Communication

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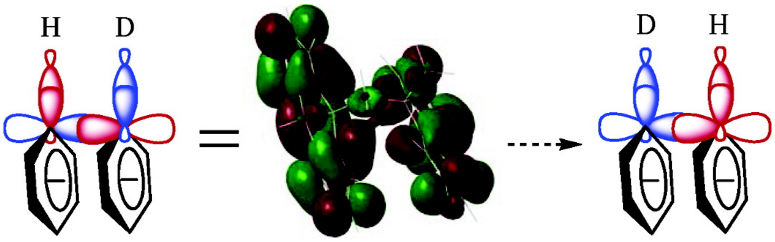

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Intramolecular C−H/C−D Exchange in Cofacially Stacked Polyfluorenes via Electron-Induced Bond Activation

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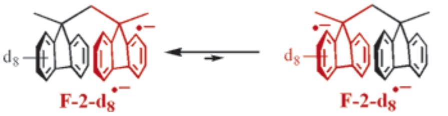
The dissociation energy of the C−H bond in benzene is 113.5 ± 0.5 kcal/mol.[1] Hence, hydrogen exchange, which is typical in acid−base and transition metal systems,[2] does not occur in uncatalyzed simple arene systems. We, however, were motivated to investigate the possibility of intramolecular hydrogen exchange in aromatic π-stacks, where extreme C−H bond activation[3] is present. It was noted five years ago that, even though heating naphthalene to more than 1000 °C results only in hot naphthalene, warming naphthalene anion radical to just 100 °C results in the evolution of hydrogen and methane gases. Now we report that analogous C−H bond activation, via electron addition, in the π-stacked polyfluorenes[4a] results in an exchange "aromatic C−H" hydrogens between adjacent fluorene moieties.

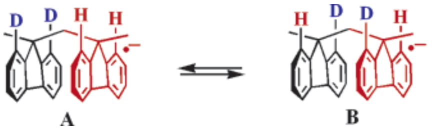
The one-electron reduction of the π-stacked difluorene (F-2) in hexamethylphosphoramide (HMPA), where ion association is absent,[4b] results in the formation of the corresponding anion radical, where all of the electron spin resides on just one of the fluorene moieties (eq 1). When one of the fluorene moieties is perdeuterated, EPR studies reveal that the odd electron resides predominantly on the isotopically light side of the molecule (eq 2), and the EPR pattern is unchanged from that of $F\text{-}2^{\bullet-}$ (Figure 1). This is the expected result, as the solution electron affinities of perdeuterated polyarenes are always much lower than those of their isotopically light analogues.[5]

(1)



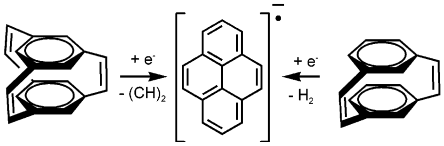
(2)

A sample of $F\text{-}2^{\bullet-}\text{-}d_8$ was stored at −15 °C, for 2 days, after which the EPR spectrum was rerecorded. The hyperfine pattern revealed the clear presence of an anion radical in which one ortho (relative to the methyne carbon) hydrogen was replaced by a deuterium (eq 3), even though the sample was kept in a frozen state (Figure 1). Over the next several days, all four ortho protons and deuteriums continued to scramble until the H and D distribution was a statistical average over the four ortho positions (eq 3). The H's and D's on the other 12 positions remained in place until days later.



(3)

Analogous σ-bond evolution has been observed in the anion radicals of rigidly enforced interacting aryl moieties. In some rigid meta-cyclophane systems, alkali metal reduction leads to the formation of σ-bonds between the opposing aryl groups and concomitant loss of molecular hydrogen or acetylene (e.g., eq 4).[6] This type of reaction and possible use in molecular electronics make face-to-face $\pi-\pi$ stacking interactions involving aromatic rings of considerable current interest.[7]



(4)

The rate of growth of the ratio, $Q = [B]/[A]$, must be independent of the total anion radical concentration, if the exchange is unimolecular. Q (1/4 in Figure 1), however, grows faster with the extent of reduction. This clearly means that the exchange takes place in the dianion, which exists only at very low concentrations, and results from anion radical disproportionation ($2F\text{-}2^{\bullet-} = F\text{-}2^{2-} + F\text{-}2$). The slow exchange is observed when much less than 1 equivalent of potassium is used. It is very fast when more than 1 equivalent is used.

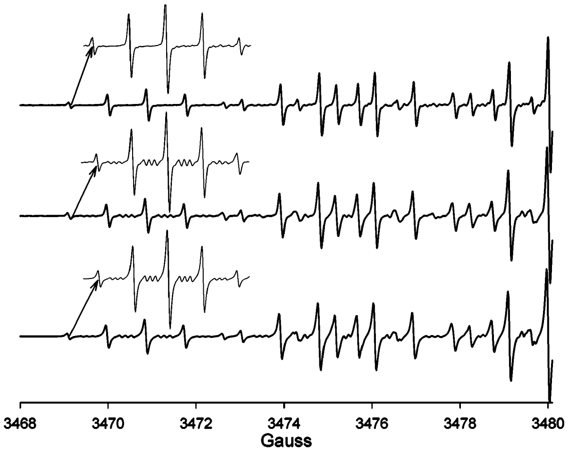


Figure 1. (Upper) Low-field half (12 G scan) of the X-band EPR spectrum of the anion radical resulting from the reduction of F-2-d_8 with K in HMPA at room temperature recorded immediately after the reduction. (Middle) EPR spectrum recorded 46 h later. Note that between each of the first five lines (expanded view in inset) there is a small 1:1:1 triplet due to a single deuterium splitting. The upper spectrum reveals only small ^{13}C splittings in these regions. (Lower) Computer simulation generated by adding two spectra together, one for $F\text{-}2\text{-}d_8^{\bullet-}$ (80%) using a_H's of 0.88 G for 4 Hs, 3.941 G for 2 Hs, and 5.2 G for 2Hs, and one (20%) with the same coupling constants except one a_H of 0.88 G is replaced by a deuterium splitting of 0.135 G ($\Delta w_{pp} = 0.065$ G).

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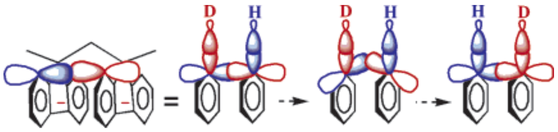
The exchange does not take place in the neutral or monoanionic molecular systems. The presence of the antibonding electrons increases the diffuse nature of the p_z orbitals and allows some overlap of the C−H and C−D σ-bonds of the opposing ring systems. This nonclassical overlap, which crosses the C_2 axis (B3LYP/6-31+G*), evolves into the new C−D and C−H σ-bonds (Scheme 1). The EPR pattern continues to evolve from that shown in Figure 1 to that due to a statistical distribution of H's and Ds in the four ortho positions. The other C−H entities are not involved in an observable exchange event until much later.

Scheme 1

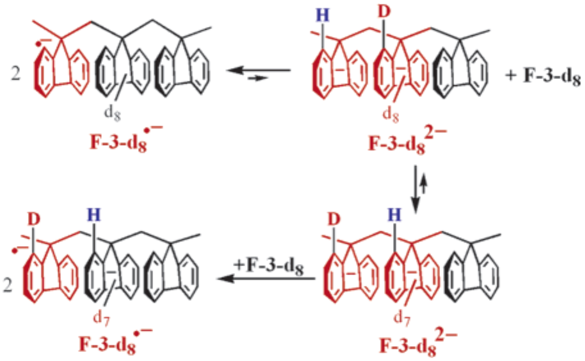


The nonclassical σ-bond−p-orbital overlap described in Scheme 1 is not particularly unusual. Spin leakage from a carbon p_z orbital into a C−H σ-bond is what gives rise to hydrogen 1s spin densities and observable EPR hydrogen coupling constants in all simple arene and polyarene anion radicals.[8]

Quantitative kinetic parameters of the H ↔ D exchange are elusive due to the unknown disproportionation equilibrium constants and inexactly known anion radical concentrations. However, samples harvested from reduced solutions were kept at 298, 258, 90, and 4 K. Only the sample stored at 4 K did not undergo H ↔ D exchange. The exchange is slower at lower temperatures, but this is complicated by the fact that the disproportionation equilibrium constant is also temperature-dependent.

F-3-$d_8^{\bullet -}$, in HMPA, reveals a virtually identical spectrum upon immediate EPR analysis. The odd electron resides exclusively in a terminal fluorene moiety, which is better solvated than a reduced internal moiety. The EPR spectrum 48 h later again reveals the presence of a deuterium on one of the ortho positions of an outer fluorene moiety (Scheme 2).

Scheme 2



Likewise, the F-4-d_{16} anion radical, formed via the reduction of the neutral π-stacked tetrafluorene with both internal fluorene moieties perdeuterated, revealed the presence of deuteriums on the ortho positions of the outer rings the day after reduction.

Interestingly, as the H ↔ D exchange proceeds in the F-2, F-3, and F-4 systems, the 1:1:1 triplets observed between the outer 1:4:6:4:1 pentets grow larger with time, but they disappear in the later stages of the reaction (Figure 2). This is the expected result, because the gyromagnetic ratio of a deuterium is only about 1/6.5 of that for a hydrogen. Thus, once two H ↔ D exchanges have taken place, the deuterium hyperfine can only be observed toward the central portion of the spectra. Computer simulations of the spectra taken after long time periods (weeks) confirm this empirical result.[9] Reduced mixtures of dimethylfluorene (F-1) and F-1-d_8 do not undergo H ↔ D exchange.

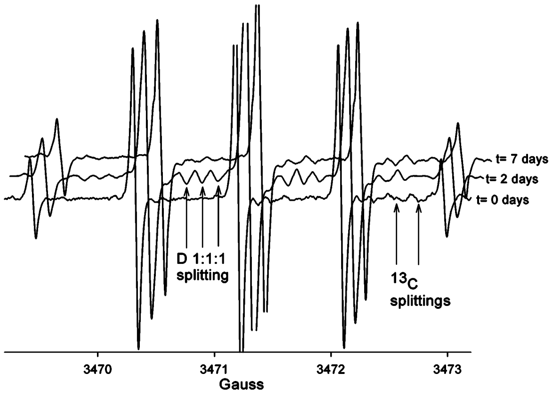


Figure 2. Low-field 1:4:6:4:1 proton pentet of the X-Band EPR spectrum of the anion radical resulting from the K reduction of F-4-d_{16} (internal fluorene moieties perdeuterated) in HMPA recorded within minutes of reduction (bottom), 2 days after reduction (middle), and 1 week after reduction (top). The vertical scale was expanded (off scale) to reveal the deuterium and natural abundance ^{13}C hyperfine patterns. Note that the deuterium splittings are most prominent in the middle spectrum.

In summary, we have demonstrated that the cofacially stacked polyfluorenes undergo H ↔ D intramolecular exchange at the ortho carbons upon one-electron reduction, even at low temperatures. This lends support to the fact that there is effective electronic coupling among various fluorene moieties due to the close proximity of the ortho carbons. However, the mechanism (i.e., heterolytic or homolytic) for the exchange remains unknown.

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(2) For examples, see: (a) Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 7635−7636. (b) Mitchell, G. P.; Tilley, T. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2524−2526.

(3) (a) To quote the experts: "In many cases, this rupture of a saturated bond is implied when the term 'activation' is used. Nevertheless, the splitting of the bond is actually a consequence of its activation, and it would be more correct to refer specifically to the splitting of the C−H bond in these situations." See: (a) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879−2932. Also see: (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245−269.

(4) The π-stacked nature of various polyfluorenes has been established in solution and in solid state by ^{1}H NMR and X-ray crystallography, respectively. See: (a) Rathore, R.; Abdelwahed, S. H.; Guzei, L. A. *J. Am. Chem. Soc.* **2003**, *125*, 8712−8713. (b) Stevenson, C. D.; Echegoyen, L.; Lizardi, L. R. *J. Phys. Chem.* **1972**, *76*, 1439−1442. (c) Shimada, K.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, *97*, 3321−3323.

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(9) After these very long time periods (weeks) there is a net loss of deuteriums to the solvent (H−D exchange between the anion radical and the HMPA). See: Stevenson, C. D.; Ballard, M. K.; Reiter, R. C. *J. Org. Chem.* **1991**, *56*, 4070.

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