Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Recent Progress in the Development of Structure-Property Correlations for κ-Phase Organic Superconductors

Jack M. Williams [a], Hau H. Wang [a], Aravinda M. Kini [a], K. Douglas Carlson [a], Mark A. Beno [a], Urs Geiser [a], Myung-Hwan Whangbo [b], Dongwoon Jung [b], Michel Evain [b] & Juan J. Novoa [b]

[a] Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, Illinois, 60439-4831

[b] Department of Chemistry, North Carolina State University, Raleigh, North Carolina, 27695-8204

Version of record first published: 22 Sep 2006.

To cite this article: Jack M. Williams , Hau H. Wang , Aravinda M. Kini , K. Douglas Carlson , Mark A. Beno , Urs Geiser , Myung-Hwan Whangbo , Dongwoon Jung , Michel Evain & Juan J. Novoa (1990): Recent Progress in the Development of Structure-Property Correlations for κ-Phase Organic Superconductors, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 181:1, 59-64

To link to this article: http://dx.doi.org/10.1080/00268949008035992

Mol. Cryst. Liq. Cryst., 1990, vol. 181, pp. 59–64
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

RECENT PROGRESS IN THE DEVELOPMENT OF STRUCTURE-PROPERTY CORRELATIONS FOR κ-PHASE ORGANIC SUPERCONDUCTORS

JACK M. WILLIAMS, HAU H. WANG, ARAVINDA M. KINI, K. DOUGLAS CARLSON, MARK A. BENO AND URS GEISER
Chemistry and Materials Science Divisions
Argonne National Laboratory, Argonne, Illinois 60439-4831

MYUNG-HWAN WHANGBO, DONGWOON JUNG, MICHEL EVAIN AND JUAN J. NOVOA
Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

Abstract An examination of the molecular packing arrangements of the electron-donor molecules in κ-phase organic conductors and superconductors [κ-(BEDT-TTF)$_2$X (X = I_3^-, $Cu(NCS)_2^-$), κ-(MDT-TTF)$_2$AuI$_2$, and κ-(BMDT-TTF)$_2$Au(CN)$_2$] reveal that the main predictors of superconductivity appear to be (i) bond-over-ring intradimer molecular packing and (ii) relatively short (~ 3.35Å) intradimer separations. These structural features in newly discovered κ-phase organic conductors may be requirements for the occurrence of ambient pressure superconductivity.

INTRODUCTION

While structure-property correlations of T_c vs. unit cell volume for β-phase (BEDT-TTF)$_2$X, [X = I_3^- (T_c = 1.5 K); IBr_2^- (T_c = 2.8 K); AuI_2^- (T_c = 5.0 K); and β*-I_3^- (p > 0.5 kbar, T_c = 8.0 K)] superconductors are now well established,[1] those for κ-phase materials are presently in an early stage of development.[2] Although similar correlations are not as well advanced for the κ-phase systems [κ-(BEDT-TTF):X, X = anion], our early analysis of the crystal and band electronic structures of these materials[2] indicates that certain structural patterns are emerging for conducting and superconducting compounds in this series (vide infra).

κ-PHASE STRUCTURAL CLASS MATERIALS

An understanding of the κ-phase materials begins with the observation that four classes of organic electron-donor molecules form κ-phase structures, viz., BEDT-TTF, MDT-TTF, DMET, and BMDT-TTF. To date, superconductivity has been observed in only the first three of these classes, [κ-(BEDT-TTF)$_2$X, X = I_3^- and $Cu(NCS)_2^-$; κ-(MDT-TTF)$_2$AuI$_2$;

and κ-$(DMET)_2AuBr_2$].[2] The κ-phase structure is composed of orthogonally packed molecular dimers (see Figure 1) such that donor molecule "stacks" do not exist when compared to β-phase systems.[1] The κ-type structure was first observed in the non-superconducting, but metallic, derivative κ-$(BMDT\text{-}TTF)_2Au(CN)_2$.[3]

Projection views of the molecular dimers along the direction perpendicular to the donor molecule plane for all four known κ-systems are shown in Figure 2. These projection views reveal that the donor molecules have a bond-over-ring (BoR) arrangement in the superconducting κ-phase salts, and a bond-over-bond (BoB) arrangement in non-superconducting $(BMDT\text{-}TTF)_2Au(CN)_2$. Furthermore, the intradimer spacing in the ambient pressure superconducting κ-phases is 3.35Å, i.e., considerably shorter than the 3.60-3.70Å spacing in the non-superconducting $(BEDT\text{-}TTF)_2Ag(CN)_2{\cdot}H_2O$ and $(BMDT\text{-}TTF)_2Au(CN)_2$ (see Table I).

Extended Hückel calculations[2] based on the crystal structure of $(BMDT\text{-}TTF)_2Au(CN)_2$, whose metal-semiconductor transition at 76 K can be driven to lower temperature with applied pressure,[4] reveal larger transfer integrals in the dimer due to better overlap between HOMO's than in other κ-phase salts and caused primarily by the bond-over-bond arrangement. However, it appears likely that the absence of superconductivity in this salt originates from weaker interactions between dimers and relatively "hard" $-CH_2\cdots$anion interactions which lower the T_c's in the corresponding BEDT-TTF β-phase materials.[5] The lack of ambient pressure superconductivity[10] in $(BEDT\text{-}TTF)_4Hg_3Cl_8$, with an intradimer separation of 3.6Å, further suggests that ambient pressure superconductivity is observed only in the κ-phase salts with the shorter intradimer separation of ~ 3.35Å! These observations are summarized in Table I.

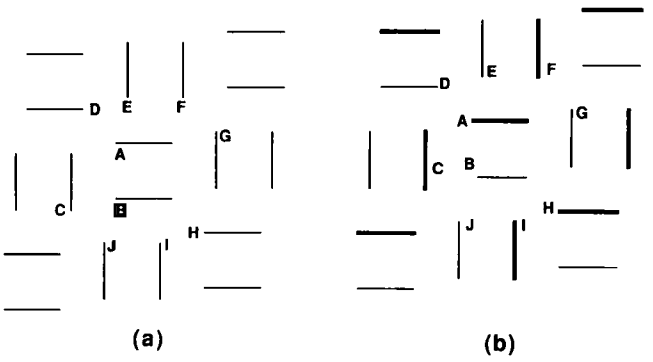

FIGURE 1 Schematic projection views (along the direction of the central C=C bond of a donor molecule) of the packing of donor dimers in the κ-phase salts: (a) κ-(BEDT-TTF)$_2$I$_3$, κ-(MDT-TTF)$_2$AuI$_2$, κ-(BMDT-TTF)$_2$Au(CN)$_2$; (b) κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The labels A through J refer to donor molecules. Darker lines refer to independent BEDT-TTF molecules which occur in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

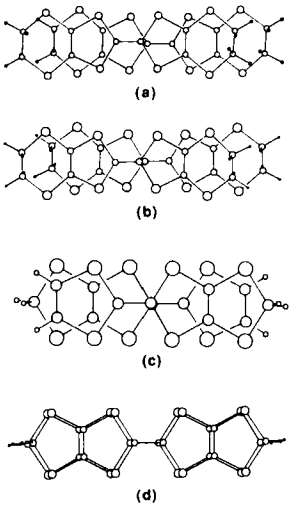

FIGURE 2 Projection views of donor dimers in (a) κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, (b) κ-(BEDT-TTF)$_2$I$_3$, (c) κ-(MDT-TTF)$_2$AuI$_2$, and (d) κ-(BMDT-TTF)$_2$Au(CN)$_2$.

TABLE I Intra-dimer Overlap Patterns, Intra-dimer Distances and Ethylene Endgroup Conformations in Known κ- or κ-like Salts.

Compound	T_c	Overlap Pattern[a]	Intradimer Distance (Å)	Ethylene Conformation[b]
$(BEDT\text{-}TTF)_2Cu(NCS)_2$	10.4 K	BoR	3.35	S,S
$(BEDT\text{-}TTF)_2I_3$	3.6 K	BoR	3.35	E,E
$(BEDT\text{-}TTF)_4Hg_3Cl_8$	1.8 K (12 kbar) 5.3K (29 kbar)	BoR	3.6	S,S
$(BEDT\text{-}TTF)_2Ag(CN)_2{\cdot}H_2O$	Non S.C. (Metal to 150 K)	BoR	3.7	E,S
$(BMDT\text{-}TTF)_2Au(CN)_2$	Non S.C. (T_{MI} 76 K)	BoB	3.6	-
$(MDT\text{-}TTF)_2AuI_2$	4.5 K	BoR	3.35	-
$(DMET)_2AuBr_2$	1.9K	BoR	-	-

[a]BoR = Bond over Ring; BoB = Bond over Bond

[b]S = Staggered; E = Eclipsed

Another important finding is that the conformations of the ethylene groups in the β- and κ-(BEDT-TTF) systems can be correlated[2] somewhat with T_c. The "staggered" ethylene group conformations are found in the molecular stacks of high-T_c β*-$(BEDT\text{-}TTF)_2I_3$ ($T_c \sim 8$ K) as revealed by a neutron diffraction study[6] below T_c ($p \sim 1.5$ kbar), and in the molecular dimers found in κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ ($T_c = 10.4$ K).[7] In the β*-phase the staggered ethylene group conformation is associated with "softer" -CH_2•••anion contacts, and hence a larger electron-phonon coupling constant (λ) and higher T_c, than in the β-$(BEDT\text{-}TTF)_2X$ [X = IBr_2^- ($T_c = 2.8$ K) and AuI_2^- ($T_c = 5$ K)] superconductors which possess lower T_c's and eclipsed ethylene group confirmations.[5] Likewise, the eclipsed conformation is found in low-T_c κ-$(BEDT\text{-}TTF)_2I_3$ ($T_c = 3.6$ K).[8] We speculate that the large negative pressure derivative[9] of T_c ($dT_c/dP = -3$K/kbar) for κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$, which strongly suggests that an enlarged unit cell for this salt will result in a higher T_c (> 10.4 K), would translate into increased interdimer spacings while maintaining the short 3.35Å intradimer distance. Such a result is exceedingly difficult to "engineer" into the preparation of new κ-phase materials, but the judicious choice of new (previously unknown?) anions may be the key to this puzzle.

CONCLUSIONS

With the highest T_c (10.1 K) in an organic superconductor having been found in a κ-phase salt, [κ-(BEDT-TTF)$_2$Cu(NCS)$_2$], one is inclined to ask if the orthogonal arrangement of molecular dimers in κ-phase materials, which may be an intrinsic structural property of κ-phase unsymmetrical electron-donors DMET and (MDT-TTF) superconductors, will eventually lead to even higher T_c's when compared to β-phase superconducting materials? This will remain an open question until a larger number of κ- and β-phase materials, and new and unknown structural phases of organic superconductors, are discovered. Until that time the main structure-property predictors for the occurrence of superconductivity in new κ-phase materials are (i) bond-over-ring intradimer arrangements and (ii) relatively short (~ 3.35Å) intradimer separations. The observation of such structural features in newly discovered κ-phase organic salts may well coincide also with the finding of superconductivity.

ACKNOWLEDGMENTS

Work at Argonne National Laboratory and North Carolina State University is sponsored by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contract W-31-109-ENG-38 and Grant DE-FG05-86ER45259, respectively.

REFERENCES

1. J. M. Williams, H. H. Wang, T. J. Emge, U. Geiser, M. A. Beno, P. C. W. Leung, K. D. Carlson, R. J. Thorn, A. J. Schultz, and M.-H. Whangbo in Prog. Inorg. Chem., edited by S. Lippard (John Wiley and Sons, New York, 1987), Vol. 35, pp. 51-218.
2. (a) D. Jung, M. Evain, J. J. Novoa, M.-H. Whangbo, M. A. Beno, A. M. Kini, A. J. Schultz, J. M. Williams, and P. J. Nigrey, Inorg. Chem., 28, 4516 (1989).
(b) M.-H. Whangbo, D. Jung, H. H. Wang, M. A. Beno, J. M. Williams, and K. Kikuchi, this volume.
(c) A. M. Kini, M. A. Beno, K. D. Carlson, J. R. Ferraro, U. Geiser, A. J. Schultz, H. H. Wang, J. M. Williams, in Proceedings of the First ISSP International Conference on the Physics and Chemistry of Organic Superconductors, Tokyo, Japan, August 27-30, 1989, edited by G. Saito and S. Kagoshima, (Springer-Verlag, Heidelberg), in press.
3. P. J. Nigrey, B. Morosin, J. F. Kwak, E. L. Venturini, and R. J. Baughman, Synth. Met., 16, 1 (1986).
4. P. J. Nigrey, B. Morosin, and J. F. Kwak in Novel Superconductivity, ed. by S. A. Wolf and V. Z. Kresin (Plenum Press, New York, 1987) pp. 171-179.
5. M.-H. Whangbo, J. M. Williams, A. J. Schultz, T. J. Emge, and M. A. Beno, J. Am. Chem. Soc., 109, 90 (1987).
6. A. J. Schultz, H. H. Wang, J. M. Williams, and A. Filhol, J. Am. Chem. Soc., 108, 7853 (1986).
7. H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, Chem. Lett. 55 (1988).

8. A. Kobayashi, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, and W. Sasaki, Chem. Lett. 459 (1987).
9. J. E. Schirber, E. L. Venturini, A. M. Kini, H. H. Wang, J. R. Whitworth and J. M. Williams, Physica C, 152, 157 (1988).
10. R. N. Lyubovskaya, R. B. Lyubovskiĭ, R. P. Shibaeva, M. Z. Aldoshina, L. M. Gol'denberg, L. P. Rozenberg, M. L. Khidekel', and Yu. F. Shul'pyakov, JETP Lett., 42, 468 (1985).