

Does Non-planarity obstruct Low-dimensional Conducting Polyarene Cation Radical Salts?

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The cation-radical salt (**3**) was prepared from bis(4*H*-cyclopenta[*def*]phenanthren-4-ylidene) (**1**); a one-dimensional behaviour, exemplified by the ESR-line-width orientational variations, was found for this conducting system, obtained from a non-planar donor.

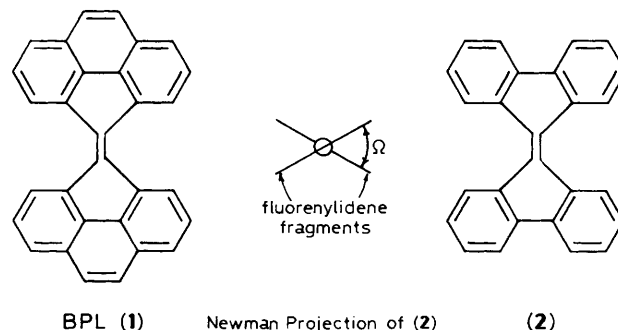
A requisite condition to the formation of highly conducting charge transfer systems is the solid-state mediated overlap of MOs. An effectual overlap is generally obtained with close-packed planar π -donors (acceptors) embedded in quasi-one-dimensional (quasi-1D) stacks involved in charge transport. In this area, non-planar molecules, as possible building blocks, have attracted little attention so far, although some sterically distorted or three-dimensionally modified tetracyanoquinodimethanes (TCNQ) and their poorly conducting charge-transfer complexes have been described.¹⁻⁴

We now report the preparation of a conducting cation-radical salt built from a highly out-of-plane distorted polyarene. Our preliminary ESR measurements point to the existence of low-dimensional properties for this solid, obtained from a non-planar donor, similar to those exhibited by the salts from planar donors.

We have used bis(4*H*-cyclopenta[*def*]phenanthren-4-ylidene) (**1**) (BPL), a known representative⁵ of the family of the distorted ethylenes,⁶ as the non-planar donor. The distortion of these ethylenes, as a consequence of severe steric overcrowding, is well documented for the parent compound bis(fluoren-9-ylidene) (**2**).⁷ In this case, the conformation of the almost planar fluoren-9-ylidene fragments, around the central distorted double bond has been determined both

experimentally⁷ and by calculation,⁸ to adopt the twisted form, the large twist angle Ω being around 50° (Scheme 1).

We have synthesized BPL (**1**),⁵ from cyclopenta[*def*]phenanthrylene ketone,⁹ by a coupling process using the McMurry reagent.¹⁰ The orange coloured crystals of (**1**) [$E_{p/2} = +1.25$ V vs. standard calomel electrode (s.c.e.) in CH₂Cl₂] were electrocrystallized in dimethoxyethane (DME), at -20 °C, with Bu₄NPF₆ as an electrolyte. The stoichiometry



Scheme 1

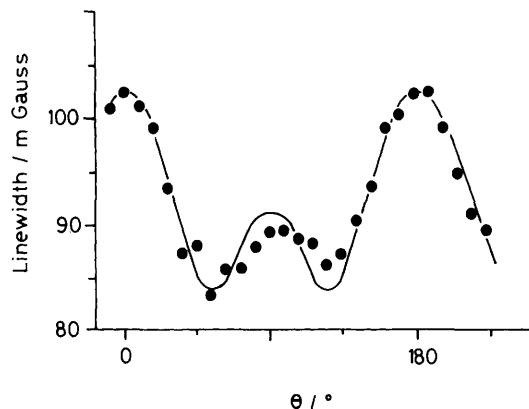


Figure 1. The anisotropy of the peak-to-peak line-width ΔH_{pp} with the orientation of the crystal (3) in the applied field, θ is the angle between the needle-axis and the field. Spectra were recorded with a Bruker ESR 300 spectrometer. ● = experimental line-width for (3); — = $\Delta H_{pp} = 88.1 + 6.54 |3 \cos^2\theta - 1|^{4/3}$.

of the black, shiny monocrystalline needles† grown in the anodic compartment was found, by microanalysis, to be [(BPL)₂PF₆, DME] (3). The d.c. conductivity was measured by the four probe method, with a platinum conductive adhesive. Moderate conductivities, ranging from $\sigma_{300\text{ K}} = 25$ to $80 \Omega^{-1} \text{ cm}^{-1}$, were found depending on the samples. The microwave conductivity at 9.2 GHz has been investigated using the cavity perturbation method,¹¹ in the 100–300 K temperature range. The same order of magnitude for the room temperature conductivity has also been found with this contactless technique, as expected for the ordered conducting systems in this frequency range.¹² On lowering the temperature, a metallic behaviour is observed down to 225 K; below 225 K, anomalies usually related to lattice distortions, appear in the dielectric response.¹³

The non-dysonian, very narrow ESR single line (around 100 m G; $G = 10^{-4}$ T) of single crystals of the salt (3) are characteristic of a strong spin exchange; such narrow ESR lines are in fact observed generally with low-dimensional

† These monocrystals were found to be stable for long periods when kept at -18°C ; the stability at room temperature was also good for shorter periods (48 h).

organic systems. The orientational variation of the line-width also supports this low-dimensional behaviour. For the quasi-1D salts prepared from planar polyarenes, such as fluoranthene,¹⁴ a similar orientational behaviour has been found in the low temperature insulating phase.¹⁵ These line-width variations are reminiscent of those described for spin-localized 1D systems which have been modelled using a $|3 \cos^2 - 1|^{4/3}$ angular variation law¹⁶ (Figure 1).

The reported 1D behaviour of the salt (3) is related to a new packing mode which we are currently studying and which is probably due to an unprecedented kind of solid-state co-operative interaction of the non-planar molecules.

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