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ORGANIC METALS ?
THE ELECTRICAL CONDUCTANCE OF ORGANIC SOLIDS

L.E. LYONS



The Royal Society of New South Wales



Lawrence Ernest Lyons

LAWRENCE ERNEST LYONS 1922-2010

Lawrence Ernest Lyons was born on 26 May 1922 in Sydney, N.S.W. After secondary education at Sydney Boys' High School (1934-1938), he went to the University of Sydney with a Liversidge Scholarship in 1939, held a Caird Scholarship during his Honours year in 1942, and graduated B.Sc. (1st. Class Hons.) in 1943. In 1943-1944 he was employed as a scientist at G.E. Crane and Sons, then served in the RAAF for the last two years of the Second World War, 1944-1945. In 1945 he was appointed as Lecturer in the Chemistry Department, University of Sydney, where he graduated M.Sc. in 1948, working with Dr. T. Iredale. In 1951 he proceeded to University College, London to work with Dr. Harry Poole and Dr. David Craig on ultra-violet spectroscopy with polarised light. During this period (1951-1952) he was Assistant Lecturer in Chemistry; he graduated Ph.D. in 1952, and held a British Ramsay Fellowship at that Institution during 1952-1953. He then returned to the University of Sydney where he was promoted to Reader in 1958. In 1963 he was appointed to the Chair of Physical Chemistry at the University of Queensland, where for the period 1970-1973 he was Head, Department of Chemistry. He was chairman of the University's Solar Energy Research Committee for the period 1977-80, a member of the Solar Energy Research council during 1980-87, and in 1979 he Reporter to the Commonwealth Department of Science on solar energy research in India and Germany. He retired in 1987 as Emeritus Professor, University of Queensland.

His researches in physical chemistry include work on organic semiconductors, electrochemistry, and various aspects of spectroscopy, including measurement of electron affinities, fluorescence, photoelectric emission, etc. During periods of leave he was Research Fellow (with a Fullbright Award) at Harvard University (1957); Visitor, Physical Chemistry Department, Oxford University (1967); Visiting Professor, University of British Columbia (1967); Leverhulme Senior Fellow, University of Tokyo (1970); Visiting Professor, Waterloo University, Canada (1985); and Visiting Fellow, Clare Hall, Cambridge University (1986).

Lawrie Lyons founded the New University Colleges Council which established New College at the University of N.S.W., and Robert Menzies College at Macquarie University. He founded also the non-profit company Iscast Ltd, an Institute to study christianity in an Age of Science and technology. He was a member of the Editorial Boards of *Molecular Crystals and Liquid Crystals* (1966-1983), and *Chemical Physics Letters* (1967-1977). The Brisbane Surface Analysis Facility was founded by him in 1980. He was President of the Chemistry Section of the Australia New Zealand Association for the Advancement of Science (ANZAAS) in 1967, and has served in various capacities for several other science, industry and community organizations.

Honours and Awards (Pre-2001)

- 1962 FRACI (Fellow of the Royal Australian Chemical Institute)
- 1964 D.Sc., University College, London
- 1966 Liversidge Research Lecture, Royal Society of New South Wales
- 1968 H.G. Smith Medal, RACI
- 1968 Burfitt Prize for Chemistry

- 1971 FAA
- 1976 Liversidge Research Lecture, ANZAAS
- 1979 Fullbright Award
- 1979 Debye Lecture, Cornell University, Ithaca (USA)

Biographical Source

Personal communication

Scientific Publications by L.E. Lyons

Between 1944 and 1991 L.E. Lyons had about 150 scientific publications, including co-authorship of two books on semiconductors (Krieger Publishing Co., 1981 and 1982).

**ORGANIC METALS ?
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L.E. LYONS

Professor of Physical Chemistry, University of Queensland, Brisbane, Australia

Introduction

This paper discusses electrical conduction in organic solids, leaving aside the spectral and photo phenomena in which I have been greatly interested for a number of years and omitting also the organic superconductivity recently discussed by Little (1964). Let us ask: How nearly can the electrical conductivity of an organic material be made to approach values typical of metals?

This question at the moment is partly but not completely answered. Therefore I hope that the discussion tonight will encourage research in what in the last few years has become a very active front in the scientific advance; thus may I fulfil Archibald Liversidge's aim in establishing this lectureship, with the award of which the Royal Society of New South Wales has honoured me this year: my gratitude goes to Liversidge now just as it did when I entered the University of Sydney with a Liversidge scholarship.

Liversidge worked in the Department of Physiology in Cambridge University and of Chemistry in the University of Sydney, and was intimately concerned with the development of science as a whole; and the subject of electrical conduction in organic materials is related to chemistry and also to certain important aspects of physiology such as vision, as well as to solid state science to photosynthesis and to the mechanisms of some enzymic processes. The breadth of application of the subject of conduction in organic materials matches the extent of Liversidge's own scientific interests.

Professor Gutmann and colleagues (1966) have recently invented a new battery which uses organic solids, and yields 1.5 V, and is of potential use for space craft, being very light. No metal is necessary. Also, The General Electric Co. in U.S.A. has made a non-metallic wire. These results indicate that some extraordinary practical developments may arise from the studies we are discussing, but they are not the subject of this talk. A recent publication discusses all aspects of the subject [Gutmann and Lyons (1967)].

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The Electrical Conductance of Metals and Inorganic Semiconductors

When there is but one type of charge carrier, an electron or a positive hole, the conductivity σ at a given temperature T and pressure p is given by the product of n , the number of carriers per cubic centimetre, and the mobility μ of the carriers:

$$\sigma = n \mu \dots\dots\dots (1)$$

If μ is measured in $\text{cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$ then σ gives the number of electrons flowing per second in a field of 1 volt cm^{-1} . The significant but relatively minor differences between the Hall mobility and the drift mobility need not concern us in this discussion.

Table 1 summarizes some of the basic data on the electrical properties of metals and inorganic semi-conductors.

TABLE 1
Data on Electrical Conductivity of Some Metals and Inorganic Semiconductors
(σ , conductivity; μ , mobility; n , concentration of carriers)

Number of Atoms (cm^{-3})	T (°K)	σ ($\text{ohm}^{-1} \text{ cm}^{-1}$)	μ ($\text{cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$)	n (cm^{-3})	n (cm^{-3})
Ag	290	6.2×10^6	(-)50	7.7×10^{22}	5.9×10^{22}
Ag	15	1.1×10^9	(-)11,000	6.3×10^{22}	
Cu	290	5.8×10^6	(-)60	2.5×10^{22}	2.55×10^{22}
Zn	293	1.7×10^6	(+) 6	19.0×10^{22}	6.6×10^{22}
Ni	293	1.4×10^6	(-)90	1.0×10^{22}	9.1×10^{22}
graphite (in plane)		10^5	(±)20,000	3×10^{18}	1.13×10^{22}
graphite (perp. to plane)		1	(+)		do.
Cu ₂ O	163	2.0×10^{-6}	(-)200	6.3×10^9	2.5×10^{22}
Cu ₂ O	373	9.9×10^{-2}	(-)20	5.6×10^{11}	
Ge (high purity)	300	2.4	(-)4,000	3.5×10^{14}	4.4×10^{22}
Ge (0.005 Al)	100	140	(+)6,000	1.5×10^{16}	4.4×10^{22}
Ge (Sn)	100	83	(-)7,000	7.8×10^{15}	4.4×10^{22}

Source: Ehrenberg (1958).

For metals, from Table 1, it is seen that

- (i) n approximately equals the number of atoms cm^{-3} ;
- (ii) σ drops as T increases;
- (iii) μ drops as T increases; and
- (iv) at room temperature, μ is often 10 to 100 $\text{cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$.

For the inorganic semiconductor Cu_2O

- (i) n is much lower than the number of atoms cm^{-3} ;
- (ii) σ and n both increase as T rises
- (iii) as in metals, $\mu = 10$ to $100 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$; and
- (iv) as in metals, μ drops as T increases.

For germanium semiconductors

- (i) μ is much higher than μ in Cu_2O or in metals
- (ii) n (and thus σ) can be determined by the concentration of an additive such as Al.

TABLE 2
Experimentally Measured Values of Mobility in Anthracene and Naphthalene

	μ^+	μ^-
Anthracene		
Crystal; $\perp(001)$	0.4	0.3
	0.98 ± 0.04	0.54 ± 0.03
	0.43 ± 0.05	
Crystal; $\parallel(001)$	1.3	2.0
Cast slab	0.48	
Crystal; ? direction	≥ 2.3	
Crystal	5×10^{-3}	
Crystal, ${}^a\mu_{aa}$	1.0	1.7
Crystal, ${}^a\mu_{bb}$	2.0	1.0
Crystal, ${}^a\mu_{c'c'}$	0.8	0.4
	$\mu^+/\mu^- =$	2.13
Crystal; $\parallel(001)$	0.8	0.4
Naphthalene		
Crystal, ${}^a\mu_{aa}$	0.9	0.7
Crystal, ${}^a\mu_{bb}$	1.4	0.7
Crystal, ${}^a\mu_{c'c'}$	0.4	0.4

${}^a\mu_{aa}$ represents the component of the mobility tensor μ_{ij} , when $i = j = a$ where a is a crystal direction ; $a, b,$ and c' are mutually perpendicular.
Source: Gutmann and Lyons (1967).

Conductivity of Organic Solids

(In this lecture the work of many workers is referred to; the contribution of our research group has been to propose and test the general theoretical framework for organic conduction.)

The general result is typical of the behaviour of semiconductors

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

E is the thermal energy necessary to form carriers. When the carriers are generated thermally within the crystal and when μ is independent of temperature

$$\sigma_0 = N\mu \dots \dots \dots (3)$$

where N is the concentration of centres capable of yielding carriers.

Measurements of σ_0 and of μ thus enable N to be deduced.

Mobility in organic crystals

The pulse method of Le Blanc (1960) and Kepler (1960) yields values of μ in anthracene and naphthalene which are all of the order of $1 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$. Positive holes and electrons differ slightly in mobility; in either cases μ is anisotropic, as is shown in Table 2.

The mobility can be explained by band theory. Essentially a band of energy levels is formed for each molecular orbital, because of the overlap of the molecular orbitals in the crystal lattice. From the widths of the bands and from a theory of scattering the mobility can be calculated. On reasonable assumptions the results of theory agree with experiment.

The "overlap" or "band" theory of mobility is supported by the observed decrease of μ with a rise in T, and by the observed increase of μ with a rise in p (Figs. 1 and 2), after Kepler (1962).

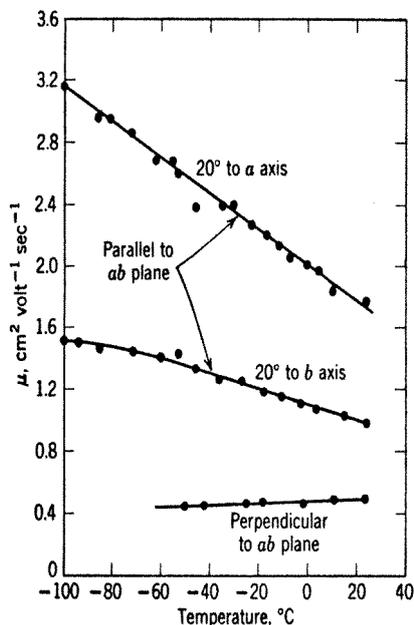


FIGURE 1
Temperature dependence of electron mobility;
after Kepler (1962)

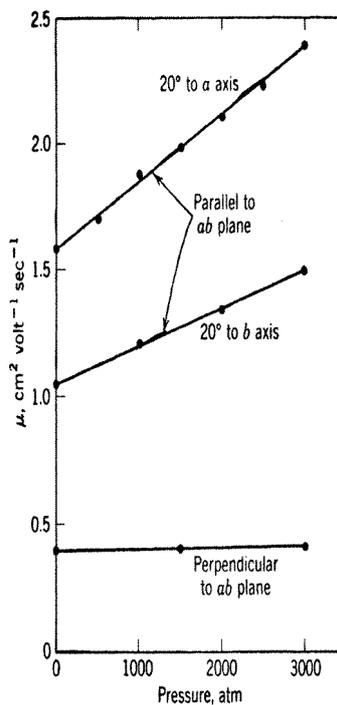


FIGURE 2
Pressure dependence of electron mobility;
after Kepler (1962)

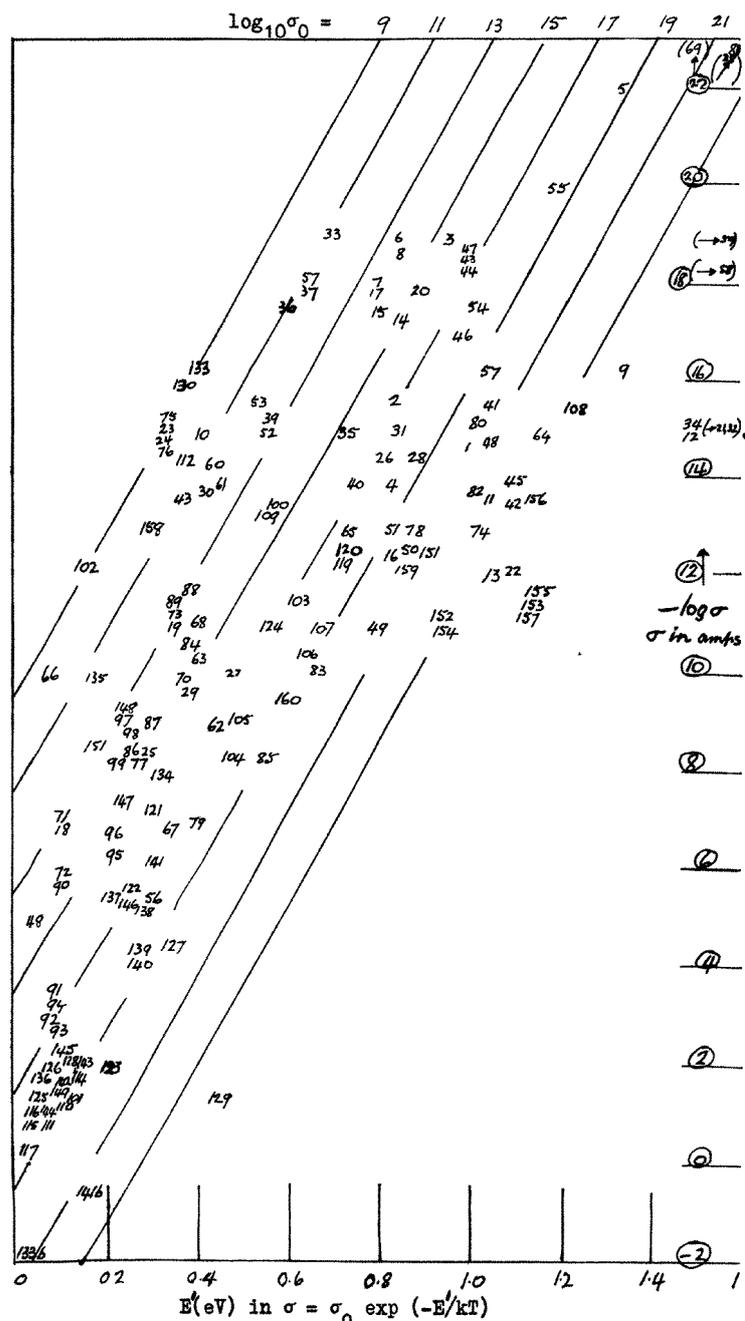


FIGURE 3

Values of σ_0 for observed E and σ in reported experiments on dark conductance.

(σ_0 is in amps $\times 10^{19}$)

Key to Fig. 3 : 1-5, anthracene ; 6-7, anthanthrene ; 8, anthanthrone ; 9, benzanthrone ; 10, benzene; 11, benzimidazole; 12, *o*-chloranil; 13, chlorpromazine; 14-17, coronene; 18, cyananthrone; 19, flavanthrone; 20, hexamethylbenzene; 21, hydroviolanthrene; 22, imidazole; 23, indanthrazine; 24, indanthrone; 25, indanthrone black; 26-27, 30, isoviolanthrene; 28-29, isoviolanthrone; 31, naphthacene; 32-35, naphthalene; 36, *m*-naphthodianthrone ; 37, *m*-naphthodianthrone ; 38, octahydroviolanthrone ; 39, ovalene; 40, pentacene; 41-47, perylene; 48, phenazine; 49, phenothiazine; 50-51, phthalocyanine; 52, pyranthrene; 53, pyranthrone; 54-55, pyrene; 56, quaterrylene; 57, α -resorcin; 58-59, β -resorcin; 60-63, violanthrene; 64, Banfield and Kenyon's radical; 65, Coppinger's radical; 66, DPPH; 67-68, violanthrone-B compound; 69, 1,9,4,10-anthradipyrimidine; 70, crystal violet; 71-72, cyananthrone; 73, flavanthrone; 74, fluorescein-Na; 75, indanthrazine; 76, indanthrone; 77, indanthrone black; 78, indigo; 79, nacrosol black; 80, orthochrome T; 81, 5,6-(*N*)-pyridino-1,9-benzanthrone; 82, acenaphthene:TCNE; 83, anthracene: TCNE; 84, azulene:TCNE; 85, β -carotene triiodide; 86, coronene:iodine; 87-89, 1,5-diaminonaphthalene:chloranil; 90-91, 1,6-diaminopyrene:chloranil; 92-93, 3,8-diaminopyrene:

bromanil; 94, 3,8-diaminopyrene:chloranil; 95, 3,8-diaminopyrene:iodanil; 96, 3,10-diaminopyrene:chloranil; 97, dimethylaniline:bromanil; 98, dimethylaniline:chloranil; 99, dimethylaniline:iodanil; 100, hexamethylbenzene:TCNE; 101, isoviolanthrene : (AlCl₃)_{3.2} ; 102, isoviolanthrone: (AlCl₃)_{3.7} ; 103, isoviolanthrone : (ICl)_{1.45} ; 104, isoviolanthrone : (ICl)_{1.90} ; 105, isoviolanthrone : (ICl)_{3.73} ; 106, isoviolanthrone : (TiCl₄)_{1.87} ; 107, lithium:anthracene; 108, naphthalene:TCNE; 109, pentamethylbenzene:TCNE; 110, perylene:SbCl₅; 111, perylene:Br₂; 112, perylene:chloranil; 113, perylene:fluoranil; 114-117, perylene:iodine; 118, perylene:metal halides; 119, perylene:TCNE; 120, phenanthrene:TCNE; 121, phenylenediamine:chloranil; 122, *p*-phenylenediamine:chloranil; 123, phthalocyanine:chloranil; 124, potassium:anthracene; 125-126, potassium:isoviolanthrene; 127, potassium:TCNQ; 128, pyranthrene:bromine; 129, pyranthrene: iodine; 130, pyrene:chloranil; 131, pyrene:iodine; 132, pyrene:TCNE; 133, pyrene:TCNQ; 133b, quinolinium:(TCNQ)₂; 134, Na:anthracene; 135, Na:3,4-benzoquinoline; 136,Na:isoviolanthrene; 137,Na:isoviolanthrene;138,tetramethyl-*p*-phenylenediamine:bromanil;139-140,tetramethyl-*p*-phenylenediamine:chloranil;141, tetramethyl-*p*-phenylenediamine:iodanil; 141b, triethylammonium (TCNQ)₂; 142, violanthrene:Br₂; 143-148, violanthrene (V) : I₂, mole ratio (V: I₂), 1: 3.7, 1: 1.9, 1: 0.118, 1: 0.01, 1: 0.0036, 1: 5x10⁻⁴; 149-150,V: I₂; 151,V:TCNE; 152, dipyrromethene-1, cobalt; 153, dipyrromethene-2, cobalt; 154, dipyrromethene-1, copper; 155, dipyrromethene-2, copper; 156, dipyrromethene-1, hydrobromide; 157, dipyrromethene-2, nickel; 158, ferrocene; 159, phthalocyanine, Cu; 160, phthalocyanine, Mg; 161, phthalocyanine, Zn.

Source of data: Gutmann and Lyons (1967)

All values of μ might be expected to be of the same order of magnitude in a given class of crystal, e.g. in similarly structured molecular crystals of aromatic hydrocarbons. *Values of σ and of E* are determined empirically from plots of $\log \sigma$ vs $1/T$.

If $\mu \approx 1$ then σ_0 indicates the number of sources of carriers. Intrinsic conductivity would require σ_0 to be *ca.* 10²¹ cm⁻³. Extrinsic conductivity would be undetectable if $\sigma_0 < ca.$ 10⁹ cm⁻³, unless E were very small.

Figure 3 summarizes the results of many workers on more than 160 substances. Nearly all lie within the expected limits for σ_0 . The conductivity itself ranges over more than 20 orders of magnitude. In Figure 3, the lower on the diagram does a number (denoting a compound) occur, the greater is $\log \sigma$; and the more to the left does a number occur, the less is σ_0 . Most observations of conductivity are therefore consistent with extrinsic rather than intrinsic mechanisms. The common occurrence of extrinsic mechanisms is consistent also with the known difficulty of obtaining hyper-pure organic compounds. None is yet available commercially in a grade comparable with that of the best germanium. From Figure 3 it is clear that less than one part in 10¹² of an active impurity in many cases can affect the observed conductivity. A new technology of purification and operation is therefore called for. Many experiments should be done in the absence both of light and of oxygen.

The Energy Gap, E

In equation (2), E ranges from 0 to more than 3 eV. An explanation of E was given by Lyons (1957). For intrinsic conductivity thermal generation of carriers requires an energy given by equation (4).

$$E = I_C - A_C \dots\dots\dots (4)$$

where I_C and A_C are the energies of subtracting and of adding an electron to the crystal.

Values of I_C can be obtained by photoemission experiments. I_C can also be related to the molecular ionization energy I_G by the polarization energy P , through equation (5);

$$I_G = I_C + P \dots\dots\dots (5)$$

We have established that I_C is less than I_G , usually by about 2 eV. Values of $I_G - I_C (= P)$ are shown in Table 3.

Calculation of P was made from the formula

$$P = \sum_{k < l} \alpha^2 e^2 r_k^{-3} r_l^{-3} r_k^{-3} [r_k \cdot r_l - 3r_{kl}^{-2} (r_k \cdot r_{kl})(r_l \cdot r_{kl})] - \sum_1^{N-1} k e^2 \alpha / r_k^4$$

More complicated expressions involving higher terms and anisotropic molecular polarizabilities are given by Mackie (1964) and by Batley (1966) who used also a

TABLE 3
Values (eV) of $I_G - I_C$ Equated to the
Polarization Energy P of a Single Charge

Anthracene	1.8	Perylene	1.9
Chrysene	2.1	Phenanthrene	1.4
Coronene	2.4	Phthalocyanine, Zn	1
9,10-Dibromo- anthracene	1.9 to 2.4	Pinacyanol	2.3
<i>n</i> -Hexane	1.7	Pyrene	1.7
Indigo blue	1.8	Quinoline blue	2.0
Merocyanine	2.2	Rhodamine 6G	1.6
Naphthacene	1.6	Water	5.6 to 7.0
Naphthalene	1.3		

Source : Gutmann and Lyons (1967).

computer programme to increase the accuracy. The theory assumes (i) crystal structures from x-ray work and (ii) molecular polarizabilities, available in many instances from the work of Professor Le Fèvre and colleagues. [Le Fèvre and Sundaram. (1963)].

When account is taken both of ion induced-dipole and dipole-dipole interaction the theory calculates P to lie within a few tenths of an electron volt of the observed difference between I_G and I_C . Since there are errors in experiments and necessary approximations in the theory, the agreement is satisfactory. In this way the theory of photoelectric emission thresholds in organic solids has been established reasonably well. Calculated values are shown in Table 4. The *electron affinities* A_C of certain dye

TABLE 4
Calculated Values of Polarization Energy (eV)

	PI Ion-dipole	PD Dipole-dipole	PI + PD
naphthalene	-2.01	+0.41	-1.60
anthracene	-2.35	+0.54	-1.81
naphthacene	-2.81	+0.66	-2.15
pentacene	-2.08*	+0.64	1.44*
coronene	-2.21*	+0.37	-1.84*
chrysene	-2.30*	+0.82	-1.48*
anthracene : TNB	-2.53*	+0.37	-2.16*

*Ion-dipole term not extrapolated to infinite radius.

crystals have been reported as 3.3 ± 0.3 eV (Nelson, 1956). There is no other direct measurement. However, A_C can be related to the corresponding molecular property A_G by equation (6) -

$$A_G = A_C - P \dots\dots\dots(6)$$

where P refers to the energy of the polarization produced by the negative charge, a quantity which will be very close to that produced by a positive charge.

Thus if we can get A_G we can determine A_C and *vice versa*. In the course of our work we have used two methods of arriving at values of A_G . The first general method derived A_G from polarographic reduction potentials in solution [Lyons (1950)], while the second derived A_G from charge-transfer spectra in solution [Briegleb (1961), Batley and Lyons (1962)]. In addition theoretical and other methods of various kinds have been used [e.g. Hoyland and Goodman (1962)].

All methods suffer from the difficulty of how to place the values on an absolute scale. However, when values relative to benzene are considered, the various methods yield values in reasonably good agreement with each other as Table 5 shows. [For absolute values, the discrepancies amongst the results of various methods have very recently been removed by Batley (1966).]

TABLE 5
*Electron Affinity Energies ΔA_G of Organic
Molecules Relative to that of Benzene*

Substance	ΔA_G	Mean
Anthracene	1.8	2.0
	1.8	
	2.0	
	2.1	
	2.0	
	2.1	
Coronene	1.8	1.85
	1.9	
	1.8	
Diphenyl	1.1	
	0.8	
	1.3	
Naphthacene	2.4	2.3
	2.4	
	2.2	
Naphthalene	1.1	1.2
	1.0	
	1.3	
	1.2	
	1.3	
	1.4	
Perylene	2.1	2.2
	2.3	
	2.2	
Phenanthrene	1.4	1.4
	1.6	
	1.6	
	1.1	
Pyrene	1.6	1.9
	1.7	
	2.3	
	2.0	

Source: Gutmann and Lyons (1967).

Thus, whilst relative molecular electron affinities are available at least for the aromatic hydrocarbons the lack of an accurate absolute value is still a problem in understanding the electrical properties of solids. This appears when equation (4) is rewritten using equations (5) and (6), as

$$E = I_G - A_G - 2P \dots\dots\dots (7)$$

The validity of this approach is seen in the case of dyes which in Figure 3 were found to obey the equation for intrinsic conductivity. Also $A_c (= A_G + P) = 3.3$ eV typically [Nelson (1956)] and $I_c (= I_{Gc} - cP) = 5.1$ eV typically. We thus predict E as

5.1 - 3.3 = 1.8 eV (eq. 4), a value which compares with the typical experimental value of 1.8 eV (Figure 3). The general mechanism is thus supported. Incidentally also, the molecular electron affinity of the dye molecule can be deduced to be 1 eV, because

$$A_G = A_C - I_G + I_C \dots\dots\dots(8).$$

There is a further set of experiments to which the same basic theoretical approach can be applied: The *effect of high pressure* upon the electrical conductivity of organic substances was observed but was unexplained until recently. It had been shown (Harada *et al.* 1964) that the greatly increased conductivity which is observed at high pressure is only 10% explicable in terms of an increased mobility. The increase in σ must therefore be caused by an increase in the number of carriers i.e. by a decreased value of E. We now use equation (7) to discuss the decrease in E.

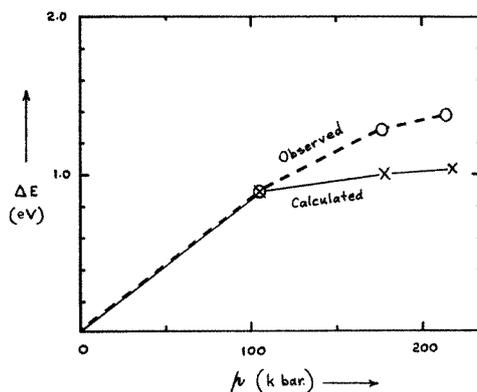


FIGURE 4
Change ΔE of the energy gap with pressure, p, for the semiconductivity of pentacene. Batley (1966)

The polarization energy, calculated as described above, is a function of the lattice parameters and must change when the crystal is compressed. Batley and Lyons (1966) have shown that the increase in carrier concentration can be explained by the change in the size of the unit cell with pressure (see Figure 4). Using the equation

$$kT \ln \left[\frac{\sigma_p}{\sigma_{o,p}} \cdot \frac{\sigma_o}{\sigma} \right] = \Delta P \dots\dots\dots(9)$$

where the subscript p denotes values at high pressure and $\Delta P \equiv P_p - P$ the theory in fact rather over explains the observations, which however are at present subject to an unknown error. Because

$$E_p = E - 2\Delta P \dots\dots\dots(10)$$

an interesting situation is predicted to arise when ΔP is sufficient to make E_p equal to zero. In this case equations (2) and (3) yield

$$\sigma = N\mu \dots\dots\dots(11)$$

so that $\sigma \approx 10^3$ to 10^4 ohm⁻¹ cm⁻¹, a value which approaches that of metals. This behaviour has been observed, e.g. in copper and metal-free phthalocyanine. On returning to atmospheric pressure the metallic behaviour disappears, again as the theory predicts.

Conductivities at p = 1 bar

Using equation (7), and requiring E to be low, it is clear that in order to increase σ we must (i) decrease I_G , (ii) increase A_G , and/or (iii) increase P. Since P varies only over a limited range we consider only I_G and A_G in this section. The dependence of I_G upon molecular structure is shown in Table 6 which presents only a sample of values. For example, I_G is lowered (i) by an increase in conjugation and (ii) by the introduction of -N.Me₂, -NH₂, -OH, and -CH₃ groups.

TABLE 6
Molecular Ionization Energy, I_G , and Molecular Structure

	I_G (eV)	Substituted benzene	I_G (eV)
benzene	9.245	-H	9.245
naphthalene	8.12	-CH ₃	8.81
anthracene	7.38	-C ₂ H ₅	8.76
naphthacene	6.88	-CHO	9.45
		-COCH ₃	9.65
		-CN	9.705
		-NH ₂	7.56
		-NH.NH ₂	7.64
pyridine	9.32	-OH	8.52
p-benzoquinone	9.67	-SH	8.33
phenothiazine	7.14	-φ	8.27
1,5-naphthalenediamine	7.2	(-NH ₂) ₂ para	7.2
bis-cyclopentadienyl Co	6.2	(-N.Me ₂) ₂	6.8

Source: Gutmann and Lyons (1967).

The dependence of A_G upon molecular structure is such that A_G increases (i) with an increase in conjugation and (ii) with the introduction, e.g., of -CN, -NO₂, or -Cl substituents.

For crystals containing only one type of molecule conduction is favoured if there is extensive conjugation. Graphite is a limiting case here: its properties are well-known (cf. Table 1). Pohl and colleagues [Pohl (1962)], as well as other workers, have made scores of polymers in which conjugation extends throughout the polymer molecule. As expected I_G is low, A_G is high and so σ is high: $\sigma = 10^{-3}$ for polydibenzpyrene ($E = 0.2$ eV); and $\sigma = 10^{-4}$ for polypyrene ($E = 0.2$ eV). The lack of a perfect single crystal lowers μ to 10^{-2} or 10^{-3} cm² volt⁻¹ sec⁻¹ and so limits σ . Polyacenequinone radicals polymers can show $\sigma = 10^{-5}$ ohm, with μ probably about 10^{-2} , and $E \geq 0.26$ eV.

Doping

The addition to a crystal of a small amount of an additive which has a lower I_G or a higher A_G than the corresponding value for the host molecule should lower E and raise

the conductivity. Figure 5 shows that this is in fact so. Table 7 indicates that it is A_G rather than I_G which is important here. The E values decrease as A_G is increased. Once again support is obtained for the usefulness of equation (7).

TABLE 7

	E_{imp}	A_G (est)	E_{imp+A_G}
<i>o</i> -chloranil	0.65	1.9	2.55
pentacene	0.95	1.2	2.1
anthraquinone	1.10	1.05	2.1
anthanthrene	1.12	?	
tetracene	1.23	0.95	2.2
perylene	1.6	0.9	2.5

Source: Johnston and Lyons (1966).

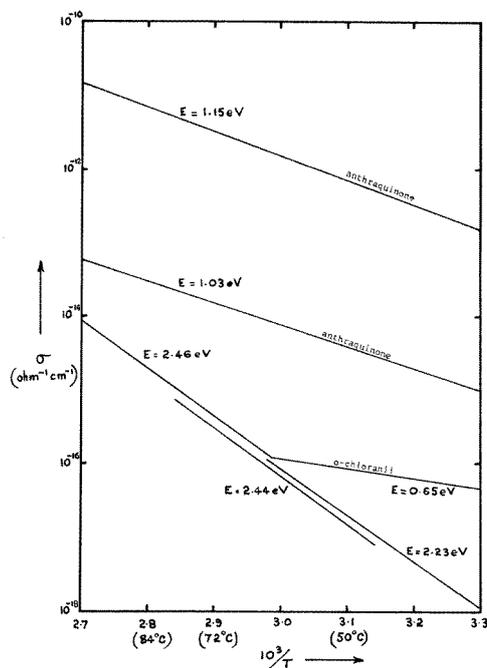


FIGURE 5

Conductivity vs inverse temperature plots for anthracene crystal containing additives. Johnston and Lyons (1966).

Doping with an alkali metal ($I_G \approx 5$ eV) is expected to give similarly increased conductivities. Amongst organic materials bis-cyclopentadienyl cobalt ($I_G = 6.2$ eV) should be worth trying and this we plan to do.

The limiting case of "doping" is found in the *donor: acceptor complexes* which can be, e.g., 1 : 1 or 1 : 2. Table 8 lists the resistivities of some donor acceptor complexes. Of those listed the lowest resistivity is that of perylene-iodine. For the 1 : 3 complex $\rho = 8$ ohm cm, while for the 2 : 3 complex $\rho = 3$ ohm cm, with $\mu < 0.01$.

TABLE 8
*Electrical Resistivities of Some Donor
Acceptor Complexes*

Donor	Acceptor	Mole Ratio	Resistivity Ohm Cm
acenaphthene	TCNE		5×10^{13}
benzidine	I ₂	1 : 1	10^6
caesium	tetrachloro pyrene		8
3,8-diaminopyrene	domanil		10^3
perylene	domanil		8
perylene	iodine	2 : 3	3

Source: Gutmann and Lyons (1967).

Some 1:1 donor complexes, such as K⁺ chloranil⁻, are completely ionic and there is a resemblance to K⁺Cl⁻ type solids. Using I_G and A_G values Mackie (1964) predicted the existence of a number of such substances. However, the resistivity is high - potassium chloride is an insulator.

For good conductivity it is necessary not only to have an abundance of ions such as chloranil⁻ but also to have neutral molecules as neighbours to the ions. The electron can then move from one site to its neighbour with practically no change in energy. Steric arrangements should be suitable for the electron transfer. A favourable arrangement has been found amongst 1 : 2 complexes. Thus the conductivity of K⁺TCNQ⁻ is *ca.* 10^{-4} ohm⁻¹ cm⁻¹, while that of K⁺(TCNQ)₂⁻ is *ca.* 10^{-2} .

Similar and even higher conductivities can be obtained with completely organic materials, e.g. for NEt₄⁺, (TCNQ)₂⁻, $\sigma \approx 7$; and for Q⁺(TCNQ)₂⁻, $\sigma \approx 100$; where Q⁺ denotes the quinolinium, ion; Et, the C₂H₅ group; TCNQ, tetracyanoquinodimethane.

In Q⁺(TCNQ)₂⁻ the mobility in pellets is rather small (10^{-2}). No good independent measurement of the mobility on single crystals exists. Such measurements would allow a study of the possibility that μ has been limited by impurities and other crystal defects. If this is so and μ could be increased by better purification of the crystals then σ would be raised to perhaps 10^4 ohm⁻¹ cm⁻¹.

Ultimate Limits on High Conductivity of Organics

Table 9 gives the number of molecules in a centimetre cube of some aromatic hydrocarbons. These values are all slightly more than one order of magnitude less than those found with metals. The simple fact that an organic molecule is bigger than a metal atom means that the number of sources for carriers must generally be less than in metals.

None the less conductivities as great as those in metals are not inconceivable. What is lost in the number of carriers may possibly be offset in the mobility. Although mobilities in the anthracene type crystals so far measured are relatively low, there are already a few experiments which point to higher mobilities in favourable directions in certain crystals. Conjugated polymers as single crystals and some hydrogen-bonded crystals are likely examples. It must be remembered that in graphite $\mu \approx 20,000 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$.

TABLE 9

Crystal	Number of Molecules cm^{-3}
anthracene	4.3×10^{21}
naphthacene	3.5×10^{21}
naphthalene	5.4×10^{21}
perylene	3.3×10^{21}

Conclusion

The day may well arrive when organic materials other than graphite will be made with conductivities of 10^4 or greater. Speaking electrically, organic metals exist already at high pressures, and the theory outlined in this paper shows that at present they are not far from existing under ordinary pressures.

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