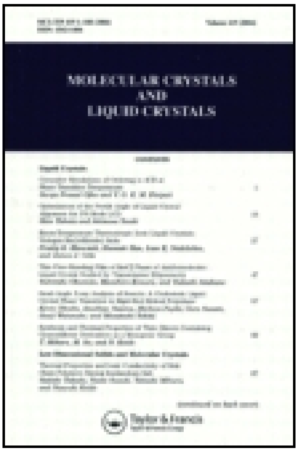

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Structural and Electronic Properties of K-Phase Organic Donor Salts: κ-$(DMET)_2AuBr_2$ and κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$

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Version of record first published: 22 Sep 2006.

To cite this article: M.-H. Whangbo , D. Jung , H. H. Wang , M. A. Beno , J. M. Williams & K. Kikuchi (1990): Structural and Electronic Properties of K-Phase Organic Donor Salts: κ-$(DMET)_2AuBr_2$ and κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 181:1, 1-15

To link to this article: http://dx.doi.org/10.1080/00268949008035988

Mol. Cryst. Liq. Cryst., 1990, vol. 181, pp. 1–15
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Printed in the United States of America

STRUCTURAL AND ELECTRONIC PROPERTIES OF κ-PHASE ORGANIC DONOR SALTS : κ-$(DMET)_2AuBr_2$ AND κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$

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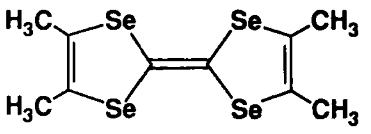
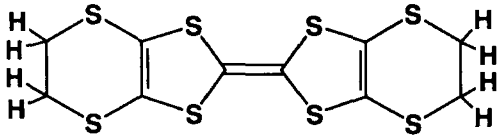
Abstract Electronic structures of κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$ and κ-$(DMET)_2AuBr_2$ were examined by performing tight-binding band calculations, and the crystal and electronic properties of the two salts were compared with those of other superconducting and nonsuperconducting κ-phase salts. A possible reason for why κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$ requires an applied pressure to achieve superconductivity was discussed.

INTRODUCTION

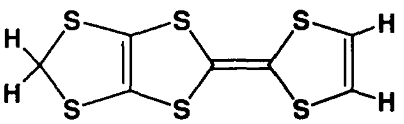
Ambient-pressure organic superconducting salts have been synthesized from symmetric donor molecules TMTSF (**1**) and BEDT-TTF (**2**) as well as unsymmetrical donor molecules MDT-TTF (**3**) and DMET (**4**).[1] These superconductors include $(TMTSF)_2ClO_4$ (T_c=1.3K),[2] β-$(BEDT\text{-}TTF)_2X$ (X^-= I_3^-, AuI_2^-, and IBr_2^- for which T_c = 1.4,[3] 2.8,[4] and 5.0 K,[5] respectively), θ - $(BEDT\text{-}TTF)_2$ I_3 (T_c=3.6 K),[6] γ - $(BEDT\text{-}TTF)_2$ $(I_3)_{2.5}$ (T_c=2.5 K),[7] κ-$(BEDT\text{-}TTF)_2$ X (X^-=$Cu(NCS)_2^-$ and I_3^- for which T_c=10.4[8] and 3.5K,[9] respectively), κ-$(MDT\text{-}TTF)_2AuI_2$ (T_c = 4.5K),[10] and κ-$(DMET)_2AuBr_2$ (Tc = 1.8K).[11] Although it has not been fully understood which structural factors govern the superconductivity of organic conducting salts, important clues for this question have been provided by studies of how applied pressure (P) influences their superconductivity. For instance, the jump in the T_c value of β-$(BEDT\text{-}TTF)_2I_3$ under pressure (i.e., T_c = 1.4 K at P = 1 bar to T_c = ~ 8K at P = 0.5 kbar)[12, 13] and the concomitant structural change[14] under pressure suggest[15] that lattice softness associated with the short C-H···donor and C-H···anion contacts are essential for the



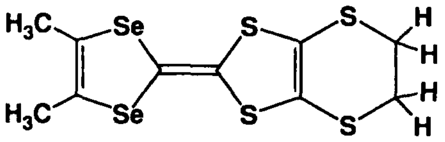
TMTSF, 1



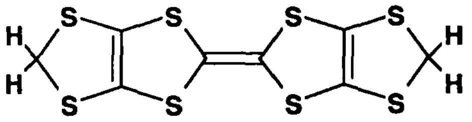
BEDT-TTF, 2



MDT-TTF, 3



DMET, 4



BMDT-TTF, 5

superconductivity of the β-phase salts β-$(BEDT\text{-}TTF)_2X$ ($X^- = I_3^-, AuI_2^-, IBr_2^-$).

The class of κ-phase superconductors has the most members and consists of several different donor molecules, including the unsymmetrical ones, and several different types of anions (i.e., discrete and polymeric). Therefore, the crystal packing of a κ-phase material appears to be most favorable in achieving superconductivity. The symmetrical donor BMDT-TTF (5) leads to a nonsuperconducting κ-phase salt, κ-$(BMDT\text{-}TTF)_2Au(CN)_2$,[16] which does not become superconducting under pressure.[17] According to a recent comparative study[18] of κ-phase salts, κ-$(BEDT\text{-}TTF)_2X$ ($X^- = Cu(NCS)_2^-$, I_3^-), and κ-$(MDT\text{-}TTF)_2AuI_2$, and κ-$(BMDT\text{-}TTF)_2Au(CN)_2$, the crystal and electronic structures of the nonsuperconducting salt differ substantially from those of the superconducting ones. In the present work, we examine the crystal and electronic structures of two other κ-phase salts, κ-$(DMET)_2AuBr_2$ and κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$[19] to learn which structural factors might control the superconductivity in the κ-phase salts. κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$ is not a superconductor under ambient pressure but, unlike κ-$(BMDT\text{-}TTF)_2Au(CN)_2$, it becomes superconducting under applied pressure with somewhat complicated pressure dependence of T_c;[19] This salt first becomes a superconductor at $P = 12$ kbar (T_c=1.8 K), with its Tc gradually decreasing upon increasing P until it loses superconductivity at $P = 23$ kbar. At $P = 29$ kbar, this salt becomes superconducting again at a higher temperature (T_c = 5.3 K). In the present study, the electronic structures of κ-$(DMET)_2AuBr_2$ and κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$ are obtained by performing tight-binding band calculations[20] based upon the extended Hückel method.[21] The atomic parameters employed in our calculations are summarized in Table 1.

TABLE 1 The exponents ζ_i and valence shell ionization potentials H_{ii} (eV) of the Slater type atomic orbitals χ_i [a, b]

χ_i	ζ_i	ζ_i'	H_{ii}
Se 4s	3.139 (0.5822)	1.900 (0.4846)	-20.5
4p	2.715 (0.5347)	1.511 (0.5553)	-13.2
S 3s	2.662 (0.5564)	1.688 (0.4873)	-20.0
3p	2.338 (0.5212)	1.333 (0.5443)	-13.3
C 2s	1.831 (0.7616)	1.153 (0.2630)	-21.4
2p	2.730 (0.2595)	1.257 (0.8025)	-11.4
H 1s	1.30		-13.6

[a] The s and p orbitals of Se, S and C are given as a linear combination of two Slater type orbitals with exponents ζ and ζ', and each is followed by a weighting factor in parentheses.

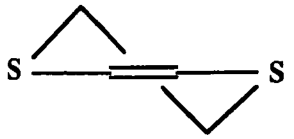
[b] A modified Wolfsberg-Helmholz formula was used to calculate the off-diagonal elements H_{ij}.[24]

CRYSTAL STRUCTURE

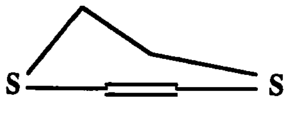
A. DONOR CONFORMATION

In 2:1 salts of BEDT-TTF the six-membered rings of BEDT-TTF are often found to adopt the conformation **6a** (i.e., the sp^3 carbon atoms above and below the π-plane) or **6b** (i.e., one sp^3 carbon atom above the π-plane and the other on the π-plane).[22] Given that both six-membered rings of BEDT-TTF have the conformation **6a**, the two ethylene groups can be arranged as in **7a** or **7b**.[15a, 22] When viewed along the central C=C bond, the two ethylene groups of **7a** and **7b** are eclipsed and staggered, respectively. In κ-(BEDT-

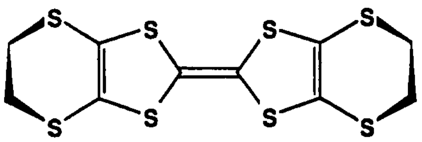
TTF)$_4$Hg$_3$Cl$_8$, one six-membered ring of BEDT-TTF has the conformation **6a**, and the other ring the conformation **6b**. The arrangement of the two ethylene groups is the same as the staggered arrangement **7b** except for a slight difference resulting from the fact that one six-membered ring has the conformation **6b**. The six-membered ring of DMET in κ-(DMET)$_2$AuBr$_2$ adopts the conformation **6a**.



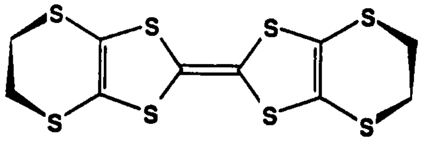
6 a



6 b



7 a

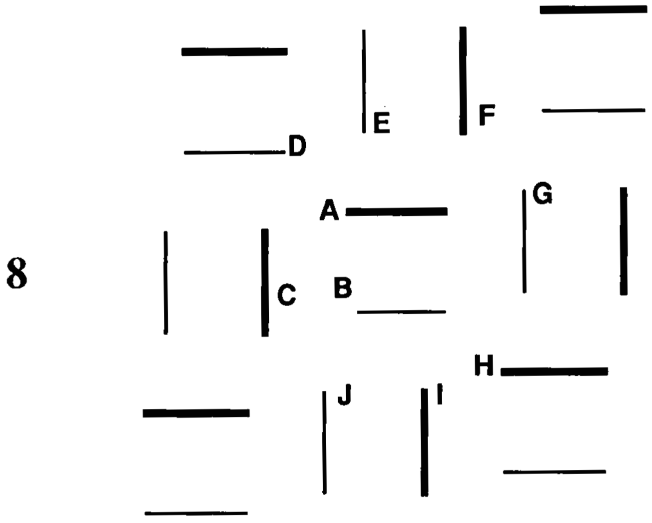


7 b

B. DONOR PACKING

A schematic projection view (along the direction of the central C=C bond of a donor) of how donor-dimers pack in κ-phase salts is shown in **8**, where the labels A-J indicate donor molecules.[18] The intradimer spacing is ~3.59Å for κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$, and ~3.54Å for κ-(DMET)$_2$AuBr$_2$. The former is quite close to the value of ~3.64Å found for the nonsuperconducting salt κ-(BMDT-TTF)$_2$Au(CN)$_2$.[18] The larger intradimer spacing of the latter originates from a bond-over-bond arrangement of donor molecules in each dimeric unit.[18] As shown in Figure 1a, donor molecules of κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$ have a bond-over-ring arrangement. Nevertheless, the intradimer spacing is much larger than the value of ~3.35Å found for the superconducting phases κ-(BEDT-TTF)$_2$ X (X^-= Cu(NCS)$_2^-$, I_3^-), in which donor molecules also have a bond-over-ring arrangement.

The intradimer spacing for κ-(DMET)$_2$AuBr$_2$ (i.e., ~3.54Å) is also large compared with the value of ~3.35Å found for the superconductors κ-(BEDT-TTF)$_2$ X (X^-=



Cu(NCS)$_2^-$, I$_3^-$) and κ-(MDT-TTF)AuI$_2$.[18] The DMET molecules in κ-(DMET)$_2$AuBr$_2$ have a bond-over-ring arrangement as shown in Figure 1b, where the methyl hydrogen atoms are not shown. Since DMET is unsymmetrical, there are two ways to have a bond-over-ring arrangement, i.e., the central C=C bond over the five-membered ring containing S atoms or over the five-membered ring containing Se atoms. The latter arrangement,

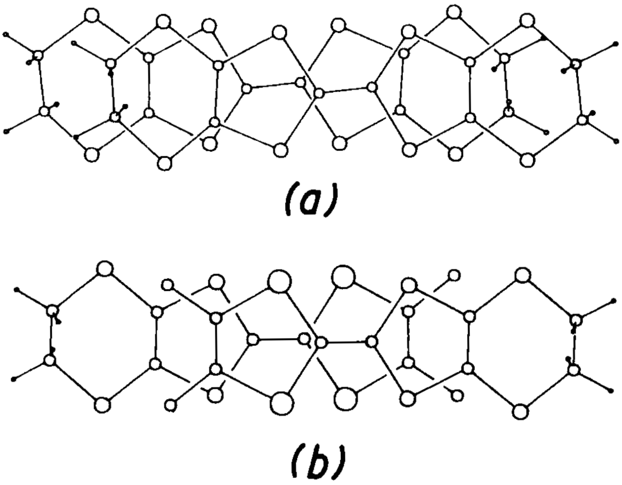


FIGURE 1 Projection views of donor dimers in (a) κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$ and (b) κ-(DMET)$_2$AuBr$_2$.

found for κ-(DMET)$_2$AuBr$_2$, is expected to be more stable than the alternative because it leads to more C-H···chalcogen atom (S, Se) interactions between donor molecules and also because the C-H···S interaction energy is larger than the C-H...Se interaction energy (0.46 *vs* 0.35 kcal/mol at the optimum H···S and H···Se distances respectively).[22] The large intradimer spacing of κ-(DMET)$_2$AuBr$_2$ (i.e., ~3.54Å) is explained by the fact that the bond-over-ring arrangement of Figure 1b leads to the intradimer Se···Se contacts, which requires greater spacing than do the intradimer S···S contacts found for κ-(BEDT-TTF)$_2$ X (X^-= Cu(NCS)$_2^-$, I_3^-) and κ-(MDT-TTF)$_2$AuI$_2$.

The extent of interaction between adjacent donor molecules i and j (e.g., i, j = A-J in **8**) may be measured in terms of their HOMO-HOMO interaction energy[23] $\beta_{ij} = \langle\psi_i \mid H^{eff} \mid \psi_j\rangle$ where ψ_i and ψ_j are the HOMO's of donor molecules i and j, respectively. The β_{ij} values calculated for various pairs of nearest-neighbor donor molecules (A-J defined in **8**) in κ-(DMET)$_2$AuBr$_2$ and κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$ are summarized in Table 2, which also lists the corresponding values in other κ-phase salts.[18] As noted earlier, the largest β_{ij} value is found for molecules within a dimer (i.e., β_{AB}) in each κ-phase salt. Except for β_{AB}, the β_{ij} values of κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$ are small, which implies that interdimer interaction are weak. In terms of the β_{ij} values, κ-(DMET)$_2$AuBr$_2$ is quite similar to κ-(MDT-TTF)$_2$AuI$_2$.

TABLE 2 HOMO-HOMO interaction energies β_{ij} (eV) in κ-phase salts

	pair (i, j)					
Salts	A-B	B-C[a]	A-G[b]	A-C[c]	B-G[d]	A-D[e]
κ-(BEDT-TTF)$_2$Cu(NCS)$_2$	0.385	0.198	0.179	0.046	0.038	0.136
κ-(BEDT-TTF)$_2$I$_3$	0.334	0.157	0.157	0.065	0.065	0.105
κ-(MDT-TTF)$_2$AuI$_2$	0.451	0.096	0.096	0.074	0.074	0.258
κ-(DMET)$_2$AuBr$_2$	0.443	0.076	0.076	0.086	0.086	0.200
κ-(BMDT-TTF)$_2$Au(CN)$_2$	0.689	0.258	0.258	0.018	0.018	0.144
κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$	0.453	0.018	0.018	0.015	0.015	0.015

[a] Equivalent to A-E. [b] Equivalent to B-I.

[c] Equivalent to A-F. [d] Equivalent to B-J.

[e] Equivalent to B-H, C-J and F-G.

C. C-H··· DONOR AND C-H··· ANION CONTACTS

The dashed lines of Figure 2a represent the short C-H···donor contacts in κ-(BEDT-TTF)$_4$-Hg$_3$Cl$_8$, and their distances are listed in Table 3. As found for the bond-over-ring arrangements in κ-(BEDT-TTF)$_2$ X (X$^-$ = Cu(NCS)$_2^-$, I$_3^-$),[18] an axial C-H bond of one donor is located above a six-membered ring of the other donor thereby leading to short C-H···H, C-H···S and C-H···C(sp^2) contacts. In κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$, the placement of the axial C-H bond is slightly slipped in a direction perpendicular to the central C=C bond so that the C-H bond makes short contacts with the H, S and C(sp^2) atoms on one side of the central C=C bond. In κ-(BEDT-TTF)$_2$ X (X$^-$= Cu(NCS)$_2^-$, I$_3^-$), the atoms on both sides of the central C=C bond are involved in making short C-H...donor contacts.[18] Figure 2b shows the short C-H···anion contacts in κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$ by dashed

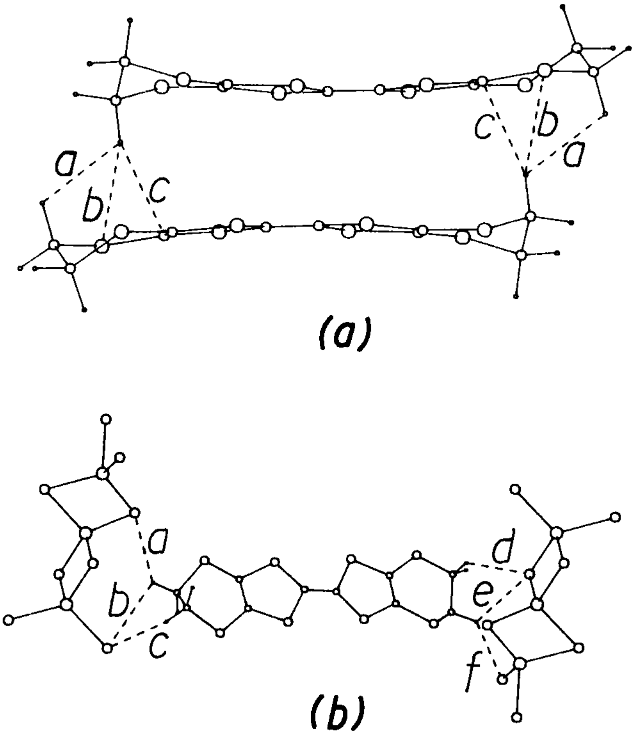


FIGURE 2 Short intermolecular contacts involving C-H bonds in κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$: (a) donor···donor contacts and (b) donor···anion contacts.

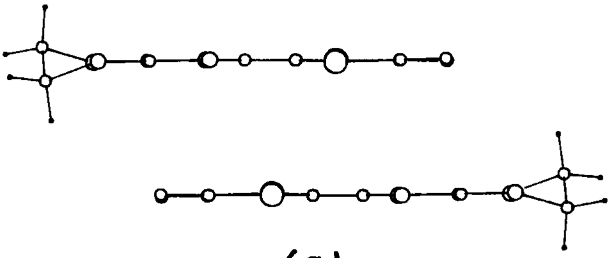
lines, and their distances are listed in Table 3. All these contacts are associated with the Cl atoms of the $Hg_3Cl_8^{2-}$ anions. Of the four C-H bonds of each ethylene group, only two C-H bonds make short C-H···Cl contacts.

TABLE 3 Selected intermolecular contact distances (Å) for κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$ and κ-(DMET)$_2$AuBr$_2$

Donor...donor contacts involving C-H bonds		
κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$		
a (H···H) 2.47	**b** (H-S) 2.89	**c** (H···C) 2.58
Donor...anion contacts associated with C-H bonds		
κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$		
a (H···Cl) 3.40	**b** (H···Cl) 2.75	**c** (H···Cl) 2.94
d (H···Cl) 2.81	**e** (H···Cl) 3.34	**f** (H···Cl) 2.90
κ-(DMET)$_2$AuBr$_2$		
a (H···Br) 3.12	**b** (H···Br) 3.17	**c** (H···Br) 2.94
d (H···Br) 2.99	**e** (H···Br) 3.28	**f** (H···Br) 3.42

† Standard deviations involving calculated hydrogen atom positions with C-H bond length of 1.09 (sp^3) and 1.08 (sp^2) are on the order of 0.01 Å

Since the positions of the methyl hydrogen atoms in κ-(DMET)$_2$AuBr$_2$ are not accurately known (due to free rotation), we are unable to discuss the short C-H···donor contacts these hydrogen atoms make. Nevertheless, it is obvious from Figure 3a, which shows the bond-over-ring arrangement of donor molecules in κ-(DMET)$_2$AuBr$_2$, that the methyl hydrogen atoms of one donor will make short C-H···S and C-H···C(sp^2) contacts with the other donor molecules. Figure 3b shows the short C-H···anion contacts associated with the ethylene groups of DMET, and their distances are listed in Table 3.



(a)

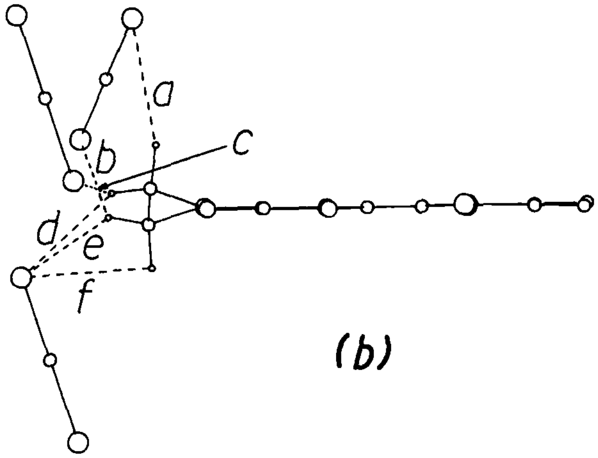


FIGURE 3 Short intermolecular contacts involving C-H bonds in κ-$(DMET)_2AuBr_2$: (a) donor···donor contacts and (b) donor···anion contacts. In (a) the contacts involve the C-H bonds of the methyl groups, but the methyl hydrogen positions are not known because of free rotation.

ELECTRONIC STRUCTURE

Figures 4a and 4b show the dispersion relations of the highest two occupied bands calculated for κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$ and κ-$(DMET)_2AuBr_2$, respectively. With the formal oxidation state of $(ET)_2^+$ for the donor layers, the highest occupied bands are each half-filled. The Fermi surfaces associated with the half-filled bands of κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$ and κ-$(DMET)_2AuBr_2$ are shown in Figures 5a and 5b, respectively. As in other κ-phase salts, these Fermi surfaces are essentially described as overlapping distorted circles.[18] Therefore, both salts are predicted to be two-dimensional metals.

The band electronic structures of Figure 4 may be described by the widths of the lower, the upper, and the overall bands (i.e., W_l, W_u, and W, respectively shown in 9). These band widths and the density of states at the Fermi level, $n(e_f)$, calculated for κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$ and κ-$(DMET)_2AuBr_2$ are summarized in Table 4, where the corresponding values for other κ-phase[18] salts are also listed for comparison. The upper bands of κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$ and κ-$(DMET)_2AuBr_2$ are narrow compared with those of other κ-phase salts, so the $n(e_f)$ values of the former are somewhat greater.

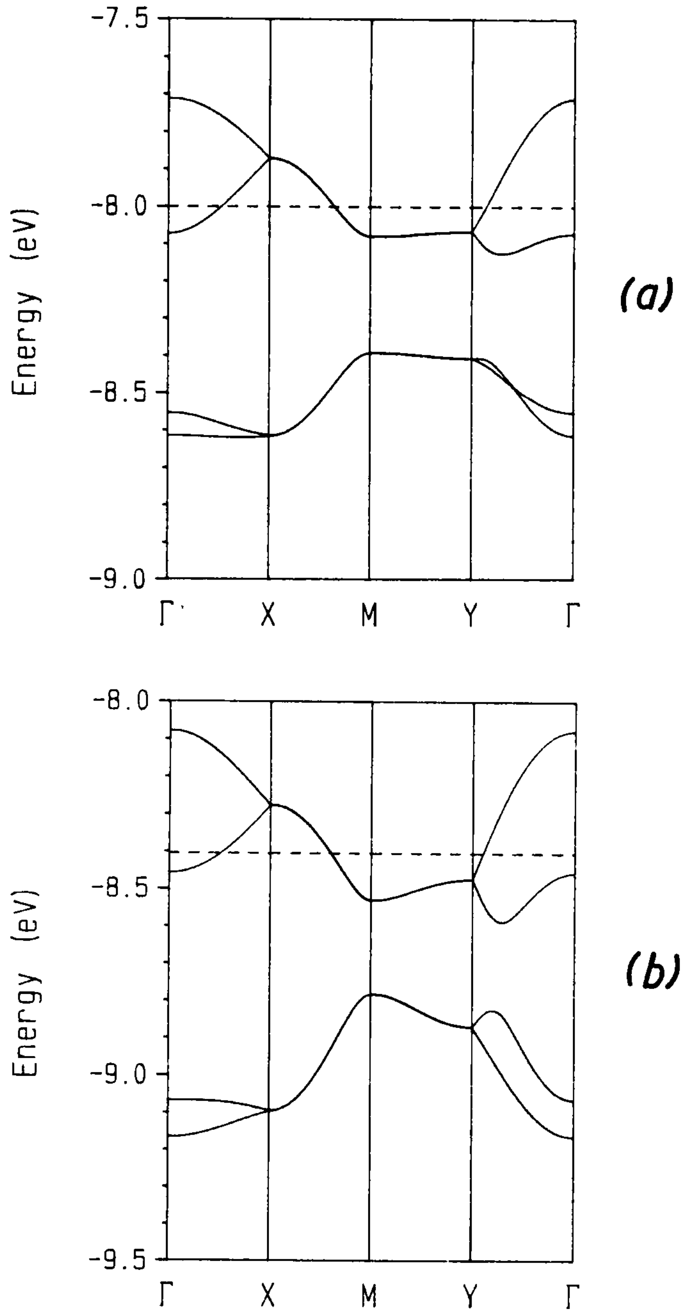
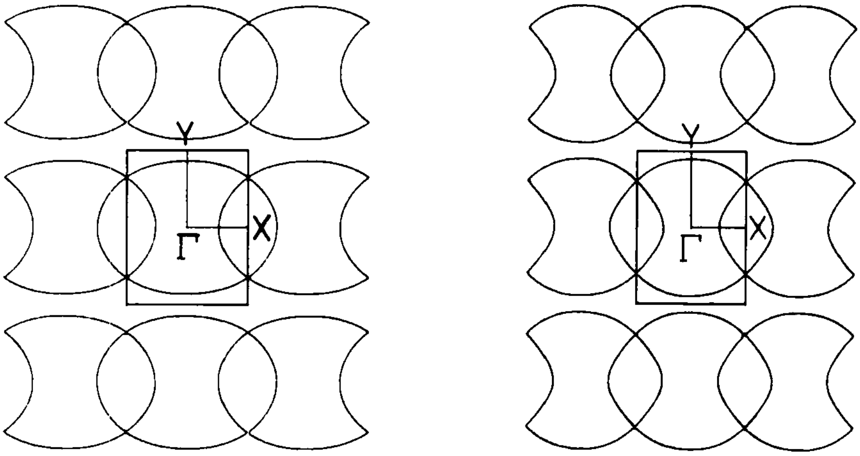


FIGURE 4 Dispersion relations of the two highest-occupied bands calculated for (a) κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$ and (b) κ-(DMET)$_2$AuBr$_2$. The dashed lines refer to the Fermi levels.



(a) (b)

FIGURE 5 Fermi surfaces associated with the half-filled bands of (a) κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$ and (b) κ-(DMET)$_2$AuBr$_2$.

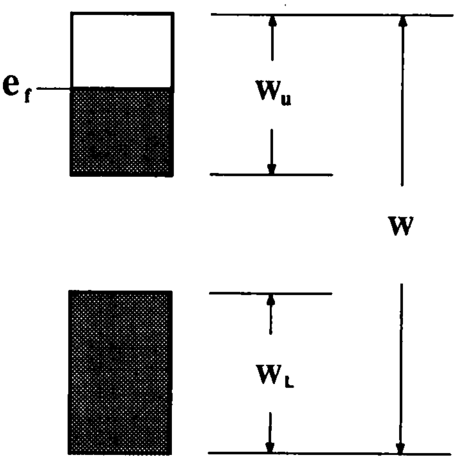


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TABLE 4 Superconducting transition temperature, band widths, and electron densities of states in the κ-phase salts.

Salt	T_c (K)	$n(e_f)$ (electron/eV)	W_l (eV)	W_u (eV)	W (eV)
κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$	10.4	7.57	0.34	0.59	1.07
κ-$(BEDT\text{-}TTF)_2I_3$	3.6	7.09	0.35	0.70	1.15
κ-$(MDT\text{-}TTF)_2AuI_2$	4.5	7.98	0.49	0.56	1.16
κ-$(DMET)_2AuBr_2$	1.8	8.92	0.51	0.38	1.09
κ-$(BMDT\text{-}TTF)_2Au(CN)_2$	--	7.30	0.55	0.74	1.69
κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$	--	10.8	0.22	0.41	1.09

DISCUSSION AND CONCLUDING REMARKS

It is evident from Table 4 that the simple relationship between T_c and $n(e_f)$, i.e., $T_c \propto \exp[-1/n(e_f)]$, does not hold. Thus, as in the case of β-phase superconducting salts β-$(BEDT\text{-}TTF)_2X$ ($X^- = I_3^-$, AuI_2^-, IBr_2^-),[15] the softness of the lattice and favorable electron-phonon coupling would be important factors for the superconductivity of the κ-phase salts. In terms of the electronic parameters β_{ij} and $n(e_f)$, κ-$(DMET)_2AuBr_2$ (T_c = 1.8K) is the closest to κ-$(MDT\text{-}TTF)_2AuI_2$(T_c = 4.5K). These salts are both based upon unsymmetrical donor molecules. Structural factors favoring the higher T_c in κ-$(MDT\text{-}TTF)_2AuI_2$ than in κ-$(DMET)_2AuBr_2$ may be that the C-H···anion interactions are softer in the former (i.e., C-H···I *vs* C-H···Br). Another important structural difference to note is that, unlike in κ-$(DMET)_2AuBr_2$, short C-H···S and C-H···C (sp^2) contacts between donor molecules are absent in κ-$(MDT\text{-}TTF)_2AuI_2$.

According to the intradimer spacing, as well as the β_{ij}, W_u and $n(e_f)$ values, the donor molecules of κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$ are loosely packed within a donor molecule layer. This could be due to the way the donor molecules make C-H···Cl contacts with the $Hg_3Cl_8^{2-}$ anions. Under applied pressure its donor packing may be tightened to become similar to that found for other κ-phase salts. It is of interest to consider a possible structural origin for the apparently complicated pressure dependence of the T_c in κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$. The donor molecules in the "low-T_c" salts β-$(BEDT\text{-}TTF)_2AuI_2$ (T_c = 5.0 K), β-$(BEDT\text{-}TTF)_2IBr_2$ (T_c = 2.8 K), and κ-$(BEDT\text{-}TTF)_2I_3$ (T_c = 3.5 K) have the eclipsed arrangement **7a** of the two ethylene groups, while those in the "high-T_c"

salts β*-(BEDT-TTF)$_2$I$_3$(T_c = ~8 K at P = 0.5 kbar) and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (T_c = 10.4 K) have the staggered arrangement **7b** of the two ethylene groups.[18] At ambient pressure the donor molecules of κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$ have the staggered arrangement **7b**. By analogy with the structural change β-(BEDT-TTF)$_2$I$_3$ (T_c = 1.4 K) experiences under pressure of 0.5 kbar to become β*-(BEDT-TTF)$_2$I$_3$ (T_c = ~ 8 K), it may be speculated that the donor molecules of κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$ have half staggered and half eclipsed arrangements at P = 12 kbar as in β-(BEDT-TTF)$_2$I$_3$, but have only the staggered arrangement at P = 29 kbar as in β*-(BEDT-TTF)$_2$I$_3$. To test this hypothesis, it would be important to determine the crystal structures of κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$ under pressures of 12 and 29 kbars in order to gain important insight into what structural factors govern the superconductivity of the κ-phase salts.

ACKNOWLEDGMENTS

Work at Argonne National Laboratory and at North Carolina State University was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U. S. Department of Energy, under Contract W-31-109-ENG-38 and Grant DE-FG05-86ER45259, respectively. We express our appreciation for computing time on the ER-Cray computer, made available by DOE.

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