1016 © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 1016—1020 (1983) [Vol. 56, No. 4

^{129}I Mössbauer Effect in Several π-σ Charge Transfer Complexes of Iodine

Hiroshi Sakai,* Tomochika Matsuyama, Hitoshi Yamaoka, and Yutaka Maeda
Research Reactor Institute, Kyoto University, Kumatori, Sennan-gun, Osaka 590-04

(Received September 6, 1982)

The ^{129}I Mössbauer spectra at 16 K have been measured for the π-σ charge transfer complexes of iodine with benzene, coronene, perylene, and poly(*p*-phenylene). It is suggested that the benzene–iodine complex in benzene prepared by slow cooling consists of alternate benzene and iodine molecules with the six-fold axial symmetry. The Mössbauer spectrum for the coronene–iodine complex (1: 1) shows only one chemical state of iodine. The acceptor orbital is described by only the σ_u-antibonding molecular orbital of iodine. The extent of charge transfer in the complex is estimated to be $0.06e^-$ in the electronic ground state. In the poly(*p*-phenylene)–iodine complex the iodine exists as almost a free molecule, indicating that the interaction between the phenylene ring and iodine is very weak.

Iodine is a typical electron acceptor and forms charge transfer (CT) complexes with various electron donor molecules.[1–3] In particular, benzene–iodine (Bz–I_2) is one of the most typical π-σ CT complexes and has been extensively treated with many experimental and theoretical investigations. However, the geometrical configuration and the electronic state of the Bz–I_2 complex are not fully understood. Two conflicting models, "resting model" and "axial model," are proposed from various experimental methods such as IR,[4] MCD,[5,6] and ^{129}I Mössbauer[7–9] spectroscopies in addition to the theoretical treatments.[10–14] From the ^{129}I Mössbauer spectroscopic studies, it is found that the iodine in benzene exhibits an anomalously high value of the quadrupole coupling constant (e^2Qq) compared to that of the free iodine molecule.[7,8] Furthermore, the same tendency is found in methylated benzene-iodine complexes.[9,15]

Shibuya[16] determined the crystal and molecular structure of the coronene–iodine (1: 1) complex by X-ray diffraction. He reported that each iodine molecule was situated between two coronene molecules and that its axis was almost normal to the plane of the coronene molecule, although it was not coincident with the C_{3v} axis of the coronene molecule. This is the only iodine-containing π-σ complex of which the molecular structure is determined. It is therefore worthwhile to compare the ^{129}I Mössbauer spectrum of Bz–I_2 with that of coronene–I_2. Recently Teitelbaum, Ruby, and Marks[17] performed the ^{129}I Mössbauer effect measurement of the perylene–iodine (2 : 3) complex, which is an organic semiconductor with relatively high electrical conductivity (≈10^{-1} S/cm).[18,19] They reported from the ^{129}I Mössbauer and the resonance Raman spectra that the perylene–iodine complex was not a well-known molecular complex, such as coronene–iodine, but rather a partially oxidized, mixed-valence compound. We have also studied the ^{129}I Mössbauer effect of the perylene–iodine (2 : 3) complex in order to elucidate the charge state and the configuration of the iodine. A comparison of the Mössbauer results of the coronene–iodine and perylene–iodine complexes will provide some information about the CT bonding formation and the electrical conductivity.

Poly(*p*-phenylene) has attracted much interest because of an increase of the electrical conductivity from about 10^{-12} S/cm of the undoped polymer to 5×10^2 S/cm with the doping of arsenic pentafluoride (AsF_5).[20] It is expected that iodine-doped poly(*p*-phenylene) may also exhibit high electrical conductivity in analogy with the iodine-doped polyacetylene. However, Mainthia *et al.*[21] were unsuccessful in obtaining conductivities higher than 4×10^{-5} S/cm.

In this paper we report ^{129}I Mössbauer effect studies on the aromatic hydrocarbon–iodine (π-σ type) complexes such as benzene–iodine, coronene–iodine (1: 1), and perylene–iodine (2 : 3) complexes. Furthermore, iodine-doped poly(*p*-phenylene) was also studied in order to elucidate the charge state and the configuration of iodine.

Experimental

All the absorber samples were prepared from Na^{129}I in Na_2SO_3 solution. After oxidizing the iodide with 3 mol dm^{-3} H_2SO_4 and 10% H_2O_2, the resulting molecular iodine ($^{129}I_2$) was extracted with benzene. The benzene solution was washed thoroughly with water and passed through a Teflon filter to eliminate a slight amount of water. The benzene solution of iodine was slowly cooled in a Teflon sample holder and used for the ^{129}I Mössbauer effect measurement as such. The other complexes, coronene–iodine (1 : 1) and perylene–iodine (2 : 3), were prepared by using the procedure of Kommandeur and Hall.[18] In the case of the coronene–iodine complex a large excess of iodine was used for preparation in order to get the brown needle-like crystals in high yields. Since these complexes decompose gradually in air, the products were immediately transferred into Teflon sample holders and kept in liq. N_2 until the Mössbauer measurement.

Poly(*p*-phenylene) was synthesized by polymerization of benzene with the $AlCl_3$–$CuCl_2$ system.[22] Iodine doping was performed by immersing the poly(*p*-phenylene) powder in hexane solution of $^{129}I_2$ at room temperature for 1 d. The content of iodine was estimated to be about 0.01 atoms per the polymer unit, $[(C_6H_4)I_{0.01}]$, from an increase of weight. The molecular iodine was doped very little in this polymer compared with arsenic pentafluoride (AsF_5).[20]

The Mössbauer source in the ^{66}Zn ^{129}Te form was prepared by irradiation of a 150 mg ^{66}Zn ^{128}Te compound at a flux of 2×10^{13} neutrons/cm^2 s for one hour in the Kyoto Univ. Reactor (KUR). The apparatus used for Mössbauer measurements was described in our previous paper.[23]

Results and Discussion

Benzene–Iodine Complex. An ^{129}I Mössbauer spectrum of iodine dissolved in benzene at 16 K is shown in Fig. 1. The spectrum was analyzed by the least-square fitting method, as indicated by the solid line. The obtained Mössbauer parameters, such as the quadrupole coupling constant (e^2Qq), the asymmetry parameter (η), the isomer shift (δ), and the line width (2Γ) are given in Table 1 together with the results of Bukshpan *et al.*[8] The e^2Qq value was converted to the ^{127}I nucleus by using the ground state quadrupole moment ratio $^{129}Q/^{127}Q=+0.70121$.[24]

As shown in Table 1, the value of $e^2Qq=-2341\pm13$ MHz is higher and the value of $\delta=0.84\pm0.02$ mm/s is lower than those for the free iodine molecule in inert matrices. Bukshpan *et al.* have observed the same tendency, but their values are slightly different from ours. The slight difference may come from the cooling procedure and the measuring temperature of the sample, that is, Bukshpan *et al.* have prepared the sample by rapid cooling and measured at liq. He temperature, while in our case the sample has been prepared by slow cooling and measured at 16 K. The value $\eta=0$ agrees with that of Bukshpan *et al.*[8] As shown in Fig. 1, only one chemical species of iodine was observed in the benzene-iodine frozen solution. Furthermore, no broadening of the line width was observed in the octet lines compared with the other spectra of crystalline materials. These observations suggest that the Bz–I$_2$ complex exists as n : n chains of alternate halogen and benzene molecules with the axial configuration in the benzene frozen solution in a similar manner to the Bz–Br$_2$ and Bz–Cl$_2$ crystalline complexes.[25] In contrast, Wynter *et al.*[15] argued from the large value of the asymmetry parameter ($\eta=0.18$) that the *p*- and *o*-xylene–iodine complexes had the resting configuration.

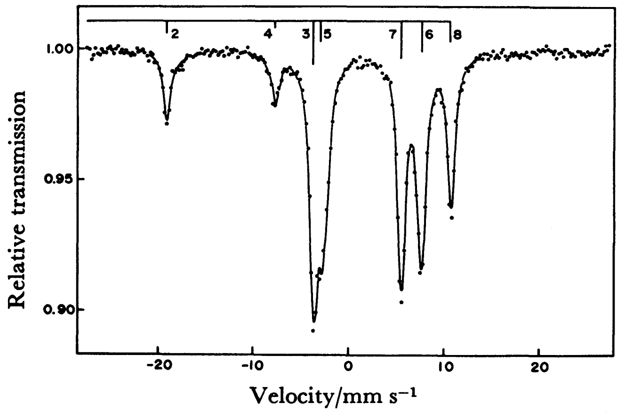

Fig. 1. ^{129}I Mössbauer spectrum of the benzene–iodine complex in the benzene frozen solution at 16 K.

In our previous paper[9] we discussed the electronic state of the Bz–I$_2$ complex by assuming axial geometry. Comparing the high value of e^2Qq and the low value of δ with those for the free iodine molecule, we found that the CT bonding orbital consisted of an *spd* hybrid orbital of iodine. The contribution of the *5d*-character to the CT bond formation was dependent on the extent of CT. This extent was not directly evaluated from the δ value. From the values of e^2Qq and δ in Table 1, and Eqs. 9 and 10 in Ref. 9, we obtain the *s*- and *d*-characters of the CT bonding orbital to be 0.8% and 8%, respectively, by assuming the extent of CT to be 0.06. This result indicates that the contribution of the *s*- and *d*-characters in the CT bond formation can not be ignored in the case of the Bz–I$_2$ complex.

Coronene–Iodine Complex. The ^{129}I Mössbauer spectrum of the coronene–iodine (1 : 1) crystalline complex at 16 K is shown in Fig. 2. The Mössbauer parameters obtained by analyzing the spectrum in the same manner as the Bz–I$_2$ complex are presented in Table 1. The spectrum shows only one chemical species of iodine, as expected from the crystal structure determined by an X-ray diffraction method.[16] The intensities of the absorption peaks are deviated from the ideal ones ($\eta=0$), which are proportional to the square of the Clebsch-Gordan coefficient $|\mathrm{CG}|^2$.[26,27] This deviation may be due to: (i) the saturation effect and (ii), the preferred orientation. The first effect depends on the absorber thickness. If the absorber is too thick, the intense peak will be relatively weakened. In our case, the absorber thickness was about 20 mg ^{129}I/cm^2, which seemed to be too thick. Since the coronene–iodine complex is a needle-like crystal, the second possibility is also not ignored.

Both values of e^2Qq and δ for the coronene–iodine complex are lower than those for free iodine molecule. This result suggests that the acceptor orbital of the iodine molecule is only the σ_u-antibonding molecular orbital, as is generally accepted. In this case we can apply the following relationship between δ and $5p$ electron populations:[7]

$$\delta(\mathrm{mm/s}) = 1.5\,h_p - 0.54 \text{ (ZnTe source)}, \qquad (1)$$

Table 1. The Mössbauer parameters for the π-σ charge transfer complexes of iodine

	$e^2Qq^{a)}$ / MHz	η	δ / mm s^{-1}	2Γ / mm s^{-1}	$U_p{}^{b)}$	$h_p{}^{c)}$	Ref.
I$_2$ in CS$_2$	-2288 ± 20	0	0.96 ± 0.03	1.08	1.00	1.00	
Benzene–I$_2$	-2341 ± 13	0	0.84 ± 0.02	1.10	1.02	0.92	
Benzene–I$_2$	-2380 ± 25	0	0.77 ± 0.03		1.04	0.87	8
Coronene–I$_2$	-2216 ± 13	0.06	0.92 ± 0.02	1.12	0.97	0.97	
Phenazine–I$_2$	-2223 ± 20	0.06	0.93 ± 0.02		0.97	0.98	29
Poly(*p*-phenylene)–I$_2$	-2296 ± 13	0	0.94 ± 0.02	1.26	1.00	0.99	

a) The e^2Qq values are converted to ^{127}I. b) $U_p=-e^2Qq_{\mathrm{obsd}}/e^2Qq_{\mathrm{at}}$, $e^2Qq_{\mathrm{at}}=2292.7$ MHz. c) $\delta=1.5\,h_p-0.54$ mm s^{-1}, relative to ZnTe source.

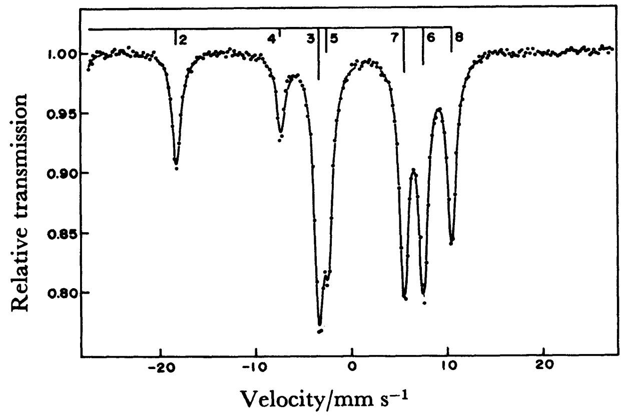

Fig. 2. ^{129}I Mössbauer spectrum of the crystalline coronene–iodine complex at 16 K.

where h_p is the number of p-holes in the $5s^25p^6$ configuration. Substituting the δ value to Eq. 1, we get $h_p=0.97$. It corresponds to the charge transfer of 0.06 electrons from the coronene molecule to the iodine molecule. On the other hand, the charge density localized on each iodine atom is also estimated from the value of e^2Qq according to the Townes and Dailey treatment.[26–28]

$$U_p \equiv -e^2Qq_{\text{obsd}}/e^2Qq_{\text{at}} \approx 1 - s^2 \pm i - \pi, \qquad (2)$$

where U_p is the number of the unbalanced p electrons, s^2 and i are the amount of s-hybridization and the ionic character, respectively, and π is the double bond character and/or the intermolecular bond. The atomic iodine quadrupole coupling constant, e^2Qq_{at}, is equal to 2292.7 MHz. With $e^2Qq=-2216\pm13$ MHz we get $U_p=0.97$. The value obtained is in good agreement with the h_p value. This agreement means that the I–I bond in this complex consists of a pure p_σ bond and the acceptor orbital can be described by only the σ_u-antibonding molecular orbital of the iodine molecule. This is also supported by the small η value.

Although the number of transferred electrons (0.06 e$^-$) is nearly equal to that for the Bz–I$_2$ complex, the electronic state of the iodine molecule is appreciably different from that for the Bz–I$_2$ complex. This result may be attributable to the difference of the geometrical configuration in the two complexes. In the case of the coronene–iodine complex, the axis of the iodine molecule is perpendicular to the coronene molecular plane but is not coincident with the six-fold axis of coronene, as shown in Fig. 3.[16] In the benzene–iodine complex, the iodine molecule is symmetrically situated along the six-fold axis of the benzene molecule.

The values of e^2Qq, δ, and η for the coronene–iodine complex are very close to those for the n-σ type complex of phenazine–iodine[29] which consists of the infinite chains of alternate phenazine and iodine molecules (in Table I). This fact suggests that the mechanism and the bond formation of the charge transfer are not essentially different between the π-σ and n-σ type complexes made up of the infinite alternative chain.

Perylene–Iodine Complex. The ^{129}I Mössbauer spectrum obtained for the perylene–iodine (2 : 3) crystalline complex (≈40 mg ^{129}I/cm^2) at 16 K is presented in Fig. 4. This spectrum has quite complicated features and is clearly different from those of the π-σ charge transfer complexes such as the benzene-iodine and coronene–iodine complexes. It is suggested from the spectrum that the iodine present in the perylene–iodine (2 : 3) complex exists as polyiodides or mixtures of the triiodide ion (I$_3^-$) and the molecular iodine (I$_2$). The possibility for the presence of the iodide ion (I$^-$) is immediately ruled out by finding no single peak at about −0.5 mm/s. The spectrum is very similar to one observed at liq. He temperature by Teitelbaum *et al.*[17] They were successful in analyzing their spectrum into five chemically different iodine sites which consisted of two interacting I$_2$ units and a distorted I$_3^-$ ion. Their analysis was also supported from the result of the resonance Raman spectra.

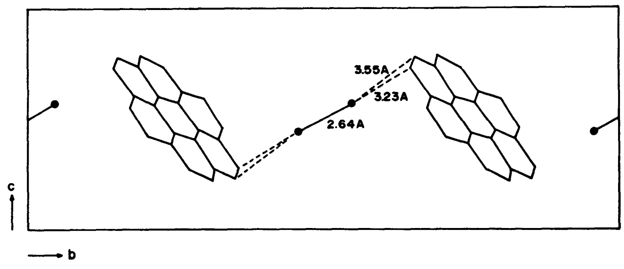

Fig. 3. Molecular structure of the coronene–iodine complex. The black circle represents the iodine atom.

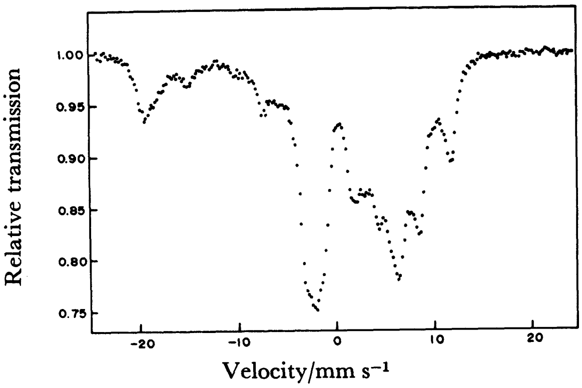

Fig. 4. ^{129}I Mössbauer spectrum of the crystalline perylene–iodine complex at 16 K.

There is little doubt that the perylene–iodine complex is not a normal molecular complex but rather an ionic, mixed-valence compound. On the other hand, the coronene–iodine complex is a typical molecular complex which consists of infinite stacks of alternate coronene and iodine molecules (Fig. 3). This difference in the complex formation may first be explained on the basis of the ionization potential of the donor molecules. That is, the ionization potential of perylene (6.85 eV) is much lower than that of coronene (7.50 eV).[30] For many of the solid complexes formed between the donors having lower ionization potential and the acceptors having higher electron affinity, there is a tendency to form ionic, radical salts which show some paramagnetic

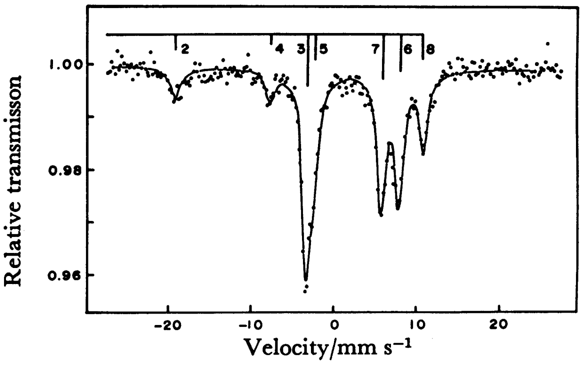

Fig. 5. ^{129}I Mössbauer spectrum of the poly(p-phenylene)–iodine complex at 16 K.

behavior and have high electrical conductivities.

*Poly(*p*-phenylene)–Iodine Complex.* Figure 5 shows the ^{129}I Mössbauer spectrum for the poly(p-phenylene)–iodine complex ($\approx$5 mg ^{129}I/cm^2) at 16 K. The solid line represents the best fitted curve obtained by the least square method. The Mössbauer parameters obtained are given in Table 1. The spectrum shows only one kind of iodine species and the values of e^2Qq and δ are in good agreement with those for the free iodine molecule. Consequently, the iodine doped in poly(p-phenylene) exists as almost free iodine molecules. It is then concluded that the iodine molecule interacts little with the phenylene ring. This finding well explains the following experimental results: (i) the electrical conductivity for poly(p-phenylene) does not increase with doping of iodine ($\approx 10^{-4}$ S/cm) as much as observed in the case of AsF$_5$-doping; (ii) the value of the conductivity for the iodine-doped poly(p-phenylene) decreases under dynamic vacuum.[20,21] The apparent activation energy for electrical conductivity is also high for Br$_2$ doping sample ($\approx$0.3 eV).

On the other hand, Matsuyama *et al.*[31] and Kaindl *et al.*[32] found from the ^{129}I Mössbauer spectroscopy that the iodine doped in polyacetylene existed as the chemical forms of I$_3^-$ and/or I$_5^-$ ions. The electrical conductivity for polyacetylene increases drastically with doping of iodine ($\approx 10^2$ S/cm).[33] The activation energy also decreases from 0.3 eV for undoped to $\approx$0.01 eV for iodine-doped polyacetylene. The difference in the doping process between poly(p-phenylene) and polyacetylene may be interpreted in terms of the ionization potential of each polymer. For doping of the very strong electron acceptor AsF$_5$, both polymers indeed exhibit the high electrical conductivity: $\approx 10^2$ S/cm for poly(p-phenylene)[20] and $\approx 10^3$ S/cm for polyacetylene.[34]

The authors wish to thank Profs. Takenobu Higashimura and Iwao Shibuya in the Research Reactor Institute, Kyoto University, for their helpful discussions and encouragements. This work was partly supported by a Grant-in-Aid for Scientific Research No. 56540259 from the Ministry of Education, Science and Culture.

References

1) R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley, New York (1969).

2) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, London (1969).

3) "Spectroscopy and Structure of Molecular Complexes," ed by J. Yarwood, Plenum Press, London (1973).

4) See, for example, L. Fredin and B. Nelander, *J. Am. Chem. Soc.*, **96**, 1672 (1974) and the references cited therein.

5) A. G. El-Kourasky and R. Gimter, *J. Chem. Soc., Faraday Trans. 2*, **72**, 1860 (1976).

6) T. J. Barton, R. Grinter, and A. J. Thomson, *Chem. Phys. Lett.*, **66**, 252 (1979).

7) S. Bukshpan, C. Goldstein, and T. Sonnino, *J. Chem. Phys.*, **49**, 5477 (1968).

8) S. Bukshpan, C. Goldstein, T. Sonnino, L. May, and M. Pasternak, *J. Chem. Phys.*, **62**, 2606 (1975).

9) H. Sakai, Y. Maeda, S. Ichiba, and H. Negita, *J. Chem. Phys.*, **72**, 6192 (1980).

10) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950); **74**, 811 (1952).

11) S. Aono, *Prog. Theor. Phys.*, **22**, 313 (1959).

12) M. W. Hanna and D. E. Williams, *J. Am. Chem. Soc.*, **90**, 5358 (1968).

13) E. G. Cook, Jr., and J. C. Schug, *J. Chem. Phys.*, **53**, 723 (1970).

14) J. McHale, A. Banerjee, and J. Simons, *J. Chem. Phys.*, **69**, 1406 (1978).

15) C. I. Wynter, Y. W. Chow, and A. Mukerji, *J. Chem. Phys.*, **72**, 5412 (1980).

16) I. Shibuya, *Bussei*, **2**, 636 (1961).

17) R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, *J. Am. Chem. Soc.*, **101**, 7568 (1979).

18) J. Kommandeur and F. R. Hall, *J. Chem. Phys.*, **34**, 129 (1961).

19) T. Uchida and H. Akamatsu, *Bull. Chem. Soc. Jpn.*, **34**, 1015 (1961).

20) D.M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, and R. H. Baughman, *J. Chem. Phys.*, **71**, 1506 (1979); L. W. Shacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, *Synth. Metals*, **1**, 307 (1979).

21) S. B. Mainthia, P. L. Kronick, H. Ur, E. F. Chapman, and M. M. Labes, *Polym. Prepr.*, **4**, 208 (1963).

22) P. Kovacic and J. Oziomek, *Macromol. Synth.*, **2**, 23 (1966).

23) H. Sakai, T. Matsuyama, Y. Maeda, and H. Yamaoka, *J. Chem. Phys.*, **75**, 5155 (1981).

24) R. Livingston and H. Zeldes, *Phys. Rev.*, **90**, 609 (1953).

25) O. Hassel and K. O. Strømme, *Acta Chem. Scand.*, **12**, 1146 (1958); **13**, 1781 (1959).

26) M. Pasternak, *Symp. Faraday Soc.*, **1**, 119 (1967).

27) H. deWaard, "Mössbauer Effect Data Index 1973," ed by J. G. Stevens and V. E. Stevens, IFI/Plenum Press, New York (1974), p. 447.

28) S. L. Ruby and G. K. Shenoy, "Mössbauer Isomer Shifts," ed by G. K. Shenoy and F. E. Wagner, North-Holland, Amsterdam (1978), Chap. 9b.

29) S. Ichiba, H. Sakai, H. Negita, and Y. Maeda, *J. Chem. Phys.*, **54**, 1627 (1971).

30) F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1956).

31) T. Matsuyama, H. Sakai, H. Yamaoka, Y. Maeda, and H. Shirakawa, *Solid State Commun.*, **40**, 563 (1981).

32) G. Kaindl, G. Wortmann, S. Roth, and K. Menke, *Solid State Commun.*, **41**, 75 (1982).

33) See, for example, C. K. Chiang, Y. W. Park, A. J.

Heeger, H. Shirakawa, E. J. Louis, and A. G. MacDiarmid, *J. Chem. Phys.*, **69**, 5098 (1978) and the references cited therein.

34) A. G. MacDiarmid and A. J. Heeger, *Synth. Metals*, **1**, 101 (1979).