

# The Effect of Structural Modifications on Charge Migration in Mesomorphic Phthalocyanines

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**Abstract:** The conductive properties of metal-free phthalocyanines, peripherally octa-substituted with *n*-alkoxy, *n*-alkoxymethyl, *n*-alkyl, and branched alkoxy hydrocarbon chains have been studied using the pulse radiolysis time-resolved microwave conductivity technique within the temperature range of -100 to +200 °C. For *n*-alkoxy-Pcs the sum of the charge carrier mobilities,  $\Sigma\mu_s$ , within organized columnar domains is estimated to be  $8.5 \times 10^{-6} \text{ m}^2/\text{Vs}$  at room temperature in the crystalline solid (K phase). This corresponds to a Pc-to-Pc intracolumnar jump time for one-dimensional charge migration of 0.14 ps.  $\Sigma\mu_s$  increases slightly with temperature in the K phase (activation energy *ca.* 0.03 eV) up to the K → D (discotic mesophase) transition at which it decreases abruptly by a factor of *ca.* 5 despite the change from tilted to horizontal stacking of the Pc macrocycles. In the D phase of the *n*-alkoxy-Pcs,  $\Sigma\mu_s$  is almost independent of temperature. The charge mobility in the tilted columnar mesophase of a *n*-alkoxymethyl-Pc is close to that found in the horizontally stacked mesophase of the *n*-alkoxy-Pcs. At the D → I (isotropic liquid phase) transition of a triply-branched alkoxy derivative  $\Sigma\mu_s$  decreases by a factor of *ca.* 7 to  $0.2 \times 10^{-6} \text{ m}^2/\text{Vs}$  which is still much higher than expected for transport via molecular ion displacement.

## Introduction

After the discovery of liquid-crystalline materials based on hexa-substituted *n*-alkanoyloxybenzene<sup>1</sup> a variety of mesomorphic materials composed of disc-shaped molecules were developed in which the solid-state stacking of the molecules is preserved on melting to the liquid-crystalline phase, forming the so-called columnar mesophase.<sup>2,3</sup> With the successful modification of the phthalocyanine (Pc) molecule to attain liquid-crystalline behavior interest in the potential conductive properties of the discotic, columnar mesophase was aroused.<sup>4</sup>

Phthalocyanine itself forms molecular crystals whose dark and photoinduced conductive properties have been studied extensively.<sup>5-11</sup> Charge carrier mobilities of electrons and holes in

single crystal, metal free Pc measured by the time of flight technique<sup>9-11</sup> are on the order of  $10^{-4} \text{ m}^2/\text{Vs}$  at room temperature (RT) with a weak temperature dependence of  $T^{-n}$  with  $0 < n < 2$ , similar to the values found for other aromatic organic molecular crystals.<sup>12,13</sup> However in microcrystalline or amorphous Pc layers, only holes have been found to be mobile with mobilities determined to lie 2-3 orders of magnitude lower.<sup>7</sup> Despite the relatively large charge carrier mobilities the dark dc conductivity of pure Pc is very low; about  $10^{-14} \text{ S/m}$  at room temperature.<sup>5,6</sup> This is due to an energy gap between the valence and conduction bands of approximately 2 eV<sup>14,15</sup> making the material an insulator. However, intrinsic conductivities of  $10^{-3} \text{ S/m}$  have been found for thin films of bis(phthalocyaninato)lutetium, Pc<sub>2</sub>Lu, and lithium monophthalocyanine, PcLi. Values as high as  $10^{-1} \text{ S/m}$  have been found for a PcLi single crystal.<sup>16</sup> A lower limit to the charge carrier mobilities in thin films of Pc<sub>2</sub>Lu has been estimated to be  $1.3 \times 10^{-4} \text{ m}^2/\text{Vs}$ .<sup>16</sup>

In addition to the intrinsically conducting derivatives just mentioned and photoconductivity studies, much research has been carried out on the conductive properties of partially oxidized phthalocyanines which are obtained by "doping" the materials with compounds such as iodine or tetracyanoquinodimethane

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(1) Chandrasekhar, S.; Sadashiva, B. K.; Suresh, K. A. *Pramana* 1977, 9, 471-480.

(2) Chandrasekhar, S. *Rep. Prog. Phys.* 1990, 53, 57-84.

(3) Chandrasekhar, S. *Liq. Cryst.* 1993, 14, 3-14.

(4) Piechocki, C.; Simon, J.; Skoulios, A.; Guillon, D.; Weber, P. *J. Am. Chem. Soc.* 1982, 104, 5245-5247.

(5) Eley, D. D. *Mol. Cryst. Liq. Cryst.* 1990, 171, 1-21.

(6) Simon, J.; André, J.-J. *Molecular Semiconductors*; Springer: Berlin, 1985.

(7) Kearns, D. R.; Calvin, M. *J. Chem. Phys.* 1961, 34, 2022-2025.

(8) Heilmeyer, G. H.; Warfield, G.; Harrison, S. E. *Phys. Rev. Lett.* 1962, 8, 309-311.

(9) Westgate, C. R.; Warfield, G. *J. Chem. Phys.* 1967, 46, 94-97.

(10) Usov, N. N.; Benderskii, V. A. *Phys. Stat. Solidi* 1970, B37, 535-543.

(11) Cox, G. A.; Knight, P. C. *J. Phys. C: Solid State Phys.* 1974, 7, 146-156.

(12) Schein, L. B. *Phys. Rev. B* 1977, 15, 1024-1034.

(13) Schein, L. B. *Mol. Cryst. Liq. Cryst.* 1982, 87, 1-12.

(14) Usov, N. N.; Benderskii, V. A. *Phys. Status Solidi.* 1967, 20, 481.

(15) Loutfy, R. O.; Cheng, Y. C. *J. Chem. Phys.* 1980, 73(6), 2902-2918.

(16) Turek, P.; Petit, P.; André, J.-J.; Simon, J.; Even, R.; Boudema, B.; Guillaud, G.; Maitrot, M. *J. Am. Chem. Soc.* 1987, 109, 5119-5122.

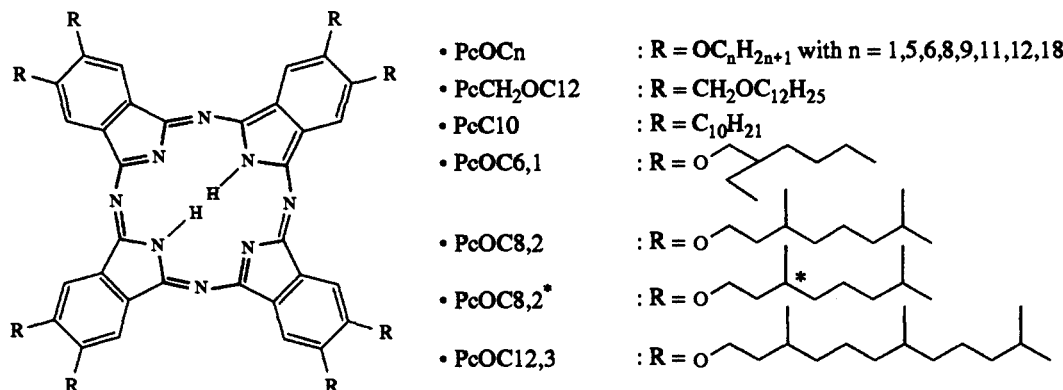


Figure 1. Molecular structures of the compounds studied. Details of the secondary and tertiary structures and phase changes are given in Table 1 and 2.

(TCNQ).<sup>17,18</sup> Via this approach very high room-temperature conductivities up to  $7 \times 10^4$  S/m for metal free Pc(I<sub>3</sub>)<sub>0.33</sub> in the Pc stacking direction have been reported with an anisotropy of  $\geq 500$ .<sup>19</sup> In such highly doped materials the supramolecular structure may however differ considerably from that of the undoped material.<sup>18</sup>

To obtain mesomorphic Pc materials, long aliphatic chains are substituted at the periphery of the macrocycle.<sup>4,20–29</sup> The compounds studied in the present paper are shown in Figure 1. On precipitation from solution the peripherally substituted Pc moieties aggregate into columnar stacks with the alkyl chains filling the medium in between. In most cases precipitation at close to room temperature results in a crystalline solid: the K phase. In this phase the Pc units are invariably tilted with respect to the columnar axis, similar to the arrangement of Pc units in pure phthalocyanine. The liquid-crystalline phase is entered at a temperature which depends on the length and type of aliphatic chain and the type of coupling to the Pc unit. In the mesophase the hydrocarbon chains are found to be liquid-like by X-ray diffraction<sup>4,20,22,24–29</sup> and solid-state NMR.<sup>30</sup> The Pc stacking, and thus the  $\pi$ - $\pi$  overlap, is however preserved. Therefore one might expect charge carriers to still be mobile in this more easily processed liquid-crystalline phase. Indeed it has been suggested that the mobility might even increase substantially at the solid to mesophase transition if the Pc moieties become horizontally stacked as they do for some of the compounds represented in Figure 1.<sup>31</sup> This expectation is based on larger cofacial  $\pi$ - $\pi$  overlap in the horizontal as compared to the tilted arrangement.<sup>32</sup>

The most highly branched of the alkoxy derivatives in Figure 1, PcOC12,3, deviates from the general behavior in that it displays liquid-crystalline behavior with horizontal stacking from  $-100$  °C up to its melting point at  $185$  °C.<sup>33</sup> This makes it a particularly interesting candidate for application in thin-film and molecular alignment studies.

Several reports have appeared in the literature describing the conductive properties of discotic liquid-crystalline materials as a function of temperature, in their different aggregation states. Papers have appeared on mesomorphic phthalocyanines,<sup>25,34–37</sup> triphenylenes,<sup>38–45</sup> porphyrins,<sup>46</sup> bis(3,4-nonyloxybenzoyl)methanocopper,<sup>43</sup> and tetrabenzyldecyldithiopyranilidene.<sup>47,48</sup> To measure the one-dimensional charge carrier mobilities along the stacking axis is however not an easy task, particularly in the solid state since large single crystals have not as yet been grown from these materials. Therefore two or four probe dc and ac conductivity studies on pressed powder pellets of the materials have most commonly been applied.

Particularly interesting is the behavior of the conductivity at the solid to mesophase and subsequent mesophase to isotropic phase transitions. The dc and ac conductivity in doped triphenylenes<sup>38–41,43</sup> have been found to remain either unchanged or to increase stepwise at the solid to mesophase transition. Similar effects are observed at the mesophase to isotropic phase transition with in addition a slight decrease being observed for some

(17) Petersen, J. L.; Schramm, C. S.; Stojakovic, D. R.; Hoffman, B. M.; Marks, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 286–288.

(18) Marks, T. J. *Angew., Chem. Int. Ed. Engl.* **1990**, *29*, 857–879.

(19) Inabe, T.; Marks, T. J.; Burton, R. L.; Lyding, J. W.; MacCarthy, W. J.; Kannewurf, C. R.; Reiser, G. M.; Herstein, F. H. *Solid State Commun.* **1985**, *54*, 501–503.

(20) Guillon, D.; Weber, P.; Skoulios, A.; Piechocki, C.; Simon, J. *Mol. Cryst. Liq. Cryst.* **1985**, *130*, 223–229.

(21) Hanack, M.; Beck, A.; Lehmann, H. *Synthesis* **1987**, 703–705

(22) Masurel, D.; Sirlin, C.; Simon, J. *New J. Chem.* **1987**, *11*, 455–456.

(23) Cook, M. J.; Daniel, M. F.; Harrison, K. J.; McKeown, N. B.; Thomson, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1086–1088.

(24) Guillon, D.; Skoulios, A.; Piechocki, C.; Simon, J.; Weber, P. *Mol. Cryst. Liq. Cryst.* **1983**, *100*, 275–284.

(25) van der Pol, J. F.; Neeleman, E.; Zwicker, J. W.; Nolte, R. J. M.; Drenth, W.; Aerts, J.; Visser, R.; Picken, S. J. *Liq. Cryst.* **1989**, *6*, 577–592.

(26) van der Pol, J. F.; Zwicker, J. W.; Nolte, R. J. M.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 615–620.

(27) Ohta, K.; Jacquemin, L.; Sirlin, C.; Bosio, L.; Simon, J. *New J. Chem.* **1988**, *12*, 751–754.

(28) Dulog, L.; Gittinger, A. *Mol. Cryst. Liq. Cryst.* **1992**, *213*, 31–42.

(29) Simon, J.; Bassoul, P. In *Phthalocyanines, properties and applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, 1993; Vol. 2, pp 225–299.

(30) Kentgens, A. P. M.; Markies, B. A.; van der Pol, J. F.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1990**, *112*, 8800–8806.

(31) Schultz, H.; Lehmann, H.; Rein, M.; Hanack, M. *Struct. Bonding* **1991**, *74*, 41–146.

(32) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.

(33) Schouten, P. G.; van der Pol, J. F.; Zwicker, J. W.; Drenth, W.; Picken, S. J. *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 291–305; *ibid* **1991**, *208*, 109.

(34) Belarbi, Z.; Maitrot, M.; Ohta, K.; Simon, J.; André, J.-J.; Petit, P. *Chem. Phys. Lett.* **1988**, *143*, 400–403.

(35) Belarbi, Z.; Sirlin, C.; Simon, J.; André, J.-J. *J. Phys. Chem.* **1989**, *93*, 8105–8110.

(36) Belarbi, Z. *J. Phys. Chem.* **1990**, *94*, 7334–7336.

(37) Kasuga, K.; Mihara, T.; Nakao, T.; Takahashi, K. *Inorg. Chim. Acta* **1991**, *189*, 11–12.

(38) van Keulen, J.; Warmerdam, T. W.; Nolte, R. J. M.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 534–536.

(39) Boden, N.; Bushby, R. J.; Clements, J.; Jesudason, M. V.; Knowles, P. F.; Williams, G. *Chem. Phys. Lett.* **1988**, *152*, 94–99.

(40) Boden, N.; Bushby, R. J.; Clements, J. *J. Chem. Phys.* **1993**, *98*, 5920–5931.

(41) Vaughan, G. B. M.; Heiney, P. A.; McCauley, J. P.; Smith III, A. B. *Phys. Rev. B* **1992**, *46*, 2787–2791.

(42) (a) Adam, D.; Closs, F.; Frey, T.; Funhoff, D.; Haarer, D.; Ringsdorf, H.; Schuhmacher, P.; Siemensmeyer, K. *Phys. Rev. Lett.* **1993**, *70*, 457–460. (b) Adam, D.; Haarer, D.; Closs, F.; Frey, T.; Funhoff, D.; Siemensmeyer, K.; Schuhmacher, P.; Ringsdorf, H. *Ber. Bunsenges. Phys. Chem.* **1993**, *97*, 1366–1370.

(43) Godquin-Giroud, A. M.; Sigaud, G.; Achard, M. F.; Hardouin, F. *J. Physique Lett.* **1984**, *45*, L387–L392.

(44) Closs, F.; Siemensmeyer, K.; Frey, T.; Funhoff, D. *Liq. Cryst.* **1993**, *14*, 629–634.

(45) Benge, H.; Closs, F.; Frey, T.; Funhoff, D.; Ringsdorf, H.; Siemensmeyer, K. *Liq. Cryst.* **1993**, *15*, 565–574.

(46) Shimizu, Y.; Ishikawa, A.; Kusabayashi, S. *Chem. Lett.* **1986**, 1041–1044; **1991**, 25–28.

(47) Kormann, R.; Zuppiroli, L.; Gionis, V.; Strzelecka, H. *Mol. Cryst. Liq. Cryst.* **1986**, *133*, 283–290.

(48) Gionis, V.; Strzelecka, H.; Veber, M.; Kormann, R.; Zuppiroli, L. *Mol. Cryst. Liq. Cryst.* **1986**, *137*, 365–372.

derivatives. An abrupt decrease in the photoconductivity of alkoxy substituted triphenylenes at the D  $\rightarrow$  I transition has recently been reported.<sup>45</sup> A dc photoconductivity study on a mesomorphic porphyrin<sup>46</sup> showed the conductivity to increase at the K  $\rightarrow$  D transition and to decrease at the D  $\rightarrow$  I transition. In the work of Giroud-Godquin<sup>43</sup> no sudden changes were observed at the phase transitions of the discotic liquid-crystalline compounds studied. The work of Belarbi et al.<sup>34-36</sup> mainly deals with mesomorphic Li and Lu substituted Pcs. They observed an increase in the ac conductivity at both K  $\rightarrow$  D and D  $\rightarrow$  I phase transitions. Impedance measurements in the  $10^{-1}$ – $6.5 \times 10^4$  Hz range by van der Pol et al.<sup>25</sup> on Cu substituted PcOC12 showed a decrease by a factor of 3 at the K  $\rightarrow$  D transition. Also in the work of Kormann et al.<sup>47</sup> using a microwave reflection technique in the 0.1–1 GHz region the conductivity was reported to decrease at the K  $\rightarrow$  D transition in a TCNQ doped columnar mesomorphic material. The literature data are clearly inconsistent with respect to the influence of phase changes on the conductive properties. This is also the case for the temperature dependence of the dc and ac conductivity in the different aggregation states.

Most of the conductivity studies referred to above were performed on doped materials and yield values for the conductivity rather than the mobility of the charge carriers since the concentration of charge carriers generated on doping is usually unknown. Furthermore, as mentioned previously, the high dopant concentrations used may cause significant changes in the phase transition characteristics of the materials and even more importantly may change the secondary and tertiary molecular ordering.<sup>34,35,38-41</sup>

In the recent work of Adam et al.<sup>42</sup> charge carrier mobilities were measured for the first time in thin films of a pure discotic liquid-crystalline material, hexapentyloxytriphenylene, using a flash-photolysis time of flight technique. Weakly temperature dependent values of  $0.8 \times 10^{-7}$  m<sup>2</sup>/Vs for the hole and *ca.*  $1 \times 10^{-9}$  m<sup>2</sup>/Vs for the electron mobility were found in the mesophase in which the discotic molecules were assumed to be oriented with the stacking axis perpendicular to the electrode surface. In the solid, mobility values could not be extracted from the current transients due to the fact that the charge carriers became deeply trapped as a result of the microcrystalline structure.

In an attempt to obtain more insight into the properties of charge carriers in undoped materials we have applied the pulse-radiolysis time resolved microwave conductivity (PR-TRMC) technique.<sup>49-54</sup> Using a short (nanosecond) pulse of high energy radiation charge carriers are homogeneously produced in the bulk material. The radiation induced charge carrier concentration is only approximately 10 micromolar or less which does not affect the structural properties of the material. The energy deposited in the sample volume is accurately known from which the initial yield of electron-hole pairs formed can be estimated. With the high, 26.5–38 GHz, microwave frequencies used in PR-TRMC measurements no field induced drift of charge carriers to domain boundaries or polarization of the sample is brought about. Therefore the microwave conductivity measured reflects the motion of the charge carriers in organized domains within the sample studied. An important practical advantage is that the TRMC-technique is a contactless method free from space charge limited currents and electrode interface effects.

Results obtained using the PR-TRMC technique have been

(49) Warman, J. M.; de Haas, M. P. *Pulse radiolysis of irradiated systems*; Tabata, Y., Ed.; CRC: Boca Raton, 1991; pp 101–133.

(50) Warman, J. M. *The study of fast processes and transient species by electron pulse radiolysis*; Baxendale, J. H., Busi, F., Eds; Reidel: Dordrecht, 1982; pp 129–161.

(51) Infelta, P. P.; de Haas, M. P.; Warman, J. M. *Radiat Phys. Chem.* 1977, 10, 353–365.

(52) Warman, J. M.; de Haas, M. P.; Wentinck, H. M. *Radiat. Phys. Chem.* 1989, 34, 581–586.

(53) Schouten, P. G.; Warman, J. M.; de Haas, M. P. *J. Phys. Chem.* 1993, 97, 9863–9870.

(54) de Haas, M. P. Ph.D. Thesis, University of Leiden, 1977.

previously reported for octadodecoxyphthalocyanine (PcOC12)<sup>55</sup> and for octanonoxethylporphyrin.<sup>56</sup> These have shown marked decreases to occur in the radiation-induced conductivity at both the K  $\rightarrow$  D and D  $\rightarrow$  I transitions. In this paper we present an extensive PR-TRMC study of the radiation induced conductivity in mesomorphic Pcs with particular attention given to the effects of chain modifications, such as varying the length, the branching, and the type of coupling of the alkyl chains to the macrocycle. The results are discussed in terms of the changes occurring in the one-dimensional, intracolumnar, charge carrier mobilities, and comparisons are made with the findings of previous dc and low-frequency ac conductivity measurements on discotic mesomorphic materials. This paper deals only with the radiation-induced conductivity determined immediately following an ionizing pulse of a few nanoseconds duration. The decay of the conductivity, due to charge carrier recombination and/or trapping, will be the subject of a subsequent article.

## Experimental Section

**Materials.** The mesomorphic phthalocyanine derivatives studied in the present work are shown in Figure 1. The methods of synthesis and characterization have been published previously.<sup>24-27,33,57-61</sup> Small angle X-ray scattering (SAXS) and polarization microscopy (PM) show that these disclike molecules stack in columns in both the solid (K) and discotic liquid-crystalline phase (D). In Tables 1 and 2 the phase transition temperatures obtained by differential scanning calorimetry (DSC) and the types of mesophase are summarized.

For the *n*-alkoxyphthalocyanines<sup>25-27</sup> the solid phase consists of molecules stacked with the Pc macrocycles tilted with respect to the columnar axis leading to a center-to-center distance of approximately 4.3 Å. In the mesophase the macrocycles change to horizontal stacking with a center-to-center distance of 3.4 Å. As a result the packing of the columns becomes hexagonal, D<sub>h</sub>. On cooling a large hysteresis is observed for the D  $\rightarrow$  K transition.

The *n*-alkoxymethyl- and *n*-alkylphthalocyanine derivatives PcCH<sub>2</sub>-OC12 and PcC12 are also found to stack with tilted Pc cores in the solid, resulting in an orthorhombic lattice of columns.<sup>27</sup> In the mesophase no reflection at 3.4 Å is found. This has been interpreted as being due to a disordered horizontal stacking of the macrocycles in the column.<sup>4,24</sup> In a recent publication<sup>62</sup> it is argued that for these compounds the tilting persists in the mesophase with a center-to-center distance of 4.9 Å and a (pseudohexagonal) rectangular packing of the columns, D<sub>r</sub>.

Branching in the hydrocarbon chains results in large changes in the phase transition temperatures and sometimes also affects the packing of the columns in the mesophases. When the alkyl chains of the hexyloxy substituted Pc are branched at the  $\beta$  carbon atom with an ethyl group, to give PcOC6,1, the K  $\rightarrow$  D transition temperature increases from 94 °C for the *n*-octa-oxy compound to 158 °C for its branched isomer.<sup>59</sup> The enthalpy change at the K  $\rightarrow$  D transition of PcOC6,1 is much smaller than for the linear chain isomer. The first mesophase at 158 °C has been reported<sup>57</sup> to consist of a tetragonal lattice of columns which undergoes a transition to a nematic liquid-crystalline phase at 224 °C.

When the *n*-alkoxy chains are branched with methyl groups as for PcOC8,2 and PcOC12,3, various effects are found.<sup>33</sup> For PcOC8,2 it was observed that when precipitated from solution a crystalline powder was obtained which showed a K  $\rightarrow$  D<sub>h</sub> transition at a temperature of 70 °C, 24 °C lower than for the linear chain PcOC8. The D<sub>h</sub> mesophase of PcOC8,2 displayed supercooling with the return to the crystalline phase taking several hours at room temperature. For PcOC12,3 a D<sub>h</sub> mesophase with horizontal stacked molecules was observed even at room temperature for the freshly precipitated material. On heating an

(55) Schouten, P. G.; Warman, J. M.; de Haas, M. P.; van der Pol, J. F.; Zwikker, J. W. *J. Am. Chem. Soc.* 1992, 114, 9028–9034.

(56) Schouten, P. G.; Warman, J. M.; de Haas, M. P.; Fox, M. A.; Pan, H.-L. *Nature* 1991, 353, 736–737.

(57) Lelievre, D.; Petit, M. A.; Simon, J. *Liq. Cryst.* 1989, 4, 707–710.

(58) Engel, M. K.; Bassoul, P.; Bosio, L.; Lehmann, H.; Hanack, M.; Simon, J. *Liq. Cryst.* 1993, 15, 709–722.

(59) Ford, W. T.; Sumner, L.; Zhu W.; Chang, Y. H.; Um, P.; Choi, H.; Heiney, P. A.; Maliszewskij, C. *New J. Chem.* in press

(60) van Nostrum, C. F.; Bosman, A. W.; Gelinck, G. H.; Picken, S. J.; Schouten, P. G.; Warman, J. M.; Schouten, A. J.; Nolte, R. J. M. *J. Chem. Soc. Chem., Commun.* 1993, 1120–1122.

(61) van der Pol, J. F. Ph.D. Thesis, University of Utrecht, 1990.

(62) Weber, P.; Guillon, P.; Skoulios, A. *Liq. Cryst.* 1991, 9, 369–382.

**Table 1.** Linear Alkyl Chains: Phase Transition Temperatures and Enthalpy Changes Determined by DSC and Structural Assignment from X-ray Diffraction and Polarization Microscopy<sup>a</sup>

compd	RT phase	T (°C) K → D	T (°C) D → K	ΔH (kJ/mol) K → D	discotic phase	T (°C) <sup>a</sup> D → I	ΔH (kJ/mol) D → I	source
PcOC1	K	<i>b</i>						61
PcOC5 <sup>c</sup>	K	121	70	36	D <sub>7</sub>	>350		this work <sup>f</sup>
PcOC6	K	119	86	72	D <sub>h</sub>	>350		25
		102		50				29
PCOC8	K	94	77	98	D <sub>h</sub>	>350		25
		94		75				29
		96		90				59
PCOC9	K	101	71	94	D <sub>h</sub>	>350		25
		107		112				this work
PcOC11	K	83	66	108	D <sub>h</sub>	334 <sup>d</sup>		25
PcOC12	K	83	65	109	D <sub>h</sub>	309 <sup>d</sup>		25
		91		130				27, 29
		91		110				59
PcOC18	K	98	65	239	D <sub>h</sub>	247	18	this work
PcCH <sub>2</sub> OC12	K	78	55	115	D <sub>r</sub>	260	4.6	24
PcC10 <sup>e</sup>	K	163	155	53	D <sub>r</sub>	282	8.2	58

<sup>a</sup> Less than 2 °C hysteresis for I → D. <sup>b</sup> This compound does not show a mesophase. <sup>c</sup> During first heating a K → K' transition is observed at 81 °C with ΔH = 19.4 kJ/mol. No X-ray diffraction was performed on this material, polarization microscopy indicated a mesophase above 121 °C. <sup>d</sup> Under polarization microscope, accompanied by decomposition. <sup>e</sup> K → K' transitions are observed at 132 and 138 °C on heating. <sup>f</sup> Use was made of a Mettler 7 DSC apparatus. <sup>g</sup> Symbols used: RT = room temperature, K = crystalline phase, D = discotic mesophase, D<sub>h</sub> = hexagonal discotic, D<sub>r</sub> = rectangular discotic, and I = isotropic liquid.

**Table 2.** Branched Alkyl Chains: Phase Transition Temperatures and Enthalpy Changes Determined by DSC and Structural Assignment from X-ray Diffraction and Polarization Microscopy<sup>c</sup>

compd	RT phase	T (°C) transition	ΔH (kJ/mol) transition	transition	source
PcOC6,1	K	158	4.6	K → D <sub>t</sub>	57–59
		224	7.6	D <sub>t</sub> → N <sub>D</sub>	
		255	3.3	N <sub>D</sub> → I	
PcOC8,2	K, D <sub>h</sub> <sup>a</sup>	70	54.6	K → D <sub>h</sub>	33
		295	8.3	D <sub>h</sub> → I	
PcOC8,2*	D <sub>h</sub> <sup>*</sup>	16	6.4	D <sub>7</sub> → D <sub>h</sub> <sup>*</sup>	60
		111	3.1	D <sub>h</sub> <sup>*</sup> → D <sub>7</sub>	
		295	10.9	D <sub>7</sub> → I	
PcOC12,3	D <sub>h</sub>	34	12.6	D <sub>h</sub> → D <sub>h</sub>	33
		173	0 <sup>b</sup>	D <sub>h</sub> → D <sub>h</sub>	
		185	4.9	D <sub>h</sub> → I	

<sup>a</sup> D<sub>h</sub> is supercooled and slowly reverts to K at RT. <sup>b</sup> Observed only by polarization microscopy. <sup>c</sup> Symbols used: RT = room temperature, K = crystalline phase, D = discotic mesophase, D<sub>h</sub> = hexagonal discotic, D<sub>t</sub> = tetragonal discotic, D<sub>h</sub><sup>\*</sup> = optically active hexagonal discotic, D<sub>7</sub> = unassigned discotic, N<sub>D</sub> = nematic discotic, and I = isotropic liquid.

irreversible enthalpy change was measured by DSC at 34 °C. SAXS data before and after this transition temperature showed the 3.4 Å reflection to change from very sharp to a more diffuse halo indicating the horizontal intracolumnar order to have decreased. Polarization microscopy indicates the D<sub>h</sub> phase to change at 173 °C, but no corresponding change in the X-ray diffraction pattern is observed. The PcOC12,3 compound was found to have a mesophase to isotropic phase transition at 185 °C, much lower than the *n*-alkoxy compounds.

In the previous paragraph PcOC8,2 refers to a mixture of stereoisomers. When PcOC8,2 was synthesized with one enantiomer of branched alkoxy chains yielding PcOC8,2\*, this material proved to be liquid-crystalline at room temperature with horizontally stacked Pc units and hexagonally packed columns even when freshly precipitated.<sup>60</sup> The SAXS pattern at 80 °C showed 3.4 Å satellite reflections at 3.2 and 3.6 Å which have been interpreted to indicate a helical superstructure with a periodicity of 55 Å which includes 16 Pc molecules. This is supported by a spiral texture under the polarization microscope. This hexagonal helical columnar phase is denoted D<sub>h</sub><sup>\*</sup>. At 16 °C a transition from an unknown phase to the D<sub>h</sub><sup>\*</sup> mesophase was found on heating from 0 °C. At 111 °C a transition to another columnar mesophase was observed whose packing could not be determined unequivocally by SAXS. The accompanying enthalpy changes of the two transitions are however very low, 6.4 and 3.1 kJ/mol, respectively. For both PcOC8,2 and PcOC8,2\* the D → I transition occurs at the same temperature of 295 °C with ΔH values of 8.3 and 10.9 kJ/mol, respectively.

**Pulse-Radiolysis Time Resolved Microwave Conductivity.** The samples were contained in a microwave cell consisting of a piece of rectangular

waveguide of cross section 7.1 × 3.55 mm<sup>2</sup> closed at one end with a metal plate.<sup>53</sup> Approximately 200 mg of a sample was compressed by hand into the cell using a close-fitting, rectangular, Teflon plunger. The weight and length of the sample were accurately measured. The temperature of the cell could be varied over the range of -100 to +200 °C. When less material was available use was made of a perspex block with a rectangular shaped cavity of 2 × 6 × 3 mm<sup>3</sup> dimension which could be filled with approximately 25 mg of material.<sup>53</sup> This perspex block was then placed in the microwave cell. Using the perspex block the upper temperature was limited to 120 °C.

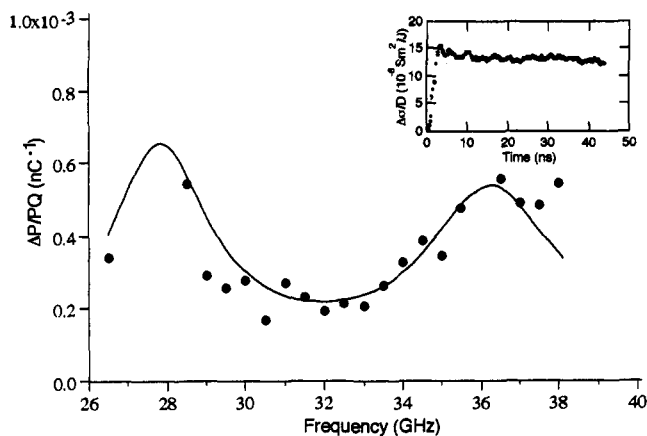
The samples were ionized by pulsed irradiation with 3 MeV electrons from a Van de Graaff accelerator using pulse widths of 2–50 ns. The integrated beam charge per pulse, *Q* (in nC), was monitored routinely. The energy deposition is close to uniform throughout the sample and equal to 0.58Q Gy (1 Gy = 1 J/kg), measured using thin-film radiochromic dosimeters (Far West technology Nr92).<sup>53</sup> A single 10 ns, 4 A pulse as used in the present study therefore corresponds to an energy deposition of 23 Gy in the material studied. Taking an average energy of 25 eV for the formation of one electron-hole pair,<sup>63–65</sup> this dose corresponds to the formation of 5.8 × 10<sup>21</sup> pairs/m<sup>3</sup> in unit density, i.e., 1 g/cm<sup>3</sup>, material, i.e., a concentration of 10<sup>-5</sup> molar of charge carrier pairs. In a separate paper<sup>53</sup> it is shown that the typical accumulated dose of 10–20 kGy used in a PR-TRMC study has no effect on the conductivity change at the end of the pulse, Δσ<sub>oop</sub>, for the present type of compounds. In fact Δσ<sub>oop</sub> was found to be unaffected up to an accumulated dose of 100 kGy.

Changes in the conductivity of a sample upon pulsed irradiation were monitored as changes in the microwave power reflected by the sample. Changes in the output of the microwave detector diode were monitored using a Tektronix 7912 digital oscilloscope with a time resolution of 1 ns. To monitor the decay kinetics, transient data from 10 ns to 5 ms could be measured using a tandem combination of a Tektronix 2205 oscilloscope (7A13 plug-in) and a Sony/Tektronix RTD 710 digitizer. A typical PR-TRMC trace at short times is shown in the inset to Figure 2.

For small changes the change in reflected microwave power, Δ*P*, is directly proportional to the radiation induced conductivity change, Δσ. In Figure 2 the fractional absorption in microwave power, Δ*P*/*P*, per unit beam charge measured at the end-of-pulse is shown as a function of the microwave frequency from 26.5 to 38 GHz. The sinusoidal variation in Δ*P*/*P* with frequency is due to interference effects resulting from the similarity between the wavelength of the microwaves and the length of the sample. The sinusoidal form of the curve is determined by the length and dielectric constant, ε', of the sample and the absolute height by the magnitude of the radiation induced conductivity. Such a frequency dependence can be fitted with ε' and Δσ as fitting parameters using

(63) Schmidt, W. F.; Allen, A. O. *J. Phys. Chem.* 1968, 72, 3730–3736.  
(64) Warman, J. M. *The study of fast processes and transient species by electron pulse radiolysis*; Baxendale, J. H., Busi, F., Eds; Reidel: Dordrecht, 1982; pp 433–533.

(65) Hummel, A. In *The Chemistry of Alkanes and Cycloalkanes*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1992; pp 743–780.



**Figure 2.** The frequency dependence of the fractional absorption in microwave power at end of pulse per nanocoulomb beam charge. The solid line is the result of the fitting procedure as described in refs 51–53 from which the absolute value of the conductivity change is determined. Inset: a typical conductivity change as monitored using the PR-TRMC technique for PcOC12 at room temperature using a 2 ns pulse.

computational procedures described previously.<sup>49–51</sup> An example of such a fit is shown by the solid line in Figure 2. The radiation-induced conductivity changes measured in the present study usually lie between  $10^{-4}$  and  $10^{-3}$  S/m. This is at least 8 orders of magnitude higher than estimated for the intrinsic conductivity due to charge carriers in the unirradiated, pure material.<sup>35</sup> A dark background microwave conductivity found in the present samples is attributed to dipolar loss and has been discussed in previous publications.<sup>66–68</sup>

## Results and Discussion

In this section first the experimental radiation-induced conductivity data are presented and discussed. This is followed by a discussion of the derivation of estimates of the concentration of charge carriers formed during the pulse which contribute to the conductivity observed. The resultant estimates of the charge carrier mobilities derived from the radiation induced conductivity are then discussed and compared with data available in the literature.

**Radiation Induced Conductivity Transients.** On pulsed irradiation readily measurable conductivity transients were observed for all of the peripherally substituted phthalocyanines studied in the present work except for PcOC1. In the inset of Figure 2 a typical nanosecond time scale conductivity transient is shown as measured for PcOC12 at room temperature. This type of trace was used to determine the value of the conductivity change in the material at the end of the pulse,  $\Delta\sigma_{\text{eop}}$  (S/m), which is normalized to the amount of energy deposited in the pulse, the dose  $D$  (J/m<sup>3</sup>). At longer times the conductivity relaxes back to zero with kinetics controlled by charge carrier localization and recombination. The after-pulse conductivity decay kinetics will be the subject of a subsequent paper.<sup>69</sup> In this paper we will focus our attention on the dose normalized end-of-pulse conductivity,  $\Delta\sigma_{\text{eop}}/D$ .

In conventional steady-state, DC conductivity measurements on molecular solids the conductivity measured is usually mainly controlled by charge carrier trapping and detrapping at domain boundaries and lattice defects as has been discussed by Silinsh.<sup>70</sup> In the context of the present nanosecond pulsed ionization, ultrahigh frequency conductivity study it is of interest to estimate the average time taken for a charge carrier formed within an

organized domain to reach the domain boundary either by diffusion or electric field induced drift. Taking the average domain dimension to be  $\langle d \rangle$ , the time for one-dimensional diffusion over this distance for a charge carrier of mobility  $\mu$  is

$$\tau_D = e\langle d \rangle^2 / 2\mu k_B T \quad (1)$$

Taking the room temperature mobility of  $1 \times 10^{-4}$  m<sup>2</sup>/Vs<sup>10,11</sup> determined along the C-axis of single crystal phthalocyanine to be a reasonable estimate of the maximum value of  $\mu$  for the present systems results in

$$\tau_D \geq 2 \times 10^5 \langle d \rangle^2 \quad (2)$$

The sharp X-ray diffraction and well defined polarization microscopy patterns for the present compounds<sup>25,26,29,33,61,71</sup> are indicative of organized domains of dimensions of hundreds of angstroms at least. An estimate of the average number of columnar stacked Pc units within a domain in the mesophase of an alkoxy substituted derivative of  $\geq 4000$  has been made.<sup>72</sup> This corresponds to  $\langle d \rangle \geq 1 \mu\text{m}$  and hence  $\tau_D > 200$  ns. This lower limit is an order of magnitude longer than the time scale on which  $\Delta\sigma_{\text{eop}}/D$  is measured.

In the presence of an electric field it is possible that charge carriers are drawn to domain boundaries more rapidly than by diffusion alone due to drift in the direction of the applied electric field. The time for field induced drift across a domain,  $\tau_E$ , is given for a DC field by

$$\tau_E = \langle d \rangle / \mu E \quad (3)$$

The maximum field strength corresponding to the microwave power levels of ca. 100 mW used in the present experiments is approximately 1000 V/m. Using  $1 \times 10^{-4}$  m<sup>2</sup>/Vs for  $\mu$  and  $\langle d \rangle \geq 1 \mu\text{m}$  results in an estimate of  $\geq 10 \mu\text{s}$  for  $\tau_E$ . This is many orders of magnitude longer than the reciprocal radian frequency of ca. 5 ps for the Ka-band microwaves used. The charge carriers are therefore subjected to only a very small perturbation from their normal diffusional motion in the presence of the microwave field. Field induced drift will therefore be negligible.

In view of the above we conclude that the values of  $\Delta\sigma_{\text{eop}}/D$  measured reflect the properties of charge carriers as initially formed within organized domains, uninfluenced by effects due to domain boundaries. Within domains there is the possibility that extrinsic impurities or radiation produced damage could influence the charge carrier mobilities. As to the former, we have for some compounds used materials from different synthetic batches and laboratories and have found no difference in the  $\Delta\sigma_{\text{eop}}/D$  values obtained. This together with general similarity in the absolute magnitudes of the conductivity transients, in particular those for the alkoxy derivatives shown in Figure 3, indicate that the results are not controlled by spurious traces of impurities.

With respect to possible effects of radiation damage, it has been pointed out that phthalocyanine is one of the least radiation-sensitive organic structures.<sup>73</sup> The absorbed energy necessary to modify a single molecule has been determined to be  $2.5 \times 10^4$  eV.<sup>74</sup> In the present experiments the dose given to a sample by a single 10 ns pulse is ca. 20 kJ/m<sup>3</sup>. The concentration of Pc units undergoing modification for this dose is therefore  $5 \times 10^{18}$  m<sup>-3</sup> or only approximately 1 molecule in  $10^8$ . In a thorough study of energy deposition and dose effects<sup>53</sup> for the present type of compounds, we have in fact found  $\Delta\sigma_{\text{eop}}/D$  to be independent of accumulated dose from 10 kJ/m<sup>3</sup> up to more than 100 MJ/m<sup>3</sup>.

(66) van der Pol, J. F.; de Haas, M. P.; Warman, J. M.; Drenth W. *Mol. Cryst. Liq. Cryst.* **1990**, *183*, 411–420; **1991**, *195*, 307–308.

(67) Schouten, P. G.; Wenning, C.; de Haas, M. P.; van der Pol, J. F.; Zwikker, J. W. *Synth. Metals* **1991**, *42*, 2665–2668.

(68) Schouten, P. G.; Warman, J. M.; de Haas, M. P.; Pan, H.-L.; Fox, M. A. *Mol. Cryst. Liq. Cryst.* **1993**, *235*, 115–120.

(69) Manuscript in preparation.

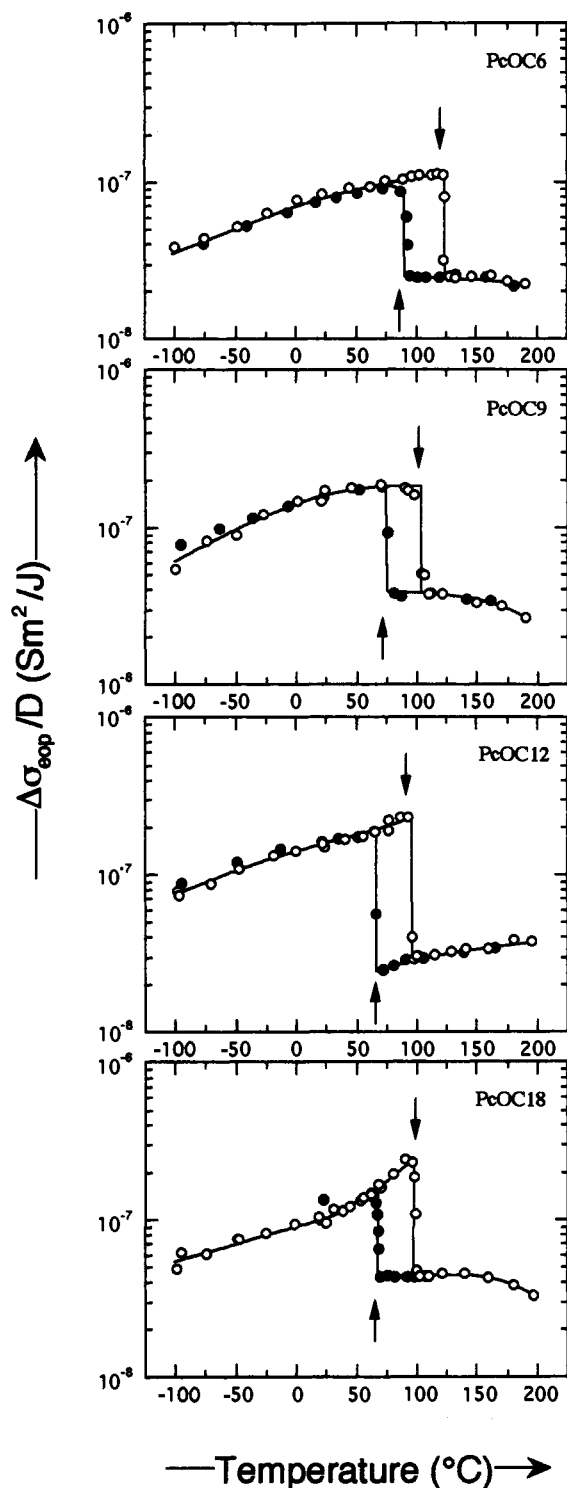
(70) Silinsh, E. A. *Organic Molecular Crystals*; Solid-State Sciences Nr 16, Springer Verlag: Berlin, 1980.

(71) Vacus, J.; Doppelt, P.; Simon, J.; Memetizidis, G. *J. Mater. Chem.* **1992**, *2*, 1065–1068.

(72) Blass, G.; Dirksen, G. J.; Meijerink, A.; van der Pol, J. F.; Neeleman, E.; Drenth, W. *Chem. Phys. Lett.* **1989**, *154*, 420–424.

(73) Zuppiroli, L. *Radiation Effects* **1982**, *62*, 53–68.

(74) Howitt, D. G.; Thomas, G. *Radiation Effects* **1977**, *34*, 209–215.



**Figure 3.** Dose normalized end-of-pulse conductivity versus temperature for the *n*-alkoxy substituted Pc derivatives shown on heating (open circles) and cooling (filled circles). The arrows indicate the K → D and D → K transition temperatures.

The latter dose is an order of magnitude larger than the total accumulated dose given to a sample in a complete PR-TRMC study. We are confident therefore that the  $\Delta\sigma_{\text{eop}}/D$  values measured are free from effects due to radiation damage.

The end-of-pulse conductivity per unit dose is related to the mobility of the charge carriers present by<sup>55</sup>

$$\Delta\sigma_{\text{eop}}/D = [\mu(+) + \mu(-)]W_{\text{eop}}/E_p \quad (\text{Sm}^2/\text{J}) \quad (4)$$

In (4),  $\mu(+)$  and  $\mu(-)$  are the mobilities in  $\text{m}^2/\text{Vs}$  of the positive

and negative charge carriers,  $E_p$  is the average energy in electron volts required to form one  $e^-h^+$  pair, and  $W_{\text{eop}}$  is the fraction of the charge carriers formed within the pulse that still survive at the end, i.e., do not undergo rapid, in-pulse recombination. Values of  $E_p$  and  $W_{\text{eop}}$  can be used to derive absolute estimates of the mobilities from the present data as will be discussed in a later section. Since  $E_p$  is independent of temperature and  $W_{\text{eop}}$  is expected to be only weakly dependent on temperature as discussed later,  $\Delta\sigma_{\text{eop}}/D$  should give at least a semiquantitative impression of the changes occurring in the mobilities of the charge carriers.

***n*-Alkoxy Substituents.** Figure 3 shows the temperature dependence of  $\Delta\sigma_{\text{eop}}/D$  for the *n*-alkoxy substituted phthalocyanines of 6, 9, 12, and 18 carbon atoms chain length from  $-100$  to  $+200$  °C. The arrows indicate the temperatures at which the K → D and D → K transitions are found to occur in DSC measurements. As can be seen all four compounds display the same general behavior.  $\Delta\sigma_{\text{eop}}/D$  increases gradually on heating in the solid phase by a factor of  $3.5 \pm 1$  in going from  $-100$  to  $+100$  °C corresponding to a small activation energy of  $0.03 \pm 0.01$  eV. A sudden decrease by a factor of between 5 and 8 is observed at the K → D transition with no apparent trend with an increasing number of carbon atoms in the aliphatic chain. In the mesophase  $\Delta\sigma_{\text{eop}}/D$  changes very little on further heating up to  $200$  °C. PcOC12, which shows the most marked drop at the K → D transition, displays a slight increase in the mesophase, while the others display a slight decrease. When the material recrystallizes on cooling from the mesophase  $\Delta\sigma_{\text{eop}}/D$  returns to the initial level. A pronounced hysteresis of  $25\text{--}30$  °C for the D → K phase transition is found as in the DSC measurements.

In Tables 3 and 4 are listed the values of  $\Delta\sigma_{\text{eop}}/D$  found at room temperature and at temperatures of  $-100$  °C,  $+200$  °C, and 10 degrees below and above the K → D transition temperature for all of the *n*-alkoxy compounds investigated.

**Branched-Chain Alkoxy Substituents.** In Figures 4–6 the temperature dependences of  $\Delta\sigma_{\text{eop}}/D$  for the Pcs with branched alkoxy chains are shown. The compounds are discussed separately below.

**PcOC8,2.** In the crystalline phase of PcOC8,2 the initial value of  $\Delta\sigma_{\text{eop}}/D$  at room temperature was close to that found for the *n*-alkoxy substituted PcOC9. The general temperature behavior on heating the freshly precipitated solid was also very similar with a gradual increase in  $\Delta\sigma_{\text{eop}}/D$  in the solid, a sharp decrease at the K → D transition, and little change on further heating. On cooling however the behavior of PcOC8,2 is quite different. No sudden increase in  $\Delta\sigma_{\text{eop}}/D$  is found at approximately  $25$  °C below the K → D transition as was the case for the *n*-alkoxy compounds. This agrees with the conclusion from DSC that the mesophase is supercooled. The fact that  $\Delta\sigma_{\text{eop}}/D$  remains at the same level in the supercooled mesophase for this compound shows that the structural disorder in the mesophase is frozen in when the temperature is lowered. At room temperature the value of  $\Delta\sigma_{\text{eop}}/D$  eventually returns to the starting level over a period of several hours, i.e., the material slowly recrystallizes to the solid-state structure.

On further cooling PcOC8,2 below room temperature after the initial heating trajectory a small increase in  $\Delta\sigma_{\text{eop}}/D$ , by a factor of 1.3, is seen at close to  $0$  °C. As will be shown in a separate paper, at this transition the lifetime of the radiation induced charge carriers is found to increase by almost two orders of magnitude.<sup>69</sup> An explanation for the small increase in  $\Delta\sigma_{\text{eop}}/D$  could be that the aliphatic chain regions become rigid in a glass transition. No phase transition is apparent at close to  $0$  °C in DSC measurements.

**PcOC12,3.** The level of  $\Delta\sigma_{\text{eop}}/D$  for freshly precipitated PcOC12,3 at room temperature is found to lie almost an order of magnitude lower than for the linear chain analogue PcOC12 and close to the level observed in the mesophase of the latter compound. This agrees with SAXS measurements which show

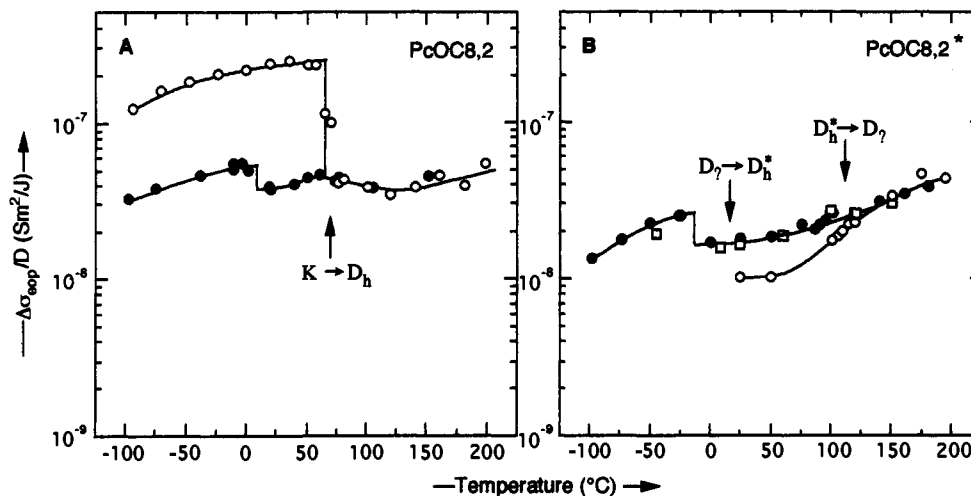
**Table 3.** Room-Temperature Values of  $\Delta\sigma_{\text{eop}}/D$  and the Minimum Mobility  $\Sigma\mu_{\text{min}}$  for the *n*-Alkoxy Pc Compounds Together with Calculated Parameters Discussed in the Text Used To Derive an Absolute Value of the Charge Carrier Mobility  $\Sigma\mu_s$  Given in the Last Column

compd	[Pc] (M)	$\Delta\sigma_{\text{eop}}/D$ ( $10^{-8}$ Sm <sup>2</sup> /J)	$\Sigma\mu_{\text{min}}$ ( $10^{-6}$ m <sup>2</sup> /Vs)	$D(R_n)/D$	$D(R_{n-2})/D$	$W_s$	$\Sigma\mu_s$ ( $10^{-6}$ m <sup>2</sup> /Vs)
PcOC1	1.30	0		0.18		0.79	
PcOC5	0.81	6.4	1.6	0.50	0.31	0.75	7.0
PcOC6	0.74	7.4	1.8	0.55	0.37	0.74	6.8
PcOC8	0.62	14.9	3.7	0.62	0.47	0.72	10.9
PcOC9	0.57	15.6	3.9	0.64	0.50	0.71	10.0
PcOC11	0.49	14.0	3.5	0.69	0.56	0.70	9.0
PcOC12	0.45	15.0	3.7	0.71	0.59	0.69	9.1
PcOC18	0.34	12.0	3.0	0.78	0.70	0.66	6.5
av $\Sigma\mu_s$ for C5–C18							8.5
av jump time (ps)							0.14

**Table 4.** Values of  $\Delta\sigma_{\text{eop}}/D$  at Selected Temperatures for the *n*-Alkoxy Pc's Together with the Corresponding Estimates of the Mobility Sum,  $\Sigma\mu_s^a$ 

compd	$\Delta\sigma_{\text{eop}}/D$ ( $10^{-8}$ Sm <sup>2</sup> /J)				$\Sigma\mu_s$ ( $10^{-6}$ m <sup>2</sup> /Vs)			
	-100	$T_{K \rightarrow D} - 10$	$T_{K \rightarrow D} + 10$	+200	-100	$T_{K \rightarrow D} - 10$	$T_{K \rightarrow D} + 10$	+200
PcOC5		11.0				11.4		
PcOC6	3.7	11.2	2.4	2.2	3.7	9.8	2.1	1.9
PcOC8		21.2	3.7			15.0	2.6	
PcOC9	6.5	17.6	3.7	2.6	5.0	11.9	2.5	1.7
PcOC11		15.6	3.6			9.6	2.2	
PcOC12	7.4	20.0	2.8	3.7	5.1	11.8	1.7	2.1
PcOC18	5.4	22.8	4.4	3.2	3.9	11.8	2.3	1.6
average $\Sigma\mu_s$					4.4	11.6	2.2	1.8
av jump time (ps)					0.47	0.08	0.28	0.27

<sup>a</sup> Also given are the average value for  $\Sigma\mu_s$  and the calculated average jump time.

**Figure 4.** Dose normalized end-of-pulse conductivity versus temperature for PcOC8,2 (A) and PcOC8,2\* (B) on heating (open circles) and cooling (filled circles). For PcOC8,2\* the open squares represent the values for the second heating. The arrows indicate the phase transition temperatures.

that even the freshly precipitated material has the hexagonal columnar stacking characteristic for the mesophase of the *n*-alkoxy derivatives. As shown in Figure 5 the conductivity is almost constant from room temperature down to  $-100$  °C with no indication of a sharp increase attributable to crystallization.

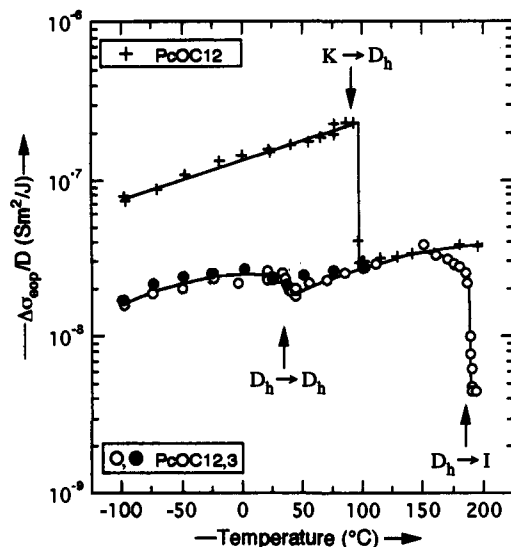
On heating from  $-100$  °C a sudden 20% decrease in  $\Delta\sigma_{\text{eop}}/D$  is observed at the  $D_h \rightarrow D_h$  transition temperature of 34 °C. On further heating, the conductivity changes very little and is close to the values found for PcOC12 in its mesophase up to the clearing point at which a sudden decrease by a factor of 7 occurs. Unfortunately the limitations of the apparatus did not allow the temperature to be increased further into the liquid phase. On cooling from the liquid,  $\Delta\sigma_{\text{eop}}/D$  regains its mesophase level with no significant hysteresis at the  $I \rightarrow D$  transition. No abrupt changes in conductivity are observed on further cooling down to  $-100$  °C.

**PcOC6,1.** The absolute magnitude of  $\Delta\sigma_{\text{eop}}/D$  and the temperature dependence for PcOC6,1 in the solid are found to

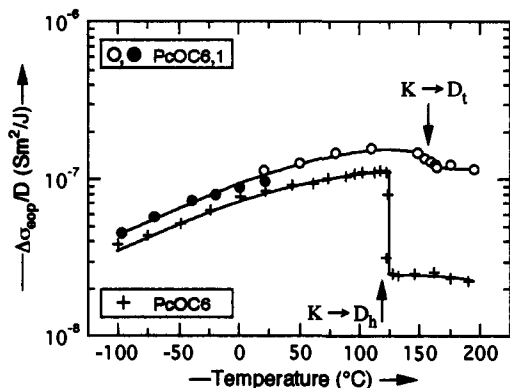
be almost identical to that for the linear chain PcOC6. The behavior of PcOC6,1 and PcOC6 at their solid to mesophase transitions is however completely different as shown in Figure 6. The latter compound shows a sharp decrease in  $\Delta\sigma_{\text{eop}}/D$  by a factor of approximately 5, whereas for PcOC6,1  $\Delta\sigma_{\text{eop}}/D$  decreases by only 20%. Furthermore  $\Delta\sigma_{\text{eop}}/D$  remains above  $10^{-7}$  Sm<sup>2</sup>/J up to 200 °C. The effect of the ethyl branch in PcOC6,1 is clearly quite different to that of the methyl branches in PcOC8,2 and PcOC12,3.

**Chiral Alkoxy Substituent.** The value of  $\Delta\sigma_{\text{eop}}/D$  for freshly precipitated PcOC8,2\* is found to be more than an order of magnitude lower than for PcOC8,2 at room temperature as shown in Figure 4. Furthermore, the optically active compound shows no sharp decrease in conductivity at elevated temperatures as found for PcOC8,2 at its solid to mesophase transition. This is in agreement with the DSC study<sup>60</sup> in which no such phase transition is found for PcOC8,2\*. Apparently a crystalline solid phase is not formed in this material.





**Figure 5.** Dose normalized end-of-pulse conductivity versus temperature for PcOC12,3 on heating (open circles) and cooling (filled circles) together with the heating values for the linear chain analogue PcOC12 (crosses). The arrows indicate the phase transition temperatures.



**Figure 6.** Dose normalized end-of-pulse conductivity versus temperature for PcOC6,1 on heating (open circles) and cooling (filled circles) together with the heating values for linear chain analogue PcOC6 (crosses). The arrows indicate the phase transition temperatures.

Above 150 °C the same value for  $\Delta\sigma_{\text{eop}}/D$  is observed as for PcOC8,2 in its liquid-crystalline phase. On cooling however  $\Delta\sigma_{\text{eop}}/D$  decreases more strongly for the optically active compound. It would appear therefore that the helical stacking of the macrocycles in PcOC8,2\* is less favorable for one-dimensional charge migration. It can be seen in Figure 4 that  $\Delta\sigma_{\text{eop}}/D$  does not return to its starting value on cooling but remains higher by a factor of approximately 2. A slight increase in  $\Delta\sigma_{\text{eop}}/D$  is found at approximately 0 °C, as was observed for PcOC8,2, indicating that also PcOC8,2\* forms a glassy state. A second heating trajectory (open squares) was found to agree with the first cooling trajectory. The low starting value found for the freshly precipitated sample at room temperature was never found again after the first heating trajectory.

***n*-Alkoxyethyl Substituent.** Figure 7A shows the first heating and subsequent cooling results for PcCH<sub>2</sub>OC12. Starting at -100 °C with the freshly precipitated sample the value of  $\Delta\sigma_{\text{eop}}/D$  is about the same as for PcOC12 as shown in Figure 7B where the heating trajectories of PcCH<sub>2</sub>OC12 and PcOC12 are compared. On heating however,  $\Delta\sigma_{\text{eop}}/D$  does not increase as found for the *n*-alkoxy Pcs but remains constant up to the solid to mesophase transition temperature. At this transition  $\Delta\sigma_{\text{eop}}/D$  decreases by a factor of 3 to a level similar to that found for the *n*-alkoxy substituted Pcs in the mesophase. PcCH<sub>2</sub>OC12 does show a

definite further increase in the mesophase which was less marked in the *n*-alkoxy-Pc derivatives.

On cooling it was found that  $\Delta\sigma_{\text{eop}}/D$  underwent a sharp increase at the D → K transition temperature but did not regain its initial value. However when the sample was remeasured a few weeks later  $\Delta\sigma_{\text{eop}}/D$  at room temperature was found to have returned to its starting level. The fact that  $\Delta\sigma_{\text{eop}}/D$  does not reach its starting level immediately when recrystallized to the solid state indicates that partial disorder of the mesophase is retained. This disorder in the stacks does not however result in a difference in the enthalpy change during the first and second heating as measured with DSC. This indicates that this enthalpy effect is mainly determined by the melting of the hydrocarbon chains and that the decrease in columnar order has no significant effect on  $\Delta H$ .

***n*-Alkyl Substituent.** In the initial measurements on freshly precipitated PcC10 at room temperature a very high value of  $\Delta\sigma_{\text{eop}}/D$  was measured; more than four times the largest value found for the *n*-alkoxyphthalocyanines. During the first heating, as shown in Figure 8A,  $\Delta\sigma_{\text{eop}}/D$  increased by more than a factor 2 in going from -100 °C to room temperature after which it remained fairly constant. At the K → D transition temperature of 163 °C a decrease was observed by about a factor of 3. On further heating a second decrease by a factor 2 was found to occur at 187 °C after which  $\Delta\sigma_{\text{eop}}/D$  reaches a value of  $1.10 \times 10^{-7} \text{ Sm}^2/\text{J}$  at 195 °C. This is still about three times higher than the *n*-alkoxy and *n*-alkoxymethyl Pc derivatives in their mesophases. Neither with DSC nor with polarization microscopy has a phase transition been observed at 187 °C for this compound.<sup>58</sup>

On cooling  $\Delta\sigma_{\text{eop}}/D$  increases abruptly at the D → K transition at 155 °C as found by DSC after which it continuously decreases on further cooling. The level attained in the solid is very much lower than found for the freshly precipitated material in the initial heating run. Apparently recrystallization from the mesophase leads to a less ordered columnar structure. As for PcCH<sub>2</sub>OC12 however no difference is observed in the enthalpy change at the K → D transition temperatures during the first and second heating cycles. During subsequent heating/cooling cycles  $\Delta\sigma_{\text{eop}}/D$  is found to behave as displayed in Figure 8B.

**Charge Carrier Yields.** In order to estimate mobilities from  $\Delta\sigma_{\text{eop}}/D$  we need to know the concentration of mobile charge carriers present at the end of the radiation pulse. As has been shown previously<sup>55</sup> in the derivation of eq 4, this amounts to a knowledge of the electron-hole pair formation energy  $E_p$  and the end-of-pulse charge carrier survival probability  $W_{\text{eop}}$ . In previous publications we have presented lower limits to the sum of the charge carrier mobilities,  $\Sigma\mu_{\text{min}}$ . These were calculated by taking for  $E_p$  a value of 25 eV, which is characteristic for hydrocarbon media,<sup>63,64,75</sup> and for  $W_{\text{eop}}$  the maximum possible value of 1. This amounts to the assumption that all primary ionization events lead to long-lived, mobile charge carriers which contribute to the end-of-pulse conductivity observed.

$W_{\text{eop}}$  would in fact be expected to be considerably smaller than 1 for the low dielectric constant, molecular materials studied in the present work. This is due to the average thermalization range of electrons from the parent radical cation subsequent to an ionization event,  $\langle r_{\text{th}} \rangle$ , being much smaller than the Onsager escape distance,  $r_o = e^2/4\pi\epsilon_0\epsilon_r k_B T$  which is 290 Å for  $\epsilon_r = 2$  at room temperature.  $\langle r_{\text{th}} \rangle$  has been determined for a large variety of molecular liquids, and typical values relevant to the present materials are those for cyclohexane and benzene of 66 and 42 Å, respectively.<sup>76,77</sup> Similar values are found in the solid phase, e.g., 48 Å in solid cyclohexane<sup>78</sup> and ca. 40 Å in anthracene.<sup>79</sup> The

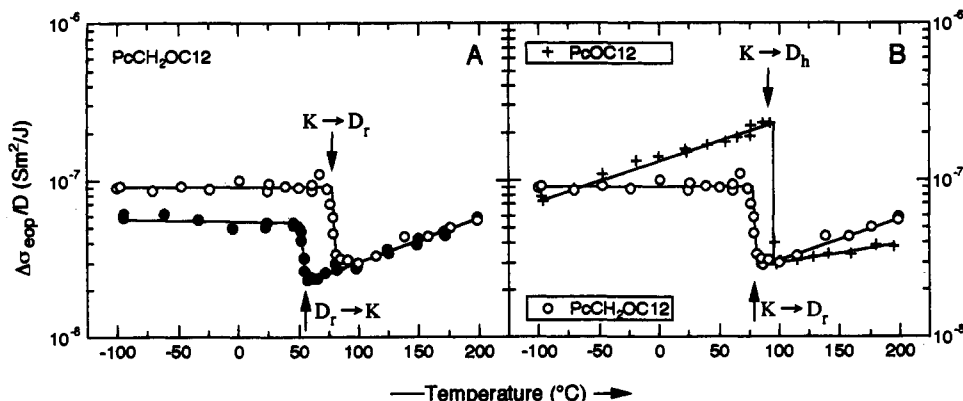
(75) Jay-Gerin, J.-P.; Goulet, T.; Billard, I. *Can. J. Chem.* 1993, 71, 287-293.

(76) Shinsaka, K.; Freeman, G. R. *Can. J. Chem.* 1974, 52, 3495-3506.

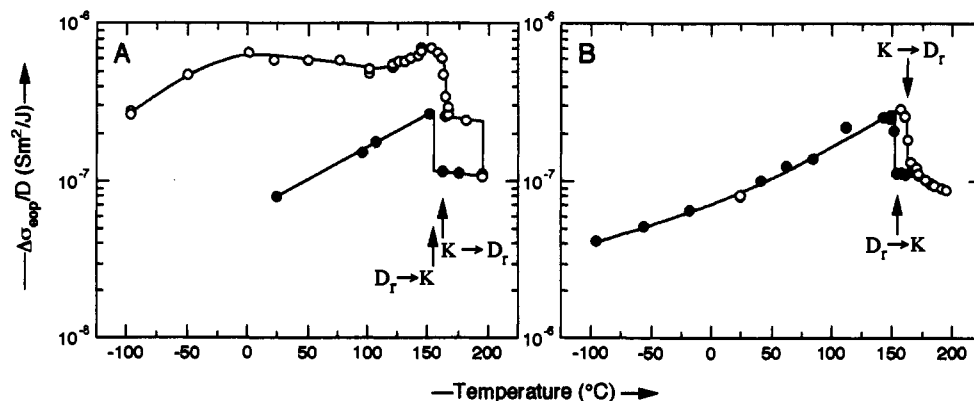
(77) Freeman, G. R. *Ann. Rev. Phys. Chem.* 1983, 34, 463-492.

(78) Namba, H.; Chiba, M.; Nakamura, Y.; Tezuka, T.; Shinsaka, K.; Hatano, Y. *J. Electrostat.* 1982, 12, 79-87.





**Figure 7.** (A) Dose normalized end-of-pulse conductivity versus temperature for PcCH<sub>2</sub>OC<sub>12</sub> on heating (open circles) and cooling (filled circles) and (B) the heating data for PcCH<sub>2</sub>OC<sub>12</sub> (open circles) plotted together with that for PcOC<sub>12</sub> (crosses). The arrows indicate the phase transition temperatures.



**Figure 8.** (A) Dose normalized end-of-pulse conductivity versus temperature for PcC<sub>10</sub> during the first heating (open circles) and cooling (filled circles) and (B) during the second heating and cooling run.

fraction of initially formed ion-pairs which escape their mutual coulombic attraction and become "free ions",  $W_{esc}$ , will therefore be small. In a previous article<sup>55</sup> estimates of  $W_{esc}$  were used as lower limits to  $W_{eop}$  in order to derive approximate upper limits to the charge carrier mobilities. In what follows we propose a model for charge carrier formation, based on the present experimental results and knowledge from the large body of previous charge carrier scavenging studies in molecular systems carried out by radiation chemists. On the basis of this we attempt to obtain more definitive values of  $W_{eop}$  and hence better estimates of the absolute mobility values.

On the basis of the very low quantum yield found for photoionization of unsubstituted phthalocyanine<sup>11</sup> and the lack of a measurable after-pulse radiation-induced conductivity for the octamethoxy-Pc substituted derivative, we conclude that electron-hole pairs formed within Pc rich regions recombine very rapidly. The observation that the end-of-pulse conductivity observed for  $n > 4$  increases with increasing alkane content of the alkoxy-Pc derivatives eventually reaching a plateau, as shown by the data in Tables 3 and 4, clearly indicates that a precondition for observing a long-lived conductivity signal in this type of medium is an extensive mantle of saturated hydrocarbon surrounding the Pc cores of the columnar stacks.

The above considerations, together with kinetic evidence discussed previously,<sup>80</sup> have led us to adopt the following model of long-lived charge carrier formation in peripherally substituted, discotic materials. The precursor  $e^-h^+$  pairs are those formed by ionization events occurring within the saturated hydrocarbon regions. For some of these pairs the electron and hole become

localized on separate phthalocyanine cores during the course of their diffusional motion prior to geminate recombination because of the relatively high electron affinity and the low ionization potential of the Pc moieties with respect to the saturated hydrocarbon region.<sup>15</sup> Subsequent charge recombination is retarded by the intervening hydrocarbon mantle which acts as an insulating barrier. While separate, the core-localized electron and/or hole undergo rapid hopping between adjacent macrocycles resulting in a large one-dimensional mobility and the radiation-induced conductivity observed. The mobilities in eq 4 refer therefore to electron (Pc radical anion) and hole (Pc radical cation) sites localized on separate columnar cores. The separated charges eventually recombine by long-distance electron tunnelling through the hydrocarbon barrier.

On the basis of this model the yield of charge carriers contributing to the radiation-induced conductivity will be equal to the yield of primary  $e^-h^+$  pairs formed in the hydrocarbon regions multiplied by the probability that the electron and hole of these pairs become localized on separate Pc cores prior to geminate recombination.

**Ionization in Hydrocarbon Regions.** On irradiation with high-energy electrons energy is deposited uniformly and nonspecifically throughout the sample in proportion to the local electron density.<sup>53</sup> The fraction of energy deposited in the alkane tail regions of the present alkoxy derivatives,  $D(R_n)/D$ , is therefore given by (5).

$$D(R_n)/D = \frac{8 \cdot Z(R_n)}{8 \cdot Z(R_n) + Z(\text{Pc})} = \frac{8 + 64n}{330 + 64n} \quad (5)$$

In (5),  $Z$  is the number of electrons per moiety, and  $n$  is the number of carbon atoms in the alkyl chain. In the derivation of (5) the alkoxy oxygen is taken to be part of the Pc macrocycle. The values of  $D(R_n)/D$  for the  $n$ -alkoxy derivatives are listed in Table 3.

(79) Hughes, R. C. *Annual report, Conference on Electrical Insulation and Dielectric Phenomena*; National Academy of Sciences: Washington, DC, 1971; pp 8-16.

(80) Warman, J. M.; de Haas, M. P.; van der Pol, J. F.; Drenth, W. *Chem Phys. Lett.* **1989**, *164*, 581-586.

As would be expected  $D(R_n)/D$  increases with increasing length of the hydrocarbon tail. The increase is however less pronounced than the increase in  $\Delta\sigma_{\text{eop}}/D$  found experimentally. In particular for the octamethoxy derivative 18% of the energy is deposited in the methyl groups but no long-lived charge carriers are observed. Clearly a peripheral methyl group is insufficient to provide a barrier to rapid, in-pulse charge recombination. The results would in fact suggest that an alkyl chain length of at least 2–3 carbon atoms is required before mobile charge carriers with a lifetime of several nanoseconds or more are formed. Therefore in addition to the value of  $D(R_n)/D$  we have listed in Table 3 the value of  $D(R_{n-2})/D$  as given by eq 6

$$D(R_{n-m})/D = \frac{8 + 64(n-m)}{330 + 64n} \quad (6)$$

This parameter is seen to reflect somewhat better the increase in  $\Delta\sigma_{\text{eop}}/D$  with increasing  $n$  observed experimentally. We will return to this point after discussing the probability,  $W_s$ , that electrons and holes formed within the hydrocarbon regions diffuse to and become trapped on the cores of the macrocyclic columns prior to geminate recombination.

**Scavenging by Pc Cores.** Calculation of  $W_s$  is made difficult by the complex, multicomponent, and multidimensional nature of the present materials. We are at present attempting to carry out Monte Carlo calculations of the diffusional motion of coulomb-correlated  $e^-h^+$  pairs in model systems representing columnar discotic materials in collaboration with W. Barczak of the University of Lodz, Poland. We present here only an approximate method of obtaining an estimate of  $W_s$  based on knowledge gained from studies of charge scavenging by solutes in homogeneous saturated hydrocarbon solutions.<sup>81</sup> These studies have led to the following empirical relationship for the probability of reaction of a primary charge carrier with a solute in competition with its geminate recombination.<sup>82</sup>

$$W_s = W_{\text{esc}} + (1 - W_{\text{esc}}) \frac{\sqrt{(\alpha c)}}{1 + \sqrt{(\alpha c)}} \quad (7)$$

In (7),  $W_{\text{esc}}$  is the probability that an initially formed  $e^-h^+$  pair undergoes complete diffusional escape from the mutual coulombic attraction. This results in the creation of what have been called "free" ions. For normal saturated hydrocarbons  $W_{\text{esc}}$  is on the order of 0.03 at room temperature.<sup>63,65</sup> Because of their long lifetime free ions are scavenged even by extremely low concentrations of added solutes.<sup>83</sup>  $W_{\text{esc}}$  has therefore been taken as a minimum value for  $W_{\text{eop}}$  in a previous publication<sup>55</sup> in order to derive maximum mobility values from  $\Delta\sigma_{\text{eop}}/D$ .

$$\sum \mu_{\text{max}} = [\Delta\sigma_{\text{eop}}/D] E_p / W_{\text{esc}} \quad (8)$$

The parameter  $c$  in (7) is the concentration of the reactive solute and  $\alpha$  is the reactivity toward scavenging of the primary charge carrier in competition with its geminate recombination. Therefore if we take the present materials to be approximated by a solution of Pc molecules in a hydrocarbon medium, then we can derive at least an approximate estimate of the probability that primary ions formed within the hydrocarbon regions will be "scavenged" by Pc units prior to their geminate recombination by applying (7) with  $c$  for the Pc concentration. For a variety of solutes and hydrocarbon liquids the value of  $\alpha$  has been found to be on the order of  $10 \text{ M}^{-1}$  for electron scavenging<sup>84</sup> at room

temperature. This value of  $\alpha$  was used to derive the values given for  $W_s$  in Table 3.

As can be seen  $W_s$  is 65% or higher for all of the alkoxy derivatives and decreases only slightly with decreasing Pc content. For high scavenger concentrations, as in the present systems,  $W_s$  is relatively insensitive to the value of  $\alpha$ . For example for PcOC9 changing  $\alpha$  from 10 to  $30 \text{ M}^{-1}$  would result in an increase in  $W_s$  from 0.71 to 0.81, i.e., by only 13%. If anything the "correct" value of  $W_s$  applicable to the present problem would be expected to be somewhat smaller than estimated on the basis of eq 7. On the one hand, because of the columnar stacking of the Pc moieties which should reduce their scavenging effectiveness compared with freely diffusing Pc molecules. On the other hand, because of the statistical chance that some electrons and holes will become localized on the same Pc column and undergo rapid intracolumnar recombination. The initial results of Monte Carlo calculations, in which we have attempted to take these complications into account, indicate that this would result in a decrease in  $W_s$  by at most approximately 20% when compared with the value derived using eq 7.

In light of the above we consider that a reasonable estimate of the charge carrier mobility can be made from the value of  $\Delta\sigma_{\text{eop}}/D$  by taking for  $E_p$  in (4) 25 eV, characteristic for saturated hydrocarbons,<sup>63–65</sup> and for  $W_{\text{eop}}$  a value given by

$$W_{\text{eop}} = [D(R_{n-m})/D] W_s \quad (9)$$

We have denoted the values of the mobility derived in this way by the symbol  $\sum \mu_s$  to indicate that they are based on the hydrocarbon scavenging model described above, so that

$$\sum \mu_s = \frac{[\Delta\sigma_{\text{eop}}/D] E_p}{[D(R_{n-m})/D] W_s} \quad (10)$$

**Temperature Dependence.** The degree to which  $\Delta\sigma_{\text{eop}}/D$  reflects temperature variations in the mobility of the charge carriers will depend on the temperature dependence of the other parameters in eq 10. The pair formation energy  $E_p$  is dependent only on the electronic transition probabilities within the molecules of the medium and should be completely independent of temperature. The term  $D(R_{n-m})/D$  is a function only of the relative electron densities of the components of the medium and should also be independent of temperature. The scavenging probability term  $W_s$  remains the only source of a temperature dependence of  $\Delta\sigma_{\text{eop}}/D$  other than that associated with  $\sum \mu$ .

While  $W_{\text{esc}}$  changes markedly with temperature,<sup>63</sup> its contribution to  $W_s$  is small. The overall temperature dependence of  $W_s$  is therefore controlled mainly by the second term in eq 7 and hence by the temperature dependence of  $\alpha$ . The reactivity parameter  $\alpha$  is given by<sup>82,85</sup>

$$\alpha = k_s / \lambda \quad (11)$$

In (11)  $k_s$  is the rate coefficient for reaction of a primary charge carrier with the solute which for the diffusion controlled case is

$$k_s = 4\pi R_s (D_{\pm} + D_s) \quad (12)$$

with  $R_s$  the reaction radius and  $D_{\pm}$  and  $D_s$  the diffusion coefficients of the reactant charge carrier (positive or negative) and the solute molecule, respectively. In general the primary electron and hole would be expected to have significantly larger diffusion coefficients than the solute molecules particularly for large solute molecules as in the present case.  $(D_{\pm} + D_s)$  will therefore be well approximated by  $D_{\pm}$ . Since the diffusion coefficient and the

(81) *Handbook of Radiation Chemistry*; Tabata, Y., Ito, Y., Tagawa, S., Eds; CRC Press: Boca Raton, FL, 1991.

(82) Warman, J. M.; Asmus, K.-D.; Schuler, R. H. *J. Phys. Chem.* 1969, 73, 931–939.

(83) Warman, J. M.; Rząd, S. *J. Chem. Phys.* 1970, 52, 485–490.

(84) Reference 81, table on p 307.

(85) Rząd, S. J.; Infelta, P. P.; Warman, J. M.; Schuler, R. H. *J. Chem. Phys.* 1970, 52, 3971–3983.

mobility are interrelated by the Einstein relation

$$D_{\pm} = \mu_{\pm} k_B T / e \quad (13)$$

eq 12 can be rewritten as

$$k_s = 4\pi R_s \mu_{\pm} k_B T / e \quad (14)$$

The parameter  $\lambda$  in (11) is the characteristic rate of geminate recombination. To a first approximation  $\lambda$  is expected to be directly proportional to the sum of the mobilities of the charge carriers undergoing recombination within the hydrocarbon regions<sup>86-88</sup>

$$\lambda = K(\mu_+ + \mu_-) \quad (15)$$

From (11), (14), and (15) we therefore have for  $\alpha$

$$\alpha \approx 4\pi R_s \mu_{\pm} k_B T / e K (\mu_+ + \mu_-) \quad (16)$$

In general the overall rates of scavenging and geminate recombination will be controlled by the most mobile primary charge carrier be it the electron or the hole. Taking the electron to be the major charge carrier we have  $\mu_{\pm} = \mu_- \gg \mu_+$  which results in the relevant value of  $\alpha$  being given by (17). The inverse condition  $\mu_{\pm} = \mu_+ \gg \mu_-$  would lead to the same relationship.

$$\alpha \approx 4\pi R_s k_B T / e K \quad (17)$$

If the electron and hole mobilities happen to be very similar in magnitude then we have the condition  $\mu_{\pm} = \mu_+ = \mu_-$  giving for  $\alpha$  eq 18

$$\alpha \approx 2\pi R_s k_B T / e K \quad (18)$$

In both cases therefore  $\alpha$  is predicted to be proportional simply to the first power of the temperature.

No thorough experimental study of the temperature dependence of  $\alpha$  in saturated hydrocarbons has appeared in the literature. Some time ago in our laboratory a study was made of electron scavenging by methyl bromide in *cis*-decalin at room temperature and  $-25^\circ\text{C}$ . These unpublished results showed that  $\alpha$  was indeed lower at the lower temperature by a factor of approximately 1.5 which is somewhat larger than the factor of 1.2 which would be expected on the basis of a first power dependence on temperature. As pointed out above the eventual value of  $W_s$  calculated using (7) is in fact quite insensitive to even large changes in  $\alpha$  for large scavenger concentrations. We have therefore taken as a first approximation  $\alpha$  to obey a linear temperature dependence with a value of  $10\text{ M}^{-1}$  at  $25^\circ\text{C}$ . As an example using this approach values of  $W_s$  for PcOC12 at the extreme limits of temperature used in the present work, i.e.,  $-100$  to  $+200^\circ\text{C}$ , are 0.62 and 0.75, respectively. This corresponds to an effective activation energy in the  $W_s$  term of only  $0.004\text{ eV}$ . One can conclude therefore that any appreciable temperature dependence found in the experimental parameter  $\Delta\sigma_{\text{eop}}/D$  must arise mainly from the temperature dependence of the charge carrier mobilities.

**Phase Changes.** Large changes in the radiation-induced conductivity are found to occur at phase transitions. The question then arises as to whether this is a result of a change in the number of charge carriers formed or a change in their mobility or both. If we consider eq 10 for the conversion of experimental  $\Delta\sigma_{\text{eop}}/D$  values into mobility values, then the question comes down to whether or not the parameters  $E_p$ ,  $D(R_{n-m})/D$ , and  $W_s$ , which determine the concentration of charge carriers present, are sensitive to phase changes.

The pair formation energy is determined by the relative oscillator strengths of the electronic transitions of the molecules above and below the ionization threshold.  $E_p$  would be expected to be completely unaffected by the types of phase transitions occurring in the present, weakly interacting materials. Even in going from the liquid phase to the gas phase of hydrocarbon systems  $E_p$  is found to change only slightly if at all.<sup>65</sup>

The fractionation of the absorbed energy between the different components of the material, as given by  $D(R_{n-m})/D$ , depends only on the relative electron densities. This parameter will therefore be completely independent of any change in phase.

The scavenging efficiency  $W_s$  might be expected to be influenced by a change in phase but there are reasons why this would be expected to be only a marginal effect. Firstly; the molecular composition, density, and dielectric constant of the materials undergo only slight changes at a solid to mesophase transition. The processes of electron hole pair separation and recombination should therefore remain basically the same. Only small changes in the thermalization distance in hydrocarbon systems have been observed on melting.<sup>89</sup> Secondly, if the mobilities of the primary charge carriers formed in the saturated hydrocarbon regions (the precursors of the charge carriers observed) were to be influenced by the phase change, then the rates of both the scavenging and the competing geminate recombination would be changed equally, i.e., both depend directly on the magnitude of the mobility. As shown above, the competitive scavenging parameter is insensitive to changes in the mobilities of the carriers. Thirdly, the scavenger (i.e., Pc) concentration is very high and the efficiency of scavenging close to unity. As a result even quite large changes in  $\alpha$  have little influence on  $W_s$ , as pointed out above.

All things considered, one would expect the yield of charge carriers contributing to the end-of-pulse conductivity signals observed to change by only a few percent, if at all, at the phase changes occurring in the present samples. There is however clearly a need to check this point, if possible by carrying out PR-TRMC and time-of-flight measurements on identical samples and under the same physical conditions.

**Charge Carrier Mobilities.** In accordance with the discussion in the previous section,  $\Sigma\mu_s$  values have been derived from experimental values of  $\Delta\sigma_{\text{eop}}/D$  using eq 10 with  $E_p = 25\text{ eV}$ ,  $D(R_{n-m})/D$  as given by eq 6 with  $m = 2$ , and  $W_s$  as given by eq 7 with  $W_{\text{esc}}$  calculated as described previously<sup>55</sup> ( $W_{\text{esc}} = 0$  is a good approximation for high scavenger concentrations) and  $\alpha = 10 \times T/298\text{ M}^{-1}$ . The values obtained are listed in Tables 3-5. While the present estimates of the mobility sum are admittedly only approximate, we think it unlikely that the true value would differ from  $\Sigma\mu_s$  by more than a factor of 2 either way. In previous reports  $\Sigma\mu_{\text{min}}$  values were given which were based on the limiting condition that all electron-hole pairs formed contribute to the conductivity observed. The  $\Sigma\mu_s$  values are found to be approximately a factor of 3 larger than  $\Sigma\mu_{\text{min}}$ .

Because of the short time scale of the observations and the ultrahigh frequency of the probing electric field,  $\Sigma\mu_s$  refers to charge carriers within organized domains. Because of the random orientation of the domains within the present samples  $\Sigma\mu_s$  is effectively an isotropic value, and the one-dimensional mobility would be expected to be a factor of approximately 3 higher along the columnar axis in oriented samples.

Since the materials studied here are being considered for applications in xerography and laser printing, it is of interest to calculate the charge carrier drift time across a well aligned thin layer on the basis of the mobilities determined. For a  $10\text{ }\mu\text{m}$  film and an applied voltage of  $100\text{ V}$ , the drift time would be approximately  $50\text{ ns}$  for the crystalline *n*-alkoxy-Pc materials at room temperature. Even for the PcOC12,3 compound, which is liquid-crystalline at room temperature and readily melted and aligned, a drift time as short as  $250\text{ ns}$  would be possible.

(86) Williams, F. *J. Am. Chem. Soc.*, 1964, 86 3954-3957.

(87) Freeman, G. R. *J. Chem. Phys.*, 1967, 46, 2822-2830.

(88) Freeman, G. R. In *Kinetics of Nonhomogeneous Processes*; John Wiley & Sons: New York, 1987; pp 277-304.

(89) Tezuka, T.; Namda, H.; Nakamura, Y.; Chiba, M.; Shinsaka, K.; Hatano Y. *Radiat. Phys. Chem.* 1983, 21, 197-208.

Unfortunately we cannot distinguish between the electron and hole contributions to  $\Sigma\mu_s$  using our technique. On the basis of time of flight (TOF) measurements on single crystal unsubstituted phthalocyanine, the mobilities of the electron and hole might be expected to be similar in magnitude.<sup>10,11</sup> However very recent TOF measurements of charge carrier mobilities in an aligned sample of the discotic liquid-crystalline material hexapentoxetriphenylene (HPT) show the hole to be almost two orders of magnitude more mobile than the electron.<sup>42</sup> We conclude that for the present compounds  $\mu(-)$  is probably approximately the same as or less than  $\mu(+)$ . In other words, at least half, and possibly considerably more, of the mobility measured can probably be attributed to positive ion migration.

**Solid.** At room temperature the  $\Sigma\mu_s$  values for the *n*-alkoxy Pcs all lie within the range  $8.5 \times 10^{-6} \pm 2.5 \times 10^{-6}$  m<sup>2</sup>/Vs supporting a common underlying mechanism for charge transport. A mobility as high as  $25 \times 10^{-6}$  m<sup>2</sup>/Vs could therefore prevail in oriented samples of the *n*-alkoxy-Pc derivatives at room temperature. This is still within the mobility range associated with small polaron motions via charge hopping between localized sites. The intracolumnar Pc-to-Pc hopping times corresponding to the values of  $\Sigma\mu_s$  are discussed in a later section.

In the K phase  $\Sigma\mu_s$  is seen to increase with temperature for all compounds which form a crystalline solid except PcCH<sub>2</sub>OC12 for which  $\Sigma\mu_s$  is almost independent of temperature. This compound is also the only one with an appreciable, thermally activated background microwave dielectric loss in the solid phase.<sup>68</sup> This loss has been attributed to high-frequency motions in the vicinity of the dipolar methoxy coupling to the Pc core.<sup>66,67</sup> The decrease in intracolumnar charge carrier mobility caused by such thermally activated side-chain motions could possibly counteract the increase in mobility with temperature that would otherwise have been expected.

The change in the average value of  $\Sigma\mu_s$  from -100 to +100 °C for the *n*-alkoxy-Pcs corresponds to an activation energy of 0.027 eV or in terms of a  $T^n$  dependence,  $n = +1.3$ . For PcOC6,1, PcOC8,2, and PcC10 the activation energies are 0.025, 0.015, and 0.044 eV respectively. In all cases the activation energies are low and of the same order as  $k_B T$ .

**Solid to Mesophase Transition.** At the K → D transition for the *n*-alkoxy derivatives  $\Sigma\mu_s$  decreases on average by a factor of 5.3. As mentioned the K → D transition for the octa-*n*-alkoxy derivatives is accompanied by a change from a tilted to a horizontal stacking of the Pc units as evidenced by SAXS.<sup>26</sup> Since the van der Waals interaction might be expected to be proportional to the area of  $\pi$ - $\pi$  overlap,<sup>32</sup> this cofacial arrangement in the mesophase has been predicted to be optimal for rapid intracolumnar energy and charge migration.<sup>31</sup> As discussed in the previous section there is no reason to believe that the concentration of charge carriers would change significantly at the phase transition. We are forced to conclude that, contrary to expectations based on  $\pi$ - $\pi$  overlap, the one-dimensional mobility of charge carriers within the columns is significantly decreased.

In addition to the change in stacking of macrocycles within the columns, other significant changes occur at the K → D transition. The large  $\Delta H$  values measured by DSC together with SAXS and solid-state NMR observations indicate the hydrocarbon mantle surrounding the macrocyclic columns to melt completely, resulting in a mobile, liquid-crystalline phase. A sudden increase in the microwave dielectric loss of these materials<sup>66-68</sup> at the K → D transition has been taken to indicate that rapid positional fluctuations occur even at the dipolar ether coupling linkages. The coupling of the motional disorder within the alkyl chains to structural disorder within the macrocyclic columns is almost certainly the reason for the marked decrease in the charge carrier mobility. Rotation of the macrocycles about the columnar axis and longitudinal and lateral motions are all expected to have a negative influence on the frequency of charge carrier hop-

ping.<sup>32,90-92</sup> In addition to the negative effect of perturbations in the columnar order it is also possible that the increased flexibility in the mesophase allows the formation of a more localized polaron state due to increased deformation of the one-dimensional lattice in the neighborhood of the radical ion site.

It is possible that the increased columnar disorder at the K → D transition overcompensates for what would otherwise have been an increase in mobility resulting from the change from tilted to horizontal stacking. We tend to discount this however on the basis of results on systems for which the solid to mesophase transition occurs without a change from a tilted to a horizontal macrocycle configuration such as the alkoxyethylporphyrins.<sup>56,68</sup> These display a smaller decrease in  $\Delta\sigma_{\text{eop}}/D$  at the K → D transition than do the alkoxy Pc materials. Our results would therefore suggest that "perfect" horizontal stacking of discotic macrocycles is not necessarily the optimal arrangement for charge transport and surprisingly might even be slightly disadvantageous. The observation that the value of  $\Delta\sigma_{\text{eop}}/D$  is about the same in the "tilted" mesophase of PcCH<sub>2</sub>OC12 as for the "horizontally-stacked" *n*-alkoxy Pc derivatives indicates that horizontal or tilted stacking of the Pc units has little influence on the charge carrier mobilities along the columnar axis. For both types of aggregation the disorder in the stacking rather than the tilt angle would seem to be the determining factor for the charge carrier mobility in the liquid-crystalline phase. This is supported by the much smaller decrease in  $\Sigma\mu_s$  at the K → D transition of PcOC6,1 a compound which displays a very low  $\Delta H(K \rightarrow D)$  indicating a mesophase with much less motional freedom.

**Mesophase.** For the *n*-alkoxy Pc derivatives little change of  $\Sigma\mu_s$  with increasing temperature is observed in the mesophase. The branched chain compounds PcOC8,2\* and PcOC12,3 are particularly interesting since they have extensive liquid-crystalline ranges. In going from -100 °C to close to +200 °C,  $\Sigma\mu_s$  increases by only a factor of approximately 2 for both compounds corresponding to an activation energy of only 0.014 eV. This relative insensitivity to temperature has also been found for a siloxane polymer derivative of an *n*-alkoxy-Pc which is also liquid-crystalline at all temperatures.<sup>55</sup> It would appear that in the liquid-crystalline phase any increase in mobility which might have arisen due to thermally induced hopping of the charge carriers is almost completely compensated by the negative effect of thermally activated perturbations in the columnar stacking.

The 20% decrease in  $\Delta\sigma_{\text{eop}}/D$  at 34 °C for PcOC12,3 during the first heating is accompanied by an endothermic peak in the DSC. SAXS measurements on the fresh sample<sup>33</sup> below (20 °C) and above (50 °C) this transition showed that the reflection corresponding to the distance of the molecules within a column at 3.4 Å, changed from sharp, FWHM (full width at half maximum) = 0.04 Å, to diffuse, FWHM = 0.14 Å. This corresponds to a change in the correlation length from 168 Å to 41 Å using the Scherrer formula.<sup>93</sup> At 34 °C therefore a change from a well organized to a more disordered horizontal columnar stacking of the macrocycles appears to occur. One would expect the charge carrier mobilities to decrease for such a transition as is observed for  $\Delta\sigma_{\text{eop}}/D$ . However the effect is not as large as one might have anticipated based on the significant change in sharpness of the 3.4 Å reflection.

Interestingly the  $\Sigma\mu_s$  values in the mesophase of PcC10 and PcOC6,1 are significantly higher than for the *n*-alkoxy- and *n*-alkoxymethyl-Pc derivatives in their mesophase. Both of these compounds have particularly high K → D transition temperatures and appear to form more rigid mesophase structures than the

(90) Whangbo, M.-H.; Stewart, K. R. *Isr. J. Chem.* **1983**, *23*, 133-138.

(91) Canadell, E.; Alvarez, S. *Inorg. Chem.* **1984**, *23*, 573-579.

(92) Pietro, W. J.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1985**, *107*, 5387-5391.

(93) Klug, H. P.; Alexander, L. E. *X-ray diffraction procedures for polycrystalline and amorphous materials*, 2nd ed.; Wiley: New York, 1974.

**Table 5.** Values of  $\Sigma\mu_s$  at Selected Temperatures for all the Pc's Studied in the Present Paper<sup>d</sup>

compd	$\Sigma\mu_s$ ( $10^{-6}$ m <sup>2</sup> /Vs)				
	-100 (phase)	RT	$T_{K \rightarrow D} - 10$	$T_{K \rightarrow D} + 10$	+200 (phase)
PcOC <sub>n</sub>	4.4 (K)	8.5	11.6	2.2	1.8 (D)
PcOC6,1	2.8 (K)	5.8	7.5	6.4	6.0 (D)
PcOC8,2	7.3 (K)	12.4	11.9	2.2	2.4 (D)
PcOC8,2*	0.8 (D)	0.9 <sup>a</sup>			2.1 (D)
PcOC12,3	0.9 (D)	1.3	(1.4) <sup>b</sup>	(0.2) <sup>b</sup>	0.2 (I)
PcCH <sub>2</sub> OC12	5.1 (K)	4.6	4.4	1.4	2.7 (D)
PcC10 <sup>c</sup>	2.3 (K)	4.3	13.2	5.0	4.0 (D)

<sup>a</sup> After first heating. <sup>b</sup> D  $\rightarrow$  I transition at 185 °C, no K phase. <sup>c</sup> Values are for the second heating. <sup>d</sup> For the *n*-alkoxy PC's the average values from Tables 3 and 4 were used.

*n*-alkoxy or *n*-alkoxymethyl compounds. This is also in accord with the lower values for  $\Delta H$  at their K  $\rightarrow$  D transitions indicating less liquid-like disorder in the hydrocarbon mantle and hence less perturbation of the Pc columnar order. Apparently the ethyl branch close to the Pc core results in the tetragonally packed liquid-crystalline phase being still relatively rigid in the case of PcOC6,1. One might even doubt if the material is really liquid-crystalline when the very low value for  $\Delta H$  of 4.7 kJ/mol is compared with the 72 kJ/mol found for PcOC6 at the K  $\rightarrow$  D phase transition. Without the ether group in the chain for PcC10 it seems that the motional freedom of the aliphatic chains and hence that of the Pc units is much more restricted resulting in the high  $T_{K \rightarrow D}$  and high charge carrier mobility. The rather small hysteresis of 7 °C for the D  $\rightarrow$  K transition suggests that for this compound the chains and Pc core act more as a single molecular unit.

**Liquid.** At the mesophase to isotropic phase transition clearly the columnar stacking must be perturbed to a very large extent, and only a very low charge carrier mobility would be expected to remain if it were indeed dependent on a well organized columnar arrangement of macrocycles. Only one of the compounds studied in the present work, PcOC12,3, had a mesophase to isotropic liquid transition within the temperature range of the experiment. As can be seen by the  $\Delta\sigma_{\text{exp}}/D$  values in Figure 5 and the  $\Sigma\mu_s$  values in Table 5, the mobility does in fact decrease dramatically at the transition temperature by a factor of 7.

From the value of  $0.20 \times 10^{-6}$  m<sup>2</sup>/Vs for  $\Sigma\mu_s$  in the isotropic phase of PcOC12,3 a diffusion coefficient of  $\Sigma D = 8.1 \times 10^{-9}$  m<sup>2</sup>/s is calculated using eq 13. This is much larger than values of approximately  $5 \times 10^{-11}$  m<sup>2</sup>/s<sup>94,95</sup> measured using NMR techniques for the molecular diffusion coefficient of analogous triphenylene derivatives in the liquid state. Even for small molecular ions in liquid cyclohexane (viscosity 1 cP) the diffusion coefficient is only approximately  $2 \times 10^{-9}$  m<sup>2</sup>/s.<sup>96</sup> It follows that the radiation induced conductivity observed in the liquid phase of PcOC12,3 cannot reflect the diffusional displacement of molecular ions but must be electronic in nature. This indicates that for the phthalocyanine macrocycles a substantial amount of transient columnar order still exists in the isotropic phase at least just above the D  $\rightarrow$  I transition.

In the case of analogous porphyrin derivatives even more dramatic decreases in mobility have been observed at K  $\rightarrow$  I or D  $\rightarrow$  I transitions. For these materials only an upper limit of ca.  $7 \times 10^{-11}$  m<sup>2</sup>/s for  $\Sigma D$  in the isotropic phase can be made.<sup>56</sup> Even this upper limit is considerably lower than  $\Sigma D$  for the Pc derivative and in fact is close to the value found for molecular diffusion. Apparently the interaction between the Pc macrocycles is stronger than between porphyrins, a fact which is also indicated

(94) Dong, R. Y.; Goldfarb, D.; Mosely, M. E.; Luz, Z.; Zimmerman, H. *J. Phys. Chem.* 1984, 88, 3148-3152.

(95) Vilfan, M.; Lahajnar, G.; Rutar, V.; Blinc, R.; Topic, B.; Zann, A.; Dubois, J. C. *J. Chem. Phys.* 1981, 75, 5250-5255.

(96) Allen, A. O.; de Haas, M. P.; Hummel, A. *J. Chem. Phys.* 1976, 64, 2587-2592.

by the much lower clearing temperatures of the porphyrin derivatives.<sup>97</sup>

**Intracolumnar Jump Times.** Since the values found for the charge carrier mobilities in the present compounds are less than  $10^{-4}$  m<sup>2</sup>/Vs the motion of the charge carriers can best be discussed in terms of hopping of charge between adjacent Pc sites within a stack.<sup>98,99</sup> For random orientation of columnar domains the diffusion of charge carriers within the material will be effectively isotropic. The diffusion coefficient is then given in terms of the jump distance,  $d_j$ , and the jump time,  $\tau_j$ , by the Einstein-Smoluchowski relation

$$D = d_j^2/6\tau_j \quad (19)$$

The jump time in (19) should possibly more correctly be called the waiting time since it is the average time that a charge remains localized at a particular molecular site. The time scale of the actual site-to-site electron-transfer process, the "jump", would be expected to be very much shorter. Combination of eq 19 with eq 13 and rearrangement yields an expression for  $\tau_j$  in terms of the mobility

$$\tau_j = \frac{ed_j^2}{6k_B T \mu} \quad (20)$$

Using  $\mu = \Sigma\mu_s$  in (20), as is done below, assumes that one of the carriers is much more mobile than the other; an assumption which results in the shortest value for  $\tau_j$ . If the positive and negative carriers were of equal mobility, then the jump time of each would be twice the values given. When for  $\mu$  the values of  $\Sigma\mu_s$  and for  $d_j$  the Pc to Pc center-to-center distance of 4.3 Å in the solid and 3.4 Å in the mesophase are used, the  $\tau_j$  values for the *n*-alkoxy-Pcs given in Table 4 are calculated.  $\tau_j$  is seen to decrease from an average of 0.47-0.08 ps for the *n*-alkoxy Pc derivatives when heated from -100 °C to just below their K  $\rightarrow$  D transition corresponding to an activation energy for  $\tau_j$  of 0.048 eV. At the K  $\rightarrow$  D transition  $\tau_j$  increases by a factor of 3.5 from 0.08 to 0.28 ps.

The charge carrier jump times determined in the present work are of the same order of magnitude as found for exciton hopping in similar materials.<sup>100</sup> In contrast to the increase in the charge carrier jump time at the K  $\rightarrow$  D transition in the alkoxy Pcs the exciton hopping time was found to decrease substantially from 45 to 0.4 ps indicating more rapid rather than slower intracolumnar transport in the mesophase. It is perhaps of interest that the estimates of exciton hopping times within organized assemblies of porphyrin derivatives in the antenna systems of photosynthesis are also on the order of tenths of picoseconds.<sup>101</sup>

From the jump time it is possible to obtain an estimate of the distance within a column a charge carrier will diffuse from its starting position in a given time,  $t$ . If the distance is counted in terms of the number of Pc units,  $n$ , then this will be simply

$$n = (t/\tau_j)^{0.5} \quad (21)$$

Conversely, the time to diffuse over a given distance can be obtained from (22).

(97) Gregg, B. A.; Fox, M. A.; Bard, A. J. *J. Am. Chem. Soc.* 1989, 111, 3024-3029.

(98) Mott, N. F. *Conductivity in Non-Crystalline Materials*; Clarendon: Oxford, U. K., 1987; pp 55-70.

(99) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals*, Clarendon: Oxford, U. K., 1982; pp 353-360.

(100) Markovitsi, D.; Lécuyer, I.; Simon, J. *J. Phys. Chem.* 1991, 95, 3620-3626.

(101) Mimuro, M.; Nozawa, T.; Tamai, N.; Shimada, K.; Yamazaki, I.; Lin, S.; Knox, R. S.; Wittmershaus, B. P.; Brune, D. C.; Blankenship, R. E. *J. Phys. Chem.* 1989, 93, 7503-7509.

$$t_n = n^2 \tau_j \quad (22)$$

The domain size in the mesophase of *n*-alkoxy-Pcs has been estimated to be approximately 4000 Pc units or 1.4  $\mu\text{m}$ .<sup>72</sup> From the above estimate of 0.28 ps for  $\tau_j$  the average time to diffuse to the boundary from the center of a domain will then be approximately 1  $\mu\text{s}$ . As will be shown in a subsequent paper the lifetimes of the mobile carriers in these materials can actually extend to milliseconds indicating that either the domains are much larger than the above estimate or that the domain boundaries are reflective for the charge carriers.

**Comparison with Previous Conductivity Studies.** It should be pointed out that the mobilities determined in the present experiments, because of the ultrahigh frequency and fast time response used, will refer to charge carrier motion within organized domains as was recently discussed by Dyre.<sup>102</sup> The electric field reverses every 1/2f seconds which for the Ka band microwaves used in the present work (26.5–38 GHz) corresponds to ca. 15 ps. At the power level of 200 mW the maximum field strength is  $3 \times 10^3$  V/m resulting in a drift of charge carriers of mobility  $10^{-5}$  m<sup>2</sup>/Vs during a cycle of less than  $5 \times 10^{-3}$  Å. Therefore charge carriers are not pulled to domain boundaries, and the mobility determined is free from interboundary hopping which can dominate the motion of charge carriers in dc and lower frequency ac conductivity measurements. The microwave field in fact simply acts as a small perturbation on the diffusional motion of the charge carriers slightly increasing the statistical probability of a charge carrier making a jump in the field direction during its otherwise random motion.  $\Sigma\mu_s$  should therefore be an upper limit to the mobility attainable for a given material. As mentioned however,  $\Sigma\mu_s$  in the present work refers to randomly oriented domains and hence pseudoisotropic charge migration. The one-dimensional mobility in fully-aligned, columnar material might be expected to be up to a factor of 3 larger.

**Time of Flight (TOF) Measurements.** The only direct TOF mobility measurements which can be related to the present results in the solid phase are the two studies mentioned previously which were carried out on aligned, single crystal samples of pure, unsubstituted phthalocyanine.<sup>10,11</sup> Both studies show the hole and electron mobilities along the "tilted-columnar", C-axis of a Pc crystal to be similar in magnitude with  $\Sigma\mu$  values of  $0.9 \times 10^{-4}$  m<sup>2</sup>/Vs<sup>10</sup> or  $3.2 \times 10^{-4}$  m<sup>2</sup>/Vs<sup>11</sup> at room temperature. As might be expected  $\Sigma\mu$  for single crystal phthalocyanine is substantially larger than the value of  $3 \times \Sigma\mu_s = 0.25 \times 10^{-4}$  m<sup>2</sup>/Vs found in the K-phase of the *n*-alkoxy-Pc derivatives at room temperature. However, considering the complexity of the present molecular aggregates, it is perhaps remarkable that the mobility does in fact come within an order of magnitude of that for the single crystal. Perhaps even more surprisingly, the mobility in the liquid-crystalline materials is only approximately two orders of magnitude lower than that for the single crystal.

In the TOF studies<sup>10,11</sup> a weak, inverse temperature dependence of both the electron and the hole mobility, corresponding approximately to  $T^{-1.5}$ , was found. This is to be compared with the weak but positive, ca.  $T^{1.3}$ , dependence found for  $\Sigma\mu_s$  for the present compounds in the K-phase. It would appear that charge migration is retarded by phonon scattering in the Pc crystal, whereas it is phonon assisted in the K-phase of the mesomorphic materials. This could be a consequence of the change from close to perfect stacking of the Pc moieties in the former to a somewhat disordered columnar stacking in the latter systems.

Only one direct, time-of-flight measurement of the mobility of charge carriers in a mesomorphic discotic material has been published. This was the work of Adam et al.<sup>42</sup> on an aligned, thin layer sample of hexa-*n*-pentoxytriphenylene, HPT. In the mesophase of this compound the hole was found to be the major charge carrier with a close to temperature independent mobility

of  $0.08 \times 10^{-6}$  m<sup>2</sup>/Vs. The very weak temperature dependence is in agreement with the present findings for the alkoxy-Pcs in their mesophase. The absolute value of the mobility in HPT is however much lower than the alkoxy-Pc value of ca.  $2 \times 10^{-6}$  m<sup>2</sup>/Vs. This difference is probably due, at least in part, to the much weaker  $\pi$ - $\pi$  interaction in the columnar stacks of the triphenylene derivative. This would be expected on the basis of the smaller size of the  $\pi$ -system and is reflected in the much lower D  $\rightarrow$  I transition temperature of HPT, 122 °C, compared with the >350 °C clearing point of octa-*n*-pentoxy-Pc. Perturbations in the one-dimensional columnar stacking such as longitudinal, lateral, and tilt displacements of the macrocyclic units would therefore be expected to be greater for HPT and lead to a reduction in the rate of intracolumnar charge carrier hopping. Unfortunately the authors were not capable of determining mobilities in the K phase of HPT because of "charge carrier localization at domain boundaries".

**Steady-State Conductivity Measurements.** The vast majority of attempts to study the charge transport properties of mesomorphic, discotic materials in their different states of aggregation have involved measurements of the steady-state conductivity. Measurements have been performed on pure and chemically doped samples and on samples irradiated with light using a variety of conductivity techniques from DC to microwave. In Table 6 we have listed those studies in which the temperature dependence of the conductivity was monitored. We have attempted in the table only to give a qualitative impression of the temperature dependence found within a given phase and the direction of the change at phase transitions. The original articles should be consulted for quantitative details.

Unfortunately Table 6 illustrates that a consistent picture cannot be derived from the conductivity measurements carried out to date; every column in the table is seen to include all possible tendencies. Somewhat surprising is the finding in several studies, including our own background microwave conductivity measurements,<sup>66-68</sup> that the conductivity remains the same or even increases at the clearing point. This observation often goes without comment despite the fact that the conductivity measured is assigned by most authors to charge carrier motion in columnar aggregates and would certainly be expected to diminish in the isotropic liquid phase. The considerable decrease in conductivity expected at the D  $\rightarrow$  I transition is clearly observed in the present work for PcOC12,3 and has previously been observed at the D  $\rightarrow$  I and K  $\rightarrow$  I transitions of analogous porphyrin compounds<sup>56</sup> using PR-TRMC.

Several problems clearly complicate the interpretation of steady-state conductivity measurements. These can be of an experimental nature involving physical contacts, medium polarization, and sample morphology. And of an interpretative nature involving a lack of accurate knowledge of the charge carrier concentrations and contributions to the AC conductivity from dipole relaxation processes. We have suggested that the latter can make a considerable contribution to the background dielectric loss even at microwave frequencies,<sup>68</sup> particularly in the liquid-crystalline phases of discotic materials. It is to be hoped that a thorough study of the dielectric properties of selected, well characterized materials, over the DC to microwave frequency range, necessary for a full interpretation can be carried out in the near future.

## Conclusions

Mobile charge carriers are formed in pulse-irradiated mesomorphic phthalocyanines. One-dimensional charge migration occurs within the columnar stacks of Pc macrocycles by a hopping mechanism. For octa-*n*-alkoxy-Pcs the Pc-to-Pc jump time decreases with increasing temperature in the crystalline-solid phase from 0.5 ps at -100 °C to 0.08 ps at close to the K  $\rightarrow$  D transition corresponding to an activation energy of 0.048 eV.

(102) Dyre, J. C. *J. Appl. Phys.* 1988, 64, 2456-2468.

**Table 6.** Temperature Dependence of the Steady-State Conductivity for Several Discotic Liquid-Crystalline Materials in Their Different Aggregation States as Found in the Literature Other Than Studied in Our Group<sup>d</sup>

macrocycle	dopant/ treatment	type of measurement	slope in solid	change at K → D	slope in mesophase	change at D → I	slope in liquid	source
triphenylene	I <sub>2</sub>	17 Hz, dc	+ / 0	+	+	+ / -	+ , 0	38
triphenylene	AlCl <sub>3</sub>	10 <sup>-3</sup> -10 <sup>7</sup> Hz	0	0	+	0	-	39, 40
triphenylene	pure and I <sub>2</sub>	dc 4-probe van der Pauw	+	0	+	0	+	41
triphenylene	pure	photoconductivity dc 2-probe	ns	+	+ / -	-	ns	44
triphenylene	pure	16 Hz	nm	nm	+	+	+	43
triphenylene	pure	photoconductivity dc 2-probe	nm	+ / -	+	-	ns	45
phthalocyanine	pure	10 <sup>-1</sup> -6.5 × 10 <sup>4</sup> Hz	+	-	+	nm	nm	25
phthalocyanine	pure	30 GHz <sup>a</sup>	+	+ / 0	+	0	0	66-68
Lu-phthalocyanine	pure	10 <sup>3</sup> Hz	+	+ / -	+	0	+	35, 36
porphyrin	pure	photoconductivity dc 2-probe	-	+	+ / -	-	nm	46
porphyrin	pure	30 GHz <sup>a</sup>	+	0	+	0	0	68
BBMCu <sup>b</sup>	pure	16 Hz	+	0	0	-	+	43
TPDTP <sup>c</sup>	TCNQ	0.1-1 GHz <sup>a</sup>	+	-	-	nm	nm	47, 48

<sup>a</sup> Microwave reflection technique. <sup>b</sup> Bisbenzoylmethanocopper(II). <sup>c</sup> Tetraphenyldithiopyranylidene. <sup>d</sup> Meaning for the symbols used: +, increase, -, decrease, 0, unchanged; nm, not measured; ns, no signal.

The transition to the mesophase is accompanied by an increase in the jump time (decrease in the mobility) by a factor of 4 to *ca.* 0.3 ps for the *n*-alkoxy derivatives. This decrease in mobility occurs despite a change from a tilted to a horizontal stacking of the Pc moieties. Any benefits of the increased  $\pi$ - $\pi$  overlap in the mesophase appear to be more than outweighed by the increased disorder resulting from the melting of the hydrocarbon tails. A comparison with derivatives for which the Pc units remain tilted in the mesophase suggests that horizontal stacking in fact provides no extra benefit for charge migration. The main controlling factor appears to be the overall rigidity of the matrix. This is thought to be the reason that the mobility in the mesophases of octadecyl-Pc and octa-2-ethylhexoxy-Pc are substantially larger than for the alkoxy or alkoxyethyl derivatives.

In the mesophase of the alkoxy derivatives the mobility is almost independent of temperature and equal to  $2 \times 10^{-6}$  m<sup>2</sup>/Vs. This is illustrated particularly well by certain branched chain derivatives which are liquid-crystalline over almost the whole temperature range studied, from -100 to +200 °C, but for which the mobility changes by only a factor of approximately 2.

For the only compound of the group studied which had a clearing point within the temperature range available the conductivity was found to decrease substantially on melting from the mesophase. A conductivity level remains however in the isotropic phase which indicates that charge migration still occurs by charge hopping on a picosecond time scale rather than by diffusion of molecular ions. Some degree of columnar order appears to persist in the isotropic phase, at least at just above the clearing temperature.

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