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CONDUCTION MECHANISM IN ORGANIC SEMICONDUCTORS

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ABSTRACT

Several theories are examined for their usefulness in predicting the mobility of charge carriers in organic semiconductors. A modified band theory using Hückel Molecular Orbitals is shown to be applicable after rejecting other available theories. The complex Molecular Orbital calculations are simplified by the use of symmetry and group theory so that they can be programmed in reasonable time on a large computer. The calculations are applied to the complex hydrogen phthalocyanine crystal structure and compared to experimental measurements. Experimental values found in the literature vary too widely to be useful. Experimental measurements are described which provide the predicted order of magnitude and the predicted trend with temperature changes. Finally, a critique of the experimental method is made with recommendations for improvements. However, it is concluded that the Hückel Molecular Orbital Theory is valid for predicting properties of organic semiconductors. Improvements in control of material purity and in measurement techniques are required before further considerations can be made regarding uses of organic semiconductors.

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PROPULSION AND VEHICLE ENGINEERING LABORATORY
RESEARCH AND DEVELOPMENT OPERATIONS

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CONDUCTION MECHANISM IN ORGANIC SEMICONDUCTORS

SUMMARY

A brief description is given of the potential uses of organic semiconductors. The two general classes of organic compounds that are semiconductors, i.e., aromatic ring structures and charge transfer complexes are discussed and characterized and examples are given of each.

A short history of the development of the theory of conduction in organic semiconductors is presented. In order, the Singlet State Theory, the Triplet State Theory, the combined Singlet-Triplet State Theory and the Donor-Acceptor Theory are discussed, and the primary weaknesses of each are pointed out, with referenced experimental data. The presently accepted Band Theory is discussed in detail along with the Hückel Molecular Orbital Theory. A procedure is developed and given for the calculation of resonance integrals and the mobility tensor by the use of a computer. This procedure is used to calculate the molecular orbitals and the band structure of hydrogen phthalocyanine.

Measurements were made of the specific resistivity and Hall mobility of a vacuum deposited sample of hydrogen phthalocyanine using the method of Vander Pauw and of a single crystal of hydrogen phthalocyanine using standard techniques. Values for the vacuum deposited sample were too low and changed with time, indicating high impurity content. Measurements on the single crystal sample yielded the correct trend of Hall mobility with temperature as predicted by theory.

Refinements of the experimental technique are required before these complex materials can be fully characterized. However, the concept of calculating molecular orbitals and the band structure as a means of predicting the potential of an organic semiconductor has been proven to be valid.

INTRODUCTION

The interest in studying organic semiconductors is related to the development of dielectrics and of materials that are suitable for thermoelectric cooling systems. Considerable effort is being spent on studying leakage and breakdown mechanisms in dielectrics in relation to environment. The subject work is expected to help clarify these studies. Also, since electrical devices generate considerable energy which must be efficiently dissipated on sealed space vehicles, various cooling techniques have been studied. Among the promising techniques being developed is the use of inorganic thermoelectric materials. Since organic semiconductors because of their low thermal conductivity may provide advantages over inorganic semiconductors, this project was started to establish the feasibility, practicality, and limitations of using organic semiconductors by investigating the electrical conduction phenomenon in single crystals of organic semiconductors. Further advantages of this project are that several hundred thousand organic materials have been prepared, and that organic chemists can fabricate organic solids with properties matched to specifications. Therefore, this project may lead to specifications for fabrication of new organic solids.

There are two general classes of organic compounds that are considered as semiconductors. They are:

1. Aromatic Ring Structures: These are mostly pure hydrocarbons with fused ring systems, although some other ring compounds are also included. Some of these are shown in Fig 1.

2. Charge Transfer Complexes: These are sometimes called "Donor-Acceptor Complexes" and are organic or semiorganic systems. Some of these are shown in Table I.

PRELIMINARY THEORETICAL CONSIDERATIONS

Organic solids are known to have low heats of vaporization and low melting points. Also, the spectra of organic materials in the solid phase are almost identical to the spectra in the gas phase. From such evidence the natural conclusion is that there is a weak interaction between the molecules and, as a consequence, an explanation can be made of most of the bulk properties of aromatic molecular solids in terms of the properties of the individual molecule. However, this is not the case. The general picture of benzene (Ref. 1) is that π-electrons of the ring form a band of energy states which is only half filled with electrons. Therefore, an electron can move around the ring without

encountering any impedance. Thus, the benzene ring acts like a 'super-conductor.' This picture can be extended to more complex molecules. A crystal formed by such molecules is called a molecular crystal because the forces holding the crystal together are weak Van der Waals forces. Such crystals have very low conductivities, therefore, the problem of bulk electrical conduction in these materials does not involve the structure of individual molecules. The problem lies in getting the charge transported from one molecule to the next.

To explain the semi- and photo-conduction of organic solids, various theories have been proposed. Most of the theories aim at explaining the experimentally observed fact that the conductivity of organic solids is represented by a relation of the type

$$\sigma = \sigma_0 \exp\ (-E/kT) \qquad (1)$$

where σ is electrical conductivity of the material.

σ_0 is a constant and may be seen as the conductivity of the material at infinitely high temperatures.

E is an energy parameter

k is Boltzmann constant

T is temperature in °K

For inorganic intrinsic semiconductors, there is a similar relation:

$$\sigma = \sigma_0 \exp(-E_G/2kT)$$

where E_G is the (energy gap) difference in energy between the highest point in the valence band and the lowest point in the conduction band.

Some authors believe that conduction in organic solids is intrinsic and that $E_G = 1/2\ E$ should be identified with some electronic term separation in the spectrum for the free molecule. As a result, there are two or perhaps three interesting theories as follows:

Singlet State Theory

Eley and Parfitt (Ref. 2), using the "electron gas" model of Bayliss (Ref. 3), determined the allowed electron states for a doughnut-shaped potential box of specified size and identified E_G with the energy of the lowest excited singlet state of the isolated molecule, $^1E_1$. Their idea seems to be that an electron in the excited state of one molecule has sufficient energy to tunnel through the intermolecular barrier to the

corresponding excited state of another molecule. An examination of this theory leads to the conclusion that the activation energy for the formation of charge carriers in a solid free radical should be very small. Therefore, the solid free radicals should be expected to be good conductors. On the contrary, the experimental results show that solid-free radicals are poor conductors, and for at least two free radicals, the activation energy is quite large (Table II). For molecular solids, the agreement between activation energy and the energy of the lowest excited singlet is very poor. The activation energy as determined from the temperature dependence of the dark conductivity is typically an electron volt smaller than the lowest excited state singlet energy. The only agreement between the singlet state theory and experiment is that the threshold for photoconduction invariably corresponds to the energy of the lowest singlet-singlet transition. However, this cannot be taken as support for the singlet state theory because this is a feature common to all of the theories. Thus, it is difficult to support the singlet state theory.

Triplet State Theory

The triplet state theory (Ref. 4, 5, 6), like the singlet state theory, is essentially a postulate that the lowest excited triplet state of a molecule is an intermediate in the formation of charge carriers and that the activation energy, E_G, is the triplet state energy, $^3E_1$. Though the reason for the participation of the triplet state is not clear, it is interesting to note that the experimental value for activation energy for conduction is often close to the energy of the triplet state. Some of the values are included in Table III. However, in many cases, this agreement is not very good since deviations as large as 0.5 e.v. are known. Small activation energies for conduction ($\sim 0.1 - 0.2$ e.v.), in the case of charge transfer-complexes (Table IV), suggest that the triplets of the donor and the acceptor molecules are not involved in the generation of charge carriers. The inverse relation between photoconductivity and phosphorescence quantum yield reported by McGlynn (Ref. 7), for a series of related compounds, further suggests that the triplet state is not a necessary intermediate in the photogeneration of charge carriers. The same conclusion has been drawn by Almeleh and Harrison (Ref. 8), from their photoconductivity measurements on pure and doped triphenylene. These measurements are important because they contradict the only evidence in support of the triplet state theory drawn from the earlier measurements by Northrop and Simpson (Ref. 9) on dark conductivity of pure and doped hydrocarbons. Rosenberg's assumption (Ref. 4, 5) that the quantum yield for photogeneration of triplet states is temperature dependent, increasing exponentially with temperature, explains the temperature dependence of photoconductivity adequately but leads to an absurd conclusion. According to Rosenberg's assumption, the yield of the triplet state at 70°K should be lower by a factor of $\sim 10^7$ compared to the yield at room temperature. This would make it impossible to detect the triplet state at (70°K or

less) low temperatures, while in practice, low temperatures are used to study the triplet state.

Combined Singlet-Triplet State Theory

Northrop and Simpson (Ref. 9, 10, 11), Simpson (Ref. 12), and Northrop (Ref. 13), consider the exciton states of hydrocarbons and the states of ionic character arising from the removal of an electron from one molecule to a neighbor. Both of these states comprise singlets and triplets, but in either case, the energy levels converge to the same limit as the electron is removed to greater distances. This limit is $(E_i - E_a)$, the difference between the ionization potential and the electron affinity of the molecules in the crystal. Northrop and Simpson (Ref. 9) argue that charge carriers are produced by the ionization of singlet and triplet states under the influence of an applied electronic field. Singlet states are presumed to be more susceptible to field ionization than triplet states and, therefore, the effective activation energy for formation of charge carriers will depend upon the relative population of singlet and triplet states. The participation of both the singlet and triplet states in the generated charge carriers fails to explain the fact that the temperature variation of conductivity in pure molecular solids is adequately represented by a single activation energy. This theory again fails in the case of highly conductive donor-acceptor systems.

To sum up these theories, it is helpful to refer to an interesting paper by Fielding and Mackay (Ref. 14). They have measured the polarized crystal and vapor spectra of several phthalocyanines and concluded that neither 'singlet' nor 'triplet' state theories can be invoked to satisfactorily explain the electrical conduction in organic semiconductors.

Donor-Acceptor Theory

One of the most elegant theories which explains the generation of charge carriers is due primarily to Lyons (Ref. 15), and is sometimes called the Donor-Acceptor theory. He has considered the general problem of exciton states in a semi-classical fashion. He has shown that the ionized states in a molecular crystal converge into a band of free states that can conduct electrons and holes. Merrifield (Ref. 16) has calculated the ionized states for a one-dimensional molecular solid and has demonstrated the existence of energy bands. Fox (Ref. 17), also, has adopted a similar approach. Recently, Kommandeur (Ref. 18, 19, 20) has used this theory to discuss the conductivity and spin resonance behavior of a variety of organic semiconductors, including charge transfer complexes. He begins by discussing the energy balance for the separation of charge within the solid by calculating a Born-Haber cycle. For this, consider

a solid made up of molecules A and B and perform the following operations:

S.N.	Operation	Energy Involved
1.	Remove Molecule A from solid to vacuum	$+S_A$
2.	Remove Molecule B from solid to vacuum	$+S_B$
3.	Ionize Molecule A	$+I$
4.	Attach electron to molecule B	$-Ea$
5.	Put A^+ back into solid keeping electrons fixed	$-S_A$
6.	Put B^- back into solid keeping electrons fixed	$-S_B$
7.	Let electrons near A^+ polarize	$-P_+$
8.	Let electrons near B^- polarize	$-P_-$
9.	Let A^+ and B^- interact coulombically	$-Q$

When these energies are summed, the energy involved in creating a separated hole and electron is obtained:

$$E_{c.s.} = I-Ea-P_+-P \qquad (3)$$

since, in the first order approximation, polarization depends only on magnitude of charge and not the sign, $P_+ = P_- = P$, so that

$$E_{c.s} = I - Ea - 2P-Q \qquad (4)$$

By estimating various quantities involved, Lyons (Ref. 15) finds for anthracene, $E_{c.s} = 5.2$ eV, which is much higher than the actual value of 1.6 eV (for dark current activation energy). Reference 17 did consider the next nearest neighbor interactions in the polarization energy. This reduced the calculated value of $E_{c.s.}$, but it remained much higher than the experimental value. Despite the failure in predicting the right order for activation energy, this theory supports the experimental evidence that conductivity in anthracene is extrinsic in nature, and explains the effects of gases on the photoconductivity. The energetic approach of Lyons (Ref. 15) also is very useful in a discussion of the properties of the donor-acceptor complexes. The only evidences against this theory are the results on mixed hydrocarbons carried out by Northrop and Simpson.

While all of these theories are concerned with explaining the activation energy, LeBlanc (Ref. 21) made the best approach to the overall problem of the conduction mechanism which is discussed in the next section.

MOBILITIES AND BAND THEORY

From a fundamental standpoint, some of the most important advances in the study of electrical properties of organic molecular solids have come from the experimental determination of carrier mobilities. LeBlanc (Ref. 22) and Kepler (Ref. 23) measured the drift mobilities of excess electrons and holes in anthracene. Their measurements showed that for anthracene the room temperature mobilities in a direction perpendicular to the crystallographic ab plane (the cleavage plane for anthracene) were 0.4 and 0.3 cm^2/volt-sec for holes and electrons, respectively. Parallel to the ab plane, these mobilities were 1·3 and 3·0 cm^2/volt-sec. The mobilities vary with temperature according to the relation

$$\mu \propto T^{-n}$$

where μ is mobility, T is absolute temperature in °K and $1 < n < 1.5$. Mobilities of the order of 1 cm^2/volt-sec and their variation in accordance with equation (5) are characteristic of semiconductors with "energy bands" rather than those with a "hopping process" conduction. Therefore, a "Band Theory" similar to that which is well known for inorganic solids to explain the electronic conduction in organic solids, also may be considered. From this work, LeBlanc (Ref. 21) developed a modified band theory. The success of his preliminary calculations sparked a great interest in Band Structure Calculations (Ref. 24, 25, 26). Another interesting experimental development was the first successful attempt at Hall measurements on organic semiconductors by Heilmeier, Warfield, and Harrison (Ref. 27). Their measurements on hydrogen phthalocyanine were followed by some Hall measurements on copper phthalocyanine (Ref. 28, 29). During the last four or five years, experimental evidence has been reported on the applicability of Band theory, so it is important to consider in some detail the actual calculations. In all the Band Structure Calculations, a tight-binding approximation (a good account of this approximation) is given by Mott and Jones.

The Theory of the Properties of Metals and Alloys

Dover, 1958, page 65 has been used and energy bands for excess electrons and holes have been calculated, instead of conventional conduction and valence bands. LeBlanc has used the Hückel molecular orbitals Simple Linear Combination of Atomic Orbital - Molecular Orbitals -

Simple(LCAO-MO) to construct crystal wave functions using a Bloch sum of MO's. For most cases, Hückel Molecular Orbitals (HMO), already exist in the literature; however, to make Band Structure Calculations, one should calculate them. Therefore, we start with a short discussion of Hückel Molecular Orbital Theory. Emphasis is placed on methods and actual calculations rather than basic theory.

Hückel Molecular Orbital Theory

In the Hückel Molecular Orbital Theory for organic solids, we begin in the customary way of separating σ-bonds from the π-orbitals (for a good discussion of σ and π-bonds, see Nature of the Chemical Bond by Pauling) and treating only the latter. In the treatment, a number of simplifying assumptions are made:

1. The π-orbitals are co-planar; i.e., they share the same nodal plane.

2. All bond distances are equal.

3. All non-neighbor interactions are negligible.

Even with these simplifying assumptions, an exact solution of Schrodinger's equation

$$H\phi = E\phi \tag{6}$$

for a polyelectronic system is not possible. In principle, although numerical expressions are possible, they provide an inefficient way of storing information. Moreover, it is difficult in the extreme to glean useful patterns from such a tabulation.

We resort, instead, to the approximation that ϕ may be factored into a set of independent or noninteracting atomic orbitals, χ, each of which describes, in effect, a separate set of electrons.

In the LCAO-MO method, each MO is constructed as:

$$\phi_j = C_{j1}\chi_1 + C_{j2}\chi_2 + \ldots + C_{jn}\chi_n \tag{7}$$

or

$$\phi_j = C_{jr}\chi_r \tag{8}$$

where ϕ_j is the j^{th} molecular orbital, χ_r is the atomic orbital for the r^{th} atom, and C_{jr} is the coefficient of the r^{th} atomic orbital in the

j^{th} molecular orbital. These molecular orbitals are eigen-functions of a Hamiltonian operator which is considered for the π-system alone. In principle, this Hamiltonian can be set up explicitly, but in actual calculations it is rarely necessary to consider the explicit form. Initially, at least, to be once taken as a one-electron Hamiltonian.

The problem is to find the best set of values for the coefficients in order to obtain the best value for the energy of the molecular orbital. This problem is approached by using the variation principle,

$$\epsilon = \frac{\int \phi H \phi d\tau}{\int \phi^2 d\tau} \geq E_o \tag{9}$$

Any wave function other than the correct one yields a value for the ground state energy which is algebraically higher than the true value. Details of the variation technique are discussed in almost every book on quantum mechanics (a good book is Quantum Chemistry by Eyring, Walter, and Kimbal). However, with the variation technique the problem is reduced to finding the set of coefficients C_{jr}, so that the function, ϵ, in equation (9) is a minimum with respect to each of the coefficients. Therefore,

$$\frac{\partial \epsilon}{\partial C_r} = 0 \tag{10}$$

On carrying out the minimization with respect to each of the coefficients, detailed algebraic calculations show the result in the following secular equation:

$$\begin{matrix} (H_{11} - S_{11}) & (H_{12} - S_{12}) \ldots\ldots\ldots (H_{1n} - S_{1n}) \\ (H_{21} - S_{21}) & (H_{22} - S_{22}) \ldots\ldots\ldots (H_{2n} - S_{2n}) \\ \ldots\ldots\ldots & \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots & \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ (H_{n1} - S_{n1} & (H_{n2} - S_{n2}) \ldots\ldots\ldots (H_{nn} - S_{nn}) \end{matrix} = 0 \tag{11}$$

where

$$H_{rs} = \int \chi_r \, H \chi_s \, d\tau \tag{12}$$

$$S_{rs} = \int \chi_r \, \chi_s \, d\tau \tag{13}$$

The definition shows that the tensors are symmetric, so that

$$S_{rs} = S_{sr}$$

and (14)

$$H_{rs} = H_{sr}$$

Thus far, no approximation has been introduced beyond the original use of a linear combination function as a solution to a one-electron Hamiltonian. At this point, some approximations which constitute the simple LCAO, or HMO, method are shown.

The terms, H_{rs}, for $r \neq s$ are called the resonance or bond integrals. From the definition, $H_{rs} = \int \chi_r H \chi_s \, d\tau$, these integrals represent the energy of interaction of two atomic orbitals. This interaction energy clearly depends on the distance of separation of the two orbitals, therefore, the following assumptions are reasonable. When atoms r and s, are not bonded in a classical structural expression, the interaction energy is likely to be small

$$H_{rs} = 0 \tag{15}$$

For atoms, r and s, bonded, H_{rs} is finite, but if all the bond distances are equal and if the atomic orbitals share the same nodal plane, the values of the various H_{rs} will have comparable magnitudes. We assume for bonded atoms

$$H_{rs} = \beta \tag{16}$$

where β is the same for all bonded atoms.

The terms H_{rr} are called coulomb integrals. From the definition, $H_{rr} = \int \chi_r H \chi_r \, d\tau$, the coulomb integral represents approximately the energy of an electron in a carbon 2p-orbital. When, as is generally the case, the π-lattice consists entirely of carbon atoms, it is assumed that all such integrals are equal and are replaced by symbol α.

$$H_{rr} = \alpha \tag{17}$$

Relative to the energy of an electron at infinity, both α and β are negative energy quantities.

The integrals S_{rs} are the overlap integrals. If we normalize the atomic orbitals, then

$$S_{rr} = 1 \qquad (18)$$

For atoms separated by a large distance the overlap integral is vanishingly small. We make the assumption that for $r \neq 2$,

$$S_{rs} = 0 \qquad (19)$$

This assumption simplifies the mathematics, although it is not a drastic measure. It is frequently referred to as the assumption of orthogonality and S_{rs} is sometimes called the non-orthogonality integral. Thus,

$$H_{rs} = \alpha \text{ for } r = s$$

$$H_{rs} = \beta \text{ for } r \neq s \text{ but bonded (i.e. } r^{th} \text{ and } s^{th} \text{ atoms are nearest neighbors)}$$

$$H_{rs} = 0 \text{ otherwise}$$

$$S_{rs} = 1 \text{ for } r = s$$

$$S_{rs} = 0 \text{ for } r \neq s$$

With these assumptions, the secular equation yields n real roots of the form,

$$\alpha - \epsilon j = -mj\beta \qquad j = 1,.....,n$$

or

$$\epsilon j = \alpha + mj\beta \qquad (20)$$

In practice, the entire secular equation is divided by β and $(\alpha-\epsilon)/\beta$ is set equal to X. This leaves only one unknown quantity, X, in the secular equation, and the mj's are n values of X obtained by solving the equation. While writing the secular determinant, one must number the atoms (this may be done by following any arbitrary sequence) and care must be taken to include all non-zero β terms. As an example, see "Calculation of Molecular Orbitals of Hydrogen Phthalocyanine" for actual calculations on hydrogen phthalocyanine.

Thus, we obtain n values for the energy given as an algebraic sum of the coulomb integral and some fraction of a bond integral. Hence, the energies can be represented as a series of energy levels above and below an energy zero taken as α. Since β is negative, negative values of the roots (i.e., positive mj) represent energy levels more negative (more stable) than the energy of an electron in a single carbon $2p$- orbital, and they represent bonding levels which correspond to the Bonding

Molecular Orbitals. For mj = 0, the energy of the molecular orbital is the same as any constituent carbon 2ρ-orbital, and such a molecular orbital is called a Non-Bonding Molecular Orbital (NBMO). Negative values of mj represent higher energies (lower stability) than an isolated carbon 2ρ-orbital, and the corresponding MO's are said to be antibonding. An energy level diagram can be drawn.

With n values of the energies, one can evaluate n sets of n C-coefficients. At first, it appears that we are determining (n+1) unknowns (n number of C's and one ϵ) with only n simultaneous equations. Actually, these equations yield only the ratios between the coefficients, e.g.,

$$\frac{C_2}{C_1}, \frac{C_3}{C_1}, \ldots, \frac{C_n}{C_1}$$

The (n+1)th equation which gives the final values is the normalization condition,

$$\int \phi^2 \, d\tau = 1 \tag{21}$$

This yields

$$\sum_r \sum_s C_r C_s \int \chi_r \chi_s \, d\tau = 1$$

or

$$\sum_r \sum_s C_r C_s S_{rs} = 1 \tag{22}$$

From the orthogonality condition,

$$\sum_r C_r^2 = 1 \tag{23}$$

Additional equation:

$$\left(\frac{C_1}{C_1}\right)^2 + \left(\frac{C_2}{C_1}\right)^2 + \ldots + \left(\frac{C_n}{C_1}\right)^2 = \frac{1}{C_1^2}$$

or

$$\sqrt{\sum_n \left(\frac{C_n}{C_1}\right)^2} = \frac{1}{C_1} \tag{24}$$

Since C_1 is known, evaluation of the C-values can be made. The application of the HMO method to a specific problem involves the following operations:

(1) Set up the secular determinant.

(2) Solve the secular equation for n values of mj.

(3) Substitute values of mj in n simultaneous equations and solve for ratios of C-coefficients.

Determination of C-coefficients can be made by using the following procedure:

(1) Pick up any one value of the root mj; e.g., m_1.

(2) Write the complete determinant for this value of the root.

(3) Find all of the co-factors (n in number) of this determinant.

(4) Find the ratio $(\text{co-factor})_n/(\text{co-factor})_1$, for $n = 1, \ldots, n$, call it (F_n/F_1).

(5) If $(\text{co-factor})_1$, with respect to the first row is zero, try co-factors with respect to any other row.

(6) Find $(F_n/F_1)^2$ for all values of n and add them.

(7) Find the square-root of $\sum_n (F_n/F_1)^2$ and call it (F_n/F_1).

(8) Divide all the (F_n/F_1) values by (F_n/F_1). This yields the required C-values for m_1, i.e. we get n C_{1n} values.

(9) Repeat the same procedure for $m_2, m_3, \ldots, m_n$. This will yield n sets of n C-values corresponding to n energy values.

One can easily take care of overlap between adjacent atoms, but this correction affects only the energy and not the C-value. Corrections for the variation of β have been tried by various workers. (A good reference is "Molecular Orbital Theory for Organic Chemists" by A. Streitwieser).

Application of Group Theory

The principal difficulty in molecular orbital calculations of molecules with any degree of complexity is the handling of the large secular determinant. However, if a large, high-speed digital computer

is available, practically any interesting π-bonded molecule can be handled by the Simple LCAO method. The molecular orbital problem can be simplified considerably by the use of group theory. Of course, it is advantageous to use group theory even though a computer is to be used, since it reduces the computer time. From a practical point, the use of group theory is proposed rather than rigorous mathematics. As an illustration, consider only the two-fold symmetry axes for no error is made by assuming that a molecule has less symmetry than it actually has. Thus, only four symmetry operations are considered.

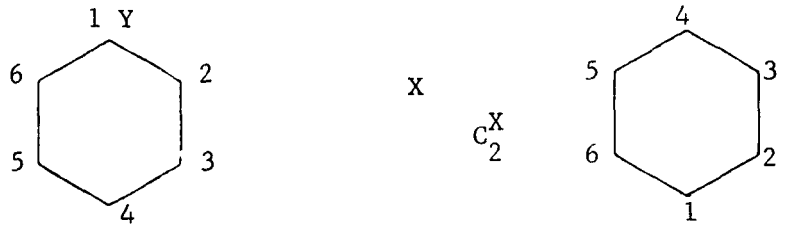
(1) Identity operation - this leaves the molecule undisturbed - operation E.

(2) Rotating the formula through 180° about X-axis - operation C_2^X.

(3) Rotating the formula through 180° about Y axis - operation C_2^Y.

(4) Rotating the formula through 180° about Z-axis - operation C_2^Z.

These operations place each of the atoms in the location of another similar atom. Results of these operations become clear by considering the case of the benzene molecule. X and Y axes are



in the plane of the molecule and Z-axis is normal to the plane. The C_2^X rotation transforms atoms 1→4, 2→3, and we can easily see the effect of other operations. The result of these operations is:

E	C_2^X	C_2^Y	C_2^Z
1	4	1	4
2	3	6	5
3	2	5	6
4	1	4	1
5	6	3	2
6	5	2	3
6	0	2	0

The numbers shown below the dotted line represent how many atomic positions remain unchanged by the operation at the head of the column. These numbers can be used in conjunction with the D_{2v} character table to simplify the problem.

The D_{2v} character table has vertical columns corresponding to D_{2v} symmetry operations E, C_2^X, C_2^Y, and C_2^Z. The horizontal rows Γ_1, Γ_2, Γ_3 and Γ_4 are various representations. These horizontal rows lead to various proper combinations of arithmetical signs of the X-functions:

	E	C_2^X	C_2^Y	C_2^Z
Γ_1	1	1	1	1
Γ_2	1	-1	-1	1
Γ_3	1	-1	1	-1
Γ_4	1	1	-1	-1

Each Γ leads to an n X n determinant where n is the dot product (sum of the products of the respective terms in Γ and their counterparts below the dotted line in the table of results of symmetry operations) divided by the number of symmetry operations (here four).

For Γ_1, $n = (1 \times 6 + 1 \times 0 + 1 \times 2 + 1 \times 0) \div 4 = 2$

For Γ_2, $n = (1 \times 6 - 1 \times 0 - 1 \times 2 + 1 \times 0) \div 4 = 1$

For Γ_3, $n = (1 \times 6 - 1 \times 0 + 1 \times 2 - 1 \times 0) \div 4 = 2$

For Γ_4, $n = (1 \times 6 + 1 \times 0 - 1 \times 2 - 1 \times 0) \div 4 = 1$

Thus, for benzene, the 6 x 6 secular determinant is reduced to two 2 x 2 and two 1 x 1 secular determinants.

Construct the trial wave functions for the separate representations (Γ's) as the dot product of each horizontal row of the character table with the table of transpositions under the symmetry operations. Thus, for Γ_1, the following trial wave functions are shown: (X = χ)

$$X_1 + X_4 + X_1 + X_4$$

$$X_2 + X_3 + X_6 + X_5$$

$$X_3 + X_2 + X_5 + X_6$$

$$X_4 + X_1 + X_4 + X_1$$

$$X_5 + X_6 + X_3 + X_2$$

$$X_6 + X_5 + X_2 + X_3.$$

Of these, only two are independent. After normalization, MO is shown as

$$\phi = (C_{1/2})\ (X_2 + X_3 + X_5 + X_6 + (C_2/\sqrt{2})\ (X_1 + X_4)$$

The elements of the determinant are found in the usual way:

$$H_{11} = \int 1/2\ (X_2 + X_3 + X_5 + X_6)\ H\ 1/2\ (X_2 + X_3 + X_5 + X_6)\ d\tau = \alpha + \beta$$

$$H_{12} = \int 1/2\ (X_2 + X_3 + X_5 + X_6)\ H\ 1/\sqrt{2}\ (X_1 + X_4)\ d\tau = \beta\sqrt{2}$$

$$H_{22} = \int 1/\sqrt{2}\ (X_1 + X_4)\ H\ 1/\sqrt{2}\ (X_1 + X_4)\ d\tau = \alpha$$

Thus, the secular equation for Γ_1 becomes

$$\Gamma = \begin{vmatrix} \alpha + \beta - \epsilon & \beta\sqrt{2} \\ \beta\sqrt{2} & \alpha - \epsilon \end{vmatrix} = 0$$

Dividing by β and putting $(\alpha - E)/\beta = \chi$

$$\begin{vmatrix} \chi + 1 & \sqrt{2} \\ \sqrt{2} & \chi \end{vmatrix} = 0$$

or

$$\chi = 1 \text{ and } \chi = -2$$

In a similar way, consider the cases Γ_2, Γ_3, and Γ_4.

For more complex molecules, proceed in exactly the same way. The use of higher symmetry (actual symmetry) is beneficial in complex molecules; however, care must be used in constructing the wave functions.

Proceed to the band structure calculations considering the procedure suggested by Le Blanc (Ref. 21).

Calculation of Band Structure

Band structure calculations for organic solids are based on the fact that the concentration of excess electrons, or holes, is very small,

therefore, a one-particle treatment is valid. Further, the binding energy of the molecular crystals is very small in relation to excitation energies of the various excited electronic states of the molecule (and crystal), so the tight binding approximation may be employed. In this method, one-electron crystal wave functions (unnormalized) are constructed from linear combinations of one-electron molecular wave functions. The possible linear combinations, adopted for the translational symmetry of the crystal, are (Ref. 19)

$$\Psi(k) = \sum_{n=1}^{n} \exp\left(i\vec{k}\cdot\vec{r}_n\right) \phi_n \left(\vec{r} - \vec{r}_n\right) \tag{25}$$

Here r_n denotes the geometrical center of molecule, n, and the sum extends over the n molecules in the crystal. The molecular wave function, ϕ_n, is understood to be oriented in the crystal in the same way as in molecule, n. Otherwise, ϕ_n is the same function for all n.

The Hamiltonian appropriate to an excess electron (or hole), has the form

$$H = \left(\frac{-h^2}{2m}\right) \nabla^2 + V(r) \tag{26}$$

where V(r), which determines the crystal field, will be approximated by

$$V(r) = \sum_n V_n(r - r_n) \tag{27}$$

where V_n is the Hartree potential of an isolated neutral molecule. For an isolated molecular ion, the Hamiltonian is:

$$H_n^\circ = \left(-h^2/_{2m}\right) \nabla^2 + V_n \tag{28}$$

from which it follows that

$$e_o = \int \phi^* \, H^\circ \, \phi \, d\tau \tag{29}$$

is the energy of the isolated negative ion relative to infinite separation of the electron and the neutral molecule. Following Balk, deBruijn and Hoijtink, (Ref. 30) the energy eigenvalue of Ψ_n is:

$$E(k) = \int \Psi^* H \Psi d\tau \tag{30}$$

$$E(k) = e_o + \sum_n^1 e_n + 2 \sum_s \mathrm{Cos}\left(\vec{k}\cdot\vec{r}_s\right) e_s \tag{31}$$

where sums are taken over all molecules except the one with its center located at the origin. The symbols appearing in the above equation are defined as follows:

$$e_o = \int \phi^* H \, \phi \, d\tau \tag{32}$$

$$e_n = \int \phi^* (\vec{r})\ V_n (\vec{r}-\vec{r}_n)\ \phi_r\ d\tau \qquad (33)$$

$$e_s = \int \phi^* (\vec{r}-\vec{r}_s)\ V_s (\vec{r}-\vec{r}_s)\ \phi(\vec{r})\ d\tau \qquad (34)$$

For calculating the mobility tensor, we are interested only in the k variation of the energy bands, therefore, it is necessary only to examine the last term in the above equation. (Integrals in this term are called resonance integrals).

Calculation of Resonance Integrals

The molecular orbitals which are used are usually linear combinations of Slater-type atomic orbitals (Ref. 31). (Recently, various other types of atomic orbitals have been used (Ref. 32).

$$\phi_n = \sum_n C_{ni}\ U_i \qquad (35)$$

The coefficients C_{ni} are determined by HMO theory, and U_i is given by Slater as

$$U_i = (\alpha^5/\pi)^{1/2}\ r_i\ \text{Cos}\ \xi_i\ \exp\ (-\alpha r_i) \qquad (36)$$

with $\alpha = 1.64$ atomic units $= 3.08 \times 10^8\ \text{cm}^{-1}$.

The potential function for the neutral molecule is usually taken as

$$V_n = \sum_i V_i \qquad (37)$$

where V_i is the Goeppert-Mayer and Sklar potential (Ref. 33) of carbon atom, i. Using Slater type orbitals, we get

$$V_i = -e^2\ r_i^{-1} \left\{4 + 6\ (\alpha\ r_i) + 4\ (\alpha r_i)^2 + 4/3\ (\alpha r_i)^3\right\} \exp\ (-2\ r_i) \qquad (38)$$

If one neglects three-center, or higher, interatomic integrals (inclusion of three-center integrals has been discussed in Ref. 14), each intermolecular integral is given by

$$\int \phi_m\ V_m\ \phi_n\ d\tau = \sum_{i,j} C_{mi}\ C_{nj} \int U_i\ V_i\ U_j\ d\tau \qquad (39)$$

Thus, the problem reduces to that of finding the integrals $\int U_i\ V_i\ U_j\ d\tau$ since coefficients C_{mi} and C_{nj} are known from HMO calculations. These integrals may be solved numerically; however, a method of calculating these integrals has been given by Murrell (Ref. 34).

Calculation of Mobility Tensor

For calculating the mobility tensor, it is assumed that carrier

scattering can be described in terms of a relaxation time function, $\tau(\vec{k})$ (Ref. 35), then consider two functional forms for $\tau(\vec{k})$, each involving one isotropic scattering parameter:

(a) $\tau(k) = \tau_o$ - constant free time

(b) $\tau(k) \times \vec{V}(\vec{k}) = \lambda$ - constant free path

Here, $\vec{V}(\vec{k})$ is the velocity associated with Ψ_k, and it is given by

$$\vec{V}(\vec{k}) = \left(\frac{1}{h}\right)[\partial E(\vec{k})/\partial k] \tag{40}$$

where $$\partial E(\vec{k})/\partial k = -2 \sum_s^1 r_s V_{mn} \sin(\vec{k}\cdot\vec{r}), \tag{41}$$

and $V_{mn} = \int \phi_m V_m \phi_n \, d\tau$(the resonance integral).

At this stage, it is assumed that λ or τ_o is isotropic. This assumption, obviously, is an oversimplification since the scattering parameters should be anisotropic in the real crystal.

For constant free time, τ_o, the components of the mobility tensor are

$$\mu_{ij} = e \tau_o \langle V_i V_j \rangle / kT \tag{42}$$

where V_i are corresponding components of V (k).

For constant free path, λ, the components of the mobility tensor are

$$\mu_{ij} = e\lambda \langle V_i V_j / |\vec{V}(\vec{k})| \rangle / kT \tag{43}$$

For a comparison of the mobility tensor with experimental values, generally we calculate μ_{ii} values along orthogonal axes.

CALCULATION OF MOLECULAR ORBITALS OF HYDROGEN PHTHALOCYANINE

Using the simple LCAO-MO (HMO) method, calculations have been made of the molecular orbitals for hydrogen phthalocyanine. The molecular structure of the material is shown in Fig 2. The various atoms have been numbered. Atoms 5, 14, 23, 32, 37, 38, 39 and 40 are nitrogen and all others are carbon atoms. For such a molecule, justification cannot be made by using the same α and β for all the integrals involved. For nitrogen atoms, the coulomb integral, α, must be replaced by α_r and resonance integrals with bonded carbons must be replaced by β_{c-n}. Following Streitwieser (Ref. 36), we have $\alpha_n = \alpha_c + \beta_{c-c}$ and $\beta_{c-n} = \beta_{c-c}$.

With these values of coulomb and resonance integrals, the complete secular equation can be written:

The correct symmetry of the hydrogen phthalocyanine molecule is D_{2h} (Ref. 37). However, little error is introduced by using the symmetry of the molecule as D_{4b} (Ref. 38). The π-electron MO's are; by definition, all antisymmetric with respect to the molecular plane, and, therefore, they belong to representations A_{1u}, A_{2u}, B_{1u}, B_{2u}, and Eg. For each of these representations trial wave functions have been constructed. The trial wave functions have been constructed in exactly the same manner as outlined for the benzene molecule with D_{2v} symmetry. However, in representation Eg, there is some freedom of choice in the forms of MO. The trial wave functions used in the calculations are listed below:

Representation A_{1u}

$$\phi 1 = \frac{C_1}{2\sqrt{2}}(X_1 + X_{19} + X_{10} + X_{28} + X_9 + X_{27} + X_{18} + X_{36}) +$$

$$\frac{C_2}{2\sqrt{2}}(X_2 + X_{20} + X_{11} + X_{29} + X_8 + X_{26} + X_{17} + X_{35}) + \frac{C_3}{2\sqrt{2}}$$

$$(X_3 + X_{21} + X_{12} + X_{30} + X_7 + X_{25} + X_{16} + X_{34}) + \frac{C_4}{2\sqrt{2}}$$

$$(X_4 + X_{22} + X_{13} + X_{31} + X_6 + X_{24} + X_{15} + X_{33}) + \frac{C_5}{2}$$

$$(X_5 + X_{23} + X_{14} + X_{32}) + \frac{C_6}{2}(X_{37} + X_{38} + X_{39} + X_{40})$$

Representation A_{2u}

$$\phi 2 = \frac{C_1}{2\sqrt{2}}(X_1 + X_{19} + X_{10} + X_{28} - X_9 - X_{27} - X_{18} - X_{36}) \times \frac{C_2}{2\sqrt{2}}$$

$$(X_2 + X_{20} + X_{11} + X_{29} = X_8 - X_{26} - X_{17} - X_{35}) + \frac{C_3}{2\sqrt{2}}$$

$$(X_3 + X_{21} + X_{12} + X_{30} - X_7 + X_{25} - X_{16} - X_{34}) + \frac{C_4}{2\sqrt{2}}$$

$$(X_4 + X_{22} + X_{13} - X_6 - X_{24} - X_{15} - X_{33})$$

Representation B_{1u}

$$3 = \frac{C_1}{2\ 2}(X_1 + X_{19} - X_{10} - X_{28} + X_9 + X_{27} - X_{18} - X_{36}) +$$

$$\frac{C_2}{2\ 2}(X_2 + X_{20} - X_{11} - X_{29} + X_8 + X_{26} - X_{17} - X_{35}) + \frac{C_3}{2\ 2}$$

$$(X_3 + X_{21} - X_{12} - X_{30} + X_7 + X_{25} - X_{16} - X_{34}) + \frac{C_4}{2\ 2}(X_4 + X_{22} -$$

$$X_{13} - X_{31} + X_6 + X_{24} - X_{15} - X_{33}) + \frac{C_5}{2}(X_5 + X_{23} - X_{14} - X_{32})$$

Representation B_{2u}

$$4 = \frac{C_1}{2\ 2}(X_1 + X_{19} - X_{10} - X_{28} - X_9 - X_{27} + X_{18} + X_{36}) + \frac{C_2}{2\ 2}$$

$$(X_2 + X_{20}\ \ X_{11} - X_{29} - X_8 + X_{17} + X_{35}) + \frac{C_3}{2\ 2}(X_3 + X_{21} - X_{12} -$$

$$X_{30} - X_7 - X_{25} + X_{16} + X_{34}) + \frac{C_4}{2\ 2}(X_4 + X_{22} - X_{13} - X_{31} - X_6 -$$

$$X_{24} + X_{15} + X_{33}) + \frac{C_5}{2}(X_{37} + X_{39} - X_{38} - X_{40})$$

Representation E_g

$$5 = \frac{C_1}{2}(X_1 + X_{18} - X_{19} - X_{36}) + \frac{C_2}{2}(X_2 + X_{17} - X_{20} - X_{35}) +$$

$$\frac{C_3}{2}(X_3 + X_{16} - X_{21} - X_{34}) + \frac{C_4}{2}(X_4 + X_{15} - X_{22} - X_{33}) + \frac{C_5}{2}$$

$$(X_5 + X_{14} - X_{23} - X_{32}) + \frac{C_6}{2}(X_6 + X_{13} - X_{24} - X_{31}) + \frac{C_7}{2}(X_7 +$$

$$X_{12} - X_{25} - X_{30}) + \frac{C_8}{2}(X_8 + X_{11} - X_{26} - X_{29} + \frac{C_9}{2}(X_9 + X_{10} -$$

$$X_{27} - X_{28}) + \frac{C_{10}}{2}(X_{38} - X_{40})$$

Proceeding in the usual way, the following secular equations are obtained:

Representation A_{1u}

$$\begin{vmatrix} (X+1) & 1 & 0 & 0 & 0 & 0 \\ 1 & X & 1 & 0 & 0 & 0 \\ 0 & 1 & (X+1) & 1 & 0 & 0 \\ 0 & 0 & 1 & X & (0.8\sqrt{2}) & (0.8\sqrt{2}) \\ 0 & 0 & 0 & (0.8\sqrt{2}) & (X+1) & 0 \\ 0 & 0 & 0 & (0.8\sqrt{2}) & 0 & (X+1) \end{vmatrix} = 0 \qquad (44)$$

Representation A_{2u}

$$\begin{vmatrix} (X-1) & 1 & 0 & 0 \\ 1 & X & 1 & 0 \\ 0 & 1 & (X-1) & 1 \\ 0 & 0 & 1 & X \end{vmatrix} = 0 \qquad (45)$$

Representation B_{1u}

$$\begin{vmatrix} (X-1) & 1 & 0 & 0 & 0 \\ 1 & X & 1 & 0 & 0 \\ 0 & 1 & (X-1) & 1 & 0 \\ 0 & 0 & 1 & X & 0.8\sqrt{2} \\ 0 & 0 & 0 & 0.8\sqrt{2} & (X+1) \end{vmatrix} = 0 \qquad (46)$$

Representation B_{2u}

$$\begin{vmatrix} (X+1) & 1 & 0 & 0 & 0 \\ 1 & X & 1 & 0 & 0 \\ 0 & 1 & (X+1) & 1 & 0 \\ 0 & 0 & 1 & X & 0.8\sqrt{2} \\ 0 & 0 & 0 & 0.8\sqrt{2} & (X+1) \end{vmatrix} = 0 \qquad (47)$$

Representation E_g

$$\begin{vmatrix} (X-1) & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & X & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & (X-1) & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & X & 0.8 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.8 & (X+1) & 0.8 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.8 & X & 1 & 0 & 0 & 0 & (0.8\sqrt{2}) \\ 0 & 0 & 0 & 0 & 0 & 1 & (X+1) & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & X & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & (X+1) & (X+1) & 0 \\ 0 & 0 & 0 & 0 & 0 & (0.8\sqrt{2}) & 0 & 0 & 0 & 0 & (X+1) \end{vmatrix} = 0 \qquad (48)$$

In these equations, $X = (\alpha - E)/\beta$ where α is the coulomb integral for carbon and β is the resonance integral for carbon. The coulomb integral for nitrogen and the resonance integral between C and N have been taken as listed earlier.

Energy eigenvalue parameters, X, and corresponding C-coefficients for various values of X have been computed by using an IBM 7094 computer. The program was written and checked by using the secular equation for representation $A_2\mu$. Only 0.62 minutes of computer time was required.

This may be compared with the time required ($\sim$ 26 minutes) for solving the 40 x 40 determinant equation obtained when the group theory was not used. Values of the energy eigenvalue parameters (X) and C-coefficients are listed in Tables IV, V, VI, VII, VIII, and IX. Figure 3 shows the energy levels. Energy levels in group specie E_g are doubly degenerate and can have up to four electrons.

CALCULATION OF ELECTRON DENSITIES AND MOBILE BOND ORDERS

From the computed values of Hückel coefficients one can calculate electron densities at various atomic sites and mobile bond orders. An electron, occupying the molecular orbital, ϕ_j, will spend a fraction of its time given by the expression $/C_{jk}/^2$ in the atomic orbital, X_k, consequently, the total average charge on the atomic site, k, will be

$$\rho = \Sigma n_j /C_{jk}/^2 \qquad (49)$$

where the summation is extended over all the occupied ϕ_j's and nj is the number of electrons in the orbital, ϕ_j. ρ is the charge in units of electronic charge. In this case, the summation is taken over 21 MO's of the lowest energies since this molecule has 42 π-electrons. (Each MO of the E_g specie has been considered equivalent to two MO's, and then, nj = 2 for all values of j). The computed values of ρ are shown in Table X. In addition to electron densities, there is another quantity used in determining the electronic structure of the molecule called the mobile bond order, and defined as

$$\rho_{rs} = 2\Sigma C_r C_s \qquad (50)$$

This is the mobile bond order of bond, rs. The calculated values for the mobile bond orders of various bonds in phthalocyanine are shown in Table X. Also, included in Table X are the values of ρ and ρ_{rs} as calculated by Basu (Ref. 37). The difference between the two sets of data is appreciable because of Basu's initial approximation of replacing all nitrogen atoms by carbon atoms. Of particular significance is the fact that, contrary to Basu's calculations, the charge density at atomic site 5 is not minimum. Instead, the charge density is minimum at atomic site 4. This explains the oxidation reaction of phthalocyanines with acyl peroxide, organic hypochlorite, etc., and the formation of various dyes from metal phthalocyanines.

CALCULATION OF BAND STRUCTURE OF HYDROGEN PHTHALOCYANINE

Crystal Structure

In previous discussion, the calculation of the band structure

essentially means evaluation of resonance integrals (refer to main topic). For evaluation of resonance integrals, it is necessary to know the orientation of molecules in a unit-cell and the coordinates of various atoms in a molecule. A detailed X-ray analysis of the hydrogen phthalocyanine crystal has been reported by Robertson (Ref. 38). The crystal is monoclinic with two centro-symmetrical molecules per unit-cell of volume 1173 Å. The space group is C_{2h}^5 ($P2_{1/a}$).

$$a = 19.85 \text{ Å}$$

$$b = 4.72 \text{ Å}$$

$$c = 14.8 \text{ Å}$$

$$\beta = 122.25 \text{ Å}$$

A schematic representation of the unit-cell which illustrates the positions of the centers of molecules is shown in Fig 4. The coordinates of various atoms in a molecule with respect to molecular axes L and M are shown in Fig 5 and Table XI. Coordinates of these atoms with respect to the monoclinic crystal axes (with center of symmetry of molecule 1 in Fig 5 as the origin) are shown in Table XII.

Calculation of Resonance Integrals

The hydrogen phthalocyanine molecule has 42 π-electrons, and each energy state is occupied by two electrons. (Energy states belonging to group specie Eg are occupied by four electrons since they are doubly degenerate states). Therefore, the energy level diagram (Fig 3) immediately suggests that an excess electron and an excess hole will go to molecular orbitals ϕ_e and ϕ_h, respectively, given by:

$$\begin{aligned}
\phi_e = {} & 0.16348\ (\chi_1 + \chi_{18} - \chi_{19} - \chi_{36}) + 0.16556\ (\chi_2 + \chi_{17} - \chi_{20} - \chi_{35}) \\
& -0.16139\ (\chi_3 + \chi_{16} - \chi_{21} - \chi_{34}) - 0.32899\ (\chi_4 + \chi_{15} - \chi_{22} - \chi_{33}) \\
& + 0.19652\ (\chi_5 + \chi_{14} - \chi_{23} - \chi_{32}) + 0.08645\ (\chi_6 + \chi_{13} - \chi_{24} - \chi_{31}) \\
& -0.04405\ (\chi_7 + \chi_{12} - \chi_{25} - \chi_{30}) - 0.04295\ (\chi_8 + \chi_{11} - \chi_{26} - \chi_{29}) \\
& +0.04351\ (\chi_9 + \chi_{10} - \chi_{27} - \chi_{28}) - 0.09906\ (\chi_{37} + \chi_{38} - \chi_{39} - \chi_{40})
\end{aligned}$$

$$\begin{aligned}
\phi h = {} & \frac{0.36639}{2\sqrt{2}}\ (\chi_1 + \chi_{19} + \chi_{10} + \chi_{28} - \chi_9 - \chi_{27} - \chi_{18} - \chi_{36}) \\
& + \frac{0.47446}{2\sqrt{2}}\ (\chi_2 + \chi_{20} + \chi_{11} + \chi_{29} - \chi_8 - \chi_{26} - \chi_{17} - \chi_{35})
\end{aligned}$$

$$- \frac{0.22644}{2\sqrt{2}} (\chi_3 + \chi_{21} + \chi_{12} + \chi_{30} - \chi_7 - \chi_{25} - \chi_{16} - \chi_{34})$$

$$- \frac{0.7677}{2\sqrt{2}} (\chi_4 + \chi_{22} + \chi_{13} + \chi_{31} - \chi_6 - \chi_{24} - \chi_{15} - \chi_{33})$$

Where χ_i is the $2p_\pi$ atomic orbital for carbon or nitrogen, as the case may be, on the ith atomic site as shown in Fig 2 and Table XIII.

EXPERIMENTAL MEASUREMENTS

Two schools have reported successful Hall measurements on copper-phthalocyanine single crystals (Ref. 28 and 29), unfortunately, the two results do not agree. The results of Heilmeier and Harrison (Ref. 29) differ from crystal-to-crystal. Therefore, there is a need for more reliable and reproducible Hall mobility measurements on hydrogen and copper phthalocyanine, with primary interest in the order of magnitude of the Hall mobility and its variation with temperature. Two different experimental techniques have been used for measuring Hall mobility.

Measurement of Specific Resistivity and Hall Mobility For a Vacuum Deposited Sample-Method I

This method is based on the theory developed by Vander Pauw (Ref. 39). It has an advantage in that we do not need any fixed geometry of the sample. In fact, the Hall mobility and specific resistivity of a flat sample of arbitrary shape can be measured without knowing the current pattern if the following conditions are fulfilled:

1. the contacts are at the circumference of the sample

2. the contacts are sufficiently small

3. the sample is homogeneous in thickness, and

4. the surface of the sample is singly connected, i.e., the sample does not have isolated holes.

In the theory, some resistance parameters are defined as follows:

Consider Fig 6 in which A, B, C, and D are four successive contacts fixed on arbitrary places along the circumference. The resistance $R_{AB, CD}$ is defined as the potential difference $(V_D - V_C)$ between the contacts D and C per unit current through the contacts A and B. The current enters the sample through the contact A and leaves it through the contact B. Similarly, defined are the resistances $R_{BC, DA}$ and $R_{BD, AC}$ where the current flows through contacts BC and BD, respectively.

Following Vander Pauw, specific resistivity, ρ, is given by

$$\rho = \frac{\pi d}{\ln 2} \quad \frac{\left(R_{AB\ CD} + R_{BC\ DA}\right)}{2} \quad f\left(\frac{R_{AB,\ CD}}{R_{BC,\ DA}}\right) \tag{51}$$

where f is a function of the ratio ($R_{AB,CD}/R_{BC,DA}$) only and can be obtained by using the graph presented by Vander Pauw (Ref. 38).

The Hall mobility, μ_H, can be determined by measuring the change of the resistance $R_{BD,AD}$ when a magnetic field is applied perpendicular to the sample. The Hall mobility is given by

$$\mu_H = \frac{d}{B} \cdot \frac{\Delta\left(R_{BD,AC}\right)}{\rho} \tag{52}$$

where B is the magnetic induction and $\Delta(R_{BD,AC})$ the change of the resistance $R_{BD,AC}$ due to the magnetic field H, d is the thickness of the sample.

Combining equations for ρ and μ_H

$$\mu_H = \frac{\ln 2}{B} \cdot \frac{\Delta\left(R_{BD,AC}\right)}{\left(R_{AB,CD} + R_{BC,DA}\right) \cdot f\left(R_{AB,CD}/R_{BC,DA}\right)} \tag{53}$$

In our measurements, we used powdered hydrogen phthalocyanine and vacuum deposited it on a glass substrate. The vacuum deposited film was of 'clover shape.' This sample shape has many advantages, it gives a relatively large Hall effect at moderate heat dissipation which is important when measuring materials of low mobility such as phthalocyanines. Electrical contacts were made by applying a fine silver paste dot at the tip of a #40 AWG wire. The wires were held in position under spring action and glued to the glass substrate with epoxy cement. A Keithley 610 R electrometer was used to measure the potential differences along with a Keithley secondary standard resistance of 10^{11} ohms which was used to measure the current. The values of resistivity obtained were much lower than the values existing in the literature. Moreover, the resistivity as well as the mobility values changed with time. Such behavior has been shown (Ref. 40) to be due to impurities. Further work with this technique was discontinued because material with greater purity was not available.

Measurement of Hall Mobility with Single Crystals - Method II

In the second method, Hall measurements were made with single crystals of hydrogen phthalocyanine. Usually, measurements with single

crystals need a proper geometry (a rectangular plate) as shown in Fig 7. If the width of the plate is b and the thickness d, a current, I, is passed through the plate and the conductivity, σ, determined by measuring the voltage, V_c, between two contacts a distance, l, apart. Then

$$\sigma = \frac{I}{V_c} \cdot \frac{l}{bd} \tag{54}$$

If the voltage produced by a magnetic induction, B, between the Hall probes, is V_H, then

$$R = \frac{V_H \, d}{B \, . \, I} \tag{55}$$

where R is Hall constant.

If we presume that there is only one type of carrier (either hole or electron) then the carrier mobility, μ_H, is given by

$$\mu_H = \left| R\sigma \right| = \frac{V_H}{V_c} \cdot \frac{1}{b} \cdot \frac{1}{B} \tag{56}$$

The phthalocyanine crystals are very small, needle shaped, and of irregular cross-section. Therefore, it is not possible to report correct values of σ, R, or μ_H. However, our measurements do provide the order of magnitude.

The crystals were mounted on a glass substrate using epoxy cement. Fine copper wire electrodes were attached to the crystals under a microscope using a silver paint. A micromanipulator was used for this purpose. The electrodes were held in position by spring action. The electrical connections are shown schematically in Fig 8. The output across the Hall probe was recorded as a function of time, and the Hall voltage was measured by using the integration technique (Ref. 27).

The IR drop ($\sim$0.8 volts) across the Hall probe was partially suppressed by using the zero-set of the electrometer. Actual dimensions of the crystal were measured by a traveling stage microscope. Results of the measurements are indicated below and in Table XIV.

Crystal Dimensions

$l \simeq 0.203$ mm.
$d \simeq 0.015$ mm.
$b \simeq 0.008$ mm.

Hall Measurement Values

Temperature	Hall Voltage	Magnetic Field	Hall Mobility
293°K	200 V	8 K Gauss	1.6 cm^2/volt sec.
328°K	180 V	8 K Gauss	1.4 cm^2/volt sec.

DISCUSSION AND RECOMMENDATIONS

These measurements show that Hall mobility is lower at high temperature, and this trend is predicted by the Band Theory; however, we cannot attach too much significance to our limited results because of the following difficulties in the experimental arrangement:

1. The minimum sensitivity of the electrometer is inadequate.

2. The potential drop between Hall probes could not be eliminated.

3. The effect of oxygen is pronounced on the conductivity of phthalocyanines, and did not control the oxygen environment.

More refined measurements are proposed employing a much more sensitive electrometer. A cylindrical heater which is capable of giving a much higher temperature than the present one has been fabricated. Inside this heater, we can maintain an inert nitrogen atmosphere. To control the IR drop, more precise Hall probes have been mounted. An arrangement for measuring the photo-Hall effect has been completed. In earlier measurements a glass substrate was used, but in the future, a quartz substrate will be used to reduce substrate effect, if any. These experimental refinements will be required along with improvements in material purity and with techniques for growing larger crystals before the practical uses of organic semiconductors can be examined in detail.

TABLE I - SOME DONOR-ACCEPTOR COMPLEXES REGARDED AS ORGANIC SEMICONDUCTORS

DONOR	ACCEPTOR
1, 6 - Diaminopyrene	Chloranil, Bromanil, Iodanil
Perylene	Iodine
Coronene	Iodine
Tetracene	TCNE
Pentacene	Chloranil
Naphthalene	TCNE
Morpholinium	TCNQ
5,8 - Dihydroxyquinolinium	TCNQ
Triphenylmethylphosphonium	TCNQ
Diphenylamine	p - benzoquinone

TABLE II. - MEASURED PROPERTIES OF FREE RADICALS

RADICAL	ACTIVATION ENERGY E, eV	RESISTIVITY ρ, ohm-cm
DPPH	0.16 - 0.36	10^9
COPLINGER'S RADICAL	1.45	10^8
BANFIELD AND KENYON'S RADICAL	2.31	10^{15}

TABLE III. - MEASURED ACTIVATION ENERGY FOR CONDUCTION

COMPOUND	E eV	FIRST EXCITED SINGLET STATE ENERGY, eV	TRIPLET STATE ENERGY eV
NAPHTHALENE	2.25 3.70 1.40	4.0	2.64
ANTHRACENE	1.94 1.93 1.50 2.7 1.65	3.30	1.88
TETRACENE	1.69 1.70	2.61	1.34
PENTACENE	1.50 1.50	2.13	1.0
PYRENE	2.01 2.02 2.40	3.32	2.02

TABLE IV. - GROUP SPECIE AND ENERGY PARAMETERS (X)

A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_g	
-2.5732165	2.1935270	2.2398093	-2.1935270	2.21845758	0.77759276
1.5732165	-1.1935271	-1.8879976	1.1935271	-2.48168329	-1.45955473
-1.8273178	1.2949629	1.3810755	-1.2949629	1.30593557	1.49007338
0.8273178	-0.29496289	0.26711276	0.29496289	-0.01267105	-1.83815014
-0.99999995		-0.99999995	-1.0000000	-0.99999998	-0.99999993
-0.99999999					

TABLE V. - C-COEFFICIENTS FOR VARIOUS ENERGY PARAMETERS (X)
(FOR GROUP SPECIE A_{1u})

	$X_{(1)}$	$X_{(2)}$	$X_{(3)}$	$X_{(4)}$	$X_{(5)}$	$X_{(6)}$
C_1	0.17177720	0.13431411	0.60636874	0.40800545	0.64676169	0.64676167
C_2	0.27024289	-0.34561947	0.50165980	-0.74555576	0.00000004	0.00000001
C_3	0.52361629	0.40942017	0.31032317	0.20880617	-0.64676165	-0.64676166
C_4	0.55351894	-0.70790731	-0.24492389	0.36400052	-0.00000001	0
C_5	0.39806038	0.31124690	-0.33493747	-0.22536833	0.28583096	0.28583097
C_6	0.39806038	0.31124690	-0.33493747	-0.22536833	0.28583096	0.28583097

TABLE VI. - C-COEFFICIENTS FOR VARIOUS ENERGY PARAMETERS (X)
(FOR GROUP SPECIE A_{2u})

	$X_{(1)}$	$X_{(2)}$	$X_{(3)}$	$X_{(4)}$
C_1	0.42308150	0.31208198	0.76770003	0.36639250
C_2	-0.50495931	0.68456036	-0.22644305	0.47446472
C_3	0.68456040	0.50495933	-0.47446469	-0.22644302
C_4	-0.31208204	0.42308159	0.36639251	-0.76770002

TABLE VII - C-COEFFICIENTS FOR VARIOUS ENERGY PARAMETERS (X)
(FOR GROUP SPECIE B_{1u})

	$X_{(1)}$	$X_{(2)}$	$X_{(3)}$	$X_{(4)}$	$X_{(5)}$
C_1	0.38531028	0.05872509	0.75459184	0.36223332	0.38401224
C_2	-0.47771136	0.16959860	-0.28755654	0.26547615	0.76802459
C_3	0.68467207	0.26147667	-0.35745454	-0.43314539	0.38401231
C_4	-0.37115143	0.58554539	0.42377372	-0.58292288	0.00000001
C_5	0.12960945	0.74602562	-0.20135658	0.52047614	-0.33942212

TABLE VIII - C-COEFFICIENTS FOR VARIOUS ENERGY PARAMETERS (X)
(FOR GROUP SPECIE B_2)

	$X_{(1)}$	$X_{(2)}$	$X_{(3)}$	$X_{(4)}$	$X_{(5)}$
C_1	0.42308160	0.31208204	0.76770002	0.36639251	0.59962535
C_2	0.50495933	-0.68456039	0.22644299	0.47446470	0
C_3	0.68456035	0.50495931	-0.47446476	-0.22644303	-0.59962535
C_4	0.31208196	-0.42308152	-0.38839287	0.76770002	0
C_5	-0.00000011	-0.00000006	0.00000011	0.00000001	0.52999894

TABLE IX - C-COEFFICIENTS FOR VARIOUS ENERGY PARAMETERS (FOR GROUP SPECIES E)

	X(1)	X(2)	X(3)	(4)	X(5)	X(6)	X(7)	X(8)	X(9)	X(10)
C_1	0.40147434	0.00558075	0.69338225	0.32696913	0.35083835	0.11254237	0.11636419	0.31779334	0.02850511	0.35083829
C_2	-0.48917950	0.01943543	-0.21213037	0.33111217	0.70167674	0.02502999	0.28620454	-0.15574221	0.08090379	0.70167676
C_3	0.68374958	0.04265189	-0.41635366	-0.32277359	0.35083838	-0.13200550	0.30136700	-0.08572601	0.12020820	0.35083842
C_4	-0.34394029	0.12906475	0.33950776	-0.65797564	0.00000001	-0.05438897	0.45502409	0.19775425	0.26026513	0.00000005
C_5	0.09908415	0.34705750	-0.03377700	0.39304543	-0.43854796	0.21787246	0.45345695	-0.26117791	0.44774774	-0.43854796
C_6	-0.05468241	0.51372187	-0.24214828	0.17289423	0	-0.42972167	-0.19453873	0.61518596	0.20883466	-0.00000001
C_7	0.02029574	0.55345375	0.20883775	-0.08810083	0.09855011	-0.14958131	-0.10485584	-0.39149905	-0.29325532	0.09855010
C_8	-0.01063853	0.30632131	-0.23941812	-0.08590973	0	0.69561632	0.14635173	0.35967540	-0.45462664	0.00000001
C_9	0.00330549	0.20673872	0.10382689	0.08701227	-0.09855010	-0.39132491	0.31846420	-0.14444370	-0.54241671	-0.09855010
C_{10}	0.01922223	0.39226327	0.11880623	-0.19811785	0.22299343	0.27350166	-0.47893195	-0.27951122	0.28189393	0.22299342

TABLE X - CHARGE DENSITIES AND BOND ORDERS

Charge Density		Bond Order	
Author's Calculations	Basu's Values	Author's Calculations	Basu's Values
1 = 1.05912	1.074	1,36 = 0.76577	0.46
2 = 1.55937	0.990	1,2 = 0.88568	0.36
3 = 1.04888	0.962	2,3 = 0.86738	0.38
4 = 0.71875	0.922	3,4 = 0.45939	0.36
5 = 1.46410	0.778	4,5 = 0.62901	0.48
37 = 1.48179	1.136	4,37 = 0.02593	0.09

TABLE XI - ATOMIC COORDINATES RELATIVE TO MOLECULAR AXES L AND M

ATOM	L	M	ATOM	L	M
1	5.07	4.20	21	-5.07	-4.20
2	4.08	5.17	22	-4.08	-5.17
3	2.75	4.77	23	-2.75	-4.77
4	2.41	3.42	24	-2.41	-3.42
5	3.40	2.45	25	-3.40	-2.45
6	4.73	2.84	26	-4.73	-2.84
7	3.43	0	27	-3.43	0
8	2.71	1.13	28	-2.71	-1.13
9	1.38	1.32	29	-1.38	-1.32
10	1.14	2.64	30	-1.14	-2.64
11	0	3.32	31	0	-3.32
12	-1.14	2.64	32	1.14	-2.64
13	-1.38	1.32	33	1.38	-1.32
14	-2.71	1.13	34	2.71	-1.13
15	-5.07	4.20	35	5.07	-4.20
16	-4.08	5.17	36	4.08	-5.17
17	-2.75	4.77	37	2.75	-4.77
18	-2.41	3.42	38	2.41	-3.42
19	-3.40	2.45	39	3.40	-2.45
20	-4.73	2.84	40	4.73	-2.84

TABLE XII - CO-ORDINATES WITH RESPECT TO MONOCLINIC CRYSTAL AXES, CENTER OF SYMMETRY AS ORIGIN

ATOM	X, A	$\frac{2\pi X}{a}$	y, A	$\frac{2\pi y}{b}$	z, A	$\frac{2\pi z}{c}$
1	6.82	123.7°	3.12	238.1°	4.22	102.7
2	6.35	115.2°	3.76	286.5°	2.80	68.1
3	4.91	89.0°	3.43	261.5	1.46	35.6
4	3.94	71.3	2.48	189.0	1.53	37.3
5	4.40	79.8	1.84	140.6	2.95	71.8
6	5.84	105.8	2.17	165.2	4.29	104.3
7	3.24	58.7	0.14	10.4	3.79	92.2
8	3.10	56.3	0.90	68.2	2.62	63.8
9	1.95	35.2	0.98	74.5	1.09	26.5
10	2.36	42.8	1.88	143.6	0.39	9.6
11	1.61	29.1	2.31	176.0	-1.10	-26.7
12	0.20	3.7	1.79	136.7	-2.14	-52.0
13	-0.66	-12.0	0.87	66.1	-1.96	-47.8
14	-2.01	-36.4	0.68	52.0	-3.37	-81.9
15	-2.76	-50.0	2.72	207.6	-6.99	-170.1
16	-1.34	-24.3	3.34	262.0	-6.21	-151.2
17	-0.28	-5.0	3.21	245.0	-4.61	-112.2
18	-0.61	-11.1	2.29	174.5	-3.80	-92.3
19	-2.02	-36.6	1.57	119.9	-4.57	-111.2
20	-3.08	-55.8	1.79	136.6	-6.16	-150.0

TABLE XIII - COORDINATES OF ATOMS IN A MOLECULE WHOSE CENTER LIES AT (A/2, b/2) POINT

ATOM			
1.	3.11	5.48	-4.22
2.	3.58	6.12	-2.80
3.	5.02	5.79	-1.46
4.	5.99	4.84	-1.53
5.	5.53	4.20	-2.95
6.	4.09	4.53	-4.29
7.	5.69	2.50	-3.79
8.	6.83	3.26	-2.62
9.	7.98	3.34	-1.09
10.	6.57	4.24	-0.39
11.	8.32	4.67	1.10
12.	9.73	4.15	2.14
13.	10.59	3.23	1.96
14.	11.94	3.04	3.37
15.	12.69	5.08	6.99
16.	11.27	5.70	6.21
17.	10.21	5.57	4.61
18.	10.54	4.65	3.80
19.	11.95	3.93	4.57
20.	13.01	4.15	6.16
1'	16.75	-0.76	4.22
2'	16.28	-1.40	2.80
3'	14.84	-1.07	1.46
4'	13.87	-0.12	1.53
5'	14.33	0.52	2.95
6'	15.77	0.19	4.29
7'	13.13	2.22	3.79
8'	13.03	1.46	2.62
9'	11.88	1.38	1.09
10'	12.29	0.48	0.39
11'	11.54	0.05	-1.10
12'	10.13	0.57	-2.14
13'	9.27	1.49	-1.96
14'	7.92	1.68	-3.37
15'	7.17	-0.36	-6.99
16'	8.59	-0.98	-6.21
17'	9.65	-0.85	-4.61
18'	9.32	0.07	-3.80
19'	7.91	0.79	-4.57
20'	6.85	0.57	-6.16

TABLE XIV - MEASUREMENTS OBTAINED ON A SINGLE CRYSTAL OF HYDROGEN PHTHALOCYANINE

CRYSTAL DIMENSIONS

0.203 mm

0.015 mm

0.008 mm

HALL MEASUREMENTS VALUES

Temperature	Hall Voltage	Magnetic Field	Hall Mobility in cm^2/volt sec.
293°K	200 V	8 K. Gauss	1.6
328°K	180 V	8 K. Gauss	1.4

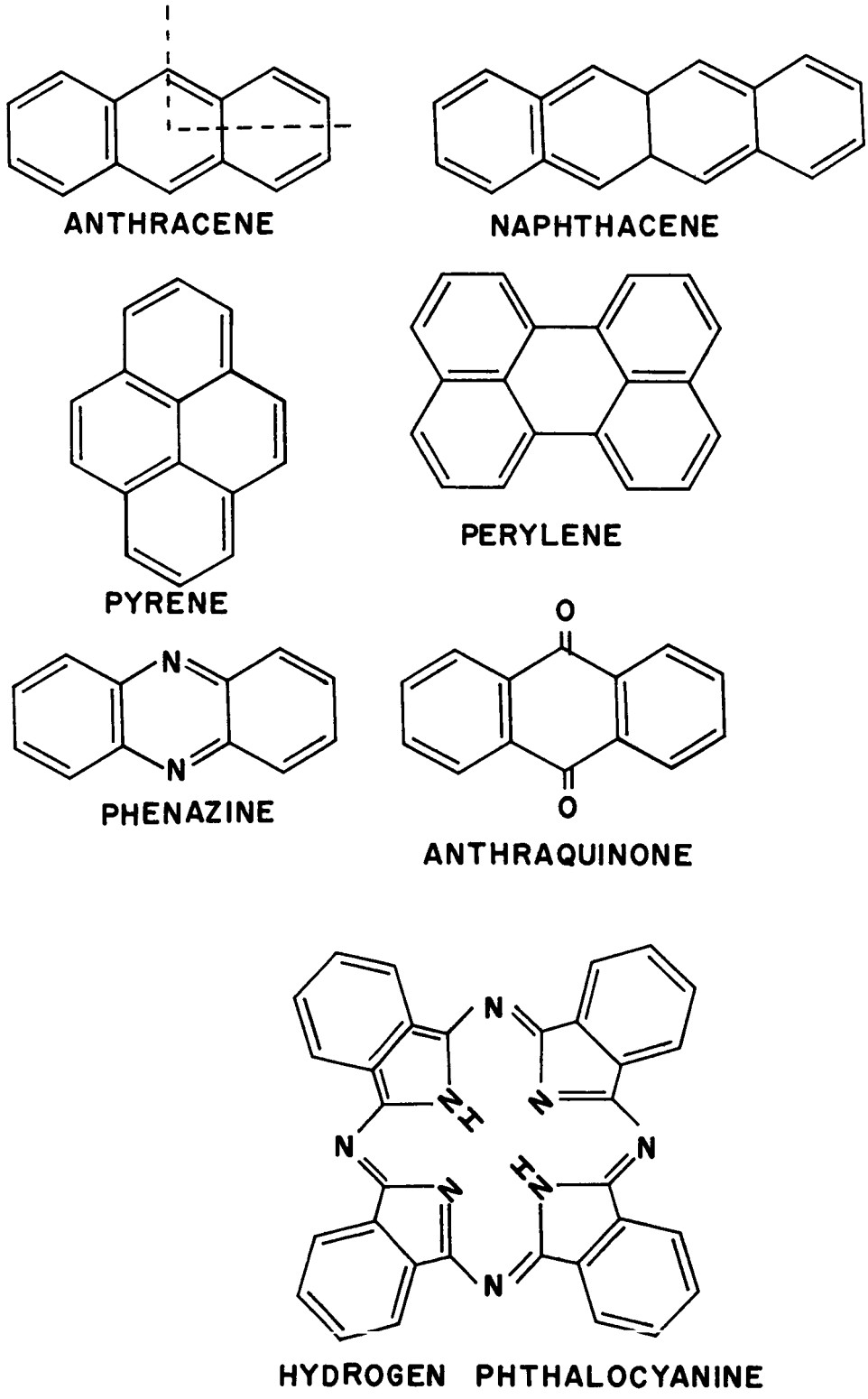


FIGURE 1 - SOME ORGANIC SEMICONDUCTORS WITH AROMATIC RING STRUCTURES

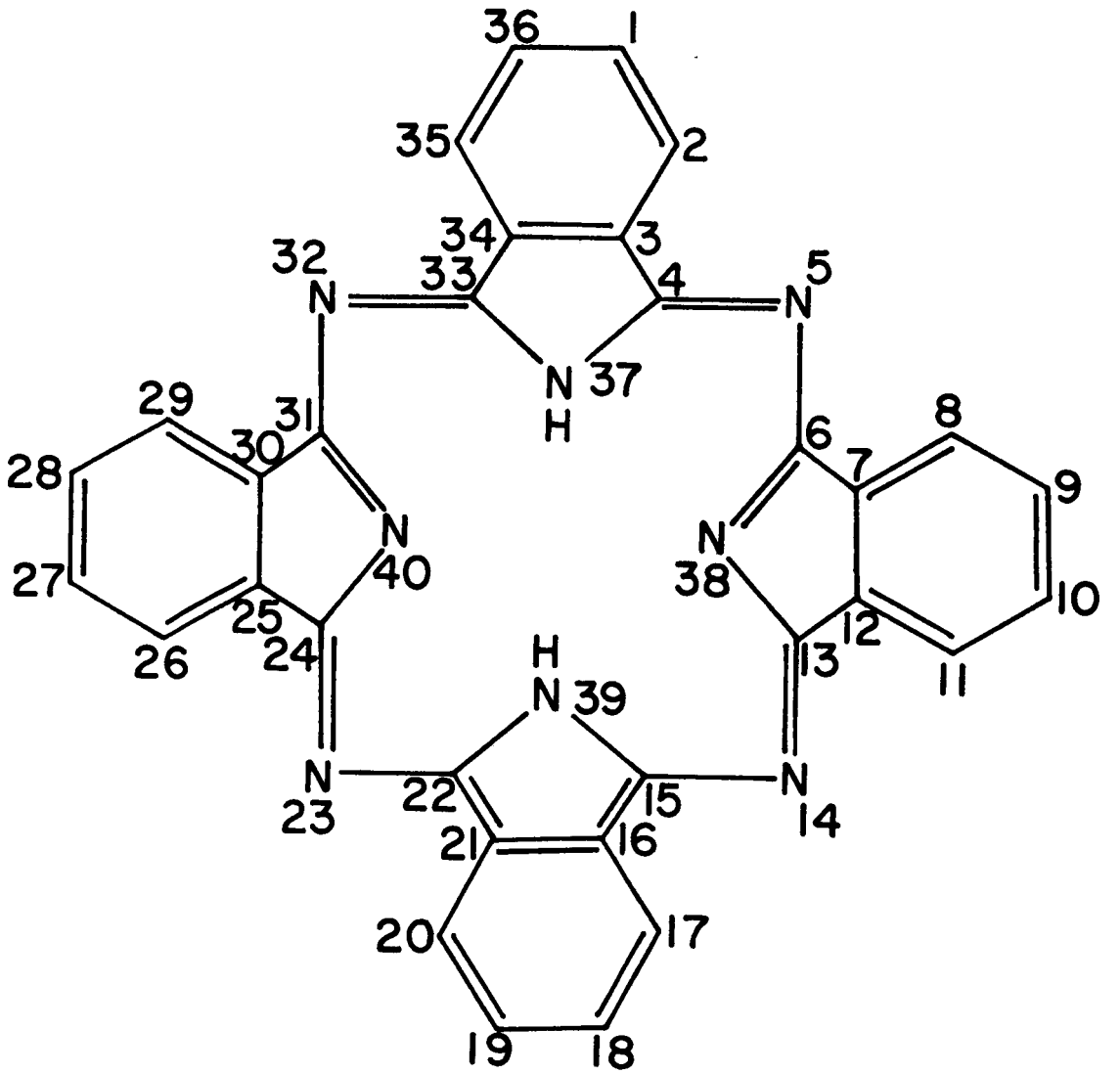


FIGURE 2 - HYDROGEN PHTHALOCYANINE

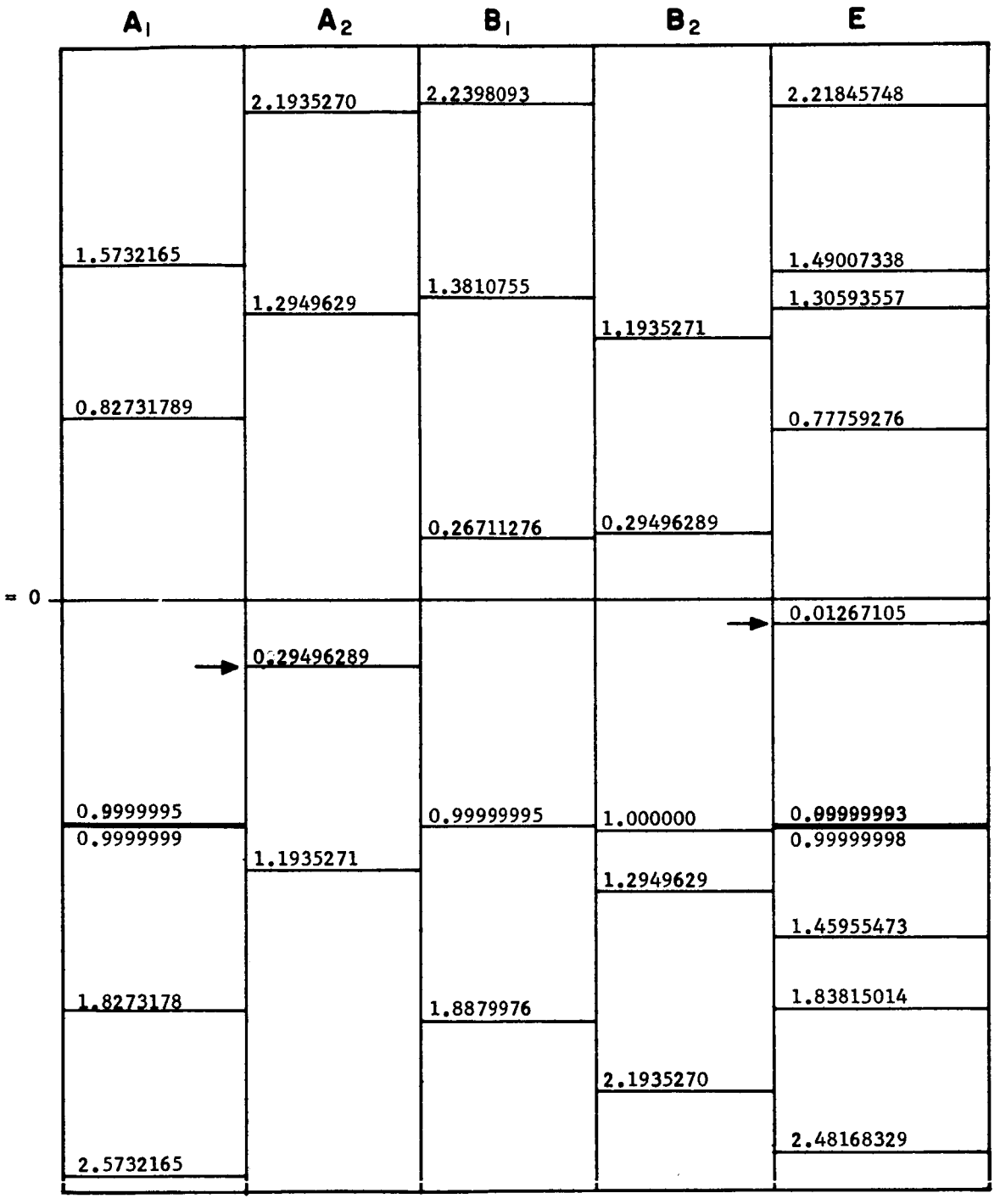


FIGURE 3- (ENERGY LEVELS ARE DRAWN WITH REFERENCE TO $\alpha = 0$ LINE AND THE SPACINGS BETWEEN THE LEVELS IS PROPORTIONAL TO THE ENERGY DIFFERENCE DIVIDED BY β)

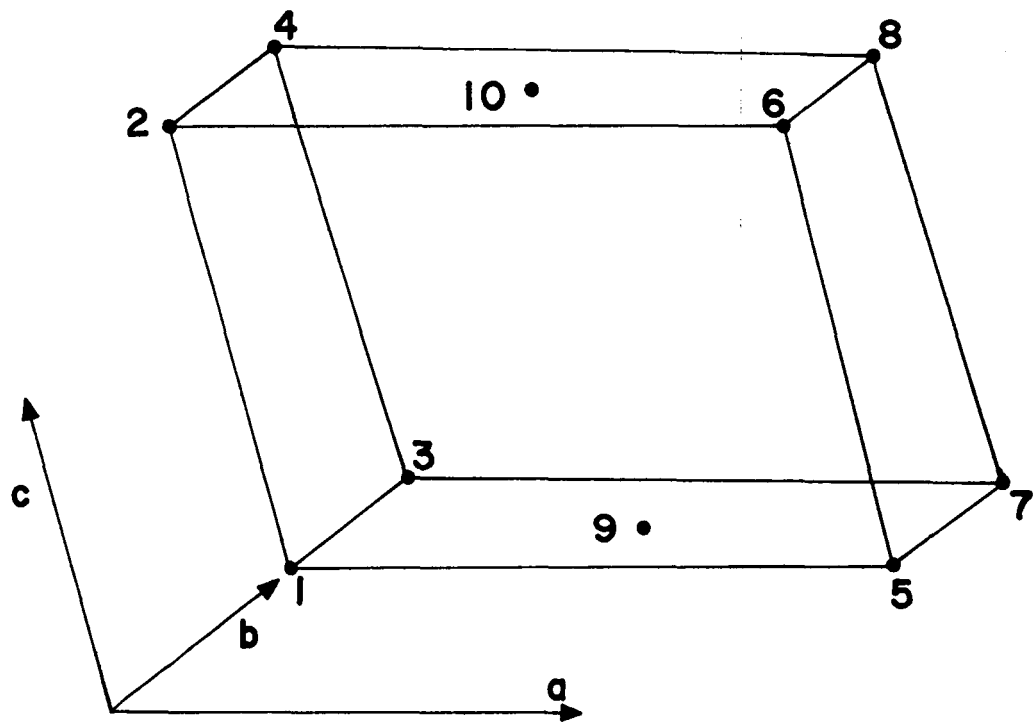


FIGURE 4 - THE UNIT CELL OF THE MONOCLINIC HYDROGEN PHTHALOCYANINE CRYSTAL

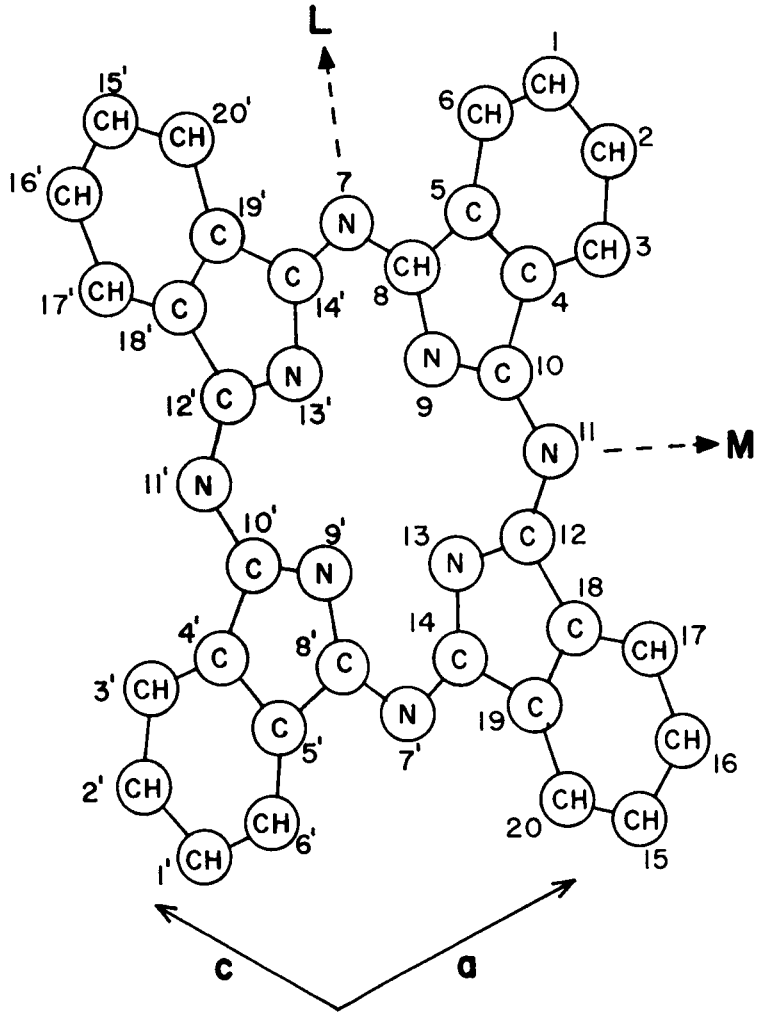


FIGURE 5 - ORIENTATION OF MOLECULAR AXES, L AND M

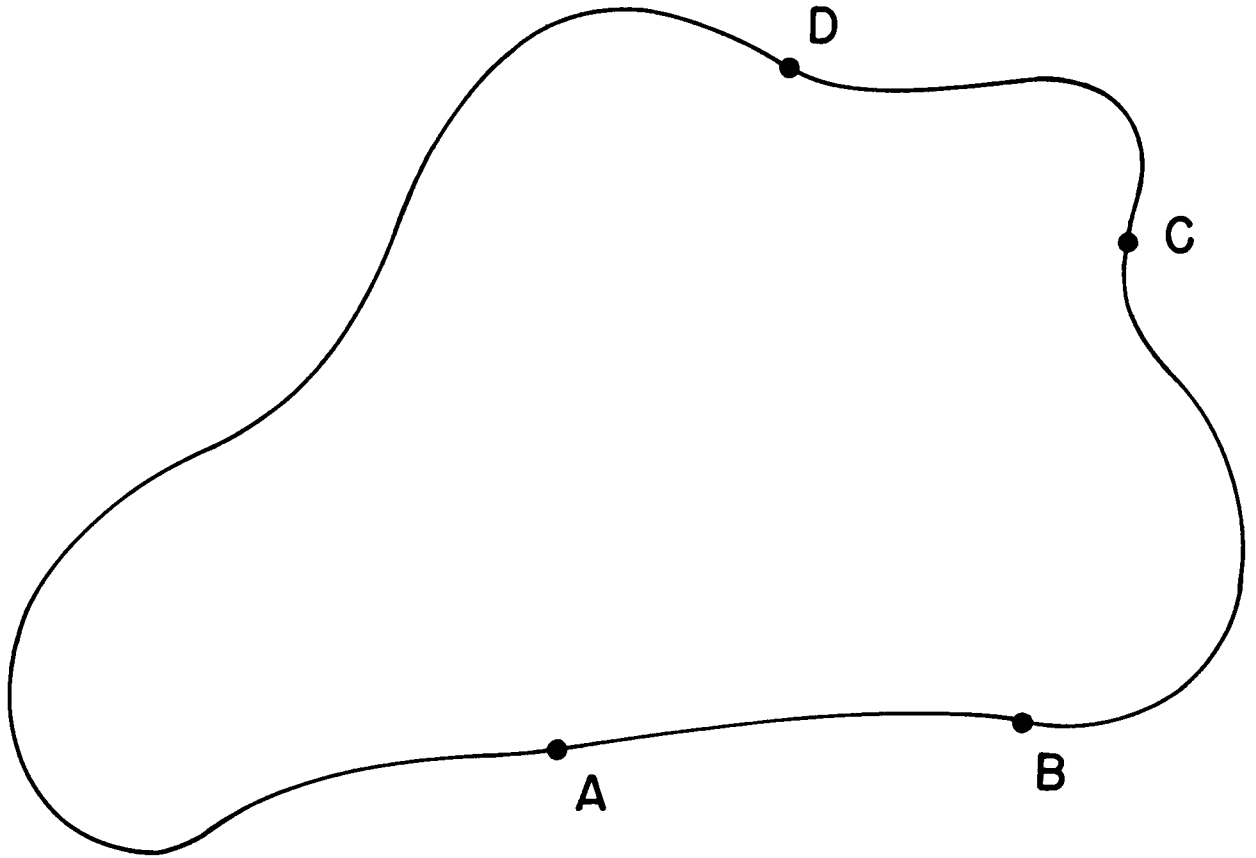


FIGURE 6 - A SAMPLE OF ARBITRARY SHAPE WITH FOUR SMALL CONTACTS AT ARBITRARY PLACES ALONG THE CIRCUMFERENCE WHICH, ACCORDING TO THIS PAPER, CAN BE USED TO MEASURE THE SPECIFIC RESISTIVITY AND THE HALL EFFECT

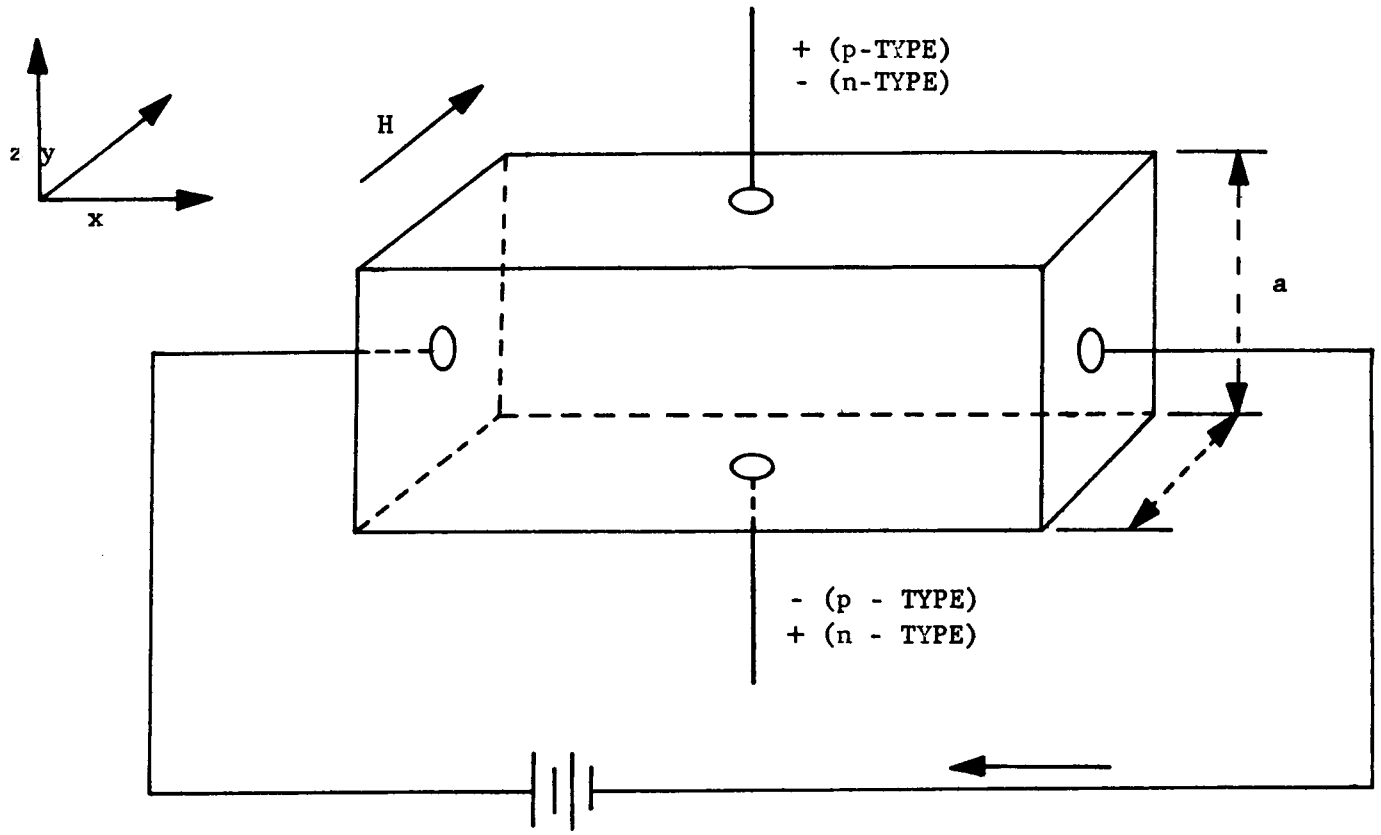


FIGURE 7 - SCHEMATIC REPRESENTATION OF HALL EFFECT MEASUREMENT

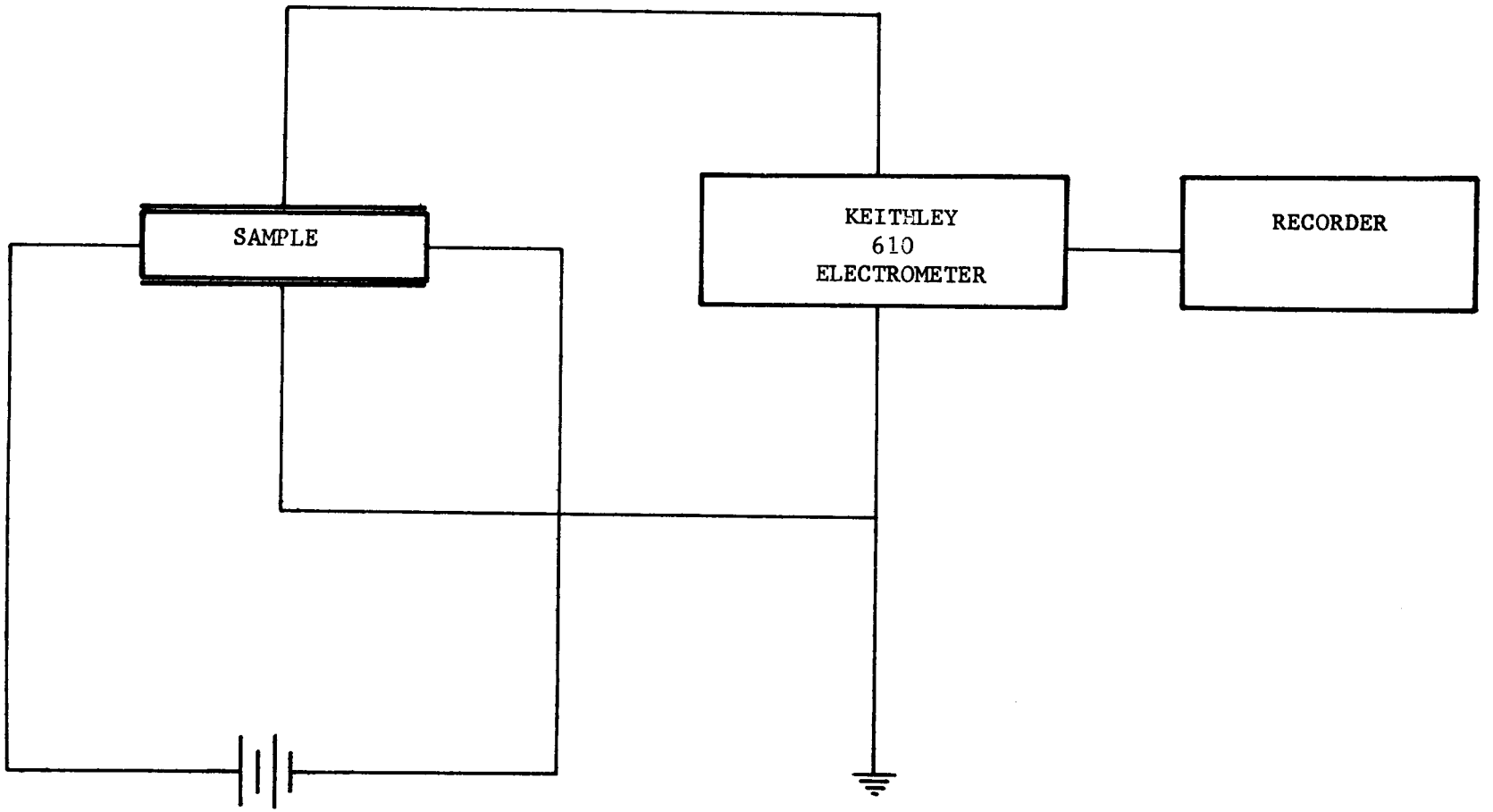


FIGURE 8 - SCHEMATIC OF ELECTRICAL CONNECTIONS FOR SINGLE CRYSTAL MEASUREMENTS

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CONDUCTION MECHANISM IN ORGANIC SEMICONDUCTORS

By Satish C. Mathur

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