Highly Conducting Organic Alloys $(NBDT)_2I_xBr_{3-x}$ {NBDT = Naphthaceno-[5,6-*cd*: 11,12-*c'd'*]bis[1,2]dithiole}

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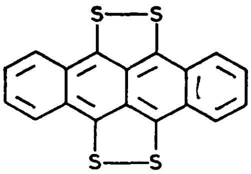
Summary Optical and conductivity measurements on the organic charge-transfer complex $(NBDT)_2I_xBr_{3-x}$ indicate that the iodine chain is not conducting and disorder is important in the parent compound $(NBDT)_2I_3$ {NBDT = naphthaceno[5,6-*cd*: 11,12-*c'd'*]bis[1,2]dithiole}.

RECENTLY, there has been considerable interest in organic conductors containing aromatic donors and halogens, especially iodine, as acceptors.[1] Because of their non-stoicheiometric and variable composition, these materials are good models for investigating the role of disorder in the transport properties. Moreover, as pointed out by Perlstein,[2] there exists a theoretical possibility of obtaining conducting iodine chains in such systems. These problems can be investigated by varying the acceptor chain either by changing the stoicheiometry or by partially replacing iodine with other halogens.

The compound $(NBDT)_2I_3$ {NBDT = naphthaceno[5,6-*cd*: 11,12-*c'd'*]bis [1,2]dithiole} is an 'organic metal' at high temperatures with one of the highest conductivities among known organic materials. In this compound relative importance of the NBDT and iodine chains and the influence of inherent disorder associated with the random I_3^- chains is unclear. In order to study these effects we have prepared new radical salts of NBDT (**1**) with mixed acceptor chains containing iodine and bromine.



(1)

The compound (NBDT)IBr was prepared by mixing nitrobenzene solutions of NBDT, iodine, and bromine, at 210 °C. The solution was then slowly cooled when needle-like crystals (typical dimensions $2 \times 0.1 \times 0.01$ mm^3) having a golden metallic lustre appeared. Depending on the initial concentrations of the solution, two different batches of crystals were obtained, both with an overall halogen content of *ca.* 1·5 mole of I_2 per 2 moles of NBDT. Elemental analyses yielded the compositions $(NBDT)I_{1\cdot1}Br_{0\cdot5}$ and $(NBDT)I_{0\cdot8}Br_{0\cdot7}$, respectively.

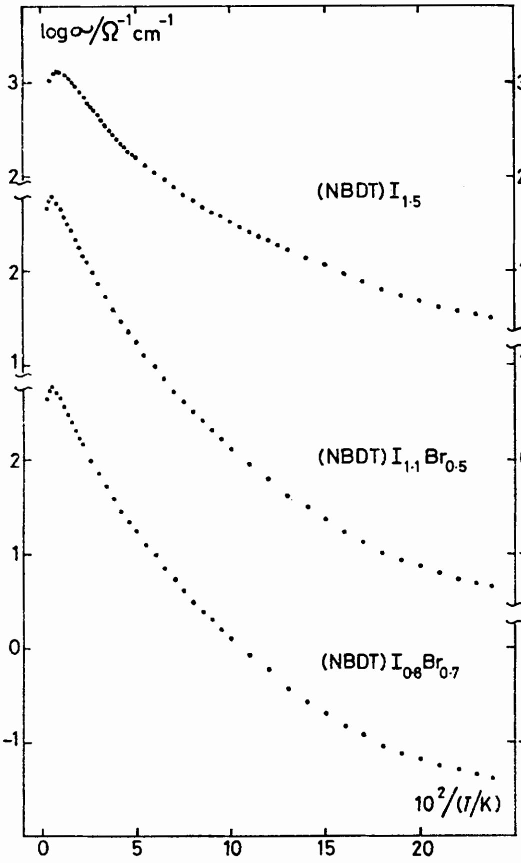


FIGURE. Single crystal conductivity *vs.* temperature of $(NBDT)_2I_3$, $(NBDT)I_{1\cdot1}Br_{0\cdot5}$, and $(NBDT)I_{0\cdot8}Br_{0\cdot7}$.

Powder *X*-ray experiments show the unit cell parameters to be the same as in the B-phase of the iodine compound whose iodine content is in the range 1·5—1·7 per mole of NBDT. U.v. spectra in dichloromethane solution show the presence of $(NBDT)^+$ and $(NBDT)^\circ$ in an approximately 1 : 1 ratio. Solid state diffuse reflectance and i.r. spectra are quite similar to those of the B-phase $(NBDT)_2I_3$, including the presence of a broad low-energy absorption band at 2500 cm^{-1} (0·3 eV), probably corresponding to the $(NBDT)^+(NBDT)^\circ \rightarrow (NBDT)^\circ(NBDT)^+$ charge-transfer process. Thus it is possible that the (NBDT)IBr systems contain NBDT stacks having the same configuration as those in $(NBDT)_2I_3$, with mixed trihalide ions in the acceptor chain, *i.e.* a random mixture of I_3^-, Br_3^-, IBr_2^-, and I_2Br^- ions.

The Figure shows a plot of the d.c. conductivity *vs.* temperature of two typical crystals containing mixed trihalides in different I : Br ratio, and that of a $(NBDT)_2I_3$ sample. The single crystal conductivities were measured by the four contact method. The samples were glued on four 10 μ thick annealed gold wires by well conducting silver paint (Dupont 4929). The temperature dependence and the absolute value of the d.c. conductivity of $(NBDT)I_{1\cdot1}Br_{0\cdot5}$ and $(NBDT)I_{0\cdot8}Br_{0\cdot7}$ are the same within the experimental error. The room temperature value is *ca.* 500 Ω^{-1} cm^{-1}. The conductivity shows a smeared maximum at 150—180 K and at lower temperatures its variation is slower than exponential. The overall behaviour is similar to that of $(NBDT)_2I_3$. Although there is a slight difference between the crystals of $(NBDT)_2I_3$ and (NBDT)IBr (T_{max} is higher in the latter case) the absolute values are somewhat lower in the (NBDT)IBr systems; these might arise from the different amounts of impurities or crystal defects owing to different conditions of preparation.

The non-stoicheiometric I : Br ratio suggests that the acceptor chains are strongly disordered in the alloys, and the conductivity is characteristic of that of a disordered material.[3] The observation that the $\sigma(T)$ curve is practically the same for $(NBDT)_2I_3$ and the alloys, suggests that there is substantial disorder even in $(NBDT)_2I_3$. We also conclude that only the NBDT chains are conducting in $(NBDT)_2I_3$. In the opposite case, the change of I_3^- for any mixed IBr trihalide would decrease the transfer integral and thus lead to strong depression of the conductivity in the $I_{1\cdot5} \rightarrow I_{1\cdot1}Br_{0\cdot5} \rightarrow I_{0\cdot8}Br_{0\cdot7}$ direction.

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[1] V. F. Kaminskii, M. L. Khidekel, R. B. Lyubovskii, I. F. Shchegolev, R. P. Shibaeva, E. B. Yagubskii, A. V. Zvarykina, and G. L. Zvereva, *Phys. Stat. Sol.* (*a*), 1977, **44**, 77; R. B. Somoano, S. P. S. Yen, V. Hadek, and S. R. Khanna, *Phys. Rev.* (*B*), to be published; L. I. Buravov, G. I. Zvereva, V. F. Kaminskii, L. P. Rosenberg, M. L. Khidekel, R. P. Shibaeva, I. F. Shchegolev, and E. B. Yagubskii, *J.C.S. Chem. Comm.*, 1976, 720; L. C. Isett and E. A. Perez-Albuerne, *Solid State Comm.*, 1977, **21**, 433; J. B. Torrance, B. A. Scott, B. Welber, P. E. Seiden, and F. B. Kaufman, preprint; J. L. Petersen, C. S. Schramm, D. R. Stojakovic, B. M. Hoffman, and T. J. Marks, *J. Amer. Chem. Soc.*, 1977, **99**, 286.

[2] J. H. Perlstein, *Angew. Chem.*, 1977, **89**, 534.

[3] K. Holczer, G. Mihály, A. Jánossy, G. Grüner, and M. Kertész, unpublished results.