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ELECTRONIC STRICTURE AND REACTIVITY OF PHENYL AND PENTAFLUOROPHENYLSUBSTITUTED N,N-DICHLOROAMIDES AND -AMINES.

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SUMMARY

The charge distribution in the polyfluoroaromatic N,N-dichloroamides and -amines and their hydrocarbon analogues has been established from the X-ray fluorescent ClK_{α} and SK_{α} - spectra and X-ray photoelectron spectra of chlorine, sulphur and nitrogen in comparoson with data obtained from NQR ^{35}Cl frequencies and semiempirical calculations by CNDO/2. The action of sulphur and selenium on the N,N-dichloroamides of pentafluorobenzenesulphonic acid and pentafluorobenzoic acid leads to the corresponding S,S-dichlorosulphimines and Se,Se-dichloroselenoimines respectively. The polyfluoroaromatic N,N-dichloroamines have been found to form polyfluorinated trans-azobenzenes under the same conditions. The mechanism of these reactions has been discussed.

INTRODUCTION

The stability and reactivity of polyfluoroaromatic compounds containing the NCl_2-group and their hydrocarbon analogues are known to be considerably different [1]. A possible reason for this can be found in the different electronic effects of the aromatic and polyfluoroaromatic ring towards the NCl_2- group as a reaction centre.

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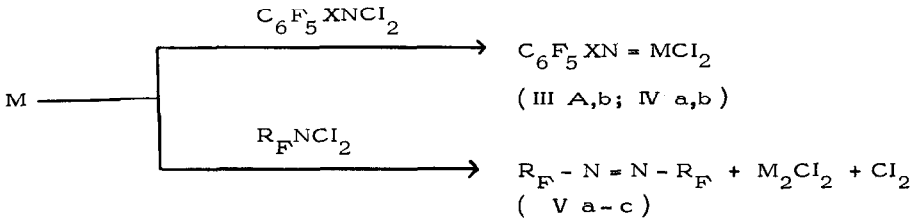
In connection with our previous systematic studies of polyfluoro-aromatic compounds containing the NCl_2 - group [1], in this paper the electronic structure of N,N-dichloroamides of pentafluorosulphonic and pentafluorobenzoic acids and their reactivity towards sulphur and selenium in comparison with the corresponding hydrocarbon analogues [2 - 4] have been investigated.

RESULTS AND DISCUSSION

The N,N - dichloroamides of pentafluorobenzenesulphonic (I) and pentafluorobenzoic (II) acids are found to react with sulphur and selenium to give S,S - dichlorosulphimines (III a,b) and Se,Se - dichloro-selenoimines (IV a,b) respectively in high yields. The products (III a,b; IV a,b) are decomposed readily by atmosphric moisture.



X = SO_2 (I), CO (II);
III a X = SO_2, M = S; III b X = SO_2, M = Se;
IV a X = CO, M = S; IV b X = CO, M = Se;
V a R_F = C_6F_5; Vb R_F = 4 - $CF_3C_6F_4$; Vc R_F = 4 - Py_F;

The action of selenium on the N,N - dichloroamides of arylsulphonic acids occurs similarly and leads to the Se,Se - dichloro - N - arylsulphonyl-selenoimines $ArSO_2N = SeCl_2$ [2, 3]. In the same time bis(arylsulphonyl)- and bis(aroyl)sulphur diimines can obtained by the reaction of arylsulphonic acids N,N-dichloroamides and benzoic acids N-chloroamides respectively with sulphur [4,5].

In view of the difference in the chemical behaviour of the polyfluoro-aromatic compounds (I) and (II) and their hydrocarbon analogues towards sulphur we have studied the reaction between sulphur and N,N - dichloro - amines containing the NCl_2 - group adjacent to polyfluoroaromatic ring. N,N - Dichloropentafluoroaniline (VI), N,N - dichloroheptafluoro - para -

toluidine and 4 - N,N - dichloroamino - 2,3,5,6 - tetrafluoropyridine were found to react with sulphur to form the corresponding azocompounds (Va - c) in high yields. The products of these reactions have shown to be trans - isomers. Their dipole moment measured in benzene was found to be equal to zero. The use of selenium instead of sulphur leads with these reagents to the same products.

The observed differencies in the reactivities of N,N - dichloro - amides and - amines are assumed to be connected with the peculiarties in the electron density distribution within their NCl_2 - groups. Therefore we have estimated by means of NQR ^{35}Cl data, X - ray fluorescent K_α - spectra of chlorine and sulphur and semiempirical calculations by CNDO/2 the effective charges on chlorine atoms in some N,N - dichloro - amides and - amines (Table 1). In the same way the effective charges on sulphur atoms for the compound (I) and the N,N - dichloroamide of benzenesulphonic acid (VII) have been estimated. The charges on chlorine atoms from NQR ^{35}Cl frequencies were calculated by Townes - Dailey theory [6,7] in assumption that the degree of s - hybridization of the chlorine atom is equal to zero. The charges on chlorine atoms from the X - ray fluorescent spectra were determined from the experimental curve obtaind by us and presenting the dependence of the ClK_α - shifts (taken from the molecular chlorine as a standart) on the values of Pauling charges on chlorine atoms in the model compounds (Fig. 1). The latter have been calculated from the data given in [8]. The bond lengths and the valence angles for CNDO/2 calculations have been taken from [9, 10].

It is nessesary to take into account that the charge values in Table 1 obtained by the various methods are not coincident. That fact can be explained, since the different methods for obtaining the effective charge are connected usually with the different definitions of the latter. Moreover, all the methods used in the present work are approximate to a greater or less degree. The general comparison of their precision [7,11,12] leads us to conclude that the most precise in our case are the X - ray fluorescent data because that method gives a direct dependence of the experimental values (for instance, ClK_α - shifts) on the effective charges on the atoms in the molecule [12, 13]. Therefore, the data from X - ray fluorescent spectra will be discussed in more detail.

TABLE 1 .

The charge values for chlorine and sulphur atoms in the N,N-dichloroamides and -amines of polyfluoroaromatic series and model compounds.

Compound	The charges on chlorine atoms					The charges on sulphur atoms	
	From NQR ^{35}Cl data		From X-ray fluorescent spectra		From CNDO/2 calculations	From X-ray fluorescent spectra	From CNDO/2 calculations
	Frequency MHz	Charge $\bar{e}$	ClK_{α}-shift eV	Charge $\bar{e}$	Charge $\bar{e}$	Charge in covalent volume, $\bar{e}$	Charge $\bar{e}$
(I)	53.632	- 0.03	0.06 ± 0.03	0.03 ± 0.01	0.06	0.96 ± 0.02	
(II)	56.278	+ 0.02	- 0.03 ± 0.03	- 0.03 ± 0.02	0.06		
(VI)	51.180	- 0.07	- 0.09 ± 0.02	- 0.09 ± 0.01	- 0.03		
(VII)	52.605	- 0.05	- 0.25 ± 0.03	- 0.28 ± 0.09	- 0.05	0.94 ± 0.03	0.48
(VIII)	53.061	- 0.04	- 0.17 ± 0.04	- 0.15 ± 0.05			
Cl_2	54.247 [7]	0.00	0.00	0.00			
C_6F_5Cl	39.410			- 0.04 ± 0.03			
C_6H_5Cl	34.621			- 0.06 ± 0.02			
SCl_2				- 0.10 ± 0.04	- 0.01	0.26 ± 0.02	0.08

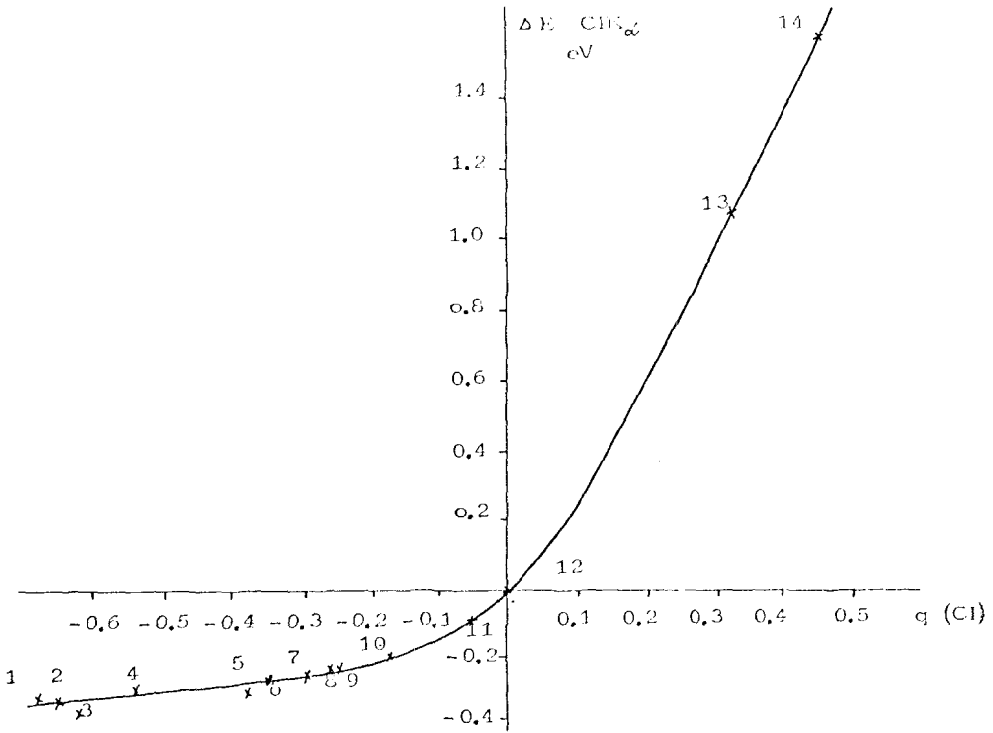


Fig. 1 . The correlation between ClK$_\alpha$- shifts and Pauling charges on chlorine atoms in model compounds (1 - KCl; 2 - NaCl; 3 - $CaCl_2$; 4 - $MgCl_2$; 5 - $CrCl_3$; 6 - $CdCl_3$; 7 - $FeCl_3$; 8 - $CuCl_2$; 9 - $CoCl_2$; 10 - PCl_3; 11 - C_6Cl_6; 12 - Cl_2; 13 - $NaClO_3$; 14 - $Co(ClO_4)_2$) .

Through the absolute charges on the chlorine atoms obtained by the various methods do not coincide, all the methods used give the same qualitative results. The NQR ^{35}Cl frequencies of the investigated N,N - dichloroamides and - amines (Table 1) are close to each other and to the frequency of molecular chlorine. The charges calculated from these data are rather small and the show the preferably covalent character of the N - Cl bond. The same conclusion can be made for the compounds (I), (II) and (VI) from the X - ray fluorescent data and for the compounds (II), (VI) and (VII) from CNDO/2 calculations. The chlorine atoms in most measurements have negative charges according to data from all methods except the compound (I) (from X - ray fluorescent spectra) and the compound (II) (from NQR ^{35}Cl frequencies and CNDO/2 calculations). Nevertheless, the effective positive charges on chlorine atoms in investigated compounds are small. At the same time the hydro - carbon analogues of compounds (I) and (II), the compound (VII) and benzoic acid N,N - dichloroamide (VIII) have a relatively large negative charge on their chlorine atoms (from X - ray fluorescent spectra). The presence of the pentafluorophenyl ring in the molecules in place of the phenyl one leads to less electron density on the chlorine atoms of the NCl_2 - group by data from all methods. The effect depends also on the fragment of the molecule which conducts the influence of pentafluorophenyl group to the chlorine atom. It can be observed most clearly from X - ray fluorescent data (Table 1).

The effective charges on nitrogen atoms in the compounds (I) and (VII) also can be estimated from the X - ray fluorescent charge data for chlorine and sulphur atoms. The charges on sulphur atoms in these compounds are practically equal (Table 1). The charges on oxygen atoms in sulphonyl group are known to be practically independent of the character of the radicals adjacent to that group [14]. Therefore the sums of charges on the fragment C_6F_5 and NCl_2 in the compound (I) and C_6H_5 and NCl_2 in the compound (VII) can be considered to be approximately equal and equal to zero. Since the Pauling electronega - tivity of sulphur atom with the charge +1 (2.8) [14] is very close to that of chlorine (3.0), the charges on C_6F_5 and C_5H_5 - fragments can be appoximated by those on the aryl fragments in pentafluorochlorobenzene (Table 1). Since the charge effects are preferentially due to the inductive interactions, the differencies in the π - acceptor properties of S^+ and chlorine atom can be taken for our degree of approximation as negligible. Hence, the positive charge on nitrogen atom for the

compound (I) is about 0.5 $\bar{e}$ less on the nitrogen atom for the compound (VII). Moreover, since the charges on the C_6F_5 and C_6H_5 groups estimated as mentioned above are close to zero, the total charge on the NCl_2 - group can be approximately considered to be also practically equal to zero, i. e. the charge on the nitrogen atom in that group is equal to the double charge on chlorine atom with opposite sith.

$$q(C_6F_5)_I + q(NCl_2)_I = q(C_6H_5)_{VII} + q(NCl_2)_{VII} = 0$$

$$q(N)_{VI} \sim q(N)_I + 0.5\ \bar{e} \qquad q(NCl_2)_I \sim_{VII} 0$$

where $q(X)_j$ - the charge on the group (atom) X in the compound

For qualitative examination of the obtained electron density distribution the values of the 2p - level energies of sulphur and chlorine and 1 s - level energy of nitrogen atom were determined by the X - ray photoelectron spectra (Table 2). The obtained energies let us conclude that in the compound (VII) relative to the compound (I) the electron density on nitrogen atom is considerably less, while on the chlorine atoms the opposite picture is observed. At the same time the charges on sulphur atoms within the limits of experimental error are equal. The comparison of the data above with correlation dependence between $E(N_{1s})$ and $q(N)$ in [15] shows that in the compound (I) the nitrogen atom is practically neutral whereas in the compound (VII) it is charged positively about + 0.2 - 0.4 $\bar{e}$*.

TABLE 2.

The X - ray photoelectron spectral data for the compounds (I) and (VII).

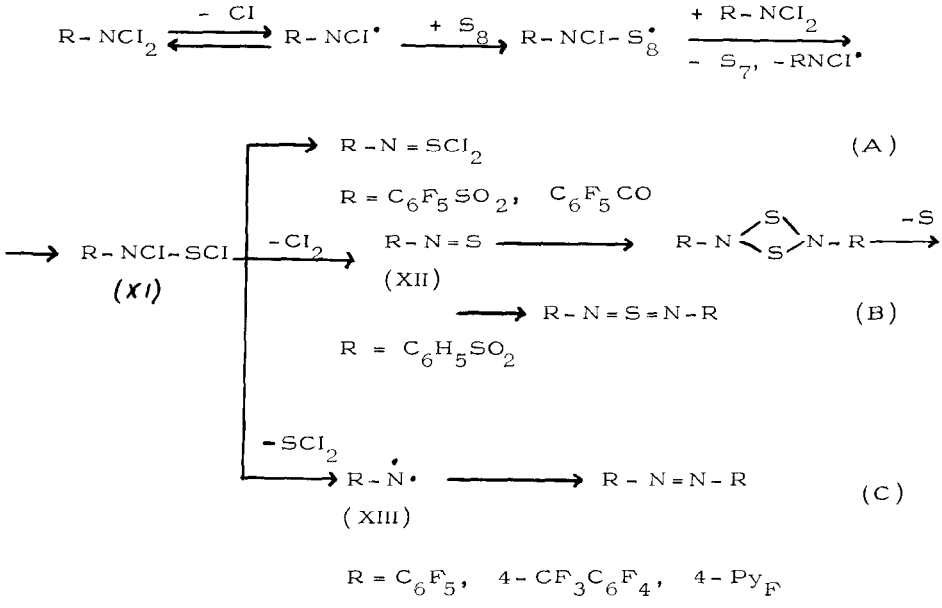
Compound	Level	The energy of level, eV
(I)	N_{1s}	400.4 ± 0.3
	Cl_{2p}	200.9 ± 0.4
	S_{2p}	169.4 ± 0.3
(VII)	N_{1s}	402.0 ± 0.3
	Cl_{2p}	199.8 ± 0.3
	S_{2p}	169.8 ± 0.3

* The data on the energies of N_{1s} - levels, obtained in [15] is necessary to increase on 1.0 eV because of incorrect calibration used for spectra [16].

The difference between the charges on chlorine atoms in the compounds (I) and (VII) is equal to approximately 0.1 - 0.2 $\bar{e}$, the chlorine atom in compound (I) being more electropositive. The latter follows from the correlation with the data observed [14].

Thus, the obtained X- ray photoelectron spectral data support qualitatively the above estimation of the charge distribution in the NCl_2- groups in the conpounds (I) and (VII). Hence the set of the obtained data leads us to conclude that in the series of compounds of the $RNCl_2$ - type the replacement of the aryl radical by polyfluoroaryl doesn't lead to the integral transfer of the electronic density between the aryl fragment and NCl_2 - group, but only to the decrease of polarity of N - Cl bond.

Since the absolute values of chlorine atom charges in compounds (I), (II), (VI - VIII) (Table 1) are sufficiently small, the homolytic splitting of N - C bonds and hence radical reactions must preferentially take place for them. Therefore the following scheme can be proposed for the reaction of these compounds with sulphur and selenium (for instance, in the case of sulphur):



Radical (R - NCl) formed by rupture of the N - Cl bond in the parent compound reacts with sulphur and after elimination of the

fragment S_7 intermediate (XI) generates. The latter can rearrange further or eliminate the stable molecules. The state of the bond S-Cl in the intermediate (XI) at the first moment of its generation can be supposed to be similar to that of the SCl_2 molecule and the state of the bond N-Cl will not differ from that in the NCl_2 - group in the initial N,N-dichloroamide or - amine. Taking into account that the most stable electronic state of chlorine is the state of anion Cl^-, one can also suppose that the intermediate (XI) must first of all undergo the rearrangements leading to the increase of electron density on chlorine atom or, if that demand is unreal, to the elimination of elemental chlorine or sulphur dichloride. In that case the electronegativity of the radical R will be the factor determinating the ability of intermediate (XI) to rearrangement or elimination. If it is so, then just at this stage the differences between polyfluoroaromatic compounds and their hydrocarbon analogues must play an important role.

When R in the intermediate (XI) is $C_6F_5SO_2$ or C_6F_5CO, the chlorine atom of the N-Cl bond has close to zero charge. The tendency of chlorine atom, bonded with nitrogen, to accept σ- electron density, can not be realized by nitrogen since their electronegativities are approximately equal. At the same time the sulphur atom bonded with the N-Cl fragment has an 'unshared' electron pair and considerably lower electronegativity than chlorine. The tendency of nitrogen and chlorine atoms to accept σ - electron density can be realized at the same time in that system only byrearrangement taking place because of interaction of chlorine atom, bonded in the intermediate (XI) with nitrogen, with non-bonding ('unshared' pair) electrons of sulphur (route A) to give S,S-dichlorosulphimines. In the case of $R=C_6H_5SO_2$ the chlorine atom of the N-Cl bond has an effective negative charge Therefore its interaction with non-bonded electrons of sulphur becomes disadvantageous and the above rearrangement is not observed. In that case the nitrogen atom is charged positively and its ability to accept electron density from the neighbouring chlorine and sulphur atoms increases. As a result of this the total electron density on the chlorine atoms of the intermediate (XI) must decrease and elimination of molecular chlorine becomes preferential and is observed experimentally [4]. This process leads to the thioanalogue of nitrosocompound (XII). The further dimerisation of conpound (XII) and the elimination of sulphur

from dimer gives sulphur diimines (route B).It should be noted that participation of thioanalogues of nitrosocompounds and their dimers has already been propesed [17, 18] . When R in the intermediate (XI) is the C_6F_5 group, the observed charge on the chlorine atom of N-Cl bond in it is equal to that for chlorine atoms in the SCl_2 molecule (Table 1). In that case the most preferable route of reaction must be elimination of SCl_2 molecule from the intermediate (XI) because any charge redistrybutions are unnecessary. Such elimination (see also [19]) leads to corresponding nitrenes (XIII), probably in triplet state, and recombination of them gives azocompounds (route C). Under the reaction conditions SCl_2 decomposes readily to form S_2Cl_2 and Cl_2 .

The probablity of pathways of intermediate (XI) stabilization depending on the effects of the radical, determines the observed differencies in the reactivity of N,N-dichloroamides and -amines towards sulphur.

In the case of selenium the state of bonds N-Se and Se-Cl in the selenium analogue of (XI) cannot differ markedly from the corresponding bonds in the intermediate (XI) because of close electronegativities of sulphur and selenium. The fact that the compounds reacting with sulphur by route B, under the same conditions react with selenium by route A, has, in our view, the following explanation.Rearrangement by route A begins with the interaction between 3p-AO 'unshared' pair of the sulphur atom and 3p-AO of the chlorine atom participating in intermediate (XI) in the formation of the N-Cl bond.Furthermore, the corresponding 4p-AO of the selenium atom has a greater size then 3p-AO of sulphur atom. Hence, in the case of the selenium-containing intermediate the initial overlap promoting the rearrangement (A) will take place easier than in the case of sulphur-containing one. Rearrangement (A) must occur by the migration of chlorine cation because of evidently ilide-like character of the bond N-S in S,S-dichlorosulphimines, similarly to sulphiniminos [20].Since the ionization potential of the 'unshared' pair of selenium is lower than that of sulphur [21], the interaction of the chlorine cation and selenium atom in the selenium analogue of (XI) must occur easier, than in the case of the sulphur atom in the intermediate (XI).That rearrangement (A) occurs preferentially for the selenium analogue of (XI) is evidently explained in that in the case of reaction of selenium with N,N-dichloroamides, route B is not observed.

EXPERIMENTAL

^{19}F NMR spectra were recorded on Varian A 56/60 A spectrometer at 56.4 MHz (p p m from internal C_6F_6). ^{35}Cl NQR frequencies were measured on impuls spectrometer - relaxometer NQR IS Sh - 1 at 77 K. The electronic spectra were recorded for heptane solutions on Specord UV - VIS spectrometer. X - ray fluorescent spectra were recorded at 77 K on X - ray spectrometer ' Stearate ' with using of quartz (the plane rhombohedre) as a crystal - analiser, the working regime of X - ray tube: voltage 8 Kv, anodic cuurent 0.4 - 0.6 a.AgL - radiation was used as an exciting radiation for the ClK_α - and SK_α - spectra. X - ray photoelectron spectra were obtained on the spectrometer [22]. For the semiempirical CNDO/2 calculations the computer BESM 6 was used. The analitical data of the new compounds prepared are shown in Table 3. Compounds (I) and (II) were obtained by known methods.

S,S - Dichloro - N - pentafluorophenylsulphonylsulphimine, (IIIa), (n.c.)

3.16 g pentafluorobenzenesulphonic acid N,N - dichloroamide and 0.32 g sulphur powder are heated on the bath 1h at 100°, cooled and distilled in vacuo. The product is dried to yield sulphimine (IIIa) (62%), b.p. 95 - 96°/ 3 torr. ^{19}F NMR spectrum: - 31.6 (2 $F_{2,6}$), - 23.9 (F_4), - 78 (2 $F_{3,5}$).

Se,Se - Dichloro - N - pentafluorophenylsulphonylselenoimine, (IIIb), (n. c.)

To a stirred suspension of the 0.79 g selenium powder in 15 ml of CCl_4 at 0° a solution of 3.16 g pentafluorobenzenesulphonic acid N,N - dichloroamide in 5 ml CCl_4 is added. After 3 h stirring at 20° the white precipitate is filtered, washed by CCl_4 and dried in vacuo to yield selenoimine (IIIb) (98%), m. p. 96 - 98°.

S,S - Dichloro - N - pentafluorobenzoylsulphimine, (IVa), (n. c.)

2.2 g pentafluorobenzoic acid N,N - dichloroamide and 0.32 g sulphur powder are heated on oil bath 1 h at 110 - 115°. The obtained oil which crystallized after cooling is dissolved in 1,1,2 - trichloro - 1,2,2 - trifluoroethane. The solution is filtered, the solvent is evaporated under reduced pressure. The product is dried to yield sulphimine (IVa), (72%), m. p. 79 - 81°. ^{19}F NMR spectrum: - 26.4 (2 $F_{2,6}$), - 16.2 (F_4), - 2.0 (2 $F_{3,5}$).

TABLE 3 .

Characteristics of compound (IIIa), (IIIb), (IVa), (IVb)

Compound	Found, %					Calcd. %				
	C	Cl	F	N	S	C	Cl	F	N	S
$C_6Cl_2F_5NO_2S_2$ (IIIa)	21.2	20.2	27.0	3.80	18.9	20.7	20.4	27.3	4.30	18.4
$C_6Cl_2F_5NO_2SSe$ (IIIb)	17.9	7.50	24.5		8.50	18.2	6.90	24.1		8.10
$C_7Cl_2F_5NOS$ (IVa)	27.4	22.2	29.8	4.80	10.9	26.9	22.7	30.4	4.50	10.3
$C_7Cl_2F_5NOSe$ (IVb)	23.0	19.8	27.0	4.23		23.4	19.8	26.5	3.90	

Se,Se-Dichloro-N-pentafluorobenzoylselenoimine, (IVb), (n. c.)

A solution of 2.8 g pentafluorobenzoic acid N,N-dichloroamide in 10 ml CH_2Cl_2 is added at 0° to a stirred suspension of 0.79 g selenium powder in 10 ml CH_2Cl_2. After 2 h stirring at 0° the obtained solution is filtered and evaporated in vacuo, to yield selenoimine (IVb) (98 %), m. p. 113-115°. ^{19}F NMR spectrum: -23.8 (2 $F_{2,6}$), - 13.5 (F_4), - 1.8 (2 $F_{3,5}$).

Reaction of polyfluorinated N,N-dichloroamines (Va-c) with sulphur and selenium.

(a). A solution of fresh-distilled 4-N,N-dichloroamino-2,3,5,6-tetrafluoropyridine in 10 ml CH_2Cl_2 is added dropwise at 0° to a stirred suspension of 1.58 g selenium powder in 25 ml CH_2Cl_2. The reaction mixture is stirred during 30 minutes at 0°, then 30 minutes at 20°. After concentrating at reduced pressure, the residue is separated on the column with silica gel and the mixture of pentane - diethyl ether (10:1) is used as an eluating solvent. After the evaporation of solvent the orange crystals are sublimed, to yield azocompound (Vc) (3.08 g, 94 % on dichloroamine), m. p. 147-148° (lit. [23] 147°). (Found: N, 17.0; M (mass-spectrum) 328. $C_{10}F_8N_4$ requires N 17.1; M 328).

(b). A mixture of 2.35 g 4-N,N-dichloroamino-2,3,5,6-tetrafluoropyridine with 0.32 g sulphur powder is heated at reduced pressure up to beginning of reaction (~90°), which is accompainied by the crystallization of the reaction mixture. The crystalline solid is cooled to room temperature, washed by small amount of pentane and dissolved in ether. After filtration the ether is evaporated and the residue is sublimed in vacuo, to yield azocompound (Vc) (1.43 g, 37 %), m. p. 147-148°. IR, UV, Raman and ^{19}F NMR spectra are identical to those for product of the above reaction with selenium and the authentical sample obtained by [23].

(c). Compounds (Va) and (Vb) are synthethized by the same methods. Their melting points and spectral data coincide with those described in the literature [24, 25].

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