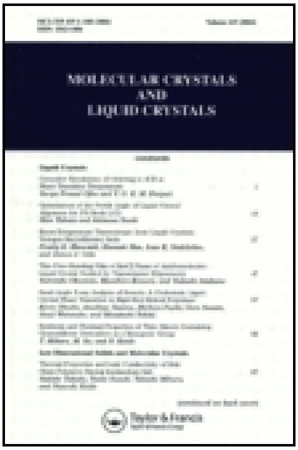

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Studies of Organic Semiconductors for 40 Years—IV

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Studies of Organic Semiconductors for 40 Years—IV

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1. INTRODUCTION

Most contributions by Australian workers in the field of electrical properties of organic solids have been discussed in (i) the excellent book[1] by Pope & Swenberg; (ii) three books[2–4] surveying the field generally; and (iii) the extensive theoretical survey by Silinsh.[5]

In Australia there has been for forty years a strong interest in the optical and excitonic properties of molecular crystals associated with (apart from ourselves) the names of e.g. D. P. Craig, I. G. Ross, G. C. Morris, J. A. Ferguson and, latterly, M. G. Sceats and Jai Singh. This work mostly does not involve charge carriers but some does. It is not possible in the present article to cover the purely spectroscopic matter, but two books[6,7] by Craig and his co-authors give an insight to much of his work.

Australian work on the electrical properties of organic molecules and their crystals dates from 1950 when a set of values of molecular electron affinities of aromatic hydrocarbons was published.[8] Those values are discussed later in this article; in 1950 there were no other values with which to compare them.

Observations of crystals (of naphthalene and hexamethylbenzene) were reported by Craig and Lyons[9,10] in 1952 when the interest lay in the absorption of polarized light and the symmetry properties of excited electronic and vibronic states. These papers built upon the work of Craig on the spectroscopy of aromatic molecules.

The first Australian publication on the photoelectrical properties of crystals of aromatic hydrocarbons was of the work[11–14] of my first Ph.D. student D. J. Carswell. It appeared in 1953, 1954 and 1955. It is discussed in Section 3 of this article. In Section 2 we look at more than a score of research findings by others, not members of my own group.

2. WORK IN VARIOUS CENTRES

1950 Fulvalene and Ferrocene

R. D. Brown published quantum mechanical calculations[15] on an "aromatic compound" $C_{10}H_8$ with two 5-membered rings, a compound not then known in any laboratory and which he named "fulvalene." Brown's paper led to Kealy & Pauson's synthetic work[16] which in 1951 found, en route to fulvalene, the compound dicyclopentadienyl—iron i.e. ferrocene. In later days the tetrathia- and tetraselena-fulvalenes became celebrated for their part in highly conductive organic solids.

1955 Polarizabilities

Molecular electric polarizabilities are needed for the calculations of polarization energies. Many values[17] were determined by the late Professor R. J. W. LeFevre in the University of Sydney.

1957 Thermoelectric Measurements—Seeback co-efficient

The first such measurements on an organic single crystal appear to be those of Fielding & Gutmann on metal-free phthalocyanine[18]; they showed that the sign of the majority carrier was positive.

1957 Phthalocyanine single crystals

Fielding & Gutmann made one of the first photoconduction measurements[18] on single crystals of phthalocyanine. They found the mobility of holes was 0.01 $cm^2 V^{-1}s^{-1}$. Fielding and Mackay[18] extended the work.

1962 Glassy regions and electrical conductivity

An unusual peak was observed[19] by Gutmann and Netschey in the electrical conductivity vs. temperature curve of solid chlorpromazine. The peak was traced to the inclusion in the solid of small glassy regions as a result of a study[20] by Ehlers & Haneman of nucleation and crystal growth in that material.

1967 CT complexes in power sources[21]

Solid charge-transfer complexes, used in cells between a reactive metal such as Mg and an inert metal such as Pt, constituted a power source having an open-circuit voltage up to 2.5V and short-circuit currents up to 25mA cm^{-2}. In the complex the donor was e.g. perylene or polyvinylcarbazole or mixtures of these with carbon black, and the acceptor was e.g. I_2 or tetracyano-quinodimethane. Moisture enhanced the performance.

1967 I_2 CT Complexes

Two types of charge transfer complexes between phenothiazine and I_2 were found.[22]

1967–70 Mobility in amorphous solids affected by long range order.

Long range order in disordered systems was shown[23,24] by Gutmann able to arise from the accumulation of small disturbances with a resultant effect on carrier mobility.

1968 Tunneling not Hopping

For electron transfer over distances of several nanometres in certain biological structures Gutmann calculated[25–27] the Christov characteristic temperature to decide that tunneling was dominant over hopping at temperatures at or near room temperature. This conclusion appears to be fairly general for barriers about 1eV high and of width c.1-2nm.

1969 First Hall effect measurements on TCNQ complexes

These[28] were made by Gutmann with some American colleagues. The resultant Hall mobility, in the complex made with the donor 1,2-bis (4-pyridyl) ethane, was 0.04 $cm^2V^{-1}s^{-1}$.

1969 Activated mobility in TCNQ complexes measured for first time.

In a series of monomer and polymer complexes with tetracyano-quinodimethane Gutmann *et al.* found[29] that the resistivity dropped eight orders of magnitude as the temperature rose from 80K to 500K, when the donor was polymerized 1,2-bis-(4-pyridyl)-ethane. Because the carrier concentration, determined from the voltage where the i-V curve changed from ohmic to parabolic, was constant as T changed, they ascribed the conductivity changes to an activated mobility, several times previously predicted as a phenomenon in the literature but apparently never observed before. From their Figure 2 the activation energy was 0.17eV.

1969 Rotational Assistance to Tunneling

Gutmann sought[30] a general understanding of charge transport for the large numbers of organic substances to which the band model is inapplicable. He suggested that often the pre-condition for tunneling to occur was a sterically favourable alignment of the molecules on adjacent sites and that their adjustment required a process of hindered rotation. Such a process is illustrated in the article's drawing which is the frontispiece to Pope and Swenberg's work[1] of art, and which is based on a Duke & Schein article[31] in 1980.

1970 Measuring Permittivity of Small Crystals

A method to determine the effective permittivity of small crystals was described[32] by Johnston & Lyons.

1972–4 Exciton Scattering

Morris & Sceats used reflectance spectroscopy to study exciton-phonon scattering events.[33–35]

1972 Interpretation of Glow-Curve Peaks

Glow-curve peaks in a number of polymers were able[36] to be correlated with the onset of particular molecular motions which liberated electrons from traps. Any peaks not so assigned were attributed to trapping by impurities.

1972 Charge Transport in PVC

In polyvinyl chloride Ranicar and Fleming found[37] charge transport occurred in two stages, the first within the chain of one molecule and the second an inter-chain hop.

1972 Analysis by Fluorescence

The effects on the fluorescent spectrum of doping anthracene with each of ten organic dopants were recorded[38] by Lyons and Warren, thus providing an analytical method for a set of doped anthracene samples.

1976–8 Cardiac Pacemakers

Primary cells based upon solid CT complexes are now commercially available as cardiac pacemakers. Polyvinyl pyridine: iodine: lithum cells have life times of 10 years in actual use.

1977 Review of Electrochemistry of Charge Transfer complexes[43,44]

1978 Dark Conductivity and Activation Energy in CT Complexes
Farges and Gutmann, in reviewing[43] charge transfer complexes, noted that, like other organics, charge transfer complexes showed an exponential rise of electrical conductivity with temperature, weak complexes having large activation energies up to more than 2eV whilst for strong complexes the activation energy was low and approached zero.

1978 Dielectric methods reviewed
The complexes between DNA and dyes were studied with dielectric methods, reviewed[43] in 1978.

1979 Application of Noise to Recombination
A method for the direct measurement of recombination processes in charge-transfer complexes might be developed from the measurement of noise, according to Farges and Gutmann.[44]

1979 Co-ordination number and Oxidation state[45]
Plastocyanin molecules in donating or accepting electrons retain the same co-ordination number of the central Cu atom.

1981 Energy gap and cohesive energy
Gutmann & Keyzer found[46] some positive evidence that for a series of organic compounds the energy gap was related to the cohesive energy density. Since for aromatic compounds, all electronic properties do tend to vary together (*see* Lyons & Morris[47]), and also the cohesive energy is describable in terms of the electronic polarizabilities, the Gutmann & Keyzer relation can be understood, at least semi-quantitatively.

1987 Trapping of carriers at charged centres
The encounter rate of oppositely charged carriers and electron trapping by charged impurities were considered by Dawes & Sceats[48] with results which are relative to the determination of the quantum yield of luminescence in semi-conductors. The theory is relevant also to superlattices made from differing semi-conductors, as it was developed for both 2- and 3-dimensions. The reduced configuration space in two dimensions gave rise to a lower encounter rate.

3. PHOTOCONDUCTION (PC)—EARLY WORK

Shortly after Akamatu and Inokuchi in Tokyo studied[49] the semi-conduction of various organic solids, the earliest work[11–14] on photoconduction in Australia was done in the 1950's. We did not know in 1950 of the work[50] of Pochettino who in 1906 had shown that anthracene was a photoconductor and who also had observed photo-electric emission. Even earlier, Stoletov[51] had detected a photo-voltaic effect with dye-films, and in 1910–3 both Volmer[52] and Byk and Borck[53] had reported on anthracene's photoconduction. Before 1950 in the U.S.S.R. Vartanyan[54] had studied dyes, and in the U.K. Eley had measured phthalocyanine films.[55,56]

In 1950, we *did* know, from polarography,[8] that an electron from a metal could be transferred to an aromatic molecule in an environment which was largely organic. This fitted easily with the work done by D. J. Carswell who undertook a study of photoconduction in anthracene crystals using metal electrodes, both on the front surface, and a circuit built around a Mullard electrometer valve. Thus we entered in the early 1950's the area of electrical conduction in "insulating" crystals. The wheel turned full-circle when the work on electrical conduction later called for, amongst other things, a greater knowledge of electron affinities.

What was new about the Australian work was (i) the use of single crystals and (ii) the use of monochromatic light, and consequently the observation of the striking resemblance of the PC excitation spectrum to the absorption spectrum of the crystal (in the "surface" cell) a resemblance which persisted[57,58] when the incident light was plane-polarized either parallel or perpendicular to the *b* direction of the crystal.

Although the resemblance of the two spectra clearly showed that the anthracene crystal was involved in the photo-generation of charge carriers, yet, because the crystal was thick enough for light of every wave-length within the absorption band system to be 100% absorbed, it was not immediately obvious why the excitation spectrum had its observed nature. Tetracene crystals showed a similar phenomenon[58,59]; indeed, the polarized PC excitation spectrum was done before the polarized absorption intensities had been measured. When later we did such measurements the Davydov splitting in the absorption explained the observed splitting of maxima in the two polarizations in the PC excitation; both were a result of Frenkel exciton motion.

Lyons in 1955 used a random walk model[60] for the exciton motion—in one dimension perpendicular to the irradiated surface—in order to explain the excitation spectrum; the further from the surface the exciton was formed, the less probably would it regain the surface where carrier generation took place.

The PC phenomenon was reduced almost (but not quite) to zero if oxygen in the ambient was replaced by nitrogen, but recovered after the return of oxygen. These observations[61] supported the notion that the PC was a surface effect and carriers were generated where oxygen was adsorbed and an exciton arrived. In fact I_{pc} was shown[61] to vary with oxygen pressure in a way represented by a Langmuir adsorption isotherm.

By much chemical analysis[59] of anthracene crystals irradiated in air, the final oxidation product found on the surface was anthraquinone, but this gave no carriers by exciton collision with it. There was an intermediate, anthracene peroxide, which was involved in carrier formation.

In 1956 naphthalene, phenanthrene, pyrene, chrysene, diphenyl and *p*-terphenyl crystals were shown[47] to yield similar photoconduction effects to anthracene; and the magnitude of the photocurrent was shown to vary through the set of molecules in exactly the same way as did any other molecular electronic property (e.g. I_G). Some afterwards, 1:2-benzanthracene and 1:2-5:6-dibenzanthracene, dibenzthiophene and acridine were added[62] to the list. Sano and Akamatu[63] added e.g.

violanthrene, indanthrazine, anthanthrone and violanthrone; the phenomenon was quite general. Besides O_2, NO and other electron accepting gases increased I_{ph} in surface cells, but H_2O and NH_3 reduced I_{ph}. Lyons's exciton diffusion theory[60] was queried by Compton *et al.* who pointed out[64] that a double layer of charge at the surface might produce a similar effect to that of adsorbed gas by affecting the carriers after their formation. Eremenko & Medwedew examined[65] the two theories and found that the diffusion length of excitons derived on the basis of exciton diffusion theory agreed with that derived from luminescence studies. They concluded that the exciton diffusion theory was to be preferred.

The early work[65] revealed the common occurrence of space-charge, but also showed that, in sandwich cells, space-charge was reduced by a sufficiently high electric field. Under these circumstances the photocurrent was constant as the wave-length varied through the absorption band and to lower photon energies beyond it. Furthermore, infra-red radiation of wave-length 1.5 to 2 micrometers released charge carriers from traps. Observations such as these showed the existence of bulk-generated photocurrents, the need for a consideration of the roles of space-charge and of traps, and also the need for a theory of how carriers could arise in the bulk of an irradiated crystal. It should be remembered that around the late 1950's there had been a large amount of work on the spectra of organic molecular crystals and none of it required the mention of any charged species. The situation with organics was quite different from that with Si or CdS where the very absorption of light meant that charge carrier pairs were being generated. A fresh approach was needed and is discussed in Section 4.

4. ENERGY GAPS IN MOLECULAR CRYSTALS

Ever since there were published[66,67] some relatively simple methods for numerical estimation of energy quantities in molecular crystals, there has been frequent use of the quantities by many workers, (see References 1–4) as well as a long-sustained and highly successful effort[5] by Edgar Silinsh to improve the calculations, to make them more exact and to extend their range of application, all this being covered in his book.[5]

A key quantity in the theory is the polarization energy P of a singly charged entity situated on a point of the molecular crystal lattice. P is approximately but not precisely the same whether the charge is positive or negative, when all neighbouring molecules are neutral. It is possible to calculate P by classical methods. The problem is an exercise in the interaction of many electrons.

Although the term E_G, the energy gap, is used for molecular crystals as well as for silicon-type semi-conductors, it has some implications which are different in the two cases. In molecular crystals the state lying at E_G above the ground state has two carriers of opposite sign separated from each other by a distance large enough (c.15nm) for the mutual interaction energy to be less than kT.

Using the symbols $I_{G,C}$ for the ionization energy of the gaseous molecule and the molecular crystal; $A_{G,C}$ the electron affinities; P_+, P_- for the polarization energy of a positive, negative, centre; D, Ac for donor, acceptor, there are various ways of using the quantities in the determination of

(i) I_C from I_G by estimating P_+
(ii) A_C from A_G by estimating P_-
(iii) E_G from $E_G = I_C - A_C$
(iv) E_G from $E_G = I_G - A_G - 2P$; if $P_+ = P_-$
(v) P_+ by measuring I_G and I_C; $P_+ = I_G - I_C$
(vi) P_+ or P_- by calculation from molecular polarizabilities.
(vii) Molecular donor or acceptor levels in a host crystal as first described in Reference 2 p. 368. In applying energy level numbers to interpret observations, here as elsewhere a proper account[2] must be taken of entropy changes.
(viii) Levels in a crystal under pressure, by calculating P.
(ix) Levels of e.g. aromatic hydrocarbons in rare gas matrices
(x) CT exciton levels.
(xi) E_G from polarographic $E_{1/2}$ values.

The whole subject has been discussed in the books.[1-4] Here I must be content with illustrations of (viii), (ix), (x) and (xi).

(viii) Pressure dependence of electrical conductivity.

High pressure changes the intermolecular spacings and consequently P increases and thereby lowers the thermal activation energy for the formation of carriers. This model[68-71] has been used to calculate the polarization energy of many organic materials assuming them to be isotropic and the increased conduction to stem at least in part from the greater polarization energy reducing the thermal activation energy. There is no question but that there is frequently a drop in the activation energy at high pressure, although in addition one must expect other pressure induced phenomena such as dimerization, increased mobilities, and sometimes, the formation of new phases or compounds.[72]

(ix) Electronic levels of aromatic molecules in rare gas matrices

Naphthalene in Ar, Kr or Xe at low temperatures was studied in Australia[73,74] and illustrates, in our present symbolism, where I_G (naphthalene) = 8.14eV, that in Ar $I_C = 7.2$; $P_+ = 0.9$; $E_G = 7.14$ and $P_- = 0.11$. In addition two Wannier states were recognised below E_C (which lay at 7.14 V above ground) by ($2.40/2^2$ =) 0.6eV and by ($2.40/3^2$ =) 0.27eV. The electron was said to be in the conduction band which is based in argon on levels with increased principal quantum members (4,5. .) above those (1,2,3) used in describing the atomic ground state. Then, too, argon differs as a host from say naphthalene in the value of I_C for naphthalene (7.25 in argon; 6.84 in naphthalene). Furthermore, argon has no intramolecular vibrations as has naphthalene. The naphthalene molecule of course has highly excited levels based on carbon orbitals with n = 3,4. . . . And all orbitals of appropriate symmetry will interact. As I write this, I can not recall any calculation of crystal levels except for the paper by Bounds and Siebrand[75] which tries to take account of all these interactions. They were outlined in the 1957 paper.[66] Vibronic levels must be included too in any full treatment of excited states. Perhaps there is here a task for the future.

(x) CT Levels and CT Excitons

These were predicted[66] in one-component molecular crystals in 1957 with estimates of their energy. In anthracene crystals also the oscillator strength of a direct optical transition to a nearest-neighbour charge-transfer (CT) state was calculated in 1957 by Lyons as 3×10^{-5}. As was then pointed out, configurational mixing with other states of appropriate symmetry, through intensity stealing from other transitions, would increase f. Ewing and Kearns[76] calculated $f = 10^{-4}$. Choi, Jortner, Rice & Silbey discussed[77] CT excitons in molecular crystals in 1964 and other references are given on p. 328 of Reference 2. From an electro-absorption experiment Sebastian, Weiser and Baessler[78] in 1981 found that $f = 10^{-2}$, and also listed various CT states. This was pre-dated by the first experimental evidence of the existence of CT excitons obtained in tetracene by Pope, Burgos and Giachino[79] in 1965. In 1974, Abbi and Hanson[80] found CT states in 9,10-dichloroanthracene by electro-reflectance.

The low permittivity of many organic solids ensures a strong tendency for ions of opposite sign to form a pair. If the lattice spacing is 0.5nm then finding a CT state with a separation distance r of 0.5nm is c.10^4 times as likely as finding one with $r = 1.0$ nm. When the relative permittivity equals four, the interaction energy of the charges equals kT at $r = 14$nm; ion pairs can be quite large and can be formed by the two charged species coming together. They can also be formed from neutral molecules by photo-generation.

C. L. Braun and his colleagues have a long and profitable record of studying the photogeneration of carrier pairs especially by 1-photonabsorption. In anthracene in 1976 Chance & Braun[81] found photons with 4.4 to 5.1 eV energy gave rise to $r_0 = 5$ nm, but 5.4 to 6.1 eV photons gave $r_0 = 6.7$ nm, in the resultant CT states. A similar experiment in the same year by Lyons and Milne[82] gave r_0 values of 1.8 to 2.5 nm (2.9 to 4.2 eV photons; relative permittivity 3.2 to 3.8) and 2.5 to 3.2 nm (4.5 to 5.0 eV; 3.2 to 3.8).

There are various ways to obtaining and treating the data obtained in these experiments. The two groups in fact did different experiments and used different methods to treat the raw data. It is not clear how the different r_0's should be reconciled for 4.4 to 5 eV photons.

To calculate the activation energy E_D of dissociation of an ion-pair using $E_D = (0.378/r_0)$, where E_D is in eV and r_0 in nm, yields, for a dielectric constant of 3.8,

for $r_{0,A} = 1.8 \pm 0.5$ nm: $E_{D,A} = 210 \pm 60$ meV;

and for $r_{0,B} = 2.5 \pm 0.5$ nm: $E_{D,B} = 150 \pm 30$ meV;

An experiment of Dr. K. A. Milne[82] varied the temperature and determined directly the activation energy of dissociation of $r_{0,B}$ as 190 ± 30 meV. Values of r_0 changed from one crystal to another and gave rise to the stated errors. It is unclear however where the entropy factor enters into these results. It would cut the activation energy to half, if both carriers were free to move. The auto-ionization process is more complicated then once it was thought to be.[88]

The auto-ionization model, used for organic molecular crystals by Pope[83] and his colleagues is intrinsically involved with CT states. Pope and Swenberg remark (Reference 1, p. 75) that in a 1980 paper[84] "Lyons estimated the band gaps of about thirty organic solids, including pentacene and tetracene, on the basis that auto-ionization was a significant mechanism and his results are consistent with the electro-absorption results."

Two long-standing results in the literature also are consistent with auto-ionization: Vartanyan (Reference 2, p. 378) studied the temperature dependence of the photo-current I_{ph} for some dyes, and found that dI_{ph}/dT lessened as the photon energy increased in the absorption region. Also, Akamatu and Kuroda[85] looked at CT solids and found that the threshold of intrinsic photoconduction was regularly 200 to 300 meV above the peak of the CT absorption.

Polarization energies and CT states: (cf. Silinsh[5]) Craig & Petelenz in 1984 proposed[86] a theory of charge-transfer (CT) states in connection with interpreting the photo current spectra of anthracene-tetracyanobenzene. They estimated that the nearest-neighbour CT state lay at a higher energy than the other CT states, thus agreeing with Samoc & Williams' view[87] that CT states were not in a coulomb-like series. Craig & Petelenz's theory explained a variety of experimental observations and indeed, if confirmed, is of quite some generality.

For chlorophyll *a*: H_2O adducts the photoconduction at $h\nu = 1.5$ eV was attributed[88] to dissociation of a CT state.

Lyons & Morris predicted[89] that one way to dissociate a CT exciton is to have it collide with a charged centre, near to which the electric field is c. 10^7 V cm^{-1}. See Petelenz (1978) for a discussion of field effects on excitons.[90]

(xi) E_G from $E_{1/2}$ values

A variation to the above methods was used by Lyons[84] who calculated E_G for about 30 dyes from the polarographic half-wave potentials. As a result it becomes possible to expect photogeneration of carriers in these solids at energies within about 0.2 or 0.3 eV of the first strong absorption maximum in the solid.

In discussing in 1966 the feasibility of organic metals Lyons made a survey[84] of the pre-exponential factors and activation energies of electrical conductance for 161 organic solids which revealed that several behaved as though they were intrinsic semi-conductors in that the pre-exponential factor was around 10^{22} cm^{-3} comparable with the molecular concentration. For this group twice the activation energy was usually about 2 eV. It would be interesting to estimate E_G from the method just discussed to see if the old experimental results for E_G are confirmed.

5. IONIZATION ENERGIES I_G OF MOLECULES AND I_C OF CRYSTALS

In 1959 C.G.B. Garrett in an article[91] on organic semi-conductors remarked that "few of the substances of interest to us have been investigated." This was true to some extent of I_G but more especially very true indeed of I_C. Lyons, Mackie and Morris therefore measured[92,93] I_C by direct photoemission of electrons from single crystals with results summarised (Reference 2, p. 693) along with numbers from Inokuchi, Vilesov, Pope and others.

Pope's adaptation[94] of the Millikan oil-drop experiment to small organic crystals was so splendidly sensitive that I must mention it for comparison with the other equipment used by most of us, it was better by 10^6.

Another development, photo-electron spectroscopy, has greatly improved the accuracy of determining both I_G and I_C; but before it became available, charge transfer spectra were used especially to find I_G and A_G, as e.g. by Lyons & Fulton[95] who measured I_G for the nucleic acid bases (amongst many others) obtaining the following values in eV which compare with Kunii and Kuroda's theoretically calculated values[96] as follows: cytosine calc. 8.8, exp. 8.0; adenine 8.0, 7.8; guanine 7.7, 7.6; uracil 8.4, 8.5.

A further piece of Australian work was the first determination,[97] in 1968, of I_C for CT complexes.

6. ELECTRON AFFINITIES A_G AND A_C

Before 1950, no electron affinity value had been obtained for any polyatomic organic molecule. So that when A_G values[8] for a number of aromatic hydrocarbons were derived from polarographic half-were potentials they were the first of their kind. Although the numbers obtained were all about 0.8eV too positive, they were quite good on a relative scale. For example, for benzene relative to naphthalene, the 1950 value $A_{G,\mathrm{rel}}$ was -1.03 eV; and to-day we accept[98] -1.17 for $A^{v}_{G,\mathrm{rel}}$ by theory, and -1.10 by expt. (Superscript v denotes vertical; a, adiabatic). For anthracene relative to naphthalene: in 1950 $A_{G,\mathrm{rel}} = +0.81$eV to-day $A^{v}_{G,\mathrm{rel}} = +0.75$ (theory) or $+0.74$ (expt.) and $A_{G,\mathrm{rel}} = +0.67$ (theory) and 0.72 (expt.).

The reasons for the 1950 absolute values being high was elucidated later.[69] Neglect of a surface potential and of a liquid junction potential accounted for about two-thirds of the error. In addition, more recent and better values of absolute electrode potentials improved the original calculations. Now the method produces agreement with experiment to within 0.1eV.

In 1955, Hush and Pople[99] obtained theoretical values for A_G for a number of aromatic hydrocarbons which to-day compare well with experiment (In addition Hush[99] considered electron removal from a positive ion and electron interactions in multiply charged ions.)

It is convenient to divide organic molecules into two classes when discussing A_G values: (i) the aromatic hydrocarbons, and (ii) molecules with electron accepting groups such as quinones, nitro compounds, and cyano compounds, especially tetracyanoethylene and tetracyano-quinodimethane. Over the years it has proved easier to get agreement on relative electron affinities than on absolute values. This is demonstrated by looking at the electron affinities of aromatic hydrocarbons relative to benzene listed in Gutmann and Lyons,[100] where e.g. $A_{G,\mathrm{rel}}$ for anthracene (vs benzene) has a mean from six different approaches of 1.97eV, with a standard deviation of 0.13eV. For naphthalene (vs benzene) six different approaches give a mean of 1.22eV with a standard deviation of 0.14eV.

As a fixed point on the A_G list for aromatic hydrocarbons Silinsh[101] selected the value for anthracene obtained by the electron capture method[102] in 1966 by Becker and Chen[103] who reported $A_G = 0.55 \pm 0.01$ eV, and then in 1968 Lyons, Morris and Warren,[104] who used the electron capture method and who investigated the methodology and the theory of it, reported $A_G = 0.57 \pm 0.02$ eV confirming the earlier result.

When attention is turned to the non-hydrocarbon compounds it is again true that values of $A_{G,\mathrm{rel}}$ are more consistent than absolute values of A_G.

Here the methods used to determine A_G include:

(i) quantum mechanical theory;
(ii) polarographic $E_{1/2}$;
(iii) charge-transfer spectra, for relative values;
(iv) Page's magnetron method;
(v) Beitz & Miller's gas phase method;
(vi) Beitz & Miller's electron survival technique (at 77K in MTHF glass);
(vii) photodetachment of electrons from negative ions.

In Australia (ii),[105] (iii)[69,106] and (vii)[107] have been used.

Let us concentrate attention on A_G values in eV for three important electron acceptors: *p*-benzoquinone, *p*-chloranil and tetracyanoethylene.

Using the collection[108] of A_G tables from various workers: Page,[109] Kloepfer & Rabenhorst,[110] Beitz & Miller[111] (three methods) and Lyons & Palmer,[108] averaging the absolute values gives for *p*-benzoquinone, 1.8 ± 0.3; *p*-chloranil, 2.4 ± 0.5; and for tetracyano-ethylene, 2.5 ± 0.4, where the error quoted is the standard deviation. (A value for *p*-chloranil) of 1.37 was corrected to 1.73 before averaging). It is seen that absolute values of A_G are no more accurate than about 0.3 to 0.5 eV. This was also about the accuracy attained by photodetachment[107] of electrons from the negative ion of tetracyanoethylene.

In 1982, there still remained the need for a precise A_G determination on several key molecules. If the need still is there, a task for the future is evident. The aim should be to attain A_G values accurate to 0.01eV or better. With present day facilities it should be possible to do this with photodetachment experiments.

Using the same data as above, relative values $A_{G,\mathrm{rel}}$, when always the same method was used for two compounds, showed the $A_{G,\mathrm{rel}}$ value of *p*-chloranil vs. *p*-benzoquinone was 0.7 ± 0.2 eV. In contrast, the difference of the means for A_G (absolute) for each compound had an error of ±0.8eV. Relative values are, as expected, more accurate when the method is kept constant.

7. POLARIZATION ENERGIES (*P*)

The early calculations of *P* by Lyons, Batley & Mackie have been summarized,[112] whilst the work[5] of Silinsh is available for the development over recent decades. It seems fair to claim that the introduction of polarization energies into the energy level calculations of organic molecular crystals has enabled numbers of different types of observations to be interpreted quantitatively.

8. MIM CELLS AS ENERGY CONVERTERS, AND SPACE-CHARGE LIMITED CURRENTS

Ghosh & Feng[113] said that the first extensive study of metal/organic insulator/metal cells was that of Lyons and Newman[114] who employed tetracene as the organic. Ghosh and Feng themselves used tetracene and porphyrins. Usov and Benderskii[115] in the earliest work of all in this area used phthalocyanine.

For nearly a decade in the 1970's there was no satisfactory theoretical approach and it was only in 1978 that a suitable theory,[116] experimentally confirmed, appeared and that only for a restricted though useful range of conditions.

In this period various authors tried to apply the solid state theories used for inorganic semiconductors like silicon. There was talk of band-bending varying with the applied voltage, of donors to the conduction band and acceptors from the valence band, etc., but no organic MIM or MI system in the 1970's behaved in all respects like Si. A new approach was needed.

In the organic cells, my colleague Dr. Jim Bonham in a fine series of papers,[117-123] using much electrostatics, looked at the various conditions which can hold for organic MIM cells. He distinguished between ohmic and blocking electrodes, included traps distributed in a number of ways, looked at the behaviour in the dark and in light, with and without an applied voltage. He allowed diffusion of carriers to occur, as it undoubtedly does at low electric field strengths. The widely used space-charge-limited-current theory[124] of Helfrich and Mark had ignored diffusion of carriers and in the end was seen to be somewhat in error. In the determination of the parameter values for a trap distribution the new theory gave numbers significantly different from the old.

Should we conclude then, that the wonderful world of silicon semiconductor theory is always irrelevant to organics? Will there never be a really good (that is, like silicon) pn junction? For some years it might have been possible to answer yes to both these questions. In recent years, however, lutetium phthalocyanine has been shown to have all the "right" capacity behaviour and doping possibilities, so that we do have to-day a "true" organic semiconductor. But let us return to organic MIM cells in the early 1970's. Because the energy conversion efficiency of those cells was very low it is of interest to examine what is the theoretical upper limit to the efficiency.

The maximum power output is given,[126] under appropriate conditions, for an open-circuit voltage of 1V, in SI units, by $J_{ph}U$, where $J_{ph} = 10^{-11}\, uf/d^3$. Here f is the ratio of free to (shallow) trapped carriers; u, the carrier mobility, and d, the interelectrode spacing. Because incident power (at 1 sun) is $1\mathrm{kWm}^{-2}$ a satisfactory power output might be $100\mathrm{Wm}^{-2}$. If $u = 10^{-4}\mathrm{m}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$, and $d = 100$ nm, then f must not be less than 10^{-4} for a useful solar cell with $J_{ph} = 20\mathrm{mAcm}^{-2}$. A rather greater mobility of $10^{-2}\mathrm{m}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$ enables, for the same value of d, the permissible value of f to be 10^{-6}, a goal which appears likely to be achievable. One line of approach therefore is to try to increase u from c.10^{-4}, a common value, by a factor of 100. This may not be impossible: in some saturated hydrocarbon liquids u is of the order of $10^{-2}\mathrm{m}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$. In the highly methylsubstituted compound, durene, $u = 0.5 \times 10^{-2}\mathrm{m}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$ at 120K and $0.08 \times 10^{-2}\mathrm{m}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$ at room temperature.

Methylation of a molecule may well reduce the coupling between the carrier and the molecule and so weaken the scattering.

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