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

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Version of record first published: 21 Mar 2007.

To cite this article: Yosihiro Aikawa , Mitsunori Sukigara & Kenichi Honda (1976): Photoconduction and Intermolecular Electron Interaction in Auramine Crystal, Molecular Crystals and Liquid Crystals, 36:3-4, 235-243

To link to this article: http://dx.doi.org/10.1080/15421407608084327

Mol. Cryst. Liq. Cryst., 1976, Vol. 36, pp. 235–243

Printed in Holland

Photoconduction and Intermolecular Electron Interaction in Auramine Crystal

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(*Received April 30, 1976; in final form July 15, 1976*)

The band structure for an excess electron and an excess hole in the auramine crystal were calculated in the tight binding approximation. Simplified formulas were derived for the interatomic resonance integrals to accomplish the calculation of band structures in molecular crystals involving hetero-atoms easily. The calculation showed the possibility that this crystal behaves as *n*-type in the a^* direction and as *p*-type in the c^* direction as expected from the molecular electron distribution and the crystal structure.

INTRODUCTION

Transport of charge carriers in organic solids has been discussed from two different points of view, i.e., the band model and the localized model. In any case, however, mobility of the charge carriers is primarily determined in terms of intermolecular electron interaction. In the band picture of tight binding approximation, the intermolecular interaction determines the shape of an excess electron band or hole band which reflects in the group velocity of carriers.[1] In the localized picture, on the other hand, the quantity of the interaction is essential in the transition probability of an excess electron or hole from one site to the neighbouring site resulting in the hopping model (high temperature) or the tunneling model (low temperature).[2]

There are many organic materials which show semiconductivity or photoconductivity in the solid state or ordered state. Many of them are compounds containing hetero-atoms, especially organic dyes which play an important roll in the sensitization of semiconductors and photographic process,[3] and some biologically important substances such as chlorophile.[4] For this

interesting group of materials only a small number of calculations of bands or even of intermolecular electron exchange interactions has been reported.[5]

A calculation of excess electron and hole bands of the auramine perchlorate crystal is given in the present study. The π-electron molecular orbitals of auramine calculated with PPP method showed the concentration of an excess electron at the central imino group of the molecule and, to the contrary, the spread over of an excess hole all around the molecule except the imino group. Such electron and hole distributions in a molecule suggest a large anisotropy in electron and hole mobilities in the solid state, i.e., a hole would have a largest velocity in the direction of the maximum overlap of aminophenyl group and an electron in the direction of the maximum overlap of the imino group. The predicted anisotropy in the mobility of electrons and holes may explain somewhat contradictory results previously reported by the authors that the majority carriers through the evaporated auramine film was electron[6] but the carriers in the photoconduction of auramine crystal were holes.[7] Though the method proposed here is the first approximation, it might be convenient for the semi-quantitative calculation of intermolecular electron exchange interactions of a large number of interesting organic systems.

BAND CALCULATION

The band structures for an excess electron and an excess hole in the auramine perchlorate crystal were calculated in the tight binding approximation using the molecular orbitals as the approximate basis functions. Goeppert-Mayer–Sklar type potential[8] was used as an average potential of a second row atom written as follows:

$$V_X(r) = \frac{N_X}{N_C} V(\alpha_X, r) + \frac{Z_X e^2}{r} \tag{1}$$

where N_X and Z_X are respectively the number of L shell electrons and the formal charge of atom X at the valence state, and V is given as,

$$V(\alpha_X, r) = \frac{e^2}{r}[4 + 6(\alpha_X r) + 4(\alpha_x r)^2 + \tfrac{4}{3}(\alpha_X r)^3]e^{-2\alpha_x r} \tag{2}$$

Here α_X is the parameter which optimizes the single parameter Slater type orbital of atom X.

An intermolecular resonance penetration integral is generally written as $\langle m|U_1 H' U_2|m\rangle$, where $|m\rangle$ is the molecular orbital of a molecule at the site m making the potential H', and U_i is an operator to bring the molecule to the ith site in the crystal. The potential H' is approximately expressed by the

sum of the potentials of atoms which construct the molecule,

$$H' = \sum_p V_p$$

and $|m\rangle$ can be written as a linear combination of the atomic orbitals,

$$|m\rangle = \sum_p c_p |p\rangle$$

where $|p\rangle$ is the p_π-atomic orbital of the pth atom in the molecule. Thus the intermolecular resonance penetration integrals can be reduced into the interatomic integrals,

$$\langle m|U_1 H' U_2|m\rangle = \sum_{p,q,r} c_p c_q \langle p|U_1 V_r U_2|q\rangle$$

Neglecting three center integrals, one needs to calculate only the integrals, $\langle p^k|V_q|q\rangle$, so long as one is concerned about the shape of the bands. Here $|p^k\rangle$ means that the atom p belongs to a molecule at the kth molecular site from a fixed position which is occupied by a molecule containing the atom q. The integral $\langle p^k|V_q|q\rangle$ can be divided into two integrals: σ-integral and π-integral,[9,10]

$$\begin{aligned}\langle p^k|V_q|q\rangle &= (t_{qp}\cdot n_p)(t_{pq}\cdot n_q)\langle \sigma_p^k|V_q|q\rangle \\ &\quad + [n_p n_q + (t_{qp}\cdot n_p)(t_{pq}\cdot n_q)]\langle \pi_p^k|V_q|q\rangle \end{aligned} \tag{3}$$

where n_p is the unit vector of the directions of p_π orbital of the atom p and t_{pq} is the unit vector from the atom q to the atom p.

In the case between two carbon atoms, the interatomic resonance integrals were calculated by LeBlanc[9] and Katz *et al.*[10] as follows,

$$\begin{aligned}\langle \sigma_C|V_C|C\rangle &= e^{-\alpha_C r}\left[-\frac{e^2}{r}P(\alpha_C r)\right] \\ \langle \pi_C|V_C|C\rangle &= e^{-\alpha_C r}\left[-\frac{e^2}{r}Q(\alpha_C r)\right]\end{aligned} \tag{4}$$

where r is the distance between two carbon atoms and,

$$\begin{aligned}P(x) &= 2^{-7}(1386x^{-2} + 1386x^{-1} + 693 - 1596x + 593x^2) \\ Q(x) &= 2^{-8}(1386x^{-2} + 1386x^{-1} - 2120 + 1072)\end{aligned} \tag{5}$$

Extension of the above formulas to more general cases results in,

$$\begin{aligned}\langle \sigma_p^k|V_q|q\rangle &= \exp\left(-\frac{\alpha_p r}{2}\right)\left[-\frac{e^2}{r}P(\alpha_q r)\right]\exp\left(-\frac{\alpha_q r}{2}\right). \\ \langle \pi_p^k|V_q|q\rangle &= \exp\left(-\frac{\alpha_p r}{2}\right)\left[-\frac{e^2}{r}Q(\alpha_q r)\right]\exp\left(-\frac{\alpha_q r}{2}\right)\end{aligned} \tag{6}$$

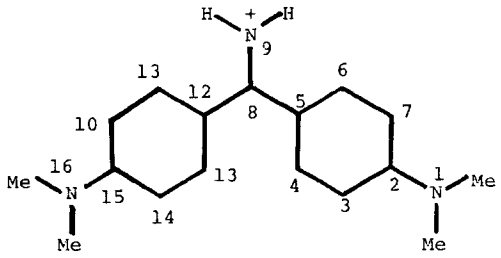

FIGURE 1 The structure of Auramine Molecule.

The formulas in Eqs. (6) are the functions of only the distance between two atoms and the Slater's parameters of atomic orbitals.

The electronic structure of an auramine molecule shown in Figure 1 was calculated with Pariser–Parr–Pople[11,12] method assuming the C_{2v} symmetry of the molecule. The distributions of an excess electron and an excess hole in a molecule within the PPP approximation are given in Table I. It is remarkable that an excess hole spreads over the molecule and that, to the contrary, an excess electron concentrates in the center of the molecule.

The auramine perchlorate crystal has the space group $P\bar{1}$ with the lattice constant of $a = 8.86$ Å, $b = 9.69$ Å, $c = 11.29$ Å, $\alpha = 97°40'$, $\beta = 99°34'$,

TABLE I

The distributions of an excess electron and an excess hole in a molecule

Atom	Excess electron[a]	Excess hole[a]
1	−0.298	0.439
2	0.268	−0.118
3	0.143	−0.308
4	−0.258	0.028
5	0.009	0.405
6	−0.231	0.015
7	0.102	−0.293
8	0.505	0.014
9	−0.334	−0.019
10	0.131	0.257
11	−0.258	−0.032
12	0.007	−0.357
14	0.124	0.271
15	0.264	0.156
16	−0.297	−0.409

[a] The numbers in the Table represent the coefficients of corresponding atomic orbitals in the lowest vacant molecular orbital (excess electron) or the highest occupied molecular orbital (excess hole).

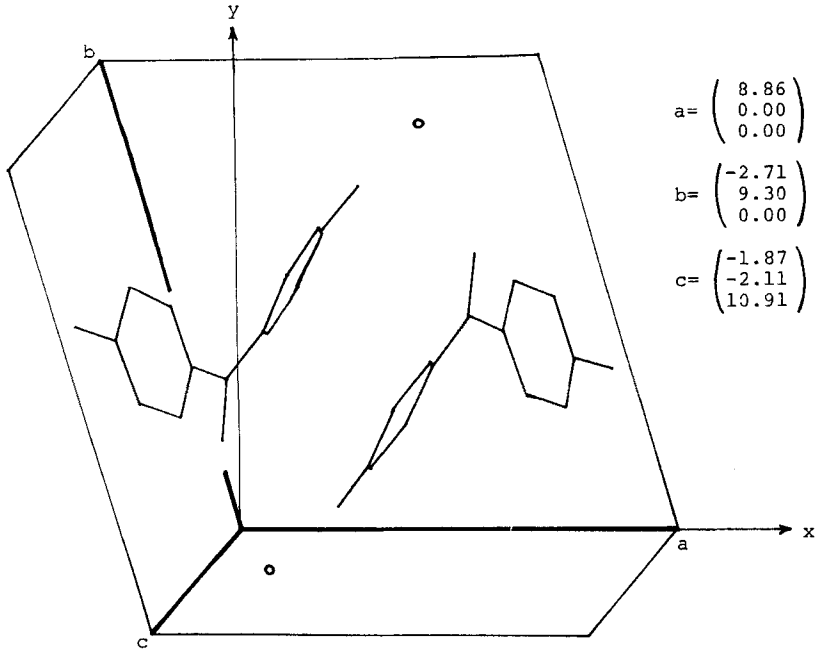

FIGURE 2 A unit cell of the auramine perchlorate crystal.

$\gamma = 106°16'$ (see Figure 2),[13] and contains two auramine molecules in a unit cell. So the operator U can be expressed by a product of the translation operator T_1 where 1 is a lattice vector and the inversion operator i. An exchange interaction between any two molecules, $|m\rangle$ and $|n\rangle$, is represented by an integral $\langle m|H'U|m\rangle$. We calculated those integrals taking $(3^3 - 1)$ unit cells into account. The resonance integrals which have significant values are tabulated in Table II. Because there are two molecules in a unit

TABLE II
The resonance integrals $\langle m|VU|m\rangle$ (10^{-4} eV)

U	Electron	Hole
iT_{-b-c}	−29.208	23.699
iT_{-a-b-c}	17.758	9.107
iT_{-b}	−0.759	12.150
iT_{a-b}	−0.022	−0.047
T_a	−0.003	−0.006
T_b	−0.002	0.000

cell, each energy band has two branches as:

$$E_{\pm}(k) = E^0 + \sum_{1 \neq 0} \langle m|H'T_1|m\rangle \cos kl \pm \left| \sum_{1} \langle m|H'iT_1|m\rangle e^{-ikl} \right| \qquad (7)$$

where E^0 is the energy of an excess electron or hole independent of wave vector k.

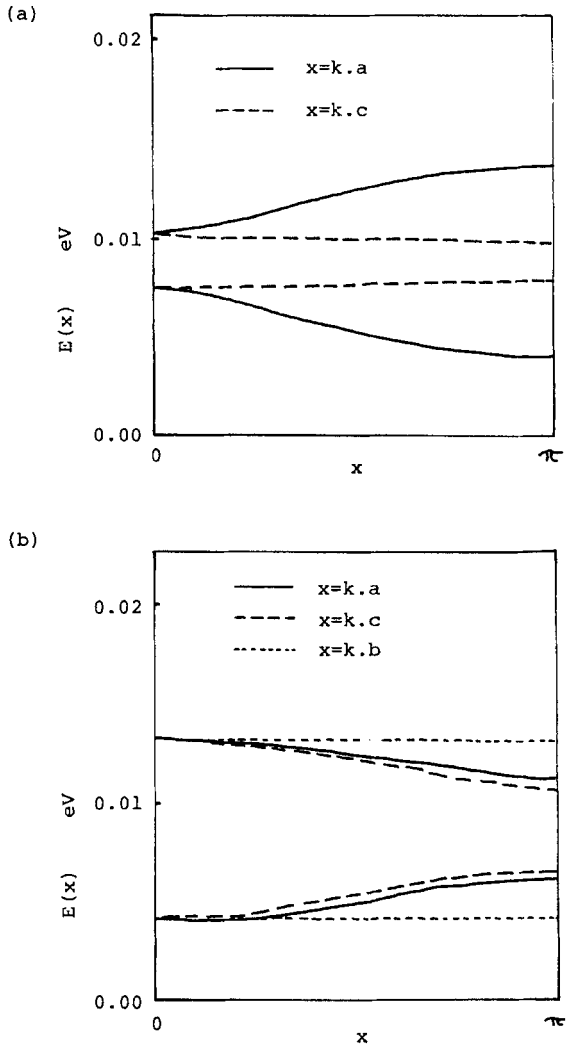

FIGURE 3 Shapes of the excess electron (a) and the excess hole (b) bands of auramine perchlorate crystal.

DISCUSSION

In Figure 4 some of the typical alignments of molecules in the crystal are illustrated. Figure 4 shows that the overlap between $|m\rangle$ and $iT_{-b-c}|m\rangle$ is almost face to face, while the overlap between $|m\rangle$ and $iT_{-b}|m\rangle$ is at the aromatic rings of the molecules. These features of the molecular overlap in the crystal, together with the electron and hole distributions in a molecule shown in Table I, reflect in the value of the intermolecular resonance integrals as listed in Table II.

The mean square velocity $\langle v_i v_j \rangle$ is calculated by

$$\langle v_i v_j \rangle = \int \left[\frac{\partial E_+}{\partial k_i} \frac{\partial E_+}{\partial k_j} \exp(-\beta E_+) + \frac{\partial E_-}{\partial k_i} \frac{\partial E_-}{\partial k_j} \exp(-\beta E_-) \right] \times \frac{d^3k}{h^2} \int [\exp(-\beta E_+) + \exp(-\beta E_-)] \, d^3k \tag{8}$$

Since the maximum width of the bands is less than the thermal energy at room temperature, we neglected the variation of the Boltzmann factors in Eq. (8). The components of the square velocity tensor thus calculated are listed in Table III. Table III shows that the velocity of an excess electron is larger than that of an excess hole in the a^* direction, while in the c^* direction the velocity of an excess hole is much larger than that of an electron. In the b^* direction velocities of both electron and hole are almost equal to zero. The above result is in good agreement with the molecular arrangement in the crystal where the transformation of iT_{-b-c} and iT_{-a-b-c} causes the movement in approximately the a^* direction, and that of iT_{-b} and iT_{-b-c} to the c^* direction (In the b^* direction there is little overlap of molecular orbitals of an electron or hole.).

The mobility tensors for an excess electron and an excess hole in the band is given by Eq. (9) assuming the constant isotropic relaxation time.

$$\mu_{ij} = \frac{e\tau \langle v_i v_j \rangle}{kT} \tag{9}$$

Under the above assumption it is predicted that the mobility of excess electrons is larger than that of excess holes in the a^* direction, while in the c^* direction the mobility of excess holes is much larger than that of excess electrons. Such a phenomenon that transfer of electrons is much easier in one direction but that of holes is much easier in other direction of the same crystal is the result of the anisotropy of the electronic interaction in the crystal, and one may not expect such a characteristic in most of inorganic semiconductors.

There has been a contradiction about the sign of charge carriers of organic materials.[14–17] For instance, Meier[14,15] classified auramine into n-type

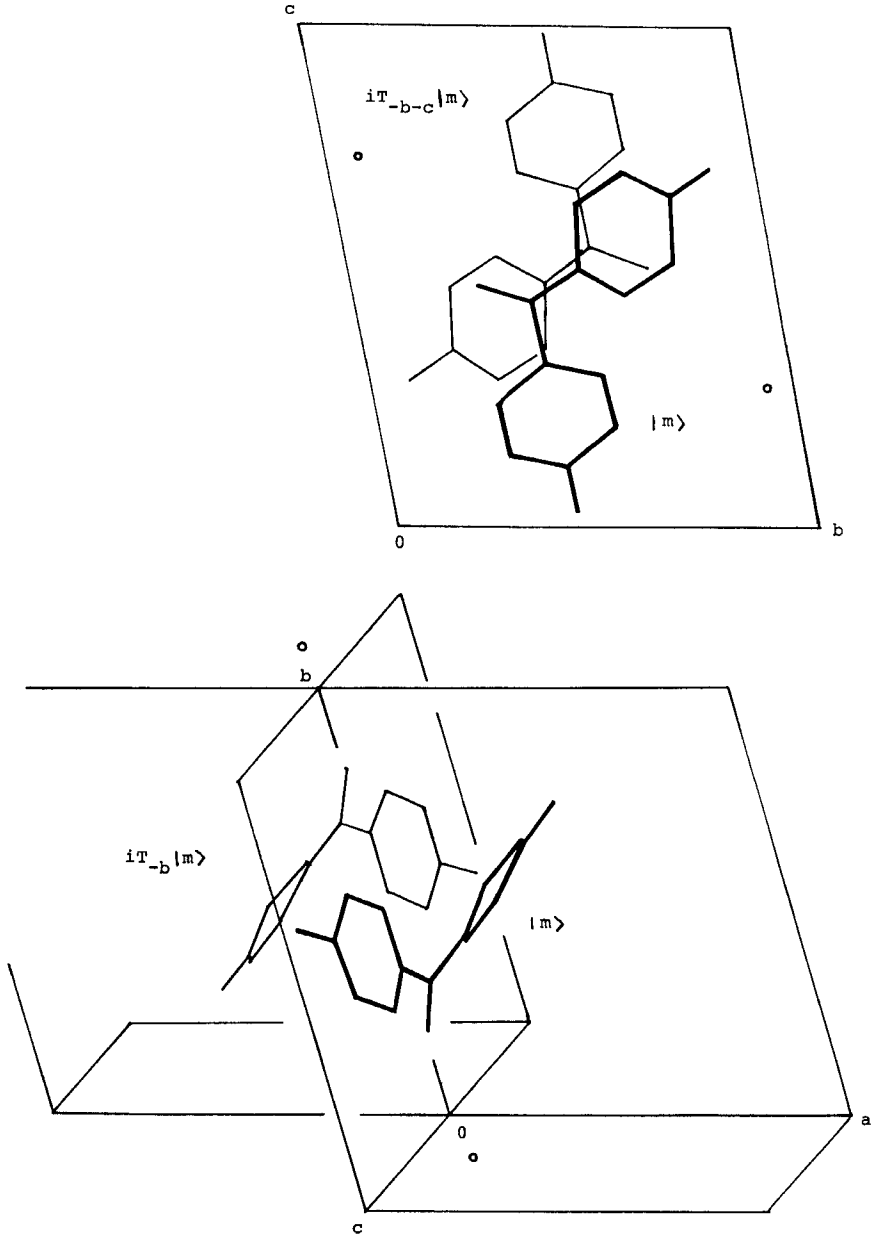

FIGURE 4 The typical alignments of molecules in the crystal.

TABLE III

The mean square velocity (10^8 cm^2/s^2)

	Electron	Hole
$\langle v_a^2 \rangle$	306.64	82.41
$\langle v_b^2 \rangle$	0.00	0.00
$\langle v_c^2 \rangle$	0.73	191.61

photoconductor on the basis of electrical measurements with a polycrystalline auramine film, while Terenin[18,19] reported that the charge carrier of the photoconduction of an auramine single crystal was holes. We reported that the electrical behavior of a vacuum sublimated auramine film on SnO_2 could be interpreted as *n*-type semiconductor,[6] but we also reported that the sign of the charge carriers of the photoconduction of an auramine single crystal was positive.[7]

Our calculation suggests the possibility that, in an auramine crystal, the sign of charge carriers may be different with crystal axis in which an electric current flows, though the densities of electrons and holes in conductive states should be taken into consideration at the same time if we talk about the type of electric conduction.

Such an anisotropy in charge transfer integrals could be expected in many organic materials, and even a semi-quantitative calculation will be of some help in understanding many phenomena with electron transport processes.

References

1. F. Seitz, Modern Theory of Solids, MacGraw-Hill, New York, (1940).
2. R. Kubo and Y. Toyosawa, *Progress Theoret.*, **13**, 160 (1955).
3. C. E. K. Mees and T. H. James, Ed., The Theory of Photographic Process, 3rd edition, MacMillan, New York, (1966).
4. B. Rosenberg, R. A. Orlando, and J. M. Orlando, *Arch. Biochem. Biophys.*, **93**, 395 (1961).
5. M. Sukigara and R. C. Nelson, *Mol. Phys.*, **17**, 387 (1969).
6. H. Shimoda, M. Sukigara, T. Sakata, and K. Honda, *J. Phys. Chem.*, **76**, 1655 (1972).
7. H. Shimoda, M. Sukigara, and K. Honda, *Mol. Cryst. Liquid Cryst.*, **20**, 165 (1973).
8. M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).
9. O. H. LeBlanc, *J. Chem. Phys.*, **33**, 626 (1960), *ibid*, **35**, 1275 (1961).
10. J. L. Katz, S. A. Rice, S. I. Choi, and J. Jortner, *J. Chem. Phys.*, **39**, 1683 (1963).
11. R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).
12. J. A. Pople, *Trans. Faraday Soc.*, **49**, 1373 (1953).
13. A. V. Fratini and I. L. J. Karle, *Applied Opt.*, **6**, 2091 (1967).
14. H. Meier, *Z. Wiss. Photo. Photophysik Photochem.*, **53**, 1 (1958).
15. H. Meier, *Z. Physik Chem.*, **208**, 340 (1958).
16. R. C. Nelson, *in* H. Kallmann and M. Silver, Eds., Symposium on Electrical Conductivity in Organic Solids, Interscience, New York, 1961, p. 18.
17. R. C. Nelson, *J. Chem. Phys.*, **29**, 388 (1958), *ibid.*, **30**, 406 (1959).
18. A. Terenin, E. Putzeiko, and I. Akimov, *J. Chem. Phys.*, **54**, 716 (1957).
19. A. Terenin, *Proc. Chem. Soc.*, 321 (1961).