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^{15}N, ^{17}O, ^{31}P AND ^{77}Se NUCLEAR MAGNETIC RESONANCE SPECTRA OF POLYFLUOROAROMATIC COMPOUNDS

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SUMMARY

The relationship between ^{15}N, ^{17}O, ^{31}P, ^{77}Se NMR spectral parameters and the electronic structure of a number of polyfluoroaromatic compounds has been discussed. Increase in nuclear shielding has been found in polyfluoroaromatic compounds investigated with respect to their hydrocarbon analogues. That effect has been discussed in terms of a decreased conjugation between the unshared electron pair of the heteroatom and the π-system of the polyfluorinated benzene ring. The influence of a polyfluoroaryl group on the character of bonds between different atoms in the functional group has been discussed on the basis of ^{17}O and ^{15}N (^{31}P, ^{13}C) NMR data for the aromatic compounds containing the M=O double bonds (M = C, N, P). Pentafluorophenyl group has been found to shield nitrogen and deshield oxygen as compared to the phenyl one. This has been observed by other spectral methods.

INTRODUCTION

One of the main trends in studies on polyfluoroaromatic compounds involves elucidation of the nature of interactions between polyfluorinated benzene rings and various substituents, as well as investigation of the effect of polyfluoroaryl rings on the properties of functional groups. In earlier works attention was paid above all to the high electron accepting ability

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of the polyfluorophenyl ring with respect to the functional groups containing heteroatoms or multiple bonds. According to numerous data [1], the inductive acceptor effect of the pentafluorophenyl group is stronger than that of the phenyl one. This is due to the fact that the greater electronegativity of ring fluorine atoms leads to a positive charge on the σ-framework of the polyfluoroaromatic ring. The π-system of the polyfluorophenyl ring is likely to be highly disturbed as compared to that of phenyl, owing to the effective π-interaction of fluorine p-electrons with the π-system of the benzene ring.

Recently the problem of influence of fluorine atoms on the electronic structure of polyfluorinated benzene systems has become the object of detailed investigation by modern physical methods. Special attention was paid to changes in the nature of the aromatic system itself under the influence of ring fluorine atoms. This problem was studied on the basis of the data of UV photoelectron [2], X-ray photoelectron [3,4] spectroscopy and quantum-chemical calculations [5]. These differencies lead to the substantial changes in the electronic structure of functional groups on the aromatic ring permitting to study the character of the aromatic π-system. Comparative studies of the electronic structure of sulphur [6,7] and phosphorus [8] in the phenyl and pentafluorophenyl derivatives by UV photoelectron and X-ray fluorescent specroscopy lead to some conclusions as to changes in the π-system of the benzene ring. Screening constants of N, O, P, Se vary within wide limits in NMR spectra, being considerably affected by small changes in the electronic environment. That makes possible application of NMR spectroscopy to study the influence of substituents on the electronic structure of the resonant nuclei. In many cases spectral parameters of organo-elemental compounds are correlated with the reactivities of the latter in reactions involving heteroatoms.

In this work we studied the effect of polyfluoroaryl substituents on ^{15}N, ^{17}O, ^{31}P and ^{77}Se NMR spectrostructural characteristics for the derivatives in which these atoms retain unshared electron pairs.

RESULTS AND DISCUSSION

The aim of the present work is to make a comparative analysis of NMR data on heavy nuclei for the aryl and polyfluoroaryl derivatives with functional groups containing heteroatoms (nitrogen,oxygen,phosphorus,selenium) attached directly to the aromatic ring and having non-bonding electron pairs or involved in multiple bonds.

NMR spectra of compounds containing heavy elements are generally recorded by means of internuclear double resonance technique [9] or by direct observation of nuclear resonance in Fourier Transform mode [10]. A number of heteroatoms are characterized by a low natural abundance of magnetic isotopes (^{77}Se - 7.5%, ^{17}O - 0.037%, ^{15}N - 0.37%),which considerably complicates the recording of spectra requiring the enrichment of organic compounds with these isotopes.In addition,greater spin-lattice relaxation times and quadrupole broadening of NMR peaks of ^{17}O (J = 5/2, ^{14}N (J = 3/2) suggest application of some special methods to increase the signal to noise ratio.

According to the theory of nuclear screening [11], in subgroup V and subgroup VI aromatic derivatives at the lowest state of oxidation,the magnetic shielding of nuclei in molecules consists of four atomic contributions : a local diamagnetic term,a paramagnetic term,neighbour anisotropy and interatomic currents and is controlled by the electronic effects of substituents bonded with heteroatoms.In particular, the increase in the electron-accepting ability of substituents leads to deshielding of the latter.Because of the greater electron-accepting ability of polyfluorinated aryl groups with respect to hydrocarbon ones, deshielding of heteroatom nuclei in polyfluoroaromatic compounds in comparison with their hydrocarbon analogues can be expected.However, ^{15}N, ^{17}O, ^{31}P and ^{77}Se NMR data obtained by us indicate that the observed dependence is complicated.

The ^{15}N signals of amino nitrogen in the aromatic amines are known to be shifted in a higher field than those of other nitrogen-containing aromatics.The chemical shift range of amines is rather small and does not exceed 30 p.p.m.for the compounds examined by now [12].According to our data,in ^{15}N NMR spectra of polyfluorinated anilines,the signals of nitrogen are shifted ~20 p.p.m. upfield with respect to their hydrocarbon analogues (Table 1).As in the case of hydrocarbon compounds,introduction of electron-accepting substituents in the fluorinated benzene ring leads to a downfield shift of ^{15}N signal of the amino group,the effect of ortho-substituents being stronger than that of substituents in para-position.Electron-donating substituents show the analogous effect of the same sign but the value of the shift is smaller (Table 1).

In ^{15}N NMR spectrum of pentafluorodimethylaniline,the ^{15}N signal is shifted upfield with respect to the same signal in the ^{15}N NMR spectrum of pentafluoroaniline.The analogous shift has been also observed earlier for hydrocarbon analogues [13],and was attributed (see [13]) to the increased electron density on nitrogen in dimethylaniline due to weakening of the π-character of the C-N bond ,reducing paramagnetic contribution to the chemical shift value.In the case of substituents at nitrogen capable of strong p_π-p_π-interaction with it,the latter may be expected to be considerably deshielded and the corresponding signal in ^{15}N NMR spectrum of N,N-dichloropolyfluoroanilines will be observed in a lower field with respect to that of pentafluoroaniline (cf.[14]).Indeed,the directions of signal shifts in NMR spectra are consistent with CNDO/2 calculated variations in charge values on nitrogen in investigated compounds. i.e. the calculated values of charges on nitrogen atoms in pentafluoroanilines and 4-amino-2,3,5,6-tetrafluoropyridine (this compound was labelled by ^{15}N isotope on amino-group) are -0.232 and -0.226 e respectively,whereas for thei N,N-dichloro derivatives,these values are -0.019 and -0.022 e respectively [15].

In Table 2 the phosphorus chemical shifts in phosphines of the type $C_6F_5PX_2$ are listed.In this case,the sensitivity of phosphorus screening to the electronic effects of the X substituents is higher than in the case of N,N-disubstituted anilines.The lowest extent of screening is observed for compounds containing the phosphorus atom bonded with some

TABLE 1

^{15}N chemical shift (p.p.m.vs.NH_3) of nitrogen-containing polyfluoroaromatic compounds

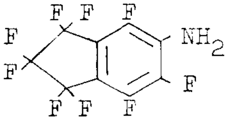
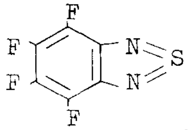
Compound	δ N	
	Polyfluorinated compound	Hydrocarbon analogue ([Lit.])
$4\text{-}N(C_2H_5)_2C_6F_4NH_2$	30.0	
$4\text{-}NH_2C_6F_4NH_2$	25.5	44.4 [16]
$4\text{-}CH_3OC_6F_4NH_2$	28.8	44.7 [16]
$4\text{-}CH_3C_6F_4NH_2$	43.2	45.2 [16]
$4\text{-}H\text{-}C_6F_4NH_2$	29.9	
$C_6F_5NH_2$	24.4	52 [16]
$4\text{-}CF_3C_6F_4NH_2$	44.4	
$4\text{-}CN\text{-}C_6F_4NH_2$	59.7	
$4\text{-}NO_2C_6F_4NH_2$	51	74.2 [16]
Py_FNH_2	48.7	63.2 [17]
$2\text{-}NO_2C_6F_4NH_2$	54	
$2\text{-}NH_2C_6F_4NH_2$	31.6	
$2\text{-}NO_2\text{-}5\text{-}CF_3C_6F_3NH_2$	52	
	41	
$2,6\text{-}F_2C_6H_3NH_2$	26.6	
$C_6F_5N(CH_3)_2$	16.7	44.6 [17]
$C_6F_5NCl_2$	104.2	
$4\text{-}CF_3C_6F_4NCl_2$	95.1	
Py_FNCl_2	100.2	
$C_6F_5NH_2$ HSO_3F	25.5	48.0 [17]
$4\text{-}H\text{-}C_6F_4NO_2$	350.4	
$C_6F_5NO_2$	350.4	370.3 [17]
$4\text{-}CF_3C_6F_4NO_2$	350.2	
$4\text{-}CH_3OC_6F_4NO_2$	354.8	369.9 [17]
Py_FNO_2	349.2	
$4\text{-}NO_2C_6F_4NO_2$	349.2	366.1 [17]
$2,6\text{-}F_2C_6H_3NO_2$	354.3	

TABLE 1 (cont.)

C_6F_5NO	893.3	913 [18]
C_6F_5NSO	292.3	319.4
$4\text{-}CF_3C_6F_4NSO$	292	
$2,6\text{-}F_2C_6H_3NSO$	293.8	
$C_6F_5N{=}S{=}NC_6F_5$	273	308.2
$C_6F_5NSF_2$	132.9	
$C_6F_5NSCl_2$	268.2	
$C_6F_5N{=}CHC_6F_5$	315.8	327.9
$C_6F_5N{=}CHC_6F_5\ HSO_3F$	165.7	
$4\text{-}CF_3C_6F_4N{=}CHC_6F_5$	322.7	
$4\text{-}CF_3C_6F_4N{=}CHC_6F_5\ HSO_3F$	165.7	
$Py_FN{=}CHC_6F_5$	321.6	
$C_6F_5N{=}PCl_3$	127.2	
$C_6F_5\underset{\downarrow \atop O}{\overset{1}{N}}{=}\overset{2}{N}C_6F_5$	305.9(1) 319.2(2)	335.7(1) 351.7(2)
$4\text{-}H\text{-}C_6F_4\underset{\downarrow \atop O}{\overset{1}{N}}{=}\overset{2}{N}C_6F_4\text{-}H\text{-}4$	315.9(1) 328(2)	
$\left[C_6F_5\overset{1}{N}{\equiv}\overset{2}{N}\right]^+$	213.2(1),333.5(2)	223.8(1),317(2)
$C_6F_5CONH_2$	113.2	105.4
$2,6\text{-}F_2C_6H_3CONH_2$	107.2	
$C_6F_5CONCl_2$	106.2	
$C_6F_5CONSCl_2$	314	
$C_6F_5CONSF_2$	181.2	
C_6F_5CN	279.3	258.7 [17]
$C_6F_5CN\ HSO_3F$	164.6	
trans-$C_6F_5N{=}NC_6F_5$	527.7	508 [17]
trans-$C_6F_5N{=}NC_6F_5\cdot HSO_3F$	386.5	360 [17]
trans-$4\text{-}CF_3C_6F_4N{=}NC_6F_4CF_3\text{-}4$	529.9	
trans-$4\text{-}CF_3C_6F_4N{=}NC_6F_4CF_3\text{-}4\cdot HSO_3F$	456.5	
trans-$Py_FN{=}NPy_F$	542.2	
	320.1	332.9 [19]

Py_F =

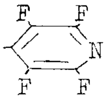


TABLE 2

^{31}P chemical shift (p.p.m.vs.85% H_3PO_4) of polyfluoroaromatic phosphines.

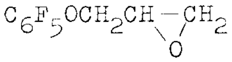
Compound	$q_{cov.}(P)$ in covalent volume [8]	δ^P Polyfluorinated compound	Hydrocarbon analogue (Lit.)
$C_6F_5PH_2$	0.02±0.02	-183.1	-122 [21]
$C_6F_5P(CH_3)_2$	0.06±0.02	-47.8	-46 [21]
$C_6F_5PF_2$	0.37±0.01	+193	+205 [21]
$C_6F_5PCl_2$	0.20±0.01	+110.9	+166 [21]
$C_6F_5P(OCH_3)_2$	0.41±0.01	+69.5	+159 [22]
$C_6F_5P(NCS)_2$	0.36±0.03	+60.8	
$C_6F_5P(CN)_2$	0.23±0.01	-121.3 [20]	
$C_6F_5P(C_6F_5)_2$	0.14±0.01	-77.9	-5.9 [22]
$C_6F_5P(C_6H_5)_2$		-26.3	
$(C_6F_5)_2PC_6H_5$		-42.5	
$C_6F_5P(C{\equiv}CC_6F_5)_2$		-29.4	-61.2
$(C_6F_5)_2PC{\equiv}CC_6F_5$	0.27±0.02	-74.7	
$P(C{\equiv}CC_6F_5)_3$		-90.0	
$C_6F_5P[N(C_2H_5)_2]_2$	0.25±0.01	+79.2	+98 [22]

electronegative atoms (e.g.,oxygen, nitrogen, halogens)The signals in ^{31}P NMR spectra of polyfluorinated aromatic phosphines lie in a higher field than those of their hydrocarbon analogues.The chemical shift difference of those two systems significantly depends on the nature of the substituent. Thus,the value of $\Delta\delta$ (^{31}P) between dimethylphenylphosphine and dimethyl(pentafluorophenyl)phosphine is 1.3 p.p.m.,whereas that between dimethylphenylphosphite and dimethyl(pentafluorophenyl)phosphite is 89.5 p.p.m.

The data presented in Table 3 show that in the case of polyfluorinated aryl derivatives of oxygen,the ^{17}O NMR signals are also observed in a higher field as compared with those of hydrocarbon analogues.In this case,there are considerable differences in oxygen chemical shifts in the whole series of compounds. Thus,the chemical shift difference between anisole and pentafluoroanisole is 39 p.p.m.The ^{17}O nuclear screening in

TABLE 3.

^{17}O chemical shift (p.p.m.vs. H_2O) of polyfluoroaromatic derivatives of oxygen.

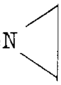
Compound	δO	
	Polyfluorinated compounds	Hydrocarbon analogue (Lit.)
$4\text{-}N(CH_3)_2C_6F_4OCH_3$	2	
$4\text{-}CH_3OC_6F_4OCH_3$	6	38 [23]
$4\text{-}CH_3C_6F_4OCH_3$	7	44 [23]
$4\text{-}NH_2C_6F_4OCH_3$	-12	36 [23]
$4\text{-}H\text{-}C_6F_4OCH_3$	13	48 [23]
$4\text{-}BrC_6F_4OCH_3$	14	51
$4\text{-}CH_3SC_6F_4OCH_3$	33	
$4\text{-}CF_3C_6F_4OCH_3$	28	54
$4\text{-}CN\text{-}C_6F_4OCH_3$	40	60 [23]
$4\text{-}NO_2C_6F_4OCH_3$	22	67
C_6F_5OH	33	
$C_6F_5OCH_3$	8	45 [23]
$C_6F_5OC(O)CH_3$	137	
$C_6F_5OCHF_2$	76.5	
$C_6F_5OCHCl_2$	109	
$C_6F_5OSi(CH_3)_3$	39	
$C_6F_5OCH_2CH{=}CH_2$	-4	
 $C_6F_5OCH_2CH(O)CH_2$	-25	
$4\text{-}CF_3C_6F_4OCH(CH_3)_2$	18	
$4\text{-}CF_3C_6F_4OCH_2CHF_2$	11	
$2\text{-}FC_6H_4OH$	52	
$2\text{-}FC_6H_4OCH_3$	29	

compounds of the type C_6F_5OR [R = H, CH_3, $COCH_3$, $CHCl_2$, CHF_2, $Si(CH_3)_3$, $CH_2CH{=}CH_2$] appeared to be rather sensitive to the nature of the R substituent at oxygen. With an increase in electronegativity of substituents at oxygen the ^{17}O NMR lines are shifted downfield. In compounds of the type $4\text{-}X\text{-}C_6F_4OCH_3$ (Table 3), replacement of fluorine in para-position by substituents without strong π-donor effect, leads, as a rule, to deshielding of oxygen which is also typical of a number of 4-substituted anisoles [23].

The data in Table 4 show that in ^{77}Se NMR spectra of polyfluoroaryl derivatives of bivalent selenium,the observed substituent effects are largely consistent with those in the case of oxygen : the ^{77}Se NMR signals are shifted upfield with respect to those of hydrocarbon analogues.And in this case, there are also considerable selenium chemical shift differences in the whole series of compounds.A chemical shift difference ($\Delta\delta$ (^{77}Se)) between selenophenol and pentafluoroselenophenol is 168 p.p.m.,that between selenoanisole and pentafluoroselenoanisole is 104.3 p.p.m.In compounds of the type C_6F_5SeR [R = H,

TABLE 4

^{77}Se chemical shift (p.p.m.vs.$(CH_3)_2Se$) of polyfluoroaromatic derivatives of selenium

Compound	δ Se	
	Polyfluorinated compounds	Hydrocarbon analogue (Lit.)
C_6F_5SeH	-16	152 [24]
$C_6F_5SeCH_3$	97.7	202 [24]
$C_6F_5SeC_6F_5$	110	402 [24]
$C_6F_5SeC_6H_5$	265	
$C_6F_5SeSeC_6F_5$	368	460 [24]
C_6F_5SeCl	812	
$C_6F_5SeN(C_2H_5)_2$	634	
C_6F_5SeN 	377.5	
$4\text{-}CH_3OC_6F_4SeCH_3$	88	
$4\text{-}CF_3C_6F_4SeCH_3$	145	
$(4\text{-}CF_3C_6F_4Se)_2$	370	
$(4\text{-}CF_3C_6F_4)_2Se$	179	
CF_3SeCF_3	361.7 [28]	
$CF_3SeSeCF_3$	528	281 [28]
$(CF_3)_2CFSeCF(CF_3)_2$	517	432 [28]

CH_3, C_6H_5, C_6F_5, C_6F_5Se, Cl, $N(C_2H_5)_2$, N◁], ^{77}Se nuclear screening has also proved to be rather sensitive to the nature of the R substituent at selenium.Similarly to the case of hydrocarbon analogues [24-26],with increased electronegativity of substituents at selenium,the ^{77}Se NMR signals are shifted downfield.The ^{77}Se nuclei are deshielded in decafluorodiphenyldiselenide relative to those in decafluorodiphenylselenide more than in hydrocarbon analogues ($\Delta\delta(^{77}Se)$ = 258 p.p.m.and 58 p.p.m.,respectively).The data in Table 4 show that the influence of the nature of a substituent introduced in the para-position of the aromatic ring on selenium screening is similar to that observed earlier for 4-substituted selenoanisoles [27].

The lowest extent of screening of ^{77}Se was observed in compounds where it is bonded to some electronegative atoms (e.g.,chlorine,nitrogen) (Table 4).Comparison with screening of ^{77}Se in perfluoroalkyl substituted compounds reveals an important role of the π-system of the aryl substituent in screening of ^{77}Se. The trifluoromethyl group that shows a strong inductive effect deshields selenium,whereas the pentafluorophenyl group shields it.In case of the phenyl substituent where the inductive effect is smaller than that of CF_3 and C_6F_5-groups, deshielding will take place only in case of a strong mesomeric effect.

This may indicate influence of other factors on screening of N, O, P, Se due to the presence of fluorine at positions 2 and 6 of the benzene ring.This influence is just the opposite to that which could be expected from the point of view of electronegativity of substituents.

The less effectiveness of the conjugation of lone electron pair with aromatic π-system in the case of polyfluoroaromatic compounds also must be taken into account as a possible reason of the unusual screening of the heteroatoms in the latter. Thus,the ^{31}P resonance of tricoordinate phosphorus compounds is mainly determined by the state of hybridization of the unshared pair of electrons on the central atom.Thus,comparison of the values of the first and the third ionization potential difference Δ_{13} for pentafluoroaniline (2.59 eV),pentafluorophenol (2.50 eV) and pentafluoroanisole (1.55 eV) with those for nonfluorinated derivatives (2.76, 3.0, 2.6 and

1.8 eV, respectively) shows a decrease of that value, indicating a reduced conjugation of unshared electron pairs of heteroatoms with the π-system of the benzene ring. Increased electronegativity of substituents in the aromatic ring must lead to a downfield shift of NMR signals of heavy nuclei, whereas reduced conjugation of unshared electron pair of heteroatom with the aromatic π-system leads to the opposite effect.

Reduced conjugation of the unshared electron pair of phosphorus with the π-system of polyfluoroaryl ring is confirmed by X-ray fluorescent spectral data (see [8,29]). In PKβ-spectrum of arylphosphines, increased intensity of transition is observed, indicating participation of 3p electrons of phosphorus in bond formation, on passing from nonfluorinated compounds to polyfluorinated ones. A similar dependence may be expected for the oxygen and selenium derivatives, too, as X-ray fluorescent spectral data for organic sulphur compounds with similar properties have shown reduced conjugation of sulphur 3p electrons with the π-system of the benzene ring involving fluorine [30]. An important role of conjugation effect in variation of screening constant is confirmed by the fact that α-nitrogen chemical shift value for 2,4,6-trinitrophenylazide is virtually the same as that for phenylazide, though the electron-accepting ability of the phenyl fragment of the former might be expected to lead to strong deshielding of nitrogen. Taking into account the absence of electric field effect of ortho-nitro groups, this may be explained by the fact that the nitrogen 2p electrons are withdrawn out of conjugation with the π-system of the benzene ring due to van der Waals interaction.

Another possible explanation of the observed direction of NMR signal shifts is based on van der Waals interactions and electric field effects of ortho-fluorine on nitrogen of amino groups. It should be noted that a similar analysis has been made in [28] for the case of CH_3-groups in ortho-positions relative to a substituent. In that work, a conclusion has been drawn about sterical interaction of unshared electron pair of nitrogen with CH_3-group in 2,6-disubstituted N-arylphosphoramides. Increased screening of nitrogen on passing from arylazide to polyfluorinated arylazides was attributed by the authors of [31] to perfluoro effect which is responsible for an increase in the energy term ($\triangle E^{-1}$).This term in approximation normally dominates the local paramagnetic screening term.The paramagnetic component of the magnetic screening of ^{31}P nuclei is described by the general equation of Jameson and Gutowsky

$$\sigma^{P} = -\frac{2\,e^{2}\hbar^{2}}{3\,m^{2}\,c^{2}} \cdot \frac{1}{\Delta E}\left(\left\langle \frac{1}{r^{3}} \right\rangle_{p} \cdot P + \left\langle \frac{1}{r^{3}} \right\rangle_{d} \cdot D\right)$$

Here $\triangle E$ represents the average value of the excitation energy of the electrons in the molecule,and $\langle 1/r^{3} \rangle$ p and $\langle 1/r^{3} \rangle$ d are also everage values,with r equal to the distance between the nucleus and a 3p or 3d electron.

In this case,the smaller is the $\triangle E$ value of excitation energy,the greater is deshielding.It was reported in [32] that the value of long-wave absorption maximum (the $n \rightarrow \pi$ transition) is smaller for polyfluoroaromatic compounds C_6F_5X (X = NH_2, OCH_3, OH, etc.) than for their hydrocarbon analogues.This suggests that the $\triangle E$ value is smaller for hydrocarbons than for polyfluoroaromatic compounds,which should lead to increased screening in the same direction.

Steric interaction of the unshared electron pair of nitrogen with ortho-fluorine does not seem to be the determining factor in the increase of screening,as for the more bulky atoms of chlorine deshielding of nitrogen (α) occurs,rather than the influence of ortho-fluorine (this has been shown in [31] on 4-azido-3,5-dichlorodifluoropyridine and 4-azido-tetrafluoropyridine).

The effect of the electric field of ortho-fluorine on the heteroatom of a substituent attached directly to a polyfluorinated benzene ring is much greater.Thus,it has been shown by us that the amino ^{15}N signal of 2,6-difluoroaniline is shifted upfield only 2.5 p.p.m. relative to that of pentafluoroaniline.

In the case of ortho-fluoroaniline,screening of nitrogen has been earlier noted,as opposed to aniline [33].But this cannot be the only explanation of the increased screening of nitrogen in pentafluoroaniline,as the increased accepting ability of the whole polyfluoroaryl substituent should bring about deshielding of nitrogen,as opposed to 2,6-difluoroaryl substituent.Accordingly,increase in screening of oxygen has been found by us for 2-fluoroanisole and 2-fluorophenol as opposed to anisole and phenol (Table 3).

The value of the positive charge on the heteroatom may also contribute to increase of screening,being considerably greater for polyfluoroaryl derivatives than for their hydrocarbon analogues (see, e.g., CNDO/2 calculations [3]).Positive charge values in covalent radius of phosphorus in arylphosphines, calculated from PKα -shifts in X-ray fluorescent spectra (see [8]),are higher for polyfluorinated derivatives than for their hydrocarbon analogues (Table 2).Screening of nitrogen in pentafluoroaniline and pentafluoroanilinium salt appears to be the same,unlike that in the pair : aniline-anilinium salt (Table 1).That fact may be explained by the greater value of positive charge on nitrogen in pentafluoroaniline than in its hydrocarbon analogue.This can affect diamagnetic contribution to screening constant.It is,however,generally accepted that the diamagnetic component remains nearly constant with a change in the chemical state of polyelectronic atoms.The growing positive charge contracts the p-orbitals of heteroatom.That is why the resonant atom should have a growing radial factor,which results in the reduced screening (this was observed for 4-substituted anilines and anisoles involving electron-accepting substituents (Tables 1 and 3).

Influence of the above factors on heteronuclear screening should also be expected for the derivatives where the heteroatom bonded directly to the benzene ring is involved into the multiple bond of the functional group.Indeed,the data in Table 1 indicate that the ^{15}N NMR signals for various nitrogen derivatives containing the N = X multiple bond are shifted upfield with respect to the signals of their hydrocarbon analogues.In this case,the direction of the ^{15}N NMR signal shift is consistent with changes in the charge on nitrogen in compounds investigated.As an example,there is a linear correlation dependence between the chemical shift of nitrogen bonded directly to pentafluorophenyl ring and CNDO/2 calculated charge densities (for compounds $C_6F_5NO_2$ and $C_6F_5NSF_2$ q_N 0.561 [3] and -0.082 [34],respectively).

$$\delta(^{15}N) = 378\ q_N + 126$$
$$r = 0.983,\ s = 23.6,\ n = 6$$

At the same time, ^{15}N signals in 2,6-difluoronitrobenzene and N-sulphinyl-2,6-difluoroaniline undergo a smaller upfield shift as compared to those of pentafluoro substituted derivatives, especially in the case of 2,6-difluoronitrobenzene ($\Delta\delta(^{15}N)$ 14 p.p.m.).This fact can be interpreted in terms of a reduced conjugation of NO_2 and NSO groups with the π-systems of 2,6-difluorobenzene rings but that effect is weaker in the case of pentafluorophenyl ones. The ^{17}O NMR spectral data of these compounds confirm the above supposition (Table 5).In the case of the other aromatic derivatives containing the N - O bonds. Deshielding of oxygen and screening of nitrogen are observed in polyfluorinated compounds with respect to hydrocarbon analogues. The case is similar with pentafluorophenyldiazonium cation,i.e. screening of nitrogen,attached directly to the ring and deshielding of β-nitrogen are observed.

For the compounds,containing the M = O bonds (M = C, N, S, P) deshielding of oxygen in polyfluorinated compounds was observed because of the weaker ability of pentafluorophenyl ring. Identical dependence of nitrogen screening on the nature of substituents in the benzene ring has been earlier demonstrated for the nitro derivatives [36] and acetophenones [35,37]. At the same time shielding of C, N, P is observed in ^{13}C, ^{15}N, ^{31}P NMR spectra (Tables 1,2,6, respectively) and the corresponding signals of these elements are shifted upfield. This fact can be explained by the less shift of the π-electron density of M = O bond to the oxygen atom as a result of the influence of pentafluorophenyl group.

Oxygen screening within the series of compounds containing the same fragment (CO, SO_2) depends essentially on the character of the substituent bonded to the latter. Increased electronegativity of the substituent leads to deshielding of oxygen (Table 5).Pentafluorobenzoic acid gives one signal in ^{17}O NMR spectrum, probably due the fast proton exchange.

TABLE 5

^{17}O chemical shift (p.p.m.vs.H_2O) of some oxygen-containing aromatic derivatives.

Compound	δ^{O} (hydrocarbon analogue [Lit.])	Line width, Hz	Temperature, °C
$C_6F_5NO_2$	627±4 (560±4)	400(390)	65
C_6F_5NSO	437±3 (410±3)	146(150)	80
C_6F_5NO	699±2 (620±2)	530(500)	65
$4-N(C_2H_5)_2C_6F_4NO_2$	644±4	520	55
$4-CH_3OC_6F_4NO_2$	633±4	340	90
$4-H-C_6F_4NO_2$	631±3	230	90
Py_FNO_2	632±3	460	55
$4-CF_3C_6F_4NSO$	441±3	146	80
$C_6F_5\underset{\overset{\downarrow}{O}}{N}=NC_6F_5$	549±6 (456±2)	1800(1200)	65
$4-CH_3C_6F_4\underset{\overset{\downarrow}{O}}{N}=NC_6F_4CH_3-4$	534±7	1800	60
$4-CF_3C_6F_4\underset{\overset{\downarrow}{O}}{N}=NC_6F_4CF_3-4$	578±15	2000	60
$C_6F_5SO_2Cl$	247±3 (221 [35])	177	80
$C_6F_5SO_2F$	195±3	73	80
$4-CF_3C_6F_4SO_2F$	194±3	200	80
$4-N(C_2H_5)_2C_6F_4SO_2F$	198±3	245	80
$C_6F_5SO_2CH_3$	180±6	292	80
$4-H-C_6F_4SO_2CH_3$	177±0.5	290	80
$C_6F_5SO_2NH_2$	183±3 (163±3)	208(146)	100
$C_6F_5SO_2C_6F_5$	191±3	250	100
$C_6F_5P(O)F_2$	120±2 J(P-O)=123±20	254	65
$C_6F_5P(\overset{*}{O})(OCH_3)_2$	112±3* J(P-O)=159	104(90)	80
	(98±3*) 37±10(35±10)		
$(C_6F_5)_3P=O$	70±1 J(P-O)=160±15	500(480)	
	(45±0.7 J(P-O)=183±15)		
C_6F_5COOH	271±0.5	410	60
$C_6F_5C(\overset{*}{O})OCH_3$	379±3* (341±3*)	250(271)	80
	144±3 (154±3)	210(210)	
$C_6F_5C(O)Cl$	552±3 (487±3)	190(167)	80
$C_6F_5C(O)CH_3$	615±4 (550±4)	250	80
$C_6F_5C(O)CF_3$	627±4	310	80
$C_6F_5C(O)H$	612±3 (562±3)	250	80

The nitro group is conjugated with the π-system of polyfluorobenzene ring and a change in the nature of the substituent in para-position of the benzene ring leads to a considerable change in nitrogen screening. In this case, the effect of the nature of a substituent in polyfluorinated and hydrocarbon series is the same. At the same time, substituent effect on ozygen screening is insignificant for para-substituted tetrafluorobenzenesulphofluorides. This is in agreement with the data in [39], where on the basis of S-O bond absorption frequency values for para-substituted fluoroanhydrides of benzenesulpho acids a conclusion has been made about insignificant degree of conjugation between the π-system of the benzene ring and the S-O bond.

As follows, from the data in Table 5 screening of oxygen is increased in the order $C > S > P$ with substituents at the element-oxygen bond being the same. This, probably, reflects the ability of the element-oxygen double bond to be conjugated with the π-system of the benzene ring, due to the fact that in ^{17}O NMR spectra, the dominating role is played by the mesomeric effect [23]. That conclusion is also confirmed by a connection between the oxygen chemical shift value of the M=O bond with noted non-symmetric stretching frequency (Table 7). It should be noted that earlier, an increase in C=O bond stretching frequency for para-substituted acetophenones was correlated with oxygen chemical shift in ^{17}O NMR spectrum [37]. In this case, an increase in C=O bond stretching frequency induced a downfield shift of the signal. Introduction of fluorine into the benzene ring leads to, an increase in the element-oxygen bond order, indicating a decreased effectivity of conjugation of these groups with the π-system of polyfluorobenzene ring.

It follows from the data in Table 1 that for the compounds with N=S bonds, nitrogen screening is increased with an increase in electronegativity of sulphur-containing fragments $S{=}O < S{=}N < SCl_2 < SF_2$. This tendency is consistent with an increase in delocalization of nitrogen unshared electron pair on S-X fragment, leading to the greater mesomeric transfer of aromatic. The π-bond order between nitrogen and carbon of the aromatic ring is decreased in the same sequence [19].

Comparison of ^{15}N chemical shifts for diarylthiodiimides shows increased nitrogen screening on sequential increase of number of fluorine atoms in the aromatic rings.In the case of polyfluorinated derivatives,an upfield shift of ^{15}N signal must be induced by weakening of the π-character of Ar-N bond. This results in a change in N=S bond order,as revealed by Raman spectral data.For decafluorodiphenylthiodiimide the N=S stretching frequencies are : symmetrical - 1202 and anti-symmetrical - 1450 cm^{-1},whereas for diphenylthiodiimide they are 980 and 1277 cm^{-1}, respectively [40].Increased N=S stretching frequency indicates increased force constant and hence increased order of these bonds in polyfluorinated compounds.A change in the interaction of sulphur and nitrogen under the influence of the aryl substituent was investigated by X-ray fluorescent spectroscopy [41].

In case of the multiple bond of nitrogen with other hetero-atoms,the order of the π-bond with an aromatic carbon will depend on electronegativity of the fragment bonded to nitrogen. The strong electronegative X elements of N-X fragment will induce nitrogen screening because of the increase of mesomeric π-electron density transfer from aromatic ring.Indeed, nitrogen chemical shifts for compounds containing groups =N=, $=\underset{O}{N}-$, =CH-, =S<, =P$\leqslant$ confirm that supposition (Table 1). In these compounds screening of nitrogen is increased with increased electronegativity of the fragment attached to nitrogen as well as the stretching frequency of the bond with nitrogen.

Table 1 lists the chemical shifts of some classes of compounds for which the opposite effect (the downfield shift of nitrogen signal due to introduction of fluorine to the aromatic ring) was observed in ^{15}N NMR spectrum.In the majority of these compounds nitrogen is not directly bonded to pentafluorophenyl ring.For the amide of pentafluorobenzoic acid,deshielding of nitrogen may be induced by a changed electronegativity of carbon of the carbonyl group (see Table 6),due to a stronger accepting effect of pentafluorophenyl ring as compared to that of the phenyl group.

When the lone electron pair of the nitrogen atom participating in the multiple bond is not conjugated with the π-system of

TABLE 6

^{13}C chemical shift (p.p.m.vs.$(CH_3)_4Si$) of the carbonyl group of polyfluoroaromatic compounds.

Compound	δ^{C}	
	Polyfluorinated compound	Hydrocarbon analogue [38]
$C_6F_5C(O)CH_3$	189.9	196.0
$C_6F_5C(O)H$	181.1	191.0
$C_6F_5C(O)Cl$	158.0	168.5
$C_6F_5C(O)OCH_3$	158.7	166.9
C_6F_5COOH	160.7	174.9
$C_6F_5C(O)N(C_2H_5)_2$	157.6	171.1

TABLE 7

^{17}O chemical shifts and stretching frequencies of the M=O bond of polyfluoroaromatic compounds containing double-bonded oxygen.

Compound	Chemical shift in p.p.m.from H_2O	Non-symmetric stretching frequency of M=O bond, $\nu_{M=O}$, cm^{-1}
$C_6F_5P(O)(CH_3)_2$	70	1193
$C_6F_5SO_2CH_3$	180	1410
$C_6F_5C(O)CH_3$	615	1720

the benzene ring,the chemical shift value must be affected by a change in the substituent inductive effect.Thus,in the case of azobenzenes,introduction of fluorine in the benzene ring induces a downfield shift of ^{15}N. The azo group,characterised by high covalency and maximal double bond character,lies in the plane of the benzene ring (trans-form of azobenzene),causing a reduction in p-π-conjugation of nitrogen nonbonding electron pair with the π-system of the benzene ring.Therefore,the major contribution to nitrogen screening constant is made by the value of electronegativity of the aryl substituent,with deshielding of nitrogen proceeding concurrently with its increase.Introduction of electron-accepting substituents stronger than fluorine (e.g., CF_3-group) in polyfluorinated benzene ring causes deshielding of nitrogen.

EXPERIMENTAL

The ^{15}N NMR spectra were recorded on a Bruker HX-90 spectrometer Fourier Transform at 9.12 MHz,with nearly saturated solutions in CH_2Cl_2 (40%).All measurements were carried out in 10 mm NMR tubes with a 5 mm NMR tube containing D_2O inserted therein at room temperature.For Fourier Transform and spectral optimization,the laboratory-type B-NC 12 minicomputer was used. Compounds were enriched with ^{15}N isotope (94-96%).Liquid NH_3 served as an external reference,because its signal lies in a higher field relative to the majority of the known diamagnetic substances.The spectrometer operation mode : scanning at 6024 Hz, pulse width - 20 μs (90° pulse angle - 30 μs),pulse period - 8 s. The ^{31}P NMR spectra were recorded on the same spectrometer at 36.43 MHz both in monoresonance mode and with spin-spin coupling to protons being inhibited.Stabilization of resonance conditions was fulfilled similarly to stabilization for ^{15}N . Spectrum recording conditions : pulse width 15 μs, pulse period - 3 s .The ^{31}P chemical shift (in p.p.m.) was calculated in comparison with 85% H_3PO_4.The ^{13}C NMR spectra were recorded on the same spectrometer at 22.63 MHz.The ^{13}C chemical shift (in p.p.m.) was calculated in comparison with tetramethylsilane ($\delta(^{13}C)$ scale).Spectrum recording conditions : pulse width - 10 μs (90° pulse angle - 15 μs),pulse period - 5 s,accumulations - 150 to 200.The ^{17}O NMR spectra were recorded on the Bruker CXP-300 spectrometer at 40.7 MHz at natural abundance of the ^{17}O isotope.The following conditions were employed : pulse width - 20 μs (90° pulse angle),pulse period - 30 μs, accumulations - 20,000 to 50,000.The ^{77}Se NMR spectra were recorded,at natural abundance of the ^{77}Se isotope,on the Bruker SXP-100-4 spectrometer at 17.18 MHz,using Fourier Transform,at pulse width 20 μs (90° pulse angle),with 10,000 to 20,000 accumulations.The chemical shifts are given relative to the signal of $(CH_3)_2Se$ as the external standard.For potimization of ^{77}Se NMR spectrum recording conditions,a relaxant, chromium acetylacetonate,was added to solutions.

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