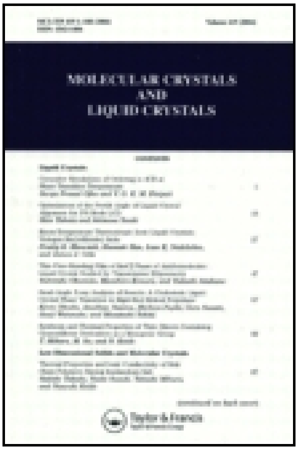

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Estimation of the On-Site Coulomb Repulsion Energy of 2,2′-Bi-1H-Imidazole System

Tomoyuki Akutagawa [a] [b] & Gunzi Saito [a]
[a] Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto, 606-01, Japan
[b] Research Institute for Electronic Science, Hokkaido University, Sapporo, 060, Japan

To cite this article: Tomoyuki Akutagawa & Gunzi Saito (1996): The Estimation of the On-Site Coulomb Repulsion Energy of 2,2′-Bi-1H-Imidazole System, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 284:1, 307-318

To link to this article: http://dx.doi.org/10.1080/10587259608037933

Mol. Cryst. Liq. Cryst., 1996, Vol. 284, pp. 307–318
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science
Publishers SA
Printed in Malaysia

THE ESTIMATION OF THE ON-SITE COULOMB REPULSION ENERGY OF 2,2'-BI-1*H*-IMIDAZOLE SYSTEM

TOMOYUKI AKUTAGAWA# and GUNZI SAITO
Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku,
Kyoto 606-01, Japan.

Abstract The 2,2'-bi-1*H*-imidazole ($H2BIM^0$) can change to 2,2'-bi-1*H*-imidazolium ($H4BIM^{2+}$) by the two-step proton-transfer, then, to 2,2'-bi(2,3-dihydroimidazolylidene) ($H4BIM^0$) by the two-step electron-transfer. From the systematic investigations of half-wave redox potentials ($E_{1/2}$) and acid dissociation constants (pK_a), we estimated the repulsion energy of electrons (U_1^{CT}) and protons (U_1^{PT}) for $H4BIM^0$ and $H4BIM^{2+}$, respectively, and other systems, p-benzoquinones (BQs), diphenoquinones (DPQs), 7,7,8,8-tetracyanoquinodimethanes (TCNQs), tetrathiafulvalenes (TTFs), aromaticdiamines, hydroquinones (H2Qs), 1,4-benzenedimalononitrile (H2TCNQ), bis(4-hydroxyphenyl) sulfides (HPSs). The U_1^{CT} and U_1^{PT} values are deduced from the linear correlation between the first $E^1_{1/2}$ (pK_{a1}) value and the second $E^2_{1/2}$ (pK_{a2}) one. The obtained U_1^{CT} of $H4BIM^0$ (4.68 eV) is comparable to that of TTF (4.65 eV), and U_1^{PT} of $H4BIM^{2+}$ (4.26 eV) is slightly larger than that of H2TCNQ (4.22 eV). The U_1^{CT} and U_1^{PT} values are correlated to the structural parameter of π-electron density and molecular length.

Present address: Research Institute for Electronic Science,
Hokkaido University, Sapporo 060, Japan.

INTRODUCTION

The multiplex proton-transfer (PT) and electron (charge)-transfer (CT) system has been studying in the 2,2'-bi-1*H*-imidazole (H2BIM) system.[1, 2] The PT and CT nature of this system is very complicated one according to the ideal existence of twenty-five independent chemical species. Among these states, we are interested to the cation and dication species of H2BIM system and examined the crystal structures and the CT complex formations with some 7,7,8,8-tetracyanoquinodimethane (TCNQ) derivatives.[3] By the occurrence of the protonation, the neutral 2,2'-bi-1*H*-imidazole ($H2BIM^0$) with 6π-6π electronic structure changes to the monocation 2-(2-1*H*-imidazolyl)-1*H*-imidazolium ($H3BIM^+$), then the dication 2,2'-bi-1*H*-imidazolium ($H4BIM^{2+}$). The dication of $H4BIM^{2+}$ varies the cation radical ($H4BIM^{+\bullet}$), then the neutral 2,2'-bi-2,3-dihydroimidazolylidene ($H4BIM^0$) with 7π-7π electronic structure by two-step CT processes (Figure 1).

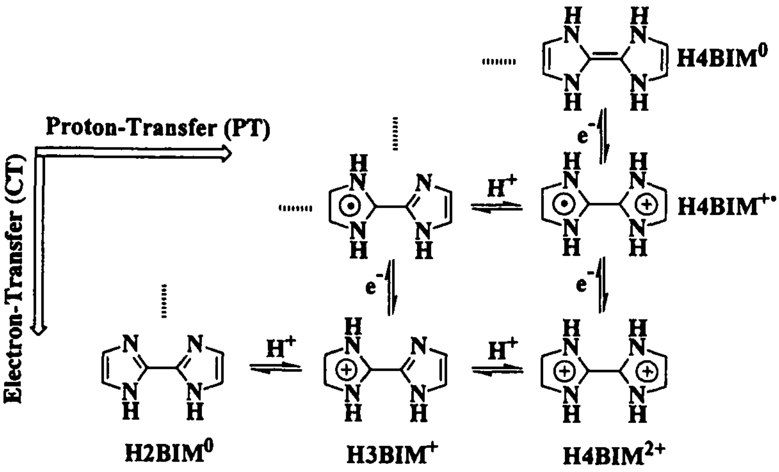

FIGURE 1 Proton - transfer (horizontal processes) and electron (charge) - transfer (vertical processes) scheme of 2,2'-bi-1*H*-imidazole system. The parts of species are omitted to simplify the figure.

In the two-step CT process, the repulsion energy between two electrons on the same molecular site, that is the bare on-site Coulomb repulsion energy (U_1^{CT}) which corresponds to the disproportional energy for $2A^{-\bullet} \rightarrow A^0 + A^{2-}$ reaction in the gas phase, is one of the molecular parameters to influence the transport properties of mobile carrier in the solid state. The effective on-site Coulomb repulsion energy (U_{eff}^{CT}) is reduced in the solid state and simply approximated by the following equation,

$$U_{eff}^{CT} = U_1^{CT} - U_2^{CT} \qquad (1),$$

where U_2^{CT} represents that between two electrons on neighbouring sites. The larger U_{eff}^{CT} value than the band-width localizes the electron on the molecule.[4] The value of U_{eff}^{CT} can be estimated from the optical or magnetic measurements,[5, 6] but there are no reports for the direct measurement of U_1^{CT} values of organic molecules. However, it has been known that half-wave redox potentials ($E_{1/2}$) can be used to obtain information on the relative magnitude of U_1^{CT} for different molecules provided that the same conditions are used for comparative measurements. Similarly, the electrostatic repulsion energy of two-step PT process (U_I^{PT}) was also considered and this was estimated from the acid dissociation constants (pK_a). The systematic researches for U_I^{CT}, U_I^{PT}, and structural parameters (molecular length and distribution of the π-electron density) induce the design of new electron and/or proton acceptors and donors having an arbitrary magnitude of U_I^{CT} and U_I^{PT} values.

We measured the $E_{1/2}$ and pK_a values of a variety of electron and/or proton acceptors and donors in the same condition. We tried to estimate the U_I^{CT} values of p-benzoquinones (BQs), diphenoquinones (DPQs), TCNQs, p-phenylenediamine (PPD), benzidine (Bz), 1,6-diaminopyrene (DAP), dimethylphenazine (Me_2PHz), tetrathiafulvalenes (TTF), 1,6-dithiapyrene (DTPY), tetrathianaphthacene (TTT), and $H4BIM^0$. The evaluations of U_I^{PT} value were done for $H2BIM^0$ ($H4BIM^{2+}$), hydroquinone (H2Q), 1,4-benzenedimalononitrile (H2TCNQ), and bis(4-hydroxyphenyl) sulfide (HPS) systems as shown in Figure 2.

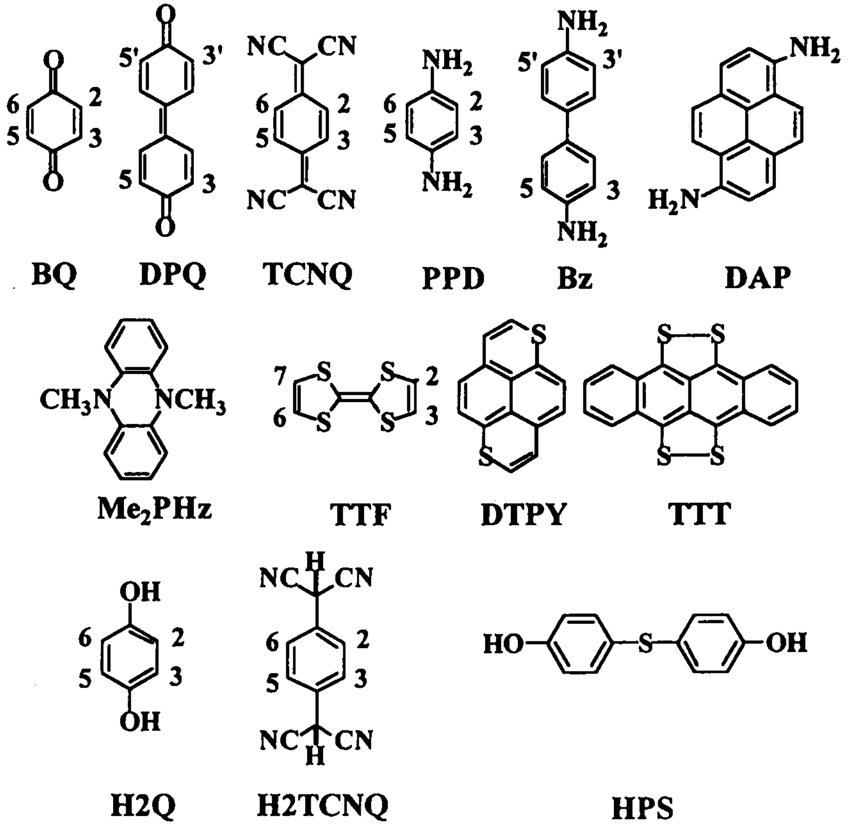

FIGURE 2 Represented molecular structures and abbreviations in this text. The substituted positions were shown as the numbers.

EXPERIMENT

All of materials used in this study were obtained by the method of our preceding paper.[2] The measurements of redox potential were done under the following conditions: solvent, dimethylformamide (DMF); supporting electrolyte, 0.1 M of tetrabutylammonium tetrafluoroborate (TBA•BF_4); scan rate, 100 mVs^{-1}; reference electrode, Ag / AgCl; working and counter electrodes, Pt; temperature, 22 ± 1°C. The titration was done at the following condition: solvent, DMF - H_2O (7 : 3), ion strength 0.1 M, temperature, 22 ± 1°C. The structural parameter (r) is the distance between the centers of gravities of π-electron density ($\Sigma\mu_{\pi i}r_i / \Sigma\mu_{\pi i}$) for a half unit of molecule, which is calculated for neutral donor and dianion states of acceptor based on Pariser-Parr-Pople (PPP) self-consistent field molecular orbital (MO) calculation.

RESULTS AND DISCUSSION

From the experimentally observed $E^1{}_{1/2}$ and $E^2{}_{1/2}$ values of donors and acceptors, the estimation of the $U_I{}^{CT}$ values was done as following procedure. The estimation of $U_I{}^{PT}$ was also done by the similar procedure using the first acid dissociation constant (pK_{a1}) and the second one (pK_{a2}) instead of $E^1{}_{1/2}$ and $E^2{}_{1/2}$. The linear relationship between $E^1{}_{1/2}$ and $E^2{}_{1/2}$ values within a same molecular framework is observed[2], thus the $E^2{}_{1/2}$ is expressed as

$$E^2{}_{1/2} = \alpha E^1{}_{1/2} - \beta \qquad (2).$$

Next, we consider the energy changes of two-step CT processes in the gas phase. The energy changes for the reaction $A^0 + e^- \rightarrow A^{-\bullet}$ and $A^{-\bullet} + e^- \rightarrow A^{2-}$ correspond to $E^t{}_1 - E^t{}_0$ and $E^t{}_2 - E^t{}_1$ where $E^t{}_0$, $E^t{}_1$, and $E^t{}_2$ indicate the total energies of A^0, $A^{-\bullet}$, and A^{2-} species, respectively. Here, the $U_I{}^{CT}$ is defined as a disproportional energy ($U_I{}^{CT} = E^t{}_0 + E^t{}_2 - 2E^t{}_1$) in the reaction $2A^{-\bullet} \rightarrow A^0 + A^{2-}$. On the other hands, in solution we need to consider the term of solvation energy as shown in Equations (3) and (4),

$$E^t{}_1 - E^t{}_0 = -E^1{}_{1/2} - \Delta G_{sol} + C \qquad (3),$$

and

$$E^t{}_2 - E^t{}_1 = -E^2{}_{1/2} - \Delta F_{sol} + C \qquad (4),$$

where ΔG_{sol} (ΔF_{sol}) is the difference in solvation energies for A^0 ($A^{-\bullet}$) and $A^{-\bullet}$ (A^{2-}) molecules, and C is a constant which depends upon the reference electrode.[7, 8] From Equations (3) and (4), the relation of $E^1{}_{1/2}$ and $E^2{}_{1/2}$ is deduced as

$$-E^2_{1/2}(2) = -E^1_{1/2} + (E^t_2 + E^t_0 - 2E^t_1) - \Delta G_{sol} + \Delta F_{sol} \quad (5).$$

ΔF_{sol} was roughly approximated as $3\Delta G_{sol}$ by Hedges and Matsen,[9] and the term in the parenthesis is equal to U_I^{CT}, so Equations (2) and (5) give

$$U_I^{CT} = (1-\alpha)E^1_{1/2} + \beta - 2\Delta G_{sol} \quad (6).$$

The U_I^{CT} value is deduced from the liner relationship of $E^1_{1/2}$ and $E^2_{1/2}$ and constant term of ΔG_{sol}. Using the same procedure, the U_I^{PT} based on the pK_a values is expressed as,

$$U_I^{PT} = -2.303RT(1-\alpha)(pK_{a1}) + 2.303RT\beta - 2\Delta G'_{sol} \quad (7),$$

where R and T are the gas constant and temperature, respectively.

We used the ΔG_{sol} value as -2.2eV from the following reason. Kebarle et al. estimated the ΔG_{sol} values for various sizes and shapes of p-benzoquinone derivatives based on the measured electron affinities and half-wave redox potentials (-2.13 eV: p-chloranil, -2.36 eV: 9,10-anthraquinone, and -2.45 eV: 2,5-$(CH_3)_2$-BQ in DMF).[7] They derived these ΔG_{sol} as a function of $E^1_{1/2}$ values. However, the $E^1_{1/2}$ dependence in ΔG_{sol} and ΔF_{sol} is already included in Equation (2) because the observed α may or may not coincide with unity according to the $E^1_{1/2}$ dependence. The constant term in ΔG_{sol} ($E^1_{1/2} = 0$) is evaluated as -2.196 eV by using the ΔG_{sol} values in Reference 7 and $E^1_{1/2}$ values for the BQ system. Assuming that ΔG_{sol} ($E^1_{1/2} = 0$) is not much different among the systems, sizes, and shapes of molecules under examination, we can represent the relationship between the U_I^{CT} and the $E^1_{1/2}$ values in Equation (6). For the estimation of U_I^{PT}, no precise values of $\Delta G'_{sol}$ for the systems under examination have been measured, unfortunately, so we roughly approximated it by the value for aromatic hydrocarbons (-2.0 eV).[9]

On-site Coulomb Repulsion Energy of CT Processes (U_I^{CT})

The U_I^{CT} values obtained by the above mentioned procedure are summarized in Table I. The results show that each molecular system (BQ, DPQ, and TCNQ) has the same extent of U_I^{CT} values. The plots of $E^1_{1/2}$ and $E^2_{1/2}$ values for two redox processes, $A^0 + e^- \rightleftarrows A^{-\bullet}$ and $A^{-\bullet} + e^- \rightleftarrows A^{2-}$, indicate the good linear correlation of these two redox processes for the BQ, TCNQ, and DPQ systems.[2] From this linearity, we can obtain the U_I^{CT} as shown Equations (8), (9), and (10).

$$U_I^{CT}(BQ) = 0.06E^1_{1/2} + 5.30 \quad (8)$$

$$U_I^{CT}(TCNQ) = 0.06E^1_{1/2} + 4.95 \quad (9)$$

$$U_I^{CT}(DPQ) = 0.06E^1_{1/2} + 4.79 \quad (10)$$

TABLE I U_I^{CT} (eV) of electron acceptors and dications.

Entry	Acceptor a)	U_I^{CT} b)	Entry	Dication a)	U_I^{CT} b)
	BQ System			***TTF System***	
a	2,3-(Cl)$_2$-5,6-(CN)$_2$-BQ	5.33	**A**	bis(trimethylene)-TTF	4.65
b	2,3-(CN)$_2$-BQ	5.32	**B**	(CH$_3$)$_4$-TTF	4.65
c	2,3,5,6-(Cl)$_4$-BQ	5.31	**C**	TTF	4.65
d	2,3,5,6-(Br)$_4$-BQ	5.30	**D**	(ethylenedithio)-TTF	4.54
e	2,3,5,6-(F)$_4$-BQ	5.30	**E**	bis(ethylenedioxy)-TTF	4.54
f	2,5-(Cl)$_2$-BQ	5.29	**F**	(CH$_3$)$_2$-TTF	4.65
g	BQ	5.27	**G**	bis(tetramethylene)$_4$-TTF	4.65
h	2,5-(CH$_3$)$_2$-BQ	5.26	**H**	bis(ethylenedithio)-TTF	4.54
i	1,4-naphthoquinone	5.26	**I**	(CH$_3$S)$_4$-TTF	4.55
j	2,3,5,6-(CH$_3$)$_4$-BQ	5.25	**J**	6,7-(ethylenedithio)-2,3-bis(methoxycarbonyl)-TTF	4.55
	DPQ System			***Diamine System***	
k	3,3',5,5'-(Cl)$_4$-DPQ	4.81	**K**	3,3'-(CH$_3$O)$_2$-Bz	4.57
l	3,3',5,5'-(Br)$_4$-DPQ	4.81	**L**	3,3',5,5,'-(CH$_3$)$_4$-Bz	4.54
m	DPQ	4.78	**M**	*N,N,N',N'*-(CH$_3$)$_4$-Bz	4.54
n	3,3',5,5'-(CH$_3$)$_4$-DPQ	4.77	**N**	3,3'-(CH$_3$)$_2$-Bz	4.58
	TCNQ System		**O**	Bz	4.58
o	2,3,5,6-(F)$_4$-TCNQ	4.99	**P**	2,3,5,6-(CH$_3$)$_4$-PPD	4.73
p	2-F-TCNQ	4.97	**Q**	PPD	4.74
q	TCNQ	4.97	**R**	DAP	4.64
r	2,5-(CH$_3$CH$_2$)$_2$-TCNQ	4.96	**S**	Me$_2$PHz	5.09
s	2,5-(CH$_3$)$_2$-TCNQ	4.96		***Another System***	
t	2,5-(CH$_3$O)$_2$-TCNQ	4.96	**T**	TTT	4.64
u	BTDA-TCNQ c)	4.95	**U**	DTPY	4.64
			V	H4BIM	4.68

a) Molecular structures and substituted positions were indicated in Figure 2. b) ΔG_{sol} = -2.2 (eV) was used for the U_I^{CT} estimations. d) BTDA-TCNQ is the 4,8-bis(dicyanomethylidene)-4,8-dihydrobenzo[1,2-c:4,5-c']bis[1,2,5]thiadiazole.

The 1-α value in Equation (6) is obtained as 0.94 within the experimental error and is less than unity.[10] The β value in Equation (2) of BQ, TCNQ, and DPQ systems decreases in the order of BQ (β = 5.30) > TCNQ (β = 4.95) > DPQ (β = 4.79).

In the BQ system, the strongest acceptor, 2,3-(CN)$_2$-5,6-(Cl)$_2$-BQ, has the highest U_I^{CT} of 5.33 eV and the weakest one, (CH$_3$)$_4$-BQ, has the lowest U_I^{CT} of 5.25

eV within our experimental data. So all BQs in Table I are included within the change of U_I^{CT} of 0.08 eV. For the TCNQ system, the change of U_I^{CT} is much less amount; 0.04 eV. The MO calculations on the U_I^{CT} values have been done by several groups for TCNQ, and it is between 2.33 and 5.44 eV.[11-13] The calculated U_I^{CT} of chloranil is reported as 3.3 and 6.1 eV.[14] Our estimated U_I^{CT} values for TCNQ (4.97 eV) and chloranil (5.31 eV) are within these range.

The same situation can be applied to the two-step electron accepting processes of the dication molecules. There are some molecular series described as the same equations having the slope of 0.94 just as the BQ, TCNQ, and DPQ systems do,[2] so we classified these dications into four representative groups **i** ~ **iv**. **i)** PPD system (P and Q). **ii)** TTF and alkyl substituted TTF (A, B, C, F, and G in addition to T, R, and U). **iii)** BEDT-TTF (bis(ethylenedithio)-TTF) system so called alkylthio (alkyloxy) substituted TTF (E, H, I, and J in addition to K and M). **iv)** Bz system (L, N, O, and D). In addition to these classifications, Me_2PHz^{2+} (S) has large U_I^{CT} value compared with above mentioned system. The $H4BIM^{2+}$ is close to PPD system and its position is far from the usual TTF^{2+} system reflecting the low electron-accepting ability. Its U_I^{CT} value (4.68eV) is close to that of TTF^{2+} (4.65eV). The molecules belong to series **i** ~ **iv** have the U_I^{CT} values in the following order, line BQ (β = 0.90) > TCNQ (β = 0.55) > DPQ (β = 0.39) > PPD (β = 0.31) > TTF (β = 0.19) > Bz (β = 0.16) > BEDT-TTF (β = 0.09).

For the case of diamine molecules, since DAP^{2+} (R) has U_I^{CT} of 4.64 eV and that of Me_2PHz^{2+} (S) is 5.09 eV, the estimated U_I^{CT} values decrease in the order of $Me_2PHz^{2+} > PPD^{2+} > DAP^{2+} > Bz^{2+}$. This order suggests the existence of a correlation between the values of U_I^{CT} and the distances of two nitrogen atoms of dication species. For the case of the TTF system, there is a slight difference between the TTF^{2+} (4.65 eV) and the BEDT-TTF (4.54 eV), the latter group has a smaller U_I^{CT} value than that of the former one.

Electrostatic Repulsion Energy of PT Processes (U_I^{PT})

In the case of two-step PT processes, the charges of molecules vary from neutral, monovalent, to divalent states or vice versa by two-step PT processes; $H2D^0 \rightarrow HD^- + H^+$ ($H2A^{2+} \rightarrow HA^+ + H^+$) and $HD^- \rightarrow D^{2-} + H^+$ ($HA^+ \rightarrow A^0 + H^+$). The individual values of U_I^{PT} at 295 K for the $H2BIM^0$ ($H4BIM^{2+}$), H2TCNQ, H2Q, and HPS systems can be represented as the following equations,

$H2BIM^0$ ($H4BIM^{2+}$) system; $U_I^{PT} = -0.00176(pK_{a1} \text{ or } pK_{a3}) + 4.26$ (11),

H2TCNQ system; $U_I^{PT} = -0.00176pK_{a1} + 4.21$ (12), H2Q system; $U_I^{PT} = -0.00176pK_{a1} + 4.13$ (13),

and

HPS system; $U_I^{PT} = -0.00176pK_{a1} + 4.06$ (14).

The estimated U_I^{PT} values decrease in the order of H2BIM^0 (H4BIM^{2+}), H2TCNQ, H2Q, and HPS systems (Table II). In each system, the differences of U_I^{PT} value are less than 0.02 eV because of its insensitivity to the pK_{a1} or pK_{a3} value.

TABLE II. U_I^{PT} (eV) of H2BIM, H2Q, H2TCNQ, and HPS systems.

Entry	Compounds[a]	U_I^{PT}[b]	Entry	Compounds[a]	U_I^{PT}[b]
	H4BIM^{2+} System		**q**	2,6-$(Cl)_2$-H2Q[c]	4.15
a	$(CH_3)_4$-H4BIM^{2+}	4.27	**r**	2,5-$(Cl)_2$-H2Q[c]	4.15
b	H4BIM^{2+}	4.26	**s**	Cl-H2Q[c]	4.15
c	$(Cl)_4$-H4BIM^{2+}	4.25	**t**	H2Q[c]	4.15
d	$(Br)_4$-H4BIM^{2+}	4.25	**u**	(CH_3O)-H2Q[c]	4.15
e	$(CN)_4$-H4BIM^{2+}	4.25	**v**	(CH_3)-H2Q[c]	4.15
	H2BIM System		**w**	2,5-$(CH_3)_2$-H2Q[c]	4.15
f	$(CH_3)_4$-H2BIM	4.29	**x**	$(CH_3)_3$-H2Q[c]	4.15
g	H2BIM	4.29	**y**	$(CH_3)_4$-H2Q[c]	4.15
h	$(Cl)_4$-H2BIM	4.28		***H2TCNQ System***	
i	$(Br)_4$-H2TBIM	4.28	**A**	F_4-H2TCNQ	4.22
j	$(CN)_4$-H2BIM	4.27	**B**	H2TCNQ	4.22
	H2Q System		**C**	$(CH_3)_2$-H2TCNQ	4.22
k	2,5-$(OH)_2$-3,6-$(NO_2)_2$-H2Q[c]	4.13		***HPS system***	
l	2,5-$(Cl)_2$-3,6-$(OH)_2$-H2Q[c]	4.14	**D**	HPS[d]	4.08
m	2,5-$(OH)_2$-H2Q[c]	4.14	**E**	HPSe[d]	4.08
n	2,3-$(Cl)_2$-5,6-$(CN)_2$-H2Q	4.14	**F**	HPDS[d]	4.08
o	$(Cl)_4$-H2Q	4.15	**G**	HPTB[d]	4.08
p	2,3-$(CN)_2$-H2Q	4.15	**H**	HPTN[d]	4.08

a) Molecular structures and substituted positions were indicated in Figure 2. b) $\Delta G'_{sol} = -2.0$ (eV) was used for the U_I^{PT} estimations. c) Cited from Reference 15. d) Cited from Reference 16.

Relation between On-site Coulomb Repulsion Energy and Structural Parameter (r)

Table III summarizes the r^{-1} and the estimated $U_I^{CT(PT)}$ values. To make the relation between the $U_I^{CT(PT)}$ and r values clear, we added data from the literature for the following molecules; *N,N'*-dicyano-p-benzoquinone diimine (DCNQI),[17] 7,7-dicyano-pbenzoquinonemethide (CNQI),[18] 9,9,10,10-tetracyano-2,6-naphthoquinodimethane (TNAP),[19] 13,13,14,14-tetracyanodiphenoquinodimethane (TCNDQ),[19] 2,5-bis(dicyanomethylidene)-2,5-dihydrothiophene (TCNT),[19] 11,11,12,12-tetracyano-2,7-pyrenoquinodimethane (TCNP),[20] and 2,5-bis(4-oxo-2,5-cyclohexadien-1-ylidene)-2,5-dihydrothiophene (BCDT).[21] And, the data for dicarboxylic acid ($HOOC(CH_2)nCOOH$; DCAR),[22] 4,4'-biphenyldiol (BPH),[23] Bz,[23] and terephthalic acid (PHTH)[23] are compared with U_I^{PT} of H2BIM system.

The relation between the estimated U_I^{CT} and r^{-1} values (Figure 3) clearly divided the examined molecules into two classes: **I**, electron acceptors (open circles) and **II**, dications (closed circles). The roughly linear relationship is observed for these two classes, though there are some exceptions, for example, TCNDQ (b) is near class **II** and BCDT (a) and TCNE (l) are between classes **I** and **II**. Two straight lines, **I** and **II** in Figure 3, the intercepts of which are fixed to 4.4 eV ($= -2\Delta G_{sol}$), are the guides to eyes to distinguish the two classes. It should be noted that a distinct difference exists in the correlation of U_I^{CT} and r^{-1} between electron acceptors (line **I**) and donors (line **II**).

In the acceptor system, the high conducting salts were obtained at about $r^{-1} < 0.18$ range, which is based on highly conducting TCNQ salts, but the DCNQI system is exception case due to the decrease of r^{-1} by the high coordinating character of cyano groups. The value of U_I^{CT} in dication molecule is found to be insensitive to the molecular size. For the sulphur-containing dication molecule, the high conducting complexes were observed at about $r^{-1} < 0.26$ range, TTF is a boundary of this. However, the Bz system has the r^{-1} value of 0.18 which is shorter than 0.25, and is not prefer to give the metallic character. The U_{eff}^{CT} value is reduced by the high polarizability of sulphur atoms,[13] thus the sulphur-containing system is advantageous to be the metallic character compared with nitrogen-containing system.

The values of U_I^{PT} of DCAR system show a linear decrease against the value of r^{-1} in the small r range and tend to saturate in the large r range ($r_c^{-1} > 0.14$). For this system, if two dissociation sites of diacidic base are perfectly independent of each other, for example $n = \infty$ in $HOOC(CH_2)_nCOOH$ molecules, the difference of pK_{a1} and pK_{a2} is equal to 0.6 (= log 4) from a statistical reason.[22] In the short r region, the ratio of K_{a1}/K_{a2} becomes larger than 4 due to the electrostatic repulsion of the two sites. From Equation (7), the U_I^{PT} ($r^{-1} = 0$) is estimated as 4.04 eV from the relation of $pK_{a2} = pK_{a1} + 0.6$.

Approximately, the same feature of U_I^{PT} vs. r^{-1} is seen among H2BIM, H2Q, HPDS, PHTH, BPH, and Bz systems, though the U_I^{PT} value of H2TCNQ system is rather out of the expected point. In the course of our titration measurements of

H2TCNQs in DMF-H_2O (7:3), the colourless solution changes to a slightly-green one in the second acid dissociation process which may suggest instability of the TCNQ^{2-} species. The general features of line **III** of Figure 3 are as follows. The value of U_I^{PT} increases as the decreasing of r value with a weak correlation and the U_I^{PT} values emerge within 4.06 ± 0.02 eV in the region $r^{-1} > 0.14$, while in the $r^{-1} < 0.14$ region the U_I^{PT} values are dominated by the distance r.

TABLE III r^{-1} ($Å^{-1}$) and estimated U_I^{CT} and U_I^{PT} (eV).

Compounds	r^{-1}	U_I^{CT} a)	Compounds	r^{-1}	U_I^{CT} a)
a: BCDT	0.127	4.61	**m**: DTPY	0.177	4.64
b: TCNDQ	0.128	4.55	**n**: BEDT-TTF	0.178	4.55
c: TNAP	0.133	4.77	**o**: Bz	0.179	4.57
d: TCNP	0.145	4.74	**p**: N,N,N',N'-$(CH_3)_4$-Bz	0.179	4.54
e: TCNT	0.180	5.00			
f: TCNQ	0.183	4.97	**q**: TTT	0.189	4.64
g: DPQ	0.187	4.78	**r**: DAP	0.190	4.64
h: CNQI	0.219	4.91	**s**: TTF	0.258	4.65
i: HCBD	0.247	4.94	**t**: H4BIM	0.283	4.68
j: DCNQI	0.270	5.03	**u**: PPD	0.315	4.74
k: BQ	0.327	5.29	**v**: Me_2PHz	0.482	5.09
l: TCNE	0.476	5.20			

Compounds	r^{-1}	U_I^{PT} a)	Compounds	r^{-1}	U_I^{PT} a)
A: H2Q	0.327	4.14	***DCAR System*** b)		
B: H4BIM^{2+}	0.307	4.27	**J**: n = 1	0.286	4.16
C: H2BIM^0	0.271	4.27	**K**: n = 2	0.203	4.09
D: H2TCNQ	0.183	4.22	**L**: n = 3	0.166	4.07
E: HPS	0.141	4.08	**M**: n = 4	0.137	4.06
F: HPSe	0.141	4.08	**N**: n = 5	0.117	4.06
G: HPDS	0.126	4.08	**O**: PHTH	0.203	4.06
H: HPTB	0.103	4.08	**P**: BPH	0.187	4.11
I: HPTN	0.103	4.08	**Q**: Bz	0.179	4.08

a) U_I^{CT} and U_I^{PT} were estimated from Equations (6) and (7) taking the α as 0.94 and 0.97, respectively. b) DCAR is $HOOC(CH_2)_nCOOH$ series and n is the number of methylenes.

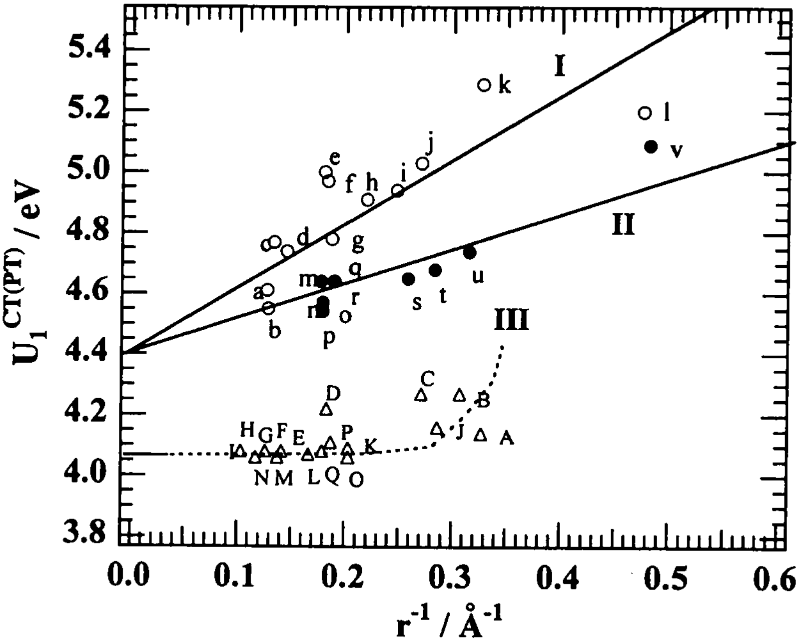

FIGURE 3 The relation between $U_l^{CT(PT)}$ (eV) and r^{-1} (Å^{-1}) for electron acceptors (open circle), dications (closed circle), and proton donor and acceptor (open triangle). The alphabets correspond to these listed in Table III.

SUMMARY

From the linear correlation of $E^1{}_{1/2}$ (pK_{a1}) and $E^2{}_{1/2}$ (pK_{a2}), we evaluated the on-site Coulomb repulsion energy (U_l^{CT} and U_l^{PT}) of two-step CT and PT processes for various types of molecules, including H4BIM^0 and H4BIM^{2+}, and examined the correlation for the molecular structures. The value of U_l^{CT} in H4BIM^0 becomes on the same order of that in TTF and smaller than that of electron acceptors; BQs, TCNQs, and DPQs systems. The distance r between the centers of gravities of π-electron at a half unit of a molecule is correlated to our U_l^{CT} values. As a result, two types of classification can be made, I) electron acceptors and II) dications. For electron acceptors, the degree of change in U_l^{CT} against the r values is bigger than dications. It is disadvantageous for the molecule having large r^{-1} value for the formation of high conducting complex. The boundary of this is estimated as about 0.18 and 0.25 for the acceptor and donor molecules, respectively. The estimation of U_l^{PT} was done for

H2BIM^0 (H4BIM^{2+}), H2Q, H2TCNQ, and HPS systems. The U_I^{PT} of H4BIM^{2+} (4.27 eV) is larger than other examined systems. The values of U_I^{PT} are also related with the distances r, and show saturation in the U_I^{PT} values in the big r region ($r^{-1} >$ 0.14).

ACKNOWLEDGEMENT

This work was partly supported by a Grant-in-Aid for Scientific Research from Ministry of Education, Science, and Culture of Japan, a Grant for the International Joint Research Project from NEDO, Japan.

REFERENCES

1. T.Akutagawa, G.Saito, H.Yamochi, M.Kusunoki, and K.Sakaguchi, Synthetic Metals, 69, 591 (1995).
2. T.Akutagawa and G.Saito, Bull. Chem. Soc. Jpn., 68, 1753 (1995).
3. T.Akutagawa and G.Saito, unpublished results.
4. D.O.Cowan in New Aspects of Organic Chemistry, edited by Z.Yoshida, T.Shiba, and Y.Oshiro (Kodansha Ltd, Tokyo, 1989).
5. A.J.Epstein, S.Etemad, A.F.Garito, and A.J.Heeger, Phys. Rev., B, 5, 952 (1972)
6. J.B.Torrance, Y.Tomkiewicz, and B.D.Silverman, Phys. Rev., B, 15, 4738 (1977).
7. E.P.Grimsrud, G.Caldwell, S.Chowdhury, and P.Kebarle, J. Am. Chem. Soc., 107, 4627 (1985).
8. P.Kebarle and S.Chowdhury, Chem. Revs., 87, 513 (1987).
9. R.M.Hedges and F.A.Matsen, J. Chem. Phys., 28, 950 (1958).
10. E.C.M.Chen and W.E.Wentworth, Mol. Cryst. Liq. Cryst., 171, 271 (1989).
11. J.Ladik, A.Karpfen, G.Stollhoff, and P.Fulde, Chem. Phys., 7, 267 (1975).
12. A.Karpfen, J.Ladik, G.Stollhoff, and P.Fulde, Chem. Phys. Lett., 31, 291 (1975).
13. A.J.Epstein, N.O.Lipari, D.J.Sandman, and P.Nielsen., Phys. Rev., B, 13, 1569 (1976).
14. A.Bieber and J.J.Andre, Chem. Phys., 5, 166 (1974).
15. P.J.Pearce and R.J.J.Simkins, Can. J. Chem., 46, 241 (1968).
16. K.Sugiura, J.Toyota, H.Okamoto, K.Okaniwa, T.Mitani, A.Kawamoto, J.Tanaka, and K.Nakasuji, Angew. Chem., Int. Ed. Engl., 31, 852 (1992).
17. A.Aumuller and S.Hünig, Liebigs Ann. Chem., 165 (1986).
18. S.Iwatsuki, T.Itoh, and H.Itoh, Chem. Lett., 1187 (1988).
19. M.L.Kaplan, R.C.Haddon, F.B.Bramwell, F.Wudl, J.H.Marshall, D.O.Cowan, and S.Gronowitz, J. Phys. Chem., 84, 427 (1980).
20. M.Maxfield, R.Heckendorn, D.O.Cowan, A.M.Kini, and M.Maxfield, J. Am. Chem. Soc., 105, 7017 (1983).
21. K.Takahasi and T.Sakai, Chem. Lett, 157 (1993).
22. P.G.Bonhomme, Bull. Soc. Chim. Fr., 11, 60 (1968).
23. H.S.Harmed and B.B.Owen in The Physical Chemistry of Electrolyte Solution, (Reinhold Publishing Co., New York, 1958).