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^{129}I Mössbauer Spectroscopic Studies of Tetrathiafulvalene-Iodine Charge-Transfer Salts

Hiroshi SAKAI,* Manabu MIZOTA,† and Yutaka MAEDA
Research Reactor Institute, Kyoto University,
Kumatori-cho, Sennan-gun, Osaka 590-04

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The Mössbauer effect of ^{129}I has been applied to investigate tetrathiafulvalene-iodine (TTF-I_n) charge-transfer salts at 16 K. The electrically conductive TTF-$I_{0.71}$ salt shows a broad single-line with the isomer shift of -0.36 mm s^{-1}, suggesting that the iodine atoms on the average are not completely ionic ($I^{-1.0}$) but are negatively charged by about 0.9 ($I^{-0.9}$) in the low temperature phase. This is due to the weak interactions of the iodine atoms with the sulfur atoms of the TTF molecules. This fact is consistent with the crystallographic data and the electron spin resonance spectra of the salt. This salt is recognized as a partially oxidized mixed-valence compound. The spectrum of the TTF-I_3 salt consists of two sets of quadrupole octets, corresponding to the central and terminal iodine atoms of the slightly distorted I_3^- ion. The charge density localized on each iodine atom of the I_3^- ion is close to that of the isolated I_3^- ion. That is, the salt is regarded as a simple ionic compound, for which a high electrical conductivity can not be expected. It is confirmed that a small amount of the TTF-I_2 salt coexists in the TTF-$I_{0.71}$ phase obtained from the solution of excess TTF and iodine. In the salt the iodine atoms exist as polyiodides consisting predominantly of I_3^- units.

Tetrathiafulvalene (TTF) is a good π-electron donor which forms highly conductive charge-transfer complexes (or salts) with various electron acceptors. The high electrical conductivity arises from the segregated donor and/or acceptor stacks and the incomplete charge-transfer from the donor to the acceptor. In the TTF-iodine system three phases have been confirmed by X-ray diffraction: TTF-$I_{0.71}$ (monoclinic),[1,2] TTF-I_2 (orthorhombic),[3] and TTF-I_3 (monoclinic).[4] However, the crystal structure of the TTF-I_2 phase is not yet established in detail. In the monoclinic TTF-$I_{0.71}$ salt, the dc conductivity at room temperaure is observed to be ≈400 S cm^{-1} along the needle c-axis, which is comparable to that of TTF-TCNQ (TCNQ, tetracyano-*p*-quinodimethane).[3,5] The salt exhibits a phase transition near 210 K between the metallic (high temperature) phase and the semiconductive (low temperature) phase. The crystallographic data of the salt in the metallic phase suggest that the TTF molecules form segregated stacks along the c-axis with an intermolecular separation of about 3.56 Å and the iodine atoms, probably iodide ions I^-, occupy the channels between the TTF stacks.[1,2] Preliminary X-ray results of the salt at low temperature reveal no major change in crystal structure.[3] According to Ref. 3, the room-temperature conductivity for the orthorhombic TTF-I_2 salt is found to be ≈10^{-3} S cm^{-1} along the TTF stacking axis. The iodine atoms seem to exist as small polyiodide species, probably predominately triiodide ion I_3^-. In the monoclinic TTF-I_3 salt,[4] the TTF molecules do not form segregated stacks but exist as completely oxidized $(TTF)^+$ dimers interspersed between pairs of triiodide ions. The electrical conductivity of the salt is observed to be ≈10^{-9} S cm^{-1} at room temperature, as one would expect from the crystal structure.

It is important to estimate the degree of charge-transfer and interactions between the TTF molecules and the iodine atoms in order to understand the electrical properties of these TTF-iodine salts. The ^{129}I Mössbauer spectroscopy is a powerful method for this purpose. The Mössbauer parameters such as the quadrupole coupling constant (e^2Qq), the asymmetry parameter (η), and the isomer shift (δ), are directly related to the charge distribution and the charge density of the iodine atom. Previously ^{129}I Mössbauer spectroscopy has been successfully applied to iodine complexes or salts exhibiting high electrical conductivity: perylene-iodine,[6,7] metal glyoximate-iodine,[8,9] metal phthalocyanine-iodine,[8,10] and oligoaniline-iodine.[11] The Mössbauer spectrum of the TTF-$I_{0.71}$ salt has been measured, but the detailed analysis and discussion are not given.[8] In this paper we report the results of the ^{129}I Mössbauer spectroscopic study of the TTF-$I_{0.71}$ and TTF-I_3 salts. The Mössbauer data of the TTF-I_2 salt coexisting in the TTF-$I_{0.71}$ phase are also presented.

Experimental

Materials. The commercially available TTF (Aldrich Chemical Co.) was recrystallized from cyclohexane. The radioisotope ^{129}I, in the standard from of Na ^{129}I in a Na_2SO_3 solution (New England Nuclear Co.), was oxidized with 3 mol dm^{-3} H_2SO_4 and 10% H_2O_2, and the resulting molecular iodine ($^{129}I_2$) was extracted with benzene. The iodine solution was thoroughly washed with water and passed through a Teflon filter to eliminate any slight amount of water. The ^{129}I-labeled TTF-iodine salts were prepared on a small scale by mixing together benzene

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† Present address: Mitsubishi Fusion Center, Mitsubishi Denki Bldg, 2-3, Marunouchi 2-Chome, Chiyoda-ku, Tokyo 100.

solutions of TTF and iodine ($^{129}I_2$) with the prescribed mole ratios. A precipitate obtained from the solution with a composition of TTF:I=1:0.71 contains the TTF–$I_{0.71}$ salt and small amounts of another salt, probably TTF–I_2. Therefore, the precipitate was recrystallized from acetonitrile. The iodine contents of the TTF–iodine salts were checked on nonradioactive (natural iodine) preparation samples by elemental analysis: Found; C, 24.52; H, 1.28; I, 30.38%. Calcd for TTF–$I_{0.71}$:C, 24.48; H, 1.37; I, 30.60%. Found: C, 11.79; H, 0.67; I, 66.31%. Calcd for TTF–I_3:C, 12.32; H, 0.69; I, 65.07%. No pure TTF–I_2 salt could be isolated by recrystallization from acetonitrile.

Measurements. A single-line $^{66}Zn^{129}Te$ Mössbauer source was prepared by irradiating 140 mg $^{66}Zn^{128}Te$ at a thermal neutron fluence rate of 2×10^{13} n cm^{-2}s^{-1} for 1 h in the Kyoto University Reactor (KUR). The source was checked by the spectrum against a single-line Cu ^{129}I absorber (10 mg ^{129}I cm^{-2}). The line width at half maximum was found to be 1.12 mm s^{-1} for the single absorption peak. The isomer shift of Cu ^{129}I was −0.42 mm s^{-1} for the source, which is in good agreement with the literature.[12] Measurements were carried out in a transmission geometry by cooling the source and the absorber to 16 K in the same way as reported previously.[11]

Results and Discussion

^{129}I Mössbauer spectra of the recrystallized TTF–$I_{0.71}$ (absorber thickness; 12 mg ^{129}I cm^{-2}) and TTF–I_3 (13 mg ^{129}I cm^{-2}) salts at 16 K are shown in Fig. 1(a) and (c), respectively. The former shows only a single absorption peak (no quadrupole hyperfine splitting), while the latter consists of two kinds of quadrupole octets. Figure 1(b) shows the spectrum of a precipitate (29 mg ^{129}I cm^{-2}) obtained from the benzene solution with a composition of TTF:I=1:0.71. The spectrum evidently consists of one singlet and two different quadrupole octets. These spectra were analyzed by the least-squares method. The solid curves in the figure represent the best-fitted Lorentzian spectra and the dashed curves indicate their components. Table 1 gives the Mössbauer parameters obtained such as the quadrupole coupling constant (e^2Qq) and its sign, the asymmetry parameter (η), the isomer shift (δ), and the line width (2Γ). Included inTable 1 for comparison are results of the isolated I_3^- ions in the $[Ru(\eta\text{-}C_5H_5)_2I]I_3$[13] and β-carotene–I_3[14] complexes and of I_3^- chains in the *N,N′*-diphenyl-*p*-phenylenediamine-iodine (DPPD–I_x) and *N,N′*-diphenylbenzidine-iodine (DPB–I_x) complexes.[11]

TTF–$I_{0.71}$ Salt. The single-line spectrum of TTF–$I_{0.71}$ with the small δ value suggests that the iodine atom exists almost as an ionic I^- ion. This result is in good agreement with that of Marks.[8] However, the δ value (=−0.36±0.05 mm s^{-1}) for this salt is slightly larger than that for the typical I^- ion in the KI crystal (δ=−0.51±0.025 mm s^{-1}).[15] This implies that a slight amount of covalency is present between the I^- ion and the TTF molecules. According to the detailed crystallographic data of the salt,[2] each iodine atom has four sulfur neighbors and there are two characteristic coordination geometries; a distorted tetrahedron and a distorted square planar. The I···S bond distances for both coordination geometries are in the range of 3.56 to 3.79 Å, less than the sum of the respective van der Waals radii (4.0 Å). Furthermore, the presence of the interaction between the iodine and the sulfur atoms has been suggested from the *g* value and the line width of the ESR spectra of the salt.[16]

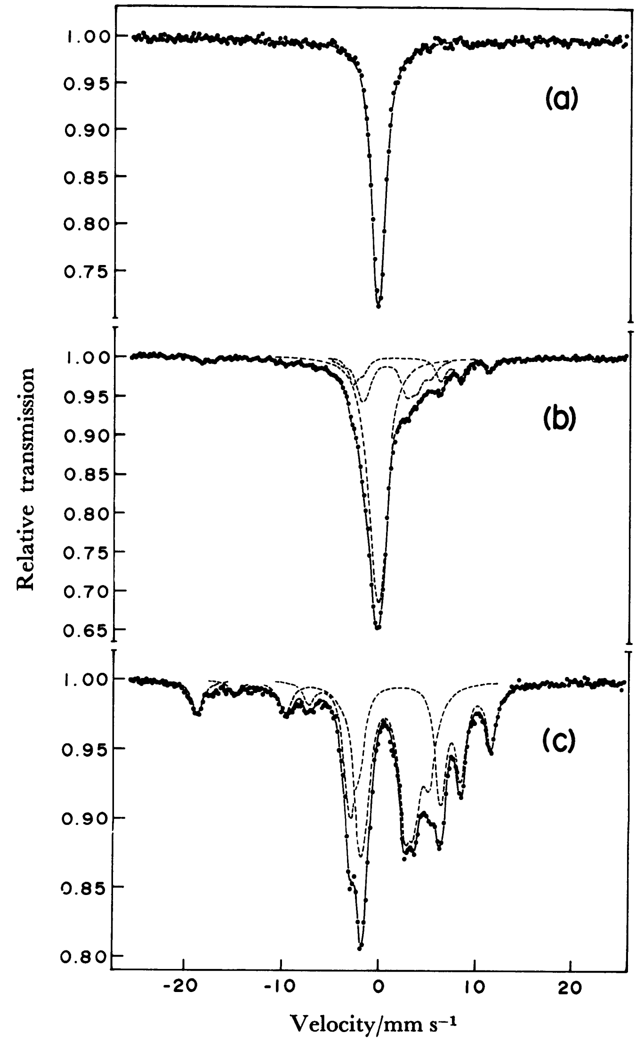

Fig. 1. ^{129}I Mössbauer spectra at 16 K of (a) the TTF–$I_{0.71}$ salt recrystallized from acetonitrile, (b) the precipitate obtained from the benzene solution with composition of TTF: I=1 : 0.71 (shows the presence of the TTF–$I_{0.71}$ and TTF–I_2 salts), and (c) the TTF–I_3 salt.

The charge density on the iodine atom can be evaluated from the semiempirical relation as follows;[12]

$$\delta(\text{mm s}^{-1}) = -9.2\,h_s + 1.5\,h_p - 0.54 \quad \text{(for ZnTe source)}, \qquad (1)$$

where h_s and h_p are the numbers of 5s- and 5p-electron holes, respectively, in the $5s^25p^6$ configuration. Therefore, the h_p is expressed as

Table 1. ^{129}I Mössbauer Parameters for the Tetrathiafulvalene-Iodine Charge-Transfer Salts, $[\mathrm{Ru}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{I}]\mathrm{I_3}$, β-Carotene-$\mathrm{I_3}$, and the Oligoaniline-Iodine Complexes

		e^2Qq[a)] / MHz	η	δ[b)] / mm s^{-1}	2Γ / mm s^{-1}	Area[c)] Ratio	U_p[d)]	h_p[e)]	Ref.
TTF-$\mathrm{I_{0.71}}$		$+\ 130\pm25$[f)]	—	-0.36 ± 0.05	1.12[f)]		0.05	0.12	*
TTF-$\mathrm{I_2}$	$\mathrm{I_c}$	-2285 ± 25	0.06 ± 0.04	1.18 ± 0.05	1.41 ± 0.10	1.0	1.00	1.15	*
	$\mathrm{I_t}$	-1060 ± 25	0.05 ± 0.04	0.15 ± 0.05	1.64 ± 0.10	1.6	0.46	0.46	*
TTF-$\mathrm{I_3}$	$\mathrm{I_c}$	-2336 ± 25	0.05 ± 0.04	1.32 ± 0.05	1.31 ± 0.10	1.0	1.02	1.24	*
	$\mathrm{I_t}$	-1153 ± 25	0.06 ± 0.04	0.18 ± 0.05	1.48 ± 0.10	1.6	0.50	0.48	*
$[\mathrm{Ru}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{I}]\mathrm{I_3}$	$\mathrm{I_c}$	-2460 ± 25	0.06 ± 0.04	1.48 ± 0.05	0.83 ± 0.08	1.0	1.07	1.35	13
	$\mathrm{I_t}$	-1152 ± 25	0.06 ± 0.04	0.25 ± 0.05	0.85 ± 0.08	1.6	0.50	0.53	
β-Carotene-$\mathrm{I_3}$	$\mathrm{I_c}$	-2445 ± 20	0.05 ± 0.04	1.59 ± 0.04	1.04 ± 0.10	1.0	1.07	1.42	14
	$\mathrm{I_t}$	-1152 ± 20	0.06 ± 0.04	0.23 ± 0.04	1.20 ± 0.10	1.4	0.50	0.51	
DPPD-$\mathrm{I_{2.4}}$	$\mathrm{I_c}$	-2347 ± 20	0.05 ± 0.04	1.32 ± 0.04	1.00 ± 0.06	1.0	1.02	1.24	11
	$\mathrm{I_t}$	-1183 ± 20	0.04 ± 0.04	0.25 ± 0.04	0.93 ± 0.06	1.6	0.52	0.53	
DPB-$\mathrm{I_{2.7}}$	$\mathrm{I_c}$	-2282 ± 20	0.10 ± 0.04	1.35 ± 0.04	1.09 ± 0.06	1.0	1.00	1.26	11
	$\mathrm{I_t}$	-1166 ± 20	0.06 ± 0.04	0.22 ± 0.04	1.60 ± 0.06	1.7	0.51	0.51	

a) The e^2Qq values are converted to the ^{127}I nucleus. b) The δ values are relative to the ZnTe source. c) The ratios are normalized with respect to the $\mathrm{I_c}$ atom. d) $U_p=-e^2Qq_{\mathrm{obsd}}/e^2Qq_{\mathrm{atom}}$, $e^2Qq_{\mathrm{atom}}=2292.7$ MHz. e) $\delta=1.5\,h_p-0.54$ (mm s^{-1}). f) The e^2Qq value is obtained by analysis with a fixed line width (1.12 mm s^{-1}).
* The errors quoted in this work include estimated systematic errors.

$$h_p = 6 - (N_x+N_y+N_z), \tag{2}$$

where N_x, N_y, and N_z are the populations of the 5p-electrons in the x, y, and z orbitals, respectively. If only 5p-electrons take part in bond formation, the h_p value is calculated to be 0.12 from the δ value. This implies that the iodine atom on the average is negatively charged by 0.88 in the TTF-$\mathrm{I_{0.71}}$ salt. The average covalency per I···S bond is, therefore, found to be 3%. The e^2Qq value is affected only a little by the slight covalency. In the tetrahedral coordination geometry the e^2Qq value would be zero, regardless of the extent of covalency. In the case of the square planar geometry, the contribution of the covalency to e^2Qq may be calculated on the basis of the Townes and Dailey approximation as follows;[12)]

$$U_p = -e^2Qq_{\mathrm{obsd}}/e^2Qq_{\mathrm{atom}} = -N_z + (N_x+N_y)/2, \tag{3}$$

where U_p is the number of unbalanced p-electrons and e^2Qq_{atom}, the atomic iodine quadrupole coupling constant. The latter is equal to 2292.7 MHz for the ^{127}I nucleus. Since the z principal axis (V_{zz}) of the electric field gradient (EFG) tensors lies along the four-fold axis in the square planar coordination, the 5pz orbital has two nonbonded electrons, i.e., N_z=2.00. Substituting the values of h_p and N_z into Eq.2, one obtains N_x=N_y=1.94. If all iodine atoms are surrounded in a square planar configuration by four sulfur atoms, the covalency of 3% for each I···S bond leads to +138 MHz for e^2Qq from Eq. 3. However, the crystallographic results of the salt suggest that about 40% of the iodine atoms have a distorted square planar coordination and the residual 60% have a distorted tetrahedral coordination.[2)] Therefore, the spectrum of the salt should have two components corresponding to two kinds of iodine atoms, one in a distorted square planar arrangement and the other in a distorted tetrahedron. Unfortunately, since the resolution of the Mössbauer spectrum of ^{129}I is not very high, it may be difficult to distinguish between them.

The line width of the spectrum is apparently broad compared with that of Cu ^{129}I with nearly the same absorber thickness. The broadening is mainly due to the slight covalency of the I···S bonds described above. When the spectrum was analyzed with the fixed line width (1.12 mm s^{-1}) determined from the single-line spectrum of Zn^{129}Te vs. Cu^{129}I and with the theoretical intensity ratios obtained from the square of the Clebsch-Gordan coefficient $|\mathrm{CG}|^2$, the e^2Qq value was found to be 130 MHz. If a larger line width, due to the saturation effect, is used for the analysis, this value would further decrease. The e^2Qq value obtained from the broadening of the line-width is in good agreement with that predicted from the δ value within experimental error. It is concluded that on the average the iodine atom in the TTF-$\mathrm{I_{0.71}}$ salt is not completely ionic ($\mathrm{I^{-1.0}}$), but is negatively charged by about 0.9 ($\mathrm{I^{-0.9}}$) in the low temperature (semiconductive) phase (16 K). The average covalency per I···S bond is estimated to be 3%, which is likely from the I···S bond distances. The ^{129}I Mössbauer spectrum in the high temperature (metallic) phase of the salt is important and interesting in order to understand the phase transition near 210 K. Unfortunately, because of a significant decrease in the Mössbauer resonance absorption, the measurement of the spectrum could not be performed above 210 K.

TTF-$\mathrm{I_3}$ Salt. The Mössbauer spectrum of the TTF-$\mathrm{I_3}$ salt is similar to those of the linear triiodide anions observed in the β-carotene-$\mathrm{I_3}$,[14)] DPPD -$\mathrm{I_x}$, and

DPB–I_x complexes.[11] The crystallographic data of the salt have revealed that the iodine atoms exist as a slightly distorted triiodide anion.[4] The bond distances between the iodine atoms in the asymmetric triiodide anion are 2.907 and 2.953 Å, respectively, while the bond angle ∠I–I–I of 175.40° deviates slightly from linearity. The distances between two terminal iodine atoms and sulfur atoms of the TTF molecules are in the range of 3.636 to 3.989 Å, suggesting weak intermolecular interactions. By analogy with the Mössbauer spectra of the other I_3^- ions, it is appropriate to assign the iodine with the larger quadrupole splitting to the central iodine atom (I_c), and the other splitting to the two terminal iodine atoms (I_t). A slight broadening of the line width has been observed for I_t compared with that for I_c, suggesting that the charge densities on the two I_t atoms are slightly different from each other, i.e., the I_3^- ion is slightly asymmetric. This is consistent with the result of the crystal structure. Therefore, the values of e^2Qq, η, and δ given in Table 1 are the means of those for two I_t atoms. The absorption area ratio of I_t and I_c was found to be 1.6:1, which is close to the values obtained for the other I_3^- ions in the $[Ru(\eta\text{-}C_5H_5)_2I]I_3$ and β-carotene–I_3 complexes, as shown in Table 1. The deviation from the composition ratio of 2:1 in the I_3^- ion is due to the differences in the recoilless fraction and in the saturation effect, as discussed in our previous paper.[11] The small η value for the I_c atom is in accord with the fact that the I_3^- ion is almost linear. The bond angle of 175.40° leads to only 0.01 for η, assuming that two I_t atoms are equivalent. In this case e^2Qq for I_c is negative in sign and the z principal axis (V_{zz}) of the EFG tensors lies along the direction of the bonding axis. The small η value for the I_t atoms implies that the interaction is little present between the I_t atoms and the sulfur atoms of the TTF molecules.

The charge density of 5p-electrons localized on each iodine atom can be estimated from the values of δ and e^2Qq using Eqs. 1—3. The U_p value is close to the h_p value on the average for two I_t atoms of the asymmetric I_3^- ion. This suggests that the bonding of I_t is mainly due to $5p_\sigma$-electrons. If $5p_\pi$ -electrons take part in an intra- or intermolecular bond formation, the relationship $U_p < h_p$ is generally observed. Therefore, the I_t atoms are unlikely to be interacting with sulfur atoms of the TTF molecules, consistent with the small η value. The I_t atom of the salt is negatively charged by about 0.50 e^- on the average due to the values of U_p and h_p. This charge density on the terminal iodine atom is in good agreement with that of the usual isolated I_3^- ion. For the I_c atom the h_p value is larger than the U_p value, which is always found in the I_c atoms of the other I_3^- ions, as shown in Table 1. This phenomenon has been successfully explained on the basis of the contribution of the core $4d_\sigma$-electrons, on the I_c atom, to the linear I_3^- bond formation, in addition to the delocalized three-center four-electron bonding scheme.[11,17] Consequently the charge density localized on the I_c atom of the I_3^- ion is computed to be +0.01 e^- from the values of δ and e^2Qq using Eqs. 4 and 5 of Ref. 17. The charge density is close to that on the I_c atom of the successive I_3^- chain in the DPPD–$I_{2.4}$ complex rather than to that on the isolated I_3^- ion. This seems to be attributed to the fact that the I_3^- ion in the TTF–I_3 salt is slightly asymmetric and bent. It is concluded that the iodine atoms of the TTF–I_3 salt exist as an almost isolated I_3^- ion and the interaction of the I_3^- ion with sulfur atoms of the TTF molecules is extremely weak. Since the TTF–I_3 salt is regarded as a simple ionic compound, a high electrical conductivity is not expected for the salt, consistent with the observed conductivity ($\approx 10^{-9}$ S cm^{-1}).[4]

TTF–I_2 Salt. A precipitate obtained from the solution with a composition of TTF:I=1:0.71 showed a complicated spectrum consisting of one broad singlet and small amounts of two different quadrupole octets, as shown in Fig. 1(b). If the broad single-line spectrum corresponds to the iodine of the TTF–$I_{0.71}$ salt, the δ value actually agrees well with that of TTF–$I_{0.71}$, the residual two quadrupole octets must arise from iodine species of another TTF–I_n salt. The Mössbauer parameters of the iodine species are evidently different from those of the TTF–I_3 salt, though of lower precision because of the weak intensities and the broad line widths of the iodine species. Warmack et al.[3,18] have reported that two different types of charge-transfer crystals are formed by slow diffusion of TTF and iodine in acetonitrile: monoclinic TTF–$I_{0.71}$ (needles) and orthorhombic TTF–I_2 (flat platelets). In the latter TTF–I_2 form the iodine columns seem to contain small polyiodide species, probably predominantly I_3^-. It is reasonable to assume that the unknown iodine species corresponds to the I_3^- unit of the TTF–I_2 salt. That is, the iodine with the larger quadrupole splitting can be assigned to the central iodine atom (I_c) of the I_3^- unit, whereas the other to the two terminal iodine atoms (I_t), in analogy with the I_3^- ion of the TTF–I_3 salt. However, the values of e^2Qq and δ for the I_3^- unit of TTF–I_2 are considerably different from those for the isolated I_3^- ion of TTF–I_3, as shown in Table 1. Further, the line widths are very broad for the I_3^- unit. The optical data for the salt have suggested the presence of monomers (I^-) and dimers (I_2) in the iodine columns, in addition to the trimers (I_3^-).[18] Accordingly, the I_3^- units in the polyiodides containing the I_3^-, I_2, and I^- species are presumably distorted significantly compared with the symmetric isolated I_3^- ion. Furthermore, the spectrum of the dimer (for free iodine molecule, $e^2Qq=-2250\pm30$ MHz, $\delta=+0.94\pm0.05$ mm s^{-1} [19]) present in the polyiodide may be superimposed on that of the I_c atom in the I_3^- unit. The spectrum of the monomer, of course, can not be distinguished from that of the coexisting TTF-$I_{0.71}$ salt. These effects may complicate the spectrum of the I_3^- unit present in the TTF-I_2 salt, and then the spectrum may not permit a quantitative discussion of the charge density of the iodine species. It is concluded that the TTF-I_2 salt is formed from the benzene solution of excess TTF and iodine, in addition to the TTF-$I_{0.71}$ salt. The iodine atoms in the iodine columns of TTF-I_2 exist as polyiodides consisting predominantly of I_3^- units. These results are consistent with the crystallographic data and the optical data of the TTF-I_2 salt.

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