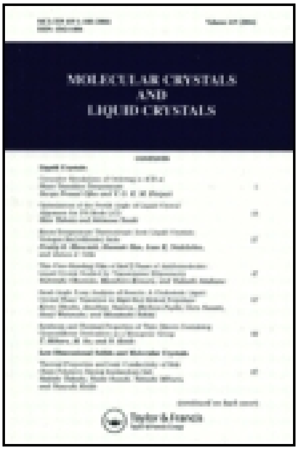

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Radical Cation Salts of Arenes. Structure, Properties and Model Character for Conducting Polymers

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RADICAL CATION SALTS OF ARENES. STRUCTURE, PROPERTIES AND MODEL CHARACTER FOR CONDUCTING POLYMERS

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Abstract Radical cation salts of arenes are obtained by anodic oxidation. They are a new family of organic conductors. Common structural principles are reviewed. Radical cation salts of oligomers of poly-p-phenylene have been prepared and characterized. The packing found in these model compounds can be used to construct models for conducting polymers.

STRUCTURAL PROPERTIES OF AROMATIC RADICAL CATION SALTS

Stable radical cation salts of arenes are obtained by anodic oxidation of arenes in the presence of suitable anions of low nucleophility, e.g. BF_4^-, ClO_4^-, PF_6^-, AsF_6^-, SbF_6^-. They represent a new family of organic metals which are built up by simple and easily obtainable components. The analysis of the electrochemical processes which lead to the growth of the crystals has revealed that the reaction may be split into three independent reactions[1-3]:

$$Ar \rightleftharpoons Ar^{\cdot +} + e^- \qquad (1)$$

$$Ar^{\cdot +} + Ar^o \rightleftharpoons (Ar_2)^{\cdot +} \qquad (2)$$

$$(Ar_2)^{\cdot +} + X^- \rightleftharpoons Ar_2X \qquad (3)$$

The key reaction in this scheme is the dimerization (2) in which the short lived intermediate monomer radical cation is stabilized. The equilibrium constant of this reaction determines not only the stability of the reactive intermediates but also the composition of the growing crystals. A large number of aromatic radical cation salts have been prepared and characterized in terms of composition, crystal structure and electronic properties[3-7]. Depending on the conditions of the electrocrystallization, e.g. concentrations, counterion, solvent and temperature the equilibrium of the dimerization (2) can be shifted and crystals with compositions differing from the ideal 2:1 stoichiometry are obtained. In these cases the ratio arene : anion is always less or equal to 2, e.g. in pyrene radical cation salts ratios of 7:4, 12:7, 19:10 and 2:1 are observed[4].

Fluoranthene (FA) is one example where the dimerization (2) is always complete so that under all experimental conditions so far only crystals with the ideal composition FA_2X have been isolated. With these comparatively simple structures common structural principles, phase transitions and electronic properties which are typical for the whole class of aromatic radical cation salts have been investigated.

All radical cation salts can be characterized as columnar structures. The aromatic rings are arranged in stacks leaving channels in which the counterions and in some cases additional molecules like solvent or neutral arenes are situated. Within the stacks extremely small interplanar spacings of 3.2 to 3.3 Å are observed. The rings are usually oriented perpendicular to the stacking direction. This gives rise to very close atomic contacts as shown for FA_2PF_6 in Fig. 1.

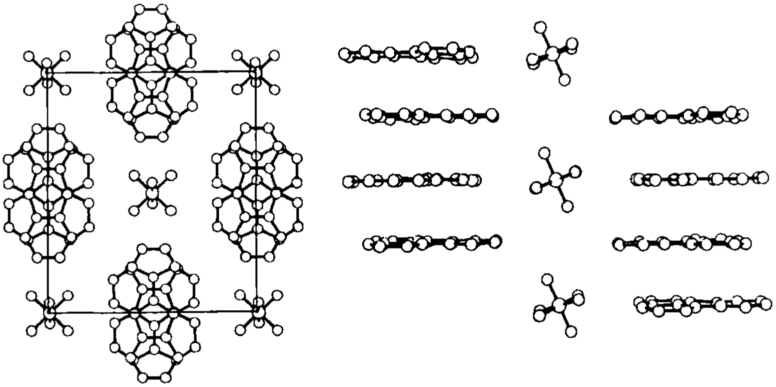

FIGURE 1 Crystal structure of FA PF at 300 K. Left: projection along the stacks, right: projection perpendicular to the stacking direction[1,2].

The geometry of the overlap of neighboring rings is intimately coupled with the high conductivity and the rapid spin exchange along the stacks. At metal-insulator transitions which usually are observed near 200 K this overlap geometry is changed. The structural changes during the phase transition have been investigated in detail for FA salts[1]. It could be shown that the molecular overlap which in the high temperature phase is strictly symmetric is distorted perpendicular to the stacking direction.

RADICAL CATION SALTS AS MODELS FOR CONDUCTING POLYMERS

The interaction found between the aromatic rings in the conducting stacks in radical cation salts can be regarded as a model for interchain interactions in conducting polymers. As a consequence many of the models which have been proposed for the structure of highly conductive polymer phases are derived from the structural principles of radical cation salts[8-13]. This concept is schematically illustrated in Fig. 2.

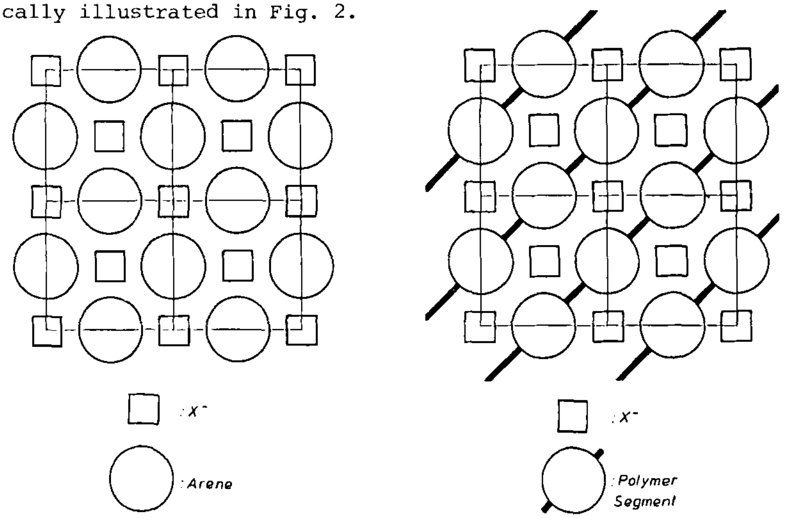

FIGURE 2 Analogy of the packing in radical cation salts (left) and conducting polymers (right).

The radical cation sites created on the polymer backbone are thought to stabilize themselves by formation of complexes with neutral chain segments in the vicinity according to eq. (2). The elements forming the stacks are here part of the polymer main chain. As a consequence the structures can be characterized as intercalation structures in which layers of polymer chains and counterions alternate. Many of the structural properties of the conducting phases of polyacetylene, polypyrrole and poly-p-phenylene (PPP) have been successfully explained using this structural model[11-16]. It should be emphasized at this point that the term "doping" used for this reaction is misleading. Metallic phases of fixed structure and composition have been observed from the very early stages of the oxidation.

It was therefore interesting to prepare radical cation salts of oligomers which could be used as models to refine the limited diffraction data obtainable from conducting polymers.

We have been able to prepare a series of radical cation salts of oligomers of PPP e.g. terphenyl (TP), quaterphenyl (QP) and substituted analogs[4,14]. To date the QP SbF_6 salt has been investigated in detail. Pertinent crystallographic data are given in Table 1 and two projections of the structure are shown in Fig. 3.

Table 1 Crystallographic data of $QP_{12}QP_4(SbF_6)_{10}$

a	20.40(2) Å		α	98.1(2) °
b	11.00(1) Å		β	81.6(2) °
c	35.24(2) Å		γ	89.2(2) °
triclinic, space group F$\bar{1}$				

The structure consists of stacks of QP molecules which are separated by layers of counterions. All QP units are nearly aligned along one direction so that the packing realized in this salt comes quite close to the structural model for conducting polymers given in Fig. 2. The composition of the crystals is $QP_{12}QP_4(SbF_6)_{10}$. Four QP molecules are incorporated in the anion sheet and are no part of the conducting stack. They are omitted in Fig. 3. On the average each QP unit carries a charge of (0.83)+ , i.e. the complex formed in the course of the electrocrystallization could be described as $QP^{2+}QP^{0}$,

The stack consists of three rings, one of which (QP1) is located on a center of symmetry. Of the 12 anion sites 4 are statistically only half occupied. As it is frequently observed in radical cation salts the stack is not uniform, i.e. wide and close spacings alternate (Fig. 3). The two types of interstack contacts are also connected with different molecular overlap patterns. In the close contact (QP1-QP2) neighboring molecules are shifted along their long axes by approximately half a phenyl ring. In the wide contact the shift is perpendicular to the long axes (Fig. 4). Similar close relations between interplanar spacing and molecular overlap geometry have been previously described for pyrene radical cation salts[4].

The packing found in this model compound was used to construct a structural model for the conducting phase of PPP. The repeat unit used is shown as dashed cell in the structure of the QP salt (Fig. 5). Unit cell dimensions and packing derived from the model

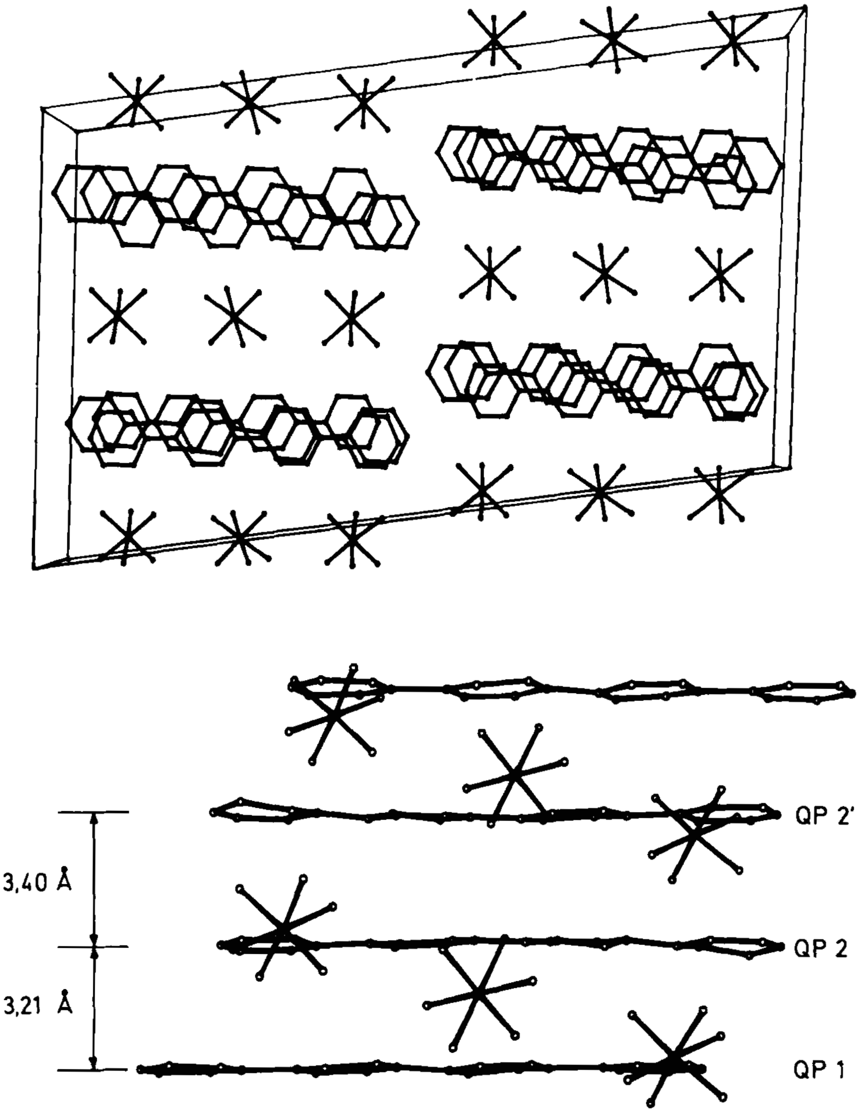

FIGURE 3 Crystal structure of $QP_{12}QP_4(SbF_6)_{10}$. Top: Projection along the stacks, bottom: projection perpendicular to the stacks.

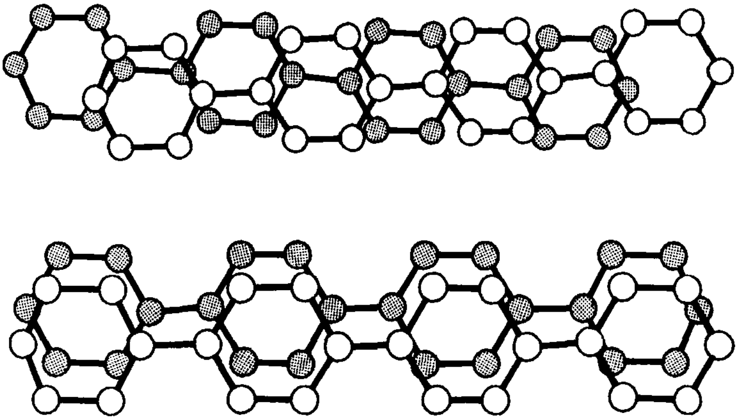

FIGURE 4 Molecular overlap in the QP stack. Top: QP1-QP2, bottom: QP2-QP2'

were used without further refinement. Unit cell dimensions are given in Table 2 and two projections of the model structure are shown in Fig. 5 in comparison with the QP salt.

TABLE 2 Crystallographic data for the model structure

a	10.0 Å	α	90 °
b	6.6 Å	β	90 °
c	16.8 Å	γ	90 °
Composition:	$(C_6H_4)_8(SbF_6)_3$		

There are two PPP chains in the unit cell which are shifted with respect to each other by half a phenyl ring repeat unit as it was found in the close QP contact. The composition is $(C_6H_4)_8(SbF_6)_3$, this corresponds to a "doping level" of about 40%. This compares well with the limiting conversion found in the electrochemical oxidation of PPP[15].

In Fig. 6 and 7 experimental x-ray and neutron scattering diagrams of oxidized PPP are compared with the curves calculated for the structural model presented in Fig. 5.

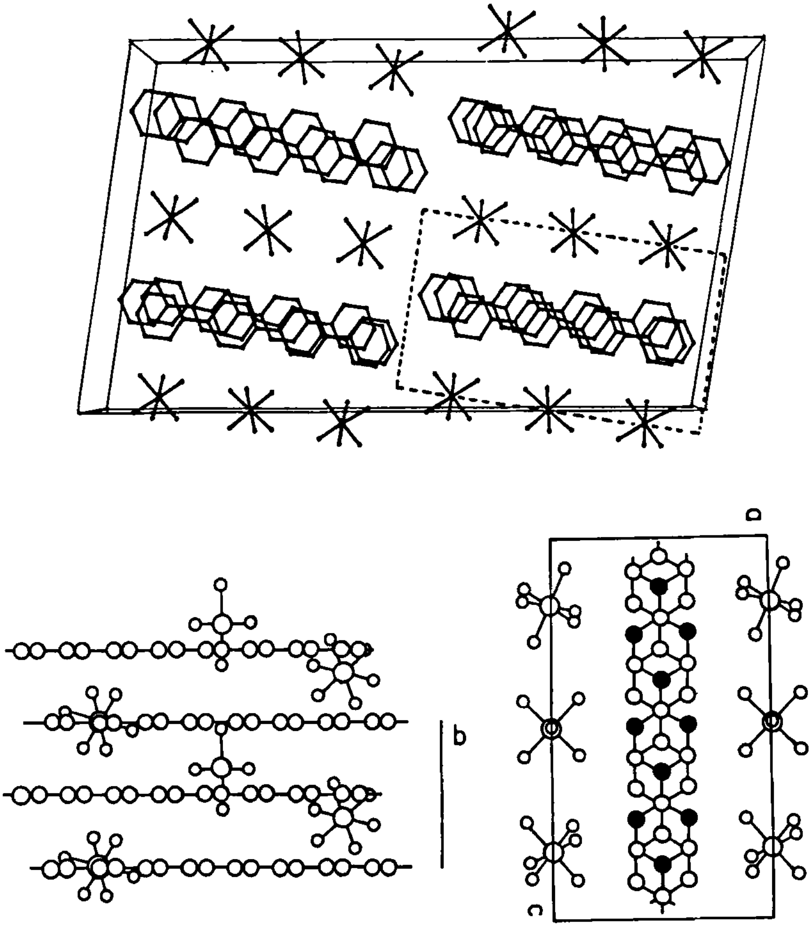

FIGURE 5 Comparison of the QP radical cation salt (top) and the structural model for conducting PPP salts.

Due to the large contributions of the anions the x-ray scattering reflects mainly the SbF_6 anion subcell whereas all atoms contribute about equally to the neutron scattering. Considering that the model has not been refined the agreement between experiment and calculation is satisfactory and the model seems to be a promising starting point for more detailed investigations.

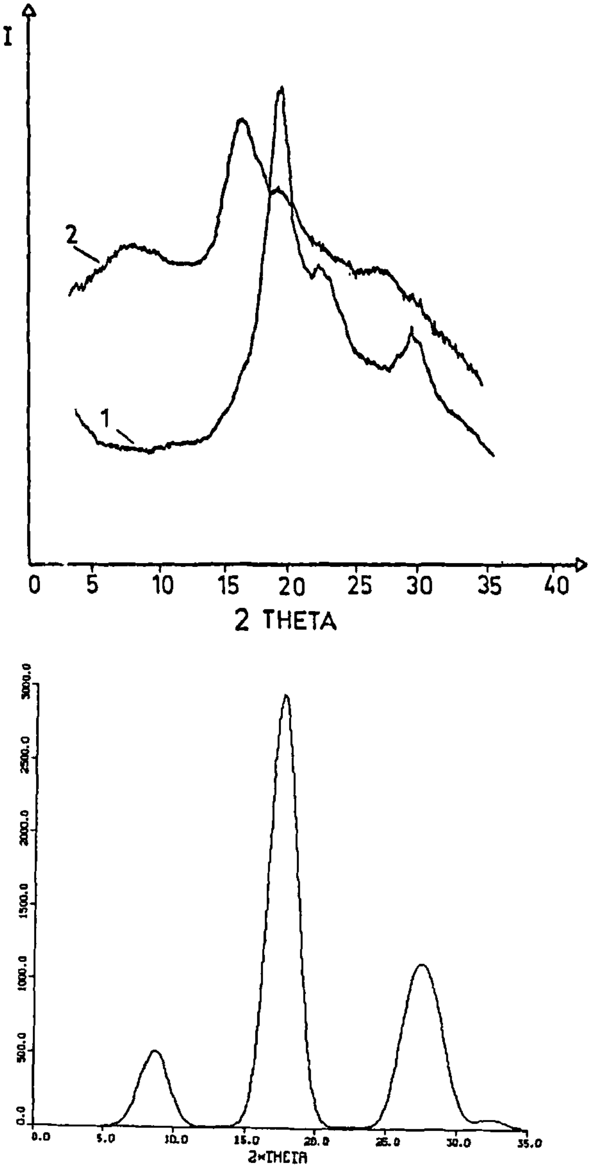

FIGURE 6 X-ray scattering of electrochemically doped PPP (top, curve 2) and the calculated scattering diagram. Experimental data were taken from J. Eiffler[15].

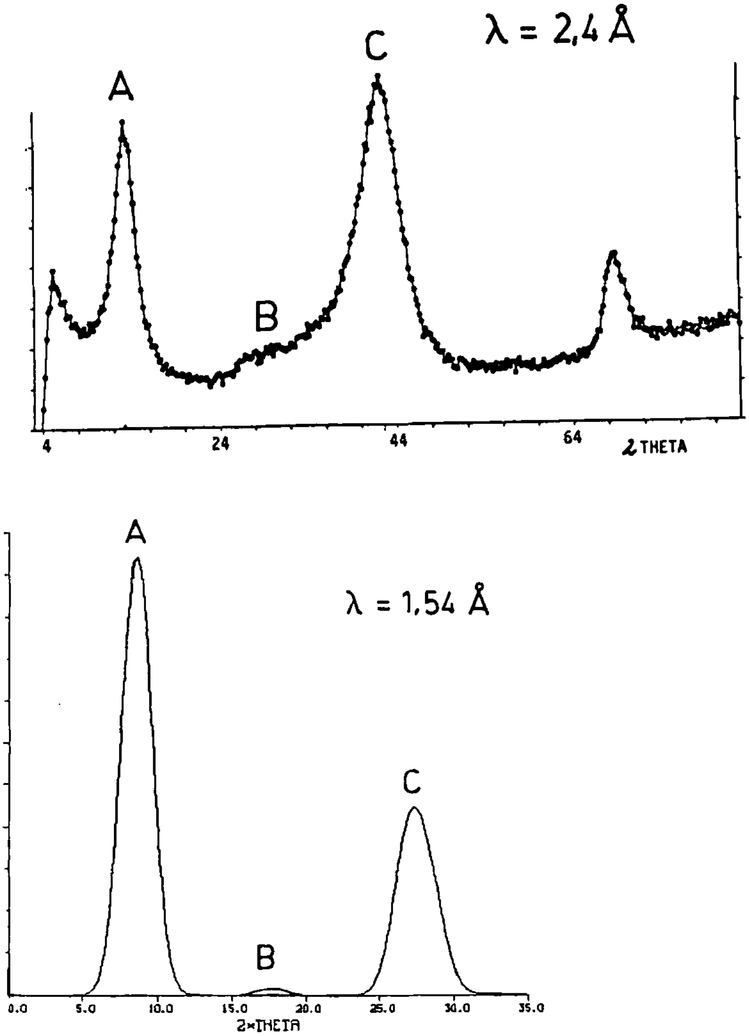

FIGURE 7 Comparison of the experimental neutron scattering curve for AsF$_6$ doped PPP and the model structure. The experimental data were taken from M. Stamm[16].

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