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Ground-state Energy Stabilization in Solid Cation Radical Salts Derived from Some Aromatic Hydrocarbons

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Synopsis. The ground-state energy stabilization due to the charge-transfer interaction between cation radicals was examined with solid cation radical salts of 9,10-dimethylanthracene, 9,10-dichloroanthracene, and perylene with antimony pentachloride and perchlorate anions.

There have been made extensive investigations concerning the optical and magnetic properties of a number of crystalline ion radical salts.[1-7] In such ion radical salts, the planar ion radical moleucles are known to form, in themselves, a segregated stacking into one-dimensional columns so as to make a large overlap between their half-occupied moleuclar orbitals. The electronic and magnetic properties of those solid salts are interesting in comparison with those of ion radical monomer. The electronic spectrum of such solid salt is found to differ distinctly from the monomer spectrum of the corresponding ion radical molecule, but shows a charge-transfer transition between ion radicals in the low-energy region.[1-5] As for the magnetic properties, an antiferromagnetic spin exchange interaction between adjacent ion radicals is known to take place in such solid ion radical salt.[1-6] These optical and magnetic properties can be understood in terms of the charge-transfer interaction between ion radical molecules in segregated one-dimensional columns of solid ion radical salts. In the present paper, we shall examine the ground-state energy stabilization due to the charge-transfer interaction between cation radicals in solid aromatic hydrocarbon cation radical salts of 9,10-dimethylanthracene (DMA) with antimony pentachloride anion, 9,10-dichloroanthracene (DCA) with antimony pentachloride anion, and perylene with perchlorate anion.[2,8]

In a previous paper,[4] we applied Hubbard model to the segregated stack of the aromatic hydrocarbon cation radicals and explained the optical and magnetic behaviors of those solid cation radical salts. As for the DMA and DCA cation radical salts, non-alternant one-dimensional half-occupied Hubbard Hamiltonian was applied to the stack of the DMA or DCA cation radicals. The Hubbard Hamiltonian is given by

$$\mathscr{H} = \sum_{i,j,\sigma} T_{ij}C_{i\sigma}{}^{+}C_{j\sigma} + I\sum_{i} n_{i\downarrow}n_{i\uparrow}, \tag{1}$$

where $n_{i\sigma}=C_{i\sigma}{}^{+}C_{i\sigma}$, and $C_{i\sigma}{}^{+}$ and $C_{i\sigma}$ are the creation and annihilation operators of an electron with σ-spin at the i-th site, respectively, and where T_{ij} is the electron transfer matrix element between the i-th and j-th sites, and the Coulomb repulsive potential, I, appears only when two electrons with up and down spins are at the same site. In this model, we take the half-occupied molecular orbital of the unpaired electron for one site of cation radical, and assume a model of regular one-dimensional column composed of infinite number of such sites. We further assume that the transfer matrix element of electron exists only between nearest neighbor sites and is denoted by $T(<0)$. In the case of regular one-dimensional half-occupied Hubbard model with $I\gg|T|$, the Hamiltonian of Eq. 1 becomes equivalent to the following effective Hamiltonian,[6]

$$\mathscr{H}_{\text{eff}} = \frac{4T^2}{I}\sum_{i}\left(S_i\cdot S_{i+1}-\frac{1}{4}\right)+0\left(\frac{T^3}{I^2}\right), \tag{2}$$

where S_i, $(S=\frac{1}{2})$, is the spin operator of an electron at the i-th site. In the limit of $I/|T|\rightarrow\infty$ and $N\rightarrow\infty$, where N is the number of sites in one-dimensional system, we can neglect such higher terms as $0(T^3/I^2)$, and the ground-state energy of Eq. 2 is given by

$$E = -\frac{4NT^2}{I}\ln 2. \tag{3}$$

The ground-state energy of the one-dimensional system of the cation radicals is found to be stabilized by the charge-transfer interaction between cation radicals through the non-zero transfer matrix element, T. Rigorously speaking, the $I/|T|$ value of one-dimensional system of actual ion radical salt is large but not infinite, so that the approximation of E in Eq. 3 has some deviation from exact ground-state energy of Eq. 2. This deviation is caused by neglecting such terms as $0(T^3/I^2)$ in deriving Eq. 3. Therefore, relative error, $\Delta E/E$, in the approximation of Eq. 3 is, at most, of the order of T/I. An advantage of our application of Hubbard model is many-body treatment, so that we can obtain ground-state energy of one-dimensional stack composed of infinite number of ion radicals.

For the DMA cation radical salt, the experimental results of the charge-transfer absorption and the magnetic susceptibilities were well explained in terms of the parameter values of $I=11600\ \text{cm}^{-1}$ and $T\approx-570\ \text{cm}^{-1}$.[4] In this case, since the magnitude of $I/|T|=20.4$ is much larger than unity, we can apply, in place of Eq. 1, the effective Hamiltonian of Eq. 2 to the one-dimensional system of the DMA cation radicals. Then, by the use of the approximation of Eq. 3, the value of E was estimated to be $-0.93\ \text{kJ mol}^{-1}$, and the error of its value was within $\pm0.046\ \text{kJ mol}^{-1}$. In a similar way, for the DCA cation radical salt, the values of $I=11200\ \text{cm}^{-1}$ and $T\approx-560\ \text{cm}^{-1}$ were estimated with the one-dimensional system of the DCA cation radicals.[4] Then, the ratio of $I/|T|=20.0$ is found to be much larger than unity, and the approximation with Eq. 3 is again applicable to our case. The ground-state energy was thus estimated as $E=-0.93\pm0.047\ \text{kJ mol}^{-1}$.

In the case of perylene cation radical salt, the perylene cation radicals are paired up to form dimers in the solid state.[2,4] Then, we applied a dimer model of Hubbard Hamiltonian, which can by written by

$$\mathscr{H} = \sum T(C_{1\sigma}{}^{+}C_{2\sigma}+C_{2\sigma}{}^{+}C_{1\sigma}) + I(n_{1\downarrow}n_{1\uparrow}+n_{2\downarrow}n_{2\uparrow}), \tag{4}$$

where the notations are common to those in Eq. 1. The suffixes, 1 and 2, denote two sites of perylene cation radicals in a dimer, and $T(<0)$ is the electron transfer matrix element between the cation radicals in the dimer. If we only take the half-occupied molecular orbital of perylene cation radical for each site, there are six bases of the wave functions for the dimer. After solving the eigen value problem, the lowest state of the dimer is the singlet state whose energy is given by $E_s = I/2 - \sqrt{(I/2)^2 + (2T)^2}$.[3] The negative value of E_s means ground-state energy stabilization due to the charge-transfer interaction between cation radicals in the dimer through non-zero transfer matrix element, T. Earlier, we explained the optical and magnetic properties of the perylene cation radical salt with the above approach, and obtained the parameter values of $I = 6330\ \mathrm{cm}^{-1}$ and $T = -1630\ \mathrm{cm}^{-1}$.[4] Therefore, the ground-state energy per one mole of perylene cation radicals can be estimated by summing the E_s value with half mole of the dimers, and is calculated to be $-8.19\ \mathrm{kJ\ mol}^{-1}$.

For the above three compounds, the ground-state stabilization energy due to the charge-transfer interaction between cation radicals becomes one of the factors for their cohesive energies. At the present time, there may be no other way to isolate and estimate its magnitude experimentally, but its magnitude is related to the absorption intensity of the charge-transfer transition between cation radicals in their solid-state spectra. In regular one-dimensional infinite stack of cation radicals, the absorption intensity is given, in the small $|T|$ limit, by $N\pi e^2 a T^2/I$,[5] where a is the lattice separation. Therefore, the absorption intensity is approximately proportional to the magnitude of the ground-state stabilization energy. In the dimer model of cation radicals, the situation appears to be similar, and the magnitude of the ground-state stabilization energy is also nearly proportional to the charge-transfer absorption intensity of the dimer. In view of the estimated values of the stabilization energies of DMA, DCA, and perylene cation radical salts. the charge-transfer absorption intensity of the perylene cation radical salt will be about nine times stronger than those of the DMA and DCA cation radical salts, and the absorption intensities of the latter two compounds will be of the same magnitude. This prediction appears to be in agreement with the experimental result of the solid-state spectra reported by Sato *et al.*[2]

All of these compounds are ionic crystals and crystal Madelung energy will be the most important factor for their cohesive energies. Although there is no information on the values of Madelung energy for those compounds, the Madelung energies of several other cation radical salts such as Würster's Blue (*N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine) perchlorate and iodide are of the order of $-4\times10^2\ \mathrm{kJ\ mol}^{-1}$.[6,7] In comparison with great contribution of the Madelung energy, the stabilization energy due to the charge-transfer interaction between cation radicals may make very small contribution to the total cohesive energy in our DMA, DCA, and perylene cation radical salts. However, it is important to note that the mechanism of the charge-transfer interaction does not act in usual ionic crystals such as alkali halides, but only takes place in solid ion radical salts.

References

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6) Y. Iida, *Bull. Chem. Soc. Jpn.*, **52**, 3447 (1979).

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8) As for the DMA–$SbCl_5$ and DCA–$SbCl_5$ crystals, in view of their optical and magnetic properties shown in Ref. 2, ion radical species should be only cation radicals of DMA and DCA, and the counter anion of $SbCl_5$ will have some diamagnetic form. Concerning this anion form, Dr. Y. Sato, who is one of the authors of Ref. 2, suggested that the disproportionation to $SbCl_4^-$ and $SbCl_6^-$ might be most probable.