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Observation of an Aromatic Radical Anion Dimer: $(C_{10}F_8)_2^{\bullet-}$

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Radical cation dimers are observed for many alkenes¹⁻⁴ and aromatic hydrocarbons⁵⁻¹⁰ as products of the reaction between the monomer radical cation and the neutral molecule,

eq. 1. In most cases, the dimer radical anions, formed via reaction of the monomer radical anion with a neutral molecule, eq 2, have not been observed. Here we report the observation of the dimer radical anion of octafluoronaphthalene, formed by reaction of $C_{10}F_8^{\bullet-}$ with the neutral parent molecules in nonpolar solvents following pulse radiolysis. Both the monomer and dimer ions have been characterized by their EPR spectra obtained by the time-resolved fluorescence-detected magnetic resonance (FDMR) technique.

Figure 1 shows FDMR spectra observed at 190 K in n-hexane solvent containing octafluoronaphthalene. In the pulse radiolysis/FDMR method, fluorescence from the recombination reaction between spin-correlated radical ion pairs is modulated at resonant magnetic field by a microwave pulse.¹¹⁻¹³ The superimposed EPR spectra of the recombining pair of ions are obtained as the magnetic field dependence of the fluorescence intensity. Thus octafluoronaphthalene anions, formed by electron capture, recombine with solvent radical cations, and the octafluoronaphthalene fluorescence is monitored. An auxiliary scintillator (d_{10} -anthracene), which contributes a signal that overlaps the center

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line of the spectrum, was added to enhance the signal intensity, or omitted to allow interrogation of the central portion of the EPR spectrum.

At 10^{-3} M $C_{10}F_8$ (Figure 1a), the spectrum of $C_{10}F_8^{\cdot-}$ is observed. This spectrum is described by two quintet coupling constants, $a_1 = 23.2$ G and $a_2 = 20.0$ G, as appropriate for two sets of four equivalent spin one-half ^{19}F nuclei. What appears as a 9-line spectrum at low resolution, clearly separates into the 25-line pattern at slightly higher resolution (expanded view of inner three line groupings, Figure 1a). The coupling constants increase slowly with temperature, and at room temperature we observe $a_1 = 28.1$ G and $a_2 = 21.6$ G. We observe no evidence for the formation of $C_{10}F_8^{*+}$ under our experimental conditions. The signal is not quenched by the addition of a positive ion scavenger, such as durene, which further supports the assignment to the radical anion.

As the $C_{10}F_8$ concentration is increased, the monomer anion signal intensity decreases, and the spectrum is replaced by a narrower spectrum with a 7 G line spacing. At 190 K and 5×10^{-3} M $C_{10}F_8$, the 7 G spectrum is dominant (Figure 1b), and is consistent with coupling to 16 nearly equivalent nuclei. The ratio of the 7 G spectrum to the monomer anion spectrum is also increased by delaying the time window of observation. This new spectrum is assigned to the dimer radical anion, $(C_{10}F_8)_2^{\cdot-}$, based on the i) reduced hyperfine splitting, ii) increased number of equivalent nuclei, iii) concentration dependence and iv) kinetic behavior. Note that a very different kind of spectrum narrowing takes place in the event of rapid electron transfer to neutral solute molecules;^{14,15} thus the self-exchange reaction is not responsible for the observed behavior. Observations i) - iv) are analogous to those pertaining to radical cation dimers studied by FDMR^{1,5,15,16} and other methods.^{2-4,7,10}

Fluorine substitution has a significant effect on the energies of the unoccupied molecular orbitals of aromatic compounds. In a series of fluorine-substituted benzene¹⁷ and pyridine radical anions,¹⁸ it has been shown that fluorine substitution destabilizes the lowest π^* orbital and stabilizes the lowest σ^* orbital and gives rise to $\sigma^*-\pi^*$ crossover.

That is, in heavily fluorinated benzene and pyridine radical anions, the excess electron occupies a delocalized σ^* orbital rather than a π^* orbital. The main signature of the σ^* ground state anion is that the hyperfine splittings are larger for the radical anion than the radical cation, which is the reverse of the ordering of $a(+)$ and $a(-)$ for lightly or unsubstituted aromatic compounds.^{7,19-23}

The reported coupling constants for $C_{10}F_8^{+\bullet}$ are 19.0 and 4.8 G.²⁴ Thus, on this basis we would conclude that the ground state of $C_{10}F_8^{\bullet-}$ is σ^* . The relatively small differences between $a(+)$ and $a(-)$ for $C_{10}F_8$, however, leave room for doubt and suggest that the σ^* and π^* orbitals are close in energy. This may explain the temperature dependence of the hyperfine splittings, for example, if the mixing of the σ^* and π^* states has a vibronic component. We cannot rule out a predominantly π^* ground state with a small amount of σ -character mixed in from a nearby σ^* state, which might be sufficient to explain the observed coupling constants.

The dimer radical anion of octafluoronaphthalene is presumed to have a sandwich-type structure by analogy to aromatic dimer radical cations. The $\sim 1/3$ ratio of $a(\text{dimer})$ to the average of the monomer coupling constants deviates from the value of $1/2$ commonly found for symmetric dimer radical cations.^{7,10} It has been shown in EPR studies of naphthalene derivatives that this ratio may vary in dimer radical cations due to rotational or translational perturbations from the geometry of highest symmetry.¹⁰ On the other hand, the balance of σ vs. π character of the SOMOs in $C_{10}F_8^{\bullet-}$ and $(C_{10}F_8)_2^{\bullet-}$ could also affect the ratio.

What about the existence of other dimer radical anions? The only reported example of an anion-molecule dimerization reaction observed by EPR is the cyclization reaction between the tetrafluoroethylene radical anion and the parent molecule to give $c\text{-C}_4F_8^{\bullet-}$.²⁵ EPR has also been used to show that the trapped electrons in crystalline acetonitrile exist as the acetonitrile dimer anions.²⁶ There is optical and kinetic evidence from pulse radiolysis

studies that radical anions of various ethylenes, substituted with strong electron-withdrawing groups, form dimer anions with absorption bands in the IR and UV.²⁷

Other fluorinated aromatic derivatives deserve investigation. The hexafluorobenzene radical anion has been reported to undergo self-exchange in nonpolar solvents at room temperature,²⁸ in contrast to our low-temperature results for octafluoronaphthalene. Our FDMR results for the radical anion of 1,2,4,5-tetrafluorobenzene in n-hexane are very similar to those for octafluoronaphthalene and suggest the formation of $(C_6H_2F_4)_2^{\bullet-}$; however, the presumed dimer anion spectrum is unresolved in this case.²⁹

To summarize, we have reported the first observation of an aromatic radical anion dimer. This result is interesting in light of the dearth of previous reports of such species and the common observation of dimers formed from aromatic radical cations. While such dimer radical ions are best characterized via their EPR spectra, they should be observable by optical absorption spectroscopy as well. In view of the fact that aromatic aggregate radical cations have been shown to lead to excimer formation,⁵ we plan to investigate the possible occurrence of excimer emission following ion recombination of the dimer radical anions.

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Figure Caption:

- Figure 1 a) FDMR spectrum observed at 190 K in n-hexane containing 10^{-3} M $C_{10}F_8$ and 10^{-4} M d_{10} -anthracene (lower experimental trace), no d_{10} -anthracene (upper experimental trace). The upper trace was obtained at higher resolution. The stick spectrum was simulated with the parameters, $a(4F) = 23.2$ G, $a(4F) = 20.0$ G.
- b) FDMR spectrum observed at 190 K in n-hexane containing 5×10^{-3} M $C_{10}F_8$. The stick spectrum was simulated with $a(16F) = 7$ G.

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