Ab Initio MO Studies on Electronic States of DCNQI Molecules

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Electronic and geometrical structures of DR-DCNQI molecules (R = H, Cl, Br, I, Me, and OMe) were studied by performing ab initio MO calculations at the HF/DZP level. We carried out DCNQI monomer calculations and found that the optimized structures are close to experimental ones within errors of 0.04 Å in a six-membered ring. We then discussed the basis set dependence of geometrical parameters and concluded that the polarization functions improve the description for double and triple bond states. Ab initio parameters such as transfer integrals were calculated for DCNQI dimers and trimers and compared with formerly calculated parameters. We found that the transfer integrals correlate well with lattice parameters of the *c* axis.

1. Introduction

Organic conductors such as (R1,R2-DCNQI)$_2$M[1–3] (Figure 1) salts show various profound features by replacing their components[4–8] such as substituents, R1 and R2, and a metal, M, or by changing temperature or pressure.[9–11] For example, the electronic states of (DMe-DCNQI)$_2$Cu salts change from metals to insulators due to the methyl deuterium isotope effect. Its substituent effect was understood in terms of the amount of charge transfer from Cu to DCNQI.[7] DCNQI salts form tetragonal crystals of space group $I4_1/a$ and their molecules are stacked face to face forming a one-dimensional (1-D) column.[5,12,13] (Figure 2) For M = Li or Ag, they show strong 1-D character of conductivity and become insulators at low temperatures due to the Peierls transition.[12] However, for M = Cu, the anisotropy with respect to the direction of stacked molecules is small because the hybridization between the d orbital of Cu and p orbital of DCNQI destroys the 1-D character.[1–3,5,13] Therefore, even at low temperatures, some of the DCNQI crystals are metallic.[14] In this paper, we investigate such properties based on ab initio molecular orbital (MO) calculations. From a first-principles approach, Miyazaki et al. calculated metallic states of DCNQI salts with use of the local density approximation (LDA) or the generalized gradient approximation (GGA) based on the density functional theory.[15–17] The first-principles Fermi surface of the (DMe-DCNQI)$_2$Cu salts obtained by them show good agreement with experimental results. They also studied the unique pressure dependence of the (DI-DCNQI)$_2$Cu salts, the existence of the metal–insulator transition under about 15 kbar, and the existence of metallic phase under pressure higher than 19.5 kbar at low temperatures.[8] Suzumura and Fukuyama employed a periodic Anderson model including the electron–phonon interactions and studied physical properties by the mean field theory.[18] Ogawa and Suzumura applied the slave boson method to the same model and examined the effect of strong correlation on the metal–insulator transition.[19–21] The same problem was also studied by Yonemitsu from the renormalization-group approach.[22] From various studies, bulk properties of the DCNQI crystals have been understood reasonably well. However, the electronic and geometrical structures of DCNQI molecules, which are necessary to understand the character of DCNQI molecules, in developing new materials
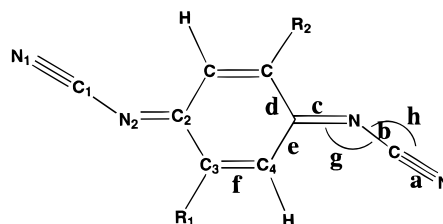

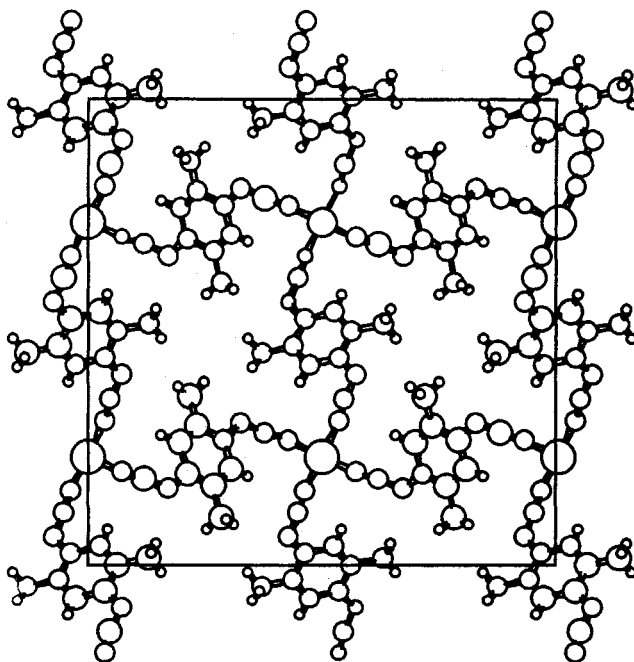**Figure 1.** Molecular structure of the 2,5 − R1,R2-DCNQI molecule.

Figure 2. The *c*-axis projection of the crystal structure of (DMe-DCNQI)$_2$Cu at room temperature.

synthetically, have not been studied yet. Thanks to recent developments of computer and algorithm technology, such information can be obtained by ab initio MO methods.[23–25] In the following, we perform ab initio MO calculations of DCNQI molecules to better understand the character of the organic systems.

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2. Method

Anionic and neutral DCNQI monomers were optimized at the Hartree−Fock (HF) with several Gaussian-type basis sets and compared with experimental data. We assumed R1,R2-DCNQI molecules (R1 = R2) are of C_i symmetry and have planar structures. Three different basis sets, the single-ζ (SZ),[26] valence double-ζ (DZ),[27−29] and DZ plus polarization (DZP)[27−29] sets, were used for comparisons. In this study, we performed the oligomer calculations to construct the effective Hamiltonian, H_{eff}. In order to obtain the parameters such as transfer integrals which are necessary for H_{eff}, we calculated the electronic structures of stacked DCNQI dimers with various formal charges $q_d = 0$ to 4. A DCNQI trimer with $q_d = -2$ was also calculated to check the size dependence of cluster. In the oligomer calculations, we used structural parameters from the X-ray diffraction experiments at various temperatures. Crystal structure at room temperature is shown in Figure 2.[5,13,30] In this study, we consider temperature effects as the changes of structural parameters. We also adopted the SZ, DZ, and DZP basis sets for the DCNQI dimer calculation. For the DCNQI trimer, the Stevens−Basch−Krauss−Jasien split valence plus polarization basis sets and their effective core potentials (ECP)[31] were used to reduce the number of basis functions.

We define two types of transfer integrals based on DCNQI dimer calculations with $q_d = -1$. Henceforward, the spatial orbital indices, i, j, ..., s, t, ..., λ, ..., and p, q, ..., are used for the doubly occupied, singly occupied (SOMO), localized (LMO), and general molecular orbitals, respectively. The transfer integral, $t(1)$, is the half of the energy difference between the ^2A_g ground and ^2A_u first excited states, i.e.,

$$t(1) = \frac{1}{2}[E(^2A_g) - E(^2A_u)] \tag{1}$$

We performed the restricted open shell HF calculations for these states whose energies are given by

$$E(S) = \langle s|f(S)|s \rangle + E_{core}(S) \tag{2}$$

where S in the parentheses means the orbitals are optimized with respect to the state, $s = a_g$, a_u, for S = A_g, A_u, respectively. In the restricted open shell HF calculations, we constrained that open shell orbitals for the ^2A_g ground and ^2A_u first excited states have a_g, a_u symmetries, respectively. f and E_{core} are defined as

$$\langle p|f|q \rangle = \langle p|h|q \rangle + \sum_i [2\langle ip|iq \rangle - \langle ip|qi \rangle] \tag{3}$$

$$E_{core} = \sum_i [\langle i|h|i \rangle + \langle i|f|i \rangle] \tag{4}$$

Here h represents the one-electron Hamiltonian of the dimer model and the Dirac notation is used for two-electron integrals. The other transfer integral, $t(2)$, is defined as

$$t(2) = \langle \lambda_1|f|\lambda_2 \rangle \tag{5}$$

where λ_1 and λ_2 denote LMOs which are equivalently located on each DCNQI molecule. As the canonical MOs and LMOs are connected via the unitary transformation

$$|a_g\rangle = (1/\sqrt{2})[|\lambda_1\rangle + |\lambda_2\rangle] \tag{6}$$

$$|a_u\rangle = (1/\sqrt{2})[|\lambda_1\rangle + |\lambda_2\rangle] \tag{7}$$

it is easy to confirm that $t(1)$ is equivalent to $t(2)$ for a given

TABLE 1: Structural Parameters (a−f, Å; g−h, deg) for R1,R2-DCNQI (R1 = R2) Molecules from the HF Calculations with DZP Basis Set

R1	charge	a	b	c	d	e	f	g	h
−H	0	1.141	1.345	1.274	1.477	1.476	1.330	120.1	176.6
−H	−1	1.151	1.323	1.329	1.437	1.435	1.359	119.0	176.3
−Cl	0	1.141	1.344	1.268	1.487	1.475	1.328	120.6	176.7
−Cl	−1	1.150	1.323	1.319	1.440	1.437	1.356	119.2	176.4
−Br	0	1.141	1.343	1.268	1.485	1.475	1.328	120.6	176.5
−Br	−1	1.150	1.323	1.319	1.438	1.437	1.355	119.2	176.3
−I	0	1.141	1.342	1.270	1.484	1.477	1.330	120.9	176.5
−I	−1	1.150	1.322	1.319	1.439	1.438	1.357	119.5	176.4
−Me	0	1.141	1.344	1.275	1.488	1.473	1.333	120.4	176.4
−Me	−1	1.151	1.321	1.330	1.443	1.435	1.361	119.4	176.1
−OMe	0	1.142	1.342	1.272	1.500	1.458	1.341	119.5	176.9
−OMe	−1	1.151	1.320	1.332	1.450	1.425	1.365	119.6	175.6

set of MOs. However, in the $t(1)$, MOs are optimized separately to the two states. Thus the orbital relaxation is therefore neglected in $t(2)$. We used the Boys localization procedure[32] for the LMOs based on the ground-state HF calculation. A similar estimation was also performed for the DCNQI trimer. Besides the transfer integrals, on-site and nearest-neighbor Coulomb interactions, $\langle \lambda_1\lambda_1|\lambda_1\lambda_1 \rangle$ and $\langle \lambda_1\lambda_2|\lambda_1\lambda_2 \rangle$, are estimated by using the same LMOs. All calculations were performed by the GAMESS[33] and GAUSSIAN[34] suites of program packages.

3. Optimized Structures

3.1. Neutral and Anionic DCNQI Molecules. Structural parameters of DCNQI monomers optimized at the HF/DZP are shown in Table 1. Andreetti et al. studied the crystal structure consisting of DCNQI molecules which have neutral charge.[35] These parameters are shown in Table 2. Comparing them, we can see that the errors of bond distances and angles are within 0.04 Å and 1°, respectively, except the parameter h, which is about 4° different from that of the X-ray diffraction experiment. One reason for this is that crystal effects are not included in our calculations. The parameters d, e of the neutral DCNQI molecule are about 1.48 Å which is shorter than the theoretical value of ethane, 1.531 Å, obtained by the HF/DZP calculation. On the other hand, the parameter f is about 1.330 Å which is a little longer than the theoretical value of ethylene, 1.325 Å, obtained by the HF/DZP calculation. These results imply delocalization of the p orbital in the DCNQI molecule. For neutral and anionic DCNQI molecules, the parameters d, and f of R = −Me, −OMe are longer than those of other DCNQI molecules, whereas, the parameter e is shorter. In the crystal, the DI-DCNQI salts show a unique phase diagram under high pressure as discussed above.[11] As far as the molecular structure is concerned, however, there is no prominent difference between DI-DCNQI and other DCNQI derivatives. The character of DI-DCNQI salts is probably due to the dimensionality as suggested by Miyazaki et al.[15] This means that the ratio of intercolumn to intracolumn interactions is different among DI-DCNQI and other DCNQI derivatives.

By comparing neutral DCNQI and anionic DCNQI$^-$ structures, we found the parameters c, f of DCNQI are longer than those of DCNQI$^-$, whereas the parameters b, d, e are shorter. Especially the parameter c of DCNQI is about 0.06 Å longer due to the antibonding nature of $-C_2-N_2-$. We will discuss this point in a later section.

3.2. Comparison with Other Results. We now compare our results with the experimental results and with the calculated results of others. DCNQI crystal structures of copper salts were studied experimentally by Sinzger et al., Kobayashi et al., and Sawa (Table 2).[5,13,30] In the metallic state, the formal charge of

TABLE 2: Structural Parameters ($a-f$, Å; $g-h$, deg) for R1,R2-DCNQI (R1 = R2) Molecules from Experiments

R1	metal	temp	charge	a	b	c	d	e	f	g	h
$-Cl$	Cu	RT[a,b]	$-2/3$	1.150	1.299	1.330	1.443	1.433	1.351	120.1	172.4
$-Br$	Cu	RT[b]	$-2/3$	1.152	1.306	1.329	1.434	1.443	1.350	120.6	172.4
$-I$	Cu	9 K[c]	$-2/3$	1.154	1.322	1.336	1.445	1.432	1.362	121.1	172.5
$-Me$	Cu	20 K[d]	$-2/3$	1.163	1.318	1.340	1.452	1.435	1.365	119.5	172.9
$-OMe$	Cu	RT[b]	$-2/3$	1.150	1.321	1.335	1.452	1.413	1.352	120.4	171.2
$-H$		[e]	0	1.150	1.334	1.303	1.446	1.450	1.336	119.5	172.8

[a] Room temperature. [b] Reference 13. [c] Reference 30. [d] Reference 5. [e] Reference 35.

TABLE 3: Structural Parameters ($a-f$, Å; $g-h$, deg) for R1,R2-DCNQI (R1 = R2)$^{-2/3}$ from the HF Calculations from DZP Basis Set (Average of Neutral and Anionic DCNQI Molecules)

R1	a	b	c	d	e	f	g	h
$-Cl$	1.147	1.330	1.302	1.456	1.450	1.347	119.6	176.5
$-Br$	1.147	1.330	1.302	1.454	1.450	1.346	119.6	176.4
$-I$	1.147	1.329	1.303	1.454	1.451	1.348	120.0	176.4
$-Me$	1.148	1.329	1.312	1.458	1.447	1.352	119.7	176.2
$-OMe$	1.148	1.327	1.312	1.467	1.436	1.357	119.6	176.0

TABLE 4: Basis Set Dependence of Structural Parameters ($a-f$, Å; $g-h$, deg) for R1,R2-DCNQI (R1 = R2) Molecules from the HF Calculations with SZ, DZ, and DZP Basis Set

| R1	basis set	charge	a	b	c	d	e	f	g	h
$-H$	SZ	0	1.179	1.413	1.315	1.507	1.507	1.344	119.5	174.8
$-H$	DZ	0	1.155	1.346	1.286	1.475	1.473	1.338	124.2	175.4
$-H$	DZP	0	1.141	1.345	1.274	1.477	1.476	1.330	120.1	176.6
$-H$	SZ	-1	1.180	1.393	1.370	1.458	1.458	1.372	117.4	173.4
$-H$	DZ	-1	1.166	1.328	1.342	1.438	1.434	1.366	122.5	175.4
$-H$	DZP	-1	1.151	1.323	1.329	1.437	1.435	1.359	119.0	176.3
$-Me$	SZ	0	1.179	1.412	1.315	1.513	1.503	1.345	119.7	174.6
$-Me$	DZ	0	1.155	1.344	1.287	1.486	1.472	1.341	124.5	175.3
$-Me$	DZP	0	1.141	1.344	1.275	1.488	1.473	1.333	120.4	176.4
$-Me$	SZ	-1	1.180	1.391	1.369	1.461	1.456	1.372	117.7	173.3
$-Me$	DZ	-1	1.166	1.327	1.343	1.443	1.436	1.368	122.7	175.3
$-Me$	DZP	-1	1.151	1.321	1.330	1.443	1.435	1.361	119.4	176.1

Cu is close to $+4/3$ and that of DCNQI molecule is $-2/3$.[1-3] In Table 3, we show the average structural parameters of DCNQI$^{-2/3}$ derived from those of neutral DCNQI and anionic DCNQI$^-$. The errors of bond distances and angles between experimental and theoretical structures are within 0.04 Å and 5°, respectively. The errors in angles are large because we neglected the Cu coordinated by cyano groups at the end of DCNQI molecule. We should stress that the structural parameters we obtained are in good agreement with experimental ones. Therefore, this may indicate that the effect of the Cu is limited to the cyano groups and does not affect the parameters such as transfer integrals very much.

Next, we compared our results with the calculations based on the density functional theory.[17] The largest discrepancies between them for bond lengths and angles are 0.03 Å and 0.7°, respectively. Most of the bond lengths are reproduced within errors of 0.01 Å and show a good agreement.

3.3. Basis Set Dependence. In Table 4, we show the basis set dependence of the structural parameters. Large errors of bond lengths are clearly seen in the SZ basis set case. The structural parameters of DZP basis set are similar to those of the DZ basis set, but some improvements are found in the bond lengths of double and triple bonds and in the angle of $-N_2-C_1-N_1$.

4. Molecular Orbitals

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the DCNQI molecule are drawn in Figure 3. In this study, the HOMO or LUMO is referred to those of neutral molecules. The antibonding characters of $-N_2-C_2-$ and $-C_3-C_4-$ are observed in the LUMO.
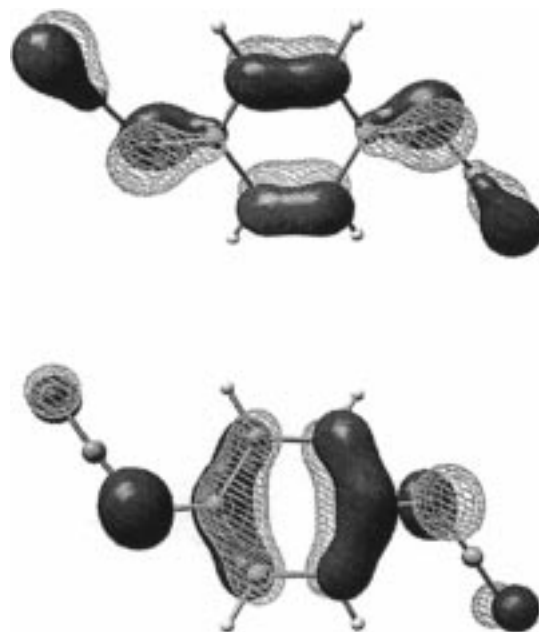
Figure 3. (top) HOMO and (bottom) LUMO orbitals of neutral DCNQI molecule at the HF/DZP level.

As seen in the previous section, these bond lengths of anionic DCNQI$^-$ molecules are longer than those of the neutral one. The LUMO coefficients of p-type orbitals in $-N_2-$ and the six-membered ring are large but those of the substituent are small. This indicates that the six-membered ring and $-N_2-C_1-N_1$ play an important role in conductivity of DCNQI crystals.

5. Ab Initio Parametrization of the Model Hamiltonian

We calculated DCNQI dimers for different q_d (from 0 to -4). The transfer integrals, $t(1)$, $t(2)$, and the on-site and nearest-neighbor Coulomb interactions are shown for DCNQI derivative dimer in Table 5. These parameters are particularly helpful in understanding the physical properties of the organic conductors. We could not obtain the $t(1)$ except DMe-DCNQI at room temperature and DI-DCNQI at 9 K because of poor convergence. In DCNQI trimer calculations, we also obtained one $t(2)$ and nearest-neighbor Coulomb interaction by considering the Ci symmetry. We could not define $t(1)$ in DCNQI trimer calculation because of the $t(1)$ definition. On-site and nearest-neighbor Coulomb interactions change slightly when the formal charge is changed. The transfer integral $t(2)$ is similar for $q_d = 0, -1$, and -2 but different for $q_d = -3$ and -4. This difference is explained by the separation of LMOs. Transfer integrals are underestimated due to unphysical charge separation for $q_d = -3$ and -4. We chose $q_d = -1$ of DCNQI dimer which is close to that of Cu-DCNQI dimer, $-4/3$. The SOMO of DMe-DCNQI dimer at room temperature with $q_d = -1$ is drawn in Figure 4. For DMe-DCNQI dimer at room temperature, $t(1)$ is calculated as 0.356 eV which is slightly smaller than the corresponding

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TABLE 5: Some Parameters (eV) from the HF Calculations

	temp	cluster	charge	basis set	lattice parameter c (Å)	$t(1)$	$t(2)$	on-site Coulomb interaction	nearest-neighbor Coulomb interaction
DMe-DCNQI	RT[a]	dimer	−1	SZ	3.871[c]		0.298	6.804	3.227
DMe-DCNQI	RT	dimer	−1	DZ	3.871		0.362	6.424	3.276
DMe-DCNQI	RT	dimer	0	DZP	3.871		0.365	6.390	3.224
DMe-DCNQI	RT	dimer	−1	DZP	3.871	0.356	0.380	6.545	3.323
DMe-DCNQI	RT	dimer	−2	DZP	3.871		0.373	6.357	3.326
DMe-DCNQI	RT	dimer	−3	DZP	3.871		0.293	6.566	3.387
DMe-DCNQI	RT	dimer	−4	DZP	3.871		0.273	6.382	3.265
DMe-DCNQI	100 K	dimer	−1	DZP	3.801[d]		0.417	6.536	3.362
DMe-DCNQI	20 K	dimer	−1	DZP	3.792[d]		0.428	6.529	3.367
DCl-DCNQI	RT	dimer	−1	DZP	3.816[c]		0.398	6.433	3.334
DBr-DCNQI	RT	dimer	−1	DZP	3.896[c]		0.366	6.431	3.305
DI-DCNQI	RT	dimer	−1	DZP	4.077[e]		0.292	6.395	3.242
DI-DCNQI	9 K	dimer	−1	DZP	4.0042[e]	0.310	0.331	6.415	3.277
DMe-DCNQI	100 K	dimer	−1	ECP	3.801		0.422	6.510	3.349
DMe-DCNQI	100 K	trimer	−2	ECP	3.801		0.416	6.338, 6.282	3.332
(DMe-DCNQI)$_2$Cu	20 K		theory[b]			−0.25			
(DBr-DCNQI)$_2$Cu	RT		theory[b]		−0.18				
(DI-DCNQI)$_2$Cu	9 K		theory[b]		−0.14				

[a] Room temperature. [b] Reference 16. [c] Reference 13. [d] Reference 5. [e] Reference 30.
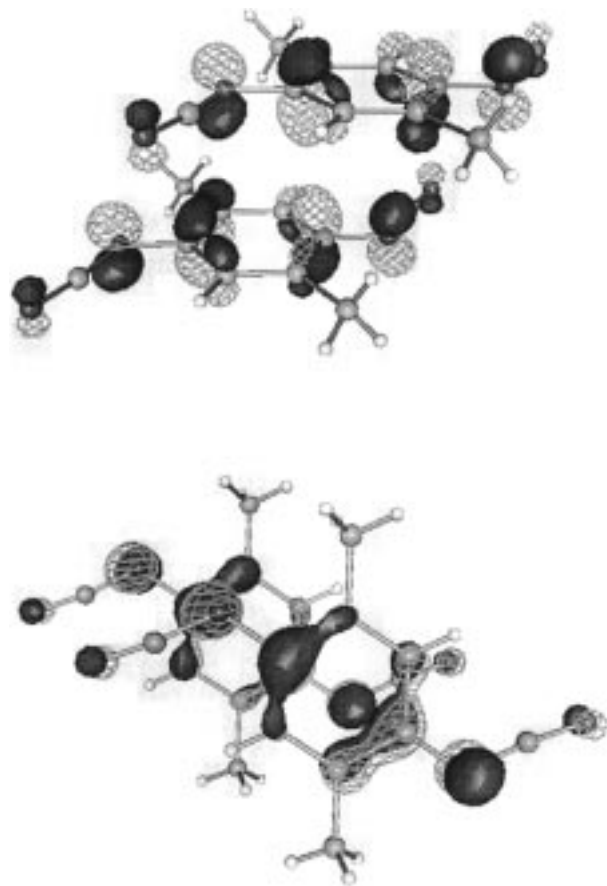
Figure 4. SOMO of DMe-DCNQI dimer at room temperature with q_d = −1 at the HF/ECP calculation.

Figure 5. Correlation between the $t(2)$ obtained from the HF/DZP calculation and lattice parameters of the c axis.

$t(2)$, 0.380 eV. This difference is mostly explained by the orbital relaxation. For DMe-DCNQI dimer at room temperature, on-site and nearest-neighbor Coulomb interactions are calculated as 6.55 and 3.32 eV. The absolute value of $t(2)$ of LUMO−LUMO (intrachain) is calculated as 0.43 eV for DMe-DCNQI at 20 K. This is larger than that of 0.25 eV calculated from density functional theory for (DMe-DCNQI)$_2$Cu.[16] Two reasons, which are related, are responsible for this discrepancy. (1) Pure model calculation parameters of DCNQI molecules were extracted in this particular work; however, the hybridization with d orbitals in the Cu atoms probably requires the multiple band
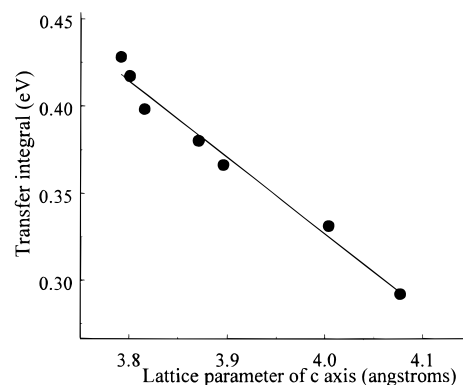
treatment in bulk calculations. (2) The tight-binding approximation used in analyzing the first-principles results may include ambiguity in their fitting band descriptions. The $t(2)$ of the DI-DCNQI dimer at room temperature is smaller than those of the other dimers. This is because the lattice parameter of the c axis of the DI-DCNQI crystal is longest among calculated DCNQI salts. Based on the discussions on HOMO and LUMO, this indicates that the substituents mostly control the lattice parameters which dominate $t(2)$. This correlation is clearly seen in Figure 5.

We checked the basis set dependence by using SZ, DZ, and DZP sets. The $t(2)$ calculated with SZ basis set is found to be small, whereas the DZ and DZP results are similar. We calculated the DMe-DCNQI salts with parameters at three different temperatures. These calculations indicate that the $t(2)$ becomes large as temperature decreases. We obtained a similar tendency in the DI-DCNQI salts. To check the accuracy of the obtained $t(2)$ with respect to the size of clusters, we performed trimer calculation of the DMe-DCNQI using the experimental structural parameters at 100 K with the ECP basis. A preliminary calculation of the dimer suggests that the ECP reproduces the $t(2)$ of DZP set accurately, 0.417 and 0.422 eV, respectively. We obtained 0.416 eV based on the trimer calculation which is slightly smaller than that obtained from the dimer calculation.

6. Conclusion

We calculated the geometrical and electronic structures of DCNQI monomers at the HF/DZP level. The theoretical

structures of the DCNQI molecules agree with the experimental ones within errors of 0.04 Å in bond length and 5° in angle. Except for the errors in the angles attributed to crystallographic packing effects, the HF method basically reproduces the experimental structures of DCNQI molecules well. Furthermore, we parametrized the H_{eff} including transfer integrals, on-site Coulomb and nearest-neighbor Coulomb, interactions from ab initio results. The obtained parameters were compared with previous theoretical ones and their differences are discussed. A clear correlation between lattice parameters of the *c* axis and theoretical transfer integrals was also discovered. Analyses of spin and charge orderings of the DCNQI salts, which can be studied by diagonalizing the H_{eff} obtained in this work, is now ongoing. [36]

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