PHYSICAL REVIEW B VOLUME 46, NUMBER 5 1 AUGUST 1992-I

Conductivity and structure of a liquid-crystalline organic conductor

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(Received 30 September 1991; revised manuscript received 23 December 1991)

We have measured the dc conductivity and lattice parameters of hexa(hexylthio)triphenylene (HHTT) saturation doped by exposure to iodine vapor, using a four-probe resistivity technique and powder x-ray diffraction. The compound was further characterized by differential scanning calorimetry, thermogravimetric analysis, and polarizing microscopy. Pure HHTT is an insulator, and displays monoclinic crystal (K), incommensurate helical (H), columnar liquid crystal (D_{hd}), and isotropic liquid (I) phases. The iodine-doped compound retains the K, D_{hd}, and I phases, but the H phase is suppressed. In addition, the conductivity rises 4–5 orders of magnitude after doping, so that the iodine-HHTT complex has a powder conductivity characteristic of a semiconducting radical-ion salt.

I. INTRODUCTION

In recent years, there has been considerable experimental interest in the preparation of conducting complexes of discotic liquid-crystal donors doped with electron acceptors.[1–6] Such complexes may be expected to combine the electrical properties of semiconductors or conductors with the anisotropic mechanical, optical, and structural properties of liquid crystals.

Discotic liquid crystals are typically[7] formed by planar molecules, with flat, conjugated cores and four or more paraffinic side chains, or "tails." In the typically observed "D_{hd}" hexagonal-disordered columnar mesophase, for example, the molecules are ordered into a long-range two-dimensional (2D) hexagonal lattice of columns. Within each column, there is only short-range positional order of the molecules; intercolumnar correlations of the intracolumnar molecular displacements are weak or nonexistent. The centers of the columns are occupied by the molecular cores, which are essentially parallel to one another. The intercolumnar space is occupied by the highly disordered tails, which have in fact structural properties resembling those of an isotropic liquid, even though they are physically attached to the cores.[8] The structure can be thought of as consisting of stacks of conjugated plates, separated by regions of a paraffin liquid.

The structure of discotics is therefore similar to that of many aromatic molecular crystals,[9] which have been intensively studied after a suggestion by Little[10] that such compounds may display high-temperature excitonic superconductivity. Although no high-temperature superconductors of this sort have been observed, some compounds of this class have been shown to have highly anisotropic conductivity in the metallic range after doping with electron acceptors. We can anticipate, therefore, that a discotic compound might also display one-dimensional conducting properties.[11] Upon doping with electron acceptors, a number of discogenic compounds have in fact been observed to retain their mesophase character while undergoing increases in conductivity up to six orders of magnitude from the insulating, undoped values.[1]

The suggested mechanism for conduction in discotics assumes that all carrier transport is along the stack of cores; the tails are thought to play little or no role in the electrical properties. Therefore, discotics should have electrical properties similar to the aromatic molecular crystals discussed above. The rigid aromatic rings which form the core of the discotics contain delocalized π electrons; the usual intracolumnar core-core distance is such that the π^* shells of adjacent molecules in the stack overlap, thereby enhancing the probability of carrier transfer. In their undoped state, aromatic compounds have a very low carrier concentration,[12] and therefore are poor conductors, the mechanism often being exciton migration liberating trapped carriers. However, the low ionization energy of these compounds facilitates formation of conducting charge-transfer or radical-ion salt complexes upon the introduction of acceptor molecules. In this state the Mott criterion, $2E = C - J$, applies: The energy gap E is reduced when the Coulomb interaction term C decreases or the conduction bandwidth J increases. The high polarizability of the aromatic cores provides the necessary reduction of C, but the small values of J found in organic molecular crystals (typically a few meV),[13] indicate that the molecular salt is more likely to be a semiconductor (with $E > 0$) than a conductor.

Motivated by these observations, we have studied complexes of a discogenic donor molecule, hexa(hexylthio)triphenylene (HHTT), with iodine. Iodine was chosen as our initial dopant based on the ease of vapor doping and the observation that iodine forms stable polyiodide ions in similar molecular crystals.[14,15] Pure

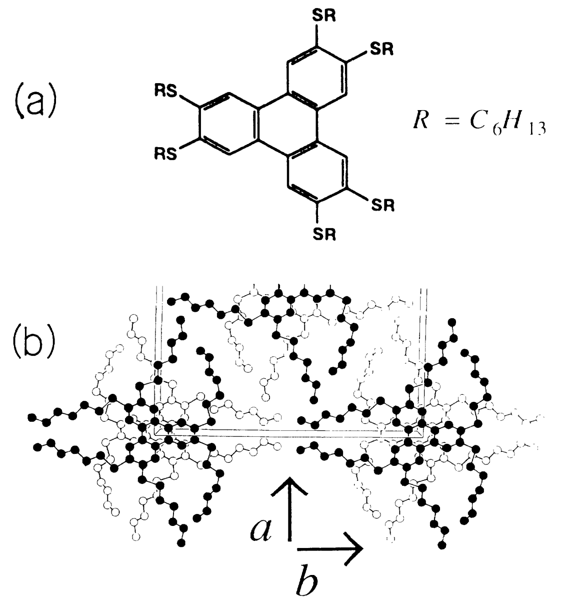

FIG. 1. (a) Molecular structure of hexa(hexylthio) triphenylene (HHTT). (b) Crystal (*K*-phase) structure of pure HHTT (Ref. 18). Half of the unit cell is shown, as viewed along the *c* axis. Atoms in the upper plane are indicated with closed circles, atoms in the lower plane with open circles.

HHTT has undergone extensive structural and thermodynamic study.[16–19] The phase sequence of the pure system at atmospheric pressure is

$$K \underset{62^\circ C}{\longleftrightarrow} H \underset{70^\circ C}{\longleftrightarrow} D_{hd} \underset{93^\circ C}{\longleftrightarrow} I \quad .$$

The crystalline (*K*) phase has a monoclinic structure with a basis of four molecules (Fig. 1). The molecules are ordered into columns, within which there is a repeat unit of two molecules. The *H* phase, although crystalline, closely resembles liquid-crystalline columnar phases. Molecules are ordered into columns with long-range intracolumnar and incommensurate helical order. In the liquid-crystalline D_{hd} phase, the molecules still form a hexagonal array of columns. However, the positional order within the columns is liquidlike, and both helical and superlattice order is lost. As usual, the isotropic (*I*) liquid phase has only short-range positional and orientational order.

II. EXPERIMENTAL

Hexa(hexylthio)triphenylene was synthesized as previously reported.[19] To prepare samples for x-ray diffraction and conductivity measurements, a flask containing approximately 50 mg of sample was placed in an evacuatable chamber together with a flask of 10 g of iodine, both of which were kept at room temperature. The chamber was evacuated to a vacuum of 10^{-3} Torr, and then isolated from the dynamic pump. We observed that the formation of iodine crystals on the sample was suppressed if the chamber was then connected to an LN_2 cold trap, which had the effect of maintaining the total pressure at 10^{-3} Torr. Several hours were sufficient to dope a powdery sample that had been recrystallized from solution, while much longer times (on the order of days) were required to dope liquid samples or solid lumps; we ascribe this rate difference to the difference in surface areas. After doping, the resulting silverish-purple powder was found by thermogravimetric analysis (TGA) to have an approximately 1:1.55 mole ratio of HHTT:I_2. The compound was stable to iodine loss through the crystal and mesophases, although the iodine rapidly diffused out after melting into the isotropic phase. X-ray diffraction showed no evidence of I_2 crystals in the sample.

For powder x-ray-diffraction measurements, the doped compound was warmed to the isotropic phase, loaded in air into 0.2- or 0.5-mm capillary tubes, and then allowed to cool to room temperature. The tubes were then sealed and mounted in a temperature-control oven[20] with better than 0.1 °C stability.

X-ray-diffraction measurements were carried out in three different configurations. Low-resolution measurements for phase identification employed an INEL XRG 3000 generator together with a CPS-120 one-dimensional linear gas detector. Further work was done on a Rigaku RU 200 rotating anode generator, utilizing the (004) reflection from a Gr monochromator with a scintillation detector. Iodine has a much lower absorption cross section for the Mo $K\alpha_1$ radiation produced by this instrument, an order of magnitude better than that for Cu x rays. Therefore, the count rate was improved using the Rigaku, although there was a substantial loss of resolution, which made it impossible to accurately determine crystallographic parameters. Higher-resolution studies employed an Elliott GX-13 rotating anode generator and an NaI scintillation detector. The Cu $K\alpha_1$ line was selected using LiF(200) vertically focusing monochromator, slits, and a flat LiF(200) analyzer, resulting in a longitudinal resolution of 0.005 Å^{-1}.

Previous transport studies on discotic liquid crystals have utilized a variety of techniques to determine the resistivity, including dc two- and four-probe methods,[5,7,21] ac radio frequency reflection techniques,[22] and gain/phase impedance determination.[1] For our resistivity measurements, we chose to use the four-probe lead configuration proposed by van der Pauw.[23] This method requires small amounts of sample, and minimizes effects of contact resistance and sample shape.

Typically, about 20 mg of powdery crystal-phase sample (either doped or neat), were placed at the bottom of a 4.6-mm diam, flat bottom test tube. The tube was then reheated in air above the isotropic transition temperature and four 0.254-mm copper leads were inserted at even spacings around the perimeter. After cooling again to room temperature, the sample was observed to make a flat disk approximately 0.5 mm thick, covering the bottom of the test tube. Finally, the cell was sealed with a Teflon stopper, and the leads secured with silicon cement around the top of the tube. The cell was then placed in the same temperature-control oven used in the x-ray studies. Since the surface of the oven consisted of grounded Al cylinders, it provided a fair degree of electric shielding. The conductivity was then measured using a Keithley 617 system electrometer/source. (This meter has an extremely high internal impedance of >200 TΩ, necessary when measuring high resistivities.) Readings were smoothed by a digital filter to minimize the effects of electronic noise. The actual applied voltages were typically on the order of a few volts across a 3–5-mm sample.

According to the treatment of van der Pauw, a potential introduced between two adjacent contacts, a and b, on the perimeter of a thin sample of arbitrary cross-sectional shape and area, and constant thickness t will induce a current between two other adjacent leads on the sample, c and d. Under these conditions, the expression for the resistivity is

$$\rho=\frac{\pi t}{\ln 2}\frac{R_{ab,cd}+R_{bc,da}}{2}f\left[\frac{R_{ab,cd}}{R_{bc,da}}\right] .$$

Here $R_{ab,cd}=V_{ab}/I_{cd}$. f is a tabulated function of $R_{ab,cd}$ and $R_{bc,da}$,[23] and is very close to 1 when $R_{ab,cd}\approx R_{bc,da}$, as was the case in all of our measurements.

Systematic errors in such a measurement can include the effects of non-point-like contacts, nonuniform sample thickness, electrical noise, thermal electromotive force, input capacity, and leakage resistance. The magnitude of the first term can be approximated from van der Pauw's treatment, and was found to be negligible. Homogeneous sample thickness is a criterion for the van der Pauw treatment to be valid. Within a given sample we observed, at most, small deviations in thickness, and the reproducibility of our data for different size samples indicates this was not a major source of error. Careful treatment of the electronics minimized the other sources of error, so that the total uncertainty from all of these factors is believed to be less than 6%. As with other four-probe methods, this configuration should give values mostly independent of contact resistance, which in any case is likely to be several orders of magnitude less than resistances in the sample.

A potentially more serious question of interpretation arises from the possibility of having a small number of oriented domains, with some preferential orientation induced by the substrate. We believe that our samples were orientationally averaged in the K and I phases. In the D_{hd} phase, there is some possibility that homeotropic alignment was induced by the glass substrate. The measurements may therefore have been made predominantly perpendicular to the columns, most likely resulting in a value of the average conductivity that was *lower* than the true "powder average," and much lower than the intrinsic conductivity along the column direction.

III. RESULTS

The saturation-doped compound was found by differential scanning calorimetry (DSC) and powder x ray to have the phase sequence

$$K \xrightarrow[54^\circ\mathrm{C}]{} D_{hd} \xrightarrow[63^\circ\mathrm{C}]{} I \ .$$

The K-phase powder-diffraction pattern was indexed, and it was found that the doped K phase remains a monoclinic lattice with a unit cell that is slightly larger in all dimensions (Table I). The mesophase is still categorized as D_{hd} in the doped sample, as demonstrated by the existence of both hexagonal (100) and (110) sharp diffraction peaks, with d spacings in the ratio of $1:\sqrt{3}$, and the absence of any sharp (00L) or (HKL) peaks. The intercolumnar distance in the doped D_{hd} phase is actually *less* than that in the undoped phase (Table I). At high scattering angles, diffuse tail-tail and core-core scattering patterns were observed, also characteristic of a discotic mesophase.[8,18,24] The helical H phase was not observed in the doped samples. Lattice constants corresponding to the reflections in the K and D_{hd} phases are shown below.

X-ray-diffraction measurements on heating indicate an extended region of K/D_{hd} coexistence between 54 and 59 °C. In this region we observe the gradual growth of the D_{hd} (100) peak at 0.3488 Å^{-1}, with the concurrent diminishing of the K (110) peak at 0.3319 Å^{-1}, while the total integrated intensity under the two peaks remains constant. This is consistent with the first-order thermal signature observed by DSC.

The conductivities measured for both doped and undoped unaligned samples are shown in Fig. 2. We found a conductivity increase of approximately 4–5 orders of magnitude upon doping; this is consistent with measurements on other unaligned doped discotics,[2] although our compounds showed a larger conductivity variance with temperature than is usually observed.[2,5] The conductivity increases exponentially with temperature in the K and I phases. Upon warming into the mesophase from the K phase, the conductivity increases rapidly through the coexistence region, and eventually reaches a consistent value when the sample is completely in the D_{hd} phase. Large resistance fluctuations, as great as ±20%, are observed in the mesophase. The fluctuations are definitely *not* an instrumental effect; while their origin is not completely certain, we believe that they arise from random movement of microaligned domains in the sample. Such domains, separated by domain walls, are observed via optical microscopy. The movement could arise from slow flow of the highly viscous sample, from gradual annealing and annihilation of domain wall boundaries, or (less likely) from random thermal fluctuations. Sluyters *et al.*[11]

TABLE I. Lattice parameters, in Å, measured from powder x-ray diffraction in pure (Ref. 18) and iodine-doped samples of HHTT. The values given for the c lattice parameter in the D_{hd} phase are the mean core-core separations.

		Undoped	Doped
K	a	28.69	28.86
	b	25.02	25.25
	c	7.88	7.95
	β	97.85°	97.85°
D_{hd}	a	21.72	20.80
	c	3.64	3.79

have observed a large enhancement of this effect when conductivity was measured over a very small region of sample with a pointlike probe. The observation of conductance fluctuations is consistent with the hypothesis of highly anisotropic conductivity in the D_{hd} mesophase; we suggest that aligned domains temporarily "short circuit" pairs of leads, depending on their orientation.

If we assume a thermally activated hopping mechanism for the K phase, where the conductivity σ is given by $\sigma=\sigma_0\exp(-\varepsilon/2k_bT)$, an activation energy of approximately $\varepsilon=1.8$ eV may be extracted. This band gap is larger than the energies in the range 0.75 eV usually seen along the best conducting direction in molecular radical-ion salts, but it should be noted that the activation energy sampled in this experiment is an incoherent sum of the activation energies parallel and perpendicular to the columns, and that the latter is expected to be quite high. It should be emphasized that our measurements were made on essentially unoriented samples, and thus the conductivity we observe represents some kind of average over any anisotropic conduction effects.

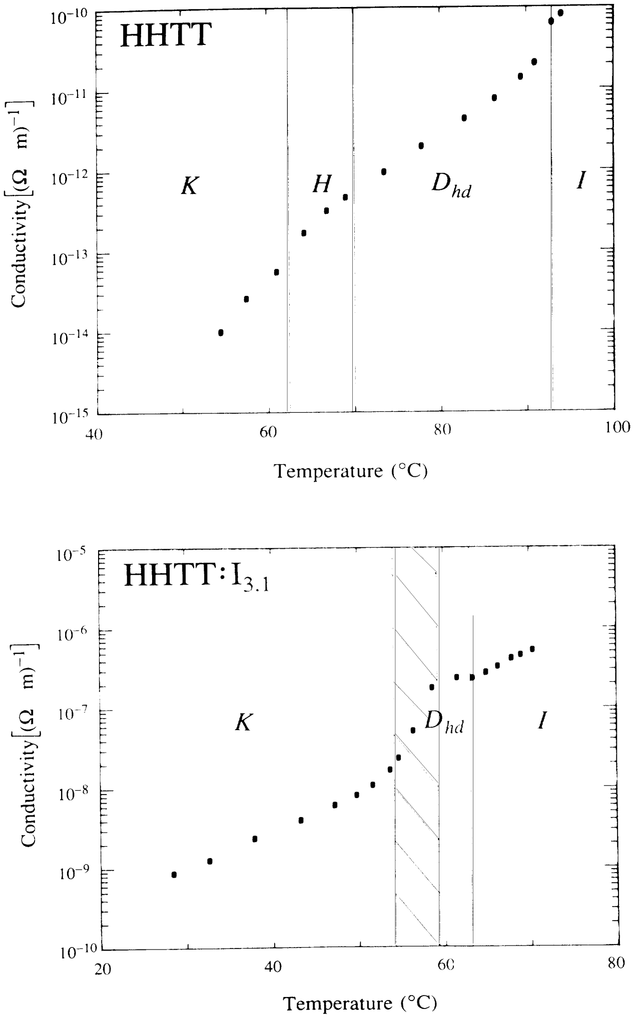

FIG. 2. Thermal dependence of dc conductivity of pure and iodine-doped HHTT, as measured by the four-probe method of van der Pauw. The shaded area in the lower graph indicates the K-D_{hd} coexistence region.

IV. DISCUSSION

Measurements of the bulk powder conductivity of anisotropic conductors are not sufficient to determine the components of the conductivity tensors of these materials, which have in general two or four independent components in systems of hexagonal or monoclinic symmetry, respectively. Since each component may have its own temperature dependence, and the dominant component may change in different temperature regimes, the behavior observed may be reflective of only certain components. In addition, no highly conducting behavior may be observed, since it will be masked by interparticle contact resistances between crystallites in the sample. Therefore, although the increase in conductivity observed after doping, as well as the color change in the sample, is indicative of some degree of charge transfer and carrier generation, the absolute conductivity in any direction remains unknown, pending work (in progress) on aligned samples.

Crystal structure refinements have not been performed on the ordered structures. Nevertheless, we can construct a plausible model for the structure based on the stoichiometry and lattice constants. It has often been observed that in a nonpolar, uniaxial environment iodine will form I_3^- ions.[15,28] The observed mole ratio from TGA is suggestive of a model of one polyiodide ion per HHTT molecule, where the iodine appears almost completely as I_3^-. The creation of this species would be consistent with the theoretical doping equation,

$$2\ \mathrm{HHTT}+3\ I_2\rightarrow 2\ (\mathrm{HHTT}+I_3^-)\ .$$

The rest of the iodine would take the form of other possible species, such as I_5^-. The enlargement of the unit cell in the K phase is greatest in the direction perpendicular to the column; the increased distance between adjacent cores is only 0.04 Å. Therefore, we propose that the monoclinic unit cell contains four HHTT molecules and four polyiodide molecules, with the linear polyiodide molecules occupying the gaps between the larger HHTT molecules, although the orientation of the iodine ions is indeterminable from our data. Such an arrangement is quite similar to the two-dimensional "staging" structure seen in polyacetylene and other doped chain polymers.[25]

The *decrease* in the intercolumn distance in the D_{hd} phase upon iodine doping seems somewhat surprising, although a similar reduction has been seen in doped polymer discotic liquid crystals.[26] In general, the intercolumnar distance in discotic columnar phases is quite "soft," due to the many degrees of freedom available in the aliphatic tails. We have previously[17,18,24] reported large *negative* thermal expansion parameters in discotic columnar and nematic phases, and associated this thermal shrinking of the lattice with increased tail disorder. Thus, the most likely model for the structure of the doped D_{hd} phase is that the iodine ions again fit themselves into gaps between columns of HHTT molecules (Fig. 3), with the aliphatic tails moving aside to make

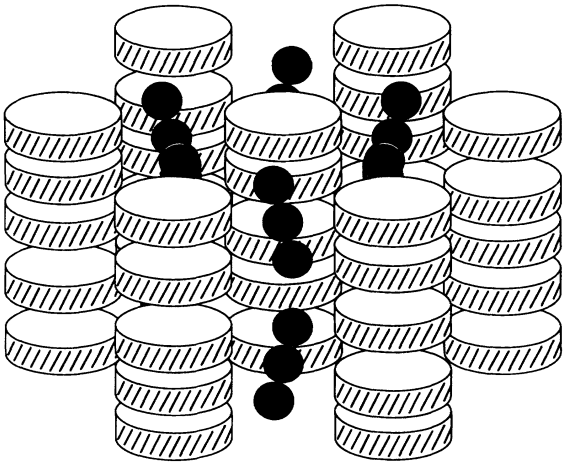

FIG. 3. Schematic of the proposed structure of the doped D_{hd} phase. The disks represent the cores of the HHTT molecules, which are assembled into columns with short-range intracolumnar order and long-range hexagonal intercolumnar order; and the black spheres represent the I_3^- ions. The iodine ions are assumed to occupy the volume between the columns in a disordered fashion. The liquidlike tails which also lie in the intercolumnar spaces are omitted for clarity.

room. The decrease in the *a*-*b* lattice constant is then explained by Coulomb interactions arising from charge transfer from the HHTT columns to the polyiodide ions.

It is of course possible that a minority of the iodine atoms or molecules are incorporated *within* the HHTT columns. For example, iodine has been observed to fit between adjacent conjugated sheets in molecular crystals.[12] However, the mean observed core-core distance in this phase of 3.79 Å leaves little space between the calculated[27] van der Waals radii of the adjacent triphenylenes for an iodine ion. With a 1:1 ratio of I_3^- ions per HHTT molecule, the majority of the iodine ions must be "intercalated" between the columns.

In summary, HHTT retains its monoclinic crystal and hexagonal columnar liquid-crystal phases upon doping with iodine. The conductivity increases by 4–5 orders of magnitude after doping, and subsequent conductivity changes are correlated with phase transition temperatures. Our observations support the premise of conductivity occuring along columns of aromatics with π orbital overlap. The structural evidence is consistent with a model of I_3^- ions interspersed between HHTT columns in both the K and D_{hd} phases. Further structural and conductivity measurements on oriented samples are anticipated.

ACKNOWLEDGMENTS

We are grateful to A. R. McGhie and S. H. J. Idziak for performing the TGA and DSC measurements. We also thank J. E. Fischer, A. F. Garito, and N. C. Maliszewskyj for useful discussions. This work was supported by National Science Foundation Grant Nos. DMR MRL 88-19885 and DMR 89-01219.

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[1] N. Boden, R. J. Bushby, J. Clements, M. V. Jesudason, P. F. Knowles, and G. Williams, Chem. Phys. Lett. **152**(1), 94 (1988).

[2] L. Y. Chiang, J. P. Stokes, C. R. Safinya, and A. N. Bloch, Mol. Cryst. Liq. Cryst. **125**, 279 (1985).

[3] P. Davidson, A. M. Levelut, H. Strzelecka, and V. Gionis, J. Phys. (Paris) Lett. **44**, L-823 (1983).

[4] V. Gionis, H. Strzelecka, M. Veber, R. Kormann, and L. Zuppiroli, Mol. Cryst. Liq. Cryst. **137**, 365 (1986).

[5] J. van Keulen, T. W. Warmerdam, R. J. M. Nolte, and W. Drenth, Recl. Trav. Chim. Pays-Bas **106**, 534 (1987).

[6] F. D. Saeva, G. A. Reynolds, and L. Kaszczuk, J. Am. Chem. Soc. **104**, 3524 (1982).

[7] For a recent review of the structural properties of discotic liquid crystals, see S. Chandrasekhar and G. S. Ranganath, Rep. Prog. Phys. **53**, 57 (1990).

[8] E. Fontes, M. Ohba, J. N. Haseltine, and A. B. Smith III, Phys. Rev. A **37**, 1329 (1988).

[9] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals* (Clarendon, Oxford, 1982).

[10] W. A. Little, Phys. Rev. **134**, A1416 (1964).

[11] J. H. Sluyters, A. Baars, J. F. van der Pol, and W. Drenth, J. Electroanal. Chem. **271**, 41 (1989).

[12] F. Gutmann and L. E. Lyons, *Organic Semiconductors* (Wiley, New York, 1967).

[13] E. A. Silinsh, *Organic Molecular Crystals, Their Electronic States* (Springer-Verlag, Berlin, 1980).

[14] A. Gleizes, T. J. Marks, and J. A. Ibers, J. Am. Chem. Soc. **97:12**, 3545 (1975).

[15] J. L. Petersen, C. S. Schramm, D. R. Stojakovic, B. M. Hoffman, and T. J. Marks, J. Am. Chem. Soc. **99:1**, 286 (1977).

[16] E. F. Gramsbergen, H. J. Hoving, W. H. de Jeu, K. Praefcke, and B. Kohne, Liq. Cryst. **1**, 397 (1986).

[17] E. Fontes, P. A. Heiney, and W. H. de Jeu, Phys. Rev. Lett. **16**, 1202 (1988).

[18] P. A. Heiney, E. Fontes, W. H. de Jeu, A. Riera, P. Carroll, and A. B. Smith III, J. Phys. (Paris) **50**, 461 (1989).

[19] W. K. Lee, P. A. Heiney, J. P. McCauley, Jr., and A. B. Smith III, Mol. Cryst. Liq. Cryst. **198**, 273 (1991).

[20] E. Fontes, P. A. Heiney, J. N. Haseltine, and A. B. Smith III, J. Phys. (Paris) **47**, 1533 (1986).

[21] H. Strzelecka, V. Gionis, J. Rivory, and S. Flandrois, J. Phys. (Paris) Colloq. **44**, C3-1202 (1983).

[22] R. Kormann, L. Zuppiroli, V. Gionis, and H. Strzelecka, Mol. Cryst. Liq. Cryst. **133**, 283 (1986).

[23] L. J. van der Pauw, Philips Res. Rep. **13**, 1 (1957).

[24] W. K. Lee, B. A. Wintner, E. Fontes, P. A. Heiney, M. Ohba, J. N. Haseltine, and A. B. Smith III, Liq. Cryst. **4**, 87 (1989).

[25] P. A. Heiney, J. E. Fischer, D. Djurado, J. Ma, D. Chen, M. J. Winokur, N. Coustel, P. Bernier, and F. E. Karasz, Phys. Rev. B **44**, 2507 (1991).

[26] H. Ringsdorf and R. Wüstefeld, Philos. Trans. R. Soc. London, Ser. A **330**, 95 (1990).

[27] J. M. Robertson, *Organic Crystals and Molecules* (Cornell University Press, Ithaca, 1953).

[28] J. M. Reddy, K. Knox, and M. B. Robin, J. Chem. Phys. **40**(4), 1082 (1964).