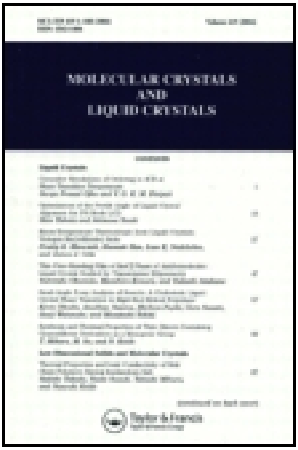

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Organic Conductors Versus Organic Photoconductors: Similarities and Differences in Their Charge Carrier Transport

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Version of record first published: 17 Oct 2011.

To cite this article: Norbert Karl, Roland Stehle & Wilhelm Warta (1985): Organic Conductors Versus Organic Photoconductors: Similarities and Differences in Their Charge Carrier Transport, Molecular Crystals and Liquid Crystals, 120:1, 247-250

To link to this article: http://dx.doi.org/10.1080/00268948508075795

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 247-250
0026-8941/85/1204-0247/$10.00/0

Printed in the United States of America

ORGANIC CONDUCTORS VERSUS ORGANIC PHOTOCONDUCTORS: SIMILARITIES AND DIFFERENCES IN THEIR CHARGE CARRIER TRANSPORT

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Abstract Are the time-of-flight mobilities obtained with suitable members of the family of organic photoconductors such as naphthalene and perylene also representative of the basic transport processes occurring in organic semiconductors and conductors? Our recent results support this idea.

The most important microscopic parameters of charge carrier transport in organic semiconductors and conductors are not easily accessible experimentally: Electrical conductivity reflects an additive superposition of electron and hole contributions, where each contribution is composed of a concentration and a mobility factor, and each of these four independent quantities may have a different temperature dependence. The two mobilities are often highly anisotropic tensors which require the determination of 4 components each for monoclinic crystal symmetry, and which are composed of 6 components for triclinic symmetry (which both occur frequently).

In the case of Hall effect or Seebeck coefficient measurements electron and hole contributions are superimposed subtractively and may even cancel eachother.

The interpretation of near IR or VIS reflectivity in terms of "optical conductivity" is sometimes not unambiguous; electron and hole contributions cannot be separated either.

With electron spin resonance and NMR methods the motion of spin carrying particles can be studied. However, only in cases of single sign, one-dimensional transport a straightforward interpretation of the data in terms of concentration and diffusion constant seems possible, cf./1/.

Since, in general, none of these methods is specific for either charge carrier sign alone, nor suitable for the determination of single microscopic parameters, a direct determination of electron and hole drift mobilities has been highly desirable.

Indeed, a direct determination of mobilities has been demonstrated to be feasible for organic photoconductors with vanishing dark conductivity, which can maintain an electric field without space charge accumulation or dielectric relaxation /2/: In the time-of-flight technique electrons and holes are produced near one face of a crystal slice (of typical thickness 0.1 ... 1mm) by a strongly absorbed light (or electron beam) pulse, and a sheet-like uncompensated space charge (of either sign) is pulled through the sample by an (appropriately poled) electric field. Its arrival time at the rear electrode is monitored on an oscilloscope as the trailing edge of an (ideally) rectangular current pulse.

Time-of-flight signals of surface-generated charge carriers have the great advantage of directly making visible electron or (independently) hole mobilities. Since no such direct method is available for dark-conductive organic materials, it is desirable to consider which general conclusions on charge carrier transport in organic molecular crystals can be drawn from time-of-flight results obtained from organic photoconductors.

Recent progress with the ultrapurification and technology of several typical photoconductors, such as naphthalene and perylene, has allowed us to observe essentially trap-unperturbed time-of-flight transits down to liq.He temperature for the first time: With decreasing temperature the electron and hole mobilities increase continuously over orders of magnitude (anisotropic power law), see figs.1,3. At high electric fields/low temperatures the charge carrier velocities display sublinear deviations from Ohm´s law and tend to saturate at approximately $2\cdot10^6$ cm/s, see figs.2,4. The highest measured mobility values ranged about 400 cm^2/Vs. Their magnitude was limited by the minimum electric field necessary for detecting a signal.

We conclude from our naphthalene and perylene results by comparing them with the scarce (and indirectly obtained) mobility data available for highly conductive materials, cf./4/, that charge carrier transport in both classes of materials, organic photoconductors and organic conductors, is very similar and governed by the same principles, as long as a single-particle description applies. We therefore propose that organic photoconductors can be suitable model systems for studying basic features of charge carrier transport in organic semiconductors and conductors.

We further believe that the entire range of three, two, and one-dimensional transport can be covered with suitably selected model crystal structures.

On the other hand, we are aware that our approach of drawing conclusions on transport in dark conductors from the transport results obtained with photoconductors becomes worse the more the former transport is governed by electron-electron (hole-hole) repulsion or electron-hole attraction, or by cooperative electron-phonon interactions.

It is worth mentioning that the observation of a subohmic transport with tendency towards high field saturation of the carrier velocity was possible because photoconductors can withstand much higher electric fields than the good conductors, and in addition since the former can be prepared in very high purity by zone-refining. Besides the other aspects mentioned, these hot carrier effects demonstrate the great value of photoconductor model systems.

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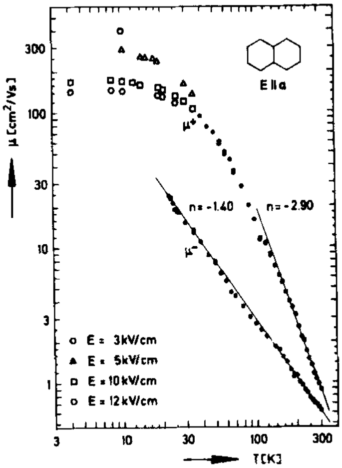

FIGURE 1 Naphthalene, mobility, μ_{aa}, versus temperature for different electric field strengths, log/log plot; /3/.

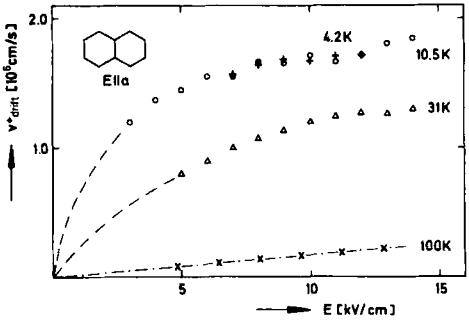

FIGURE 2 Naphthalene, hole velocity versus electric field; the crystallographic orientation, E parallel [100], is the same as in fig. 1.

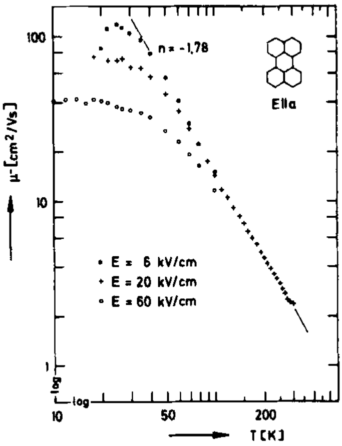

FIGURE 3 Perylene, electron mobility versus temp. for different electric field strengths, log/log plot; /3/.

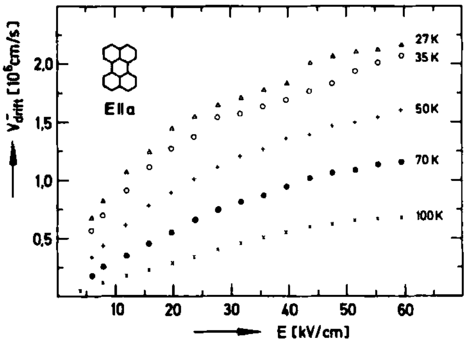

FIGURE 4 Perylene, electron velocity versus electric field; the crystallographic orientation, E parallel [100], is the same as in fig. 3.

ACKNOWLEDGEMENT

This work has been supported by the Deutsche Forschungsgemeinschaft.