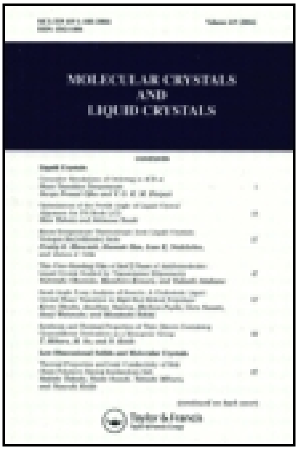

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Studies of Organic Semiconductors for 40 Years—I The Mobile π-Electron—40 Years on

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Studies of Organic Semiconductors for 40 Years—I
The Mobile π-Electron—40 Years on

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The earliest studies concerned photoelectric emission of negative charges from dyestuff solutions,[1,2] and anthracene layers.[3] The negative charges were identified as electrons,[4] then in 1911 Goldmann and Kalandyk[5] separated photoconduction from photoelectric emission, observing it in anthracene under U.V. irradiation, while Pauli[6] and Volmer[7] studied photoconduction in anthracene in the visible. Petrikaln[8] discussed gas effects on visible light photoconduction in dyestuffs, Koenigsberg and Schilling[9] studied dark conduction in anthracene, naphthalene and alizarine and also deduced the formula linking specific conductivity σ with absolute temperature T, $\sigma = \sigma_o \exp(-E_{act}/kT)$. Further dark conduction studies were carried out by Rabinowitsch.[10]

In spite of some references in Hughes and DuBridge,[11] by 1948 this work was largely overlooked or forgotten. My own interest originated in catalysis studies on phthalocyanine,[12] which had proved irreproducible.[13] I had suggested the presence of active sites formed from extended π-electron surface polymers.[14] This led me to investigate π-electron mobility in phthalocyanine crystals by semiconduction studies. Further, pre-war studies on haemoglobin[15] had interested me in energy and electron transfer in the oxidation enzyme chain. Thus I read the papers of Möglich and Schön[16] and Szent-Györgyi,[17] proposing electron energy bands in biochemical systems. The ease of purification of phthalocyanine, its great thermal stability, and its close relation to the biochemically important porphyrins, see Section I in the Appendix, made it ideal for semiconduction work, and so it remains today.[18,19] By 1948 the necessary background theory of intrinsic and extrinsic semiconductors,[20] and π-electron molecular orbital theory[21] was in place. In this review I concentrate on dark or semiconduction, and invoke photoconduction only in a supporting role, in spite of its great importance. Studies on phthalocyanines appear to have started in the U.K. and U.S.S.R., and studies on polyacenes in Japan, followed by rapid developments worldwide.

Phthalocyanine and Closed Shell Compounds

We shall seek to see how far the early ideas and results are still relevant. The thermally stable β polymorph of metal free phthalocyanine, β-H_2Pc, has planar molecules packed parallel to each other, separation 3.38A, in rows arranged her-

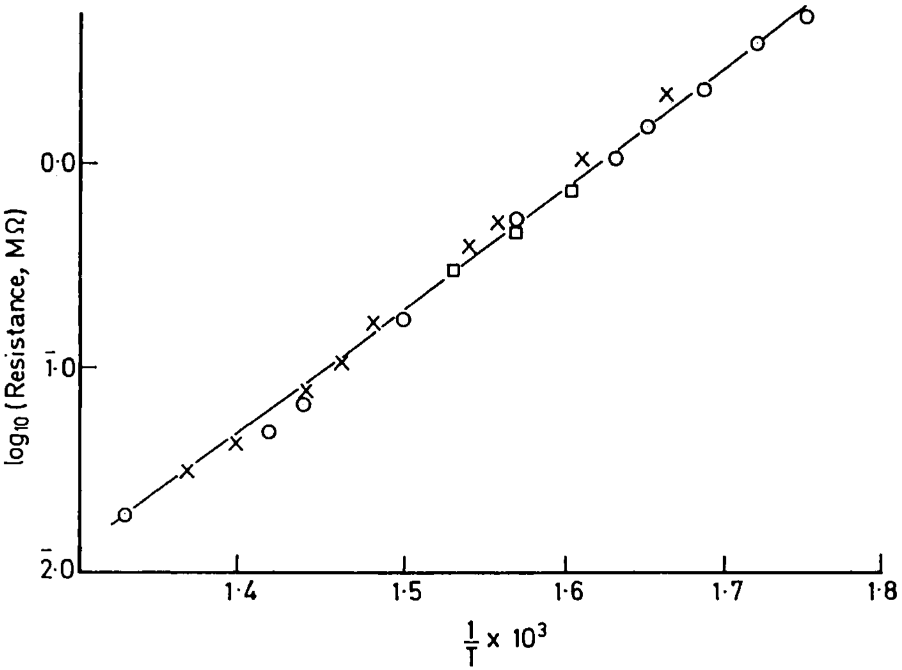


FIGURE 1 Resistance of metal-free phthalocyanine (Ref. 23). ⊙ descending T°K, × ascending T, ☐ after 24 hours at 360°C.

ringbone fashion along the *b* or needle axis.[22] In our first experiments[23] these powdered crystals were lightly compressed between Pt electrodes, area A separation l, in a cell, under H_2 or N_2 gas. The resistance was taken with a war-surplus megohm-meter, over 300–480°C. Figure 1 shows the original plot of resistance R, lg R vs. T^{-1}/K^{-1}, demonstrating a fit of the specific conductivity $\sigma = l/RA$ to the equation[20]

$$\sigma = \sigma_o \exp(-E_{act}/kT) = \sigma_o \exp(-\Delta\epsilon/2kT)$$

Since β-H_2Pc gave $E_{act} = \Delta\epsilon/2 = 1.2$ eV, it was suggested "that the electrons lie in energy bands common to the whole crystal, arising perhaps by intermolecular overlap of the π-orbitals of the porphyrin [sic!] rings. The observed activation energy (E_{act}) is then one-half the energy gap ($E_G = \Delta\epsilon$) between the full ground band and the empty first excited band." Results for CuPc were similar emphasizing the importance of π electrons, but they were affected by heat treatment, and development of impurity centers was suspected. In the USSR Vartanyan[24] found a rubbed film of H_2Pc on quartz gave a similar straight line graph between 10 and 100°C, with $\Delta\epsilon = 0.9$ eV. Further work with an electrometer valve circuit[25] in our laboratory confirmed $\Delta\epsilon = 2.4$ eV over 480–300°C, with a change of slope to $\Delta\epsilon = 1.7$ eV over 300–100°C characterizing an impurity conduction over the lower range. Compression of the electrodes to 80 kg cm^{-2} lowered both Δε values. Single crystal studies gave $\Delta\epsilon = 1.44$ to 1.87 eV over 20 to 160°C[26] and 1.63 to 1.93 eV over 50 to 390°C.[27] The currents were all Ohmic, but later studies showed a transition to space charge limited currents (q.v. later), giving a band gap of 1.68 eV and trapping states 0.38 eV below the conduction band,[28] and $E_G = 2.00$ eV, with trapping and donor levels 0.32 eV below the conduction band.[29] At this time the consensus is that $E_G = 2.00$ eV for H_2Pc[19] and 2.0 eV for CuPc.[30] FePc and MnPc are much more highly conducting than H_2Pc and CuPc.[31] Careful attention to preparation and purity later on resulted in $\Delta\epsilon$ values for the metal Pc's of the first transition period,[32] shown in Figure 2. The μ^* values are estimated values of the mobility following Many *et al.*[33] The unstable α polymorph α-H_2Pc, had a much higher conductivity than β-H_2Pc,[34] with $\Delta\epsilon = 0.5$ eV.[32,35] It may be that the metals Co, Fe and Mn provide states in the band gap of β-MPc's, while in α-H_2Pc oxygen atoms may provide impurity levels.

Reference to Table I shows that although β-$Fe^{II}Pc$ and Fe^{III}haeminCl each have inner rings of 18 π-electrons their $\Delta\epsilon$ values are very different, a difference which may turn on Fe:Fe spacings or the oxidation state of Fe.

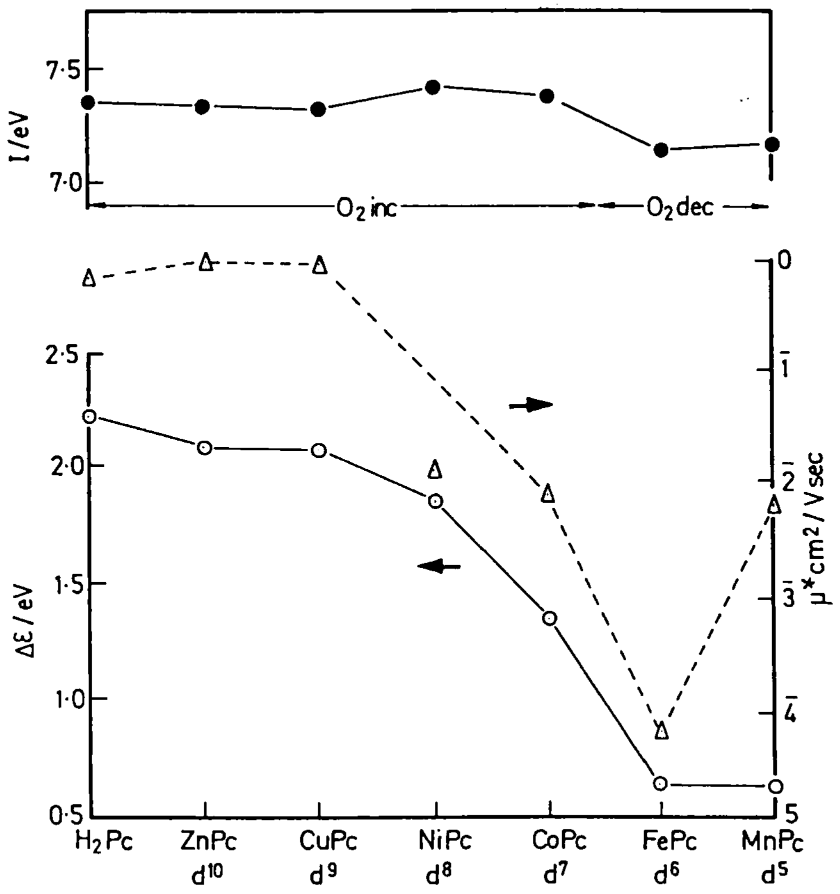


FIGURE 2 Experimental values of $\Delta\epsilon$, μ^* estimated from σ_o, and Ionization Potentials, across the series of phthalocyanines (Ref. 32).

TABLE I

A selection of semiconductor data

Substance	*n*	Form	σ_o, cm^{-1}	$\Delta\epsilon$, eV	Ref.
PolyCuPc	140?	*p*	0.5	0.26	59
α-H$_2$Pc	18(42)	*p*	7.7×10^{-3}	0.48	32, 35
β-Fe^{II}Pc	18(42)	*s*	7.3×10^{-2}	0.68	32
Isoviolanthrone	36	*p*	6.8×10^{-4}	0.75	36
Isoviolanthrone	36	*p*	1.9×10^{-3}	1.36	38
Trans β-carotene	22	*s*	3.3×10^{-5}	1.45	53
Trans β-carotene	22	*s*	0.34	1.8	54
DPPH	27	*p*	0.28	1.54	60
		$s, \parallel c$	4.6	1.60	60
		$s, \perp c$	0.84	1.61	60
Fe^{III}haeminCl	18(26)	*p*	6.4×10^{-2}	1.74	61
		p	0.16	1.81	62
Cu^{II}aetioporphyrin	18(26)	*p*	0.81	1.82	62
H$_2$-aetioporphyrin	18(26)	*p*	9.8×10^{-2}	1.99	62
β-H$_2$Pc	18(42)	$s \parallel b$	0.4	2.0	29
β-H$_2$Pc		*p*	0.8	2.2	32
β-Cu^{II}Pc	18(42)	$s \parallel b$	1.7×10^{1}	2.0	30
		p	1.3×10^{2}	2.1	32
Adeninephosphate	12	*p*	2.0×10^{3}	2.0	63
Adenosinemonophosphate	12	*p*	1.0×10^{2}	2.0	63
Ribose 5-phosphate	—	*p*	2.0×10^{1}	2.1	64

n, number of conjugated π-electrons, (n) total number of π-electrons. All dc, Ohmic dark conduction values, *s* single crystal, *p* compressed disc sandwiched between Pt electrodes at 80.0 kg cm^{-2}, in 10^{-6} torr vacuum, in very dry state.

Pc phthalocyanine, DPPH diphenylpicrylhydrazyl.

Turning to polyacenes, Akamatu and Inokuchi[36] investigated isoviolanthrone (Formula II) and two similar molecules, under 80 kg cm^{-2}, finding $\Delta\epsilon = 0.75$ eV, violanthrone 0.78 eV and pyranthrone 1.06 eV. Following results on 8 more compounds[37] they concluded the substances were intrinsic semiconductors whose conductivity was determined mainly by the number of π-electrons, and little influenced by molecular shape. A spectrographically analyzed isoviolanthrone gave an a.c. value $\Delta\epsilon = 0.99$ eV,[34] there is a further d.c. value $\Delta\epsilon = 1.36$ eV,[38] and a photoconduction energy gap of 0.93 eV.[39] Addition of 0.1% benzanthrone markedly lowered $\Delta\epsilon$ for isoviolanthrone.[40] Unlike phthalocyanines, polyacenes cannot be purified by sublimation.

Early dark conduction studies on anthracene (Formula III) gave $\Delta\epsilon = 1.65$ eV (powder),[25] 1.65 (single crystal),[41] 1.92 (film)[42] and 2.7 eV (film).[43] Liquid electrodes such as $I_2/NaI_{(aq)}$ will inject large hole currents into anthracene crystals.[44] Metal electrodes appear to inject surface currents over anthracene crystals, since they are completely suppressed by a guard ring, see a later discussion of semi-insulating crystals.[45,46] Addition of 0.1% naphthacene to anthracene, induced a change of slope in the temperature plot to a lower $\Delta\epsilon$ value characteristic of the impurity, in film specimens.[42] Thomas and Williams[47] used liquid electrodes to inject bulk space charge limited hole currents (q.v.) into anthracene, calculating the number of traps by the Mark-Helfrich equation,[48] which were found to correlate with the dislocation densities (etch pit technique).[49]

As to linear polyenes, currents observed with diphenyl butadiene, and four stilbene derivatives, were considered to be limited by electrode injection.[50] It is possible, although not certain, that the Ohmic currents in all-*trans* β-carotene arise by intrinsic ionization of the π-electrons. Some $\Delta\epsilon$ values are 1.52 eV,[52] 1.65 eV,[52] 1.45 eV (single crystal with guard ring),[53] 1.8 eV (single crystal with guard ring),[54] 1.5 eV,[55] but σ_o values are inconsistent (Table I). At higher voltages, space charge limited currents give evidence of voltage sensitive traps of depth c. 0.6 eV,[56] which might relate to the high voltage low frequency current pulses observed in some crystals[54,57] and to anomalous photovoltaic effects.[58]

In an early paper[34] we used a high frequency a.c. method ostensibly to short out the resistance of interparticle contacts in a powder, and with this we derived $\Delta\epsilon = 0.26$ eV for diphenyl picrylhydrazyl DPPH, Formula IV. The method was effectively criticized by Huggins and Sharbaugh.[65] We later found that many organic crystals with a high $\Delta\epsilon$ d.c. conduction, show a low activation energy high frequency loss[66,67] probably due to electron hopping between localized, possibly defect, sites.[68]

Electron Gas Theory and $\Delta\epsilon$

The model is shown in Figure 3a.

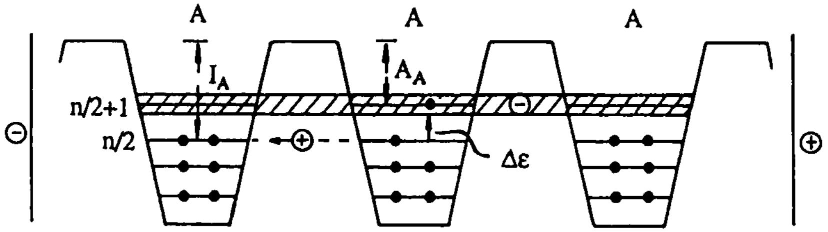
The molecule is regarded as a potential energy box, in which the n π-electrons fill up the lowest $n/2$ levels, two in a level according to Pauli's principle, although spins are not considered in the model. The energy levels are calculated by electron gas theory,[69–71] for an electron wave moving on an open or closed path of length $a = nd$, where $d = 1.39$A, the C—C distance in aromatic compounds. The conduction occurs by an electron being excited from the $n/2$ level to the $(n/2+1)$th level, from which it may tunnel to the next molecule in the direction of the positive electrode. A positive hole or electron vacancy is left at the $n/2$th level which may tunnel towards the negative electrode. If the intermolecular overlap of wave functions is sufficient an energy band, width δ may form; this is shown for the $(n/2+1)$th level as the conduction band. If a similar band forms at the $n/2$th level this will be the valence band. Neglecting band width

$$\Delta\epsilon = E_G = \frac{h^2}{8ma^2}(n+1) = \frac{h^2}{8md^2}\cdot\frac{(n+1)}{n^2}, \quad \text{open path}$$

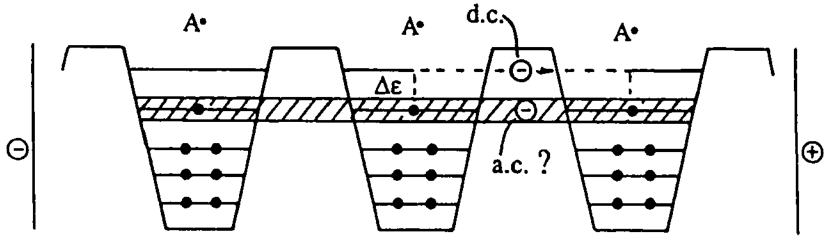
$$\Delta\epsilon = E_G = \frac{h^2}{4ma^2}n = \frac{h^2}{4md^2}\cdot\frac{1}{n}, \quad \text{closed path}$$

The graphs of these functions[34] will not be repeated here. They represented in broad terms the way $\Delta\epsilon$ decreases over a series of compounds with increasing numbers of π-electrons n. However, for H_2Pc is $n = 42$, the total number of π-electrons, or the number in the inner ring 18, since C—C bond-lengths in the pyrrole rings show little double bond character? A closed path of 22A with $n = 18$, gives $\Delta\epsilon = 2.79$ eV, an open path (here inappropriate) 1.47 eV, the experimental value being 2.00 eV. Crude as it is, it does predict the low $\Delta\epsilon$ for polyCuPc.

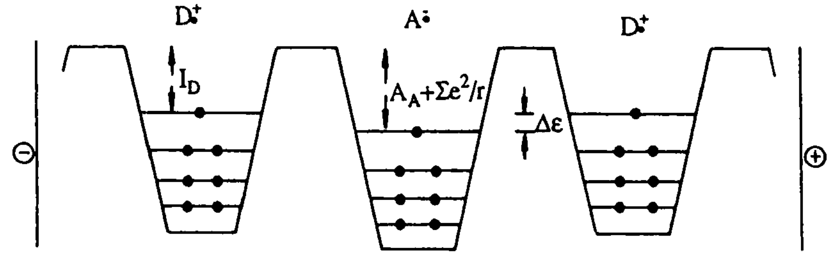
(a) e.g. H_2Pc



(b) Solid Free Radicals



(c) e.g. $TMPD^+$ $Iodanil^-$



(d) Proteins, DNA, Polymers

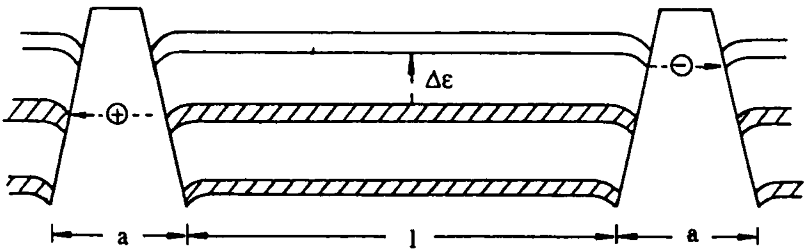


FIGURE 3 Electron in a box model (a) for closed shell molecules (b) for open shell and free radical molecules (c) for a charge transfer complex, e.g., $TMPD^+$ $iodanil^-$ (d) for proteins and biopolymers.

Its main shortcoming is that it neglects the polarization energies of the charge carriers P_+ and P_-, calculated by Lyons.[72] If I_A is the ionization potential of the molecule, A_A is the electron affinity we should write, in place of

$$E_G = \Delta\epsilon = E_{(n/2+1)} - E_{(n/2)} = I_A - A_A$$

the expression[72]

$$E_G = \Delta\epsilon = I_A - A_A - P_+ - P_- = E_{(n/2+1)} - E_{(n/2)} - P_+ - P_-$$

Using the latest I_A, A_A, and P values[73] we calculate $E_G = 3.85$ eV for anthracene, much larger than the observed $\Delta\epsilon$ values. The theory further neglects the electron spin in the excited state, whether it is a singlet or triplet state. Northrop and Simpson[42] found $\Delta\epsilon$'s for pure polyacenes were equal or greater than the optically determined triplet state energies of the free molecules, or equal for the molecules as solutes. Lyons[72] also noted this correlation, but could see no reason why the triplet-state should be involved in the thermal production of charge carriers. Finally, the band width δ was shown by a tight-binding calculation based on $2p_z$ atomic orbitals for anthracene to be 0.014 eV at room temperature,[74] therefore negligible in the present context.

Solid free radicals and open shell complexes

Figure 3b shows the model for a solid free radical like DPPH Formula IV, where the unpaired electron forms part of the conjugated π-electron system. It predicted $\Delta\epsilon \simeq 0$ and the early a.c. value of $\Delta\epsilon = 0.26$ eV was taken to confirm this. When the single crystal d.c. values came out as 1.60 eV,[60] and values for a number of other solid free radicals were all similar, we realized the model must neglect certain factors. These are a) since steric factors will probably cause the molecules to pack badly, δ will be less than the anthracene value of 0.01 eV and b) the single electron theory neglected charge correlation, i.e., the large repulsive energy between two electrons on one site $A^=$. We expect the value of $\Delta\epsilon$ in these cases to be $\Delta\epsilon = C - \delta$,[76,77] which will give rise to the observed values. The low $\Delta\epsilon$ for a.c. probably refers to electron tunnelling between two otherwise empty defect sites. Since the d.c. data were very reproducible, the correlation explanation seems more rational than our first idea of electrode injection with surface states.[60]

The idea of the half-filled energy band in free-radical solids, led on to work on the charge-transfer complexes. Akamatu and co-workers had already established the very high conductivity of certain non-stoichiometric polyacene-halogen complexes,[78] with a definite free-radical character.[79] We studied a series involving 2 planar donors dimethyl aniline (DMA) and tetramethylphenylenediamine (TMPD) and 3 planar acceptors, chloranil, bromanil and iodanil.[80] All 1:1 complexes and chemically stable, X-ray crystallography had established their structure as mixed stacks DADADA etc., with intra-stack spacings of 3.4A for the DMA and 3.26A for the TMPD complexes.[81,82] ESR studies had demonstrated the DMA complexes as non-paramagnetic, and the partially ionic character of the TMPD complexes, with free-radical character 0.2% TMPD-chloranil, 2.0% bromanil and 20% iodanil.[83,84] In Figure 3c we show the free-electron model we suggested for TMPD-iodanil. In summary the van der Waals' DMA complexes had room temperature $\sigma \simeq 10^{-8}$–10^{-9} Scm^{-1} and $\Delta\epsilon = 0.45$–0.47 eV, the partially ionic TMPD complexes $\sigma \simeq 10^{-4}$–10^{-5} Scm^{-1}, but higher $\Delta\epsilon$'s 0.53–0.59 eV. Since the higher conductivity of the TMPD complexes is due to σ_o, we suggested this arose from easier electron tunnelling through the narrower barriers. If $\Sigma e^2/r$ is the Madelung energy of the ions in the lattice, notional in the sense that the complexes in the ground state were at most partially ionic, I_D ionization potentials of donor and A_A electron affinity of acceptor we put (Figure 3c)

$$\Delta\epsilon = I_D - A_A - \Sigma e^2/r$$

Using the latest I_D and A_A values[85] and a Madelung energy of 4.43 eV[86] we calculate for TMPD-chloranil $\Delta\epsilon = 0.29$ eV.

By contrast, alkali metal complexes of anthracene gave rather high $\Delta\epsilon$ values, e.g., $Na_{1.08}An$ 2.40 eV, the differences again being determined by σ_o.[87] Isoviolanthrene complexes however gave very low values for the K and Na doping, also with acceptors like $AlCl_3$, but the effects were less marked with isoviolanthrone.[38] The authors suggested the donor electrons were respectively ring π and oxygen n or lone pair.[38]

Pre-exponential factors and mobilities

If n, p are the concentrations of electrons and holes, mobilities μ_e, μ_p and charge e then[88]

$$\sigma = e(\mu_e n + \mu_p p) \text{ Scm}^{-1}$$

For intrinsic conduction $n = p = n_i$; then with N_c, N_v densities of states in conduction and valence bands, and E_G the energy gap

$$n_i = (np)^{1/2} = (N_c N_v)^{1/2} \exp - (E_G/2kT) \text{ cm}^{-3}$$

If m_e, m_p are the effective masses of electrons and holes, m_o the free electron mass

$$(N_c N_v)^{1/2} = 2\left(\frac{2\pi m_o kT}{h^2}\right)^{3/2}\left(\frac{m_e m_p}{m_0^2}\right)^{3/4} = 2.5 \times 10^{19} \text{ cm}^{-3}$$

for T = 298 K, $m_e = m_p = m_o$. Hence

$$\sigma = \sigma_o \exp(-E_G/2kT), \quad \text{where } \sigma_o = 2.5 \times 10^{19} e(\mu_e + \mu_p)$$

i.e.

$$\sigma_o = 4.0(\mu_e + \mu_p), \quad \text{for T} = 298 \text{ K}, \quad m_e = m_p = m_o$$

Using Le Blanc's methods,[74] electron and hole band widths for anthracene are 0.01 eV,[89] coronene 0.05 eV, ovalene 0.1 eV,[90] 0.07 to 0.6 eV depending on direction for H_2Pc.[91] So while we used[34] the broad-band value above to derive $\mu^* = \mu_e + \mu_p$ values of 10^{-2} cm^2 V^{-1} s^{-1} for violanthrone, 1.4 – 16.8 for H_2Pc. Many,[33] preferred to take $(N_c N_v)^{1/2} = 10^{21}$ cm^{-3}, the number of molecules per unit cell times the number of π electrons in a typical molecule. On this basis he summarized μ^*, $\Delta\epsilon$ data for 29 organic molecules, and concluded that μ^* increased from 10^{-12} cm^2 V^{-1} s^{-1} for $\Delta\epsilon = 0.6$ eV to 10^2 for $\Delta\epsilon = 1.70$ eV. Many *et al.*[33] concluded that the tunnelling probability through intermolecular barriers increased with electron excitation energy $\Delta\epsilon$. These ideas could be further developed by direct measurement of mobilities, and by model barrier-tunnelling calculations, described below.

The direct timing of photoexcited electrons and holes across crystals of zone-refined anthracene,[92,93] gave results set out on p250 of Reference 89. Briefly, μ_e and μ_p were about 1 cm^2 V^{-1} s^{-1}, with precise values of μ and dμ/dT depending on the lattice direction.

A second method studied the space charge limited currents which set in at higher voltages, when the number of electrode injected carriers exceeds n_i. If V is the voltage drop across a crystal of thickness d, then in the absence of traps, Child's Law holds, current density j, $j \propto V^2/d^3$.[96] The theory was further developed by Rose, Lampert and others, and applied to organics by Mark and Helfrich.[47] The latter authors assumed an exponential distribution of traps, total concentration H, and mobility μ_p, in the case of hole injection with liquid electrodes. A study of the pulse transients gave $\mu_p = 3 \times 10^{-2}$ cm^2 V^{-1} s^{-1} for tetracene, which substituted into the steady-state current equation below, with the disorder parameter $l = 2$, gave $H = 3.4 \times 10^{16}$ cm^{-3}. In hole injection the equation is

$$j = N_v \mu_p e^{(1-l)} \left[\frac{\epsilon\epsilon_o l}{H(l+1)}\right]\left[\frac{2l+1}{l+1}\right]^{l+1}\left[\frac{V^{l+1}}{d^{2l+1}}\right]$$

ϵ is the relative permittivity, ϵ_o the permittivity of free space.[48]

In a third method Hall coefficients are combined with conductivities, to give sign and Hall mobility μ_H of the carriers. As examples, CuPc single crystals gave the two-carrier Hall mobility $\mu_H = -75$ cm^2 V^{-1} s^{-1},[98] supported by a recent microwave Hall value $\mu_H = -40$ cm^2 V^{-1} s^{-1}, at 300 K.[99] In H_2Pc $\mu_H = -0.1$ to 0.4 cm^2 V^{-1} s^{-1}.[100] The difference was ascribed to mixing of the Cu 3*d* orbital with the ring π-system.[98] By contrast poly CuPc gave $\mu_H = +10$ cm^2 V^{-1} s^{-1},[59] which may reflect a disorder in the polymer system.

Seebeck coefficients have been used for polycrystalline compactions and single crystals. For example, the thermoelectric power Q as a function of T for a compaction of the segregated stack complex salt $DEBP^{2+}$ $(TCNQ)_4^{2-}$ [101] fits the band theory equation[102] for a *p*-type-extrinsic semiconductor which becomes intrinsic above 215 K, the equation being

$$Q = \frac{-k}{e}\left(\frac{\mu_e - \mu_p}{\mu_e + \mu_p}\right)\left(\frac{E_G}{2kT} + 2\right)$$

Together with conductivity data this gave $\mu_e = 10 - 25$ and $\mu_p = 4 - 8$ cm^2 V^{-1} s^{-1}, at 298 K, in the intrinsic region, with temperature dependencies $\mu_p \propto T^{-1.1}$ and $\mu_e \propto T^{-1.6}$, confirming applicability of band theory with neutral lattice scattering of carriers (theoretical dependence of $T^{-1.5}$). The mean free path $L = 3\mu\,(2\pi m kT)/4e$ is greater than the inter TCNQ-spacing, satisfying the Joffé criterion for band conduction.

In connection with changes in slope for the $lg\sigma$ vs. T^{-1} plot, already referred to[25,42] for dark conduction, due to impurity levels (donor or acceptor) and trapping levels in the band gap, Schmidlin and Roberts[103,104] have analyzed a general model of a semi-insulator, with "Ohmic contacts." They show how the thermal activation energies of both Ohmic and space charge limited currents, can lead to values for the depth and concentration of localized levels in the band gap, as well as a value for the band gap E_G. They applied their method to a reanalysis of H_2Pc data (Barbe and Westgate) and CuPc (Heilmeir and Harrison) deriving band gaps $E_G = 1.72$ eV and $E_G = 1.83$ eV respectively.

The Compensation Effect and Barrier Tunnelling

Eley and Willis[105] suggested the model shown in Figure 4, a development of the earlier idea, in which a π-electron is thermally activated from the $n/2$ or HOMO level to the $n/2 + 1$ or LUMO level, then tunnelling through the intermolecular barrier to the corresponding level in the next molecule. If a is the barrier width at the tunnelling level the transmission probability down field is

$$T_f - T_b \simeq \phi[\exp - \gamma(V_o - E - aeV)^{1/2}a - \exp - \gamma(V_o - E + aeV)^{1/2}a]$$

Here we restrict ourselves to electron (rather than hole) currents.

The current density j is then

$$j = A \sinh bV \exp(-\Delta\epsilon/2kT) = AbV \exp(-\Delta\epsilon/2kT), \quad (bV < 1.0),$$

Ohm's Law holding for typical parameters for $V < 5 \times 10^7$ V cm^{-1}. A model calculation for a 20 π-electron molecule gave $\mu_e = 0.9 \times 10^{-3}$ cm^2 V^{-1} s^{-1} (square barrier) and $\mu_e = 1.5 \times 10^{-1}$ cm^2 V^{-1} s^{-1} (triangular barrier), the latter value being similar to those found in practice. In a further model calculation[106] to investigate $\sigma_o - \Delta\epsilon$ compensation laws, a triangular barrier was taken, with energy zero shift from Z_1 to Z_2 so that $\Delta\epsilon = E = h^2(n + 1)/8ml^2n^2$, the open path case. As a result it was found that for $n = 20$ π-electrons, $\sigma_o = 5 \times 10^{-4}$ Scm^{-1}, $\Delta\epsilon = 1.0$ eV, which changed for $n = 2$ π-electrons, to $\sigma_o = 10$ Scm^{-1}, $\Delta\epsilon = 14.5$ eV. Later Kemeny and Rosenberg[107] were able to extend the range to $\sigma_o = 10^{16}$ Scm^{-1} by choosing $V_o = 6$ eV rather than 20 eV, and replacing the effective mass m_o by 100 m_o. However, we have taken it that the "astronomically" large σ_o values found in some data on small aromatic molecules called for another approach (see later). The theory was further developed[108-110] to include electron-phonon interactions through variations in barrier thickness, resulting in $\mu = 4.6 \times 10^{-3}$ cm^2

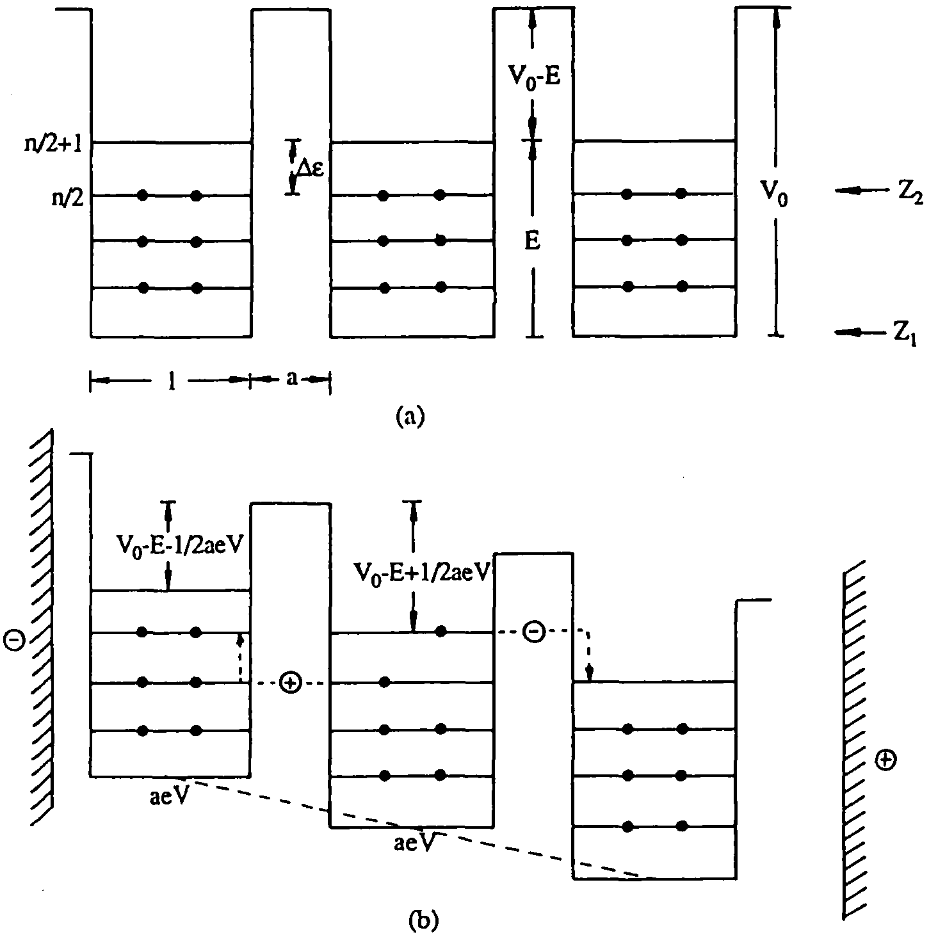


FIGURE 4 The Electron Tunnelling Model.

V^{-1} s^{-1} independent of temperature. Tredgold's view,[111] however, was that μ should increase with temperature. The theory was applied to discuss mobilities in proteins, using the models of Figure 3d,[112] to charge transfer in octacosane,[113] and to derive an upper value for the effective mass in organic semiconductors of 25 m_o.[114] It has also been used to discuss j/V behavior in organic films.[115]

Electrode limited currents

The compensation law, for different preparations of the same substance (Meyer-Neldel rule) may be written[106] $lg\sigma_o = \alpha\Delta\epsilon + \beta$, where $T_c = 1/4.606\, k\alpha$. We have found that the currents through some small aromatic semi-insulating crystals with metal electrodes are surface currents,[45] and single crystals without guard rings, and also compactions, can yield compensation plots extending to very high σ_o values.[46]

TABLE II

A selection of semi-insulator data

Substance	n	Form	σ_o, Scm^{-1}	$\Delta\epsilon$, eV	Ref.
Anthracene	14	s, (g.r.)	$\sigma < 10^{-15}$ at 180°C		45
		s −	66 to 3.5×10^3	1.68 to 1.94	46
		s, film	1.6	1.95	118
Glycine	—	s, (g.r.) $\perp$ac	—	3.26	119
		s, $\perp$, ac	—	3.26(3.12)	119(61)
		s, $\parallel$, ac	—	3.26(2.82)	119(61)
Benzoic Acid	8	s, (g.r.)	$\sigma < 10^{15}$ at 120°C		45
		s	2.5×10^6 to 4.0×10^{10}	2.8 to 3.4	46
Adenosine	12	p	4×10^{10}	3.9	64(63)
D-ribose	—	p	4×10^{16}	3.6	64
D-glucose	—	p	1.4×10^{18}	4.6	120
Adenine	12	p	10^{18}	5.0	64
Diphenylbutadiene	16	film	50 to 10^{30}	1.9 to 6.3	116

All dc dark conduction, ohmic currents to 2000 V cm^{-1} except for anthracene and benzoic acid, where the currents were mainly surface currents.

(g.r.) signifies guard ring

Selected data are collected in Table II, and 5 examples[116] shown in Figure 5. Values of T_c calculated for these and a further 7 substances are plotted in the inset. Clearly there is some correlation (coefficient = 0.61) between T_c and the melting point of the substance T_m (the plot of Reference 116 is here corrected). This suggests the effect relates to surface states at the electrode-semiconductor interface. In the thermionic emission of electrons from a metal surface into a vacuum, occasional anomalously large pre-exponential constants arise in the Richardson equation, which relate to the desorption of adsorbed films from the metal.[117] In the present case it was suggested that the increase in molecular vacancies at the surface with temperature, causes the activation energy, for charge-carrier injection, associated with band bending at the interface, to decrease with temperature. The following equation was derived

$$= 41 \exp\text{-}(E_{act}/kT) = 41 \exp\text{-}(E_{act}(0) - aT/kT)$$

$$= 41 \exp(a/K)\exp - (E_{act}(0)/kT)$$

A reasonable value of $a = 2.5 \times 10^{-3}$ eV K^{-1} gives rise to a σ_o value of 2.6×10^{14} Scm^{-1}. The mechanism can be applied to both hole and electron injection.

Biological molecules[120]

Early observations were due to Baxter[121] and Szent-Györgyi himself.[122] Baxter found that dry wool obeyed the semiconductor equation, being "almost a perfect

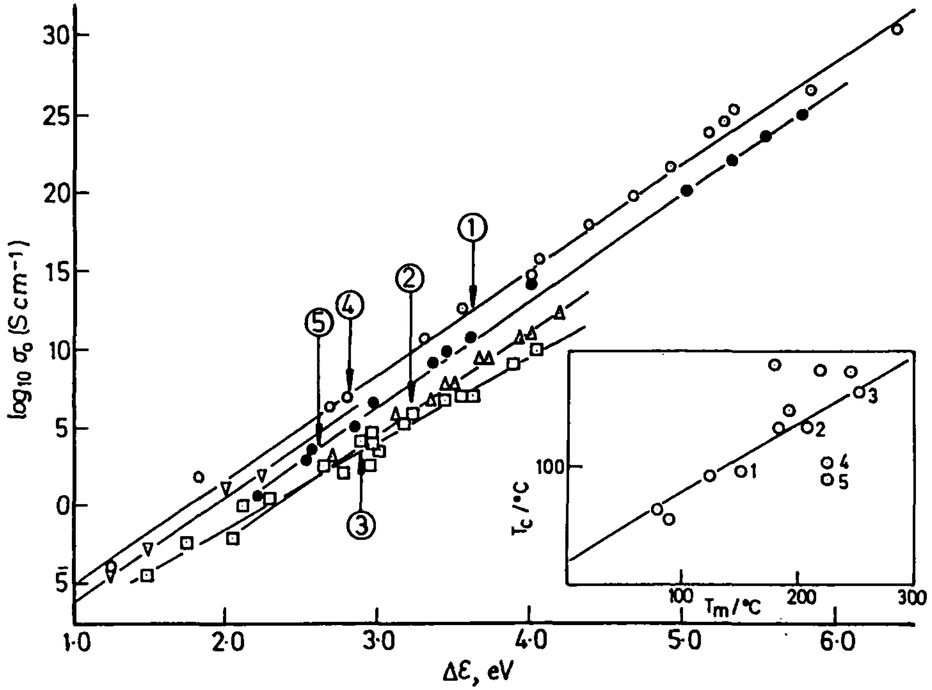


FIGURE 5 Compensation law plots for

(1) $C_6H_5CH{=}CHC_6H_5$;
(2) $NO_2C_6H_4N{=}CHC_6H_4N(CH_3)_2$;
(3) $NO_2C_6H_4CH{=}CHC_6H_4N(CH_3)_2$;
(4) $NO_2C_6H_4CH{=}NC_6H_4N(CH_3)_2$;
(5) $NO_2C_6H_4N{=}NC_6H_4N(CH_3)_2$.

Arrows indicate $^1E_1$ first singlet state excitation energies. *Insert*, AT_c vs. T_m plot for compounds 1–5 plus 7 other compounds.

insulator" with $\Delta\epsilon = 2.2$ eV. The large increase in conductivity due to adsorbed water, was attributed to electrons jumping between bound water molecules, separation d, with a jump rate varying as exp-(γ_d').

Szent-Györgyi found that illumination caused an increase in conductivity of protein films containing dyestuff molecules. After some preliminary work on proteins[25] we established a reliable technique, in which compressed discs of globular proteins, sandwiched between Pt-electrodes under a pressure of 80 kg cm^{-2}, were examined in 10^{-6} torr vacuum. Good straight lines for $lg\sigma$ vs. T^{-1} were obtained for haemoglobin, globin, heme, polyglycine and some amino-acids.[61] There were no polarization effects, Ohm's law was obeyed, and there was no evidence for conduction by protons or by adventitious ions. Thermoelectric power results made haemoglobin p-type, and glycine single crystal n-type.[61] Similar results were obtained for a range of proteins,[123] and a selection of data is given in Table III. The dry proteins all had $\Delta\epsilon$'s in the range 2.57 to 3.12 eV, and "free electron mobilities" μ^* (calculated from σ_o) as 10^3–10^5 cm^2 V^{-1} s^{-1}. Evans and Gergely[124] had made LCAO band

TABLE III

Dark conductivity, dry biopolymers

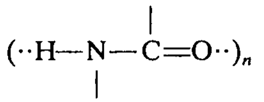
Biopolymer	σ_o, Scm^{-1}	$\Delta\epsilon$ eV	Ref.
K Polyadenylate (KPolyA)	7.9×10^1	2.2	152
NaDesoxyribonucleate (NaDNA)	2.2×10^2	2.36	152
Ribonucleic acid (RNA)	2.3×10^2	2.36	152
Cytochrome C	6.4×10^4	2.60	112
Lysozyme	8.0×10^4	2.62	112
Hemoglobin (natural)	1.0×10^5	2.66	112
Hemoglobin (denatured)	1.3×10^6	2.89	112
Globin	1.0×10^5	2.97	112
Bovine Plasma Albumin	2.5×10^6	2.90	132
Poly *L*-Tyrosine (helical)	4.0×10^6	2.99	112
Poly *L*-Tyrosine (random coil)	1.3×10^6	2.98	112
Polyglycine	2.0×10^6	3.12	61
Polyglycine	1.3×10^6	2.99	112
Silk (⊥ fibre axis > 121°C)	—	2.78	[a]
Silk (‖ fibre axis > 139°C)	—	3.73	[a]

The data were obtained on compressed discs between Pt electrodes (except Ref. 132, also Cu, Al, In), apart from silk.

[a] There was a change-over below temperatures indicated to $\Delta\epsilon = 2.1$ eV in each case (W. P. Williams, Thesis, Nottingham, 1964).

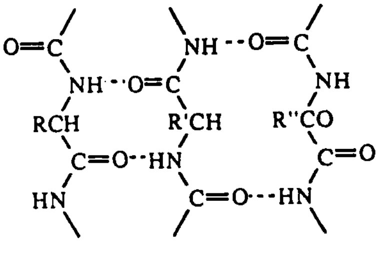
Low temperature, ranges were used, e.g., 70–130°C, DNA (Ref. 152) nucleic acid (Ref. 122), 60–130°C proteins (Ref. 112).

theory calculations for the H-bond system

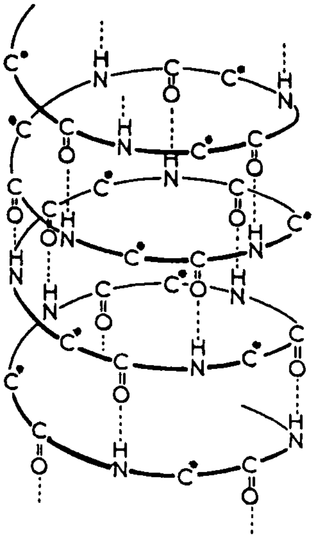


$$(\cdot\cdot\mathrm{H{-}\underset{|}{N}{-}\overset{|}{C}{=}O}\cdot\cdot)_n$$

found in α-helices and β-protein structures, see Figure 6. The result was 3 narrow energy bands, 0.2 eV wide, the bottom two filled by the 4 π-electrons of the peptide unit, the upper conduction band empty. The calculated band gap of 3.05 eV agreed with our experimental findings. We modified the model by addition of energy barriers terminating the H-bond systems, e.g., between α-helices, as in Figure 3d. Mobilities were then determined by barrier tunnelling as before, but the resulting large net displacement led to the high "mobilities" calculated from σ_o. However, when it became possible to measure such mobilities by the microwave Hall method, no such large values were found.[125–127] Furthermore, improved quantum chemical calculations for the H-bond system gave larger band gaps,[128] and similarly for conduction along the main polypeptide chain.[129–131] Although the electrode injection mechanism may operate for amino acid crystals,[119] it seems ruled out for proteins. Bovine plasma albumin has $\Delta\epsilon = 2.90$ eV and $lg\sigma_o = 6.4$ pretty accurately for Cu, Pt, Al and In electrodes.[132] Our present view is that the charge carriers in proteins arise by internal electron transfer within the molecule, e.g., from an S atom or CO group to a distant NH, giving rise to a charge-transfer energy band.[133] This leaves unsolved the problem of the high values of σ_o. Attempts to establish

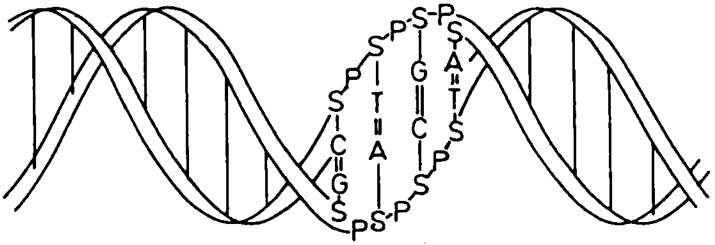


β-pleated sheet

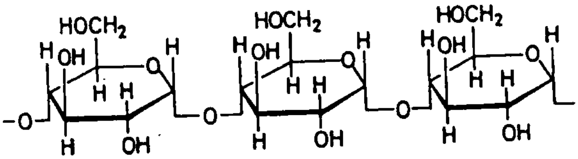


α-helix

H bonds in proteins



DNA



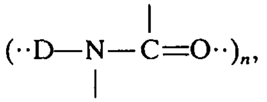
Amylose

FIGURE 6 The Biopolymer Structures.

an anisotropy in $\Delta\epsilon$, with a lower value along the H-bonds, which means $\parallel$ ac plane for glycine, and $\perp$ fibre axis for silk fibroin, indicates a possible effect at least for fibroin (Tables II and III), but more work is necessary.

Adsorbed water[134] and electron accepting molecules,[135-137] raise the conductivity of proteins. (The suggestion that an oxidizing agent might inject a hole into the valence band of a protein was made early on.[61]) Rosenberg[138] concluded that adsorbed water raised the conductivity of haemoglobin, by lowering $\Delta\epsilon = I\text{-}A\text{-}2P$, through increasing the dielectric constant of the protein and hence the polarization energy of the charge carriers P. It was our view that water molecules donated electrons into the conduction band,[139] while acceptors injected holes into the valence band of the protein. One argument is that methanol, with a lower dielectric constant but higher electron donor potential than water, gives a somewhat larger increase in conductivity than water when absorbed on bovine plasma albumin.[140] The electron donation idea has been used to interpret the kinetics of water uptake,[140] and the change from *p*-type to *n*-type behavior on adsorbing water on haemoglobin.[133] However, a new time-of-flight method applied to bovine plasma albumin recently led to the view that it is the mobility (not the number) of carriers that increases exponentially with adsorbed water,[141] and further work is necessary.

It is interesting that polyamides show much larger conductivities, departures from Ohm's law and polarization effects,[142] all supporting proton conduction as originally postulated.[143] So far as haemoglobin is concerned, charge-carriers are electrons and holes until adsorbed water molecules form a nearly complete monolayer (ca. 3–4 B.E.T. monolayers, or >15 wt.% H_2O) over the protein molecular surface, when H^+ conduction sets in Reference 139. Deuteration, changing the peptide link to

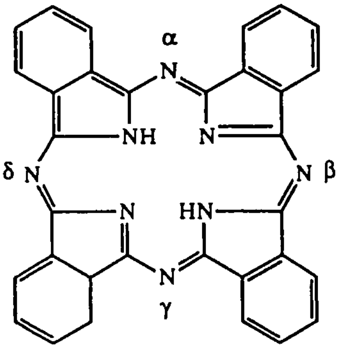


$$(\cdot\cdot D\text{—}\underset{|}{N}\text{—}\overset{|}{C}\text{=}O\cdot\cdot)_n,$$

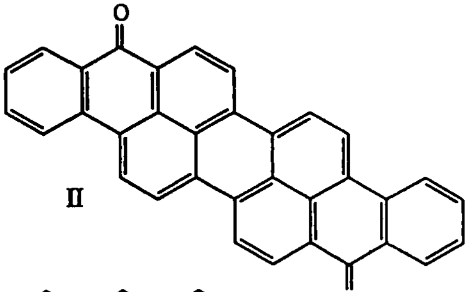
has negligible effect on σ and σ and $\Delta\epsilon$ in the dry state for a number of proteins.[144] For lysozyme a recent paper states proton conduction is important for water contents >5 wt.%.[145]

Referring to Table III, the electron transfer protein cytochrome C in our own work was similar in behavior to ordinary globular proteins. However, cytochrome C as a dry film, thickness 1.1 to 1.5×10^3 nm in a surface cell, gives a 10^2-higher Ohmic conductivity in the Fe^3 and 10^4-higher conductivity in the Fe^2 state, both with a lower $\Delta\epsilon$ of 1.2 eV.[145] Cytochrome C_3, containing four hemes per molecule gives even higher conductivities, with a negative activation energy under certain conditions where an equilibrium $Fe^2 \rightleftharpoons Fe^3 + e^-$ is found to exist.[147] The differences from the earlier behavior presumably turns on Fe. . Fe spacings and the higher Fe^2 content of the films, over the powder compactions of cytochrome C. Microwave Hall mobility measurements have been made on components of the mitochondrial oxidation chain,[148] but further work is needed.[133] Direct measurements of dc, conductivity, ac, loss and Seebeck coefficients confirm the charge carriers in mitochondrial particles as electrons,[149] but again much more work is required.

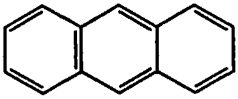
Appendix of relevant formulae



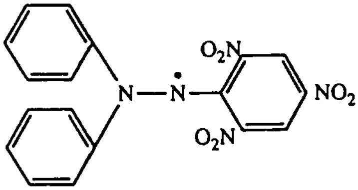
I



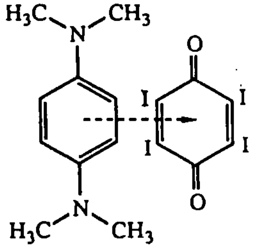
II



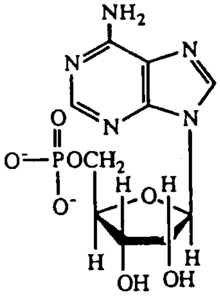
III



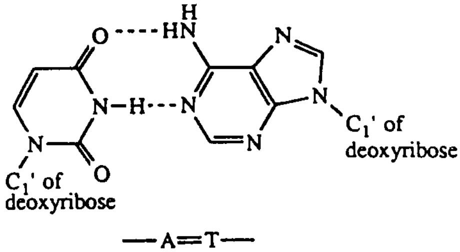
IV



V



VI



VII

I H_2 phthalocyanine (for H_2 porphyrin omit peripheral benzene rings and replace $\alpha,\beta,\gamma,\delta$–N='s by –CH='s)

II Isoviolanthrone (isodibenzanthrone) III Anthracene IV Diphenylpicrylhydrazyl

V Tetramethyl *p*-phenylene diamine - iodanil VI Adenosine monophosphate (adenine ribose 5-phosphate) VII The adenine-thymine (AT) base pair in DNA

Turning to the nucleic acids, the molecule of DNA, see Figure 6, with its double-helix of sugar-phosphate chains held together by the hydrogen-bonded base pairs adenine-thymine (22 π-electrons) and guanine-cytosine (24 π-electrons) (see Appendix), might be expected to show semiconduction down the axis of the helix across the base pairs, spacing 3.4A.[150-152] Although in the dry state the double helices must be disordered, compactions do show a small but very reproducible semiconductivity, see Table III. Dry NaDNA has $\Delta\epsilon = 2.36$ eV,[153] the low value of 1.8 eV[150] arising probably from traces of adsorbed water. A study of the nucleotide components[63,153], cf. Tables II and III, establishes a key role for the phosphate groups, which will induce a $\Delta\epsilon = 2$ eV conductivity in the base adenine, the sugar *d*-ribose, and the ribose-sugar compound adenosine. Initially we attributed an electron bridging role to the phosphate group.[63] Subsequently we changed this to a suggestion that the phosphate group acts as an electron acceptor, inducing a hole conduction in the second component, and in the case of DNA, in the base-pairs along the axis.[153] There is theoretical support for this idea,[154] and also Seebeck coefficients have established dry NaDNA as *p*-type.[133] The effect of adsorbed water is to increase the conductivity of NaDNA, initially without change in $\Delta\epsilon$, and then with a decrease in $\Delta\epsilon$[155] similar to that already observed for haemoglobin.

There is a definite need for quantum chemical bond calculations as a guide to work on polysaccharides, from our experience. Thus, cellulose is made of chains of β1:4 glucose units and amylose of chains of α1:4 glucose units, while $\Delta\epsilon$ values are 4.6 eV for *D*-glucose,[120] 2.73 eV for dry cellulose[120] and 1.7 eV for dry amylose (Subramanyan and Eley, unpublished). This suggests an interaction between glucose units in spite of an absence of conjugated π-electrons. Again, further experimental work is needed.

In conclusion, the compelling needs of space and a coherent theme which has caused me to concentrate on our own work on dark conductivity, has meant omitting many important references. For this, my apologies. My heartfelt thanks are due to Martin Willis and Stephen Wallwork, my colleagues over many years, and to my past research students, including our host Professor Hiroo Inokuchi, for their friendship and collaboration.

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Note added in proof. The $\Delta\epsilon$ of *c* 1.5 eV for all-*trans* β-carotene is similar to the presently accepted band gap for polyacetylene, and probably arises in the same way from bond length alternation, as first noted by Kuhn.[71]