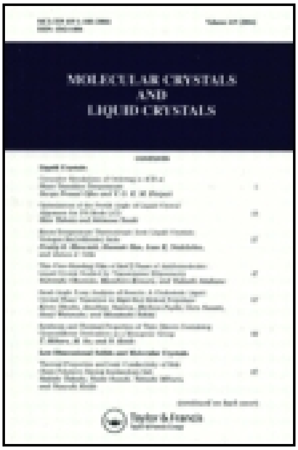

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ESP- and Conductivity Measurements on the Radical-Cation-Salt $(PYRENE)_{12}(SbF_6)_7$

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ESR- AND CONDUCTIVITY MEASUREMENTS ON THE RADICAL-CATION-SALT $(PYRENE)_{12}(SbF_6)_7$

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Abstract Conducting radicalcation salts (rcs) containing pyrene exhibit a pronounced polymorphism in crystal-structure and composition due to the high symmetry of the hydrocarbon. On this basis we associate the doublet structure of the ESR-signal in $Pyrene_{12}(SbF_6)_7$ with microclusters, alternating in the pyrene stack, which are turned to each other by exactly 90° around the stacking direction.

INTRODUCTION

Rcs of pure hydrocarbons belong to the class of low dimensional organic conductors: conductivities[1] up to $10^3 (\Omega\ cm)^{-1}$ are accompanied with ESR linewidths as narrow as 2.5 milliGauss[2]. The latter effect is due to motional averaging of the hyperfine interaction (hfs), to less effective spin orbit coupling in the 1-d case and to the low Z-values of the nuclei. If, and this is here the case, ESR-doublets are found which are split less than the static hfs which is averaged, structural imperfections must be taken into account.

EXPERIMENTAL RESULTS

All experiments were performed on $Pyrene_{12}(SbF_6)_7$-crystals, grown by anodic oxidation from 1,1,2-trichloroethane at 0° C. The physical properties, as there are

ESR-intensity, ESR-linewidth, DC and AC-conductivity are only weakly dependent in a metallic regime 300 ≧ T ≧ 200 K to be thermally activated below a phase transition at about 200 K[3]. This is in accordance to the behaviour of most of these salts[1,2].

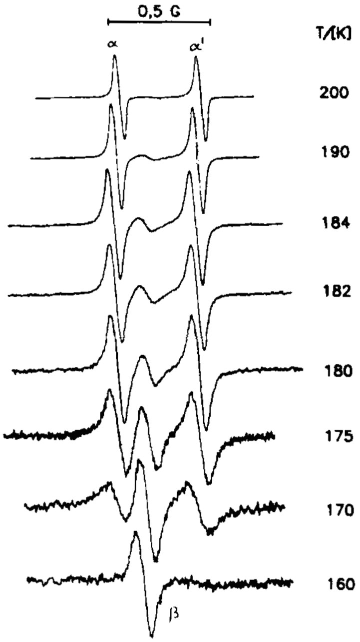

FIGURE 1 The ESR-signals of $Py_{12}(SbF_6)_7$ at different temperatures (normalized representation), B_o to the needle axis.

A unique peculiarity of $Py_{12}(SbF_6)_7$ is the occurance of a doublet - or even triplet - structure of the ESR-signal as demonstrated in Fig. 1. At T ≧ 200 K there are two lines, labeled α and α', about 25 milliGauss in width and split maximally by 0,5 Gauss. The third line (ß) in between is seen best at temperatures where the two others are lowered in intensity.

α and α' behave totally analogous: both have the same intensity, the same linewidth and the same temperature dependence of I_{ESR} and ΔB_{pp} as given in Fig. 2. Both disappear thermally activated ($\Delta E=0{,}023$ eV) below 200 K whereas the properties of the ß-line are nearly temperature independent.

The angle dependence of the field positions of α and α' are phaseshifted by 90° having $B_o \perp$ to the stacking direction of the pyrenes[4], Fig. 3. Turning aroung

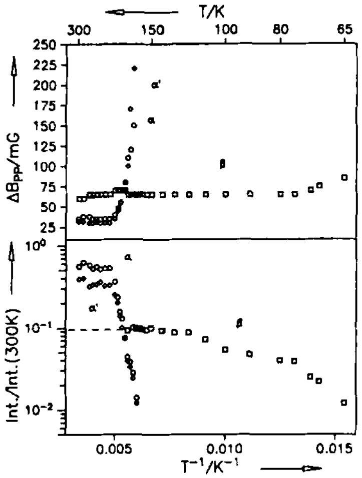

FIGURE 2 The temperature dependence of ESR-intensity and linewidth of the signals given in Fig. 1.

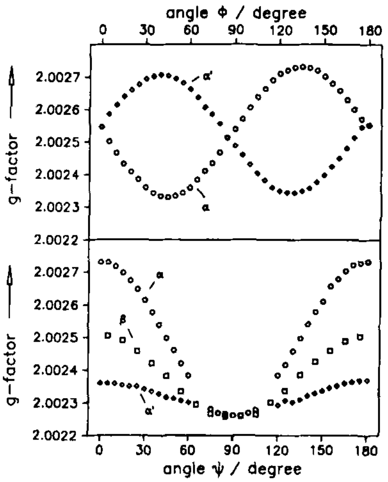

FIGURE 3 The g-factor-angle dependence of the α, α' and ß-signals.

the canonian directions, the g-factors are in phase, the ß-signal always in between.

DISCUSSION

α, α' and ß cannot belong to adjacent stacks because there is no exchange detectable if the lines coincide on the magnetic field scale.

A correlated motion of two electrons (triplet) within the same stack which could explain the splitting although the hyperfine interaction - much larger in magnitude - is averaged out, can be dropped by some reasons: i) the angle dependence of the splitting does not follow the law of dipolar interaction (i. e. the splitting is largest for $B_o \perp$ stacking direction).

ii) the e-e-distance, corresponding to 0,5 Gauss is 16Å and may be unreasonable large.
iii) the g-factor anisotropy of "one-ESR-line Pyrene salts" just fit the 0,5 Gauss!

We therefore assume that α and α' result from different regions of the sample. A macroscopic twinning can be excluded, because α and α' are always comparable in intensity and width as long as the crystal size exceeds 1 μg.

Microclusters of α and α' orientation seem to alternate, perfectly oriented in respect to each other over macroscopic distances. Such a behaviour is only possible if the zone bounderies are reproducible and reversible and this can happen only in the individual stacks. Columns of pyrene molecules in α orientation are followed by such in α' orientation and vice versa. The parallel arrangement of pyrene molecules seems to be nearly isoenergetic to that, in which the molecules are turned to each other by 90° around the out of plane axis, favorized by the high symmetry of the hydrocarbon. The ß-signal, always occuring between α and α' may result from this twisted configuration.

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