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A MARY study of radical anions of fluorinated benzenes

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The paper reports the results of two studies centred on the properties of radical anions of polyfluorinated benzenes in liquid dodecane solutions at room temperature using level crossing (MARY) spectroscopy of spin-correlated radical ion pairs generated in nonpolar solutions by ionizing radiation. The first study takes advantage of the large, nearly two orders of magnitude, span of hyperfine couplings in the series of otherwise similar radical anions to probe into the peculiarities of degenerate electron exchange reaction for system with large hyperfine couplings. The second study provided the first observation of radical anion of 1,3,5-trifluorobenzene and yielded a hyperfine coupling constant of 7.2–7.5 mT with three equivalent fluorine nuclei and coherent lifetime of the radical anion about 20 ns at room temperature, which has thus far precluded its observation by other techniques.

1. Introduction

Radical ions of fluorinated benzenes have attracted much attention and effort by both theoreticians and experimentalists because of their electronic and spatial properties ([1] and references therein). On the one hand, disturbance of the planar structure of the benzene ring because of strong perturbation of its σ-system by fluorine atoms produces substantial, up to tens of mT, hyperfine couplings with fluorine nuclei in radical ions of polyfluorinated benzenes [1] that are easily detectable by ESR. On the other hand, weak perturbation of the π-system of such a radical ion by fluorine substituents results in only minute energy splitting of the frontier π molecular orbitals that are degenerate in unsubstituted benzene, producing a pair of close-lying π states, the terms of which can cross [2, 3]. The movement of the system along potential energy surface (PES) through the resulting avoided crossings results in modulation of the magnetic interactions in the radical ion, detectable as characteristic spectral features in ESR spectra. Most studies of the radical ions of fluorinated benzenes have thus been centred either on quantum-chemical calculations of PES and the details of its traversing, or on ESR studies of the corresponding radical ions, and often combined these two approaches.

By far the most studied of the discussed species is the radical anion (RA) of hexafluorobenzene (HFB), C_6F_6. First abnormally large hyperfine coupling constants (HFC) of 13.7 mT for HFB RA were reported in adamantane matrix at 218 K [4]. This investigation was continued in subsequent works by several groups [5–13] turning to quantum chemistry techniques for theoretical insights and to ESR in frozen matrices for experimental data. The work [5] also reported ESR spectra and INDO study of RA from pentafluorobenene, 1,2,4,5-tetrafluorobenzene, and p-difluorobenzene in adamantane matrix. A classical study of 10 radical cations of fluorinated benzenes from mono- to hexafluorobenzene in freon matrices is also available [14], and the work [12] reported both HFB radical anion and cation.

Development of optically detected spin chemistry techniques opened the possibility to study RA of fluorinated benzenes in liquid, even warm, non-polar solutions. The first Optically Detected ESR (OD ESR) study of HFB RA appeared in 1980 [15]. In this work a resolved isotropic spectrum for HFB RA in squalane at 296 K with neatly resolved second-order structure was obtained, yielding a HFC constant of 13.36 mT. Further studies [16, 17] confirmed this observation and commented that the discrepancy in the value of the HFC constant is not too large and may come from the differences in local environment and temperature. Apart from HFB, RA of p-difluorobenzene and 2,3,5,6-tetrafluoro-p-xylene were reported in the first

of these works [16], and RA of *p*-difluorobenzene, 1,2,4,5-tetrafluorobenzene, 2,3,5,6-tetrafluoro-*p*-xylene, 2,3,5,6-tetrafluoroanisole, pentafluorobenene, penta-fluoroanisole, and phenylthio-2,3,5,6-tetrafluoroben-zene were reported in the second [17]. A study of dimeric anions of 1,2,4,5-tetrafluorobenzene was performed using a time-resolved counterpart of OD ESR, the Fluorescence Detected Magnetic Resonance (FDMR) technique [18]. Very recently successful OD ESR studies and quantum-chemical calculations were reported for RA of 1,2,3-trifluorobenzene [19].

RAs of fluorinated benzenes, and especially HFB RA, have also been the models of choice for calibrating new optically detected spin chemistry techniques in situations where large hyperfine couplings were needed for one reason or another, and for studying fast reactions of radical ions in solutions, such as the ubiquitous reaction of degenerate electron exchange (DEE) between a radical ion and its parent neutral molecule, with these techniques. As representative examples the works on OD ESR [20, 21], MARY spectroscopy [22, 23], time-resolved electric [24, 25], magnetic [26, 27], and microwave [28, 29] field effects in recombination fluorescence are suggested. In other words, RA of fluorinated benzenes are normally considered to be test systems with known, either measured or calculated, properties.

Our initial motivation for the study of RAs from a series of polyfluorobenzenes came from the desire to have access to a series of radical anions having similar properties with respect to radiation chemistry under X-irradiation in nonpolar solutions [30] as used by MARY spectroscopy and other optical detection techniques, but covering a wide range of hyperfine couplings. In these conditions RA is formed as the anion partner of the spin-correlated radical ion pair. After ionization of solvent molecule S, in our case dodecane, producing the primary radical ion pair 'S$^+$/e$^-$', the highly mobile electron e$^-$ is captured by a molecule of the fluorinated benzene to produce the target RA. The other partner of the pair, solvent hole S$^+$, is captured by a suitable acceptor to produce the radical cation (RC) partner of the pair, preferably with negligible hyperfine couplings and appreciable quantum yield of fluorescence. This role in our studies was played by RC of perdeuterated aromatic compounds. The selection of six fluorinated benzenes that we used is shown in figure 1 together with HFC in their RAs.
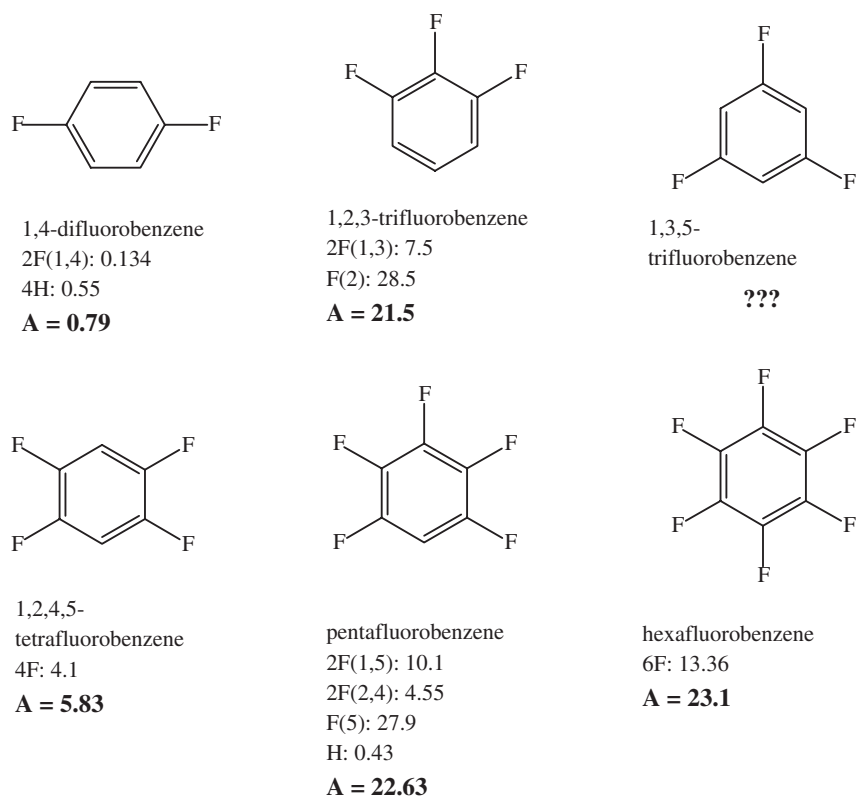

1,4-difluorobenzene
2F(1,4): 0.134
4H: 0.55
A = 0.79

1,2,3-trifluorobenzene
2F(1,3): 7.5
F(2): 28.5
A = 21.5

1,3,5-trifluorobenzene
???

1,2,4,5-tetrafluorobenzene
4F: 4.1
A = 5.83

pentafluorobenzene
2F(1,5): 10.1
2F(2,4): 4.55
F(5): 27.9
H: 0.43
A = 22.63

hexafluorobenzene
6F: 13.36
A = 23.1

Figure 1. Six fluorobenzenes discussed in this work. Also given are HFC constants and effective HFC constant $a_{eff} = \sqrt{2/3 \Sigma a_i^2 I_i(I_i + 1)}$ in mT for their radical anions. The values of HFC constants for radical anion of 1,3,5-trifluorobenzene are not known, HFC constants for radical anion of 1,2,3-trifluorobenzene were taken from work [19], and for all other radical anions – from work [17].

All these molecules are fairly good electron acceptors, do not capture solvent holes in dodecane solution due to rather high ionization potential [14], and most likely have similar mobilities, thus creating similar molecular carriers for the radical anion partner of the pair. However, effective hyperfine couplings in their RA $a_{\text{eff}} = \sqrt{2/3 \Sigma a_i^2 I_i (I_i + 1)}$ vary from about 0.8 mT for p-difluorobenzene to about 23 mT for hexafluorobenzene, thus providing the desired series of 'test systems' with known properties. We followed this methodology in our recent study of RC of methyl-substituted benzenes to obtain a similar series of radical cations [31]. Thus defined effective HCF constant that differs by $\sqrt{2}$ from the conventional definition of the second moment of ESR spectrum of the radical was introduced in the description of MARY spectra when systems with arbitrary hyperfine structure were considered in semiclassical approximation [32] as it turned out to be slightly more convenient.

However, as this project progressed, two important factors gradually surfaced. First, as was pointed out in recent theoretical work [33, 34], increasing hyperfine couplings in a radical ion can qualitatively change spectral manifestations of the DEE reaction in which it takes part. We shall describe this effect later in a dedicated section, but mention here that from theoretical estimates HFB RA in dodecane comes close to the limit of detectability of this effect, rendering our series of 'test systems' not so ideal. Since this situation can be rather common and is not limited to MARY studies, we describe this reasoning and our experimental findings on it in the present work.

Second, we found that to the best of our knowledge RA of symmetric 1,3,5-trifluorobenzene (TFB) has not thus far been reported by any spin-sensitive technique, which explains bold question marks instead of hyperfine couplings for it in figure 1. Such studies have been attempted, both with matrix isolation [5] and in OD ESR [17], but the authors had to admit that they could not detect these species. Furthermore, in the matrix isolation study of radical cations of fluorinated benzenes [14], although the authors provide the g-values and HFC constants for TFB RC, they comment on the poor resolution of its spectrum compared to other studied RC, and it is the only RC for which they do not produce the spectrum itself. Apparently, radical ions of the symmetric TFB are difficult to observe using magnetoresonance techniques. Although the real reason for it in this particular case is not known precisely, usually the argument of enhanced spin relaxation due to Jahn-Teller effect in a highly symmetric (having at least a threefold symmetry axis) molecule is invoked. Such effects have been reported both for aromatic [35–37] and aliphatic [27, 38–40] radical ions. We have observed this radical

anion and indeed found rather short, about 20 ns, relaxation time for it.

The paper is organized as follows. First we provide a brief description of the technique of MARY spectroscopy as it is applied in this work. Then in two dedicated sections we discuss the problem of coupling DEE reaction to effective hyperfine interaction in the radical ion and the problem of obtaining magnetoresonance parameters from MARY spectra for radical ions with equivalent magnetic nuclei, starting from theoretic and methodological considerations and concluding with our original experimental results.

2. Materials and methods

2.1. *MARY spectroscopy technique*

A detailed description of MARY (Magnetically Affected Reaction Yield) spectroscopy as applied in this work was published recently [31, 41], and in this subsection we only briefly summarize the method. MARY spectrum is essentially a conventional stationary magnetic field effect (MFE) curve – dependence of the yield of recombination fluorescence from radical ion pairs in irradiated solutions on external static magnetic field – with sharp lines at zero and low fields due to degeneracy of the spin energy levels of the pair. Similar techniques that we are aware of have also been implemented in Oxford [42, 43], RIKEN, Japan [44], Graz, Austria [45], Minneapolis, USA [46, 47], and Leicester [48]. To amplify the weak and narrow zero field MARY line against the slowly changing background of the MFE, magnetic field modulation with lock-in detection of the signal and symmetric passage through zero of the field is used, producing a first derivative experimental spectrum resembling CW ESR lines. A time-resolved modulation-free realization of MARY spectroscopy is now being developed [49] using the switched magnetic field approach similar to the methology of stroboscopic/SEMF studies [50–53].

For MARY, spin evolution in the pair leading to the observed effect is driven by hyperfine interactions in the pair partners, rather than by the B_1 field of a spectrometer, and radical ion partners of the pair living as short as nanoseconds can be readily registered for species with large hyperfine couplings, e.g., radical anions of hexafluorobenzene ($A_{6F} = 13.5$ mT) [54] or perfluorocyclobutane ($A_{8F} = 15.1$ mT) [55], provided that one of the partners yields a fluorescing excited state upon recombination. The technique is sensitive only to spin-correlated radical ion pairs and is thus best suited to study the reactions of geminate radical ions on the time scale from nanoseconds to tens of nanoseconds.
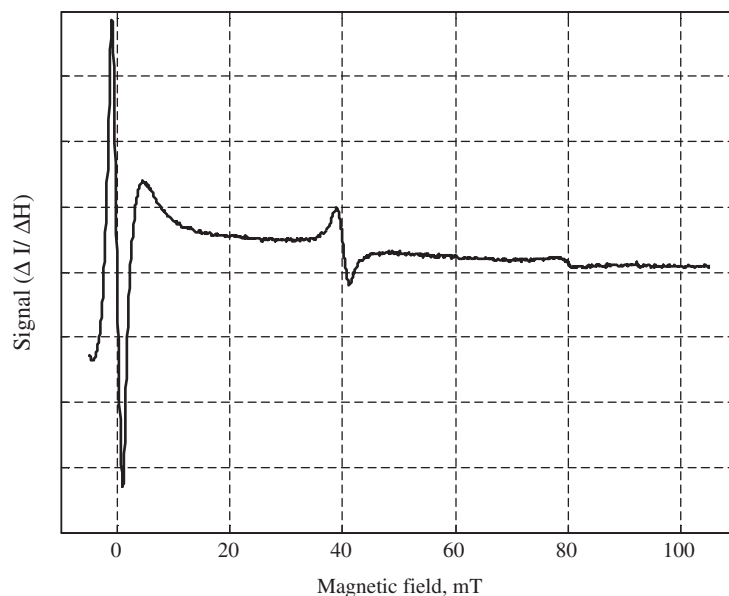
Figure 2. Experimental MARY spectrum for solution of 5×10^{-2} M C$_6$F$_6$ and 1×10^{-3} M *p*-terphenyl-d_{14} in dodecane, room temperature, modulation amplitude 2 mT. No microwave power was applied to the sample. Note the satellites at 40 mT and 80 mT. The zero field line is overmodulated in these conditions.

The width of MARY lines is determined by chemical decay and spin relaxation of radical ions and the processes of geminate radical ion pair recombination, and the former two give additive contribution to the width, assuming that they are exponential [22]. For the strongest MARY line in zero magnetic field the kinetics leads to apparent scaling of the exponential processes (decay and relaxation), which is accounted for by dividing the measured peak-to peak width of the experimental line by a constant factor, typically equal to 2 in our experimental conditions [23]. Thus obtained figure corresponds to the width of an imaginary Lorentzian contour determined by the exponential processes in the radical ion pair. A typical MARY study was an estimation of the lifetimes of primary radical cations of *n*-alkanes in neat liquids [56], which were found to vary from 1 to 30 ns in the series *n*-pentane–*n*-hexadecane.

Although normally only MARY line in zero field, or the so called Low Field Effect (LFE) is observed, for systems with equivalent nuclei additional lines in fields – multiples of the single HFC constant can be observed. This effect has the same origin as LFE, the crossing of eigenlevels of the spin system as magnetic field is varied, and is essentially a transposition of the LFE to nonzero fields. The effect was predicted theoretically in 1983 [57], first experimental lines were reported in 1995 [46, 58], and weaker further lines were reported in 1998 [55]. A representative spectrum for hexafluorobenzene radical anion is shown in figure 2. Although much weaker than the zero field line, lines in nonzero field bear specific spectroscopic information – the value of the HFC constant, while retaining the sensitivity to short lifetimes inherent in MARY spectroscopy. We shall use this effect to chase down the radical anion of 1,3,5-trifluorobenzene.

2.2. Experimental

Detailed description of the experimental set-up can be found elsewhere [31, 41]. About 1 cm^3 of degassed solution in a quartz cuvette is placed in the field of a Bruker ER-200D ESR spectrometer equipped with an offset coil with a separate DC power supply to provide the 'negative' shift of magnetic field required to sweep the field through zero using the standard field controller of the Bruker spectrometer, an X-ray tube for sample irradiation (Mo, $40 \, \text{kV} \times 20 \, \text{mA}$ for this work), and a photomultiplier tube assembly to detect fluorescence (FEU-130). The external magnetic field was modulated at a frequency of 12.5 kHz with an amplitude of up to 2 mT taking care not to over-modulate the lines. A Stanford SR-810 Lock-In Amplifier and computer averaging over 20–100 scans were used to get the presented MARY lines as the first derivatives of the actual field dependencies. No micro-wave power was ever applied to the samples. All experiments were carried out at room temperature.

The solvent – *n*-dodecane – was stirred with concentrated sulphuric acid, washed with water, distilled over sodium and passed through a column of activated alumina. 1,3,5-Trifluorobenzene was synthesized by

Dr V.V. Knyazev, NIOCh SB RAS, Novosibirsk, other acceptors were commercially available: hexafluorobenzene (Avocado, 99%), pentafluorobenzene (Avocado, 98+%), 1,2,4,5-tetrafluorobenzene (Avocado, 99%), 1,2,3-trifluorobenzene (Avocado, 99%), 1,4-difluorobenzene (Aldrich, 99+%), benzene-d_6 (Aldrich, 99.6 atom% D), toluene-d_8 (Aldrich, 99 atom% D), and p-terphenyl-d_{14} (Aldrich, 98 atom% D). All acceptors were used as received without further purification. All fluorobenzenes were checked with a chromatomass-spectrometer (Agilent Technologies 6890N Network GC System) using n-hexane as solvent, the dominant impurities (within the specified purities) found were minute amounts of other polyfluorobenzenes (e.g., pentafluorobenzene in hexafluorobenzene and vice versa), which did not lead to any artefacts in the described experiments. To extract parameters all experiments were modelled as described later.

3. Results and discussion

3.1. *Peculiarities of DEE reaction for systems with large hyperfine couplings*

Degenerate electron exchange (DEE), or ion-molecular charge transfer, reaction

$$A^{+/-}(n) + A(j) \Leftrightarrow A(n) + A^{+/-}(j)$$

is one of the most ubiquitous processes in radical ion chemistry occurring under high energy irradiation and has rather specific spectral manifestations [59]. A convenient theoretical description of its coupling to radical ion processes in magnetic field was provided in the framework of spin correlation tensor approach [60, 61]. Since then DEE reaction has been incorporated into description of most experiments in spin chemistry, such as Chemically Induced Dynamic Nuclear Polarization [62], Stimulated [63] and Dynamic [64] Nuclear Polarization, as well as already mentioned OD ESR [20] and MARY Spectroscopy [22].

Theoretical treatment of the DEE influence on spin dynamics of radical ions is usually based on the non-correlated frequency migration (NFM) approach, that is, on the concept of non-correlated jumps over the HyperFine Structure (HFS) of the radical ion, with exponential distribution over mean residence time τ:

$$dW(\tau) = \frac{1}{\tau_0}\exp\left(-\frac{\tau}{\tau_0}\right).$$

Typically, for diffusion-controlled DEE reaction the frequency of the jumps is identified with the frequency of diffusion encounters of $A^{+/-}$ and A in liquid phase:

$$\frac{1}{\tau_0} = C_A k_D, \quad k_D = 4\pi RD,$$

where C_A is the concentration of parent molecules A, k_D is the diffusion-controlled rate of jumps over the HFS spectrum, and R and D are the reaction radius and the mutual diffusion coefficient for the two reagents, respectively. Just as in conventional CW ESR, in MARY spectra DEE reaction in the limit of slow exchange leads to additional line broadening of $1/\tau_0$ [22], which provides a means of measuring DEE rate constants from the plots of line width as a function of concentration.

However, as has been pointed out in theoretical work [33, 34], the conventional approach meets certain difficulties. First, k_D is the rate constant of diffusion-controlled *irreversible* reaction represented as a sink, a black sphere of radius R, while the DEE reaction is obviously reversible and the rates of forward and backward processes are equal to each other. Intuitively it can be understood that in the limit of diffusion control, i.e. infinitely efficient reaction, the probability of passing the spin and charge from the radical ion to a neutral molecule as a result of diffusion encounter is equal to the probability of retaining them on the original radical ion, and thus k_D should be halved. A more general expression for τ_0 is given by [33, 34]:

$$\tau_0 = \frac{2k + k_D}{k k_D C} = \frac{k + (k_D/2)}{k(k_D/2)C},$$

where k is the kinetic rate constant. This result can also be exactly reproduced by a simple collision complex approach [65].

Furthermore, it is well-known that the diffusion encounter of two particles is not instantaneous and consists of a large number of collisions (re-contacts). As a consequence, during the encounter electron repeatedly jumps between the two different hyperfine states, and HFC of the electron with the nuclei is strongly modulated. These effects will become important if effective HFC constant a_{eff} of the radical ion is large enough as compared to the inverse duration of the encounter τ_d, and a new dimensionless parameter should be introduced into theory:

$$\xi = a_{\text{eff}}\tau_d, \quad \tau_d = \frac{R^2}{D}.$$

As a rigorous treatment within the framework of encounter theory (ET) shows [33], for $\xi \ll 1$ the conventional non-correlated frequency migration over

the spectrum takes place, but the rate constant of jumps should still be replaced by $k_D/2$ in the diffusion-controlled limit. Keeping this in mind, we shall call NFM approach the limiting result of the ET for $\xi \ll 1$.

For larger values of ξ the rate of transverse electron spin magnetization transfer between two spectral components depends on their frequencies, and the frequency migration becomes correlated. Here the change in electron spin precession phase in external magnetic and nuclear fields during the encounter can no longer be neglected. HFC between electron and nuclear spins is modulated due to repeated random electron jumps from one nuclear structure to another during re-contacts. Such a random HFC modulation results in additional electron spin dephasing and requires refinement of the description beyond the NFM theory. For $\xi \gg 1$ this modulation is so strong that the encounters irreversibly dephase the electron spins at a rate $C_A k_D$ [33], curiously enough cancelling the 'reversibility factor' of $1/2$ in the effective rate constant.

While at high magnetic field the projections of spins on the Z axis (direction of the magnetic field B_0) are conserved and only the precession frequency of the electronic spin is modulated during the encounter, at low fields relevant for MARY studies the situation is qualitatively different. Electron and nuclear spins undergo flip–flop transitions, and their projections on the Z axis are no longer conserved. The flips of the electron spins are modulated by switching of the nuclear spin state of radical ion in the course of DEE reaction. As a consequence, electron spin projections may change during the encounter if a_{eff} is large enough. Rigorous ET treatment of the DEE reaction at arbitrary magnetic fields taking into account diffusional motion of reactants was performed recently [34] with particular attention to special cases of systems with one magnetic nucleus and semiclassical [60] systems. The result is also additional electron dephasing, albeit the situation is more complicated here and depends on the HFS of the system, restoring to the high field limit of 2 for a semiclassical system.

From experimental perspective this means that, other factors being equal, the rate constant of broadening caused by the DEE reaction can change by a factor of as much as two, depending on the complexity of the HFS of the system and on the applied external magnetic field, as effective hyperfine couplings in the system are increased. Most radical ions in common alkane solutions correspond to the limit of systems with weak hyperfine couplings, $\xi \ll 1$. However, simple estimates show that for radical anion of hexafluorobenzene in dodecane solution at room temperature ξ already approaches 1, and a noticeable deviation of the apparent

rate constant from the NFM limit can in principle be expected. This effect for HFB RA was treated theoretically in the limit of high external field [33], but these predictions still wait to be verified experimentally. In this work we turned to low field (MARY) studies, comparing several radical anions with (presumably) similar molecular carriers but with hyperfine couplings covering the situations of weak to moderate couplings in terms of this effect.

Figure 3 summarizes the representative results of these studies, giving selections of three spectra for increasing concentrations of acceptors for three out of six fluorobenzenes studied in the field range $+/-5\,\mathrm{mT}$ and comparing the situations of weak (*p*-difluorobenzene) and moderate (penta- and hexafluorobenzenes) couplings in the radical anion. $5 \times 10^{-2}\,\mathrm{M}$ benzene-d_6 was added to solutions of di- and hexafluorobenzene, and $10^{-3}\,\mathrm{M}$ toluene-d_8 to the solutions of pentafluorobenzene as fluorescing hole acceptors. The concentration of fluorobenzenes in solutions was varied from 5×10^{-4} to $5 \times 10^{-1}\,\mathrm{M}$. Spectra for other concentrations are very similar and do not add to the understanding, and were thus omitted to help keep the figure comprehensible. The set of spectra for tetrafluorobenzene is also very similar and is not presented, but the results of its simulation are (*vide infra*) also included in the width *vs.* concentration graph. The concentration transformations of spectra for the two trifluorobenzenes could be sensibly taken only using *p*-terphenyl as hole acceptor and luminophore because of the very low yield of recombination fluorescence, but such spectra, although nice looking and good for qualitative consideration, contain artefacts and cannot be adequately modelled (see the section on 1,3,5-trifluorobenzene later on).

The spectra and their transformations with concentration are rather typical for MARY. Difluorobenzene produces the spectra consisting of the broad wings of conventional MFE with the superimposed zero field MARY line in the opposite phase. Penta- and hexafluorobenzene produce only MARY lines, as the couplings in their radical anions are so large that the wings of the MFE become too broad and practically do not show up in a modulation experiment. The spectra become progressively broader as the concentration of acceptor is increased due to gradual acceleration of the DEE processes, and we wish to extract the rates of DEE reaction from their simulation.

The results of simulation for each presented spectrum are shown with smooth lines. The simulations were performed in the simplest possible model: exponential kinetics of recombination, equivalent magnetic nuclei, and DEE reaction described in the formalism of spin correlation tensors [22]. Radical ions with
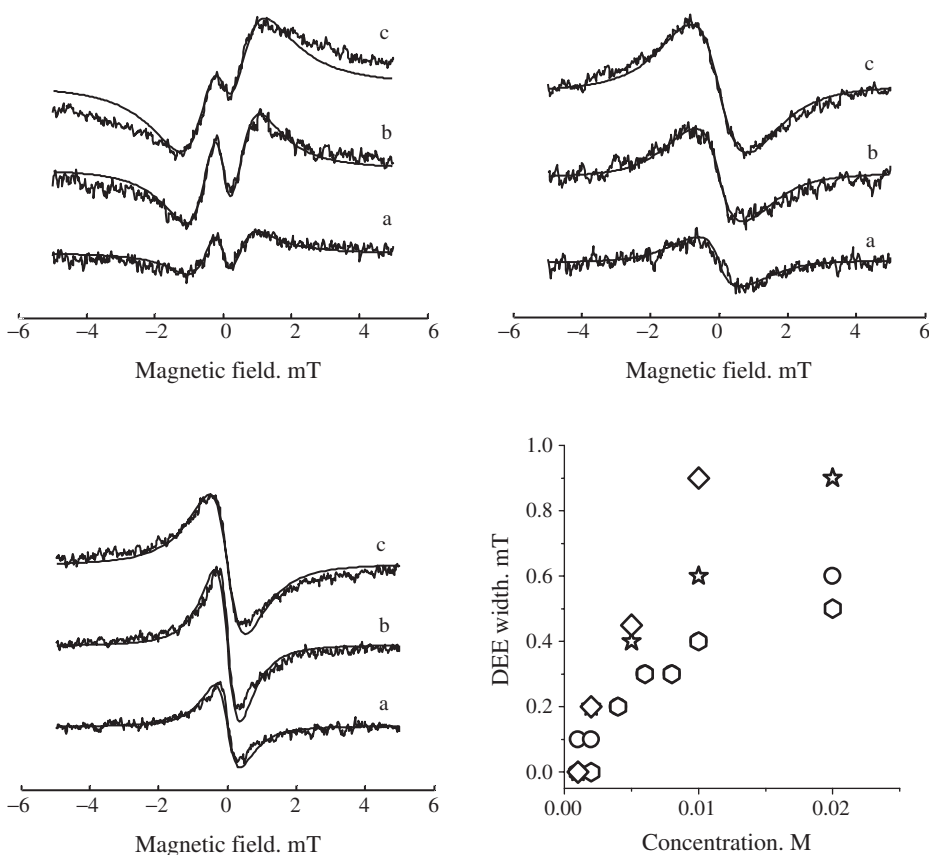
Figure 3. Typical concentrational transformations of MARY spectra for three fluorobenzenes, in dodecane solutions at room temperature. The concentrations for each panel are a – 5×10^{-4} M, b – 2×10^{-3} M, c – 1×10^{-2} M. Smooth lines – results of simulation. Top left panel: $C_6H_4F_2$, 5×10^{-2} M benzene-d_6 added as hole acceptor; modulation amplitude 0.25 mT; model for simulation: $C_6H_4F_2^{\bullet -}$ – 6×0.455 mT, $a_{\text{eff}} = 0.79$ mT, second partner – 6×0.05 mT, $a_{\text{eff}} = 0.085$ mT (DEE-narrowed benzene-d_6); simulation yielded $(1/\tau_R, 1/\tau_0) = (5, 0)$, $(5, 1)$, $(5, 4)$ for spectra a, b, c, respectively. Top right panel: C_6HF_5, 10^{-3} M toluene-d_8 added as hole acceptor; modulation amplitude 0.5 mT; model for simulation: $C_6HF_5^{\cdot -}$ – 12×9.25 mT, $a_{\text{eff}} = 22.6$ mT, second partner – 8×0.375 mT, $a_{\text{eff}} = 0.75$ mT (toluene-d_8); simulation yielded $(1/\tau_R, 1/\tau_0) = (5, 0)$, $(5, 1)$, $(5, 2)$ for spectra a, b, c, respectively. Lower left panel: C_6F_6, $5 \cdot 10^{-2}$ M benzene-d_6 added as hole acceptor; modulation amplitude 0.25 mT; model for simulation: $C_6F_6^{\cdot -}$ – 6×13.36 mT, $a_{\text{eff}} = 23.1$ mT, second partner – 6×0.05 mT, $a_{\text{eff}} = 0.085$ mT (DEE-narrowed benzene-d_6); simulation yielded $(1/\tau_R, 1/\tau_0) = (5, 0)$, $(5, 1)$, $(5, 4)$ for spectra a, b, c, respectively. Lower right panel: plot of $1/\tau_0$ *vs.* concentration for $C_6H_4F_2$ (circles), $C_6H_2F_4$ (diamonds), C_6HF_5 (stars), and C_6F_6 (hexagons).

non-equivalent nuclei were represented as sets of a large enough number of equivalent nuclei producing the same value of effective HFC constant, e.g. pentafluorobenzene RA was modelled as 12 spin 1/2 nuclei with HFC constant 9.25 mT producing the target value of $a_{\text{eff}} = 22.6$ mT. This emulates the semiclassical limit [60] for description of spin motion in the pair, and extensive checks have shown that after going beyond eight equivalent nuclei to build up the hyperfine spectrum while keeping a_{eff} constant the results of modeling stabilize. We have already used this approach [66], and the results for the description of MARY spectra in the vicinity of zero field are quite satisfactory. In fact, it is the spectra for pentafluorobenzene that were modelled best (see figure 3). This model can be solved

analytically and, provided the HFC constants are known, leaves only two parameters to vary, the characteristic recombination time of exponential kinetics τ_R and the mean residence time of DEE jumps τ_0. All spectra were modelled using the same value of τ_R with $1/\tau_R$ equal to 0.5 mT in the field units (1 ns^{-1} corresponds to 6.6 mT, and the product of time and field remains constant), rather normal for alkane solutions, which left only one parameter to vary among the set of 50+ spectra – just τ_0, which is extracted with relative accuracy of 15–20%.

Although the recombination kinetics is in fact not exponential, this leads only to transparent multiplicative corrections [23], and as we are interested here in comparing the rate constants for different systems

rather than obtaining their absolute values, this limitation is in this case not very serious. Furthermore, although much more elaborate simulations with explicit account taken of the HFS of each species and more realistic kinetics [67] could have been attempted, our recent experience with them shows [68] that they do not provide substantial improvement for modelling MARY spectra in the vicinity of zero field in a radiation chemical setting as opposed to photochemical studies [67], while the computational costs increase quite dramatically, let alone the necessity to explicitly code every possible subensemble of nuclei. The problem seems to be not in the description of spin motion or recombination, but rather in the necessity to take into account the full range of ion–molecular reactions from DEE to formation of clusters between the radical ion and one or more of its parent molecules as the concentration of acceptor is increased, the point, already raised [68–70] and not yet sorted out. The sign of these discrepancies can be seen in the top trace shown for difluorobenzene: being the system with the smallest hyperfine couplings, it is the first one to fall out of the region of slow DEE, which is accompanied by characteristic changes in the line shape.

The plot in the lower right part of figure 3 summarizes the results of these measurements. The plot is limited to concentrations up to 20 mM, where all studied systems can be considered to be in similar conditions of slow DEE reaction. As already noted, the spectra for higher concentrations still cannot be adequately modelled, and if such a fit is attempted, the extracted apparent DEE rates are too low. This fact was already noted in studies of HFB RA in squalane by OD ESR [20] and MARY [22], in which a bilinear plot of line width versus concentration was obtained. Since it is not yet clear whether this is an artefact of the simplistic model of ion-molecular processes or a real effect, we shall refrain from referring to the high concentration region in this work. The linear portion of the plot in the range of low concentration is sufficient to determine the rate constant of DEE reaction.

We are bound to conclude that we did not find the sought effect: the points for di-, penta-, and tetrafluorobenzene all lie close together, without clear separation for systems with weak and moderate hyperfine couplings. The points for tetrafluorobenzene go higher for reason that is not presently clear, and this behaviour was also reproduced in a different solvent (cyclohexane). The sought effect in our experimental conditions probably turned out to be so weak that we could not notice it with this technique, and the analysis tools that we used thus far are too crude for it and need to be refined, which will be a major undertaking. Still we

believe that the approach of comparing radical ions with similar properties but substantially varying hyperfine couplings that we followed in this study is valid and can be successfully used by other, more discriminating but also more demanding techniques. We in turn plan to return to these studies after improving the model for simulation of our spectra. Another experimental possibility is also increasing the solvent viscosity to shift the boundary between 'weak' and 'strong' hyperfine couplings towards lower values, where more systems are available for investigation.

3.2. *Exploiting equivalence of nuclei to detect RA of 1,3,5-trifluorobenzene*

As has already been mentioned, for systems with equivalent nuclei, additional satellite MARY lines can sometimes be observed that are characteristic of the single HFC constant (figure 2). The best conditions for this are created when equivalent nuclei with substantial HFC constant are collected in only one partner of the pair, and the counter-ion has negligible magnetic interactions and just completes the spin-correlated radical ion pair [58]. The conditions required to observe the satellites were formulated in the original theoretic work [57]. Their position is determined by the single HFC constant a_{hf}, the possible values of the total spin of the sub-ensembles of equivalent nuclei I, and its projection m, with additional limitations that $I > 1$ and $0 < m < I$:

$$H^* = \frac{a_{hf}I(I+1)}{2m}.$$

We shall use the notation $(I, m, H^*/a_{hf})$ for identifying the satellites. Up to now, the experimental satellites have been reported only for systems with integer values of I having even number of spin 1/2 magnetic nuclei, such as hydrogen or fluorine, and/or spin 1 nuclei, such as nitrogen [46, 58]. In this case the proportionality factors between the HFC constant and the positions of the first, strongest satellites become simple integers and the lines for different values of I coincide, which simplifies their experimental observation. For example, for the radical anion of hexafluorobenzene (figure 2) the following satellites are predicted: $(3, 1, 6)$, $(3, 2, 3)$, $(2, 1, 3)$, yielding the observed lines in the fields about 40 mT ($H^* = 3a_{hf}$) and about 80 mT ($H^* = 6a_{hf}$).

However, the simplest system that would produce a satellite is a set of three spin 1/2 nuclei yielding the line $(3/2, 1/2, 15/4)$. The scheme of energy levels illustrating this crossing is given in figure 4. The subset of energy levels shown corresponds to total nuclear spin of three nuclei $I = 3/2$ and total spin projection of the pair
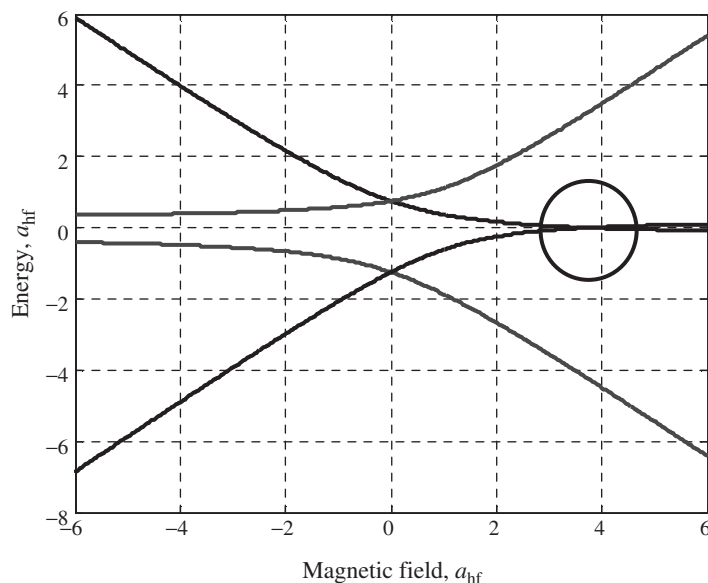
Figure 4. Subset of energy levels corresponding to total nuclear spin $I = 3/2$ and total spin projection of the radical pair (nuclear plus electronic) $M = -1/2$ for a pair with one partner containing three equivalent spin 1/2 nuclei and the other partner containing no magnetic nuclei. Magnetic field and energy are measured in units of HFC constant a_{hf}. Note the crossing in the field $15a_{hf}/4$.

(nuclear plus electronic) $M = -1/2$. Since I and M are the two conserved quantum numbers for this system in the applied magnetic field, its eigenstates are divided into subsets of non-interacting states with the corresponding subsets of energy levels (eigenvalues of the hamiltonian). The states within subset can be populated simultaneously upon formation of the pair and thus can interfere. If the corresponding levels cross, this crossing will lead to interference extremum on the field dependence – the satellite MARY line, so such crossings are referred to as 'active'. The figure shows that the levels cross in zero field, producing the zero field MARY line, and in the field $3.75a_{hf}$ ($15a_{hf}/4$). The subset with $I = 3/2$ and $M = 1/2$ produces the symmetric active crossing in the field $-3.75a_{hf}$, as the system is apparently symmetric with respect to change of direction of the applied field. Other subsets do not produce active crossings in finite nonzero fields, so the line $(3/2, 1/2, 15/4)$ is indeed the only expected satellite for such a system.

We now note that radical anion of 1,3,5-trifluoro-benzene (TFB) in isotropic non-viscous solution is likely to have three equivalent fluorine nuclei. Of course, there will also be three equivalent protons, but since HFC with fluorines in the already reported RA of polyfluorinated benzenes are typically rather large, we hope that they will also dominate in this case. So, the suggested model for RA of TFB is a set of three equivalent spin 1/2 nuclei, which are expected to produce a satellite line. The results of successful

experimental verification of this hypothesis are shown in figure 5.

The left panel shows MARY spectra from solutions of 10^{-3} M p-terphenyl-d_{14} (PTP) in dodecane (upper noisy trace), 10^{-2} M TFB and 10^{-3} M PTP in dodecane (lower noisy trace with shoulder), and simulation for three spin 1/2 nuclei with HFC constant 7.3 mT. It can be seen that the shoulder in the experimental trace is indeed reproduced by simulation, however, there is a strong background that is not present in the simulation and that qualitatively looks like the spectrum for the same solution but without TFB. This background apparently comes from the pairs PTP$^-$/dodecane$^+$. PTP was used in these experiments because of its good luminescing properties (quantum yield 0.96). Unfortunately, as most good luminophores, it is a fairly good acceptor of both negative and positive charge in alkane solutions, and pairs PTP$^-$/dodecane$^+$ are formed in abundance here contributing their own signal to the observed spectrum. As MARY spectra are generally not additive, it is not a good idea to simply subtract the background from the spectrum, and thus the spectra of TFB with PTP can only serve as an illustration, but it is a very stimulating illustration.

To obtain more unambiguous experimental data, we reverted to using benzene-d_6 (BZ, concentration 5×10^{-2} M) as luminophore instead of PTP, and the results are shown in the right-hand panel of figure 5. Benzene (and toluene) in these conditions is only capable of capturing solvent holes, so the only signal
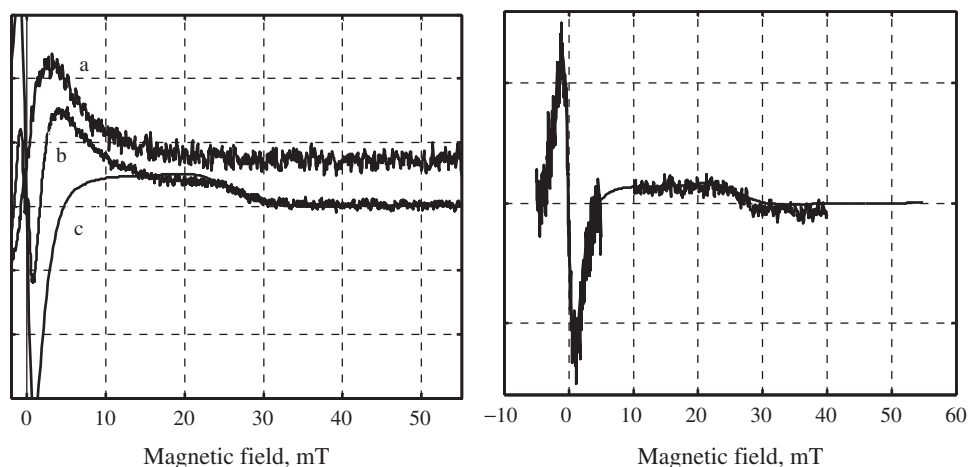
Figure 5. Left panel: MARY spectra for dodecane solutions of: a – 2×10^{-4} M *p*-terphenyl-d_{14}, modulation amplitude 0.5 mT; b – 1×10^{-3} M *p*-terphenyl-d_{14} and 1×10^{-2} M 1,3,5-$C_6H_3F_3$, modulation amplitude 0.5 mT; c – simulation for 3 nuclei with HFC constant 7.3 mT, $a_{\text{eff}} = 8.9$ mT, second partner – 8×0.045 mT, $a_{\text{eff}} = 0.09$ mT (*p*-terphenyl-d_{14}); simulation parameters $(1/\tau_R, 1/\tau_0) = (9, 4)$. Right panel: MARY spectra for dodecane solutions of 5×10^{-2} M benzene-d_6 and 1×10^{-2} M 1,3,5-$C_6H_3F_3$, experimental trace for zero field line: modulation amplitude 0.7 mT, experimental trace for satellite: modulation amplitude 2 mT, simulation for 3 nuclei with HFC constant 7.3 mT, $a_{\text{eff}} = 8.9$ mT, second partner – 6×0.05 mT, $a_{\text{eff}} = 0.085$ mT (DEE-narrowed benzene-d_6); simulation parameters $(1/\tau_R, 1/\tau_0) = (9, 4)$.

in this case comes from the pairs TFB^-/BZ^+. The intensity of the signal dropped drastically, and the spectrum was recorded as two separate portions, in the vicinity of zero field and in the vicinity of the expected satellite that we saw with PTP. Experimental conditions were optimized for each portion separately: the narrower but stronger line in zero field was recorded with modulation amplitude 0.7 mT after checking that this does not distort the line because of overmodulation, and the broader and weaker satellite line was taken with maximal available modulation amplitude of 2 mT. Each spectrum fragment is the result of averaging over 100 scans and took about 20 hours, totalling to 40 hours for the presented spectrum. This should be compared to about 2 hours for all other spectra shown in this work. The situation was similar for the other trifluorobenzene as well. This explains why DEE rates were not analysed for these two radical ions: getting spectra with acceptable signal to noise ratio for modelling that are free from artefacts from solvent holes turned out to be rather impractical.

As the figure shows, the simulation and experiment are in rather good agreement, so we conclude that we indeed have registered the spectrum from the radical anion of 1,3,5-trifluorobenzene having three equivalent fluorine nuclei with HFC constant of 7.2–7.5 mT and much smaller couplings with the three protons. We give the constant as a range of values, since the characteristic satellite line is rather broad and allows a certain margin for modelling.

Another important consideration is the time τ_R that produces the best fit to experimental spectrum.

As discussed in the preceding section on DEE reaction, we simulated the entire set of spectra for the four fluorobenzenes keeping $1/\tau_R$ constant and equal to 0.5 mT by varying the DEE residence time τ_0, and the extracted values of τ_0 are fairly consistent between the different species. For the concentration of 10^{-2} M used in the discussed experiment for TFB the resulting $1/\tau_0$ values fall in the range from 0.4 to 0.6 mT. However, the spectrum for TFB could not be modelled with the pair $(1/\tau_R, 1/\tau_0)$ of $(0.5, 0.4)$ to $(0.5, 0.6)$ mT. A good fit was produces after increasing the $1/\tau_R$ value to about 0.9 mT. This is illustrated in figure 6 showing the experimental zero field line from figure 5 simulated with parameters $(0.5, 0.4)$, and with parameters $(0.9, 0.4)$. The simulated curve of figure 5 was also produced with parameters $(0.9, 0.4)$. Although the actual numbers should be taken with some caution, the definite conclusion is that some additional process that destroys coherence in the radical pair is present for TFB as compared to other studied fluorobenzenes, which we model as a shortening exponential recombination time. Its characteristic time is about 20 ns at room temperature, corresponding (after correction for nonexponential kinetics of recombination [23]) to an additional width of 0.3–0.5 mT that must be introduced in the simulation.

4. Conclusions and outlook

In this work, we attempted to experimentally verify theoretical predictions about the connection between the apparent rate of the reaction of degenerate electron
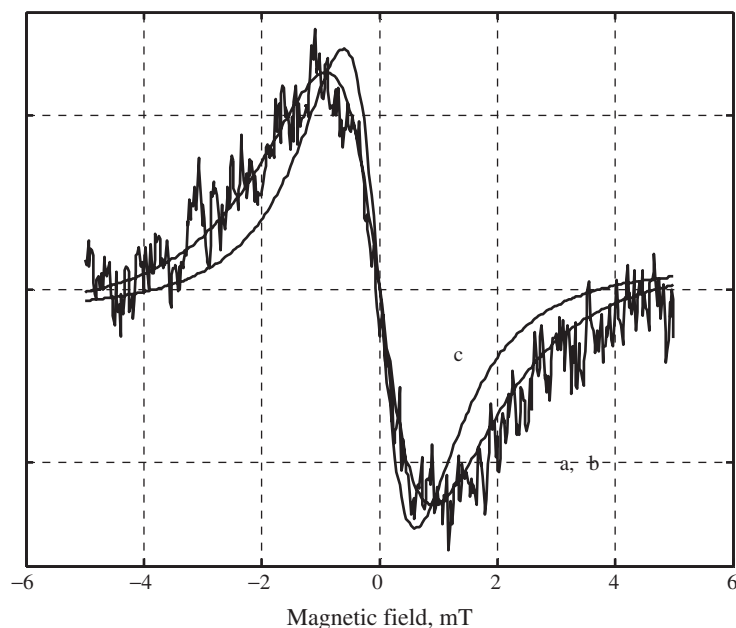
Figure 6. Zero field line for solution of 5×10^{-2} M benzene-d_6 and 1×10^{-2} M 1,3,5-$C_6H_3F_3$ in dodecane: a – experimental trace from figure 5; b – simulation for three nuclei with HFC constant 7.3 mT, $a_{\mathrm{eff}} = 8.9$ mT, second partner -6×0.05 mT, $a_{\mathrm{eff}} = 0.085$ mT; simulation parameters $(1/\tau_R, 1/\tau_0) = (9, 4)$, c – simulation for 3 nuclei with HFC constant 7.3 mT, $a_{\mathrm{eff}} = 8.9$ mT, second partner -6×0.05 mT, $a_{\mathrm{eff}} = 0.085$ mT; simulation parameters $(1/\tau_R, 1/\tau_0) = (5, 4)$.

exchange between a radical ion and its parent molecule, and the strength of hyperfine interactions in the radical ion. Using a set of polyfluorobenzene radical anions with similar properties of their molecular carrier but with effective couplings varying by a factor of 30, we could experimentally recreate in dodecane solution the situations of weak and moderate hyperfine couplings in the radical ions and followed them using MARY spectroscopy. Although conclusive experimental confirmation of the sought connection was not yet obtained, this is believed to be due to the relative weakness of the effect and the crudeness of current models used for interpretation of experimental data. The models need to be refined, and a more viscous solvent will probably help amplify the effect and expand the range of available test systems.

A positive finding was the detection of radical anion of 1,3,5-trifluorobenzene that as far as we know has thus far eluded experimental observation. In dodecane solution at room temperature this radical anion has three equivalent fluorine nuclei with hyperfine coupling constant 7.2–7.5 mT, the couplings with the three protons are much weaker. Furthermore, a rather short coherent lifetime of about 20 ns in weak magnetic fields was found for this radical anion, which probably explains its experimental obscurity. This result may be interesting for quantum chemists seeking understanding

of distorted molecular structures, and we hope it will help stimulate further effort in this direction.

Acknowledgements

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