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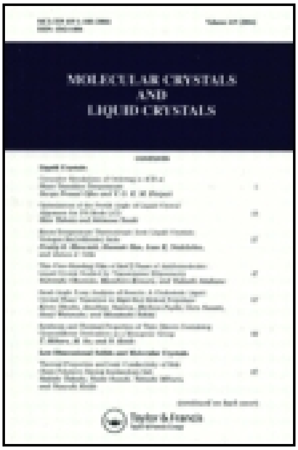

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Studies of Organic Semiconductors for 40 Years—X

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Studies of Organic Semiconductors for 40 Years—X

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The paper reports on results of studies on organic semiconductors carried out in Czechoslovakia, Hungary, Poland, Romania and Yugoslavia. Obviously, it was impossible to describe results reported in all publications which appeared during these years, thus we only cite representative papers. We also found it impossible to maintain a strict "geographic" code, as some research carried out by authors mentioned in this review was inspired by and/or carried out in collaboration with groups from other countries. With few exceptions, the review does not cover research on polymers unless it is related to low-molecular weight organic solids.

EARLY RESULTS

The first papers on semiconducting properties of an organic material appeared as early as in 1954, reporting on the measurements of the conductivity of thin films of methylene blue.[1,2] In Poland, systematic studies of organic semiconductors were initiated in Poland by K. Gumiński, and then continued by him, K. Pigoń, M. Kryszewski and their collaborators. Early papers described mainly measurements of temperature dependences of electrical conductivities of several simple organic materials (e.g., [3–10]). Specific electric behaviour of organic solids and, consequently, inapplicability of "textbook" semiconductor models was recognized quite early. In this context, it is interesting to mention the concept of the "redox wave" put forward by Gumiński as early as in 1957[11] which is, essentially, a qualitative description of the transport of injected charges. It was also realized that the arrangement of the molecules in the crystal lattice, and interactions between them (in particular, the hydrogen bonding) play an important role in the charge transport.

As shown by Pigoń and Chojnacki, they manifest themselves in anisotropy of the conductivities measured on single-crystalline samples,[12-15] and in discontinuities of electrical conductivity in the vicinity of structural phase transitions (e.g., [3,16]). The latter authors studied also the charge transport in single crystals of anthracene and gave reasonable estimates of the ratio of ranges of free electrons and holes.[17]

In Czechoslovakia, measurements of electrical properties of organic materials were initiated in the sixties by J. Honzl, K. Ulbert and their collaborators,[18] who studied properties of aniline black (polyaniline), its low-molecular weight oligomers (oligoanilines), and their CT complexes with iodine, TCNQ, ClO_4^- etc. A series of papers then followed, reporting on results of measurements of temperature dependences of dark and photoconductivity, Seebeck coefficient etc. (e.g., [19–23]. The experiments were supplemented with quantum-chemical calculations of the band structure of oligoanilines[24] and with structural reports (e.g., [25,26]).

As pointed out in 1941 by A. Szent-Györgyi,[27] organic semiconductors may be considered models for biologically active molecules, thus another obvious direction of studies were investigations of biologically important materials. J. Ladik and collaborators published a series of papers (cf., e.g., [28–31]) devoted to quantum-chemical calculations of the band structure of DNA models within the tight-binding approximation. Beleznay *et al.*[30] attempted to calculate the pre-exponential factor and the activation energy of the conductivity in DNA.

ELECTRONIC STRUCTURE AND TRANSPORT OF CHARGE CARRIERS

Independently of the calculations of the band structure of biopolymers carried out by Ladik *et al.*,[28-31] similar calculations were also performed for simple organic crystals. Chojnacki[32,33] estimated the temperature dependence of the mobilities of electrons and holes in anthracene. The computed temperature dependences of the mobility correctly predict the mobilities in the a and b directions to be decreasing functions of temperature.

Similar calculations were carried out by Chojnacki[34-37] for molecular crystals with specific interactions (extended chains of H-bonds or charge transfer). The values of the mobility anisotropy calculated for imidazole crystals point out to an important role of extended chains of hydrogen bonds in the transport of charge carriers, confirming the experimental results, published earlier by the same author.[14,15] A similar approach was also used to calculate the band structure in the weak CT complex anthracene-trinitrobenzene.[37] The anisotropy found from the calculations was found to agree well with that determined from the time-of-flight experiment.[38,39] Petelenz[40] considered the effect of the polarization of "soft" molecular crystal. Having calculated the transfer integrals in a simple "anthracene-like" molecular dimer, he showed that the field-induced polarization of molecular orbitals results in a decrease of the transfer integrals.

The influence of the hydrogen bond was also explicitly taken into account in quantum-chemical calculations of the band structures and carrier mobilities performed for several model biopolymers by the Hungarian group (cf., e.g., [41–44]).

Although the absolute values of the charge carrier mobilities obtained from the calculations appear unrealistically high, their anisotropy seems to reflect the fact that, contrary to the situation in molecular crystals, it is the main chain direction (and not that of the H-bond) which is favoured in the carrier transport.

The carrier transport in a molecular crystal is more adequately described in terms of polaron motion. This problem was considered by P. Gosar and his collaborators in a series of papers.[45-50] The approach used by Gosar, Vilfan *et al.* was employed in later publications. Pesz and Luty[51] extended the Gosar's model by taking into account the quadratic coupling of carriers with lattice phonons. The quadratic coupling was shown to decrease the mobility without otherwise changing the character of its temperature dependence. The diffusion of charge carriers interacting with lattice phonons was considered within both hopping and band regime by Čapek and Munn.[52,53] Čapek published also a series of papers where quantum corrections to the Lyons's electrostatic model were considered (e.g., [54,55]). The corrections were found to be of the order of 10^{-2} to 10^{-1}eV in the linear polyacene series increasing with the molecular dimension.

Direct measurements of the mobility of charge carriers in several molecular solids were carried out, in most cases aiming at finding a correlation between the molecular structure and interactions, and the carrier mobilities (or, more precisely, its anisotropy and temperature dependence). Zboiński[38,39] determined the anisotropy and temperature dependence of electron and hole mobilities in the single-crystalline samples of the charge-transfer complex: anthracene-trinitrobenzene. The carrier mobilities were of the order of 10^{-2}cm^2/Vs at room temperature, the largest electron mobility being along the stack; for the holes, however, the longest axis of the mobility tensor formed the angle of ca. 33° with the stack direction.

Carrier mobilities were also determined in tetracyanoethylene, dibenzothiophene and iodoform.[56-58] At sufficiently high temperatures, the mobilities were decreasing functions of temperature, and in the two former crystals they could be fitted assuming an $\exp(\epsilon_a/kT)$ -type dependence, with ϵ_a of the order of 0.1 eV. No lattice phonons can be associated with these energies, thus the mechanism which could account for these results remains obscure.

Kondrasiuk and Szymański,[59] found apparent hole mobilities in thin flakes of tetracene to be field-dependent. They amounted to ca. 1cm^2/Vs at 100 V/cm, and decreased with the field as F^{-1}. A similar behaviour was also observed in polycrystalline samples of several other materials,[60-62] being probably associating with imperfections of the samples' structure.[63-65]

LOCAL LEVELS

Basing on the approach put forward by Lyons, Sworakowski[66] and, independently, Silinsh put forward a model allowing one to predict depths of traps formed in molecular materials by structural defects and chemical impurities. According to the model, "chemical" traps for electrons are formed by guest molecules having electron affinity higher than that of the host molecules; similarly, hole traps are formed by impurity molecules having lower ionization energy. This simple model yielded results in a good agreement with available experimental data, confirming indeed the applicability of the Lyons's concept.

Structural traps may be formed by host molecules in the vicinity of defects due to modifications of local values of the polarization energy. The depth of traps formed by molecules close to the defect core may, in principle, be calculated if the positions and orientations of molecules in the imperfect crystal are known. Such calculations of the structure of imperfect crystals, carried out by Sworakowski[67,68] under several simplifying assumptions, showed that structural traps of polarizational origin are likely to form distributions of the same depths for both electrons and holes. However, there exist experimental results seemingly confirming an opposite point of view. Zboiński[69] measured the temperature dependences of electron and hole mobilities in anthracene crystals. The electron mobility was found to fulfill the $T^{-1.7}$ power law, whereas the hole transport was controlled by traps. The hole traps were identified as associated with "incipient dimers", i.e. with defects of undoubtedly structural origin. Recently, it was suggested[70] that the sandwich pair of anthracene molecules may be considered as a species having a lower ionization energy and higher electron affinity than those of single molecules. The depths of hole traps formed by such species were found to markedly exceed those of electron traps.

Much effort was directed towards the determination of the parameters of local states. Usually, the authors of the papers cited below used the space-charge-limited curents (SCLC), thermally stimulated currents (TSC) in their various modifications, and measurements of temperature dependences of the carrier mobilities.

The concept of SCL currents was used as early as in 1965 by Kryszewski and Szymański to explain the shapes of current-voltage characteristics in polymeric materials.[71] Later, the same group measured SCLC characteristics on thin sublimation flakes and polycrystalline thin films of *p*-terphenyl, *p*-quaterphenyl and *p*-hexaphenyl,[72-74] attempting to correlate trap structures in these materials with that of poly(*p*-phenyl). Steady-state SCLC characteristics were also measured in crystals of chloranil, anthracene, tetracene and *N*,*N'*-diphenyl-*p*-phenylenediamine.[75-79] The parameters of traps were determined from a fit of the experimental current-voltage characteristics to equations derived assuming *a priori* a given energetic distribution of traps (cf., e.g., [76,80–83]). However, such fits were found to yield results of a questionable quality, thus several papers appeared dealing with the "inverse problem": a determination of parameters of traps without assumptions concerning their distributions. Nešpurek and Sworakowski[84,85] put forward so-called "differential method". This method, in its original form and modified by Schauer *et al.*[86,87] ("thermally modulated SCLC"), was used in the determination of the energetic structures of local states in several inorganic (amorphous) and organic semiconductors (e.g., [87,88]).

Parameters of local states in organic solids were also determined employing the TSC technique. Here, only the papers dealing with a choice of a method of extraction of trap parameters from thermally stimulated currents will be quoted. This problem was considered by several authors (e.g.,[89–94]). It is worth mentioning the work by Samoć *et al.*,[94] who experimentally verified the concept of "transport TSD peak" introduced by Plans *et al.*[92]

Samoć and Zboiński[95] used the drift mobility measurements in their study of the trapping of charge carriers in deliberately damaged anthracene crystals finding a qualitative difference between the behaviour of electrons and holes. An interesting result was obtained by Samoć[96] who found an anisotropy of the depth of perylene traps in perylene-doped anthracene crystals. Such a result, similar to that observed earlier by Karl, might be explained assuming a rotation of the mobility tensor around its b axis; however, a similar (and even more pronounced) effect was observed in iodoform,[58] where the hexagonal symmetry of the crystal lattice prevents any rotation of the axes. It seems that the effect might be associated with the dimensionality of the systems studied. At present, no direct evidence exists supporting this point of view but recent investigations of trapping in model one-dimensional insulators[97,98] show that the behaviour of such systems should qualitatively differ from that of "conventional" ones.

PHOTOGENERATION

Upon excitation, in addition to neutral (small radius) excitons, states may be created in which electrons, having been transferred to neighbouring molecules, remain correlated with holes localized on generation sites. These states (CT excitons) can be formed via a direct excitation from the ground state,[99,100] or by the ionization of higher excited neutral states. The lifetime of CT excitons is commonly believed to be ca. 10^{-9}s but the existence of long-lived CT states in molecular complexes was also postulated.[101] They can be transformed into neutral excitons (cf.[102]) or dissociate into pairs of free charge carriers. The field dependence of the charge carrier photogeneration is governed by the efficiency of the dissociation which, in many cases, may be adequately described by the Onsager mechanism. This model was applied by Nešpurek *et al.* to describe the photogeneration in metal-free phthalocyanine,[103,104] iodoform,[105,107] as well as in some polymeric materials. There have also been reports on one-photon photogeneration processes in tetracene, linear oligoanilines, phenazine and weak CT complexes of tetracyanobenzene (TCNB).[23,108-112] Samoć and Williams[110] considered the photogeneration of charge carriers in anthracene-TCNB complex and put forward a kinetic model well describing all features of the experimental results. Nešpurek[108,113] investigated the effect of acceptor molecules on a donor-acceptor junction, finding an increase of the separation distance of the CT exciton and the primary quantum efficiency.

Photogeneration associated with multiphoton absorption was investigated in anthracene,[114] where photoionization of triplet excitons was shown to play an important role, and in thianthrene,[115] where the dc photoconductivity was attributed to interactions between singlet and triplet exciton.

A limited volume of this article makes it impossible to review papers dealing with excitons, their generation, dynamics and interactions; the Reader is thus referred to a collection of representative papers.[116-123]

PHOTOINJECTION AND DARK INJECTION

As was mentioned above, the absorption of light creates excitons which may participate in a variety of physical processes, one of possible processes being photoinjection. This process was studied in more detail on tetracene, in which long-living triplet excitons, generated by the singlet exciton fission, play a major role.[124,125] The importance of triplet excitons was confirmed by the measurements of exciton-charge carrier interactions, and in particular those of the magnetic field effect.[126-129] The steady-state and pulse photoconduction, as well as photovoltaic effect measurements in tetracene[130] demonstrated the complexity of the process of production of charge carriers in tetracene films. One of parameters that should be taken into account is the spatial inhomogeneity of the films, the other being associated with, e.g., differences in the efficiency of the injection processes[131] or in the carrier dynamics. Similar difficulties were encountered in explaining features of the photovoltaic effect in metal-free phthalocyanine (e.g., [132,133]). Thus it seems that a model taking satisfactorily into account all features of the photovoltaic effect in organic materials still remains to be put forward.

The spatial behaviour of photoinjected carriers at liquid electrodes–organic crystals interfaces was studied in References 124, 134, 135. Kalinowski and Godlewski[135] determined the spatial distribution of the space charge generated at the water/organic crystal interface upon illumination, and showed it to be well described by the Mott-Gurney relation.

Godlewski and Kalinowski[136] considered the effect of traps on emission-limited currents in narrow-band insulators. The same authors[137] studied the effect of illumination on SCL currents in anthracene and tetracene interpreting the results within the model simultaneously taking into account thermal and optical detrapping. Their model was then used by Miniewicz *et al.*[138,139] to explain photoinjection into trinitrobenzene crystals. Nešpurek *et al.*[140] described the transition from electrode-limited to SCL currents showing that it should manifest itself as a change of the activation energy.

Injection from liquid redox electrodes into pure and perylene-doped anthracene and chloranil crystals was investigated by Sworakowski *et al.*,[74-77,141,142] who determined the reorientation energy of the solvation layers of some simple redox systems.

Simultaneous injection of carriers of both signs results in a recombination and subsequent electroluminescence was measured by Kalinowski, Godlewski *et al.*[143-147] on pure and doped anthracene, and tetracene. The authors described a method of determination of the spatial distribution of the intensity of electroluminescence.[144,145] Sworakowski *et al.*[148] measured the double injection current-voltage characteristics in anthracene crystals and showed it to be influenced by surface states. Miniewicz, Nowak *et al.*[149,150] studied the electroluminescence in the perylene-doped anthracene crystals and in the anthracene-trinitrobenzene system.

Describing the research on injection and related processes, one must not leave unmentioned the work concerning switching in organic substances. Szymański *et al.*[151] reported on switching in tetracene thin films. The phenomenon was then observed also in thin films of *p*-quaterphenyl by Kasica *et al.*[152] and by Swiatek.[153]

Studies of electrical properties and switching in metal-free phthalocyanine films were carried out by Füstoss-Wegner (e.g.,[154]). It was demonstrated that, depending on the film thickness and ambient atmosphere, negative resistance, bistable switching or emission/SCL characteristics were observed.

CHARGE TRANSFER COMPLEXES AND ION RADICAL SALTS

As was mentioned in the initial section of this review, electrical properties of charge-transfer complexes have been extensively studied since early sixties, and the interest markedly increased after the discovery of high (metallic) conductivity in this class of organic solids. The number of papers that have been published is of the order of hundreds. In particular, the attention was focused on organic one-dimensional (1D) systems, tetrathiofulvalene tetracyanoquinodimethanide (TTF-TCNQ) being an example of such systems. The dielectric function in this material was for the first time determined using the backward-wave-oscillator transmission spectroscopy.[155] Several papers report also on results of magnetic measurements (e.g., the pressure dependence of the EPR signal).[156]

Interactions between electrons in a 1D system (e.g., *N*-methylphenazinium-TCNQ) were considered by Suhai and Biczó.[157] It was postulated that the Coulomb repulsion may be substantially reduced by attractive terms arising from the polarization of electronic systems of both TCNQ and NMP chains.

Several papers were devoted to studies of the metal-insulator transitions in TTF-TCNQ and related 1D systems. This problem was dealt with by Barišić *et al.* (e.g.,[157–160]) from the theoretical point of view. Experimental papers were also published concerning this point (e.g.,[161–164]). Theoretical aspects of electronic and vibronic excitations and electronic structure of doubly charged TCNQ dimers, trimers and tetramers were discussed by Málek, Král *et al.* (e.g., [166–168]). Many papers were published describing results of measurements of electrical, optical and magnetic properties of systems with dimerized molecular stacks (see, e.g., [169–176]).

A phenomenological model allowing one to calculate the charge transfer in organic ion-radical salts and adequately reproducing accepted experimental data was put forward by Komorowski.[177,178] The same author considered also the lattice energy of ion-radical salts.[179]

The irradiation of organic conducting materials results in creation of defects which markedly influence optical, electrical and magnetic properties of these materials. The effect of irradiation was reported in several papers by the Hungarian group (Grüner, Jánosy, Kamarás *et al.* (e.g., [180–185]), and by Graja *et al.* (e.g., [186,187]).

Among other low-molecular systems studied were *N*-methyl-derivatives of pyridine-TCNQ,[188,189] and methyl-derivative of 1,4-diazabicyclo[2,2,2]-octane $(TCNQ)_2$.[190] We shall also mention measurements of electrical properties of iodine complex of tetraaza[14]annulene (σ up to 10^{-5} S/cm),[191] and those of TCNQ with quinolines (σ up to 1 S/cm)[192,193] and bis(tetrathiotetracene) triiodide.

Finally, we shall briefly mention a series of papers describing an interesting use of low-molecular weight organic metals in polymeric composites. Kryszewski *et al.* published a series of papers,[194-199] describing properties of so-called "reticulate-doped" polymers. Essentially, these systems consist of crystallites of low-molecular weight highly conducting systems grown under appropriate conditions during the polymer casting. Due to a particular, needle-like arrangement of the conducting material, the conduction threshold may be achieved at a very low amount of the organic metal (sometimes below 1 wt.%). In this way, several conducting systems were prepared: e.g., tetrathiotetracene-TCNQ in polycarbonate ($\sigma \sim 2\times10^{-2}$ S/cm at 1 wt.%),[194] 1-methyl-3-alkylimidazolinium $(TCNQ)_2$ ($\sigma\sim10^{-1}$S/cm at 7 wt.%),[200] etc. Additional advantage of these systems is their increased stability with respect to conducting polymers. These new highly conducting composite systems open a new field in both polymer and organic solid state research.

FINAL REMARKS

This review aimed at pointing out to the paths, along which the research of electrical properties of organic solids proceeded in several laboratories during over thirty years. Apart from the publications cited in this paper, there appeared many more which we had to omit due to a limited space. Several review articles and monographs were also published; here, we shall mention only the books by Pigoń, Gumiński and Vetulani[201] (probably one of the earliest books devoted entirely to organic semiconductors), by Kryszewski[202] (devoted mainly to polymeric semiconductors but with extensive reference to the research carried out in low-molecular weight organic materials), and by Simionescu[203] (giving report only to research on polymeric systems but being representative of the research on organic semiconductors in Romania). It is equally important to mention some scientific events: the IUPAC International Symposium on Macromolecular Chemistry held in Prague in 1965,[204] where two subsections were devoted to electronic structure and electron properties of organic systems, two International Conferences on Organic Conductors and Semiconductors held in Siófok, Hungary, in 1976[205] and in Dubrovnik, Yugoslavia, in 1978,[206] a series of international conferences "Electrical and Related Properties of Organic Solids", organized in Poland since 1974,[207-209] and many others.

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