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J. B. Webb [a] , N. S. Dalal [a] & D. F. Williams [a]

[a] Division of Chemistry, National Research Council of Canada, Ottawa, Canada

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CHARGE CARRIER TRANSPORT IN 1:1 COMPLEXES OF TETRACYANOBENZENE WITH NAPHTHALENE ANTHRACENE AND DURENE

J.B. WEBB, N.S. DALAL AND D.F. WILLIAMS
Division of Chemistry, National Research
Council of Canada, Ottawa, Canada
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It is well established that crystals of charge transfer (CT) complexes formed between aromatic donors and acceptors are built up of linear stacks of closely packed molecules . There are two main types of CT crystal structure, (i) a parallel arrangement of linear stacks made up of the individual component molecules, AAAA...DDDD... and (ii) a parallel arrangement of linear stacks made up of alternating molecules, ADADA... In each case it is to be expected that the intermolecular forces between the face to face packed molecules in each stack are far greater than those forces between stacks.

A considerable anisotropy in physical properties which are a strong function of intermolecular interactions is a natural result of these crystal structures. Such anisotropy has been reported in the few crystals of the ADAD structure which have been examined, for example, in triplet exciton motion in biphenyl[2] and anthracene tetracyanobenzene (TCNB) complexes[3,4] and in charge carrier mobilities μ in anthracene[5] and phenthrene-pyromellitic-acid-dianhydride[6] as well as anthracene-trinitrobenzene[7]. Carrier mobilities which were reported were all low, < 0.1 cm^2/V sec., and though the major interesting questions were posed, such as what is the effect of different donors on μ?; or are there separate conduction and valence bands for acceptors and donors?; the dearth of mobility data on a range of materials leaves these questions unanswered.

We have recently measured the mobilities of holes in several TCNB complexes as a first step towards understanding carrier transport in such materials.

These are a particularly interesting series of materials in that triplet motion is said to be primarily two dimensional in anthracene TCNB[3], and unidimensional in biphenyl TCNB[2]. Since the transport of charge, like triplet exciton motion, is dominated by exchange interactions, and since CT triplet excitons carry an appreciable dipole moment - hence electron-phonon interactions are important - it is reasonable to expect some correlation between CT triplet and charge carrier transport properties.

A typical structure of one of our complexes is shown in Fig. 1. The crystals which were solution grown always exhibited a dominant c or stack axis. In the naphthalene complex the naphthalene and TCNB molecules lie perpendicular to this axis, whereas in the anthracene and durene complexes the molecules are tilted ~22° and ~20° to the c axis respectively[8,9].

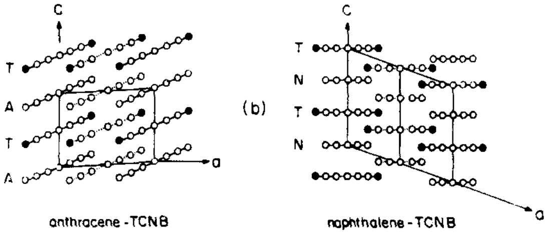

Fig. 1. Crystal structure of anthracene and naphthalene TCNB. c is the crystal stack axis.

The carrier mobilities were measured from photocurrent transients generated by a nitrogen laser pulse. The shape of the transient indicated a surface generation of charge, as expected, since the laser light 3371 A^o is strongly absorbed in all three complexes. Some trapping and thermal detrapping is evident in Fig. 2 and this is to be expected for solution grown crystals, but the kink in the current pulse can still be clearly seen. Only hole transients could be resolved however, and some residual space charge always remained on the crystal surface, presumably due to trapped electrons. In this case the mobilities were calculated from $t_t = L^2/\mu(v-v_o)$ where t_t is the current transit time, v the external voltage and v_0 the internal potential resulting from trapped charge and L is the crystal thickness. The transit time was found to scale with crystal thickness according to the above relation. Some typical changes of t_t^{-1} with applied field are shown in Fig. 2 for a naphthalene TCNB crystal with

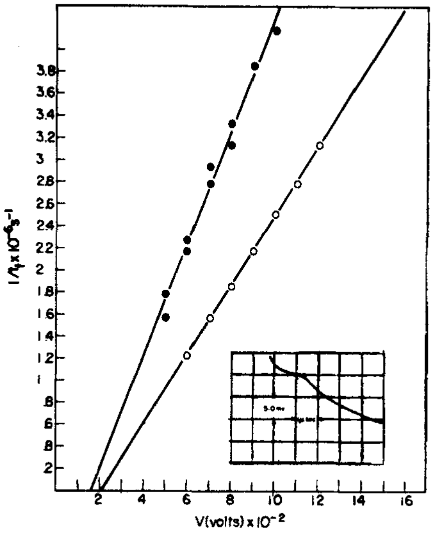

Fig. 2. Typical observed current transient and voltage dependence of transit time^{-1} on voltage for naphthalene TCNB.
○ E||, ● E⊥ c.

E|| and ⊥ to the c axis. The samples were always detrapped between measurements by reversing the field and illuminating the sample. In this manner the internal field v_0 was found to be constant for each transit measurement, Fig. 2. The calculated mobilities shown in Table I are quite large for aromatic mobilities. Unfortunately the temperature range of these measurements, 260-300°K, was not sufficient to accurately determine the mobility temperature dependence. Nevertheless, the lack of any significant mobility anisotropy and the relatively high mobilities indicate the carriers are probably delocalized. No trend of mobility variation paralleling that in the pure parent donor hydrocarbon is found. These results show that for charge transport studies in these materials one should consider the donor-acceptor pair as an entity, and hence expect that the drift mobility along the stack axis would show a considerable temperature dependence due to strong electron-phonon coupling.

TABLE I

Observed hole mobilities for anthracene, naphthalene and durene TCNB crystals where $\mu_{||}$ is along the stack direction and $\mu_{\perp}$ is perpendicular to the stack axis.

Complex	$\mu_{||}$ (cm^2/v-s)	$\mu_{\perp}$ (cm^2/v-s)	Error
A-TCNB	2.8	3.3	± 10%
D-TCNB	2.7	3.3	± 10%
N-TCNB	2.9	4.8	± 10%

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