THE hfi PARAMETERS AND STRUCTURE
OF RADICAL-ANIONS OF SUBSTITUTED TETRA- AND PENTAFLUOROBENZENES.
THEORY AND EXPERIMENT (OD ESR)

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Optically detected electron spin resonance (OD ESR) of radical pairs has been employed to take ESR spectra of short-lived radical-anions of substituted fluorobenzenes in liquid non-polar solutions at nearly room temperatures. The quantum-chemical hfi analysis has been taken into account possible manifestations of pseudo-Jahn–Teller effects. As shown by comparison with experiment, $C_6F_5OCH_3^-$, $p\text{-}H\text{-}C_6F_4OCH_3^-$ and $p\text{-}(CH_3)_2\text{-}C_6F_4^-$ are pseudo-π-radicals with non-planar distortions. A peculiar feature of these radicals is that their structure corresponds to the Jahn–Teller stabilization of excited Π^* states. The effect results from a stronger interaction of the Σ^* state with Π^* than with the ground Π state, because the SOMO space localizations coincide in the Σ^* and Π^* states.

1. Introduction

Recent experimental and theoretical investigations on hyperfine interactions (hfi) in radical-anions (RA) of polyfluorinated benzenes [1–7] have demonstrated some peculiarities of their electronic and spatial structure as compared to their unsubstituted analogues. The hfi constants in $C_6F_6^-$, $C_6F_5H^-$ and $1,2,4,5\text{-}F_4C_6H_2^-$ prove to be unexplainable in terms of their planar π and σ structure [1–5]. The whole scope of magnetic-resonance parameters can be fairly well described under the assumption that the fluorine atoms leave the planar benzene ring due to the pseudo-Jahn–Teller effect (the interaction between the ground Π and the lower excited Σ^* states of a planar RA) [6]. The character and the size of this deformation depend on the orbital symmetry and structure of an unpaired electron orbital in the Π and Σ^* state, as well as on the size of their energy splitting. An unpaired electron orbital in the ground state of deformed $C_6F_6^-$, $C_6F_5H^-$ and $1,2,4,5\text{-}C_6F_4H_2^-$ is a mixture of the π and σ orbitals of the planar structures, the former prevailing. This fact has

allowed these RAs to be termed pseudo-π radicals [6]. Amongst these there are also some fluorobenzonitrile RAs [7]. On the other hand, $C_6F_5X^-$ (X = Cl, Br, J) are known [8] to be planar σ radicals, with the unpaired electron chiefly on the σ^* orbital of the C–X bond. At the same time, the hfi data for ^{19}F in RAs of polyfluorinated nitrobenzenes [9] and benzophenones [10] do not contradict the assumption of their planar π-electronic structure. Thus, substituents other than fluorine in polyfluorobenzene RAs can essentially affect their electronic structure.

The present paper describes experimental and theoretical investigations on RAs of tetra- and pentafluorobenzenes with CH_3, OCH_3 and SPh groups as substituents.
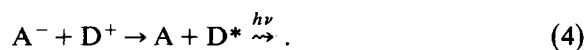
Until recently, the short lifetimes of fluorosubstituted RAs allowed one to detect their ESR spectra only in frozen matrices [1–5]. It has been shown, using $C_6F_6^-$ RAs, that the optically detected ESR (OD ESR) method is helpful in solving this problem for liquid solutions. The OD ESR technique has been employed in the present investigations. A characteristic feature of this

technique is that only the spectra from partners of spin-correlated radical-ion pairs are detected. The secondary uncharged radicals, that may result from either radical-ion decay or some other processes, cannot contribute to the OD ESR spectra [11].

A required radical-ion pair arises under hard irradiation of the solvent S with subsequent charge transfers to admixture molecules A and D

$$S \rightarrow S^+ + e^-, \tag{1}$$

$$A + e^- \rightarrow A^-, \tag{2}$$

$$D + S^+ \rightarrow D^+ + S. \tag{3}$$

Here A is an electron acceptor molecule, whose RA is of interest; D is a hole acceptor chosen so that the D^+ radical-cation spectrum overlaps that of RAs under study as little as possible. Besides, the D molecule must be fluorescent. In this case, as a D^+/A^- pair recombines, a portion of the Coulomb energy of radical-ion interaction is released as a photon

$$A^- + D^+ \rightarrow A + D^* \overset{h\nu}{\leadsto}. \tag{4}$$

The recombination fluorescence intensity depends on an external microwave field in a resonance manner [12], which allows detection of ESR spectra from recombining partners. In the present investigation we used p-terphenyl ($-h_{14}$ and $-d_{14}$) and anthracene-d_{10} as D, and squalane (2,6,10,15, 19,23-hexamethyltetracosane) as a solvent.

2. Experimental

Optically detected ESR spectra were taken with the arrangement described earlier [13] at microwave source of frequency 9.096 GHz and modulation amplitude of 5 G. The spectra were detected at various temperatures, room temperature included. The samples were cooled with a nitrogen gas flow somewhat below room temperature in order to increase the solvent viscosity and thereby the signal intensity [14]. The temperature was monitored with a thermocouple accurate to $\pm 2°C$. The ESR spectra were simulated on a Mera-60 minicomputer under the assumption of Lorentz hfs components.

We used polyfluoroaromatic compounds synthesized by the following techniques: pentafluoro- and hexafluorobenzenes [15], pentafluoro- and 2,3,5,6-tetrafluoroanisole [16], tetrafluoro-p-xylene [17], 1,2,4,5-tetrafluorobenzene [18], phenylthio-2,3,5,6-tetrafluorobenzene [19]. Physical characteristics of the above compounds coincided with those available in literature.

3. Experimental results

Figs. 1–7 show OD ESR spectra for radical-ion pairs in squalane solutions. The intensive central line in all the spectra belongs to anthracene (figs. 1 and 2) and to p-terphenyl (figs. 3–7) radical-cations. In most cases, the ESR spectra from radical-cations of the fluoro-compounds under study are not observed; most likely, because of a low-efficient hole transfer (3) for fluoro-compounds [20]. However, the spectra detected in irradiated C_6H_4HSPh solutions (fig. 7) show a signal with a shifted g factor – the low-field

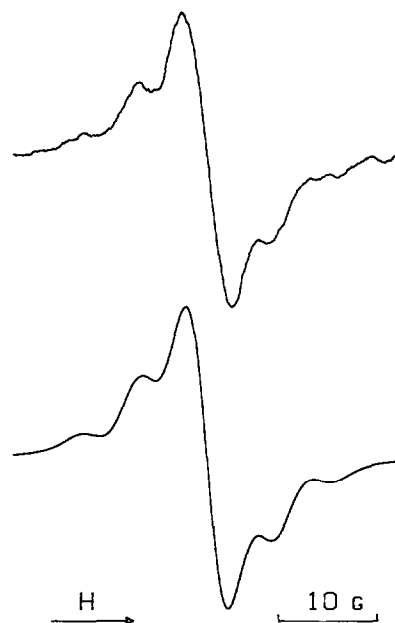Fig. 1. The first derivative of the OD ESR spectrum of liquid solution of 6.5×10^{-3} M difluorobenzene and 3.4×10^{-3} M anthracene-d_{10} in squalane under X-rays at 270 K. Top: experimental; bottom: simulated.
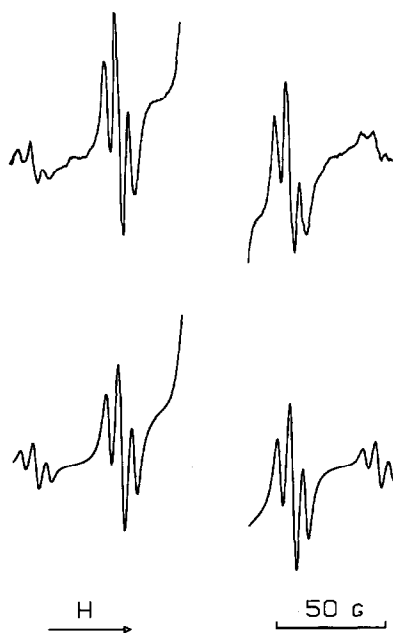
Fig. 2. The first derivative of the OD ESR spectrum from liquid solution of 7.5×10^{-3} M tetrafluorobenzene and 3.1×10^{-3} M anthracene-d_{10} in squalane under X-rays at 240 K. Top: experimental; bottom: simulated.
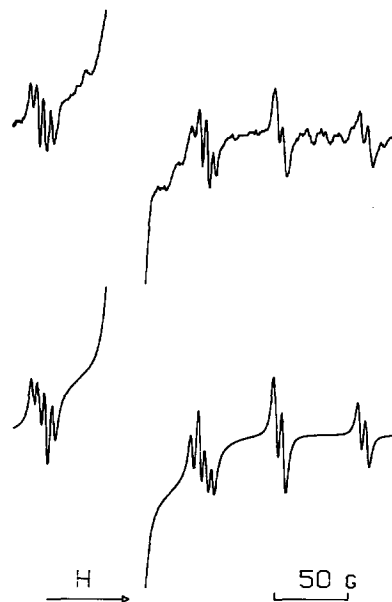

Fig. 4. The first derivative of the OD ESR spectrum from solution of 0.18 vol% tetrafluoranisole and 1.3×10^{-3} M p-terphenyl in squalane under X-rays at 287 K. Top: experimental; bottom: simulated.
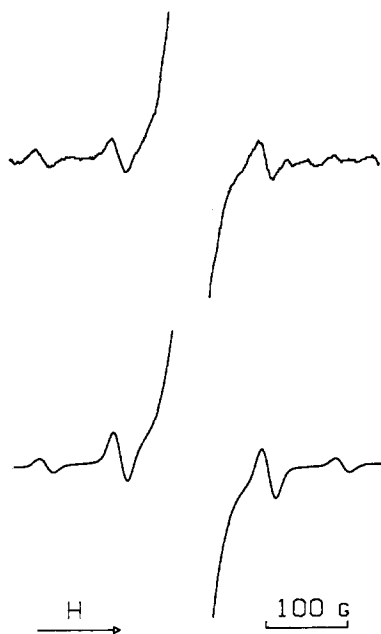

Fig. 3. The first derivative of the OD ESR spectrum from liquid solution of 3.4×10^{-3} M tetrafluoroparaxylene and 2.5×10^{-3} M p-terphenyl in squalane under X-rays at 260 K. Top: experimental; bottom: simulated.

Fig. 5. The first derivative of the OD ESR spectrum from solution of 0.2 vol% pentafluorobenzene and 1.5×10^{-3} M p-terphenyl in squalane under X-rays at 286 K. Top: experimental; bottom: simulated.
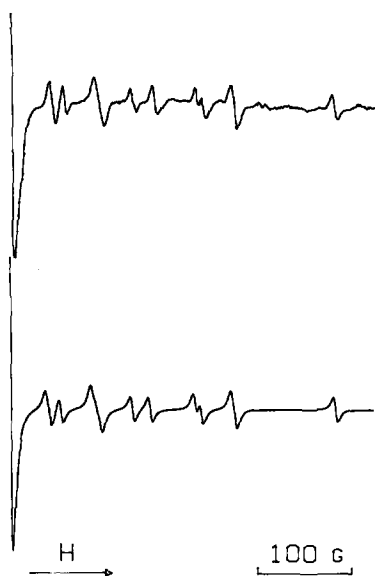
Fig. 6. The first derivative of the OD ESR spectrum from solution of 0.2 vol% pentafluoranisole and 1.4×10^{-3} M p-terphenyl in squalane under X-rays at 287 K. Top: experimental; bottom: simulated.
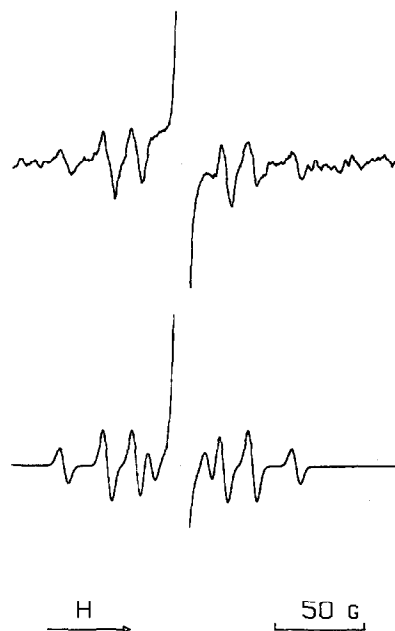

Fig. 7. The first derivative of the OD ESR spectrum from solution of 0.4 vol% phenylthiotetrafluorobenzene and 8×10^{-4} M p-terphenyl-d_{14} in squalane under X-rays at 265 K. Top: experimental; bottom: simulated.

shoulder of the central line in fig. 7. A signal with this g factor is typical for radical-cations of sulfur compounds [21] and seems to belong to either C_6F_4HSPh or sulfur-admixture cations. The other lines in the spectra are from RAs of the compounds under study.

Table 1 lists the hyperfine splitting constants

determined from the RA OD ESR spectra taken. Some of the ESR spectra have been detected earlier by a standard ESR method in frozen matrices [1,2]. The data obtained [1,2] are also listed in table 1. The slight difference in the constants in liquids and solids is not fundamental and

Table 1
Experimental hfi constants for substituted fluorobenzene

Radical-anions	Temp. (K)	Isotropic hfi constants (G)	Refs.
p-difluorobenzene	110	$a_F(1) = a_F(4) = 1.75$, $a_H(2) = a_H(3) = a_H(5) = a_H(6) = 5.3$	[2]
	270	$a_F(1) = a_F(4) = 1.34$, $a_H(2) = a_H(3) = a_H(5) = a_H(6) = 5.5$	present paper
1,3,5-trifluorobenzene		no spectrum is detected	present paper, [2]
1,2,4,5-tetrafluorobenzene	125	$a_F(2) = a_F(3) = a_F(5) = a_F(6) = 51.0$, $a_H(1) = a_H(4) = 7.8$	[2]
	240	$a_F(2) = a_F(3) = a_F(5) = a_F(6) = 41.0$, $a_H(1) = a_H(4) = 6.0$	present paper
2,3,5,6-tetrafluoroparaxylene	260	$a_F(2) = a_F(3) = a_F(5) = a_F(6) = 91.0$, $a_H(CH_3) < 5$	present paper
2,3,5,6-tetrafluoranisole	287	$a_F(2) = a_F(6) = 107.0$, $a_F(5) = a_F(3) = 57.0$, $a_H = 5.0$	present paper
pentafluorobenzene	223	$a_F(2) = a_F(6) = 101$, $a_F(3) = a_F(5) = 45.5$, $a_F(4) = 279.0$, $a_H = 4.0$	[2]
	286	$a_F(2) = a_F(6) = 107.0$, $a_F(5) = a_F(3) = 48.0$, $a_F(4) = 295.0$	present paper
pentafluoroanisole	287	$a_F(2) = a_F(6) = 108.0$, $a_F(3) = a_F(5) = 146.0$, $a_F(4) = 197.0$	present paper
phenythio-			
2,3,5,6-tetrafluorobenzene	263	$a_F(2) = a_F(3) = 40.6$, $a_F(5) = a_F(6) = 24.0$	present paper
hexafluorobenzene	218	$a_F(1) = a_F(2) = a_F(3) = a_F(4) = a_F(5) = a_F(6) = 137$	[2]
	293	$a_F(1) = a_F(2) = a_F(3) = a_F(4) = a_F(5) = a_F(6) = 133.6$	[22]

may be ascribed to different solvents and temperatures. The sharp rise in the splitting constants on fluorine nuclei observed when passing from difluorobenzene RAs to those involving more fluorine atoms results from distortions of the planar radical structure [6] and is discussed below in detail.

In view of the large splitting observed in the spectra for $C_6F_5H^-$, $C_6F_5OCH_3^-$ and $C_6F_4HOCH_3^-$ RAs, their constants were calculated taking account of the second-order perturbation theory. For some radicals the fluorine nuclei in ortho- or meta-positions of a benzene ring were equivalent either in pairs or completely with respect to their coupling with unpaired electrons. For other radicals deviations from equivalence occurred due to symmetry of substituents. In the case of nonequivalent fluorine nuclei, the splitting constants can be reliably identified only for para-fluorine featured by the highest constant $a_F(4)$. Some ways of identifying the other fluorine nuclei are discussed in the section 4 when comparing experiment and calculation. The experimental hfi con-
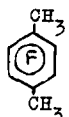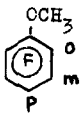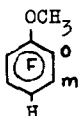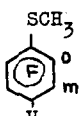
stants at ortho- and meta-fluorine nuclei, denoted in table 1 as $a_F(2)$, $a_F(6)$, $a_F(5)$, and $a_F(3)$, are given accurate to the ortho- and meta-state exchange.

4. Quantum-chemical calculations. Comparison with experiment

The experimental a_F values unambigously demonstrate all the newly generated polyfluorobenzene RAs, involving CH_3, OCH_3 and SPh, not to be π radicals. There are either distorted pseudo-π-radical structures, like $C_6F_6^-$, $C_6F_5H^-$ and $C_6F_4H_2^-$ [6], or planar σ radicals. To make the problem clear, the quantum-chemical hfi analysis was carried out by the approach developed [6]. The approach was to study the electronic structure and relative energies of planar π and σ RAs and also non-planar deformations caused by the interactions of these states within the pseudo-Jahn–Teller effect. The symmetry of possible deformations depends on the symmetry of the interacting

Table 2

Isotropic hfi constants a_F and a_H (G) and relative energies ΔE (eV) for π- and σ-electronic states of planar radical-anions of substituted fluorobenzenes [a]

Radical-anion	Parameter	Planar $^2A_2$	π-rad. $^2B_1$	Planar σ-rad. $^2A_1$	Exp.	Unpaired electron orbital in σ-state
CH₃/F/CH₃ (structure)	a_F	2.8	0.1	285.9	91.0	
	$a_H(CH_3)$	−3.3	12.7	−0.5	5	
	ΔE	0.49	0.00	2.84	–	
OCH₃ o m p (structure)	$a_F(o)$	3.9	−0.4	202.1	108.0	
	$a_F(m)$	4.3	0.4	152.0	146.0	
	$a_F(p)$	−2.6	5.8	597.7	197.0	
	ΔE	0.00	0.19	1.57	–	
OCH₃ o m H (structure)	$a_F(o)$	3.5	−0.3	171.8	107.0	
	$a_F(m)$	3.1	0.2	129.0	57.0	
	a_H	2.5	−8.0	13.7	5.0	
	ΔE	0.00	0.02	1.70	5.0	
SCH₃ o m H (structure)	$a_F(o)$	3.3	0.6	54.8	40.6	
	$a_F(m)$	2.1	0.2	44.4	24.0	
	a_H	2.3	−8.4	0.1	–	
	ΔE	1.16	0.89	0.00	–	

[a] Calculated hfi constants for o- and m-F atoms were averaged over two o- or m-positions.

Π and Σ states, its probability depending on their energy splitting and on the coincidence of the preferable localizations of an unpaired electron in these states (see also ref. [23]).

The radicals were calculated following the un-restricted Hartree–Fock method in the INDO ap-proximation using the SPIN-HAMILTONIAN program [24]. The SCH_3 group was considered as a model for the SPh substituent. We used fixed bond lengths: R_{CC}(aromat.) = 1.39 Å, R_{CH}(aro-mat.) = 1.08 Å, R_{C-CH_3} = 1.51 Å, $R_{CH}(CH_3)$ = 1.09 Å, R_{CF} = 1.40 Å, R_{C-OCH_3} = 1.36 Å, R_{O-CH_3} = 1.43 Å, R_{C-SCH_3} = 1.81 Å, R_{S-CH_3} = 1.81 Å. The atomic constants a_F^0 used for planar and distorted radicals were taken from ref. [23].

Table 2 lists calculated characteristics of π and σ states for the planar RAs investigated. As seen, the planar structures do not account ·for the hfi constants observed: for π radicals the calculated a_F values are more than one order of magnitude lower, whilst for σ radicals they are much higher than the experimental ones. The only exception is $C_6HF_4SCH_3^-$ of which the hfi constants calculated for the σ state approximate the experimental ones. Note that this is the only case of the σ state being the ground state. The unpaired electron orbital of $C_6F_4HSCH_3^-$ is strongly deformed compared to other RAs, and located chiefly on the σ C–S bond. The substantial weight of the $2s_{C1}$ AO in the σ SOMO (see ref. [23]) and the presence of the low-lying excited $^2B_1$ π state, with the unpaired electron located mainly on C_1, all point to the probability of non-planar deformation of the radi-cal primarily due to the C_1-SCH_3 bond deflec-tion. This deformation does result in a slight fall of energy and in a better fit of experimental to calculated hfi constants. For instance, at θ_{S-CH_3} = 20°, $a_F(2, 6)$ = 51.6 G, $a_F(3, 5)$ = 36.5 G, ΔE = −0.04 eV. Since for the distorted structure the contribution from the σ component to the SOMO remains basic, this radical should be classed with pseudo-σ-radicals.

In contrast to the SCH_3 group, the CH_3 and OCH_3 substituents in tetra- and pentafluoroben-zene RAs do not lead to π- and σ-term inversion, and therefore the Π state remains basic in the planar structure. This fact, together with the pres-ence of the low-lying excited Σ* state, points to
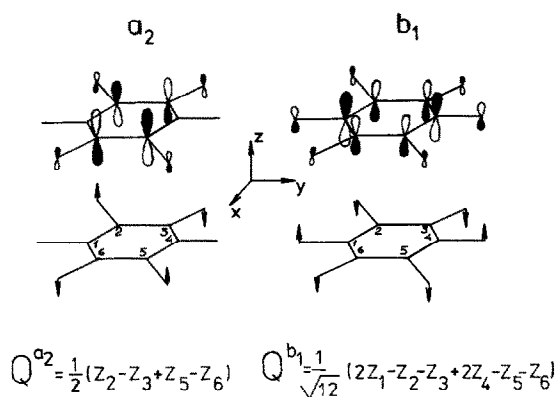

Fig. 8. Structure of degenerate π orbitals for an unpaired electron in a $C_6F_6^-$ radical-anion and the corresponding non-planar pseudo Jahn–Teller deformations Q_{a_2} and Q_{b_1}.
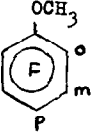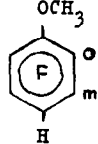
the pseudo-π-radical nature of these RAs, similar to hexa-, penta- tetrafluorobenzene RAs [6]. How-ever, there still remains the question on the type of non-planar deformation in each particular case.

In $C_6F_6^-$ the Π state of the planar D_{6h} structure is twice degenerate and has $^2E_{2u}$ symmetry, while the Σ state is totally symmetrical ($^2A_{1g}$). Here the degenerate non-planar deformation $Q_{e_{2u}}$ arises, as shown in fig. 8 (to describe the whole scope of hfi data, it is sufficient [6] to consider only non-planar displacements of F atoms, whose ratios in the Q_{b_1} and Q_{a_2} components are determined completely by symmetry considerations). In less symmetrical RAs the degeneracy is removed, and either Q_{b_1} or Q_{a_2} deformations can occur. At the same time, the ratios of F displacements are not controlled by the D_{6h} symmetry and thus can differ from those for $C_6F_6^-$. Nevertheless, the hfi constants in penta- and 1,2,4,5-tetrafluorobenzene RAs can be well reproduced even neglecting this factor, i.e., using one of the $C_6F_5^-$ Q_{2u} deformation components (Q_{b_1} for $C_6HF_5^-$, and Q_{a_2} for $C_6H_2F_4^-$ [6]). This allows one to hope to describe hfi effects in terms of standard Q_{b_1} and Q_{a_2} deformations also in the case of p-$(CH_3)_2$–$C_6F_4^-$, $C_6F_5OCH_3^-$ and p-H–$C_6F_4OCH_3^-$ RAs.

Taking into account the limitations of the INDO method as applied to small energy dif-ferences and also the possibility of crossing the terms under deformation [6], we considered defor-mations of both types for the above RAs. When

Table 3
Isotropic hfi constants a_F, a_H (G) for some angles θ^{a_2} characterizating non-planar Jahn–Teller deformations of A_2 and B_1 type [a]

Radical-anion	Deformation symmetry	Parameter [b]	θ^{a_2} (deg)					Exp.
			5	10	15	16	20	
CH3 ... F ... CH3	B_1	a_F	2.5	6.9	13.1			
		a_H	12.6	12.5	12.4			
		ΔE_{st}	0.020	0.066	0.143			
	A_2	a_F		63.5	86.7			91.0
		$a_H(CH_3)$		−3.3	−3.3			5
		ΔE_{st}	−0.015	−0.014	0.078			
OCH3 ... F ... o, m, p	B_1	$a_F(o)$	34.4	78.8	102.8	106.5		108.0
		$a_F(m)$	37.2	88.0	118.8	124.0		146.0
		$a_F(p)$	80.4	161.2	198.4	205.0		197.0
		$a_H(CH_3)$	0.1	0.15	0.2	0.2		
		ΔE_{st}	−0.056	−0.129	−0.099			
	A_2	$a_F(o)$		101.7	125.4			
		$a_F(m)$		100.3	125.8			
		$a_F(p)$		73.3	104.0			
		$a_H(CH_3)$		0.0	0.0			
		ΔE_{st}	−0.052	−0.118	−0.082			
OCH3 ... F ... o, m, H	B_1	$a_F(o)$	11.3	40.8	74.2		102.1	107.0
		$a_F(m)$	13.9	37.1	51.4		54.8	57.0
		a_H	−7.1	−5.4	−3.8		−2.8	5.0
		$a_H(CH_3)$	0.1	0.2	0.3		0.3	
		ΔE_{st}	−0.010	−0.023	−0.001		0.053	
	A_2	$a_F(o)$	40.7	86.6	111.6			
		$a_F(m)$	40.1	85.6	109.4			
		a_H	5.5	10.9	15.7			
		$a_H(CH_3)$	0.0	0.0	0.0			
		ΔE_{st}	−0.038	−0.078	−0.021			

[a] See footnote to table 2. [b] a values in gauss, ΔE_{st} in eV.

deciding between them, we took into account the fit of calculated to experimental hfi constants rather than the energy data. Table 3 lists structure dependences of the hfi constants and the energy of the radicals under study for the Q_{b_1} and Q_{a_2} deformations.

As can be seen from table 3, the Q_{a_2} deformation of a $p\text{-}(CH_3)_2\text{-}C_6F_4^-$ radical leads to a sharp increase in a_F, and at $\theta_F^{a_2} \approx 15°$ fairly well reproduces experimental values of both a_F and a_H. On the contrary, under the Q_{b_1} deformation a_F increases slowly, whilst a_H is too large compared with experiment. Note also the energy-unfavoured deflection of the CH_3 group from the ring plane.

The hfi constants for $C_6F_5OCH_3^-$ and $p\text{-}H\text{-}C_6F_4OCH_3^-$ RAs are satisfactorily described in terms of the Q_{b_1} deformation for $\theta_F^{a^z} \approx 16°$ and $20°$, respectively. The angle of deflection for OCH_3 in these RAs is assumed to equal that for the $p\text{-}F$ atom. Though leading to a slight decrease in energy, θ_{OCH_3} variations impair noticeably the agreement between calculated and experimental hfi constants.

Thus, the use of standard Q_{a_2} and Q_{b_1} deformation does allow one to qualitatively describe the hfi situation in the RAs under study. By our analysis, the radical $p\text{-}(CH_3)_2\text{-}C_6F_4^-$ shows the non-planar Q_{a_2} deformation, as would be expected by analogy with $C_6H_2F_4^-$ [6]. At the same time, tetra- and pentafluorobenzene RAs involving OCH_3 groups undergo the Q_{b_1} deformation. Since, by electronic effects, OCH_3 can be considered to

be a F analogue, the result obtained for p-H-$C_6F_4OCH_3^-$ agrees with the Q_{b_1} deformation obtained [6] for $C_6HF_5^-$.

An interesting fact following from the energy data of tables 2 and 3 is that for all the three pseudo-π radicals discussed the deformation type obtained from hfi analysis corresponds to the symmetry of the excited Π^*-state planar structure. Under deformation the energy of the excited state reduces (as in the case of $C_6H_2F_4^-$ [6]). The deformation corresponding to the ground state neither results in its stabilization (the case of $C_6H_2F_4^-$ and p-$(CH_3)_2$-$C_6F_4^-$), nor the degree of stabilization is lower in the ground than in the excited state (in $C_6F_5OCH_3^-$ and p-H-C_6F_4-OCH_3^-). However, in neither case do the ground and excited π terms cross. The abovementioned discrepancy between the energy data and hfi analysis seems to result from INDO errors in estimating small energy differences, namely:

(1) the method distorts the inductive-to-resonant effects ratio of substituents, which leads to an incorrect order of $^2B_1$ and $^2A_2$ terms and an incorrect ground state of the planar RA structure;

(2) the ground state of the planar structure is determined correctly; however, the method overestimates the energy splitting of the π terms (and, perhaps, underestimates the pseudo-Jahn–Teller stabilization of the excited π^* state).

As a result, it fails to reproduce the crossing of the ground and excited π terms under deformation.

The former error seems less probable, since the INDO method gives reliable hfi constants for low-fluorinated p-difluorobenzene [2,6] and m-fluoro- and m-difluorobenzonitryl RAs [7] having planar structures. In the case of π-type polyfluorinated radicals, the method gives a correct ground state of fluorobenzene radical-cations [2,25]. At the same time, the inductive-to-resonant effect ratio of substituents is different for vacant and occupied MOs. Therefore, in the general case one cannot say a priori which of the effects will prevail in a given RA. However, sometimes it is possible to predict the consequence of replacing one substituent by another. This is the case of $C_6F_6^-$ replaced by $C_6F_5OCH_3^-$. A fall in the inductive and a rise in the resonant effect with OCH_3 sub-
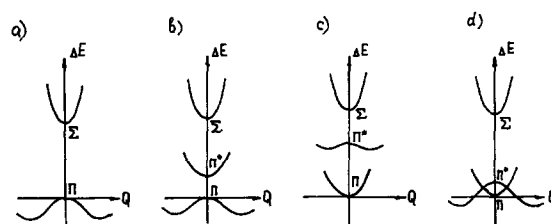

Fig. 9. Basis cases of the pseudo-Jahn–Teller stabilization in the π states of RAs of fluorinated benzene derivatives: stabilization of the ground π state with (a) and without (b) degeneration; stabilization of the excited π^* state with $\Delta E_{st}^{\Pi^*}$ < $\Delta E_{\Pi\Pi^*}$ (c) and $\Delta E_{st}^{\Pi^*}$ > $\Delta E_{\Pi\Pi^*}$ (d).

stituted for F produce the same result, that is push the b_1 component of e_{2u} π MO $C_6F_6^-$ upwards. Hence, the ground state of $C_6F_5OCH_3^-$ must be $^2A_2$, which coincides with the INDO analysis of the planar RA (see table 2). At the same time, such a high hfi constant on a p-F (197.0 G) can be explained only in terms of the Q_{b_1} deformation (see table 3). Consequently, it is possible to state that in $C_6F_5OCH_3^-$ the ground and excited π terms cross, and thus the pseudo-$^2B_1$ π state becomes the ground state of the distorted structure. Most likely, the π terms do cross in the case of p-$(CH_3)_2$-$C_6F_4^-$, p-H-$C_6F_4OCH_3^-$ and $C_6H_2F_4^-$ RAs [6].

Summing up the results of quantum-chemical hfi analysis of RAs of fluorobenzenes and their substituted derivatives obtained earlier [6,7] and in the present investigation, it is possible to draw the following general conclusion. To explain a nonplanar deformation of $C_6F_6^-$ RAs [6], it is sufficient to consider the interaction between two planar structure terms – the degenerate ground Π state and the low-lying excited, totally symmetrical, Σ^* state (see fig. 9a). The absence of degeneration in the less symmetrical substituted of the RAs leads to two Π states of close energy, Π and Π^*. The radical structure depends on two factors: (1) $\Delta E_{\Pi\Pi^*}$ splitting of these states, and (2) their stabilization, ΔE_{st}^{Π} and $\Delta E_{st}^{\Pi^*}$, due to the pseudo-Jahn–Teller effect. Depending on the unpaired electron MO structure in the Σ^* state, determined, in turn, by the number and the position of F atoms and other substituted (see table 2 and refs. [6,7]), the following situations are possi-

ble. (1) Pseudo–Jahn–Teller stabilization of the ground RA states (fig. 9b). This is the case with $C_6HF_5^-$ [6] and benzonitril RAs involving o- and/or p-F atoms [7]. Since the Σ^* state is fully symmetrical, the non-planar deformation symmetry coincides with that of the ground state ($\Gamma_Q = \Gamma_\Pi$). (2) Pseudo–Jahn–Teller stabilization of the excited Π^* state. The final result depends on the relationship between $E_{st}^{\Pi^*}$ and $\Delta E_{\Pi\Pi^*}$: (a) if $\Delta E_{st}^{\Pi^*} < \Delta E_{\Pi\Pi^*}$ (fig. 9c), the system remains planar ($C_6H_4F_2^-$ [6], and m-fluoro- and m-difluorobenzonitril RAs [7]); (b) if $\Delta E_{st}^{\Pi^*} > \Delta E_{\Pi\Pi^*}$ (fig. 9d), the system is distorted according to the excited Π^*-state symmetry ($\Gamma_Q = \Gamma_{\Pi^*}$), i.e. the deformation type, in fact, depends on the unpaired electron MO structure in the Σ^* states: the π-state corresponding to the greatest matrix element of π–σ interaction, $\langle \psi_\pi \,|\, \partial \hat{H} / \partial Q \,|\, \Psi_\sigma \rangle$ is preferred out of the two π states (this situation is observed in $C_6H_2F_4^-$ [6] and p-$(CH_3)_2$–$C_6F_4^-$ RAs). (3) The pseudo–Jahn–Teller stabilization occurs in the ground and in the excited π states. Depending on the relationship of ΔE_{st}^Π, $\Delta E_{st}^{\Pi^*}$ and $\Delta E_{\Pi\Pi^*}$, the result is similar to either case (1), or case (2b). For example, in $C_6F_5OCH_3^-$ RA the stabilization size is greater in the excited than in the ground state, $\Delta E_{st}^{\Pi^*} > E_{st}^\Pi$ (table 3). Since $\Delta E_{\Pi\Pi^*}$ is small, the terms cross: $\Gamma_Q = \Gamma_{\Pi^*}$. Most likely, this situation occurs also in p-H–$C_6F_4OCH_3^-$, although, by INDO calculations, in this case $\Delta E_{st}^\Pi > E_{st}^{\Pi^*}$. This discrepancy might result from the use of the standard Q_{a_2} and Q_{b_1} deformations. Though not optimal from the energy considerations, these deformations allow a qualitatively satisfactory description of hfi.

5. Conclusion

The experiments described have demonstrated potentialities of the radical-pair OD ESR method in structural studies on short-lived radical-ions. Our quantum-chemical analysis has shown 1,4-disubstituted perfluorobenzene RAs to be pseudo-π-electron radicals with non-planar deformations, their type and degree depending on the substituent. The only exception is p-H–C_6F_4–SPh$^-$ radical which is a pseudo-σ radical with the σ component prevailing in the SOMO.

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