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^{15}N AND ^{17}O NMR SPECTRA OF SOME NITROGEN- AND OXYGEN-CONTAINING POLYFLUOROAROMATIC COMPOUNDS

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SUMMARY

The effect of substitution of hydrogen by fluorine on the ^{15}N and ^{17}O NMR chemical shifts in N-sulphinylarylamines, azoxybenzenes, C,N-diarylnitrones and aromatic azomethines has been studied. Changes in nitrogen screening are controlled mainly by the radial factor $\langle r^{-3} \rangle_{2p(N)}$, which depends on the electron density on nitrogen, those in oxygen screening - by the two factors, the excitation energy ΔE^{-1} and the radial factor $\langle r^{-3} \rangle_{2p(O)}$, which may operate in the same or opposite directions. The ^{15}N and ^{17}O NMR spectra of the above compounds did not show any specific effects of perfluorination.

INTRODUCTION

Despite recent progress in the molecular orbital concept of the mechanism of the effect of fluorine in a polyfluoroaryl ring on the electronic structure of a heteroatom functional group bonded with it [1], the problem is still far from being solved. These studies require comprehensive investigation of the electronic structure of the molecules by a variety of independen methods giving altogether complete information. One of the most effective and widely used methods for studying the electronic and steric structure of molecules is multinuclear magnetic resonance. Experimental parameters, the chemical shift values

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and spin-spin coupling constants may be interpreted (and, in principle, calculated) by MO LCAO theory [2].

It has been found earlier that the ^{15}N[3-9], ^{17}O, ^{31}P and ^{77}Se[9] NMR signals of polyfluoroaromatic compounds, where the heteroatoms are directly bonded with the ring, are shifted upfield relative to the signals of their hydrocarbon analogues. For compounds containing two heteroatoms connected by a multiple bond, on passing from hydrocarbons to their polyfluorinated analogues the spectra showed increased screening of the heteroatom directly bonded with the aromatic group, and deshielding of the second heteroatom of the multiple bond, for example oxygen in $-N=O$, $\equiv P=O$ or $=C=O$ groups [9]. The present work, which is a continuation of these studies, deals with the effect produced by substitution of hydrogen by fluorine on the ^{15}N and ^{17}O NMR chemical shifts in N-sulphinylarylamines, azoxybenzenes, C,N-diarylnitrones and aromatic azomethines, and attempts to give a qualitative interpretation of the results in terms of the Pople-Karplus theory. In some cases we also used the data of various types of electron spectroscopy and semiempirical quantum chemical calculations.

The Pople-Karplus theory (see, for exsample [2,10,11]) represents the spatially averaged constant σ^A of nucleus A screening as an algebraic sum of three terms:

$$\sigma^A = \sigma^d_{AA} + \sigma^p_{AA} + \sum_{B \neq A} \sigma_{AB}$$

where σ^d_{AA} and σ^p_{AA} are local atomic diamagnetic and paramagnetic terms respectively, and σ_{AB} is the contribution of other atoms B to screening of atom A. The main term, that determines variation in screening of nucleus A in the series of the related compounds, is the paramagnetic term σ^p_{AA} having a large negative value, i.e. a deshielding term. The paramagnetic contributions to screening arise from mixing of the ground and excited states under the influence of the applied field. In mean energy approximation the local paramagnetic term for atom A of a second row element is given by the equation:

$$\sigma^p_{AA} = -\frac{2e^2\hbar^2}{3m^2c^2} \cdot \Delta E^{-1} \cdot \langle r^{-3} \rangle_{2p_A} \cdot \left[Q_{AA} + \sum_{B \neq A} Q_{AB} \right]$$

where ΔE is the mean energy of magnetically active electronic excitations, r is the distance from the nucleus to the 2p-electron (2p-AO radius); Q_{AA} and $\sum_{A \neq B} Q_{BA}$ are the terms obtained from the charge density-bond order matrix for the ground state of a molecule; the equation sums over all MO's and all atoms B bonded with atom A.

The radial factor $\langle r^{-3} \rangle_{2pA}$ depends on the electron density on atom A and increases with the positive charge on the atom. The one-atom term Q_{AA} varies insignificantly in a series of the related compounds, and the terms Q_{AB} are significant only when atoms A and B are coupled by a multiple bond. In general, factor $\sum Q = Q_{AA} + \sum_{B \neq A} Q_{AB}$ specifies the asymmetry of the charge density distribution of the valence electrons of atom A. The factor that often determines the σ^{p}_{AA} value is ΔE, the mean energy of virtual excitations accompanied by rotation of the electron around the nucleus, which occurs, for example, in the case of $\sigma \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. These three factors are not fully independent of each other. Thus ΔE tends to decrease with increased asymmetry of charge distribution, so the factors ΔE^{-1} and $\sum Q$ may operate in the same direction.

In general, the deshielding is larger the closer the electronic circulation is to the nucleus, the greater the asymmetry of the valence electrons and the easier the magnetically active electronic excitations.

RESULTS AND DISCUSSION

N-Sulphinylarylamines*

Examination of nitrogen and oxygen chemical shifts of these compounds (Table 1) shows that introduction of fluorine into on N-sulphinylaniline leads to increased shielding of nitrogen and deshielding of oxygen. In most of the compounds, with the exception of N-sulphinyl-2-fluoro- and N-sulphinyl-3-fluoro-anilines, the oxygen chemical shift correlates well with λ_{max}

* For the preliminary communication see [12].

of the long-wavelength band in the UV spectrum, which on passing from N-sulphinylaniline to its fluorinated analogues undergoes a bathochromic shift: $\delta_{^{17}O} = 0.77\ \lambda_{max} + 161$ where $r = 0.985$, $s = 2.36$, $n = 7$.

TABLE 1
^{15}N and ^{17}O NMR and UV data for N-sulphinylarylamines, ArNSO

Ar	$\delta_{^{15}N}$, ppm	$\delta_{^{17}O}$, ppm	λ_{max}, nm
C_6H_5	319.4	410	315
$2\text{-}FC_6H_4$	311.1	422	314
$3\text{-}FC_6H_4$	300.6	421	312
$4\text{-}FC_6H_4$	300.2	412	319
$2,4\text{-}F_2C_6H_3$	297.3	418	324
$2,5\text{-}F_2C_6H_3$		427	340
$2,6\text{-}F_2C_6H_3$	293.8	437	346
C_6F_5	292.3	437	346
$4\text{-}H_3COC_6F_4$		440	356
$4\text{-}F_3CC_6F_4$	292.0		338

The bathochromic shift of λ_{max} of the long-wavelength band on passing from hydrocarbons to their polyfluorinated analogues is rather unusual: more typical is a hypsochromic shift [13]. For example, on going from 1,3-bis(phenyl)-1,3-diaza-2-thiaallene to its 1,3-bis(pentafluorophenyl)-derivative, the electronic absorption spectrum shows a 30 nm blue shift of λ_{max} of the long-wavelength band [14,15].

The correlation of $\delta^{17}O$ with the energy of transition to the first excited state suggests that deshielding of oxygen results, at least partly, from virtual excitations which involve rotation of charge about the oxygen nucleus.* If we approximate the excited states by virtual orbitals, we can consider the electronic transitions between the oxygen lone-pair orbital,

* It has been earlier suggested [34] that this transition is $n_S \longrightarrow \pi^*$

n_O, the nodal plane of which is orthogonal to the molecular σ-plane , and the π^*-MO, involving both the NSO-group and the aromatic ring, the nodal plane of which coincides with the σ-plane (N-sulphinylarylamine molecules in general have a planar syn-configuration of C_s point symmetry [16]). Since the nodal planes of these orbitals are mutually orthogonal, the electronic transitions between them are equivalent to the rotation of the electron around the oxygen nucleus, i.e. they are magnetically active (see Fig.1). It should be noted that, though for the $n_O \rightarrow \pi^*$ transition shown in Fig.1, the selection rule $|\Delta l| = 1$ is not valid, in the case of N-sulphinylarylamines this is not forbidden. The C_s point group of symmetry has only two irreducible representations, A and B, with vectors x and y transforming as A and vector z transforming as B. Therefore all the transitions will have, in the transition integral, a subintegral expression of A_1 symmetry, and will be allowed [17].

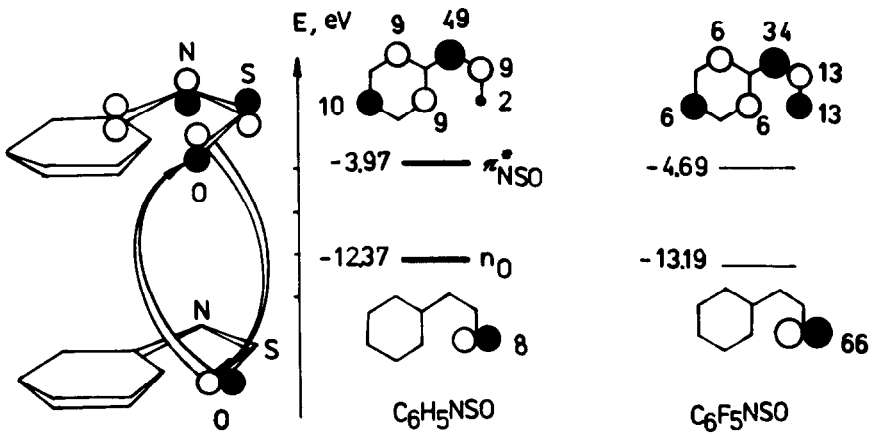

Fig.1. The electronic $n_O \rightarrow \pi^*_{NSO}$ transition and the one-electron energies and structure of the respective MO s in C_6H_5NSO and C_6F_5NSO (The relative p-orbital contribution of each MO is indicated to the nearest percent).

In this model the bathochromic shift of λ_{max} of the long-wavelength band on going from N-sulphinylaniline to N-sulphinylpentafluoroaniline is explained by the fact that the π-fluoro effect [18], which has an electrostatic nature, does not affect the energy of n_O, separated from the nearest fluorine atoms by four σ-bonds, but decreases the energy of π^*-LVMO. However this model has two disadvantages. First, the energy of n_O would be unaffected by the π- fluoro effect only on condition of 100% localization of n_O on the oxygen atom. This may not be possible, since it is known [19] that even in the water molecule, the orbital of the oxygen lone-pair that lies in the σ-plane is not a pure n_O - orbital, but contains a hydrogen 1s-AO contribution as well. Second, the electronic transitions actually occur not between two orbitals, but between two states of a molecule, so in specifying the excited states by virtual orbitals it is necessary to take into account changes in interelectron repulsion. The experimentally observed transition energy is expressed through the difference of one-electron orbital energies in the following way [20]:

$$\Delta E = \varepsilon_j - \varepsilon_i + 2K_{ij} - J_{ij}$$

where J_{ij} is a coulombic integral, K_{ij} is an exchange integral. This suggests that the bathochromic shift of the long-wavelength band in the UV spectrum of N-sulphinylpentafluoroaniline as compared to N-sulphinylaniline may not result from the decreased difference of one-electron energies of orbitals involved in the transition, as the $2K_{ij}-J_{ij}$ value may be different for molecules of these compounds.

The assumption that the energy of n_O changes insignificantly on going from N-sulphinylaniline to N-sulphinylpentafluoroaniline, implies, when the Koopmans theorem is valid [20], that one of the first ionization potentials (IP) of the molecule also changes insignificantly. The corresponding MO then could be identified with n_O. However, as follows from the UV photoelectron spectral data for N-sulphinylaniline and N-sulphinylpentafluoroaniline (Table 2), transition from the first compound to the second one is accompanied by a considerable increase of all vertical IPs, and the IP_6 value of N-sulphinylaniline is close to the IP_3 value of N-sulphinylpentafluoroaniline.

TABLE 2
UV Photoelectron spectral data and the results of CNDO/S calculations for C_6H_5NSO and C_6F_5NSO

Compound	Vertical IPs, eV *		One-electron energies of MOs (with an opposite sign) *		Charge on atoms			Wiberg indices for bonds		
					N	S	O	CN	NS	SO
C_6H_5NSO	9.12	9.06	9.35	9.37	0.04	0.12	-0.5	1.28	1.22	1.01
	9.65	9.52	10.09	10.19						
	10.62	10.38 10.87	11.21	10.57						
	11.09 11.42	11.18	11.61	11.39						
	12.37	12.26	12.41	13.14						
	12.71	12.85		13.45						
		13.75								
C_6F_5NSO	9.97	9.97		10.05	-0.03	0.21	-0.48	1.19	1.34	1.1
		11.78		10.84						
		12.29		11.54						
		13.19		12.23						
		13.98		14.03						

* Taken from [21].

Moreover, IP_6 of N-sulphinylaniline is in good agreement with IP = 12.52 eV in the UV photoelectron spectrum of HNSO associated with the $n_O - n_N$ orbital [21].

The SCF MO LCAO CNDO/S calculations of N-sulphinylaniline lead to MOs of complex structure, among which there are no clear-cut n_O orbitals. The oxygen $2p_y$-AO contribution to the sixth occupied MO (MO_6) is only 8%, and it has also contributions from ring carbon atoms, therefore this orbital can be considered as n_O only conventionally. It should be noted that the case is typical for oxygen compounds [19].

The ring carbon contributions make the MO_6 of N-sulphinylaniline subject to the action of a π-fluoro effect and on going to N-sulphinylpentafluoroaniline its energy should decrease.

This means that the proximity of the IP_6 and IP_3 of N-sulphinylaniline and N-sulphinylpentafluoroaniline is casual and that not MO_3, but some lower lying MO of N-sulphinylpentafluoroaniline corresponds to MO_6 of N-sulphinylaniline associated with n_O. The SCF MO LCAO CNDO/S calculations suggest that in N-sulphinylpentafluoroaniline it is MO_4 with a 66% contribution of oxygen $2p_y$-AO that may be associated with n_O. This is the largest contribution of oxygen 2p-AO to 10 high-lying occupied MOs. The lowest virtual MO (LVMO) in both molecules, as shown by the calculations, is antibonding orbital π^*_{NSO} (see Fig.1).

It is seen from Fig.1 that if, using the Koopmans' theorem, one takes for the n_O energies the values of the corresponding IPs with an opposite sign, then on going from N-sulphinylaniline to N-sulphinylpentafluoroaniline the one-electron energy difference between orbitals π^*_{NSO} and n_O does not decrease, it even somewhat increases (by 0.11 eV).

This indicates no controversy with the experimentally observed bathochromic shift of λ_{max} of the long-wave band in the UV spectrum of the second compound relative to that of the first, but suggests a substantial change of the $2K_{ij}-J_{ij}$ factor, which defines changes in the interelectron repulsion when the molecule passes from the ground state to the excited one.

The virtual $n_O \rightarrow \pi^*_{NSO}$ excitations, the energy of which decreases on going from N-sulphinylaniline to its fluorinated analogues, is only one reason for the observed deshielding of oxygen. The analysis of the electronic structure of the compounds involved reveals some other effects. As follows from Fig.1, the contribution of the oxygen 2p-AO to the n_O and π^*_{NSO} orbitals is larger for N-sulphinylpentafluoroaniline than for N-sulphinylaniline. This implies that the paramagnetic $n_O \rightarrow \pi^*_{NSO}$ circulation of the electron in N-sulphinylpentafluoroaniline will be closer to the oxygen nucleus than in N-sulphinylaniline, which increases the radial factor $\langle r^{-3} \rangle_{2p(O)}$ and, consequently, the deshielding of oxygen. Another factor is the change of the negative charge on oxygen q(O). On the basis of the indirect data, such as the NSO vibration frequencies identified by the ^{15}N and ^{18}O isotope shifts, the ^{13}C NMR chemical shifts and the chemical shifts of $SK\alpha$-lines in the X-ray fluorescent spectra, it has been recently suggested that on passing from

N-sulphinylaniline to N-sulphinylpentafluoroaniline, the electron density is redistributed between the ArN fragment and the oxygen atom, on which the electron density is decreased [12]. The CNDO/S calculations confirm this suggestion. As seen from Table 2, q(O) in N-sulphinylpentafluoroaniline is 0.11 electron charge units lower than that in N-sulphinylaniline. This leads to increased $\langle r^{-3} \rangle_{2p(O)}$ in the former compound and to deshielding of oxygen.

A change of the ΣQ term may be estimated by changes in the Wiberg indices defining multiplicity of the bonds [22]. The Wiberg index for the SO bond (W_{SO}) and q(O) in N-sulphinylaniline shows that the SO bond in this compound is the ordinary σ-bond, and the electron pair, which could build the σ-bond, is localised on oxygen, which may be represented by the formula $C_6H_5-N=S-O^-$. The same results were obtained earlier [21]. On passing to N-sulphinylpentafluoroaniline, the SO bond acquires the π-component, which results in the increased W_{SO}, probably due to delocalization of the aforementioned electron pair, since q(O) is decreased (Table 2). Delocalization of the pair implies increased asymmetry of the valence electron charge density distribution relative to the oxygen nucleus, which leads to increased ΣQ and, consequently, to enhanced deshielding.

Thus deshielding of oxygen observed for fluorinated N-sulphinylanilines is caused by several effects. It is difficult to estimate the relative contribution of each of these factors, and it seems to vary with compounds. For most of the compounds studied, the main reason for oxygen deshielding is, presumably, the decreased energy of virtual $n_O \rightarrow \pi^*_{NSO}$ excitations, but this is not the case for N-sulphinyl-2-fluoro- and N-sulphinyl-3-fluoroanilines, for which the correlation $\delta^{17}O / \lambda_{max}$ does not hold.

The fact that the nitrogen chemical shifts do not correlate with λ_{max} of the long-wavelength band in the UV spectrum, and change in the reverse direction with respect to the oxygen chemical shifts, suggests another reason for screening of the ^{15}N nucleus in fluorinated N-sulphinylanilines in comparison with screening of the ^{17}O nucleus. That reason may be the increased

electron density on nitrogen in fluorinated N-sulphinylanilines (the example is given in Table 2). It should be noted that previously equations have been derived which relate the charge on nitrogen to the $\langle r^{-3} \rangle_{2p(N)}$ value [8], or directly with $\delta\,^{15}N$ [9].

Another reason may be the change of ΣQ. If we postulate that the valence electron charge density distribution on nitrogen is most symmetric in cases when both of its bonds have the same multiplicity, i.e. when $W_{CN} = W_{NS}$, then the extent of deviation of that distribution from the most symmetric one may be measured by the module of difference between the Wiberg indices for the CN and SN bonds (Table 2). For N-sulphinylaniline that value is lower than for N-sulphinylpentafluoroaniline (0.06 and 0.15 respectively), which suggests greater screening of nitrogen in the first compound as compared with the second.

The upfield shift of the ^{15}N NMR signal of completely fluorinated nitrogen-containing aromatic compounds has been generally recognised [3-9]. However the data in Table 1 show no specific perfluorination effects in the ^{15}N and ^{17}O NMR spectra of the compounds studied, and it is seen that the difference between the chemical shifts of oxygen and nitrogen of N-sulphinylaniline with one, two or five fluorine atoms, are only quantitative.

Azoxybenzenes

The chemical shifts of nitrogen and oxygen of these compounds (Table 3) show that introduction of fluorine into an azoxybenzene leads to increased screening of both nitrogen atoms and deshielding of oxygen. It is worthwhile to note the shifts of λ_{max} of the long-wave length band in the UV spectrum of 2,2',3,3',5,5',6,6'-octafluoroazoxybenzene with hydrogen atoms in positions 4 and 4' substituted by the π-donor (F, CH_3) and π-acceptor (CF_3) substituents. For azoxybenzenes this band corresponds to $n_O \rightarrow \pi^*$-transitions [25]. The donor substituent CH_3 gives rise to the bathochromic shift of λ_{max} and screening of oxygen, whereas the acceptor substituent CF_3 leads to the

TABLE 3

^{15}N and ^{17}O NMR and UV spectral data for azoxybenzenes

Compound	$\delta^{15}N$, ppm N(1)	$\delta^{15}N$, ppm N(2)	$\delta^{17}O$, ppm	Line width Hz	λ_{max}, nm
$C_6H_5\overset{1}{N}(\rightarrow O)=\overset{2}{N}C_6H_5$	335.7*	351.7**	456	1200	322
4-$FC_6H_4N(\rightarrow O)=NC_6H_4F$-4			456	600	
2,4-$F_2C_6H_3N(\rightarrow O)=NC_6H_3F_2$-2',4'	316.9	326.0	495	600	
4-$HC_6F_4N(\rightarrow O)=NC_6F_4H$-4	315.9	328.0	549	2000	288**
$C_6F_5N(\rightarrow O)=NC_6F_5$	305.9	319.2	549	1800	294**
4-$CH_3C_6F_4N(\rightarrow O)=NC_6F_4CH_3$-4'			534	1800	300
4$CF_3C_6F_4N(\rightarrow O)=NC_6F_4CF_3$-4'			578	2500	282

* Taken from [23]; ** taken from [24].

hypsochromic shift of λ_{max} and deshielding of oxygen. This indicates opposed effects $\langle r^{-3} \rangle_{2p(O)}$ and ΔE^{-1} factors on ^{17}O NMR chemical shifts in azoxybenzenes. Moreover, the first factor producing the largest effect and the observed deshielding of oxygen is the decrease in electron density on this atom.

Decrease in electron density on the oxygen of the azoxy group, which may be defined by the formula $-N=\overset{+}{N}-\overset{-}{O}$ as above for the N-sulphinyl group, may be accompanied by increase in the asymmetry of valence electron charge distribution on the oxygen nucleus, which follows the same machanism. Contribution to deshielding of oxygen then is from factor ΣQ.

Increased screening of nitrogen observed for fluorinated azoxybenzenes is possibly due to the increased electron density on this atom.

As in the case of N-sulphinylarylamines, the ^{15}N and ^{17}O NMR spectra did not show any specific perfluorination effects.

C,N-Diarylnitrones

On going from C,N-diphenylnitrone to C-pentafluorophenyl-N-phenylnitrone, screening of nitrogen is decreased, that of oxygen is increased, and λ_{max} of the long-wavelength band in the UV spectrum undergoes a hypsochromic shift (Table 4).

TABLE 4
^{15}N and ^{17}O NMR and UV spectral data for C,N-diarylnitrones

Compound	$\delta^{15}N$ ppm	$\delta^{17}O$ ppm	Line width Hz	λ_{max}, nm
$C_6H_5CH{=}\overset{\downarrow}{N}C_6H_5$ (O)	263.1	446	9000	318
$C_6F_5CH{=}\overset{\downarrow}{N}C_6H_5$ (O)	276.9	406	1600	307
$(C_6F_5)_2C{=}\overset{\downarrow}{N}C_6H_4F\text{-}4$ (O)	283.9	594	1500	
$(C_6F_5)_2C{=}\overset{\downarrow}{N}C_6F_4H\text{-}4$ (O)	257.6	612	1900	288
$(C_6F_5)_2C{=}\overset{\downarrow}{N}C_6F_5$ (O)	255.8	631	380	290

The strong electron-withdrawing properties of the pentafluorophenyl group, decreasing electron density on nitrogen and oxygen, and increasing factors $\langle r^{-3}\rangle_{2p(N)}$ (and $\langle r^{-3}\rangle_{2p(O)}$) explain the deshielding of nitrogen. The observed screening of oxygen possibly arises from the fact that increase of the energy of $n_O \rightarrow \pi^*$-transitions and, accordingly, decrease of the ΔE^{-1} factor dominates increase of the $\langle r^{-3}\rangle_{2p(O)}$ factor.

The presence of the second pentafluorophenyl ring at the carbon atom brings about further slight deshielding of nitrogen and tremendous deshielding of oxygen. The latter fact may be explained if we assume domination of increase of the $\langle r^{-3}\rangle_{2p(O)}$ factor over the decrease of the ΔE^{-1} factor. Accumulation of

the fluorine atoms in the phenyl ring bonded with nitrogen increases screening of nitrogen with further deshielding of oxygen (Table 4). It seems that when the polyfluoroaryl group and the nitrogen atom, both strong electron acceptors, are directly bonded they act jointly, to increase the electron density on the ArN fragment (with respect to the hydrocarbon analogue) but decrease this in other fragments of the molecule. Such redistribution of the electron density explains the observed change in screening of ^{15}N and ^{17}O.

Azomethines with aromatic substituents*

Introduction of the fluorine atoms into the aromatic ring bonded to nitrogen in benzylidene aniline increases the nitrogen screening (Table 5). The effect of fluorine in the 2-position (reduction of the nitrogen chemical shift by 13.8 ppm) is considerably stronger than that of fluorine in the 4-position (reduction of the nitrogen chemical shift by 3.9 ppm). The effect of fluorine is additive: in the 2,4-difluoro derivative nitrogen undergoes 18.3 ppm screening in comparison with benzylidene aniline, which is in good agreement with the sum of the individual effects of *ortho* and *para* fluorine atoms equal to 17.7 ppm.

Introduction of five fluorine atoms into the aromatic ring bonded to carbon in benzylidene aniline leads to deshielding of nitrogen (Table 5). The further introduction of fluorine into the ring bonded with nitrogen leads to increased screening of the ^{15}N nucleus. The effect of fluorine in the 2-position is much stronger than that of fluorine in the 4-position, with practically the same upfield shifts $\delta\,^{15}N$ as above (13.7 and 4.2 ppm respectively). The influence of fluorine here is also additive: in 2,3,4,5,6-pentafluorobenzylidene-(2,4-difluoro-aniline) nitrogen shows 17.2 ppm screening in comparison with 2,3,4,5,6-pentafluorobenzylidene aniline, which is in good agreement with the sum of the separate effects of *ortho* and *para* fluorine atoms, equal to 17.9 ppm.

* For the preliminary communication see [26].

TABLE 5

^{15}N NMR and UV spectral data for aromatic azomethines

Compound	δ_{15_N}, ppm	λ_{max}, nm
$C_6H_5CH{=}NC_6H_5$	328.7	308
$C_6H_5CH{=}NC_6H_4F$-2	314.9	310
$C_6H_5CH{=}NC_6H_4F$-4	324.8	314
$C_6H_5CH{=}NC_6H_3F_2$-2,4	310.4	312
$C_6H_5CH{=}NC_6F_5$	294.0	306
$C_6F_5CH{=}NC_6H_5$	352.8	320
$C_6F_5CH{=}NC_6H_4F$-2	339.1	
$C_6F_5CH{=}NC_6H_4F$-4	348.6	314
$C_6F_5CH{=}NC_6H_3F_2$-2,4	335.6	315
$C_6F_5CH{=}NC_6F_5$	318.4	316
$(C_6F_5)_2C{=}NC_6H_4F$-4	354.4	334
$(C_6F_5)_2C{=}NC_6F_4H$-4	321.1	320
$(C_6F_5)_2C{=}NC_6F_5$	318.0	325

On going from benzylidene aniline to benzylidene pentafluoroaniline, screening of nitrogen is increased by 34.7 ppm, whereas on passing to 2,3,4,5,6-pentafluorobenzylidene aniline it is decreased by 24.1 ppm. On going from benzylidene aniline to 2,3,4,5,6-pentafluorobenzylidene pentafluoroaniline, screening of nitrogen is increased by 10.3 ppm (Table 5), which is in good agreement with the value of 10.6 ppm calculated according to the additive scheme.

In the series of compounds studied, the ^{15}N NMR chemical shift does not correlate with λ_{max} of the long-wavelength band in the UV spectrum (Table 5). It is known [27] that in the UV spectra of azomethines the $n_N \rightarrow \pi^*$-transition bands have low intensities and are masked by more intensive bands of $\pi \rightarrow \pi^*$ transitions. Due to this, any correlation of $\delta 15_N/\lambda_{max}$, might be irrelevant to the interpretation of changes in nitrogen chemical shifts.

Thus in the series of benzylidene anilines, the influence of fluorine on the ^{15}N NMR chemical shift is additive, which

indicates its invariance to the possible structural (see references given in [26]) and orbital [28] effects, and suggests that the observed changes in nitrogen screening result mainly from changes in the electron density on that atom.

Introduction of the second pentafluorophenyl ring at the carbon atom of (2,3,4,5,6-pentafluorobenzylidene)(4-fluoroaniline) leads to deshielding of nitrogen (Table 5). Further accumulation of the fluorine atoms in the ring bonded with nitrogen results in increased screening of the latter. It is interesting to note that in perfluorobenzohydrylidene aniline, the ^{15}N NMR chemical shift is practically equal to that in 2,3,4,5,6-pentafluorobenzylidene pentafluoroaniline, i.e. substitution of a hydrogen atom in the latter by the pentafluorophenyl group does not affect $\delta\,15_N$. It seems that in this case several effects compensate for one another.

EXPERIMENTAL

The ^{17}O NMR spectra were recorded on a Bruker CXP-300 spectrometer at 40.7 MHz in natural abundance of the ^{17}O isotope from D_2O as an external standard. The following conditions were employed: pulse width - 20 ms (90° pulse angle), pulse period - 30 ms, accumulations - 20,000 to 50,000. The ^{15}N NMR spectra were measured for the enriched compounds (94-96%) at 30.414 MHz from liquid NH_3 as an external standard; the spectrometer setting: pulse width 20 μs (90° pulse - 30 μs), pulse period - 20 s.

UV photoelectron spectra were recorded on a spectrometer designed at the Institute of Physics of the Leningrad State University. A resonance He (I) line with λ = 584 Å (21.21 eV) was used as ionization source. The spectra were calibrated by Xe lines (12.13 and 13.43 eV). The accuracy of IP's is ±0.02 eV (or for broad bands ±0.05 eV).

Quantum-chemical calculations have been performed by the SCF MO LCAO CNDO/S method using a set of quantum-chemical programs 'Viking' described in [29].

Fluorinated aromatic azomethines were obtained as described in [30,31], azoxybenzenes in [32], nitrones in [33].

CONCLUSION

Thus the ^{15}N and ^{17}O NMR specra of the compounds studied did not reveal any specific perfluorination effects. This is not surprising. The perfluoro effect, which is one of the types of π-fluoro effect, is of an elecrostatic nature [18], whereas the physical nature of magnetic screening of nuclei is different [2]. Therefore there are no reasons to expect the same specific and clear-cut perfluoro effect in the ^{15}N and ^{17}O NMR spectroscopy as in the ultraviolet photoelectron spectroscopy.

Changes in screening of nitrogen induced by introduction of fluorine into nitrogen-containing aromatic compounds are controlled mainly by the radial factor $\langle r^{-3} \rangle_{2p(N)}$, whose value depends on the electron density on nitrogen. When the pentafluorophenyl group and nitrogen, both strong electron acceptors, are directly bonded with each other, they act jointly, leading to increase of electron density on the ArN fragment with respect to the hydrocarbon analogue, decreasing it on other fragments of the molecule. Increased electron density on nitrogen of polyfluorinated derivatives in comparison with their hydrocarbon analogues shows itself in the ^{15}N NMR spectra as an upfield shift of the signal of the first compound relative to that of the second one.

An exception which confirms the rule is provided by the azobenzenes, since their fluorinated analogues show deshielding of nitrogen [7,9]. It is clear that in such compounds the pentafluorophenyl group can withdraw electrons only from nitrogen The data on azobenzenes show that the electron-accepting properties of the pentafluorophenyl group exceed those of nitrogen. Therefore, when the nitrogen atom is not directly bonded to the aromatic group, the electron density is increased only on the aromatic fragment of a polyfluorinated compound: on all other parts of the molecule, including nitrogen, it is decreased. This explains all known cases of nitrogen deshielding ([7,9] and the present work) on passing from nitrogen-containing aromatic hydrocarbons to their polyfluorinated derivatives.

Changes in screening of oxygen for fluorinated compounds are controlled mainly by two factors: inverse excitation energy

ΔE^{-1} and the radial factor $\langle r^{-3} \rangle_{2p(O)}$, which may operate in the same or opposed directions.

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