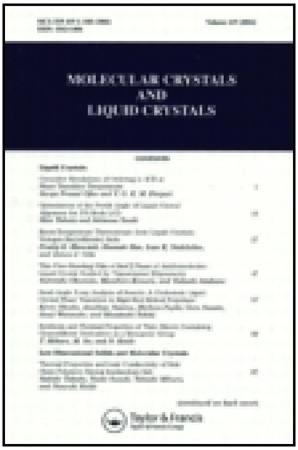

Molecular Crystals and Liquid Crystals

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Radical Cation Salts - A New Family of Organic Metals

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RADICAL CATION SALTS - A NEW FAMILY OF ORGANIC METALS

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Stable radical cations of arenes can be generated by anodic oxidation and can be separated at the anode in the presence of suitable anions as radical cation salts $[\mathrm{aryl}_2]^{+\bullet}X$ in the form of shiny black crystals.
Crystal structures and phase transitions in fluoranthenyl radical cation salts,a new family of organic conductors,are reported.The metal to semiconductor transition which is observed seems to be related to a distortion of the stacks of aromatic molecules perpendicular to the stacking direction.

INTRODUCTION

One of the common structural principles of electrically conducting molecular crystals is the crystallization of donor and acceptor molecules in separate stacks with equal distances between molecules within one stack but with only a partial charge transfer between the stacks.

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In the synthesis of the more common "organic metals" like TTF/TCNQ the charges are generated by redox reactions between the partners. In order to obtain partial charge transfer the oxidation potentials of donor and acceptor have to be carefully matched1),2). This restricts the number of possible complexes with high electric conductivity. Electrochemical oxidation seems to be a useful method to produce the charges in a more controlled fashion.

THE ELECTROCHEMICAL SYNTHESIS

Stable highly conducting radical cation salts of simple aromatic hydrocarbons can be obtained by anodic oxidation followed by the crystallization of the complex with suitable anions 3)-6). The reaction mechanism is shown in the following scheme:

$$Ar^{o} \overset{-e^{-}}{\rightleftharpoons} Ar^{+\bullet} \qquad (I)$$

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

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

Ar: naphthalene, fluoranthene, perylene, pyrene, triphenylene etc.
X^-: BF_4^- , ClO_4^- , PF_6^-, AsF_6^- , SbF_6^- etc.

Investigations of the electrocrystallization show that the oxidation of the aromat (I) is followed by a complex formation between the radical cation and a neutral molecule (2) which then crystallizes at the anode as shiny black needles of the composition Ar_2X (3) 7).

CRYSTAL STRUCTURES

The crystal structures of this new class of conducting materials can be described as a columnar packing of the aromatic rings leaving channels in which the anions are located. Anions of different sizes can be incorporated in the structure with only slight chances of the lattice parameters and consequently the structures are isomorphous. Pertinent lattice parameters for a series of fluoranthenyl radical cation salts are shown in Table I.

Table I Crystallographic Data of Fluoranthenyl Radical Cation Salts FA_2X

X^-	PF_6^- (298 K)	SbF_6^- (298°K)	AsF_6^- (298 K)	(I20 K)
a/Å	6.6I(2)	6.62(2)	6.58(2)	6.50(I)
b/Å	I2.57(I)	I2.73(I)	I2.63(I)	I2.49(I)
c/Å	I4.77(I)	I5.09(I)	I4.89(I)	I4.75(I)
β/°	I04.0(5)	I04.0(5)	I04.0(5)	I04.0(5)
D_x/Mgm^{-3}	I.53	I.72	I.64	I.69
T_c/K	I92(2)	I99(3)	203(2)	
space group	A2/m	A2/m	A2/m	$P2_I/c$

One of the interesting features of these crystals are phase transitions which are observed near 200 K5),7). Projections of the crystal structures of FA_2PF_6 and FA_2AsF_6 above and below the transition are shown in Fig.I and Fig.2. In the high temperature phase the orientation of the fluoranthene rings which are alternately rotated by I80 degrees is fixed by the site symmetry (2/m). At the phase transition which is well correlated with a change from metallic to semiconducting behaviour6),8) the space group changes from A2/m to $P2_I/c$ and a rotation of the cation stack of about 8 degrees is observed.

It should be noted that the stacking distance of the aromatic rings is not uniform. The difference of 0.05 Å which is observed in the high temperature phase is virtually retained during the phase transition (Fig.3).

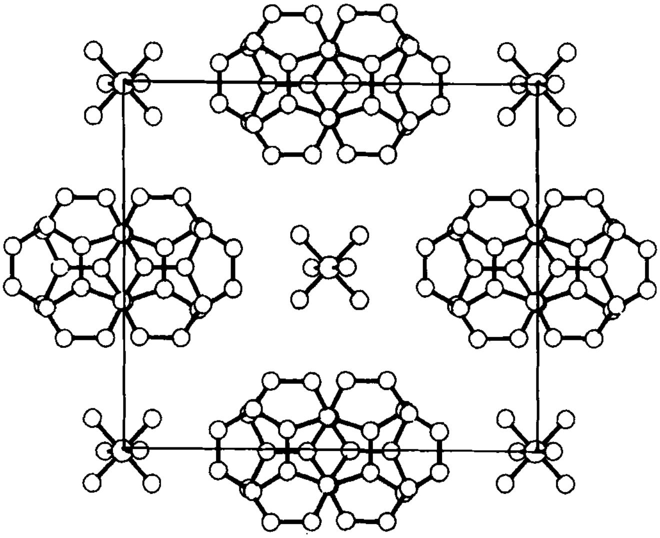

Figure I Projection of the crystal structure on the b-c plane of FA_2PF_6 at 298 K

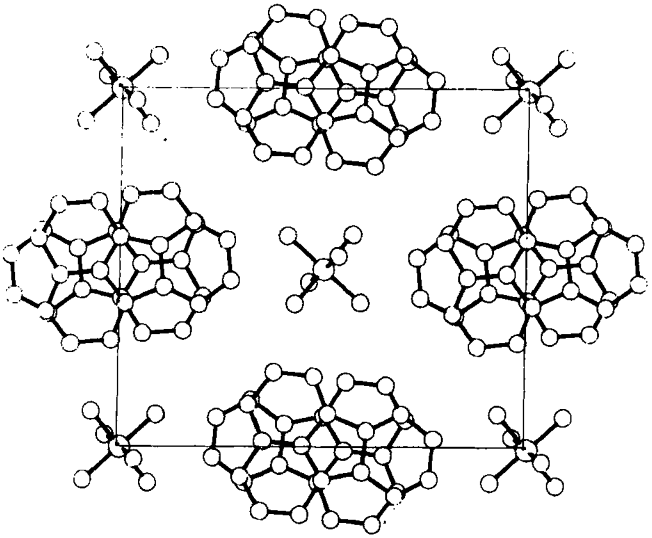

Figure 2 Projection of the crystal structure on the b-c plane of FA_2AsF_6 at I2o K

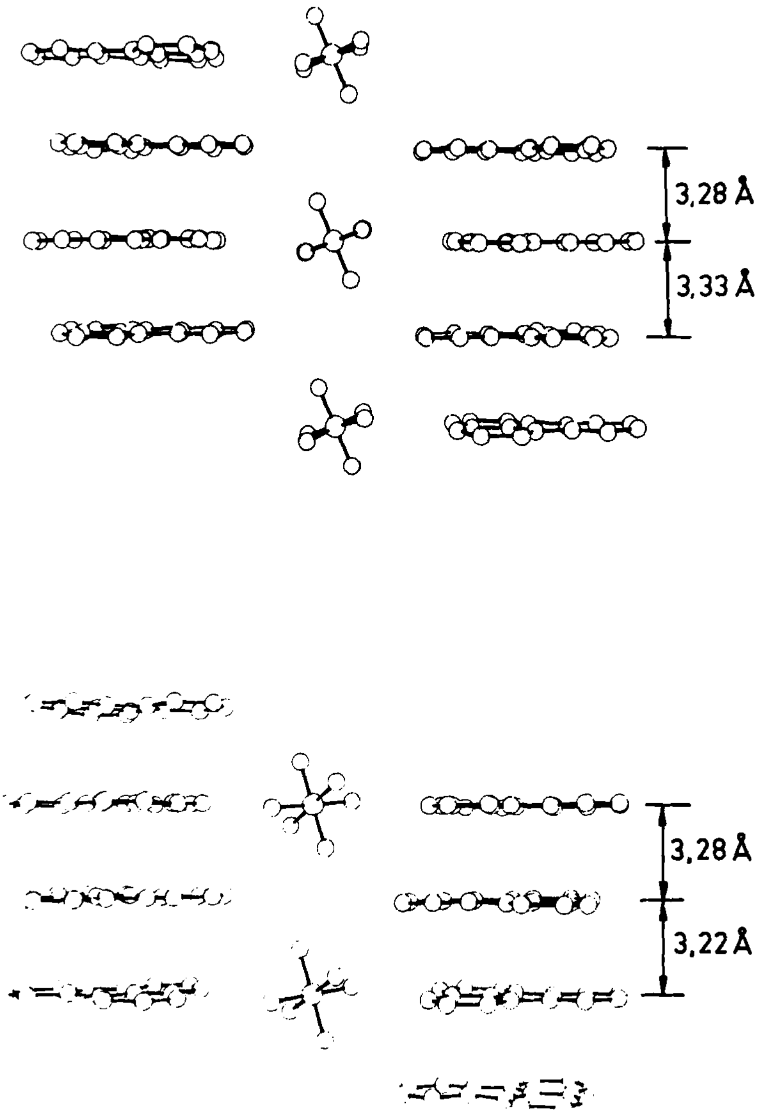

Figure 3 Projection of two crystal structures perpendicular to the stacks. Top: FA_2PF_6 (298 K), bottom: FA_2AsF_6 (120 K)

The temperature dependence of the lattice parameters is shown in Fig.4. In a temperature range of about 40 degrees below the phase transition temperature T_c small anomalies of $\underline{b}$ and $\underline{c}$ are observed.

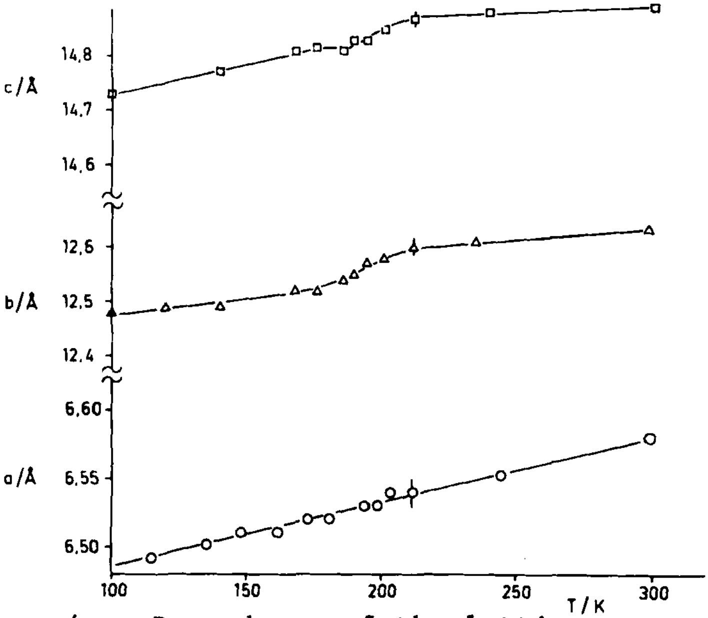

Figure 4 Dependence of the lattice parameters of FA_2AsF_6 on the temperature

Among the most interesting features of these crystals is the unusual packing of the rings which are oriented perpendicular to the stacking axis $\underline{a}$ and are arranged remarkable close to each other. As it can be seen in Fig.3 a distortion along the stacking direction cannot account for the change of the electrical properties.However, the high conductivity and the rapid spin exchange along the stack seems to be very sensitive to the geometry of the molecular overlapping. This is shown for 2 temperatures in Fig.5.

As mentioned before in the high temperature phase the rings are located on mirror planes so that the molecular overlap is strictly symmetrical. This restriction vanishes at the transition and in addition to the rotations of the stacks a small distortion perpendicular to the stacking direction is observed which is responsible for

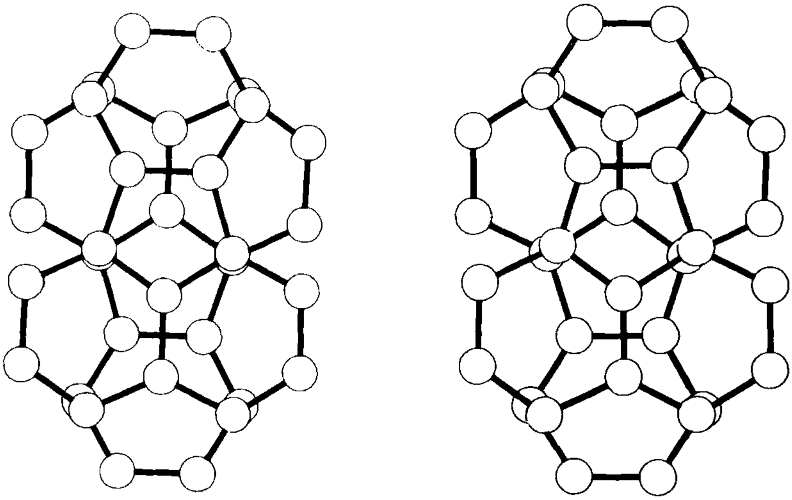

Figure 5 Projections of the crystal structures on the plane of the fluoranthene molecules; left: FA_2PF_6 at 298 K, right: FA_2AsF_6 at 120 K

the change of electrical and magnetic properties8).

We believe that the interactions between the molecules in a stack is a good model for an interchain charge transport process in conducting polymers like poly(acetylene) and poly(p-phenylene) or poly(p-phenylene sulfid).

REFERENCES

1. J.B.Torrance,Acc.Chem.Res. 12 , 79 (1979)
2. D.J.Sandman,Mol.Cryst.Liq.Cryst. 50,235 (1979)
3. H.P.Fritz,H.Gebauer,P.Friedrich,P.Ecker,R.Artes and U.Schubert,Z.Naturforsch.B 33,498 (1978)
4. T.C.Chiang,A.H.Reddoch and D.F.Williams, J.Chem.Phys. 54, 2051 (1971)
5. C.Kröhnke,V.Enkelmann and G.Wegner,Angew.Chem. 92,941 (1980)
6. H.J.Keller,D.Nöthe,H.Pritzkow,D.Wehe,M.Werner, P.Koch and D.Schweitzer, Mol.Cryst.Liq.Cryst. 62,181 (1981)
7. V.Enkelmann,B.S.Morra,C.Kröhnke,G.Wegner and J.Heinze,Chem.Phys.,in press

8. H.Eichele,M.Schwoerer,C.Kröhnke and G.Wegner, Chem.Phys.Letters 77,3II (I98I)