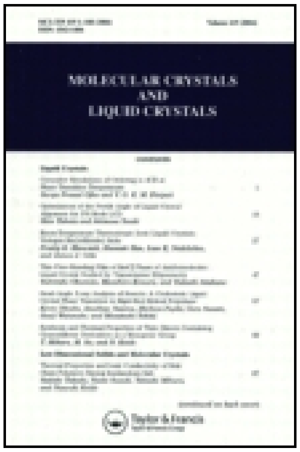

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On the Tight Binding Calculations for Anthracene Crystal

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On the Tight Binding Calculations for Anthracene Crystal

(Reply to Comment)

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The problem of the theoretical prediction of the temperature dependence of current carriers mobilities in molecular solids has been studied in general within the framework of the band theory for both narrow and broad band cases giving $n < 2$ in the relation $\mu \sim T^{-n}$ when only single acoustic phonon scattering processes are considered.[6] A possible role of the intermolecular resonance integrals (transfer integrals T.I.) for an explanation of the temperature dependence of mobilities in anthracene crystal has also been studied recently.[3]

We have found an error in the former machine computation process and the recalculated values of T.I. obtained for 290 °K and 95 °K with the same assumptions as before[3] are listed in Table 1. The results are also compared with those obtained for Sinclair *et al.*[12] crystal structure of anthracene. It will be noted that the LeBlanc's T.I. cited by Delacôte[5] were evaluated by an incorrect formula[7] (also in Thaxton *et al.*[14] calculation). A small divergence between the results of Delacôte and ours may arise from another set of Mason's coordinates[10] taken in (5). We have shown that the differences are within the limits of the accuracy of the anthracene crystal structure determination.

The new values of n in the equation $\mu \sim T^{-n}$ are quoted in Table 2 both with the existing experimental data. The theoretical slopes seem to be correct except the c′ direction for electron. The comparison made between the results of experiments with one

TABLE 1 Values of Transfer Integrals (in Units of 10^{-4} eV) between the Molecule Situated at the Origin of Coordinate System and Molecules Described by the Indices (010), (0.5 0.5 0), and (0.5 0.5 1) Respectively

Temp.	(010)		(0.5 0.5 0)		(0.5 0.5 1)	
	Hole	Electron	Hole	Electron	Hole	Electron
Room[12]	− 20.72	15.64	− 18.34	− 24.80	4.13	0.67
290 °K[10]†	− 23.20	17.60	− 17.43	− 25.00	4.40	0.71
95 °K[10]†	− 23.84	17.59	− 26.33	− 33.41	6.07	0.78
290 °K[10]‡	− 23.04	17.57	− 16.95	− 25.16	4.47	0.77
95 °K[10]‡	− 23.32	17.10	− 26.48	− 33.07	5.95	0.73

† Calculated for the arithmetic mean of the Mason's coordinates.
‡ Calculated for the " complete " Mason's coordinates.

TABLE 2 Calculated and Experimental Values of n in the Equation $\mu \sim T^{-n}$

Direction	Calculated		Experimental	
	Hole	Electron	Hole	Electron
a	0.7	0.5	—	1.1[8]
b	0.2	0.3	—	0.8[8]
c′	0.6	0.2	1[9]; 2[2]; 1.1[8](?)	1[9]; − 0.3[8]; 1.8[8](?)

another and with those of Bepler for the pyrene crystal[1] suggests, however, that the temperature dependence of electron mobility along the c′-axis is not ascertained. A scattering parameter may also play a role but for this effect allowance is not made on our calculation.

The tight binding model may be inadequate for molecular solids especially with the use of not good in tail STO's.[7] In such a case only a few atomic components in the T.I. are usually taken into account for the (0.5 0.5 1) molecule of anthracene. The SCF $2p$ functions (e.g. Clementi-Roothaan orbitals[7] seem to be much better but then the three-center integrals are of great importance[7] revised[11]). On the other hand the approximation is only a π-electron approach. The results of Schmidt's orthogonalization for naphthalene[13] point out (as well as our calculations for anthracene[4] do) that the crystal field of the form

$$V(\mathbf{r}) = \sum_{l} V^{\mathrm{C}}(\mathbf{r} - \mathbf{r}_l) + \sum_{l,m} V^{\mathrm{H}}(\mathbf{r} - \mathbf{r}_{lm})$$

where not only carbon potentials (V^{C}) but also m hydrogen potentials each of l molecules (V^{H}) are taken into account may be a better approach for hydrocarbon crystals. The hydrogen potentials seem to be most of importance just along the $\mathbf{c}'$-axis where intermolecular interactions are realized greatly by hydrogens. Hence, this may be another reason that the transport properties are more difficult to explain along the $\mathbf{c}'$ direction.

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