The Electrical Conductivity of Some Nitrogen Containing Heterocyclic Polymers

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*Factors which could influence the energy gap ΔE of an organic semiconducting polymer have been investigated by a study of the electrical conductivity of some nitrogen heterocyclic polymers, in particular paracyanogen, macrocyclic polymers and poly[benzo*bis*(aminoiminopyrrolenines)]. The electrical behaviour of paracyanogen is similar to that of the related polyacene suggesting that the energy gap ΔE is not appreciably affected by replacement of methine groups by nitrogen in the polymer. The macrocyclic polymers have larger ΔE than the polypyrrolenines and for each series the energy gaps of the polymers derived from 4,4′-diaminodiphenyl ether and paraphenylene diamine are comparable, whilst the metaphenylene diamine is lower.*

TO PREPARE an organic polymer that is predictably either a good insulator or conductor of electricity would require a knowledge of the factors which determine its limiting energy gap. Some factors which might be important have been examined in the present work.

Studies on some organic semiconducting polymers have shown that the energy gap (ΔE) is dependent on the number of units in the chain as well as the mode of combination. In the linear polyacene series for example (*Figure 1*), ΔE decreases markedly from monomer to tetramer and thereafter decreases gradually, approaching a limiting value at hexacene (1·14 eV). Further increase in the molecular weight has little effect on the energy gap[1]. Although the structure proposed for pyrolysed polyacrylonitrile[2-6] [*Figure 1*(c)] is related to that of polyacene, after prolonged heat treatment it is a semiconductor with an energy gap as low[6] as 0·06 eV. Apparently the introduction of nitrogen into the polyacene structure lowers the energy gap. To test this conclusion paracyanogen [*Figure 1*(a)] which has a proposed structure related to both polyacrylonitrile and polyacene has been studied.

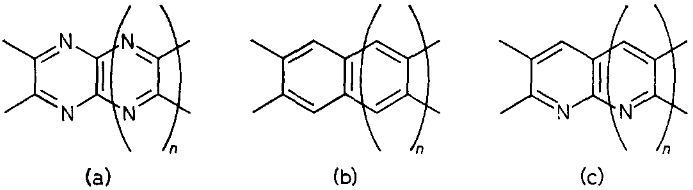

Figure 1—The proposed structures of paracyanogen (a), polyacene (b) and pyrolysed polyacrylonitrile (c)

The order of limiting energy gap in the series poly-*p*-phenyl > polyacene > condensed naphthalenes[1] suggests an inverse relationship between polymer width and ΔE. For this reason the electrical characteristics of two series of related polymers which differ in width, the poly[benzo*bis*-

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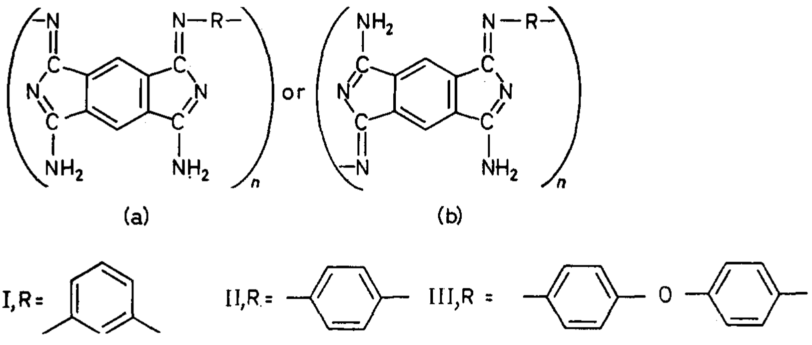

Figure 2—The proposed structures of the poly[benzo*bis*(aminoiminopyrrolenines)] studied

(aminoiminopyrrolenines)][7] (*Figure 2*) and macrocyclic polymers[7] (*Figure 3*) have been examined. The choice of the units R (I–III, *Figure 2*) was made in order to study the effect of meta-(I)- and para-(II)-phenylene linkages as well as the effect of the ether linkage (III) upon the limiting energy gap.

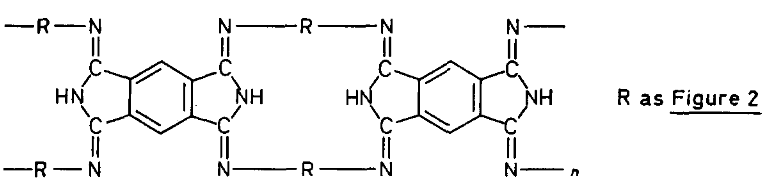

Figure 3—The proposed structures of the macrocylic polymers studied

EXPERIMENTAL

Materials

Paracyanogen was prepared by pyrolysis of either mercuric cyanide or oxamide[8]. The product, a black or dark brown powder, was purified by heating at 350°C/10^{-4} N/m^2 for 24 hours. It was characterized by its infra-red spectrum[8], and by its X-ray powder pattern which was found to contain one very strong line at a d spacing of $3{\cdot}3 \times 10^{-10}$ m.

The poly[benzo*bis*(aminoiminopyrrolenines)] and macrocyclic polymers were prepared by methods previously reported[7], and purified by Soxhlet extraction with methanol for 24 hours followed by drying at 150°/10^{-4} N/m^2 for up to 70 hours.

Measurements

Discs of the materials 1·3 cm in diameter and about 1 mm thick were prepared in an evacuable die by compression at $3{\cdot}5 \times 10^7$ N/m^2. The discs were mounted between the polished faces of two cylindrical copper electrodes, and good contact was achieved by a screw clamp arrangement. Thermocouples were embedded in each electrode close to the sample face. The upper electrode could be heated to adjust the temperature gradient across the sample. The sample holder was mounted in an evacuable (10^{-4} N/m^2) silica or stainless steel vessel and the whole assembly heated in a small furnace.

The resistance of the sample was determined by measurement of the current passing through it at applied voltages of 1 to 100 V, with a Vibron 33C electrometer (E.I.L.) to measure the voltage developed across a standard resistance in series with the sample. A guard ring made from a circlip which fitted the outer edge of the disc was attached to the sample for some of the measurements. The changes in resistivity with temperature were determined in the range 20° to 400°C.

RESULTS

D.C. resistivity

The variations of resistivity ρ of the materials with temperature T are shown in *Figures 4* and *5*. Within the temperature range measured the results generally obeyed the relationship $\rho = \rho_0 \exp(\Delta E/2kT)$. The calculated energy gaps ΔE and values of $\log \rho_0$ are listed in *Table 1*.

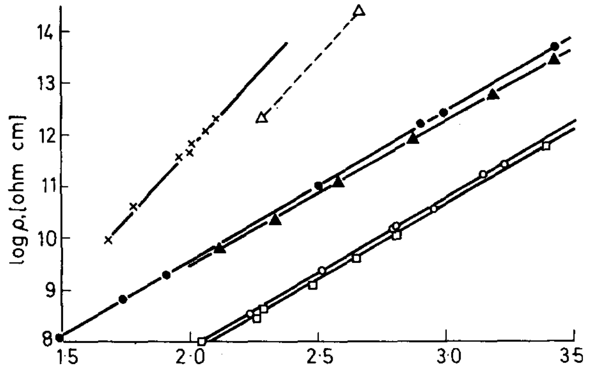

Figure 4—Temperature coefficient of resistivity ρ plots for some of the polymers studied. □ Paracyanogen prepared from mercuric cyanide; ○ paracyanogen prepared from oxamide; ▲ polypyrrolenine prepared from *p*-phenylene diamine; ● polypyrrolenine prepared from 4,4′-diaminodiphenyl ether; △ macrocyclic polymer from *p*-phenylene diamine; × macrocyclic polymer from 4,4′-diaminodiphenyl ether

Reproducibility of data

The two samples of paracyanogen studied, prepared by different routes, behaved similarly (*Figure 4*). In the resistivity range 10^8 to 10^{12} ohm cm one sample gave values of $\log \rho$ 0·2 to 0·3 higher than the other. Polymer samples from two different preparations of the macrocyclic polymer derived from *m*-phenylene diamine gave a similar order of reproducibility. One sample was studied with a guard ring and the second sample without (*Figure 5*). The resistances of the samples were essentially the same in each case.

The effect of drying

The polypyrrolenine made from *m*-phenylene diamine and the polymers derived from *p*-phenylene diamine gave variable results depending upon the time for which they were dried. Although the energy gap of the

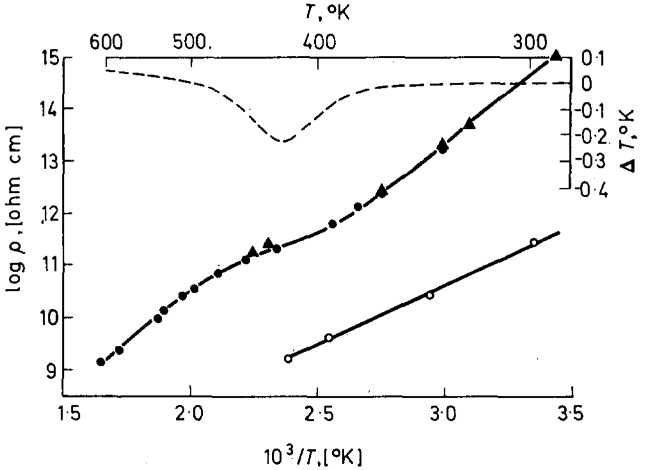

Figure 5—Temperature coefficient of resistivity ρ plots for *m*-phenylene diamine polymers. ○ Polypyrrolenine; ▲ macrocyclic polymer with guard ring; ● macrocyclic polymer without guard ring; —·—— DTA of the macrocyclic polymer

Table 1. D.C. Resistivity of polymers

Material	$\log \rho_0$* ohm cm	ΔE† eV	*Temperature range, °C*
Paracyanogen;			
from mercuric cyanide	2·13	1·12	20–220
from oxamide	2·14	1·14	20–175
Macrocyclic polymers;			
R=			
m-phenyl	2·43	1·61	230–330
p-phenyl	0–00	2·15	20–165
4,4′-diaminodiphenyl ether	0·95	2·13	200–320
Polypyrrolenines;			
R=			
m-phenyl	4·00	0·88	20–150
p-phenyl	3·98	1·09	20–200
4,4′-diaminodiphenyl ether	3·82	1·14	20–400

*$\log \sigma_0 = -\log \rho_0$. †1eV=1·602×$10^{-19}$ joules.

materials did not alter, their resistivities increased with more extensive drying. In the case of the *m*-phenylene diamine polymer values of $\log \rho_0$ of 1·8, 2·8 and 4·0 were obtained after six, 24 and 70 hours drying at 150°/10^{-4} N/m^2 respectively, whilst the energy gap was constant. After extensive drying the macrocyclic polymer from *p*-phenylene diamine could not be satisfactorily pelleted. The data given for this material were obtained on a sample dried for twelve hours at 150°/10^{-1} N/m^2. The polypyrrolenine derived from *p*-phenylene diamine was dried in 24 hours at 150°/10^{-4} N/m^2 and pelleted satisfactorily.

The effect of temperature

When the macrocyclic polymer or the polypyrrolenine derived from *p*-phenylene diamine were heated above 200° *in vacuo* and then cooled, a lower energy gap was observed.

A similar effect was noted with the polypyrrolenine from *m*-phenylene diamine. A sample heated at 160°C was found to have an energy gap of 0·88 eV. After a further sixteen hours at 315° ΔE was found to be 0·54 eV. Above 400°C *in vacuo* a gas was evolved (0·23 moles/kg in three hours), identified by infra-red spectra as a mixture of ammonia and hydrogen cyanide in a 2:1 molar ratio. Room temperature resistivities as low as 15 ohm cm were obtained on pyrolysed samples of this polymer.

Electron spin resonance (e.s.r.) measurements indicated $2 \cdot 3 \times 10^{21}$ spins/kg for unheated polymer whilst a sample heated at 300° for one hour in nitrogen contained $1 \cdot 7 \times 10^{22}$ spins/kg. In contrast the macrocyclic polymer derived from *m*-phenylene diamine had $3 \cdot 1 \times 10^{21}$ spins/kg before heating changing only to $4 \cdot 2 \times 10^{21}$ spins/kg after one hour at 300°C. This example is somewhat surprising since a reversible change occurs on heating, as shown by the resistance measurements (*Figure 5*) and differential thermal analysis (DTA).

The resistances of the polymers derived from diaminodiphenyl ether in both series were unaffected by heating over the temperature range studied.

Correlation of energy gap, ΔE, and pre-exponential factor $\log \sigma_0$

A correlation was found to exist between the energy gap ΔE and $\log \sigma_0$ $(= -\log \sigma_0)$ for the polymers derived from pyromellitonitrile (*Figure 6*).

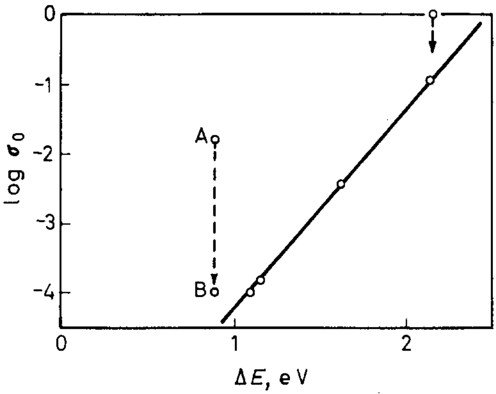

Figure 6—Correlation of energy gap ΔE with log σ_0 for the polymers derived from pyromellitonitrile

DISCUSSION

The behaviour of paracyanogen

The energy gaps determined for the two samples of paracyanogen (1·12 and 1·14 eV) are in good agreement with those reported for hexacene (1·14 eV[1] and 1·3 eV[10]). As hexacene should have much the same energy gap as the higher polyacenes[1] these results suggest that the introduction of nitrogen into an aromatic polymer does not alter the limiting energy gap. This is paralleled by the observation that the electronic spectra of nitrogen heterocycles closely resemble their benzenoid hydrocarbon counterparts[11]. In an alternant hydrocarbon the charge densities of the ground and excited electronic states are identical at any given atomic position. Replacement of carbon by an atom of different nuclear charge such as nitrogen will alter the energies of the ground and excited states to an equal extent, and to a first approximation the difference in energies should not change.

The observed energy gaps for polyacrylonitrile pyrolysed at temperatures above 400°C are low and for specimens pyrolysed in the range 550° to 675°C are typically 0·2 eV[6]. From a comparison of the energy gaps of paracyanogen and polyacene [*Figures 1*(a) and (b)] a material of the proposed structure [*Figure 1*(c)] should have an energy gap of about 1·1 to 1·3 eV. The structure proposed[2-6] for pyrolysed polyacrylonitrile would therefore seem inappropriate.

The behaviour of the polymers derived from pyromellitonitrile

The correlation which exists between $\log \sigma_0$ and ΔE for the six polymers studied (*Figure 6*) is not unusual; several such correlations have previously been reported[9]. This correlation is helpful, however, in deciding if the behaviour of individual polymers can be related to the proposed polymer structure. The range of $\log \sigma_0$ noted for the polypyrrolenine prepared from *m*-phenylene diamine on extensive drying is shown by a broken line AB (*Figure 6*). The possible change in $\log \sigma_0$ for the macrocyclic polymer prepared from *p*-phenylene diamine if it could have been more extensively dried is shown similarly. The correlation indicates that the values of $\log \sigma_0$ reported for these two polymers are probably correct within an order of magnitude.

The three macrocyclic polymers studied (*Figure 3*) had larger ΔE than their corresponding polypyrrolenine (*Figure 2*), by a factor of 1·83 to 1·97. There is no parallel therefore between the behaviour of aromatic hydrocarbon polymers[1] and the polymers studied. For in the former series there appears to be an inverse relationship between polymer width and ΔE. The reason why the macrocyclic polymers have the larger ΔE is not clear.

In the two series the behaviour of the corresponding *p*-phenylene diamine and 4,4′-diaminodiphenyl ether polymers was similar, *Figure 4*. Apparently the *p*-phenylene and 4,4′-diphenyl ether linkages (*Figure 2*, II and III) are equivalent as far as d.c. conductivity is concerned. It would be of interest to establish if these groups exhibit similar properties when present in other polymer systems and, if they do, to determine if other equivalent groupings exist. Such knowledge would help in 'tailoring' polymer molecules to individual requirements.

The behaviour of the *m*-phenylene diamine macrocyclic polymer was unique. An inflection occurred in its $\log \rho$ versus $1/T$ plot (*Figure 5*) centred at about 150°C. There was also an endothermic peak in the DTA trace of the compound at the same temperature (*Figure 5*). Only a slight change in the spin concentration in the material ($3{\cdot}1 \times 10^{21}$ spins/kg) was observed after heating to 300°C for one hour ($4{\cdot}2 \times 10^{21}$ spins/kg). This unusual behaviour could be due to tautomerism as indicated in *Figure 7*.

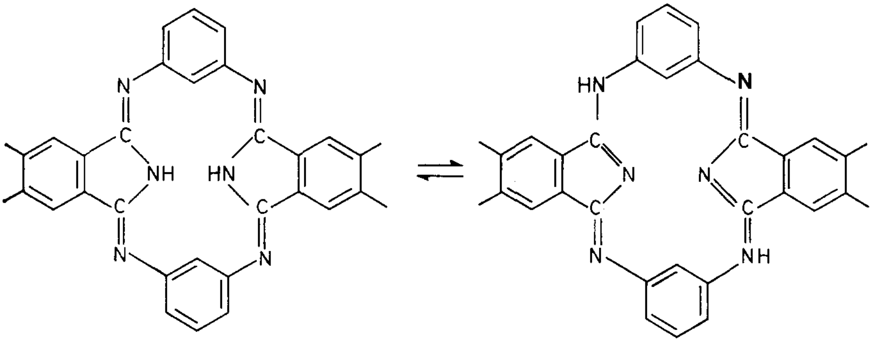

Figure 7—Tautomerism in the macrocyclic polymer prepared from *m*-phenylene diamine

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REFERENCES

[1] Okamoto, Y. and Brenner, W. *Organic Semiconductors*, pp 42–45. Reinhold: New York, 1964
[2] Vosburgh, W. G. *Textile Res. J.* 1960, **30**, 882
[3] Burlant, J. and Parsons, J. L. *J. Polym. Soc.* 1956, 249
[4] Becher, M. and Mark, H. F. *Angew. Chem.* 1961, **73**, 641
[5] Shod, W., Schurz, D. and Bezer, G. *Z. phys. Chem.* 1959, **210**, 35
[6] Brennan, W. D., Brophy, J. J. and Schonhorn. H. *Organic Semiconductors*, Ed. J. J. Brophy and J. W. Buttrey. Macmillan: New York, 1962
[7] Packham, D. I. and Rackley, F. A. *Chem. & Ind.* **1967**, 1254, 1566
[8] Bircumshaw, L. L., Tayler, F. M. and Whiffen, D. H. *J. chem. Soc.* **1954**, 931
[9] Eley, D. D. *J. Polym. Sci. C*, 1967, **17**, 73
[10] Northrop, D. C. *Proc. phys. Soc., Lond*, 1959, **74**, 756
[11] Streitweiser, A. *Molecular Orbital Theory for Organic Chemists*, pp 230–233. Wiley: New York and London, 1961