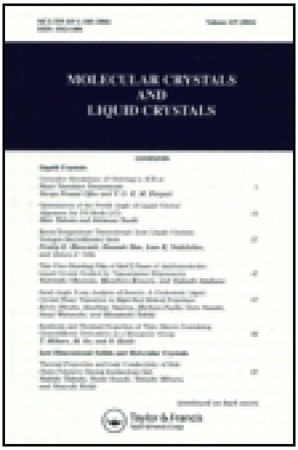


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Electronic Conductivity in a New Class of Polyiodide Complexes of 5-Dibenzosuberenone with Iodine and Alkali Iodide

Hsin-Sheng Yang [a] & Chi-Ming Wang [a]
[a] Department of Chemistry, Tamkang University, Tamsui, Taiwan, 25137, R.O.C.

Version of record first published: 19 Dec 2006.

To cite this article: Hsin-Sheng Yang & Chi-Ming Wang (1988): Electronic Conductivity in a New Class of Polyiodide Complexes of 5-Dibenzosuberenone with Iodine and Alkali Iodide, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 159:1, 315-322

To link to this article: http://dx.doi.org/10.1080/00268948808075281

Mol. Cryst. Liq. Cryst., 1988, Vol. 159, pp. 315–322

Printed in the United States of America

Electronic Conductivity in a New Class of Polyiodide Complexes of 5-Dibenzosuberenone with Iodine and Alkali Iodide

HSIN-SHENG YANG and CHI-MING WANG†

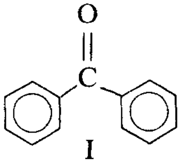
Department of Chemistry, Tamkang University, Tamsui, Taiwan 25137, R.O.C.

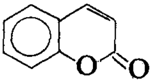
(*Received August 17, 1987*)

A new class of polyiodide complexes of 5-dibenzosuberenone with iodine and alkali iodide (DIMI complexes, M = Na, K, Rb or Cs) has been prepared for the first time. The single crystals of the DIMI complexes are needle shaped with a shiny metallic luster along the needle axis. Their longitudial dc conductivities are in the order of 10^{-4} Scm^{-1} at room temperature. They behave in a semiconductive manner from 250 to 300 K with activation energies of 0.6 to 0.9 eV. Resonance Raman spectroscopic studies show that the iodine species exist as symmetric I_3^- units in one-dimensional polyiodide chains, which are probably the conducting strands in these complexes.

INTRODUCTION

Polyiodide complexes of benzophenone (I) and coumarin (II) with iodine and alkali iodide have recently stimulated interest. These complexes are unique in having mixed electronic and ionic conductivities,[1,2] which are strongly frequency dependent with the microwave conductivities ranging up to 10 Scm^{-1}. An unusual conducting behavior[3] is that both alkali and iodide ions are mobile in the coumarin complexes (abbreviated CIMI), but only the cation is mobile in the benzophenone complexes (BIMI).


I


II

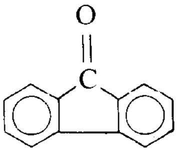
---

† To whom correspondence should be addressed.

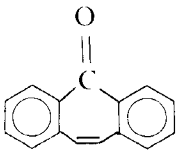
Crystallographic studies[4,5,6] indicate that both BIMI and CIMI complexes consist of column-like polyiodide chains surrounded by the hydrophobic (aromatic) part of the organic molecules and columns of cations coordinated by the polar carbonyl oxygen atoms. Although the organic framework is believed to be responsible for the unusual conducting behavior, the reason for the different behavior between BIMI and CIMI complexes is not clear.[3].

In an effort to study the effect of the organic molecules on the conducting behavior in these polyiodide complexes, a benzophenone analog, 9-fluorenone (III), has been used to form a new class of complexes with iodine and alkali iodide (FIMI).[7,8] Their conductivities at room temperature are in the order of 10^{-3} to 10^{-5} Scm^{-1}. Interestingly, the conductivity of FIMI complexes increases with decreasing cation size. This is the first time that a correlation between the conductivity and the cation size is reported in these polyiodide complexes. However, unlike BIMI and CIMI series, no ionic conductivity is found in the FIMI complexes. Thus, the organic molecules have striking effects on the conducting behavior in these complexes.

In this paper, another benzophenone analog, 5-dibenzosuberenone (IV), is used to form complexes with iodine and alkali iodide, and their conducting properties are reported.



III



IV

EXPERIMENTAL

The crystals of 5-dibenzosuberenone complexes were grown by slow evaporation of chloroform solution of stoichiometric amounts of 5-dibenzosuberenone, iodine and alkali iodide. The melting point was determined by a Mel-Temp melting point apparatus. The resonance Raman spectra were obtained at 300 K on a Spex model 1401 double spectrometer. The 5145 Å line of an argon ion laser was used as the excitation source. The dc conductivity was measured by the standard four-probe technique.[9]

RESULTS AND DISCUSSION

Elemental analyses and stoichiometries of the DIMI complexes are given in Table I. As in the coumarin series,[1] the stoichiometries are cation dependent, and no general stoichiometry is found. It is noted that the ratio of iodine to cation in the stoichiometries for all DIMI complexes is 3:1, indicating the existence of I_3^- ions. Interestingly, the ratio of 5-dibenzosuberenone to cation in the stoichiometries increases as the increasing cation size. A likely cause is that the cations may be surrounded by the oxygen atoms of 5-dibenzosuberenone. Thus, it is necessary to have more organic molecules to surround the larger cations. As in the FIMI series,[7] there is no evidence for the incorporation of solvent molecules in the DIMI series. The existence of water molecules in the DINaI complex is also indicated by O–H stretching vibration in the infrared spectrum at about 3500 cm^{-1}. Water molecules are probably absorbed by the sodium iodide salt from the atmosphere during preparation of the DINaI complex.

The crystals of DIMI complexes are needle shaped with metallic luster along the needle axis. Their dimensions are as large as 1.0 cm in length and 0.1 cm in cross-section, and are suitable for performing conductivity measurements. The melting point of DINaI, DIKI, DIRbI and DICsI is 91°C, 106°C, 103°C and 107°C, respectively. They are in between the melting points of 5-dibenzosuberenone (88°C) and iodine (114°C). Like FIMI complexes,[7] DIMI complexes are remarkably stable. Their metallic luster can be maintained for more than one month in the air. In contrast, BIMI complexes are unstable tending to lose iodine if exposed to the air.[10] To keep their metallic

TABLE I

Stoichiometry and elemental analysis of DIMI complexes

Cation	Best formula		C%	H%	I%	Cation %
Na	$D_5Na_2I_6{\cdot}6H_2O$	Found	46.40	3.19	38.87	2.40
		Theor.	46.27	3.21	39.11	2.36
K	$D_5K_2I_6$	Found	47.45	2.59	40.14	4.22
		Theor.	48.15	2.69	40.70	4.18
Rb	$D_8Rb_3I_9$	Found	46.97	2.66	36.77	8.23
		Theor.	47.27	2.64	37.46	8.50
Cs	D_3CsI_3	Found	48.04	2.62	34.02	12.19
		Theor.	47.73	2.67	33.62	11.73

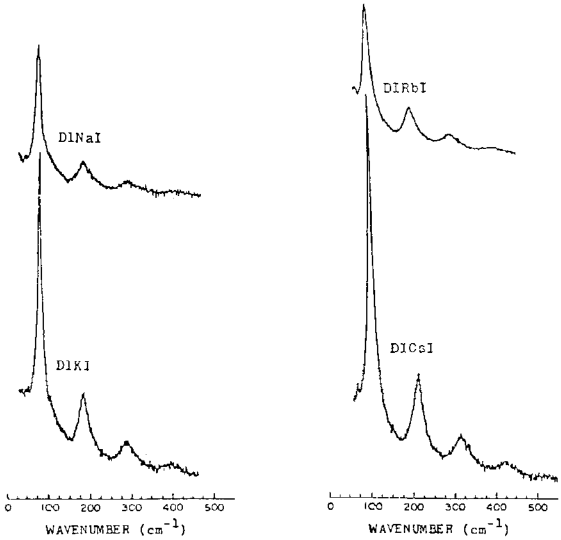


FIGURE 1 Resonance Raman spectra of DIMI complexes.

luster, BIMI complexes must be stored in sealed ampoules. The relative stabilities of DIMI and BIMI complexes suggest that the nature of iodine species is different in these complexes.

Resonance Raman spectroscopy has been shown to be a useful tool in determining the nature of iodine species in the polyiodide complexes.[11] It is found that two types of iodine species: I_3^- and I_3^-/I_2 units are present in the BIKI complex.[12] The model is consistent with the observation of thermal dissociation of the I_3^-/I_2 unit.[12] The Raman spectral data for the DIMI complexes are given in Figure 1 and Table II. The intense stretching fundamental at about 108 cm^{-1} accompanied by the characteristic overtone progression is typical for symmetric stretching mode of I_3^- units in the polyiodide chains as com-

TABLE II

Resonance Raman vibrational data of DIMI complexes

Complex	$\nu(cm^{-1})^a$
DINaI	328w, 215m, 108s
DIKI	326w, 216m, 109s
DIRbI	326w, 215m, 107s
DICsI	325w, 214m, 107s

[a] S = strong, m = medium, w = weak.

pared with the spectrum of (benzamide)$_2$HI$_3$.[11] Since the Raman spectra are very similar for the entire DIMI series, it appears that the substitution of the cation has no effect on the nature of the iodine species. The assignment of I_3^- units is in agreement with the stoichiometry shown in Table I. Unlike I_3^-/I_2 units in the BIKI complex,[12] symmetric I_3^- units in both DIMI and FIMI[7] complexes are stable for much longer period.

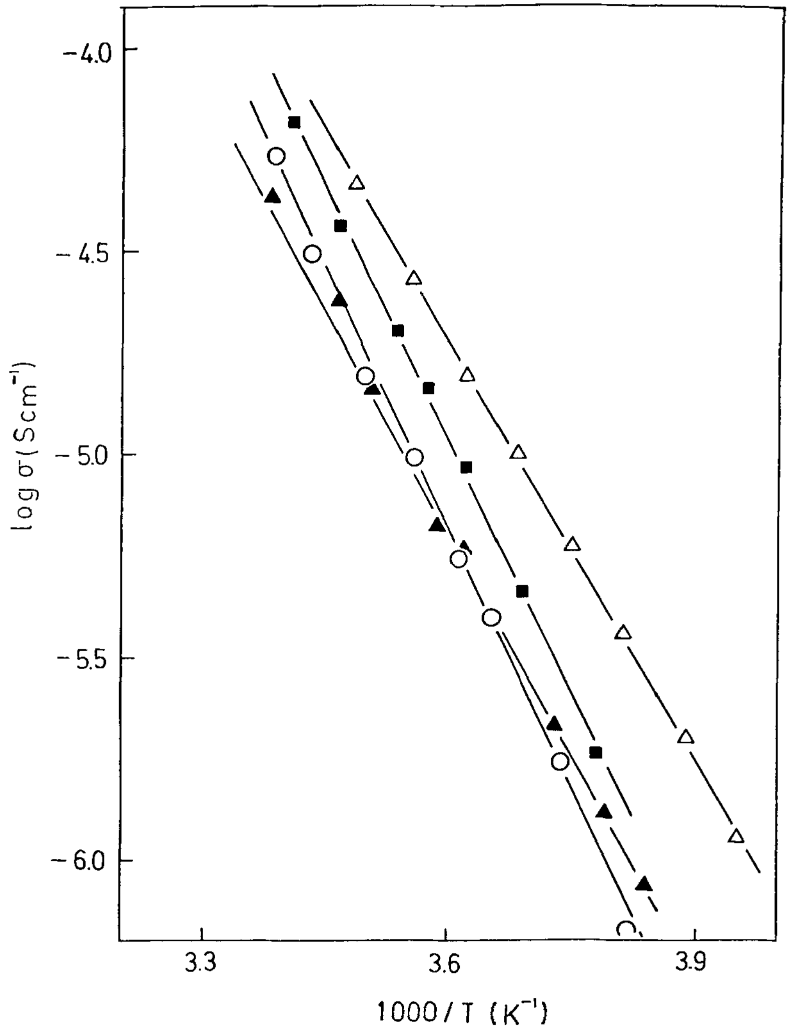


FIGURE 2 Temperature-dependent conductivity of DINaI (▲), DIKI (○), DIRbI (■) and DICsI (△).

Figure 2 shows the temperature dependence of the dc conductivity (σ) of DIMI complexes. It is clear that the conductivity can be fit well to the Arrhenius equation: $\sigma = \sigma_0 \exp(-Ea/kT)$, yielding activation energies (Ea) of 0.6 to 0.9 eV. The increase in conductivity with increasing temperature is typical for semiconducting behavior. Under an applied dc field at room temperature, the conductivity does not decrease over a period of six hours, indicating no ionic conductivity in DIMI complexes. Similar results are obtained in FIMI complexes.[7] On the contrary, significant ionic conducting is observed for both BIMI and CIMI complexes.[3] This surprising difference implies that a small change in the structure of the benzophenone skeleton has a dramatic effect on the properties of the resulting complexes.

For comparison, the room temperature conductivities of DIMI and FIMI complexes[7] are reported in Table III. It is emphasized that the conductivity of the DIMI complexes is in the order of 10^{-4} Scm^{-1}. In contrast, the conductivity of FIMI complexes decreases with increasing cation size. Since both DIMI and FIMI complexes do not yield suitable single crystals for X-ray diffraction measurements, it is very difficult to say with certainty, at this stage, what the conduction mechanism is in these complexes. Nevertheless, it is tempting to believe that the different effect of the cation on the conductivity in DIMI and FIMI complexes is probably due to different stacking patterns of the organic molecules in these complexes. The 9-fluorenone molecule is planar,[13] whereas the 5-dibenzosuberenone molecule has a folded configuration,[14,15] indicated by their crystal structures. As shown in Figure 3, the two benzene ring planes of the 5-dibenzosuberenone molecule are inclined toward each other at an angle of about 39° and the seven-membered ring is in the boat conformation.[15] In

TABLE III

DC conductivity and activation energy of DIMI and FIMI[a] complexes

Complexes	Conductivity (Scm^{-1}, at 25°C)	Activation energy (eV)
DINaI	8.3×10^{-5}	0.73
DIKI	1.1×10^{-4}	0.87
DIRbI	1.5×10^{-4}	0.82
DICsI	1.7×10^{-4}	0.69
FINaI	1.9×10^{-3}	0.62
FIKI	3.5×10^{-4}	0.65
FIRbI	3.8×10^{-5}	0.52
FICsI	3.0×10^{-5}	0.43

[a] Reference 7.

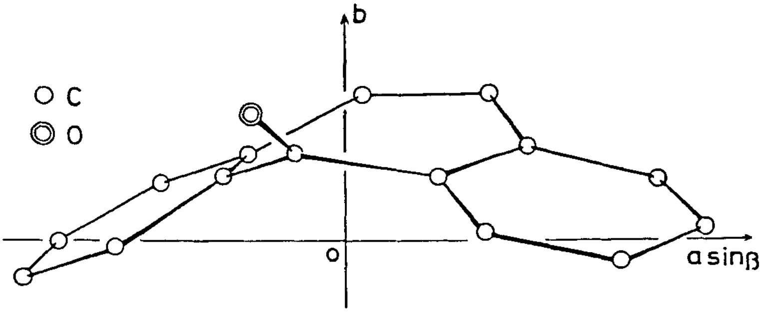


FIGURE 3 The structure of 5-dibenzosuberenone, reproduced from Reference 15.

FIMI complexes, it is assumed that the planar 9-fluorenone molecules form successive stacks with their carbonyl groups pointing to the center of a column where the cations are located, in a manner similar to the BIKI complex.[5] If such is the case, the larger cations then tend to increase the intrastack distances, which, in turn, results in weaker intrastack interactions between 9-fluorenone molecules, and lower conductivities. In DIMI complexes, it is conceivable that the cations may still coordinate to the carbonyl groups, but the folded 5-dibenzosuberenone molecules are not expected to form successive stacks as one expects from 9-fluorenone molecules. Thus, the cations have relatively small effect on the interactions between 5-dibenzosuberenone molecules. The conductivity in the entire DIMI series is probably dominated by the polyiodide chains, and is of the same order of magnitude.

In conclusion, organic molecules, indeed, have striking effects on the conducting behavior of the polyiodide complexes discussed in this paper. A model is proposed to explain the different effect of the cation on the conductivity between DIMI and FIMI complexes. In contrast to the benzophenone and coumarin series, there is no evidence for ionic conductivity in both the 5-dibenzosuberenone and 9-fluorenone series. The reason for this interesting difference is not clear for the present. It will be fruitful to obtain crystal structures of DIMI and FIMI complexes.

Acknowledgments

We wish to thank the National Science Council of Republic of China for the support of this work (NSC 76-0208-M32-11). The determinations of the Raman spectra by Prof. H. Chang of National Tsing Hua University and the technical assistance in conductivity measurements by Prof. H. I. Kao of Tamkang University are gratefully acknowledged.

References

1. C. Wu, B. Kim, H. I. Kao, C. W. Griffin, M. Jones and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **88**, 317 (1982).
2. M. M. Labes, M. Jones, H. I. Kao, L. Nichols, C. Hsu and T. O. Poehler, *Mol. Cryst. Liq. Cryst.*, **52**, 115 (1979).
3. C. Wu and M. M. Labes, *J. Phys. Chem.*, **90**, 4199 (1986).
4. P. Coppens, L. Li, V. Petricek and J. A. White, *Synth. Met.*, **14**, 215 (1986).
5. P. Coppens, P. C. W. Leung, R. Ortega, W. S. Young and C. Laporta, *J. Phys. Chem.*, **87**, 3355 (1983).
6. P. Leung, R. F. Boehme and P. Coppens, *Mol. Cryst. Liq. Cryst.*, **78**, 319 (1981).
7. H. S. Yang and C. M. Wang, *J. Chin. Chem. Soc.*, **34**, 283 (1987).
8. C. K. Hu and C. M. Wang, Proceedings of the Third International Conference on Electrochemistry, pp. 137–140, Taipei, R. O. C., April 30–May 1 (1986).
9. L. B. Coleman, *Rev. Sci. Instrum.*, **46**, 1125 (1975).
10. H. I. Kao, Ph.D. Thesis, Department of Chemistry, Temple University, Philadelphia, PA, 1978.
11. T. J. Marks and D. W. Kalina, *Extended Linear Chain Compounds* (Plenum Press, New York, 1982), J. S. Miller, Ed., Vol. 1, Chap. 6, pp. 197–331.
12. B. A. Bolton and P. N. Prasad, *Mol. Cryst. Liq. Cryst.*, **76**, 309 (1981).
13. H. R. Luss and D. L. Smith, *Acta Cryst.*, **B28**, 884 (1972).
14. P. Y. Oddon, N. Darbon, J. P. Reboul, B. Cristau, J. C. Soyfer and G. Pepe, *Acta Cryst.*, **C40**, 524 (1984).
15. H. Shimanouchi, T. Hata and Y. Sasada, *Tetrahedron Lett.*, 3573 (1968).