Coexistence of neutral and charged arenes in conducting diperylene hexafluorophosphate

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In the quasi-one-dimensional organic conductor diperylene hexafluorophosphate charged and neutral perylene (PE) molecules coexist. The molecular charge can be correlated with the distance between the PE molecule's two naphthalene moieties accessible by x-ray structural analysis. The electronic distinction is proved by magic angle sample-spinning proton-enhanced high-resolution ^{13}C nuclear magnetic resonance. The locally resolved ^{13}C-shift data in addition reveal the occurrence of two inequivalent PE molecules in the conducting stack of diperylene hexafluorophosphate. [S0163-1829(98)06936-7]

The occurrence of a Peierls transition to a low-temperature charge-density wave (CDW) state is well established in quasi-one-dimensional organic conductors built up from stacked radical cations of pure hydrocarbon molecules (arenes) like fluoranthene in difluoranthene hexafluorophosphate.[1] The deviation from the average arene charge of $+0.5e$ in the CDW phase is weak, however. We have shown that in nonmetallic radical cation salts of perylene (PE), (Fig. 1), neutral, diamagnetic PE molecules may coexist with charged pairs carrying a charge $+1e$ and a spin 1/2 localized on the ''dimer'' with the closest intradimer separation. This was derived for hexaperylene hexafluorophosphate. The $(PE)_6PF_6$ unit cell contains three mutually orthogonal PE pairs.[2,3] It was proved by a detailed analysis of the anisotropy of electron spin resonance (ESR) g tensor and line width that the ''dimer'' with the closest intradimer separation carries the charge and spin, thus $(PE)_2^+ \cdot (PE)_2(PE)_2PF_6^-$ would give an appropriate description of the electronic properties.[4] Seo and Whangbo showed by extended Hückel molecular orbital calculations that the highest occupied molecular orbital (HOMOs) of the PEs in each pair (dimer) interact to give a bonding and an antibonding level. The pair with the shortest separation gives the highest antibonding level, which consequently is emptied when an electron has to be transfered from the arenes to the PF_6 counter ions in the radical cation salt.[5] The HOMO of the individual PE molecule is antibonding between the carbon atoms 4 and $4'$ combining the two naphthalene moieties of the PE molecule (Fig. 1). Thus partial oxidation of PE strengthens and shortens the C_4-$C_{4'}$ bond[5] as can be substantiated by inspection of the x-ray structural analysis.[2]

Recently, it was argued that likewise for the ''metallic'' diperylene hexafluorophosphate the anisotropy of the electrical conductivity and of the ESR g tensor as well as the periodicity of the Peierls-distorted low-temperature phase indicate the coexistence of neutral and charged PE molecules.[6–9] The description of the electronic properties of the conducting salt requires the formula $(PE)_4^{3+}\cdots(PE)_2(PF_6^-)_3\cdot 2THF$ (THF: built in tetrahydrofurane solvent molecules): Four PE molecules form the periodic unit along the one-dimensional stack in the high-temperature phase; they transfer three electrons to the three PF_6^- counter

ions (which thus become closed shell and diamagnetic). The conducting stacks are surrounded and separated by additional diamagnetic, neutral PE molecules. The proof of this description is presented below based on locally resolved high-resolution ^{13}C nuclear magnetic resonance (NMR), molecular orbital calculations including geometry optimization (TURBOMOLE),[10,11] and a careful analysis of recent x-ray structural information.[6]

Seo and Whangbo concluded—based on the extended Hückel MO method—that the bond length C_4-$C_{4'}$ decreases almost linearly with increasing positive charge of the PE molecule.[5] Our *ab initio* molecular orbital calculations were carried out with the TURBOMOLE program of Ahlrichs *et al.*[10] The molecular structure was optimized for different molecular charges. For the investigation of the electronic structure, density functional theory calculations were performed.[4,11] These calculations indicate the contraction of the PE molecule's naphthalene-naphthalene bond C_4-$C_{4'}$ with increasing oxidation by more than 4% (Fig. 2). The experimental data for the neutral and the $+0.5e$-charged PE molecules of hexaperylene hexafluorophosphate give experimental support for this correlation. Based on this theoretical and empirical structural correlation it may be concluded that in diperylene hexafluorophosphate the PE molecules in the conducting stack carry an average charge of $+0.75e$ and those in the ''walls'' of the conducting channels definitely are neutral (Fig. 2).
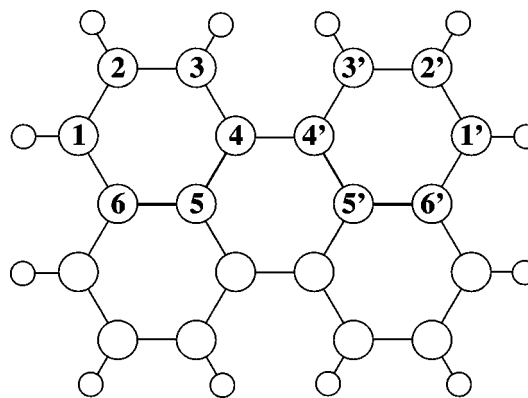

FIG. 1. Schematic presentation of a perylene molecule ($C_{20}H_{12}$) with numbering of the C atoms.
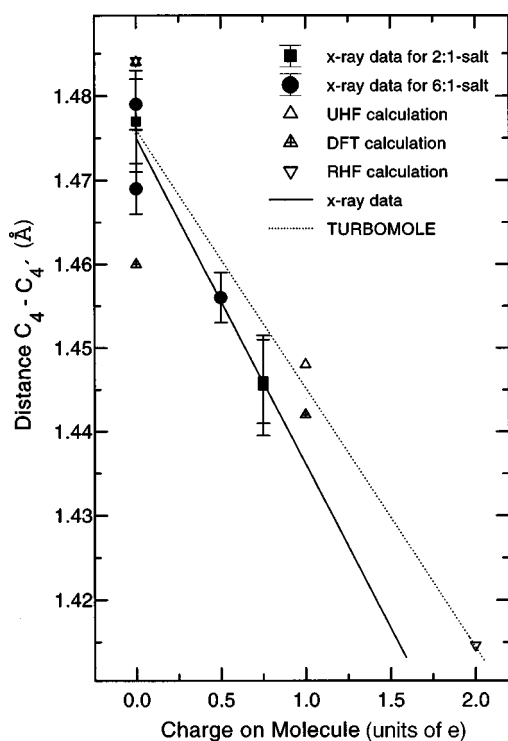
FIG. 2. Correlation between the distance C_4-$C_{4'}$ of the two carbon atoms combining the two naphthalene moieties of the perylene molecule (Fig. 1) and the molecular charge. Calculated data based on TURBOMOLE program (Refs. 10 and 11) [UHF (RHF): unrestricted (restricted) Hartree-Fock calculation, DFT: density functional theory] and experimental data based on x-ray analysis (Refs. 2 and 6).

FIG. 3. Temperature dependence of locally resolved isotropic ^{13}C shifts in diperylene hexafluorophosphate (right scale relative to pure Perylene). The broken lines confine the range of the chemical shifts observed for the neutral PE molecules (rhomb-shaped symbols: center of gravity). For the numbering of the Knight minus chemical shift data of the two inequivalent PE radical sites see Fig. 1. The solid lines were calculated using the local spin densities given in Table I and the conduction electron susceptibility determined experimentally (Refs. 6–8).

More detailed information on the electronic structure of the charged PE molecules is obtained by high-resolution ^{13}C NMR at 75.5 MHz using magic angle-sample spinning, proton-cross polarization, and proton decoupling as was introduced by Mehring and Spengler in the difluoranthene hexafluoroantimonate.[12] Our conclusions are summarized in Fig. 3 and Table I. A detailed description of the analysis will be reported elsewhere. In order to differentiate Knight shifted lines and spinning-side bands, spinning frequencies between 2 and 4.5 kHz were used for temperatures varying between 170 and 270 K in the "metallic" phase. Gated proton decoupling was applied in order to distinguish the carbons C_1 to C_3 bound with protons from C_4 to C_6 having only carbon neighbors. Shifts were determined relative to tetramethylsilane (TMS). The two lines of built-in THF solvent
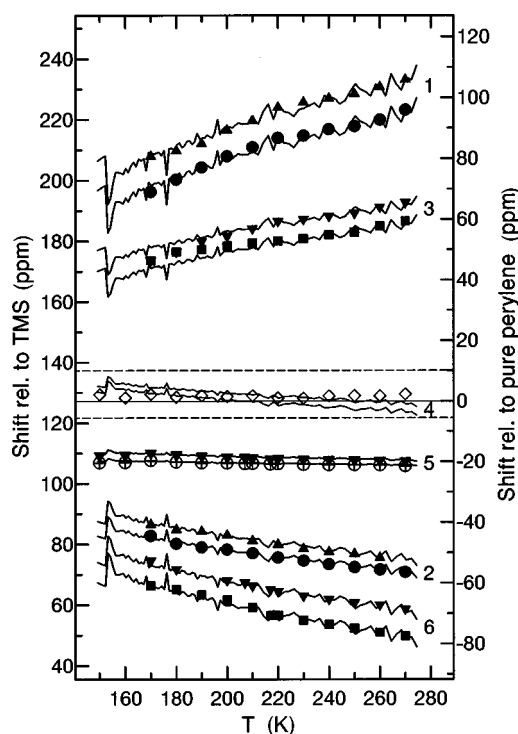
were used as internal reference. For the separation of locally differing Knight shift and chemical shift contributions the correlation of the experimentally derived temperature dependence of the conduction electron part of the magnetic susceptibility[6] and the ^{13}C line shifts was analyzed as familiar from the Jaccarino-Clogston plot. Thus, it was proved that the ^{13}C NMR spectrum of PE in diperylene hexafluorophosphate consists of the chemical shift spectrum of neutral PE molecules plus the spectra of two inequivalent PE radicals. The latters differ in their chemical as well as in their Knight shifts, however.

The ^{13}C Knight shift in aromatic radicals is not a purely local probe, but reflects also the spin density of the neigh-

TABLE I. Comparison of calculated [Hückel (Ref. 5) or TURBOMOLE (Ref. 4)] and experimental spin densities of the stacked PE radicals in diperylene hexafluorophosphate. Assignment of the locally resolved ^{13}C NMR line shifts K_i to the positions named in Fig. 1 is given in Fig. 3.

Position	K_i/ppm	ρ_{calc} (Ref. 4)	ρ_{calc} (Ref. 5)	ρ_{NMR}
1	93.7/90.9	0.144	0.103	$0.189 \pm 0.001/0.192 \pm 0.003$
2	$-43.8/-41.7$	-0.011	0.012	$0.031 \pm 0.001/0.034 \pm 0.001$
3	55.3/52.8	0.097	0.087	$0.096 \pm 0.001/0.088 \pm 0.001$
4		0.051	0.046	$-0.046 \pm 0.001/-0.056 \pm 0.003$
5	$-8.0/-4.8$	-0.015		$-0.053 \pm 0.001/-0.046 \pm 0.003$
6	$-63.6/-56.8$	-0.029		$0.012 \pm 0.001/0.034 \pm 0.001$

boring carbon sites according to the Karplus-Fraenkel relation[13]

$$K_i = \left(Q\rho_i + \sum_{j=i\pm1} Q_N \cdot \rho_j \right) \chi^{PE} / (g_e \mu_B {}^{13}\gamma\hbar) \qquad (1)$$

with $Q = 99.7$ MHz for C_1, C_2, and C_3, $Q = 85.4$ MHz for C_4, C_5, and C_6, and $Q_N = -38.9$ MHz, χ^{PE} the magnetic susceptibility per PE radical molecule, g_e: conduction electron g factor, μ_B: Bohr magneton, and ${}^{13}\gamma$: ${}^{13}C$ gyromagnetic ratio. Thus, there is no unique derivation of the spin densities (normalized to 1 per PE molecule) from the Knight-shift data K_i. Therefore a tentative assignment of the positions C_1-C_6 and the shifts had to be based on the calculated spin densities. Thereafter, the final adjustment of the experimental densities ρ_i was unique for unvaried assignments of NMR lines and carbon positions. Evidently the agreement between calculated and experimental NMR line positions is convincing.

In conclusion, we have shown by the combination of high-resolution NMR, accurate x-ray structural analysis and *ab initio* molecular orbital calculations that neutral diamagnetic and charged (Pauli) paramagnetic perylene molecules coexist in the quasi-one-dimensional organic conductor diperylene hexafluorophosphate, a representative member of radical cation salts of simple arenes. The neutral PE molecules have a longer (weaker) C_4-$C_{4'}$ bond between their two naphthalene subunits. They are arranged in between the conducting PE stacks, with their molecular plane orthogonal to that of the stacked molecules. The stacked PE radicals $(PE)_4^{+3} \cdots$ carry an average charge of $+0.75e$ and show a shorter (stronger) C_4-$C_{4'}$ bond than $(PE)_2^{+\cdot}$ dimers. NMR analysis gives the proof that the four PE molecules are not equivalent—two different sets of NMR lines are distinguished. This is in agreement with the existence of two crystallographically inequivalent sites in the PE stacks. Detailed spin-density distribution is derived by ${}^{13}C$ NMR. This analysis shows the variety of electronic structures accessible for organic molecules in organic conductors and proves the necessity of a careful characterization when aiming at real understanding of their electronic properties.

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