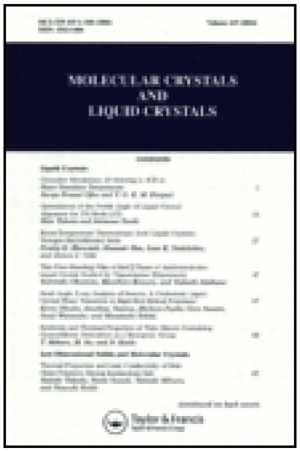

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SUDDEN CONDUCTION AT THE SOLID TO MESOPHASE TRANSITION OF OCTA-*n*-ALKOXY SUBSTITUTED PHTHALOCYANINES

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Abstract The microwave conductivity of powder samples of peripherally octa-*n*-alkoxy substituted phthalocyanines increases abruptly to approximately 0.1 Sm^{-1} at the temperature corresponding to the transition from the solid to the discotic mesophase. The conductivity increases further above the transition temperature with an activation energy of approximately 0.1 eV. Conduction is attributed to the ordered columnar stacking in the mesophase which results in optimal pi-system overlap of neighbouring Pc moieties and the thermal generation of charge carriers in the absence of deliberate doping.

INTRODUCTION

Considerable interest has been shown in the physical properties of substituted phthalocyanine compounds in particular because of their suggested potential application as molecular, one-dimensional semiconductors[1-3]. Intrinsic conductivities as high as 10^{-3} Sm^{-1} have been demonstrated recently for thin films of bis(phthalocyaninato)-lutetium, Pc_2Lu, and lithium monophthalocyanine[4], PcLi. Even larger values were reported for the single crystals of these compounds[4]. The conductivities of these "free-radical" phthalocyanine derivatives are more than six orders of magnitude greater than the values found for the crystalline solids of phthalocyanine itself or its normal monometallic derivatives[4-6].

We have recently found that the microwave conductivity (dielectric loss) of peripherally octa-*n*-alkoxy substituted phthalocyanines increases suddenly from less than 10^{-3} Sm^{-1} to approximately 0.1 Sm^{-1} at the temperature for which the transition from the crystalline solid to the ordered columnar mesophase is known to occur. This somewhat unexpected behaviour is the subject of the present report.

EXPERIMENTAL

The compounds studied in the present work are illustrated in figure 1.The materials were prepared and purified as described previously[7]. X-ray diffraction analysis carried out on the liquid crystalline phase of the C_6 and C_{12} compounds at 200°C has shown the molecules to be aggregated into ordered columns with the columns forming a hexagonal matrix as shown in figure 1. The heart-to-heart distance between molecules within the columns has been found to be well defined and equal to 3.4 Å [7,8]. The axis-to-axis intercolumnar distances have been determined to be 27.6 and 35.2 Å for the C_6 and C_{12} compound respectively[8]. The C_1 derivative showed no evidence of a phase transition from the crystalline solid for temperatures up to

200°C.

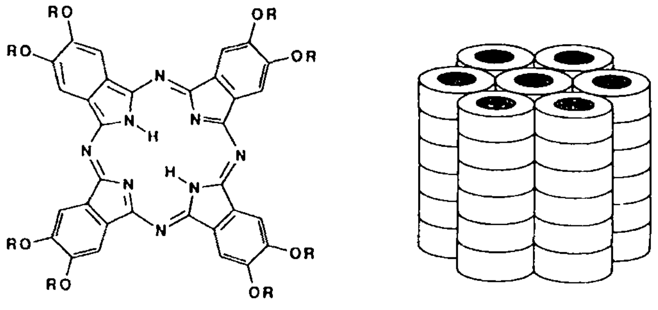

FIGURE 1 The molecular structure of the octa-n-alkoxy phthalocyanine derivatives used in the present work. R is a normal alkyl chain, C_nH_{2n+1}, with n = 1, 6 or 12. On the right is an illustration of the ordered columnar packing of these molecules found in the liquid-crystalline phase for the C_6 and C_{12} compounds. The methyl derivative shows no evidence for a solid to mesophase transition.

The powder samples were compressed into a piece of rectangular, 3.55x7.1 mm^2 waveguide, which was closed at one end with a metal short circuiting plate, using a close-fitting rectangular teflon rod. The sample length, approximately 11 mm, and weight, approximately 200 mg, were measured. The fraction of the volume filled by the solid, 70 to 75%, was determined based on an estimated bulk density of 1.0 g/cm^3. The temperature of the samples was varied over the range 20 to approximately 200°C.

The microwave power reflected by the sample was measured as a function of frequency over the range 30 to 38 GHz using a simple, source ---> circulator ---> cell ---> circulator ---> power meter, waveguide circuit. Any absorption of microwave power by the sample, corresponding to a dielectric loss, could in this way be monitored and the value of the microwave conductivity determined using calculation procedures developed previously for the quantitative analysis of time-resolved microwave conductivity changes occurring on pulsed-irradiation of samples[9-11]. Typical loss curves and calculated fits are shown in figure 2.

RESULTS AND DISCUSSION

None of the phthalocyanine compounds investigated displayed a measureable microwave loss at room temperature in agreement with the general insulating properties of the normal crystalline solids of undoped phthalocyanine derivatives[4-6]. In the case of the C_1 compound no loss was observed even up to a temperature of 174°C. For the C_6 and

C_{12} compounds however a sharp decrease in the reflected power (increase in the dielectric loss) was found to occur at temperatures close to those at which other measurements have indicated a solid to mesophase transition to occur[7,8,12]. The loss was found to increase gradually with further increase in temperature above the transition point. This dependence on temperature is discussed in more detail below.

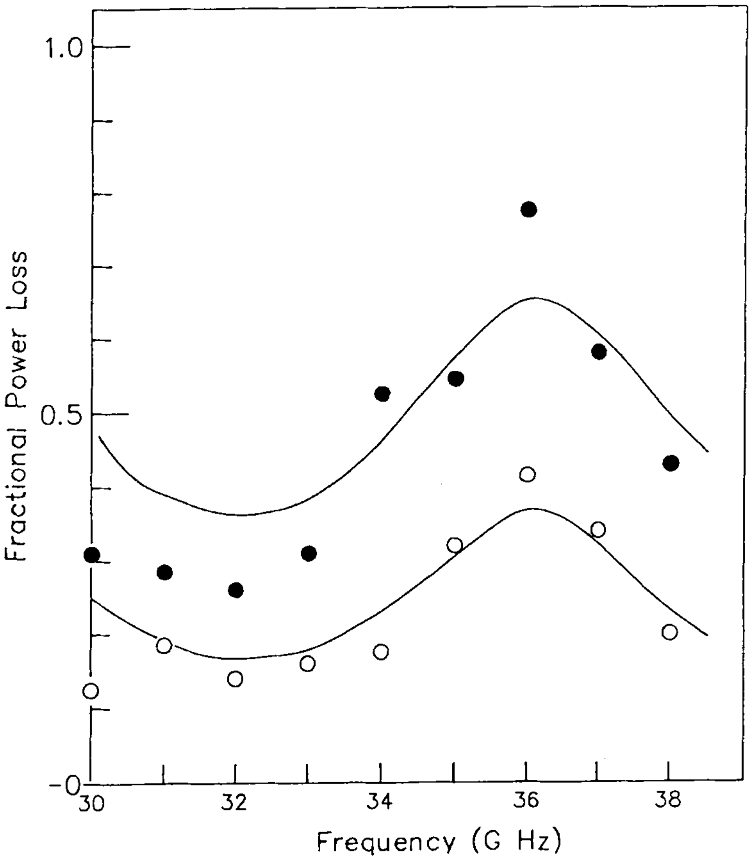

FIGURE 2 The frequency dependence of the fractional loss of microwave power reflected by a sample of the C_{12} phthalocyanine derivative at 93°C, open circles, and 215°C, filled circles. The full lines are calculated dependences for an effective uniform medium 11.7 mm long with a dielectric constant of 1.9 and conductivities of 0.040 and 0.095 respectively.

In figure 2 are shown frequency dependences of the fractional decrease in reflected power, $-\Delta P/P_o$, for two temperatures within the liquid-crystalline phase of the C_{12} compound. Also shown in figure 2 are calculated curves for the expected frequency dependence of the loss. Since the sample dimensions were known the only variables required to fit the data were the effective conductivity of the medium, σ_{eff}, which determines the absolute magnitude of the loss and the effective dielectric constant, ϵ_{eff}, which determines the form of the frequency dependence[9-11], in particular the positions of maxima and minima.

The effective dielectric constants of the samples determined from the fits were 2.1 and 1.9 for the C_6 and C_{12} compounds respectively, independent of temperature. The relative dielectric constants of the solid component in the compressed powders can be estimated from these effective values and the known fraction of the sample volume occupied by the solid (the "fill factor") by applying the Bruggeman relation[13,14] for the effective dielectric constant of a composite medium consisting of flake shaped microcrystals. The values found for the solids are 2.6 and 2.3 respectively which are values which might be expected for non-polar, aromatic organic materials.

The conductivity values required to fit the loss data for the compressed powders were divided by the fill factor in order to obtain the bulk conductivity within the solid phthalocyanine component. For fill factors close to unity, as in the present case, this should be a good first approximation. The conductivity values obtained are plotted as a function of temperature in figure 3.

For the C_{12} compound a sharp rise in conductivity is found at 91°C with a dispersion of less than one degree. For the C_6 compound the rise, which is most pronounced at 115°C, shows a dispersion of a few degrees. After the initial abrupt change both compounds show a further gradual increase in conductivity with increasing temperature with the values for the C_6 compound being in general approximately twice those for the C_{12} derivative.

Preliminary experiments with a polysiloxane derivative of the C_8 compound, which was formed by thermal polymerisation of the dihydroxy silane monomer within the mesophase region, indicate that the ordered columnar stacking can be "fixed" in this way and the conducting behaviour, observed for the present non-polymerised materials only in the mesophase, can be extended to much lower temperatures.

The temperature dependence of the conductivity can be seen to be characterised by a large hysteresis with the sharp decrease on cooling occurring at a temperature approximately 25°C lower than found for the increase on warming the sample. This marked hysteresis effect has also been found in differential scanning calorimetry measurements[7] and for the quenching of the fluorescence of these compounds[12] and related alkoxy-methyl derivatives[15]. At the transition temperature on cooling the complete disappearence of the dielectric loss could be seen to occurr on a timescale of a few minutes. This relaxation time presumably reflects the time constant for the rearrangement of the ordered columnar stacks in the liquid-crystalline phase to a tilted configuration which is thought to characterise the crystalline solid[8,16]. A more detailed study of the kinetics of this readily time-resolvable phase transition could prove to be of interest from the point of view of the liquid-crystal dynamics of these aggregates.

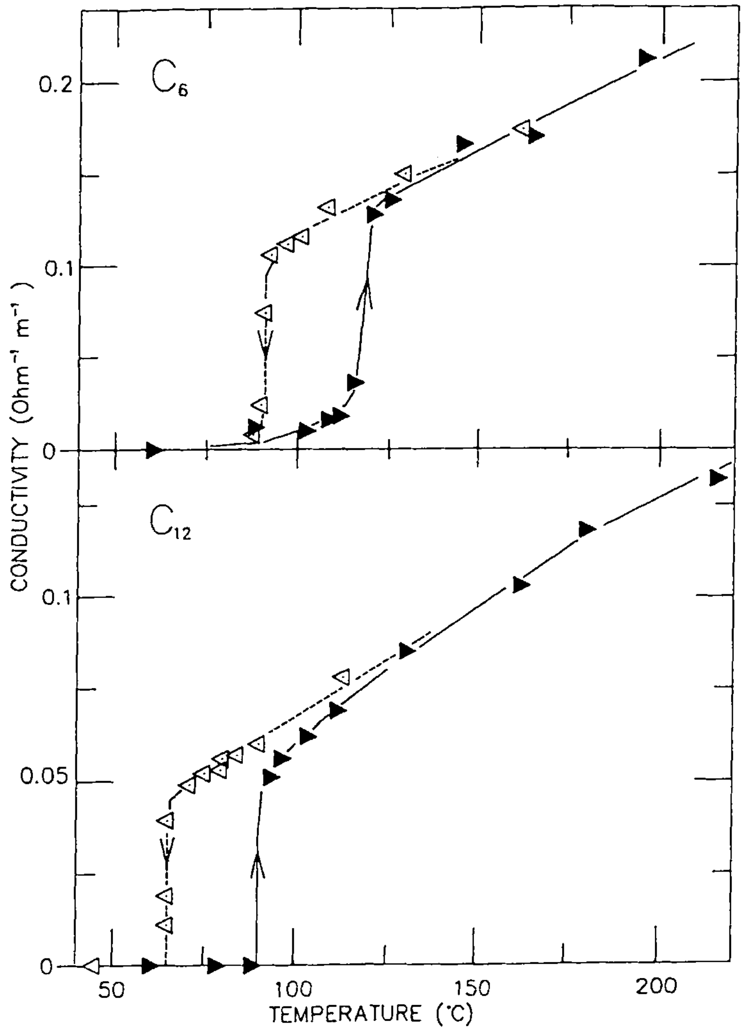

FIGURE 3 The temperature dependences of the microwave conductivities of the C_6 and C_{12} phthalocyanine derivatives. The filled triangles represent points taken as the sample was heated and the open triangles as the sample was subsequently cooled.

In figure 4 the conductivity data have been plotted in an Arrhenius fashion.

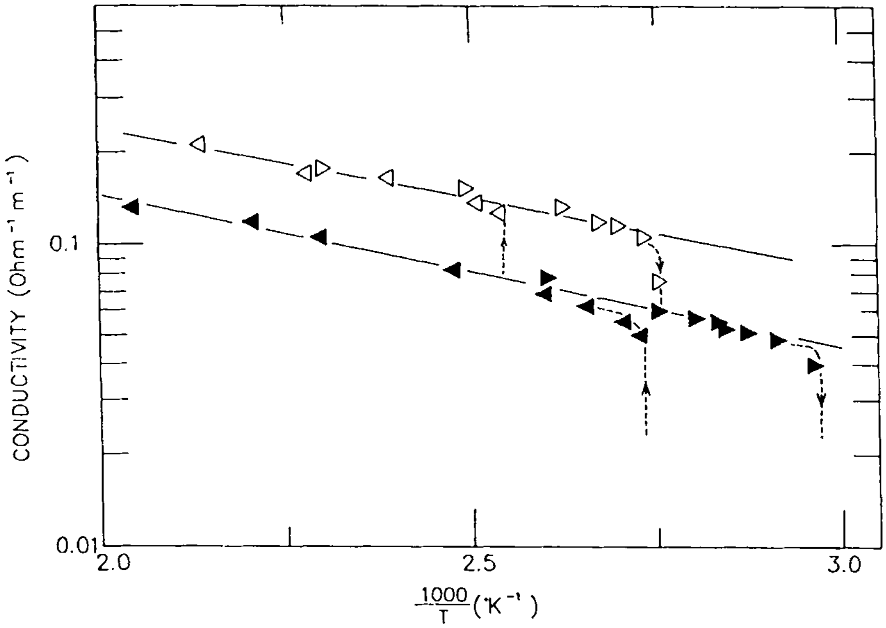

FIGURE 4 Arrhenius type plots of the temperature dependence of the conductivities for the C_6, open triangles, and C_{12}, filled triangles, phthalocyanine derivatives with the direction of the temperature change being indicated by the orientation of the triangle. The solid lines drawn through the data correspond to activation energies of 0.09 and 0.11 electron volts respectively.

The straight lines drawn through the high temperature points correspond to dependences of the form

$$\sigma(T) = \sigma(\infty)\exp\{-E_a/kT\} \qquad (1)$$

The values of $\sigma(\infty)$ found are 1.9 and 1.7 Sm^{-1} for the C_6 and C_{12} compounds respectively. The corresponding activation energies are 0.09 and 0.11 eV. In the case of the polysiloxane-octa-C_8 derivative mentioned above, a dependence of the form given in (1) has been found to be applicable down to at least -50°C with similar parameters, 1.5 Sm^{-1} and 0.11 eV, to those found for the monomer aggregates above the transition to the mesophase.

The conductivity observed within the mesophase of the present compounds could result from either the thermal creation of mobile charge carriers or the freeing of the movement of molecular dipoles. The latter would appear at first sight to be unlikely in view of the symmetry of the individual molecular units. It might be argued however that the freedom of motion of the alkoxy chains which occurs in the mesophase could result in a dipolar loss mechanism. The magnitude of the loss due to dipolar movement would be given by

$$\sigma(\omega) = N_D(\epsilon + 2)^2 p^2 F[\omega\tau]/27k_B T\tau \qquad (2)$$

In 2 ϵ is the relative dielectric constant of the medium k_B is the Boltzmann constant, T the absolute temperature, p the dipole moment, τ the dipolar relaxation time, ω is the radian frequency of the microwaves, N_D the dipole concentration and $F[\omega\tau] = (\omega\tau)^2/[1 + (\omega\tau)^2]$ is the Debye dispersion term.

From 2 we can calculate the maximum value of the dielectric loss from a dipolar source by substituting for the parameter $F[\omega\tau]/\tau$ its maximum possible value at 30 GHz of $\omega/2 \approx 10^{11}$ s-1 and for N_D a concentration equal to eight times the concentration of phthalocyanine units. This results in the condition

$$\sigma(\omega) \leq 7\times10^{-4}\ p^2 \qquad [\mathrm{Sm}^{-1}] \qquad (3)$$

for p in Debye units. Clearly the magnitude of the dipole moment of an R-O-R group, which can't be much larger than 1 Debye, is insufficient to result in a high frequency conductivity even close to the values of on the order of 0.1 Sm^{-1} found. We therefore conclude that explanation of the present observations in terms of dipolar species can be ruled out.

If, as it would appear, the conductivity observed is due to the thermal generation of free charge carriers with an equilibrium concentration N_C and mobilities $\mu(+)$ and $\mu(-)$ m^2/Vs, then the conductivity will be given by

$$\sigma(\omega) = eN_C[\mu(+) + \mu(-)] \qquad (4)$$

If the mobilities are assumed to be of the same order of magnitude as determined for phthalocyanine single crystals(17), i.e. *ca* 10^{-4} m^2/Vs, then the conductivities observed in the present compounds could be explained by an equilibrium concentration of charge carriers as low as 3×10^{21} m^{-3} (5 micromolar). This would require however that the band gap be only a few tenths on an electron volt, which is much lower than the 2 eV which has been estimated(18) for phthalocyanine derivatives.

It is always difficult to exclude completely the possibility that the conductivity observed in phthalocyanine materials is due to inadvertently present oxidative dopants including even oxygen. We can not therefore say with certainty that the conduction observed is intrinsic. What however is certain is that the change from the tilted arrangement of the Pc moieties in the solid state to the parallel stacking, with a 3.4 Å separation, in the ordered columnar mesophase must result in a considerable reduction in the barrier to charge-carrier formation whether it is intrinsic or not. This almost certainly is ascribable to the much better π-system overlap in the mesophase.

A further reduction in the energy required for the formation of electronic charge carriers could result from the greater flexibility of the matrix in the liquid-crystalline phase which might allow the formation of more tightly bound (i.e. "smaller") polaron states. This process is illustrated very schematically in figure 5.

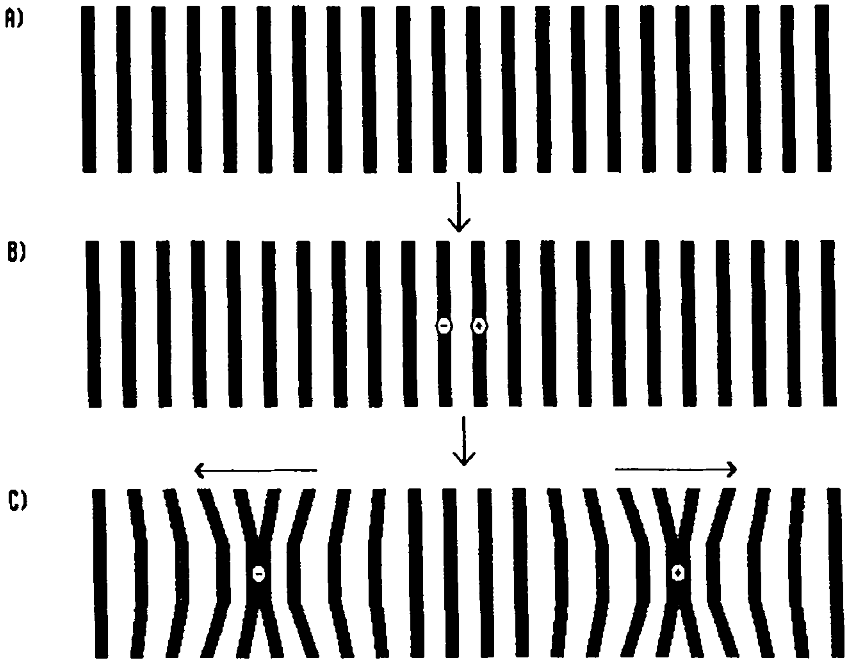

FIGURE 5 A schematic illustration of a possible energetically favourable route for the thermal production of mobile charge carriers within a columnar stack of peripherally substituted phthalocyanine molecules in the liquid crystalline phase, involving first the formation of a contact radical ion pair, (b), followed by dissociation into a polaron pair, (c).

While this would reduce the energy required for charge carrier formation it would have a detrimental influence on the mobility of the charge carriers due to the increased coupling with the matrix.

The fact that one-dimensional conduction does occur in the mesophase of the present compounds has recently received support in a DC microprobe conductivity study in which conduction has been found to occur stochastically in thin, undoped samples of these compounds above the transition temperature[19].

It is possible that the hydrocarbon mantle surrounding the central phthalocyanine core may play a more active role in charge separation than simply inducing the ordered columnar structure of the liquid crystal required for optimal π-system overlap. Thus if interstack charge separation were in some way possible, for example at domain boundaries, then the back recombination reaction could be considerably retarded by the intervening saturated hydrocarbon mantle allowing a greater build-up of separated charge carriers than might be expected.

Whatever the eventual explanation of the present phenomenon, the potential availablity of undoped one-dimensional conductors could have an important impact in the area of molecular electronics where such aggregates could function as the coaxial leads required for the controlled transmission of energy and/or information between devices and to-and-from the macroscopic world. The bistability of the compounds at close to the transition temperature may also present possibilities for the application of such materials in the bulk or as thin layers for regulation of temperature or for pattern recognition and duplication devices. The fact that the conducting properties appear to be able to be fixed by coaxial polymerisation should increase considerably the potential usefulness of this type of material.

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