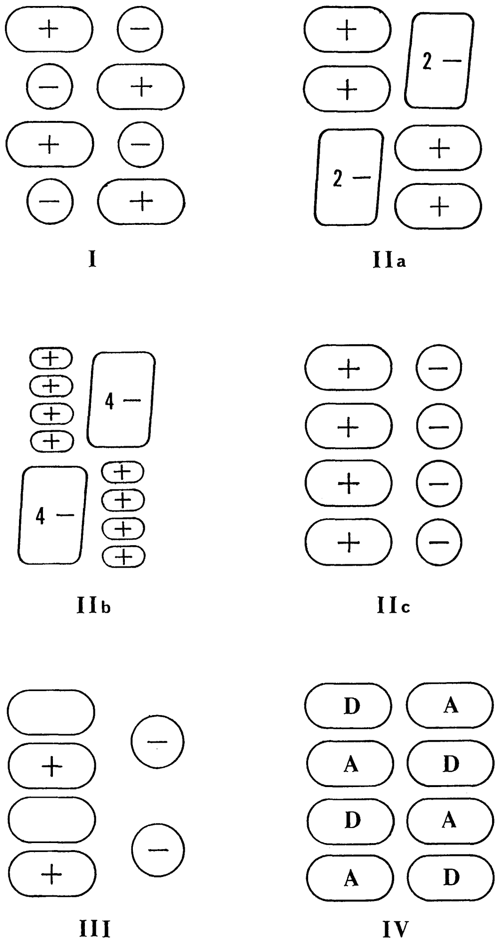

Fig. 3. Classification of crystal structure of the complexes of PT derivatives. I: Simple ionic crystal type; IIa: dimer; IIb: tetramer; IIc: segregated stack of donors with unit charge per molecule; III: segregated stack of donors with fractional charge per molecule; IV: mixed stack of π-π type CT complex.

We found that the physical properties and crystal structures of PT complexes were closely correlated if we classified them into four groups. The classification was made based on the value of λ_E as defined above. Namely, Group I: $\lambda_E \leqslant 950$nm, Group II: 1200 nm$\leqslant \lambda_E \leqslant 1700$ nm, Group III: $\lambda_E > 2500$ nm, those complexes mainly between PT derivatives and iodine, and Group IV: complexes between PT derivatives and π-acceptors. Table 3 presents the physical properties of the complexes along with the crystal structures so far determined. Schematic structures for each group of complexes are shown in Fig. 3.

Group I: Substances classified in this group possess very high electrical resistivity (actually unobservable), and their absorption edges are in a shorter wavelength range than those of the other three groups. The commonly observable absorption band with its edge at 900 nm can be assigned to the intramolecular transition of the corresponding cation radical by reference to its

Table 3. Physical Properties, Crystal Structures, and Oxidation States of PT Derivative Complexes in Crystals

Group	No.	λ_E/nm	$\rho_{25^\circ C}/\Omega$ cm	E_a/eV	Cryst. struct.	Cation radical[a]
I	**1-7a**	900	—	—	Ionic monomer[b]	○
	1-7b	850	—	—	Ionic monomer[c]	○
	1-7c	900	—	—	Ionic monomer[c]	○
	2-7	950	$>10^{11}$[d]	—	Ionic monomer[e]	○
	3-7	690	$>10^{11}$	—	—	○
II	**1-6a**	—	—	—	Tetramer[f]	○
	1-6b	1400	$>10^5$ ($\parallel c$)	0.3—0.2	Column[f]	○
	1-9	1200	10^7	0.5—0.6	—	○
	2-6	1200	10^9	0.6—0.8	—	○
	2-9	1300	10^9	0.7	—	○
	3-6	1500	10^5	0.2	—	○
	3-9	1450	10^5	0.3—0.4	Dimer[c]	○
	3-10	1200	10^4	0.4	—	○
	4-7	1700	10^4	0.2	—	○
	4-8	1700	10^4	0.2	—	○
	5-6a	1250	10^6 (s.c.)	0.2	Column[c]	○
	5-7	1350	10^{10}—10^{11}	0.7	—	○
	5-9	1400	10^5	0.3—0.4	—	○
	5-10	1200	10^5	0.4	—	○
III	**1-11**	>2500	19 (20 °C)	0.19[g]	—	—
	2-11	>2500	10^{-2} (s.c.)	0.20[h]	—	—
	3-11	>2500	34 (20 °C)	0.16[g]	—	—
	4-11	>2500	10^{-2} ($\parallel c$) 30 ($\parallel a$) 60 ($\parallel b$)	Metallic 0.02 0.03	Column[i]	—
	5-6b	>2500	40	0.14	—	—
	5-11	>2500	18 (20 °C)	0.14[g]	—	○
IV	**1-12**	>2500	2×10^4	0.36[j]	—	—
	1-13	2200	7×10^7	0.67[k]	Mixed stack[l]	—
	2-12	>2500	2×10^5 6×10^8[l]	0.33[j]	—	—
	2-13	1900	2×10^9 7×10^9	0.83[k] 0.48[n]	Mixed stack[m]	—
	3-12	>2500	10^9	1.0	—	—
	3-13	2200	10^{10}	0.3—0.4	—	—
	4-13	1700	2×10^9	0.6	—	—
	5-12	>2500	2×10^4	0.35[k]	—	—
	5-13	2100	10^6	0.3	—	—

a) A circle in this column means that the cation radical peaks were observed in its solution spectrum. A hyphen means that the peaks were not observed there. b) Ref. 7. c) Ref. 18. d) Ref. 20. e) Ref. 21. f) Ref. 8. g) Ref. 22. h) Ref. 23. i) Ref. 5. j) Ref. 24. k) Ref. 25. l) Ref. 13. m) Ref. 14. n) Ref. 26.

solution spectra (Table 2).[7] All the crystal structures so far determined of the substances belonging to this group are simple ionic crystal types similar to NaCl. They are almost spherical anions and plate-like cation radicals arranged alternately without any overlap between the donor planes (see Fig. 3). This is the reason why the substances belonging to Group I are good insulators.

A typical example of this group is **1-7a**. Polarized absorption spectra, observed with its single crystal, and observation of ESR absorption clearly indicate the existence of stable cation radicals in the crystal.[7]

Group II: As illustratively shown in Fig. 3, there are various kinds of crystal structures in this group, namely, dimers(IIa), tetramers(IIb), or segregated stacks of donors(IIc). In these solids, plate-like cation radicals overlap each other in a face-to-face manner. However, attractive interactions between donors can not be very large because of the Coulomb repulsion between fully ionized donors. It is obvious that the mean interplanar distance of 3.47 Å in **1-6b** is rather large in spite of its structure of segregated stacks.[8]

Anions in Group II crystals also exist as dimers, tetramers or polyanions, having a unit negative charge per one chemical unit (see Fig. 3). Since all the complexes so far studied in this group had a donor/acceptor mole ratio of 1:1, donors also should have a unit positive charge per molecule. Consequently, the absorption bands ranging from 950 nm to 1700 nm, between the λ_E's of Group I and Group II, can be interpreted as a charge transfer absorption band between the cation radicals.

Measurement of electrical resistivity, performed with single crystals of **1-6b** and **5-6a**, proved that they were semiconductors with anisotropy. The observed rather high resistivity and comparatively large spacing in the column, in spite of its one-dimensional structure, can be understood by considering that the amount of charge transfer is very close to unity. Since other complexes of this group possess electrical resistivity of a similar magnitude, their structures should be similar to those already determined.

Group III: As shown in Table 3, most iodine complexes of PT derivatives belong to this group. The crystal structure determination of the complexes of this group has been successful with only one complex: **4-11**, though it is not yet complete.[5] Its structure (Fig. 4) and characteristics are briefly described below.

The crystal structure of **4-11**, $(\mathrm{B}[b]\mathrm{PT})_2(\mathrm{I}_3^-)(\mathrm{I})_2$, consists of infinite stacks of B[*b*]PT molecules (stack direction is parallel to the *c* axis), separated by univalent I_3^- anions, and linear polyiodide chains (also parallel to the *c* axis). Though the electronic state of the polyiodide has not yet been precisely determined, the amount of charge transfer from B[*b*]PT to the iodine species is probably less than unity. This presumption is supported by the observation of metallic conduction along the *c* axis, and a plasma-edge-like dispersion of reflection spectra in the near-IR region with polarized light parallel to the *c* axis. The observations of ESR spectra and electronic absorption spectra indicate the existence of B[*b*]PT cation radicals.

All the Group III complexes, except **4-11**, are semiconductors. Though they have not yet been structurally analyzed, their structures and electronic states in the solid state are thought to be very similar to those of **4-11**. The structural feature common to Group III complexes is probably an infinite stack of PT derivatives with a fractional charge as shown in Fig. 3 III. Our observations, such as an absorption band extending to the near infrared range, fairly good electrical conductivity with small activation energy, positive Seebeck coefficients etc., support this assumption. Moreover, we propose that all of the Group III iodine complexes have the possibility of possessing metallic conduction, which is hidden by the semiconductive behavior in the observable room temperature range, namely, by the existence of the metal–insulator transition point at a higher range than room temperature.

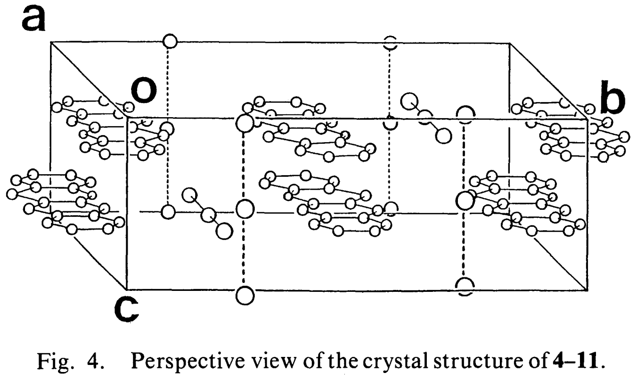

Fig. 4. Perspective view of the crystal structure of **4–11**.

Next, we compare the infinite donor stacks of Group II and Group III. Since the charge on PT derivatives per molecule is fractional in Group III, they have a smaller Coulomb repulsion than those of Group II. In fact, an observed interplanar distance of 3.22 Å between B[*b*]PT moieties in **4-11** is smaller than the value of the Group II complex cited above.

Group IV: Since both donor and acceptor molecules have a π-electron system in this group, both mixed column structure and segregated column structure are possible in the solid state. In the former structure, charge transfer interaction occurs between the donor and acceptor species, and in the latter structure, charge transfer interactions are of the donor–donor or acceptor–acceptor type. Several structural studies have been published describing the complexes between PT and π-acceptors: PT–pyromellitic dianhydride (PMDA),[9] PT–(PMDA)$_2$,[10] PT–trinitrobenzene,[11] and PT-*cis*-bis(trifluoromethylene-1,2-dithiolato)nickel.[12] All of these structures, including **1-13**[13] and **2-13**,[14] are made up of mixed stacks, as shown in Fig. 3 IV, in which PT molecules and flat acceptors stack alternately. The observed absorption band in the near infrared region is probably caused by some intermolecular interaction as cited above, though its precise assignment was not performed at this stage of our research.

The electrical resistivities of this group are in the range of "organic semiconductors". However, the variety of ρ values suggests that there are some possible crystal structures other than a 1:1 mixed column or a simple segregated column; for example, (perylene)$_3$ (DDQ)$_2$,[15] (perylene)$_3$ (TCNQ),[16] and TTF·TCNQ.[17] More structural information should be accumulated for further investigation of this group.

Configuration and Arrangement of PT Derivatives. Since a thiazine ring has an S atom as a member of the ring, PT and its derivative molecules are consequently folded in two planes with creasing through the N and S atoms, in their neutral state. However, we found that these molecules were easily flattened by incorporating their thiazine rings into conjugated systems, such as being oxidized to their cation radicals. Such enlargement of a conjugated system onto the whole molecule is favorable for stabilizing the cation radicals in the solid state, and the flattened molecules can be stacked easily to make dimers or tetramers or segregated columns. In Groups I and II, where all the PT derivatives are flattened cation radicals, their aggregate manner probably depends on the characteristics of the anions. Namely, PT derivatives combined with hexa-coordinated globular anions, such as $SbCl_6^-$ in Group I, exist as monomers. In Group II, the aggregate manner of PT derivatives are the same as those of the anions; dimeric pairs with dimer anions (**3-9**), tetrameric stacks with tetramer anions (**1-6a**), and infinite stacks with infinite polyanions (**1-6b**). By analogy with **4-11**, we presume that the crystals in Group III are composed of segregated columns of fractionally charged donors, which are also flattened.

In conclusion, the aggregate manner of PT derivatives in solids can be somewhat controlled by choosing Lewis acids which form polyanions.

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