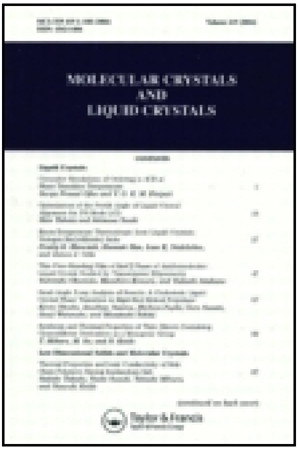

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Holes and Electrons Mobilities in 9-Methylanthracene Single Crystals

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Holes and Electrons Mobilities in 9-Methylanthracene Single Crystals

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Holes drift mobilities have been measured in 9-methylanthracene, in a temperature range comprised between 170 and 300 K, using transient techniques. For holes, room temperature values of 0.93, 0.85 and 0.64 $cm^2/Vsec$ along b, a, and c′ directions have been obtained. For electrons the mobility, measured only at room temperature along the c′ direction, has a value of 0.7 $cm^2/V.sec$. The hole mobility presents a T^{-x} dependence, with $x = 2.2, 1.7$ and 1.1 for b, a and c′ directions. These results are discussed in terms of band or hopping models, by taking into account the crystal structure and the excimeric properties of 9-methylanthracene.

1 INTRODUCTION

In the organic solid state field anthracene is one of the most extensively studied substances, both theoretically and experimentally. The studies on anthracene derivates show clearly that the introduction of substituents in the anthracene molecule leads to noticeable changes of photophysical and photochemical properties.[1,2]

Since some anthracene derivatives are also photoconductors, it would be interesting to know how and in which measure the chemical substitution affects the transport properties. With regard to this, the existing data are limited to 9, 10-dichloroanthracene,[3-5] and the mobility values found have been correlated with the crystallographic structure and with his excimeric properties. In this paper we report the result of a study of carrier transport properties of 9 methylanthracene (MeA).

2 EXPERIMENTAL

Mobility measurements were performed on single crystals of MeA grown from the melt, after careful purification (chromatography, sublimation and zone refining) of the starting material. Great care was taken in order to avoid the photochemical transformation of the substance. MeA belongs to the monoclinic space group P $2_1/c$,[6,7] with $a = 8.909$, $b = 14.625$, $c = 8.060$, $Z = 4$ and $\beta = 96.54°$.[6]

Oriented crystal samples, whose thickness ranged between 0.5 and 3.5 mm, were placed in a crystal holder, between a semitransparent conducting glass (front electrode) and a copper plate (back electrode) which was also the cold finger of a liquid nitrogen dewar. The temperature of the sample, monitored with a copper-constantan thermocouple, was varied by changing the dripping speed of liquid nitrogen inside the dewar.

An EG. & G. Microflash was used for excitation, providing a short (0.5 μsec pulse width) light flash. Space charge free conditions were obtained by lowering the light intensity with suitable filters. The voltage was applied at the crystal by means of a Keithley 246 H.T. power supply. The current pulses following the light flash were fed into a cathode follower and finally displayed into a Tektronik 549 oscilloscope.

3 RESULTS AND DISCUSSION

When the semitransparent electrode is positively biased, and the input resistence of the cathode follower is low (47–22 KΩ), the light flash produces typical current pulses, showed in Figure 1 (lower part). The time corresponding to the change in slope of the current pulse, which is inversely proportional to the voltage, indicates the arrival of the holes at the back electrode, and represents the hole transit time t_d. In space-charge-free conditions, the carrier mobility is calculated from the relation $\mu = d^2/Vt_d$, where d is the crystal thickness and V the applied voltage. In this way, room temperature mobility values of 0.93 $cm^2/V.sec$ along b, 0.85 cm^2/V sec along a and 0.64 $cm^2/V.sec$ along c' are obtained.

Figure 2 shows the temperature dependence of the holes mobility for the three different crystal directions.

In the range comprised between 170 and 300 K, the mobility increases when the temperature of the crystal decreases, and the log-log plot of the mobility vs temperature gives a T^{-x} dependence, with $x = 2.2$ for the b direction, $x = 1.7$ for the a direction and $x = 1.1$ for the c' direction.

When the illuminated electrode is negatively biased the current pulses obtained (Figure 1, upper part) show a fast decay due to strong trapping and permit the determination of the electron transit time only along the c' direction. In this case, at room temperature, an electron mobility of 0.7 $cm^2/V.sec$ is obtained. Below room temperature, however, the magnitude and the shape of the pulses doesn't allow anymore the determination of the transit time.

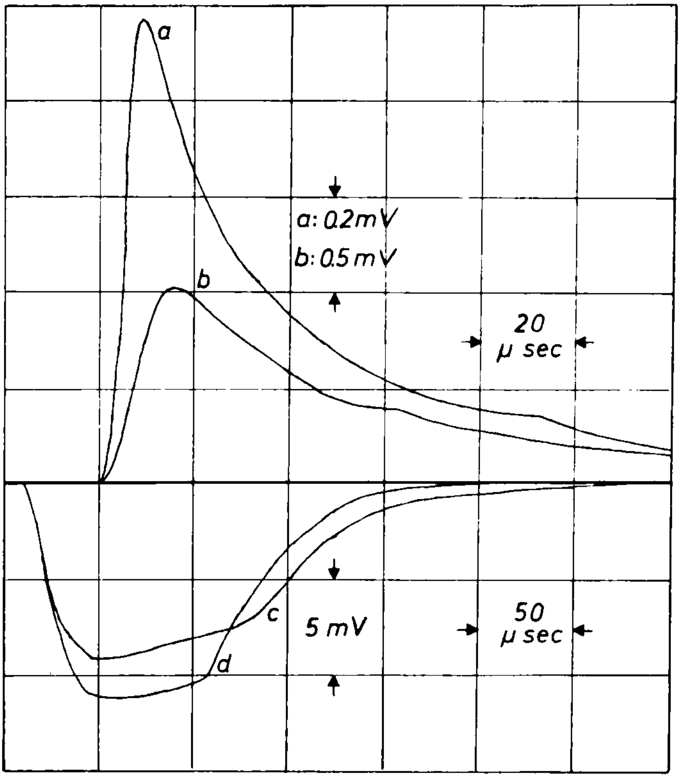

FIGURE 1 Typical electron and hole transients (upper and lower part, respectively), with the electric field in the c' direction. Voltage applied; a, 1000 V. b, 1500 V, c, 750 V, d, 1000 V, across a sample 2.44 mm thick. $T = 283$ K.

The results of mobility measurements carried out on molecular crystals have been generally explained in term of band or hopping models.[8] As Glarum[9] pointed out, for mobility values higher than 1 $cm^2/V.sec$ the band model seems to be the correct description of the charge motion, while for mobility values $\leqslant 1$ $cm^2/V.sec$ the hopping model is more adequate.

From these considerations, however, only in few cases, i.e. durene,[10] p-diodobenzene[11] and 9,10 dichloroanthracene (α-form),[4,5] in which the room temperature mobilities are ≥ 2.8 $cm^2/V.sec$, the band model can be considered the realistic model for charge transport.

In the case of MeA the room temperature mobilities, comprised between 0.93 and 0.64 $cm^2/V.sec$, are on the borderline between the two models.

The temperature dependence of mobility, however, may help the choice of the correct model. In fact, in the band model the mobility is proportional to T^{-m}, with $m \geq 1$, while in the hopping models the mobility is generally

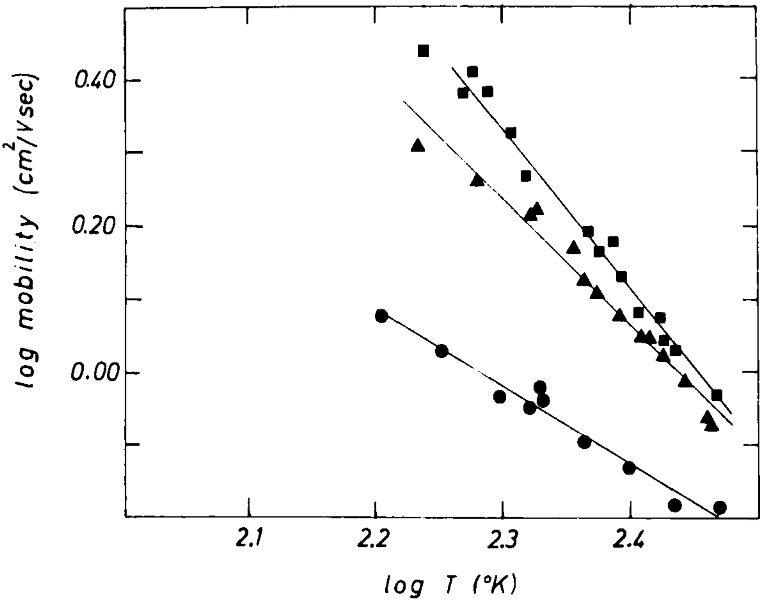

FIGURE 2 Log-log plots of hole mobilities vs temperature for a (▲), b (■) and c′ (●) crystal directions.

proportional to $T^{-n} e^{-E/KT}$, where $n \simeq 1$ and E is the activation energy.[12]

In MeA the mobility changes proportionally to T^{-x}, where $x = 2.2$ for the *b*, 1.7 for the *a* and 1.1 for the *c′* direction. The band model should therefore describe in a reasonable way the hole transport along the *a* and *b* directions, while in the *c′* direction the hopping model cannot be completely ruled out. Till now there is no theoretical calculation of the hole bandwidth of MeA in this direction, which could indicate the proper mechanism of charge motion.

MeA belongs to the same space group of anthracene, but with four molecules per unit cell. Following Robertson classification,[13] anthracene has a A type structure, where adjacent molecules are slightly overlapped, while MeA has a B type structure, with considerable overlap between adjacent molecules which are arranged in pair. For this reason MeA, unlike anthracene, shows only excimer emission and readily yields photodimers.[1,2] Our results, compared with those obtained by others on anthracene,[14,15] deserve some remarks.

The mobility in MeA is less anisotropic than in anthracene (Table I) and the values are slightly lower. It is not clear if the lower anisotropy of the hole band depends only on intermolecular spacing, or is due also to excimer formation along the b direction of the crystal, which could enhance the electron phonon coupling with the lattice modes and reduce the mobility in that direction.[3]

TABLE I

Substance	carrier	μ^{a}_{max}	μ^{a}_{min}	μ_{max}/μ_{min}	Ref.
Anthracene	+	1.3 (//ab)	0.4 (⊥ab)	3.25	14
Anthracene	+	2.1 (//b)	0.7 (⊥ab)	3.0	15
Perdeut. anthracene	+	2.0 (//a)	0.78 (//c)	2.56	18
9-methylanthracene	+	0.93 (//b)	0.64 (//c)	1.45	This work

[a] Room temperature values. ($cm^2/V.sec$)

From the few data available, the effect of excimer formation on charge transport cannot be exactly estimated. In fact in some cases (perilene and dichloroanthracene, β form) the excimer formation seems to affect strongly the mobility, leading to a hopping motion of carriers.[3,16] In the case of pyrene, instead, the experimental results indicate that the effect is not so strong and the carrier motion may be described by a band type model.[17]

In MeA the mobility values, and the temperature dependence found, means probably that the electron-phonon coupling, in spite of the excimer formation, is not so strong to lead towards a hopping motion.

Finally, even if the mobility is not strongly affected by the crystal direction, our results clearly show that, as in anthracene, the highest mobility and temperature coefficent are along the *b* direction, where the interplanar distance between adjacent molecules is only 3.5 A,[6] while the lowest values are along *c*′, which approximately corresponds with the long axis of the molecule[6] and should be the direction of lowest intermolecular interaction.

Further work is now in progress on MeA for a better understanding of the effect of crystal structure and excimer formation on carriers mobility.

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