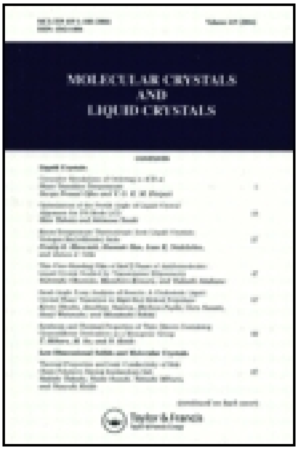

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# ORIENTATION OF THE POLARIZABILITY AND ABSORPTION TENSORS. - INTRA- AND INTERMOLECULAR EXCITATIONS IN ORGANIC CONDUCTORS *

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Indicatrix measurements in the VIS and NIR show that the orientation of the polarizability tensor is governed by the orientation of the planar molecules of the stack in the whole frequency range. But the shape of the indicatrix changes significantly: In the case of intramolecular excitation the optic sign is positive and the absorption is greatest for light vibrating parallel to the long axes of the molecules. In the case of intermolecular excitation the optic sign is negative and the absorption is greatest for vibrations perpendicular to the planes of the molecules, not parallel to the stack. The temperature dependence of the absorption obeys Urbach's rule. This makes possible the investigation of the CT-process.

## INTRODUCTION

Organic conductors consisting of chainlike stacks of planar molecules are considered. The flat planar molecules are characterized by the longitudinal axis L, transversal axis T, and the axis N normal to the molecule plane, in most cases inclined to the stack direction. The orientation of the polarizability tensor related to these molecule axes i.e. to the crystal structure are investigated by measuring the orientation and dispersion of the indicatrix.

The principal axes of the polarizability coincide with the directions (optical directions X, Y, and Z) of the three principal axes of the indicatrix. The indicatrix is a tri-

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axial ellipsoid formed by three principal axes of the length $2n_\alpha$, $2n_\beta$, and $2n_\gamma$ which lie along the X, Y, and Z optical directions, respectively. $n_\alpha$, $n_\beta$, and $n_\gamma$ are the three principal indices of refraction ($n_\gamma > n_\beta > n_\alpha$). Perpendicular to each of the two circular sections of radius $n_\beta$ is an optic axis OA. The optic axes intersect at acute angle 2 V and define the optic plane (XZ-plane).

The maximum absorption is found always parallel to one of three optical directions X, Y, or Z.

The following chapter represents the results of measurements of four excamples.

## RESULTS OF MEASUREMENTS

### $(MTPA) \cdot (TCNQ)_2$

All TCNQ molecules have the same orientation (TCNQ stacks, triclinic). The optical directions coincide with the directions of the TCNQ molecule axes[1] : X parallels N, Y parallels T, and Z parallels L. There is only a small sinusoidallike rotatation ($\lesssim 9^\circ$) on T probably due to interaction between the molecules (mixing of molecular excitations). The upper curve in Figure 1 shows the angle $\measuredangle$ (Z,L)

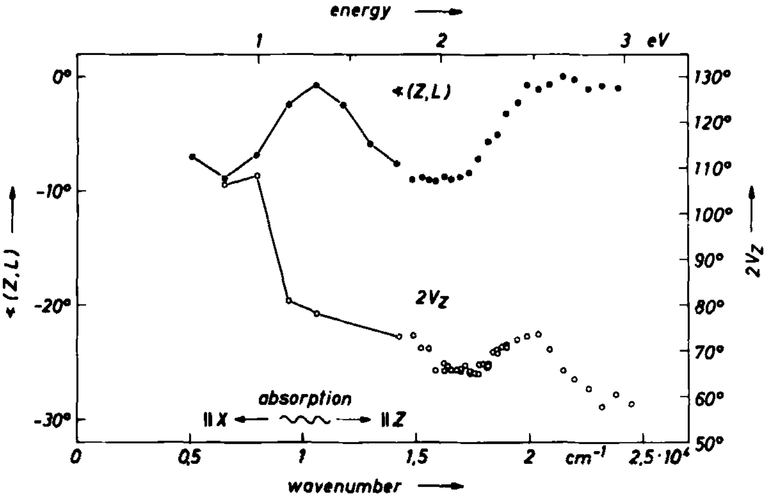

FIGURE 1 Angle $\measuredangle$ (Z, L) and axial angle $2\ V_z$ vs. wavenumber for $(MTPA) \cdot (TCNQ)_2$

in the VIS and IR range.

The lower curve in Figure 1 represents the axial angle 2 $V_z$ (related to bisectrix Z). The angle changes drastically from VIS (< 90°) to IR (> 90°) at about $1\cdot10^4$ cm$^{-1}$, that means the shape of the indicatrix changes from "rod-like" parallel Z(L) to "plate-like" normal X(N). The $n_\gamma$-dispersion[2] (intra-molecular excitation along L) can be recognized at $1.8\cdot10^4$ cm$^{-1}$.

Maximum absorption is found parallel Z(L) in the VIS and parallel X(N) in the IR. The change lies also at about $1\cdot10^4$ cm$^{-1}$ (transition from intra- to inter-molecular excitations (change transfer CT)).

## TTF•TCNQ

The TTF and TCNQ molecules are arranged in a herring-bone

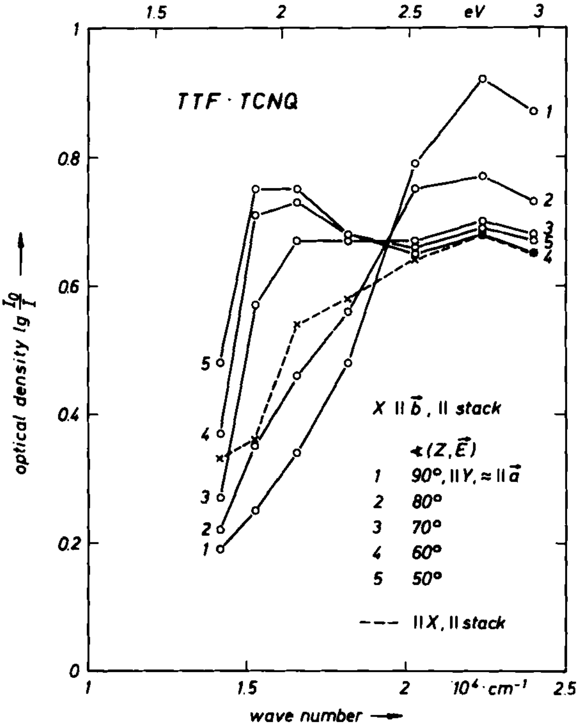

FIGURE 2 Optical density vs. wavenumber at different angles of incidence ∢ (Z, $\vec{E}$) for TTF·TCNQ

structure (segregated stacks, monoclinic). The indicatrix orientation is also directed by the orientation of the stack molecules: X parallels $\vec{b}$ (bisector of ∡ (N, N'), stack direction), Y parallels $\vec{a}$ (T), and Z parallels $\vec{c}^*$ (bisector of ∡ (L, L'), without dispersion in the VIS (L, L' and N, N' are the symmetric directions of the longitudinal axes and of the normal axes of the molecules, respectively). The axial angle 2 $V_x$ (related to bisectrix X) is smaller than 90° (optic sign negative).

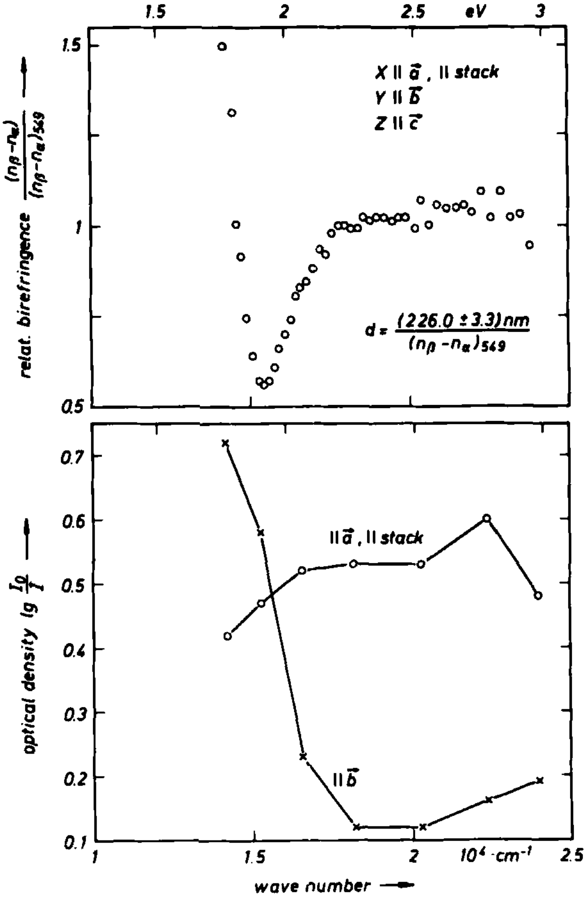

FIGURE 3 Relative birefringence (related to birefringence at 549 nm) and optical density vs. wavenumber for $(Perylen)_2 \cdot AsF_6$, $PF_6$ (d crystal thickness)

Figure 2 shows the absorption for different angle of incidence: maximum absorption is found parallel Y (T) at about $2.3\cdot10^4$ $cm^{-1}$ (probably intra-molecular excitation $4b_{1u} \to 3b^*_{3g}$ in $TTF^+$, T polarized) and parallel Z (bisector of ∡ (L, L')) at about $1.6\cdot10^4$ $cm^{-1}$ (probably intra-molecular excitation $3b_{1u} \to 3b^*_{2g}$ in $TCNQ^-$, L polarized).

### $(Perylen)_2$ $AsF_6$, $PF_6$

The perylene molecules lying herring-bone-like in the orthorhombic crystal and determine also the indicatrix orientation: X parallels bisector of ∡ (N, N') ($\vec{a}$, stack), Y parallels T ($\vec{b}$), and Z parallels bisector of ∡ (L, L') ($\vec{c}$). The axial angle 2 $V_x$ is smaller than 90° (optic sign negative).

Maximum absorption is found parallel X ($\vec{a}$, stack) in the range $\gtrsim 1.9\cdot10^4$ $cm^{-1}$ and parallel Y ($\vec{b}$, T) for $\lesssim 1.7\cdot10^4$ $cm^{-1}$ (Figure 3, lower part).

At about $1.5\cdot10^4$ $cm^{-1}$ there is a strong $n_Y$-dispersion (compare with relative birefringence in the upper part of Figure 3) (probably intra-molecular excitations $a_u \to b_{3g}$ and $b_{1u} \to b_{2g}$ in perylene, T polarized, degenerated).

### (Anthracen)•(Picric Acid)

The molecules are arranged in a herring-bone structure (monoclinic) in mixed stacks. The orientation of the indicatrix is determined by the orientation of the anthracen molecules: X parallels bisector of ∡ (N, N') (orientation

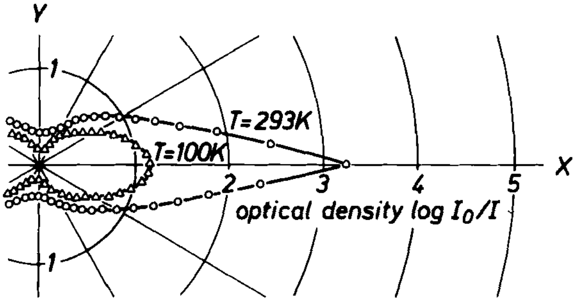

FIGURE 4 Directional dependence of the optical density in the (X,Y) plane of (Anthracen)•(Picric Acid) at the CT edge ($1.62\cdot10^4$ $cm^{-1}$)

angle ∡ (X, $\vec{a}$) = 24.6°), Y parallels bisector of ∡ (T, T') ($\vec{b}$), and Z parallels bisector of ∡ (L, L'), without dispersion in the VIS. The axial angle $2\,V_x$ is 75.7° (observable in the range $\lesssim 1.7\cdot 10^4$ $\mathrm{cm}^{-1}$, optic sign negative).

Maximum absorption at $1.6\cdot 10^4\,\mathrm{cm}^{-1}$ (CT edge) is strongly directed parallel X (Figure 4). The temperature dependence of absorption obeys Urbach's rule[3]

$$\alpha(E) = \alpha_o \exp -\gamma(E_o - E)/kT$$

with

$$\gamma = \gamma_o\ (2kT/\hbar\omega_p)\ \tanh(\hbar\omega_p/2kT)$$

($\alpha$ absorption coefficient, E photon energy, $\alpha_o$, $\gamma_o$, $E_o$ material parameters) which gives the energy $\hbar\omega_p$ of the phonon involved in the exciton-phonon interaction. In the present case $E_o = 2.1$ eV and $\gamma_o = 0.59$ are estimated following for the phonon energy $\hbar\omega_p \approx 42$ meV $\hat{=}$ 340 $\mathrm{cm}^{-1}$ (roughly approximated from yet only two temperature curves).

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