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# Conductivity and Optical Properties of a Polyiodine Canal Complex $(Benzophenone)_9(KI)_2I_7CHCl_3$†

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$(Benzophenone)_9(KI)_2I_7CHCl_3$ single crystals have a golden metallic reflection on the surfaces parallel to the polyiodine chain axis. The compound is a member of a large class of channel-like inclusion compounds in which isolated iodine atom chains are the only possible conducting strands in an otherwise insulating matrix. The (contactless) microwave conductivity is $\sim 10\ \Omega^{-1}\ cm^{-1}$ at room temperature with an activation energy of $\sim$0.03 eV down to 70°K, while the dc conductivity is $\sim 10^{-6}$. Conductivity is strongly frequency dependent and contact problems are severe.

There is a large group of channel-like inclusion compounds in which a polyiodine atom chain is established as a "guest" within the lattice of an organic "host," such as the starch-iodine complex. If the iodine atoms are equidistant in such a chain, and if there is one negative charge per three iodine atoms, a simple band-model picture suggests a 2/3 filled band, i.e. a 1-D metal.[1] Little[2] has speculated that such iodine chain compounds are attractive model systems for high temperature superconductors, if the organic host were highly polarizable. Indeed *any* conductivity arising in such a structure, in which the polyiodine strands are separated by relatively large

† These results were presented in part at the Electrochemical Society, 152nd Meeting, October 9–14, 1977, Atlanta, Georgia.

distances would most likely be of a 1-D nature. We wish to report that one member of this class of compounds, $(benzophenone)_9(KI)_2I_7CHCl_3$(BIKI), forms strongly dichroic crystals with golden metallic reflection on the surfaces parallel to the polyiodine chain axis. These crystals have a room temperature microwave conductivity (10 GHz) of $\sim 1$ to $10\ \Omega^{-1}\ cm^{-1}$ and an activation energy of $\sim 0.03$ eV from 70°K to room temperature. The dc conductivity, on the other hand, appears to be quite low, but may be contact-dominated.

Early structural views of the starch- and sugar-polyiodine complexes, as well as a number of organic hosts such as trimesic acid, coumarin, 2,6-diphenyl-γ-pyrone, benzophenone and benzamide suggested that the iodine atoms were equidistantly spaced.[3] As more detailed studies were made, it became apparent that zig-zag chains of alternate $I_3^-$ and $I_2$ units could exist with non-equivalent bond distances. In $(phenacetin)_2HI_5$,[4] for example, the I—I distance in the $I_3^-$ moiety is 2.907 Å, slightly shorter than the standard value of 2.920 Å in the free $I_3^-$ ion, whereas in the $I_2$ molecule the bond length is 2.748 Å, as compared to 2.715 Å in crystalline $I_2$.[5] The distance between $I_2$ and $I_3^-$ in the chain is 3.550 Å, and the distance between chains is >4.1 Å. Obviously such a structure has highly localized electronic states and one would not expect the system to show high conductivity.

The most detailed crystal structure information is available for metal iodide-iodine compounds with α-cyclodextrin (α-CD).[6] In $(\alpha\text{-CD})_2 \cdot LiI_3 \cdot I_2 \cdot 8H_2O$, there is a disorder caused by statistical occupancy of sites in the iodine chain, which, in this case, extends through the hole in the middle of the stacked α-CD molecules. Unfortunately we do not as yet have a structure determination for BIKI, but a strong set of reflections is found without any of the streaking characteristic of many of the other complexes suggesting a *uniform* I—I spacing of 3.07 Å. *If* this uniformity does indeed exist, it may be caused by some charge-transfer between benzophenone and iodine, an interaction known to occur in solution.[7]

BIKI was first reported by Clover in 1904,[8] and subsequently mentioned briefly in a thesis by Kapon.[4] Clover's method of preparation consisted of melting the ingredients together and recrystallizing the melt from chloroform. The crystals used in this study were prepared in an isothermal diffusion apparatus: two bulbs, one containing a stoichiometric quantity of benzophenone, another containing $I_2$, each containing $\frac{1}{2}$ of the KI, were connected by a chloroform solvent column and the reagents allowed to diffuse in a freezer. Well-formed rod-like crystals of dimensions as large as 1 cm in length and 2–3 mm in cross-section grew in the column over a period of two weeks. The crystals had a golden luster along the long direction and were black in cross-section and had no observable striations at 400 X. Analytical data are presented in Table I.

TABLE I

Analytical data on BIKI

| Authors | %C | %H | %I | %K | Best formula |
|---|---|---|---|---|---|
| Clover | 47.61 | 3.08 | 37.89 | 2.56 | $(C_{13}H_{10}O)_9(KI)_2I_7 \cdot CHCl_3$ |
| Herbstein (Kapon) | | | | | $(C_{13}H_{10}O)_9(KI)_2I_6$ |
| This work | 47.44 | 2.92 | 37.36 | 2.51[a] | $(C_{13}H_{10}O)_9(KI)_2I_7 \cdot CHCl_3$ |
| Theoretical | 47.57 | 3.08 | 38.33 | 2.62 | $(C_{13}H_{10}O)_9(KI)_2I_7 \cdot CHCl_3$ |

[a] This value obtained by atomic absorption analysis; all other data via microchemical analysis.

For comparison purposes, the dc conductivities (four-probe measurements except where indicated) of a number of canal compounds are listed in Table II. Contact problems are very severe for these compounds. Gold and platinum paints are modestly satisfactory, and graphite suspensions ("Dags"), in some cases saturated with $I_2$ are somewhat better. Electrolyte contacts ($I_2$—KI—$CHCl_3$ saturated aqueous solutions) to benzophenone complex crystals embedded in a matrix were also evaluated; although the measured conductivities were somewhat higher ($10^{-2}$ to $10^{-4}\ \Omega^{-1}\ cm^{-1}$), we could not assure ourselves of the absence of electrolyte leakage at the crystal-matrix bond.

The conductivity-frequency dependence is very marked and is plotted in Figure 1, whereas Figure 2 presents a plot of the temperature dependence of the (contactless) microwave conductivity.[9] It is interesting to note the

TABLE II

Room temperature (~25°C) D.C. conductivity[a] of a number of organic-iodine inclusion complexes

| Complex | Long Axis Cond. ($\Omega^{-1}cm^{-1}$) | Transverse Cond. ($\Omega^{-1}cm^{-1}$) | Activation Energy (eV) |
|---|---|---|---|
| (2,6-Diphenyl-γ-pyrone)$_2$HI$_5$ | $1.0 \times 10^{-5}$ (2-probe) | $1.0 \times 10^{-8}$ (2-probe) | 0.66 |
| (Coumarin)$_4$KI·I$_2$ | $2.0 \times 10^{-5}$ | | 0.60 |
| (Trimesic Acid·H$_2$O)$_{10}$HI$_5$ | $2.6 \times 10^{-8}$ | $5.0 \times 10^{-10}$ | 0.60 |
| (α-Cyclodextrin)KI·I$_2$4H$_2$O | $1.4 \times 10^{-7}$ | $4.8 \times 10^{-8}$ | 0.70 |
| (Benzamide)$_2$HI·I$_2$ | $1 \times 10^{-5}$ | | |
| (Benzamide)$_3$KI·I$_2$ | $1 \times 10^{-4}$ | | 1.3 |
| (Benzophenone)$_9$(KI)$_2$I$_7$(CHCl$_3$) | $6.0 \times 10^{-6}$ | $4.6 \times 10^{-7}$ (2-probe 1 KHz) | 0.24 |

[a] Four probe measurements except where indicated.

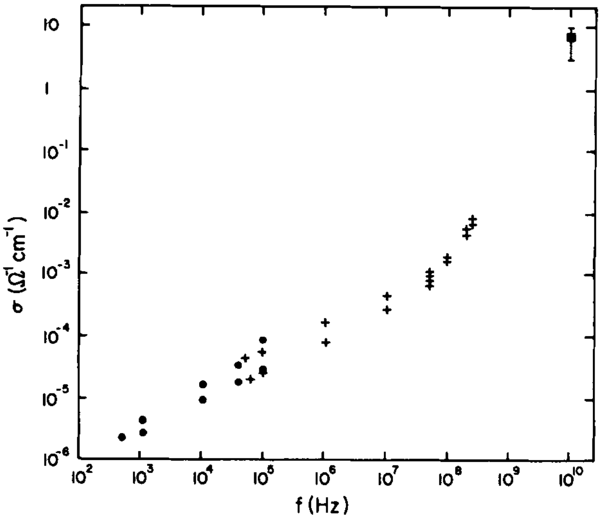


FIGURE 1 Frequency dependence of the conductivity of BIKI at room temperature. Measurements were performed by the following techniques: 0.5–40 KHz, impedance bridge; 60 KHz-50 MHz, Q-meter; 50 MHz-250 MHz, RX-meter; 9.35 GHz, microwave cavity loss.

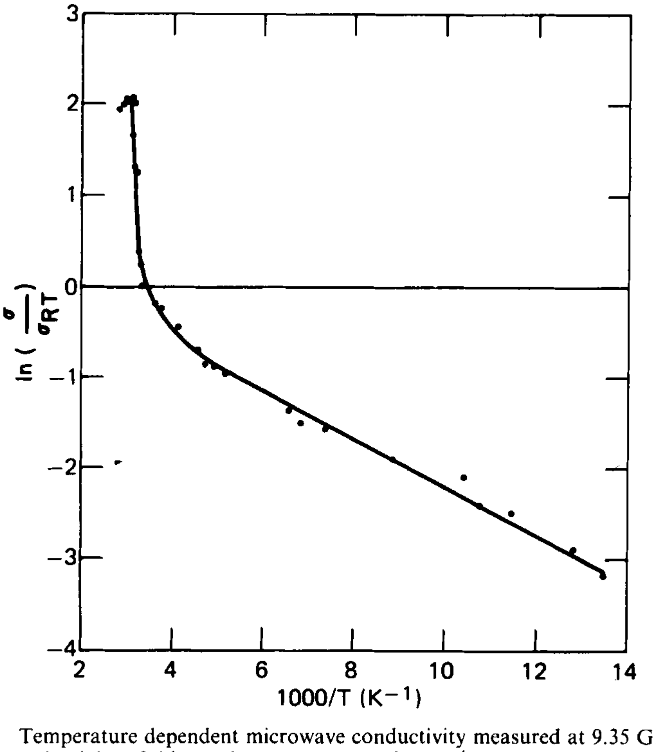


FIGURE 2 Temperature dependent microwave conductivity measured at 9.35 GHz. Room temperature conductivity of this specimen $\sigma_{RT} = 1.1\ (\Omega\ \text{cm})^{-1}$.

abrupt change in activation energy $E_a$ around room temperature; unfortunately crystal decomposition is quite rapid at 330 K. From these microwave measurements $E_a$ is 0.03 eV from room temperature to 70 K while above room temperature $E_a$ is 0.55 eV. Neither of these values are consistent with the estimated $E_a$ from dc measurements over the small temperature range 276 to 318 K of 0.24 eV. Measurements of the microwave conductivity of the compounds (2,6-Diphenyl-$\gamma$-pyrone)$_2$HI$_5$ and ($\alpha$-Cyclodextrin)KI$\cdot$I$_2$4H$_2$O yield room temperature conductivities of $2 \times 10^{-5}$ $(\Omega\,\text{cm})^{-1}$ and $1 \times 10^{-5}$ $(\Omega\,\text{cm})^{-1}$, respectively. These values are larger than the dc values as has been observed in many organic compounds, but the degree of difference between dc and microwave values does not compare to that observed in BIKI. The relatively high microwave conductivity in BIKI is clearly consistent with the increasing conductivity as a function of frequency observed throughout the radio frequency spectrum.

Preliminary measurements of the reflectance of BIKI in the visible and infrared have been conducted on both single crystals and polycrystalline pellets. The reflectance spectrum of a single crystal specimen is shown in Figure 3 for light polarized parallel and perpendicular to the conducting axis. The spectra do not show the degree of anisotropy characteristic of many one-dimensional conductors. The parallel reflectance shows a steep edge with a strong minimum at 1050 m$\mu$ with additional minima at 1700, 2100, and 2400 m$\mu$ (not shown). A weak maximum is observed in the visible near 700 m$\mu$ with a maximum reflectance of 10 to 20% depending on the sample. These spectral features have been measured reproducibly in a series of single crystal specimens. The perpendicular reflectance has a similar reflectance rise in the infrared, a lower maximum reflectance, and several minima beyond the edge. It does not, however, show a distinct minimum

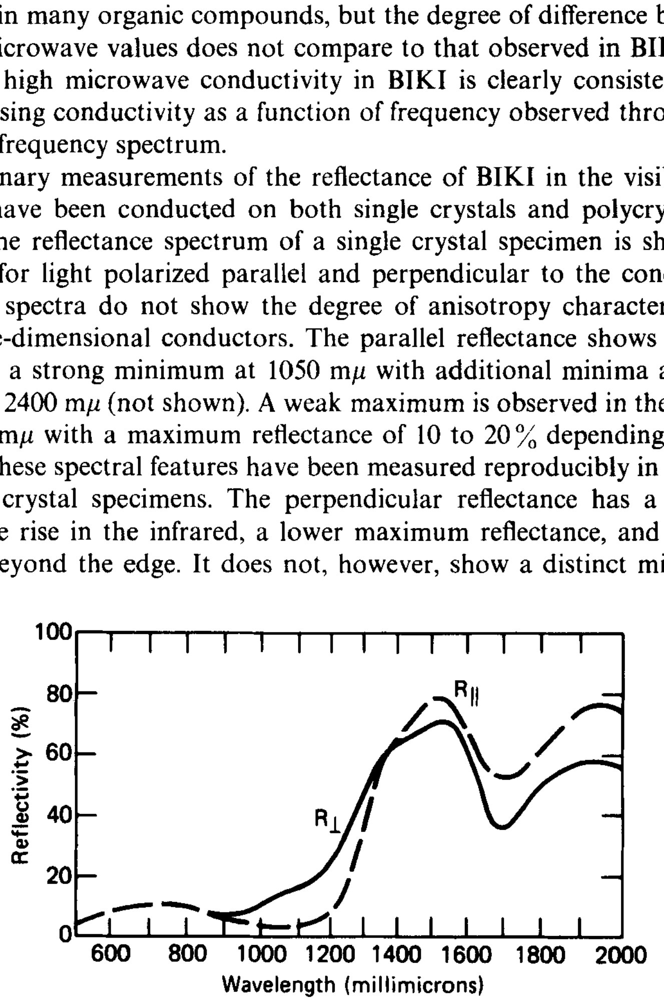


FIGURE 3 Normal incidence room temperature reflectivity (MgO standard) of single crystal specimen in the near infrared. Relative values of reflectance are accurate to within 0.01.

near 1050 m$\mu$, and the visible reflectance is small. In all samples the reflectivity at wavelengths shorter than 500 m$\mu$ is small. The structure observed in the reflectance can arise either from strong interband transitions or from plasma effects. If the reflectivity can be attributed to a plasma reflection edge, it would imply an optical conductivity substantially greater than the dc values, but consistent with the trend of the measured frequency dependence of the conductivity. However, the lack of anisotropy in the reflectance data may not support this interpretation.

The reflectance spectrum of a polycrystalline pellet of BIKI shows the strong reflectance edge as in the crystalline specimens although it is shifted to shorter wavelengths. The shift toward short wavelengths is presumably the result of a large number of surface defect states or change in composition arising from the mechanical process of grinding and pressing the pellet specimen.

The data suggest that polyiodine canal complexes represent a class of conductors where, in most cases, disorder or bond alternation interrupts the delocalization required for high conductivity. Nevertheless, in the benzophenone complex, the microwave and optical conductivity results imply that *some* structures may not suffer this interruption. We are undertaking an intensive investigation of the optical and electrical properties in this systems to further elucidate what may represent a new interesting class of low-dimensional conductors.

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