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UNUSUAL ELECTRICAL PROPERTIES OF 1,6-DIAMINO-PYRENE CHARGE-TRANSFER COMPLEX CRYSTALS

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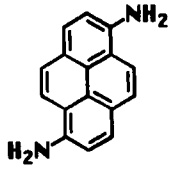
Abstract 1,6-Diaminopyrene (DAP) is a strong electron donor which can form charge-transfer complexes with many electron acceptors. When the acceptor is TCNQ, a highly conducting crystal comprising segregated-stacks of DAP and TCNQ is obtained. The temperature dependence is semiconducting with anomalously large activation energy for conduction. When the acceptor is *p*-chloranil (CHL) or 2,5-dibromo-3,6-dichloro-*p*-benzoquinone (DBDCQ), polymorphic crystals comprising mixed-stacks of DAP and CHL or DBDCQ are obtained. One of the polymorphs, α-form, is not conducting at the initial state, but becomes conducting after a mild heat treatment. It also becomes highly conducting only by fracture of the crystals. The ground state of the low-resistance phase has been found to be mainly neutral, despite its high conductivity.

INTRODUCTION

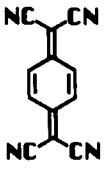
Charge transport in π-conjugated molecular crystals, especially charge-transfer complex crystals, is highly correlated with the crystal structure and the oxidation state of the constituents. When one attempts to obtain a metallic conductor, the difference between the oxidation potential of the donor and the reduction potential of the acceptor, which is related to a requirement for realizing a partial charge transfer,[1] and the symmetry of the HOMO of the donor and the LUMO of the acceptor, which is related to another requirement for realizing the segregated stacking of donors and acceptors,[2] have to be considered. In general, half fulfillment of the above requirements, i.e., completely ionic segregated stacking or partially oxidized mixed stacking, leads non-conducting crystals.

1,6-Diaminopyrene (DAP) is a rather early donor of conducting charge-transfer complexes.[3-7] Its oxidation potential is quite low; both the first and second oxidation potentials are about 0.1 V lower than each corresponding potential of TTF. We have revived this donor molecule with the intention of constructing an intermolecular hydrogen-bonded charge-transfer system. Such a system may be utilized to design

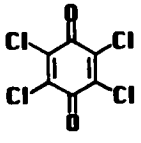
novel molecular devices.[8] We have found that DAP can actually form charge-transfer complex crystals with various acceptors, in which hydrogen bonds are formed when the acceptor has proton accepting sites. Systematic investigation of their properties has revealed that their charge transport properties are considerably different from those expected for ordinary charge-transfer complex crystals. In this paper, we describe their structures and properties with emphasizing how anomalous they are.



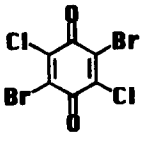
DAP



TCNQ



CHL



DBDCQ

DAP-TCNQ[9]

High-quality single crystals of DAP-TCNQ have been grown by co-sublimation of the components. The crystal obtained comprises segregated columns of DAP and TCNQ, as shown in Fig. 1. The crystal data at 295 K are as follows; triclinic, space group $P\bar{1}$, a = 7.937(1), b = 17.307(3), c = 3.898(1) Å, α = 90.38(2), β = 93.82(2), γ = 109.77(1)°, V = 502.6(2) Å^3, Z = 1, and R = 0.044 for 2290 independent reflections with $F_o > 3\sigma(F_o)$. Hydrogen bonds are formed between the columns; between the

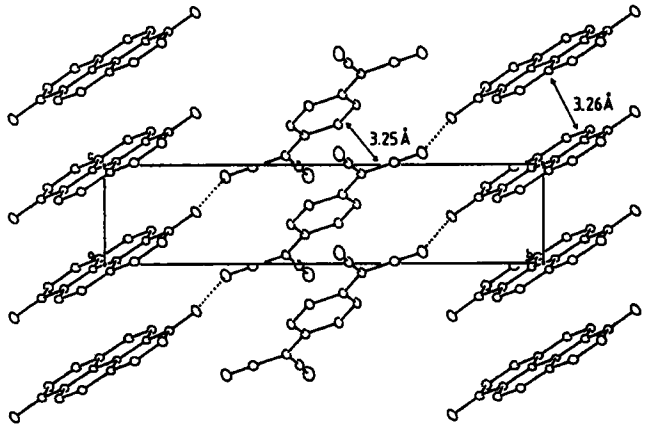


FIGURE 1 Crystal structure of DAP-TCNQ.

amino group of DAP and the cyano group of TCNQ. Since the repeat distance in each column corresponds to the *c* dimension of the unit cell, the molecules are separated with an equal distance in the column. This situation does not change down to 118 K; no signs of dimerization were observed.

The degree of ionization can be estimated both from the geometry of TCNQ and from the frequency of the CN stretching vibrational mode of TCNQ. The former gives a value of -0.96, and the latter does -1. Consequently, this crystal comprises completely ionized segregated stacks, and can be regarded as one of the non-conducting crystals.

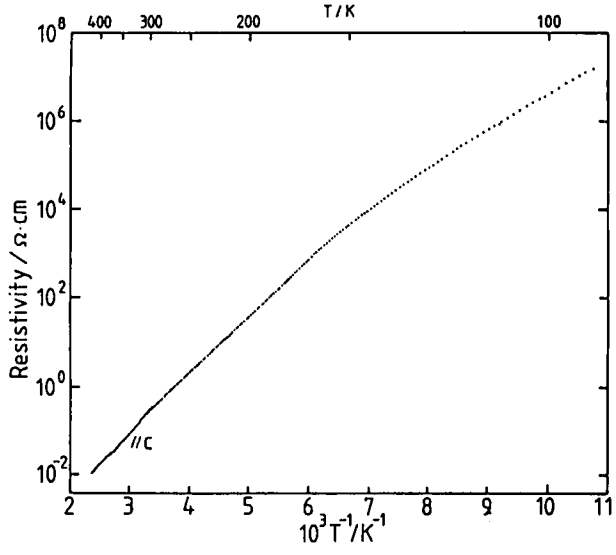


FIGURE 2 Temperature dependence of the resistivity of DAP-TCNQ.

The temperature dependence of the electrical resistivity is shown in Fig. 2. This complex is actually a semiconductor. However, the value at room temperature, 10^{-1} Ω cm, is unusually low as a Mott-type insulator. The activation energy for conduction is 0.26 eV. If one calculates the conductivity using this energy for thermal activation of charge carriers and a typical value for mobility, 1 cm^2 V^{-1} sec^{-1}, one can find that the resistivity at room temperature must be higher than 10 Ω cm. If one assumes that there already exist an appreciable number of charge carriers at the initial state by slight deviation from the complete ionization, the origin of the activation energy then becomes mysterious. It is not clear yet whether the hydrogen bonds play some critical role in the charge transport, it is notable that the anisotropy of conduction is small; $\rho_{\perp c}/\rho_{//c} \leq 10$. This indicates the possibility of charge transport through the hydrogen bonds.

DAP-TETRAHALO-*p*-BENZOQUINONE

A combination of DAP and *p*-chloranil (CHL) gives two kinds of 1:1 charge-transfer complex crystals from a benzene solution.[10] Similarly, a combination with 2,5-dibromo-3,6-dichloro-*p*-benzoquinone (DBDCQ) gives four kinds of crystals. Two polymorphs of the four have been found to be isomorphous with the two forms (α- and β-forms) of DAP-CHL. Structures and electrical properties of α-form of these two are given below.

The crystal structure of α-DAP-CHL is shown in Fig. 3. The crystal data are as follows; triclinic, space group $P\bar{1}$, a = 8.963(1), b = 9.112(2), c = 6.730(1) Å, α = 99.59(1), β = 99.65(1), γ = 114.43(1)°, V = 476.0(1) Å^3, Z = 1, and R = 0.040 for 2423 independent reflections with $F_o > 3\sigma(F_o)$. The crystal data for α-DAP-DBDCQ are quite similar; a = 8.996(4), b = 9.284(5), c = 6.809(3) Å, α = 99.30(4), β = 99.14(4), γ = 115.39(3)°, V = 490.2(4) Å^3, and Z = 1. Molecular arrangement in α-DAP-DBDCQ is practically the same as that in Fig. 3. The donors and acceptors form mixed-stacks along the *c*-axis. The hydrogen bonds between the amino group of DAP and the carbonyl oxygen of the acceptor are formed along the [221] direction. The N···O distance is only slightly shorter than the sum of the van der Waals radii. The degree of ionization has been estimated from the geometry and the frequency of the CO stretching mode of the acceptor. Both clearly indicate that the component molecules are completely neutral.

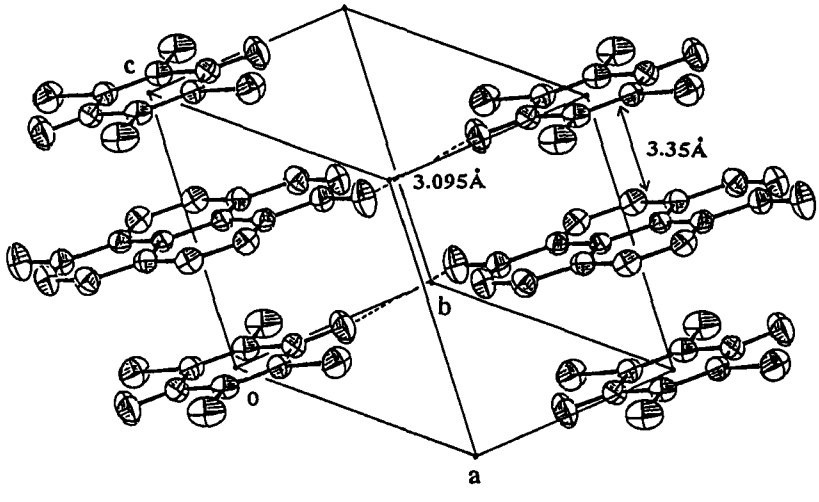


FIGURE 3 Crystal structure of pristine α-DAP-CHL.

The electrical resistivity of the pristine crystal is high (>10^8 Ω cm for both α-DAP-CHL and α-DAP-DBDCQ), which is consistent with the neutral ground state of the complex and the mixed-stack structure. When the resistivity of α-DAP-CHL was measured with increasing the temperature, a drastic resistivity change was observed, as shown in Fig. 4. The temperature at which point the resistivity drops abruptly is not the same for all the crystals; some crystals become low-resistance state at relatively low temperature, while some others persist in the high-resistance state near to 380 K. In all cases, the low-resistance state does not return to the high-resistance state after cooling.

It was also noted that the resistivity of pristine α-DAP-CHL was dramatically decreased by compression of the single crystals into a pellet. Since the resistivity is almost independent of the applied pressure, this change is considered to result from mechanical crushing of the crystals. The resistivity is almost comparable to those values of single crystals transformed into the low-resistance state by a heat treatment, as shown in Fig. 5. This suggests that the anisotropy of conduction must be small, and in fact, the anisotropy, $\rho_{\perp c}/\rho_{//c}$, has been found to be less than 10 by the single-crystal measurements.

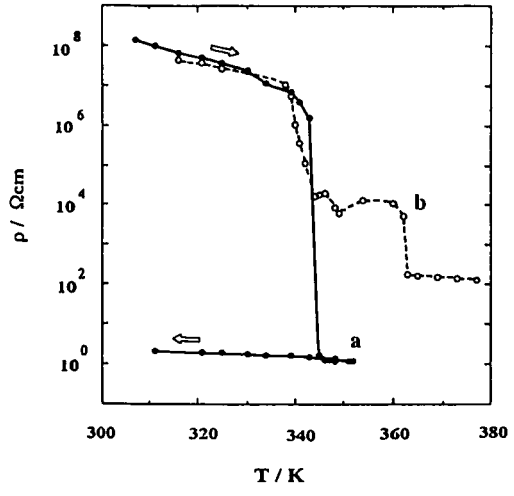


FIGURE 4 Electrical resistivity of α-DAP-CHL single crystals. **a** and **b** are independent runs for different crystals.

The X-ray crystal structure analysis of low-resistance α-DAP-CHL indicates that no structural change occurs by a transformation into the low-resistance state. The geometry of CHL is perfectly consistent with its neutral state. The infrared spectrum of low-resistance α-DAP-CHL consists of newly grown electronic absorption bands

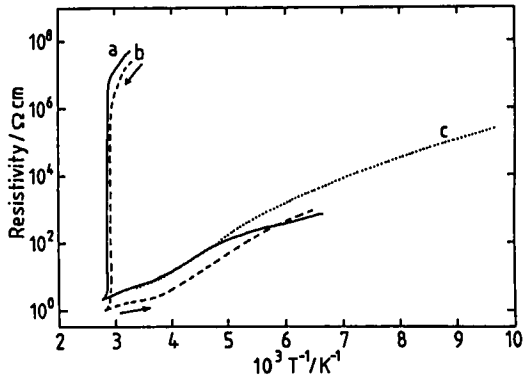


FIGURE 5 Temperature dependence of the resistivity of α-DAP-CHL; single crystals, **a** and **b**, and powder compaction, **c**.

and vibrational bands, which are the same as those of the neutral components. The ESR signal of pristine α-DAP-CHL is quite weak, indicating very low concentration of the ionized species. When the temperature is increased, the signal intensity suddenly becomes larger at nearly the same temperature region where the resistivity drop was observed, as shown in Fig. 6. More detailed study of the magnetic susceptibility of

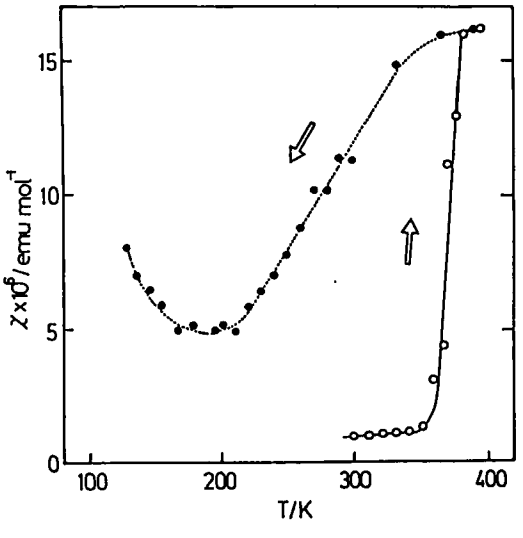


FIGURE 6 Paramagnetic susceptibility of single crystal α-DAP-CHL evaluated from the ESR signal intensity.

low-resistance α-DAP-CHL using a SQUID susceptometer indicates that the paramagnetic susceptibility consists of 0.8% of the Curie-type component and 3.3% of the singlet-triplet-type component with J/k = 500 K. Though these paramagnetic

components are arisen from a transformation into the low-resistance state, the concentration of the ionized molecules is still very small. The homogeneity of low-resistance α-DAP-CHL was checked by solid-state high-resolution NMR. The ^{13}C NMR spectrum of low-resistance α-DAP-CHL indicates that the peaks are only slightly shifted by a transformation into the low-resistance state, indicating that the molecules are essentially neutral, there is no appreciable structural change, and the low-resistance phase is fairly homogeneous. These observations confirm that the low-resistance state essentially comprises the neutral mixed-stacked molecules. Then, the reason why low-resistance α-DAP-CHL is so conductive comes into question. The resistivity value of 10^0 Ω cm is far from the achievable value for a crystal comprising mixed-stacks of donors and acceptors even when the component molecules are appreciably ionized. There could be another charge transport mechanism in which a charge carrier can travel in a crystal comprising neutral mixed-stacked molecules.

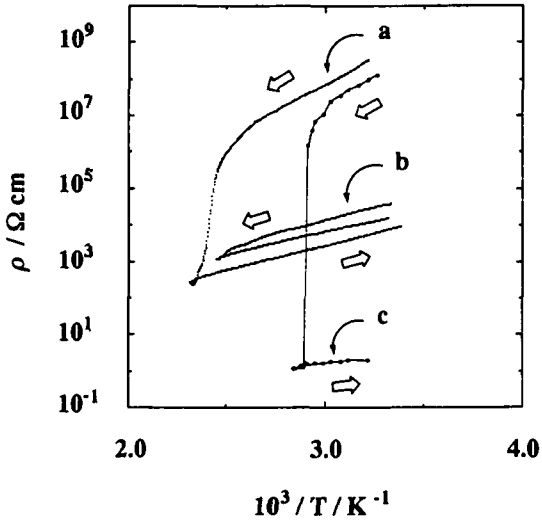


FIGURE 7 Electrical resistivity of α-DAP-DBDCQ (single crystal, **a** and powder compaction, **b**) and α-DAP-CHL single crystal, **c**.

The temperature dependence of the resistivity of α-DAP-DBDCQ is shown in Fig. 7. The resistivity drop occurs at much higher temperature compared with α-DAP-CHL. The final value of the low-resistance state is not so low as that of α-DAP-CHL. The compacted sample has been found to be also the low-resistance state, but the value is again much higher than that of α-DAP-CHL. Other physical properties are also slightly different. The signal intensity of the ESR spectra increases in the low-resistance state, but the paramagnetic susceptibility consists of only a Curie-Weiss-type component. The

electron accepting ability and the shape of DBDCQ are practically the same as those of CHL. It is not clear yet whether the replacement of CHL by DBDCQ results in such differences in property. Since the combination of DAP and DBDCQ gives four kinds of polymorphs simultaneously, it is not quite sure that each crystal obtained is composed of the pure single structural form even in the micro domain region. If there were domains which prevent the charge transport between the other regions, transport properties might be dominated by these domains.

CONCLUSIONS

It has been found that both DAP-TCNQ and α-DAP-CHL shows unusual electrical properties which cannot be interpreted with ordinary conduction mechanisms so far applied to other organic conductors. A common feature is the existence of hydrogen bonds, which seems to make the conduction anisotropy small. If this is a key of these unusual electrical properties and of an unconventional conduction mechanism, hydrogen bonding will be a powerful tool for designing charge transport in molecular crystals.

ACKNOWLEDGEMENT

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