The Crystal Structure and Intramolecular Electron Transfer of 1′,1‴-Diethylbiferrocenium Triiodide at 298 and 140 K

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The crystal structure of 1′,1‴-diethylbiferrocenium triiodide, $(EtFcFcEt)^+ I_3^-$, was determined by means of X-ray diffraction. The crystals at 298 and 140 K are found to be monoclinic, with the $P2_1/c$ space group and with $Z=2$. At 298 K, $a=9.7557(10)$, $b=9.9772(12)$, $c=13.8216(13)$ Å, $\beta=107.625(9)°$, and $U=1282.18(23)$ Å^3, while at 140 K, $a=9.6931(17)$, $b=9.8065(22)$, $c=13.7373(19)$ Å, $\beta=107.642(15)°$, and $U=1244.4(4)$ Å^3. The structures are refined to $R=0.049$ at 298 K and $R=0.036$ at 140 K. The $(EtFcFcEt)^+$ cations and I_3^- anions sit on a crystallographic center of symmetry both at 298 and at 140 K, and the two ferrocenyl(Fc) units are crystallographically equivalent. The ethyl group in each ethylcyclopentadienyl(EtCp) group is not parallel to the fulvalene moiety, but the terminal CH_3 group moves away with the 60° inclination from the Cp plane. An appreciable interaction seems to exist between the Cp ring of the cation and the I_3^- anion along the $a+c/2$ direction, but the interaction among the cations along the a axis seems to be so weak as to be negligible.

Recently, a number of monooxidized salts of binuclear ferrocene derivatives have been studied in order to clarify the mechanism of the intramolecular electron transfer between the metal atoms through the bridged ligands by measurements of the ^{57}Fe-Mössbauer, IR, and EPR spectra. It has been reported[1,2] that biferrocenium and 1′,1‴-dialkylbiferrocenium (alkyl=ethyl, propyl, butyl) triiodides show the temperature dependences of the valence state of iron atoms. We ourselves have previously reported[3] that the crystal structure of 1′,1‴-dipropylbiferrocenium($Pr^nFcFcPr^n$) triiodide changes from the state of an equivalent set of two Fc units and a triiodide anion with a symmetric I–I–I structure at 298 K to the state of an unequivalent set of ferrocene- and ferrocenium-like units and a triiodide anion with an unsymmetric structure I–I···I, showing positional disorder in the triiodide anions on the (110) plane at 110 K. These results agree with the Mössbauer spectroscopic data, which show a change from two doublets to one doublet around 240 K. On the other hand, 1′,1‴-dihalobiferrocenium salts[4] show no temparature dependence of the valence state of iron atoms. A comparison of the crystal structures of 1′,1‴-diiodo- or 1′,1‴-dibromobiferrocenium cations, which show an averaged valence state, with the structure of 1′,1‴-dichlorobiferrocenium$^+$ cations, which show a trapped valence state, suggests that the valence state of iron atoms is greatly affected by the symmetric or unsymmetric interaction of the triiodide anions with the cations. The Mössbauer spectra of biferrocenium salts[5] show that the transition temperature is lowered by 150 K when the I_3^- anions are replaced with Br_2I^- anions. The crystal structure of biferrocenium triiodide, which shows a trapped valence state at 296 K, indicates that the two Fc units are crystallographically equivalent. The 1′,1‴-diethylbiferrocenium (EtFcFcEt) triiodide shows a transition from the trapped to the averaged valence state around 270 K, as $(Pr^nFcFcPr^n)^+I_3^-$ does around 240 K in the Mössbauer spectra. In the present paper, we will report the crystal structures of $(EtFcFcEt)^+I_3^-$ at 298 and 140 K and discuss the differences in the crystal structures and IR spectra between $(EtFcFcEt)^+I_3^-$ and $(Pr^nFcFcPr^n)^+I_3^-$ in order to elucidate the infuluence of molecular packing and the effects of the triiodide anion and of different substituted groups on the intramolecular electron transfer in the cations and, therefore, on the valence state of iron atoms.

Experimental

X-Ray Measurements. The crystals of $(EtFcFcEt)^+I_3^-$ were kindly supplied by Dr. Seiichi Iijima. A dark-green thin plate crystal was sealed into a Lindemann-glass capillary for the intensity measurements. Preliminary oscillation and Weissenberg photographs taken at room temperature by means of Cu $K\alpha$ radiation showed that the crystal is monoclinic with the space group of $P2_1/c$. The final lattice constants were determined by the least-squares procedure based on the θ values of 33 reflections at 298 K and of 20 reflections at 140 K measured by a diffractometer using Ag $K\alpha$ radiation. The crystal specimen was cooled by a stream of cold N_2 gas surrounded by a warmer N_2 gas curtain. The temperature was controlled electrically at 140±2 K by monitoring with a chromel-almel thermocouple throughout the experiment. The intensities were collected on a Rigaku automated four-circle diffractometer using graphite-monochromated Ag $K\alpha$ radition ($\lambda=0.5609$ Å). Three standard reflections ($10\bar{2}$ 300 020) were measured for every fifty reflections. The intensity data were corrected for Lorentz and polarization effects, but no corrections for absorption and extinction were made. The crystal data and experimental conditions are summarized in Table 1.

Infrared Measurements. The infrared spectra were recorded on a Fourier-transform spectrometer (NICOLET 7199). All samples were prepared as KBr pellets 13 mm in diameter. For the low-temperature measurements, the sample mounted in a holder was cooled by means of a copper plate linked to liquid nitrogen in a Dewar apparatus with KRS-5 windows.

Table 1. Crystal Data
$(Fe_2C_{24}H_{26})^+I_3^-$, M.W. 806.88

Temperature/K	298 Monoclinic	140 Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	9.7557(10)	9.6931(17)
b/Å	9.9772(12)	9.8065(22)
c/Å	13.8216(13)	13.7373(19)
β/°	107.625(9)	107.642(15)
U/Å^3	1282.18(23)	1244.4(4)
Z	2	2
D_x/g·cm^{-3}	2.090	2.153
μ(Ag $K\alpha$)/mm^{-1}	2.48	2.55
Crystal size/mm	0.08×0.20×0.28	0.075×0.23×0.31
Scan method	ω–2θ	ω
$\sin\theta/\lambda_{max}$	0.753	0.682
Independent reflections ($\|F_o\| \geq 3\sigma(F_o)$)	2420	2698
Maximum repeating number	3	1
$R=\sum\|\|F_o\|-\|F_c\|\|/\|F_o\|$	0.049	0.036
$R_2=\{\sum(\|F_o\|-\|F_c\|)^2/\sum\|F_o\|^2\}^{1/2}$	0.070	0.056

Table 2. Positional Parameters for Non-Hydrogen (×10^4, for I, Fe ×10^5) and Hydrogen Atoms (×10^3) in $(EtFcFcEt)^+I_3^-$ at 298 K
For Non-Hydrogen Atoms, $U_{eq}=1/3\sum_i\sum_j U_{ij}a^*_i a^*_j \boldsymbol{a}_i\cdot\boldsymbol{a}_j$

	x	y	z	10^4U_{eq}/Å^2 (298 K)	10^4U_{eq}/Å^2 (140 K)
I(1)	0(0)	0(0)	50000(0)	452(3)	192(2)
I(2)	29658(8)	−8282(8)	59762(5)	605(3)	246(1)
Fe	13387(13)	4562(13)	18701(8)	351(4)	151(2)
C(1)	71(11)	−1120(10)	1165(6)	451(32)	207(17)
C(2)	−324(11)	−706(11)	2038(7)	499(35)	235(18)
C(3)	−731(10)	663(10)	1907(7)	455(32)	215(17)
C(4)	−638(9)	1111(10)	951(6)	423(30)	195(17)
C(5)	−171(9)	−2(9)	471(5)	368(25)	181(16)
C(6)	3430(11)	−157(12)	2201(8)	564(38)	232(18)
C(7)	3052(17)	94(21)	3106(12)	670(54)	255(18)
C(8)	2685(11)	1401(14)	3131(8)	593(42)	251(18)
C(9)	2819(11)	2011(11)	2247(8)	536(37)	241(18)
C(10)	3298(10)	1036(11)	1681(7)	507(34)	213(17)
C(11)	3589(23)	1300(31)	683(14)	876(78)	340(24)
C(12)	5129(17)	1689(20)	832(12)	1188(87)	539(37)
				10^3U/Å^2	
H(C1)	35(10)	−205(10)	107(7)	51(28)	
H(C2)	−19(13)	−154(13)	277(9)	101(43)	
H(C3)	−91(11)	130(11)	234(8)	67(32)	
H(C4)	−83(10)	199(10)	65(7)	49(27)	
H(C6)	386(14)	−82(14)	195(10)	99(47)	
H(C7)	305(17)	−18(17)	336(10)	68(61)	
H(C8)	232(11)	185(11)	351(8)	70(35)	
H(C9)	260(8)	298(9)	212(6)	33(22)	
H(C11a)	360(13)	50(12)	41(10)	72(43)	
H(C11b)	323(19)	176(18)	40(13)	125(87)	

Structure Determination

The position of the Fe and I atoms were deduced from three-dimensional sharpened Patterson maps. The electron density Fourier maps using the phases calculated on the basis of the coordinates of these atoms revealed the position of all the C atoms. Difference Fourier maps were used to locate the position of all the H atoms. The structure was refined by a full-matrix least-squares program RADIEL[6] on the basis of F magnitudes with unit weight for all the reflections. Anisotropic thermal parameters and isotropic thermal parameters were applied to the non-hydrogen atoms and the hydrogen atoms respectively. Atomic scattering factors for the non-hydrogen atoms were taken from International Table for X-Ray Crystallography,[7] and those for H atoms, from the data reported by Stewart et al.[8] The initial atomic

coordinates at 140 K were readily deduced from those at 298 K. Refinements at 140 K were carried out in the same way as those at 298 K. The *R* factors converged to 0.049 at 298 K and to 0.036 at 140 K. The final atomic parameters are given in Table 2.††

Results and Discussion

Description of the Crystal Structure. The projections of the structure along the a and b axes at 140 K are shown in Figs. 1 and 2 respectively. The $(EtFcFcEt)^+$ cations have a trans-configuration, with the two iron atoms on opposite sides with respect to the fulvalene moiety. Both the $(EtFcFcEt)^+$ cations and the I_3^- anions sit on a crystallographic center of symmetry at 298 and 140 K. The presence of the center of symmetry requires two Fc units in a cation which are crystallographically equivalent at both temperatures. The interplanar distances between the two five-membered rings in each Fc unit in the cation and their dihedral angles are, respectively, 3.351 Å and 4.8° at 298 K and 3.355 Å and 4.6° at 140 K. The distances from the iron to the least-squares planes of the two

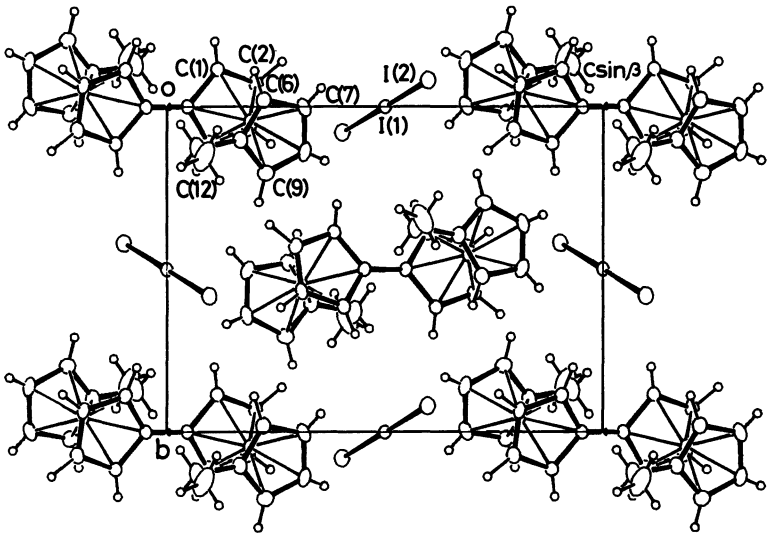

Fig. 1. The projection of the structure at 140 K along the a axis.

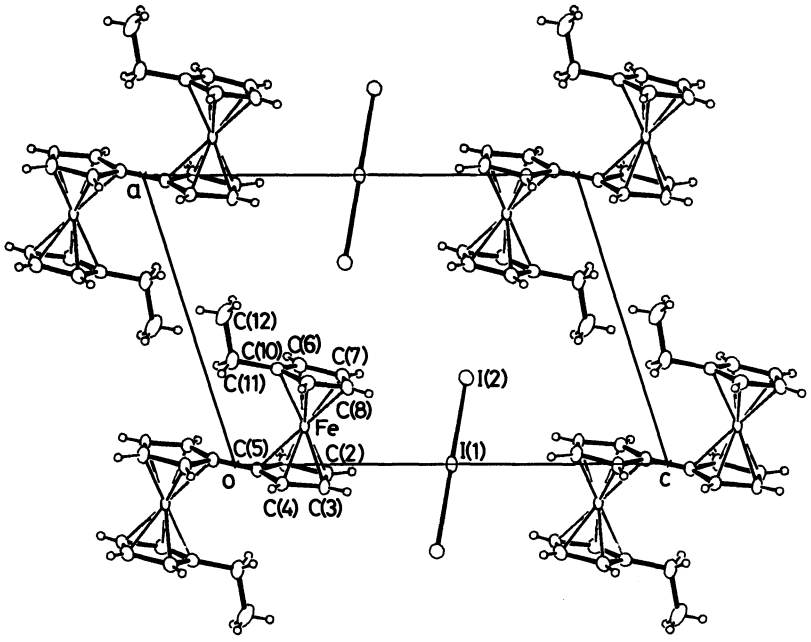

Fig. 2. The projection of the structure at 140 K along the b axis.

†† Lists of the structure factors and anisotropic thermal parameters at 298 and 140 K and the atomic coordinates at 140 K are kept in the Chemical Society of Japan as Document No. 8788.

Table 3. Bond Distances and Bond Angles with e.s.d.'s in Parentheses

(a) Bond distances at 298 and 140 K

	l/Å	l/Å		l/Å	l/Å
Temperature/K	298	140		298	140
I(1)-I(2)	2.917(1)	2.921(1)	C(2)-C(3)	1.418(14)	1.413(9)
Fe-C(1)	2.054(9)	2.062(6)	C(3)-C(4)	1.423(13)	1.422(8)
Fe-C(2)	2.063(11)	2.051(7)	C(4)-C(5)	1.437(13)	1.432(9)
Fe-C(3)	2.046(10)	2.053(6)	C(1)-C(5)	1.443(12)	1.443(8)
Fe-C(4)	2.068(8)	2.079(5)	C(5)-C(5′)	1.439(16)	1.443(12)
Fe-C(5)	2.096(7)	2.094(5)	C(6)-C(7)	1.429(21)	1.438(9)
Fe-C(6)	2.045(11)	2.063(6)	C(7)-C(8)	1.356(25)	1.403(10)
Fe-C(7)	2.028(14)	2.049(5)	C(8)-C(9)	1.406(17)	1.421(9)
Fe-C(8)	2.065(10)	2.064(6)	C(9)-C(10)	1.413(16)	1.431(9)
Fe-C(9)	2.075(10)	2.089(6)	C(6)-C(10)	1.376(16)	1.407(9)
Fe-C(10)	2.088(10)	2.097(6)	C(10)-C(11)	1.513(24)	1.499(10)
C(1)-C(2)	1.435(14)	1.433(9)	C(11)-C(12)	1.504(29)	1.501(14)

(b) Bond angles at 298 K

	φ/°		φ/°
C(2)-C(1)-C(5)	107.8(8)	C(7)-C(6)-C(10)	107.3(12)
C(1)-C(2)-C(3)	107.8(9)	C(6)-C(7)-C(8)	109.3(12)
C(2)-C(3)-C(4)	109.1(9)	C(7)-C(8)-C(9)	107.4(13)
C(3)-C(4)-C(5)	107.7(8)	C(8)-C(9)-C(10)	108.5(10)
C(1)-C(5)-C(5′)	124.6(8)	C(6)-C(10)-C(9)	107.5(10)
C(4)-C(5)-C(5′)	127.5(8)	C(6)-C(10)-C(11)	127.8(12)
		C(10)-C(11)-C(12)	112.1(15)

Primed and unprimed atoms are related by the inversion center at the center of the molecule.

five-membered rings are 1.670(7) and 1.683(3) Å at 298 K and 1.674(3) and 1.684(1) Å at 140 K for inner or fulvalene and outer or ethylcyclopentadienyl(EtCp) rings respectively. The bond distances (298 and 140 K) and bond angles (298 K) are given in Table 3. The mean Fe-C distances are estimated to be 2.065 and 2.060 Å at 298 K and 2.068 and 2.072 Å at 140 K for the inner and the outer rings respectively. These values agree well with the mean Fe-C distances of 2.059, 2.071, and 2.060 Å observed in the $(Pr^nFcFcPr^n)^+$,[3] 1′,1‴-diiodobiferrocenium$^+$,[4] and biferrocenium$^+$[2] cations respectively. The C-C bond distances in the fulvalene moiety are distributed from 1.418(14) to 1.443 (12) Å, with the mean bond distance of 1.431 Å, while those in the cyclopentadienyl(Cp) ring are found in the range from 1.356(25) of C(7)-C(8) to 1.429(21) Å of C(6)-C(7) at 298 K. These large deviations found in the Cp ring are to be ascribed to the interaction between the Cp ring and the I_3^- anion along the $a+c/2$ direction; that is, the linear I_3^- anions come close to the Cp rings, with distances of 3.709 Å (298 K) and 3.641 Å (140 K) from the Cp plane and inclinations of 60.3° (298 K) and 61.1° (140 K) to its plane pointing to the middle of the C(6)-C(7) bond.

It has previously been reported that two Mössbauer doublets converge to one doublet above 270 and 240 K in $(EtFcFcEt)^+I_3^-$ and $(Pr^nFcFcPr^n)^+I_3^-$ respectively, revealing that a trapped valence state, Fe(II) and Fe(III), at low temperatures become an averaged valence state with two iron atoms which cannot be distinguished in the Mössbauer time scale, ca. 10^{-7} s, above the transition temperatures. The results of the Mössbauer spectra of $(EtFcFcEt)^+I_3^-$ require two kinds of valence states of Fe atoms in the Fc units below 140 K in the Mössbauer time scale, while the crystal structure at 140 K indicates that $(EtFcFcEt)^+$ cations sit on the center of symmetry and are crystallographically equivalent, contradicting the results of the Mössbauer spectra. If an electron was hopping between the two Fc units more slowly than the Mössbauer time scale, ca. 10^{-7} s, or was localized in a static state to form Fe(II) and Fe(III), disordering the cations in space, it should be reflected in an unusually high thermal motion and a large anisotropy of each atom, especially those of the Cp rings in the cations. The thermal parameters are, however, very well defined, with equivalent thermal parameters, U_{eq}, in the range from 0.0181(16) to 0.0255(18) Å^2 for C atoms in Cp rings and fulvalene moieties and 0.0192(2) and 0.0246(1) Å^2 for I atoms at 140 K, in comparison with the range from 0.0368(25) to 0.0670(54) Å^2 for C atoms and 0.0452(3) and 0.0605(3) Å^2 for I atoms at 298 K. These values for the C atoms at 140 K correspond to the root mean-square amplitudes from 0.13 to 0.16 Å. The anisotropic temperature factors of U_{11} and U_{22} for all the atoms except the C(9) and C(10) atoms are larger than those of U_{33} at 140 and 298 K respectively, and their U_{11}/U_{33} and U_{22}/U_{33} rations at 140 K become slightly larger than those at 298 K. In 1′,1‴-dibutylbiferrocenium$^+I_3^-$ and 1′,1‴-dichlorobiferrocenium$^+I_3^-$, both with a trapped valence state, Fe(II)-Fe(III), the interplanar distances between two five-membered rings in ferrocene- and ferrocenium-like units are found to be 3.313 and 3.390 Å for the 1′,1‴-dibutylbiferrocenium salt[2] and 3.26 and 3.38 Å for the 1′,1‴-dichlorobiferrocenium salt[4] respectively.

The difference between ferrocene- and ferrocenium-like units is about 0.10 Å, therefore, the displacement in the position of the Cp rings between ferrocene- and ferrocenium-like units is estimated to be about 0.05 Å. The overall amplitude of about 0.15 Å due to the thermal motion of the molecules and the mosaicity of the crystal may sufficiently smear this positional difference.

In $(Pr^nFcFcPr^n)^+I_3^-$, the cations and the anions sit on the crystallographic center of symmetry at 298 K, while the center of symmetry is lost on the (110) plane and two unequivalent Fc units are observed at 110 K. However, if the whole crystal has no center of symmetry, a dipole moment will remain in only one direction. Hence, one ordered structure on the (110) plane and its reversely ordered structure, in which Fe(II) and Fe(III) units in a cation and an I_3^- anion are inverted in relative to the former structure, are stacked at random or in an orderly manner along the $\boldsymbol{a}+\boldsymbol{b}$ direction, and the whole structure should have a center of symmetry. The comparison of the molecular structure and the packing in $(EtFcFcEt)^+I_3^-$ with those in $(Pr^nFcFcPr^n)^+I_3^-$ or biferrocenium$^+I_3^-$ gives an important suggestion with regard to investigating the effect of anions on the electron-transfer process between the two Fc units. The packings of the cations and anions on the (100) plane of $(EtFcFcEt)^+I_3^-$ and biferrocenium$^+I_3^-$ and on the (001) plane of $(Pr^nFcFcPr^n)^+I_3^-$ are the same as that on the (100) plane of the NaCl type, but different inclinations of the two ions in the direction perpendicular to these planes are found because substituent groups give rise to different stacking modes on the (010) plane for $(EtFcFcEt)^+I_3^-$, the $(\bar{1}11)$ plane for biferrocenium$^+I_3^-$, and the (110) plane for $(Pr^nFcFcPr^n)^+I_3^-$ as is shown in Fig. 3. In the $(EtFcFcEt)^+$ cations, the ethyl group of ethylcyclopentadienyl(EtCp) is found not to be parallel to the fulvalene moiety, but the terminal CH_3 moves away with the 60° inclination from the Cp plane, as observed in neutral 1′,1‴-diethylbiferrocene.[9] The ethyl groups in a cation contact ethyl groups in adjacent cations along the a axis in a longer distance than the van der Waals' contact, hence, the intermolecular interaction among cations along the a axis should be very weak, while an appreciable interaction between the Cp ring of a cation and an I_3^- anion is found along the $\boldsymbol{a}+\boldsymbol{c}/2$ direction. In $(Pr^nFcFcPr^n)^+$ cations, the propyl groups of Pr^nCp go parallel to the fulvalene moiety, and a π–π interaction between the Cp rings between the adjacent cations along the c axis is found to exist with the interplanar distance of 3.47 Å, providing a segregated column structure of cations and anions along the c axis. In biferrocenium$^+I_3^-$, an interaction between the Cp rings of adjacent cations and an overlapping between a fulvalene moiety of the cation and an I_3^- anion are observed on the $(\bar{1}11)$ plane. If one Fc unit in a cation has a more positive charge, one of the I atoms in an I_3^- anion in the vicinity of the cation along the $-\boldsymbol{a}+\boldsymbol{b}$ direction will have a more negative charge and one of the I–I bonds in the anion will get a longer bond distance, such as I(1)–I(2)=2.948 Å and I(2)–I(3)=2.902 Å at 110 K in $(Pr^nFcFcPr^n)^+I_3^-$, whereas a symmetric relative position is found with respect to a Fc unit and an I_3^- anion along the $\boldsymbol{c}$ and $\boldsymbol{b}+\boldsymbol{c}$ directions, putting a more negative charge in the central I atom in the I_3^- anion in both $(EtFcFcEt)^+I_3^-$ and biferrocenium$^+I_3^-$. The intermolecular distances between iron and iodine atoms given in Table 4 show the symmetric relative position in $(EtFcFcEt)^+I_3^-$.

The segregated column structrue and the presence of a rotational disorder of propyl group in a Pr^nCp in $(Pr^nFcFcPr^n)^+I_3^-$ may provide the driving force for an ordered structure on the (110) plane with the distinguishable Fe(II) and Fe(III) states observed at 110 K. On the other hand, the presence of isolated cations and the weak interaction between the cations and anions may bring about a disordered symmetric structure of the cations at low temperatures in $(EtFcFcEt)^+I_3^-$.

Infrared Spectroscopy. It is difficult to judge whether both the ground states of the $(EtFcFcEt)^+$ and

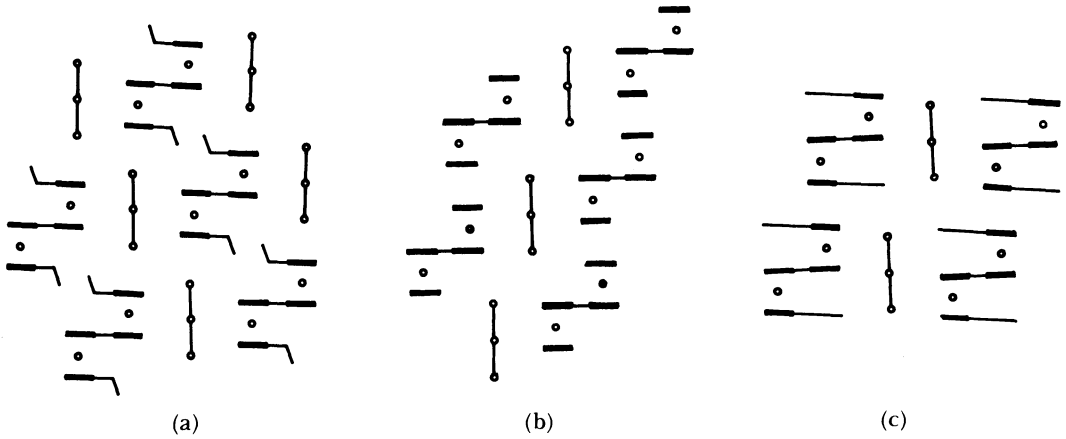

Fig. 3. The stacking models for (a) $(EtFcFcEt)^+I_3^-$, (b) biferrocenium$^+I_3^-$, and (c) $(Pr^nFcFcPr^n)^+I_3^-$.

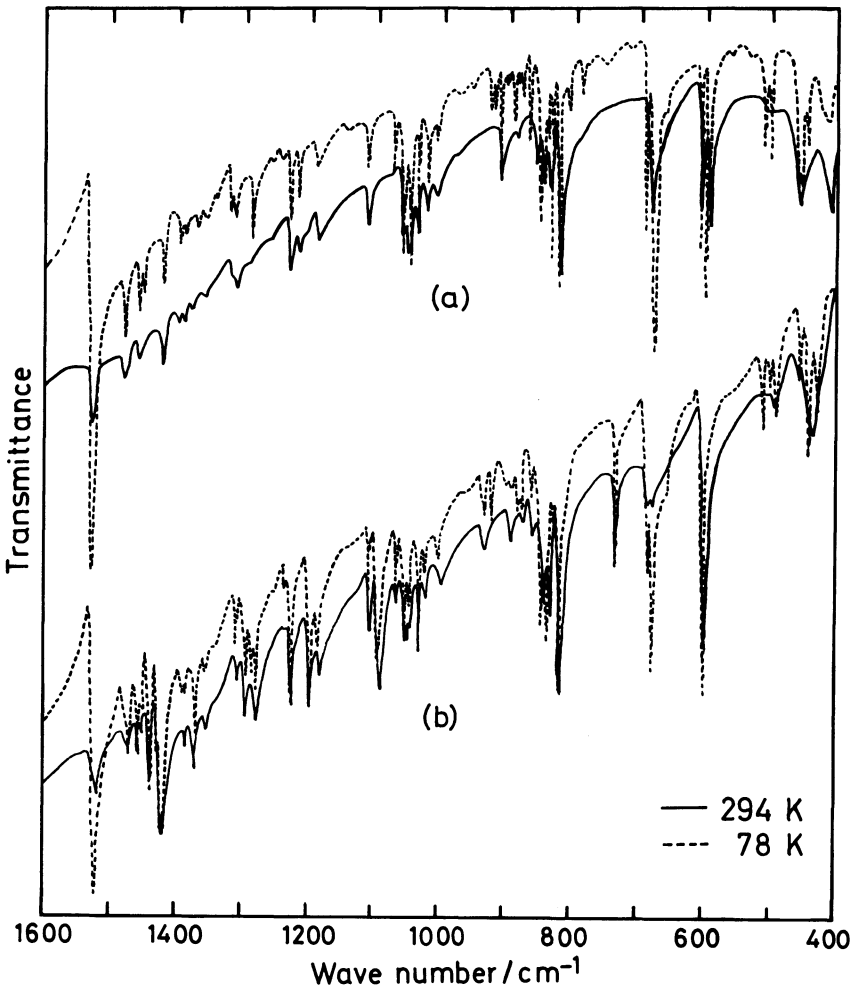

Fig. 4. IR spectra of KBr pellets of (a) 1′,1‴-diethylbiferrocenium$^+I_3^-$ and (b) 1′,1‴-dipropylbiferrocenium$^+I_3^-$.

Table 4. Intermolecular Distances between Iron and Iodine Atoms

Symmetry code
None x, y, z (i) $1-x$, $-y$, $1-z$
(ii) x, $1/2-y$, $1/2+z$ (iii) $-x$, $1/2+y$, $1/2-z$

	l/Å	l/Å
Temperature/K	298	140
I(1)···Fe	4.904(1)	4.843(1)
I(2)···Fe	5.560(1)	5.492(1)
I(2^i)···Fe	5.464(1)	5.395(2)
I(1)···Fe^{ii}	5.186(1)	5.127(1)
I(2)···Fe^{ii}	5.828(2)	5.747(2)
I(2^i)···Fe^{ii}	6.070(1)	6.050(1)
I(1)···Fe^{iii}	5.998(1)	5.912(2)
I(2^i)···Fe^{iii}	5.153(1)	5.114(2)

$(Pr^nFcFcPr^n)^+$ cations at 300 K are to be ascribed to the complete delocalization of the electrons or to the rapid intramolecular electron hopping. The IR spectra of $(EtFcFcEt)^+I_3^-$ and $(Pr^nFcFcPr^n)^+I_3^-$ at 294 and 78 K are illustrated in Fig. 4. Strong, new bands are observed in the vicinity of 680 and 1525 cm^{-1} in the IR spectra when the neutral $Pr^nFcFcPr^n$, EtFcFcEt, 1′,1‴-diiodo-, 1′,1‴-dibromo-, and 1′,1‴-dichlorobifferocene[4] are monooxidized. Moreover, the intensities of these two bands are very strong in their trapped valence states, while they become weak in their averaged valence states, judging from the Mössbauer spectra. The single bands at 700 and 703 cm^{-1}, observed in the IR spectra[10] of fulvalene(Cp_2) and carbene(Cp) respecively, are assigned to an out-of-plane C–H deformation. Two new bands around 680 cm^{-1} may be the same bands as those for the Cp and fulvalene moieties. The intensity of the single band at 1525 cm^{-1} is unusually strong in the trapped valence states. The C=C skeletal stretching vibrations are observed from near 1500 to 1600 cm^{-1} in aromatic compounds. The fulvalene has a center of symmetry in the unoxidized compounds, but loses it in monooxidized cations if the cations are not in a delocalized ground state. Hence, the band at 1525 cm^{-1} may be assigned to a C=C stretching mode of the fulvalene ring, and the coupling of this vibration mode with the electrons distributed unsym-

metrically in the fulvalene moiety may be considered to give rise to the unusually strong intensity at 78 K. On the other hand, this band does not vanish at 294 K. This indicates that the hole of the cation in the averaged-valence state is not completely delocalized.

Conclusion

Alkyl groups in the monooxidized biferrocenium derivatives affect the packing between the cations and anions, and the different interaction of anions with cations gives a different phase transition temperature. The electronic state of cations will couple with a phonon mode because a positive charge of a cation and a negative charge of an anion attract each other. However, in 1′,1‴-dibromo- and 1′,1‴-diiodobiferrocenium$^+I_3^-$, a strong intramolecular interaction resulting from the overlap between the iodine or bromine group and one of the Cp rings of the fulvalene moiety will generate an averaged valence state, even at a low temperature.

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