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Optically detected ESR spectrum of decafluorobiphenyl radical anions

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The radical anion of decafluorobiphenyl was detected by the OD ESR technique for the first time; the spectrum was interpreted on the basis of quantum-chemical calculations as a result of fast exchange among equivalent asymmetrical structures.

Fluoroarene radical ions attract much attention as key intermediates responsible for the chemical transformations of fluoroarenes.¹ For instance, such synthetically important polyfluoroarene reactions as $S_{RN}1$ nucleophilic substitution and reductive dehalogenation involve the stage of radical anion formation.^{2,3} The route of these reactions is determined by the structure of radical anion intermediates. Thus, the regularities of fluoride ion elimination from polyfluoroarene radical anions determine the regioselectivity of polyfluoroarene dehalogenation.⁴ Interest in these radical ions is due to their electronic and spatial structures. The large values of hyperfine coupling (hfc) constants of fluoroarene radical anions testify to the disturbance of their planar structure due to vibronic coupling between the anion ground π and low-lying excited σ states (pseudo-Jahn–Teller effect).⁵ The out-of-plane distortions are caused by a strong perturbation of the aromatic molecule σ -system by fluorine atoms, which generates the low-lying excited σ -states of radical anions.

One of the main obstacles to the ESR study of fluoroarene radical ions is the instability of these particles. For instance, the fragmentation rate constant of the radical anions of pentafluorophenol, pentafluoroaniline and polyfluorinated benzoates in water exceeds 10^6 s^{-1} .^{6,7} At the same time, the optically detected ESR (OD ESR) spectroscopy, being highly sensitive for radical ion pairs, provides the detection of unstable radical ions with lifetimes as short as 10 ns.^{8–10} The extremely high sensitivity of this method is due to optical detection through the fluorescence of excited molecules, which are produced by the recombination of radical ion pairs in irradiated solution.

Here, the OD ESR method was used to detect the ESR spectrum of the decafluorobiphenyl radical anion in a liquid squalane (2,6,10,15,19,23-hexamethyltetracosane) solution at room temperature. The solution contained deuterated *p*-terphenyl used as a positive charge acceptor and an emitting probe. The measurements were performed using an OD ESR spectrometer¹¹ based on an ER-200D Bruker ESR spectrometer equipped with a source of ionizing radiation (an X-ray tube) and a photomultiplier to measure fluorescence intensity. Modulation amplitude and microwave power of 0.36 mT and 2.5 W, respectively, were used to increase the intensity of very expanded ESR spectrum of

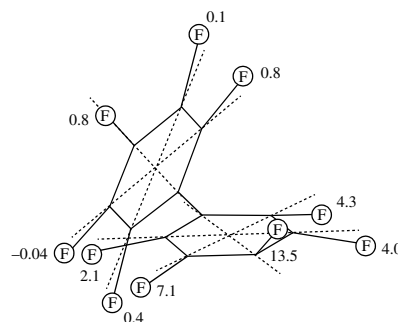


Figure 1 Structure corresponding to local PES minima of the $(C_6F_5)_2^-$ radical anion and respective calculated ^{19}F hfc constants (mT).

the decafluorobiphenyl radical anion. Under these conditions, the individual line widths were determined mainly by the microwave power broadening.

Experimental results were compared with the hfc values predicted by quantum-chemical calculations. The calculations were performed with the GAMESS program.¹² The geometry of the $(C_6F_5)_2^-$ radical anion was optimised at the PBE/6-31+G* level of calculations. The hfc constants were estimated at the PBE geometries by the B3LYP method (UB3LYP/EPRIII//PBE/6-31+G*).

According to the calculations, the structure of the $(C_6F_5)_2^-$ radical anion exhibits pseudo-Jahn–Teller distortions of two types: out-of-plane deviation of fluorine atoms (which is peculiar to radical anions of fluorobenzenes) and the nonequivalence of aromatic rings. The former distortion results from the interaction between the ground π and the excited σ state of the radical anion, while the latter one arises from the interaction between the ground and excited π states. The disturbance of fragment equivalence in radical ions of symmetric molecules was discussed previously.^{5,13}

The energy minimum corresponds to the totally asymmetric C_1 structure (Figure 1), where a dihedral angle between the planes of aromatic rings is $\sim 45^\circ$, the out-of-plane deviations of

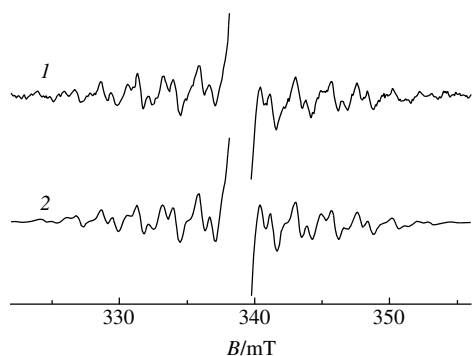


Figure 2 (1) Experimental OD ESR spectrum and (2) its simulation for a squalane solution of 10 mmol dm^{-3} of $(\text{C}_6\text{F}_5)_2$ + 1.5 mmol dm^{-3} of *p*-terphenyl- d_{14} at room temperature. The spectrum was recorded at a microwave power of 2.5 W and a modulation amplitude of 0.36 mT.

C–F bonds in one of the rings being more pronounced than in the other. The more distorted ring bears the most part of the unpaired electron density. The values of ^{19}F hfc constants calculated for this structure are also shown in Figure 1.

The unpaired electron location in one or the other ring combined with inversion of the out-of-plane distortion gives rise to four equivalent C_1 structures, which correspond to minima on the radical anion potential energy surface (PES). These four minima of equal energy are separated by transition states of two types. The upper limit for the heights of the energy barriers is determined by energy of symmetric D_2 structure of the radical anion, where an unpaired electron is delocalised over two planar C_6F_5 fragments. According to our calculations, the heights of the barriers do not exceed $1.5 \text{ kcal mol}^{-1}$, which provides the possibility of fast transitions among the PES minima. Averaging of hfc constants due to the transitions involved will give rise to three groups of effectively equivalent ^{19}F nuclei: *meta*, *para* and *ortho*, respectively.

The OD ESR spectrum obtained for a squalane solution containing 10 mmol dm^{-3} of $(\text{C}_6\text{F}_5)_2$ + 1.5 mmol dm^{-3} of *p*-terphenyl- d_{14} (pTP) is shown in Figure 2 (curve 1). The concentration of $(\text{C}_6\text{F}_5)_2$ substantially exceeding that of pTP was used in order to ensure predominance of $(\text{C}_6\text{F}_5)_2^-$ radical anions. It is evident that the principal contribution to this spectrum is made by $(\text{C}_6\text{F}_5)_2^-/(\text{pTP})^+$ radical ion pairs, the radical anions of $(\text{C}_6\text{F}_5)_2$ being responsible for the multiplet demonstrating large hyperfine splittings. As for radical cations of pTP, they give rise to the central single line with an integral intensity close to 50% of the overall spectrum intensity. As follows from Figure 2, there is no signal from radical cations of $(\text{C}_6\text{F}_5)_2$, whose ESR spectrum is known¹⁴ to be a multiplet with splitting about 0.8 mT. The absence of the signal of $(\text{C}_6\text{F}_5)_2^+$ radical cations is explained by inefficiency of positive charge transfer from the primary radical cation of solvent to $(\text{C}_6\text{F}_5)_2$ molecule due to a large $(9.4 \pm 0.02 \text{ eV})^{15}$ ionization potential of $(\text{C}_6\text{F}_5)_2$. At the same time, sufficiently large electron affinity value of the $(\text{C}_6\text{F}_5)_2$ molecule $(0.82 \pm 0.11 \text{ eV})^{16}$ provides effective formation of $(\text{C}_6\text{F}_5)_2^-$ radical anions.

Simulation of the experimental spectrum with the WinSim-2002 program¹⁷ shown in Figure 2 (curve 2) gives the following hfc values for $(\text{C}_6\text{F}_5)_2^-$ radical anion: $a(4\text{F}) = 1.9 \text{ mT}$, $a(4\text{F}) = 2.6 \text{ mT}$ and $a(2\text{F}) = 7.2 \text{ mT}$. The presence of groups of equivalent nuclei consistent with the effective symmetry of the radical anion may be caused by fast thermally activated transitions among the equivalent asymmetrical structures. In this case, the fast exchange will result in the averaging of the observed ^{19}F hfc values over all the exchanging structures. The calculated hfc constants (Figure 1) averaged in this way give the following values: $a_{\text{calc}}(4\text{F}) = 1.9 \text{ mT}$, $a_{\text{calc}}(4\text{F}) = 2.8 \text{ mT}$ and $a_{\text{calc}}(2\text{F}) = 7.1 \text{ mT}$.

A fair agreement of the hfc values obtained by averaging the calculated hfc constants with experimentally measured ones proves that a fast exchange between energetically equivalent structures of $(\text{C}_6\text{F}_5)_2^-$ radical anion takes place under the conditions of our experiments. No changes in hyperfine pattern were observed across the temperature range available in our

experiments (240 to 310 K), which provides further evidence for the activation barrier of the exchange being low.

Previously, we established a fast exchange among stationary structures to be the case for the radical anion of 1,2,3-trifluorobenzene in liquid solutions.¹⁸ Analysis of PES shape of this species demonstrates the fast exchange to be enabled by small ($2\text{--}4 \text{ kcal mol}^{-1}$) energy barriers separating the PES minima. For the $(\text{C}_6\text{F}_5)_2^-$, because of the large size of the system, quantum-chemical calculations required for energy barriers to be determined are much more expensive.

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