Journal of Fluorine Chemistry, 17 (1981) 103–111

Received: March 3, 1980

^{15}N AND ^{31}P NMR SPECTROSCOPY OF TRICLOROPHOSPHAZO-POLYFLUOROARYLS.

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SUMMARY

^{15}N and ^{31}P NMR spectra of trichlorophosphazopolyfluoroaryls obtained by the interaction between polyfluoroanilines and PCl_5 in benzene (Kirsanov reaction) have been investigated. The interconversions of monomeric and dimeric forms of trichlorophosphazopolyfluoroaryls by ^{31}P NMR are also shown.

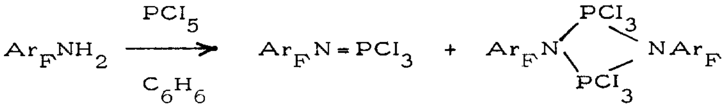
INTRODUCTION

The investigation of the nature of N–P bonds in phosphazo-compounds with the help of physical methods has not been carried out very extensively, and conclusions about it have so far been made mainly by studying of their chemical behavior [1]. The ability of trichlorophosphazoaryls to exist in dimer and monomer form has been shown to depend on the electronic effects of the aryl group. The melting or the solution of dimers in non-polar solvents leads either to their total depolymerization or to the formation of an equilibrium mixture of dimer and monomer [1,2]. NMR spectroscopy on the ^{15}N and ^{31}P nuclei can serve as a convenient method for the investigation of such transformations and for the establishment of the structures of dimer and monomer forms. Owing to the insufficiently developed theory of chemical shifts for the heavy nuclei, the values of chemical shifts for the various forms of trichlorophosphazoaryls can't be predicted thoroughly at the present time. Therefore the accumulation and establishment of spectrostructural correlation from NMR ^{15}N and ^{31}P spectral data represent an important problem.

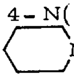
RESULTS AND DISCUSSION

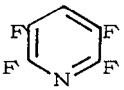
In this paper we have undertaken an investigation of NMR ^{15}N and ^{31}P spectra in a series of trichlorophosphazopolyfluoroaryls to reveal the factors determining the chemical shifts of the phosphorus and nitrogen in the NMR spectra and the stability of the monomer and dimer forms of trichlorophosphazoaryls. Study of the 4-substituted derivatives of trichlorophosphazopolyfluoroaryls is of particular interest, because of the constant substitution situation close to the group P=N, showing the influence of varying substituents as a relationship to the effects of π-conjugation.

Trichlorophosphazopolyfluoroaryls were synthetized by the Kirsanov reaction of the corresponding polyfluorinated anilines with PCl_5 in benzene.

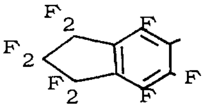


Ia-r IIa-r IIIa-e

Ar_F = 4-$N(C_2H_5)_2C_6F_4$ (Ia,IIa,IIIa), 4-$N(CH_3)_2C_6F_4$ (Ib,IIb,IIIb), 4-$CH_3OC_6F_4$ (Ic,IIc,IIIc), 4-N-C_6F_4 (Id,IId,IIId), 4-$CH_3C_6F_4$ (Ie,IIe,IIIe), 4-Cl-C_6F_4 (If, IIf), C_6F_5 (Ig,IIg,IIIg 4-H-C_6F_4 (Ih,IIh,IIIh), 4-$CF_3C_6F_4$ (Ik,IIk), 4-CN-C_6F_4 (Il,IIl), 4-NO_2-C_6F_4 (Im,IIm), 4-CH_3SO_2-C_6F_4 (In,IIn), 2-NO_2-C_6F_4 (Io,IIo), 2-NO_2-5-CF_3-C_6F_3 (Ip,IIp),



(Iq,IIq),



(Ir,IIr)

Trichlorophosphazopentafluorophenyl has been shown earlier in our laboratory to exist in the individual state as dimer (IIIg), whereas in solutions in non-polar solvents it reverts to monomer form (IIg) [3-5]. Therefore the establishment of the structures of the synthethized phosphazocompounds was carried out for each compound. In the NMR ^{31}P spectra of the solutions of trichlorophosphazocompounds obtained from anilines (Ia-f), containing electron-donor substituents, two signals are observed (Table 1), which can be attributed to the dimer (IIIa-e) and monomer (IIa-e) forms.

TABLE 1.
^{31}P and ^{15}N NMR data of trichlorophosphazopolyfluoroaryls in benzene at 30^{o}.

Compounds	Chemical shift, p.p.m		$J_{^{15}N-^{31}P}$, Hz
	$\delta_{^{31}P}$ from 85 % H_3PO_4*	$\delta_{^{15}N}$ from CH_3NO_2 **	
IIa	33.6		
IIb	33.5		
IIc	32.4	251.4	22.5
IId	33.5		
IIe	32.9	245.5	21.4
IIf	29.4	244.9	20.1
II g	30.3	252.0	20.1
II h	30.6 [6]		
II k	22.8	245.5	16.3
II l	19.9	244.4	16.4
II m	18.6	245.5	16.3
II n	17.6		
II o	22.0	244.3	12.6
II p	21.5	248.6	11.3
II q	16.5	242.2	17.6
II r	22.2	243.6	15.1
III a	71.0		
III b	68.7		
III c	71.8		
III d	70.1		
III e	73.0		

* Chemical shifts ^{31}P in high field from 85 % H_3PO_4 are positive;
** Chemical shifts ^{15}N in high field from CH_3NO_2 are positive.

The fact that the relation dimer-monomer depends on the temperature. (Table 2), proves that this relation is controlled by thermodynamic factors. At the same time the proportion of dimer form increases for the strong electron-donor substituents. In the case of polyfluoroanilines containing strong electron-acceptor substituents in the para position to the amino group, only monomer forms of trichlorophosphazopolyfluoroaryls (II k-n) are obtained under the action of PCl_5 on the former.

TABLE 2.

The influence of the temperature on the dimer-monomer equilibrium for trichlorophosphazopolyfluoroaryls in benzene.

Compound	Temperature, °C	Reaction mixture, %	
		monomer	dimer
II a	30	60	40
	60	78	22
II b	30	79	21
	60	84	16
II e	30	82	18
	60	95	5

The aromatic amines containing an ortho-nitro group are known to form only monomeric trichlorophosphazoaryls under the action of PCl_5 [1]. The formation of the monomer forms of phosphazocompounds (II o, and II p respectively) would be expected to occur in the reaction of 2-nitro-3,4,5,6-tetrafluoroaniline (I o) and 2-nitro-5-trifluoromethyl-3,4,6-trifluoroaniline (I p) with PCl_5 in benzene. The compounds (II o) and (II p) really correspond to the monomeric form of trichlorophosphazoaryls by their chemical properties and spectral data.

The electron acceptor character of the substituent at the nitrogen atom is an important factor determining the relative stability of the various trichlorophosphazocompounds forms [1]. The increase of that parameter has been shown to facilitate the preferable formation of the monomeric form. Therefore the formation of trichlorophosphazocompounds (II q) and (II r) in the monomeric form could be predicted in the reaction of PCl_5 with 4-amino-2,3,5,6-tetrafluoropyridine (I q) and 5-aminononafluoroindane (I r). That prediction was proved experimentally.

^{31}P and ^{15}N NMR data for trichlorophosphazoaryls have been shown in the Table 1. The change in the chemical shifts for phosphorus depends on the distribution of the electron density in the molecule with the increase of electron-donating power of the substituent. Attention must be paid to the presence of phosphorus signals both of monomeric and dimeric forms of trichlorophosphazopolyfluoroaryls at lower field with respect to their hydrocarbon analoques [7]. The ^{31}P chemical shift in the spectrum of a solution of trichlorophosphazophenyl in tetrachloroethane is for the monomeric form equal to 47.6 ppm and 80.2 ppm - for dimeric one. The ^{31}P chemical shift of the monomeric form of the compound (II g) in benzene is 30.3 ppm , while for the known dimeric forms, of trichlorophosphazoaryls it is equal to 68.7-73.0 ppm (Table 1). This is caused by the greater electron - withdrawal properties of polyfluoroaryl substituents relative to the phenyl group. The pentafluorophenyl ring is known to exhibit a stronger σ- acceptor character than the phenyl one while the π - effects of former are negligible [8]. Therefore for the case of a constant substituent at the phosphorus atom the decreasing of electronegativity of the substituents at the nitrogen atom must lead to a greater double bond character of the P=N bond. In agreement with the theoretical conceptions about the nature of ^{31}P chemical shift [9] the additive screening of the phosphorus atom must increase in the same direction and the signal of the phosphorus atom must be displaced to upper field.

The consideration of the ^{31}P NMR data for monomeric forms of 4- substituted trichlorophosphazotetrafluorophenyls in which the influence of the substituent on the double bond character of the P=N bond is due to π- conjugation effects shows that electron- withdrawing substituents shift the ^{31}P signal to the lower field relative to electron- donating ones. Thus the decreased degree of the aryl substituent conjugation with the P=N fragment is observed with the presence of electron- donating substituent in the benzene ring. It leads according to the conclusions of Kirsanov et.al. [10] to the facilitating of the dimerization of trichlorophosphazoaryls containing substituents with strong elecrton- donating properties. Our data support that conclusion, the more electron- donating substituents in the molecules of trichlorophosphazoaryls promote the greater percentage of dimeric form (Table 2).

The increasing of conjugation of the aryl substituent with the P=N fragment due to a strong electron- withdrawing substituent in the benzene ring leads to a lower degree of double bond character between phosphorus and nitrogen and to the lower field shift of ^{31}P signal.The P=N bond has in that case more ionic character with respect to unsubstituted compounds and the dimerization of such trichlorophosphazopolyfluoroaryls becomes disadvantageous. The fact that the tetracoordinated state for the pentavalent phosphorus is more preferable energetically than the pentacoordinated one [1] allows us to confirm that a highly ionic character of the P=N bond is necessary for the existence of monomeric form. The latter can be caused by the greater electronegativity of the aryl substituent as a whole, for instance as a result of the action of the strong electron-withdrawing ring substituents. All trichlorophosphazocompounds containing electron-withdrawing substituents as strong as the CF_3-group are present just as the monomeric form (Table 1). The compounds (II o-r) are of course, also monomers.

A satisfactory correlation must be noticed to exist between the ^{31}P chemical shift and Hammett constants of substituents in the compounds (I a-n).

$$\delta\,^{31}P = 11.1\ \sigma_{para} + 2.0$$

$$r = 0.967,\ s = 2.12,\ n = 12$$

The signals of phosphorus atom in the monomeric forms of trichlorophosphazoaryls are found to be split to triplets due to the spin-spin coupling between phosphorus and ortho-fluorine atoms. The increase of the corresponding coupling constants is observed with the increase of electronegativity of substituent (6.2, 6.5, 6.9 Hz respectively for the series $CF_3 < CH_3SO_2 < NO_2$). The values of that coupling for the compounds (II g) and (II r) are 5.6 and 4.4 Hz respectively.

The phosphorus atom signal of the dimeric form of trichlorophosphazoaryls is observed in the upper field with respect to the monomeric one (Table 1). The ^{31}P shifts of the dimeric forms of pentafluorophenyldifluorophosphazomethyl [11] and bis(pentafluorophenyl)fluorophosphazomethyl [12] are known to be equal to 65.6 and 80.0 ppm respectively. Therefore the chemical shifts of ^{31}P may indicated the assignment of the phosphazocompounds to monomeric or dimeric forms.

The chemical shifts of ^{15}N nuclei, as follows from our data, are less sensitive to ring substituent influence (Table 1). At the same time the observed signal gives a doublet due to the spin-spin interaction between nitrogen and phosphorus atoms. The signs of the coupling constants have not been determined. Nevertheless, the absolute values of these coupling constants are sensitive to the electronegativity of substituents (Table 1). They are decreased for the strong electron-withdrawing substituents with respect to weak ones which is found to be in accordance with the data [13]. Steric factors also seem to have influence upon the values of these constants. Thus, for the ortho- and para-substituted derivatives the constant changes from 12.6 to 16.3 Hz respectively. The value of that constant can indicate the presence of P=N fragment being higher for the cyclic forms [14, 15].

EXPERIMENTAL

^{19}F NMR spectra were recorded on Varian A 60/56 A spectrometer at 56.4 MHz (ppm from internal C_6F_6); ^{31}P and ^{15}N NMR spectra were recorded on a Bruker HX- 90 spectrometer at 36.4 and 9.12 MHz respectively. The pure compounds or their solutions in benzene were put into a 5 mm tube placed into a 10 mm one with D_2O. The signal of latter served as a signal of deuterium stabilization. The optimal regime of work of the spectrometer was used. The following parameters were used for ^{31}P spectra : pulse width 12 μs (90° - pulse- 17 μs), the delay time- 3 s. The value of memory for the data accumulation was equal to 8 k. The sweep width was 3000 Hz (in some cases 6000 Hz was used). For ^{15}N nuclei the parameters were the next : sweep width 6024 Hz, pulse width 20 μs (90°-pulse- 30 μs), the delay time- 8 s. The laboratory computer B- NC 12 was used for the Fourier- transformation and the optimization of spectra.

Labeled compounds used for recording of ^{15}N NMR spectra were synthethized from anilines obtained by interaction of polyfluorinated aromatic compounds with 30 % aqueous solution of $^{15}NH_3$ (enrichment by ^{15}N 95- 96 %) [16]. The degree of ^{15}N enrichment of obtained compounds has been found equal to 95- 96 % by mass- spectral method.

Trichlorophosphazocompounds have been prepared by known reaction of polyfluorinated anilines with PCl_5 in benzene [5]. The physical constants and analytical data of all new compounds have been listed in Table 3.

REFERENCES

1 G.I.Derkach, I.N. Zhmurova, A.V. Kirsanov, V.I. Shevchenko, A.S. Shtepanek, Phosphazocompounds, Naukova Dumka, Kiev, 1965, p. 177.

2 Yu.P.Egorov, I.F. Tsimbal, Yu.Ya. Borovikov, I.N. Zhmurova, V.G.Yurchenko, Theor. Exp. Khim., 15 (1979) 324.

3 Yu.G. Shermolovich, O.M. Polumbrik, L.N. Markovsky, E.P. Saenko, G.G.Furin, G.G. Yakobson, Zh.Org.Knim., 13 (1977) 2589.

4 T.D.Petrova, V.E.Platonov, T.I.Savchenko, L.M.Meshalkina, Izv.Akad.Nauk S.S.S.R., Ser. Khim., (1978) 2635.

TABLE 3.

New trichlorophosphazocompounds - physical and analytical properties.

Compound	B.p. (pressure)	Yield %	^{19}F, ppm*	Found, % C	Found, % F	Found, % P	Calcd. % C	Calcd. % F	Calcd. % P
$C_8H_6Cl_3F_4N_2P$ (II b)	98 - 99 (3)	75	- 11.0	27.34	22.00	9.44	27.95	22.13	9.02
$C_7H_3Cl_3F_4NOP$ (II c)	92 - 93 (3)	88	- 11.0, - 3.0	25.30	22.84	9.02	25.42	23.00	9.38
$C_{11}H_{10}Cl_3F_4N_2P$ (II d)	120 - 122 (3)	80	- 11.0	34.20	19.62	7.83	34.42	19.82	8.08
$C_7H_3Cl_3F_4NP$ (II e)	152 - 154 (7)	90	- 17.4, - 11.3	26.58	24.00	9.53	26.71	24.16	9.85
$C_7Cl_3F_4N_2P$ (II l)	118 - 120 (3)	87	- 27.9, - 15.6	25.70	23.05	9.40	25.81	23.35	9.52
(II m)	150 - 152 (3)	90	- 14.5, - 14.2	20.62	21.74	8.53	20.84	22.00	8.97
$C_6Cl_3F_4N_2O_2P$ (II o)	150 - 152 (3)	94	- 19.7, - 16.2, - 13.8, - 3.2	20.71	21.80	8.62			
$C_7Cl_3F_6N_2O_2P$ (II p)	114 - 115 (3)	95	- 40.7, - 21.6, - 13.6	21.09	28.64	7.70	21.24	28.82	7.84
$C_5Cl_3F_4N_2P$ (II q)	85 - 86 (3)	96	- 74.1, - 14.3	19.80	25.00	10.11	19.90	25.21	10.28
$C_9Cl_3F_9NP$ (II r)	104 - 106 (6)	96	- 57.5 (2), - 56.5 (2), - 36.1 (1), - 33.6 (2), - 30.7 (1), - 21.5 (1)	24.94	39.51	7.00	25.09	39.72	7.20

* The relative intensity of signal has been noted in brackets.

5 Yu.G. Shermolovich, E.A. Romanenko, T.D. Petrova, M.I. Povolotsky, G.G. Furin, Izv. Sib. Otd. Akad. Nauk S.S.S.R., Ser. Khim. Nauk (1980) (4) 141.

6 K. Ulvary, M. Bermann, Monatsh. Chem., 99 (1968) 2369.

7 H. A. Klein, N. P. Latscha, Z. anorg. allg. Chem., 406 (1974) 214.

8 R. Filler, in P. Tarrant (Editor), Fluorine Chemistry Rev., vol. 8, Marcel Dekker, Interscience, New York, 1977, p. 1.

9 J.R. van Weser and J.H. Letcher, in M. Grayson and E.J. Griffith (Editor), Topics in Phosphorus Chemistry, vol. 5, Interscience Publishirs, New York, 1967, p. 169.

10 I.N. Zhmurova, A.V. Kirsanov, Zh. Org. Khim., 30 (1960) 3044.

11 M. Fild, W.S. Sheldrick, T. Stankiewicz, Z. anorg. allg. Chem. 415 (1975) 43.

12 M. Fild, R. Kurpat, T. Stankiewicz, Z. anorg. allg. Chem., 439 (1978) 145.

13 G.A. Gray, T.A. Albright, J. Am. Chem. Soc., 98 (1976) 3857.

14 J.R. Schweiger, A.H. Cowley, E.A. Cohen, P.A. Kroon, S.L. Manatt, J. Am. Chem. Soc., 96 (1974) 7122.

15 B. Thomas, G. Grossmann, Z. anorg. allg. Chem., 448 (1979) 107.

16 Syntheses of Fluoroorganic Compounds. I.L. Knunyants and G.G. Yakobson (Editor), Khimia Publishers, Moskow, 1977, p. 190.