fluoromethane (δ_F). Phosphorus chemical shifts are reported in ppm relative to external 85% phosphoric acid (δ_P). It was noticed that monofluorophosphoric and (especially) difluorophosphoric acids reacted with glass, so 5-mm quartz nmr sample tubes were used in experiments with fluorophosphoryl compounds as precursors and in acid solutions. Direct ^{31}P nmr spectra were recorded, except that the ^{31}P chemical shift of phosphinic fluoride was obtained by the indor technique.[2d] Wide-range HR-mode direct ^{31}P spectroscopy (sweep widths 2000–13,000 Hz) was useful in monitoring the various reactions; the HA mode was used whenever possible to determine more precisely individual peak positions. All spectra could be interpreted on a first-order basis. The use of fluorosulfuric acid as a reaction medium introduced into ^1H spectra, besides absorption peaks due to protonated molecules and reaction products, only an extra low-field singlet absorption (δ 10–13); in ^{19}F spectra the solvent absorption singlet at δ_F *ca.* −40 was well removed from absorptions of fluorophosphorus species.

Preparation of Ions.—Most of the phosphorus compounds were dissolved in a tenfold molar excess of fluorosulfuric acid or Magic Acid solution with stirring and ice bath cooling. Ten per cent (w/w) solutions of potassium pyrophosphate and polyphosphoric acid in fluorosulfuric acid were also prepared in this manner. Dry Ice–acetone cooling was used to suppress decomposition in the cases of phosphonic and phosphinic acids. The same cooling was used to condense phosphorus oxyfluoride for use in making mixtures and to aid dissolution of phosphorus trifluoride as it was bubbled through fluorosulfuric acid.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER 8, BRITISH COLUMBIA, CANADA

Phosphonitrilic Derivatives. XX.[1] The Electronic Properties of Fluorophosphonitrilic Substituents

BY T. CHIVERS AND N. L. PADDOCK*[2]

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Three series of (fluoroaryl)fluorophosphonitriles have been prepared, of the type $N_nP_nF_{2n-1}Ar_F$ (n = 3–8; Ar_F = C_6F_5, p-FC_6H_4, m-FC_6H_4). The ^{19}F nmr spectra of the fluoroaryl groups indicate strong inductive and conjugative electron withdrawals by the fluorophosphonitrilic ring, both effects being similar to those exerted by a cyano group. For the pentafluorophenyl series, the alternation of $\delta^F{}_p - \delta^F{}_m$ as the phosphonitrilic ring size is increased is consistent with conjugation of the homomorphic π system of the pentafluorophenyl group with a homomorphic π system in the phosphonitrilic ring.

Among the many series of cyclic inorganic compounds, phosphonitrilic derivatives are distinguished by the number and variety of the substitution reactions which they undergo and by the different types of orientation pattern observed. Substituents can be broadly classified into electron withdrawing and electron releasing, but such a division, while useful, is too simple to explain all the known facts. On this basis it might be expected, for instance, that the tendency to geminal substitution of the chlorophosphonitriles by amines would decrease with increasing base strength of the amine,[3] but this is not always so; for example, the course of substitution of $N_3P_3Cl_6$ by *tert*-butylamine (pK_{BH^+} = 10.45) is exclusively geminal,[4] whereas aniline (pK_{BH^+} = 4.58), although giving predominantly geminal isomers with $N_3P_3Cl_6$, reacts nongeminally with $N_4P_4Cl_8$.[5] There is clearly a need for a more detailed study of reaction mechanisms and of the interaction of the phosphonitrilic ring with its substituents. The results can be expected to differ from those found for benzene derivatives because the atoms and their polarizabilities are different and the reaction centers are bifunctional. The π interactions, both inside and outside the ring, can also be of a different type.

Inductive effects require no net electron transfer to or from the ring, and appear to form an adequate basis for the explanation of some substitutional behavior. For instance, the predominantly geminal antipodal substitution of octafluorocyclotetraphosphonitrile by methyllithium, although unexpected in terms of purely electrostatic or σ-inductive interactions, follows naturally from a consideration of the perturbation of the π-electron density of the fluorophosphonitrile by the methyl substituent, the π-inductive effect being simulated by a reduction of the electronegativity of the substituted phosphorus atom.[6] Similarly, the variations in the lengths of the ring bonds in *gem*-$N_4P_4F_6Me_2$, which are much greater than in benzene derivatives, correlate well with polarizability calculations based on the same model.[7] By contrast, π-conjugative effects are less well established. Neither spectroscopic nor structural evidence indicates strong conjugative interaction between a phenyl group and a phosphonitrilic ring; for example, the P–C bond length is nearly the same in $N_3P_3Ph_6$ (1.804 Å[8]) as it is in $N_4P_4Me_8$ (1.80 Å[9]). The

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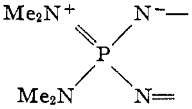
crystal structures of $N_4P_4(NMe_2)_8$[10] and $N_6P_6(NMe_2)_{12}$,[11] on the other hand, show evidence of appreciable exocyclic π bonding in the sense



which is enhanced when the ring is protonated, even at a remote site.[12] Electronic influences of potential chemical importance can therefore be transmitted between the ring and an exocyclic π system and can have important directing effects on substitution.[13] From these results, it seemed likely that conjugative interactions would be most easily detected when the phosphonitrile was a strong acceptor, and we have therefore investigated the interactions of fluorophosphonitrilic rings with attached fluoroaryl groups, in which the substituents act as sensitive and well-established probes of π-electron density. The spirit of the work has been to investigate the behavior of the phosphonitriles as substituents in the benzene ring, rather than conversely, and, in part, to place them in a wider chemical perspective. Apart from their expected acceptor properties, the choice of fluorophosphonitriles is appropriate, because the existence in them of a delocalized π system has been established by measurements of ionization potentials,[14] and its chemical[6] and structural[7] effects have been demonstrated. Conjugation with a benzene ring is likely to show more clearly than with other phosphonitrilic derivatives, since the rings in both $N_3P_3F_6$ and $N_4P_4F_8$ are planar,[15,16] and that in $N_6P_6F_{12}$, on the evidence of its vibrational spectra, is nearly so, at least in the vapor phase.[17] A preliminary account of some of this work has been published.[18]

Experimental Section

Phosphonitrilic fluorides were prepared as described previously.[19] Pentafluorobenzene, *p*-bromofluorobenzene, *m*-bromofluorobenzene, and *n*-butyllithium in hexane were obtained commercially.

Preparative Procedures.—With the exception of $N_3P_3F_5(p\text{-}FC_6H_4)$ and $N_4P_4F_7(p\text{-}FC_6H_4)$, the experimental procedure was essentially the same for each member of a series, so only a typical example is recorded in detail; comparable reactions have been used for the preparation of the series $N_3P_3F_{6-x}Ph_x$ (x = 1–5).[20] Monosubstituted derivatives were obtained in 20–30% yield and were easily separated from more highly substituted products by distillation *in vacuo*. For Ar = *p*-FC_6H_4 and n = 3, 4, only the disubstituted compounds $N_nP_nF_{2n-2}Ar_2$ were obtained when the reaction was carried out by the dropwise addition of an ethereal solution of the phosphonitrilic fluoride to an ethereal solution of *p*-fluorophenyllithium. In these cases, monosubstituted derivatives were obtained by reverse addition, and it is probable that higher yields of the other monosubstituted compounds could be achieved in this way.

(Pentafluorophenyl)pentafluorocyclotriphosphonitrile.—*n*-Butyllithium (0.015 mol) in hexane (6.8 ml) was added dropwise to pentafluorobenzene (2.65 g, 0.016 mol) in diethyl ether (50 ml) at −78°. The reaction mixture was stirred for 30 min before addition of hexafluorocyclotriphosphonitrile (3.84 g, 0.015 mol) in ether (30 ml). Stirring was continued at −78° for 5 hr and then at 25° for 10 hr. The lithium salts were removed by filtration, and the solvents were removed at 20 mm, to give a pale yellow liquid (3.47 g) from which (pentafluorophenyl)-pentafluorocyclotriphosphonitrile $N_3P_3F_5(C_6F_5)$ was obtained by distillation as a colorless liquid (1.35 g, 23%).

(*p*-Fluorophenyl)pentafluorocyclotriphosphonitrile.—*n*-Butyllithium (0.015 mol) in hexane (6.4 ml) was added dropwise to *p*-bromofluorobenzene (2.59 g, 0.015 mol) in diethyl ether (70 ml) at −78°. The reaction mixture was stirred for 45 min and was then added dropwise, by syringe, to hexafluorocyclotriphosphonitrile (4.38 g, 0.018 mol) in ether (70 ml) at 0° The addition took 30 min, the reaction mixture being stirred at 25° for a further 2 hr. Lithium salts were removed by filtration, and the solvents by evaporation at 20 mm. Distillation of the colorless liquid residue gave (*p*-fluorophenyl)pentafluorocyclotriphosphonitrile $N_3P_3F_5(p\text{-}FC_6H_4)$ as a colorless liquid (0.89 g, 14%). (*p*-Fluorophenyl)heptafluorocyclotetraphosphonitrile was prepared similarly.

Measurements.—Microanalyses were carried out by standard methods and, with boiling points, are given in Table I. Fluorine nmr spectra of solutions in CCl_3F at 25° (concentration range 20–40% by volume) were measured at 94.07 MHz on a Varian HA100 spectrometer. The shifts were found to vary by less than 0.1 ppm over the concentration range 10–50%.

TABLE I

ANALYSES AND BOILING POINTS OF (FLUOROARYL)FLUOROPHOSPHONITRILES

		%					
		Calcd			Found		
	Bp, °C (mm)	C	N	F	C	N	F
$N_3P_3F_5(C_6F_5)$	40–43 (0.05)	18.2	10.6	47.9	18.2	10.5	47.9
$N_4P_4F_7(C_6F_5)$	48–50 (0.007)	15.0	11.7	47.5	14.9	11.8	. . .
$N_5P_5F_9(C_6F_5)$	65–66 (0.01)	12.8	12.4	47.2	12.8	12.3	47.0
$N_6P_6F_{11}(C_6F_5)$	73–74 (0.02)	11.2	13.0	47.1	11.3	13.2	46.6
$N_7P_7F_{13}(C_6F_5)$	85–86 (0.02)	9.9	13.5	46.9	9.9	13.6	46.7
$N_8P_8F_{15}(C_6F_5)$	92–94 (0.03)	8.9	13.8	46.8	8.9	13.9	47.2

		%			
		Calcd		Found	
		C	H	C	H
$N_3P_3F_5(m\text{-}FC_6H_4)$	44 (0.03)	22.2	1.2	22.0	1.2
$N_4P_4F_7(m\text{-}FC_6H_4)$	47–48 (0.02)	17.7	1.0	17.6	1.0
$N_5P_5F_9(m\text{-}FC_6H_4)$	59–60 (0.03)	14.7	0.8	14.5	0.8
$N_6P_6F_{11}(m\text{-}FC_6H_4)$	67–68 (0.05)	12.6	0.7	12.5	0.7
$N_7P_7F_{13}(m\text{-}FC_6H_4)$	71–73 (0.04)	11.0	0.6	11.0	0.7
$N_8P_8F_{15}(m\text{-}FC_6H_4)$	80–82 (0.03)	9.7	0.5	9.7	0.6
$N_3P_3F_5(p\text{-}FC_6H_4)$	114–115 (50)	22.2	1.2	22.1	1.5
$N_4P_4F_7(p\text{-}FC_6H_4)$	70–71 (3)	17.7	1.0	18.3	1.2
$N_5P_5F_9(p\text{-}FC_6H_4)$	45 (0.03)	14.7	0.8	14.3	0.9
$N_6P_6F_{11}(p\text{-}FC_6H_4)$	58–60 (0.04)	12.6	0.7	12.5	0.8
$N_7P_7F_{13}(p\text{-}FC_6H_4)$	72–74 (0.03)	11.0	0.6	10.5	0.7
$N_8P_8F_{15}(p\text{-}FC_6H_4)$	66–67 (0.005)	9.7	0.5	9.2	0.6

Results and Discussion

The presence of fluorine atoms in both the phenyl and phosphonitrilic rings provides, in principle, a wealth of information for the interpretation of electronic effects. We shall rely chiefly on the fluoroaryl shifts, which have been studied extensively both theoretically and experimentally, but a number of regularities also appear in the phosphonitrilic part of the spectrum which illustrate some otherwise recognized features of pπ–dπ bonding. All the PF_2 groups in a particular unsubstituted phosphonitrilic fluoride are equivalent; details of their ^{19}F nmr spectra are given in Table II. The shifts decrease with increase in ring size, but not regularly; they oscillate, in the sense that the shifts of the even-numbered rings exceed the mean shift of their odd-numbered neighbors, and the same is true of the PF(X) and PF_2 resonances of the (*p*-fluoroaryl)fluorophosphonitriles

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TABLE II

CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS (HERTZ) OF THE PHOSPHONITRILIC FLUORIDES $(NPF_2)_n$

	n						
	3	4	5	6	7	8	9
δ^F	71.90	71.85	69.05	68.60	68.00	68.00	67.95
J'_{PF}	868	836	874	885	901	903	901

[a] Neat liquid, ppm, relative to internal CCl_3F, to nearest 0.05 ppm.

(Figure 1). The oscillatory behavior can be given a qualitative explanation. Interactions of the pπ–dπ type may be either heteromorphic or homomorphic,[21] and the π-electron density at fluorine is expected to vary smoothly with ring size for the first and to oscillate for the second. For particular arbitrary values of the relevant parameters, π-charge densities at fluorine are given in Figure 2. If we assume, temporarily, that chemical shifts reflect π-electron densities, it can be seen that an additive combination of homomorphic and heteromorphic contributions could give the oscillation about a descending curve characteristic of the phosphonitrilic fluorides. The monosubstituted derivatives (Figure 1) show additional features. The oscillatory behavior remains, as it does also for the PF(X) and PF_2 groups in other monosubstituted phosphonitrilic fluorides[1] (X = Br, Cl, NCS, NMe_2), so that, although the balance of the π systems is clearly altered by substitution, their essential nature is unchanged. Further, all the fluorine resonances are shifted downfield relative to that of the simple fluoride of the same ring size, the PF(X) group most, then the nearest pair of PF_2 groups, where distinguishable, and then the remaining PF_2 groups. The general lowering is probably to be attributed to a reduction in mean ligand electronegativity, so expanding the phosphorus d orbitals, tending to localize π electrons on nitrogen, and weakening the π system generally (ν_{as}(PNP) for $N_nP_nF_{2n-1}$-(p-FC_6H_4) is less, by 20–30 cm^{-1}, than in the parent fluorides). Such an effect, in the reverse sense of the enhancement of the acceptor properties of the phosphorus by electronegative ligands, has been detected by Rakshys, Taft, and Sheppard[22] and here prevents more than a qualitative interpretation of the fluorine shifts of the phosphonitrilic ring.

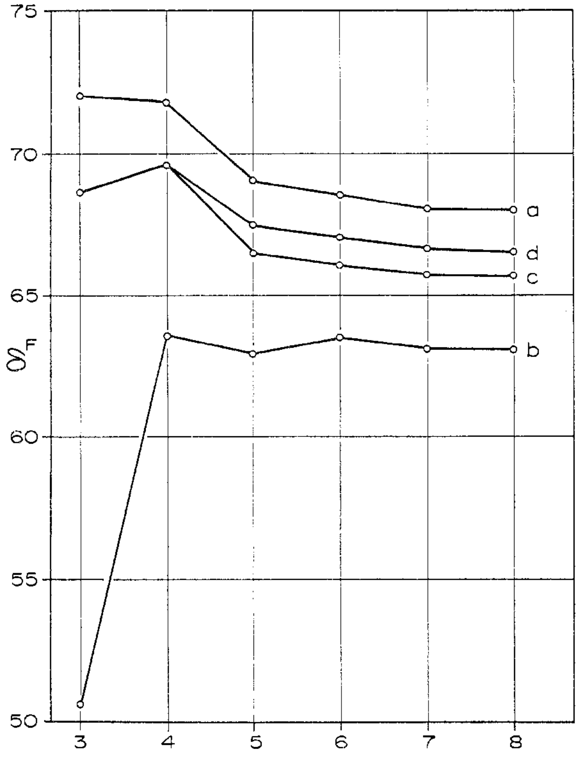

Figure 1.—The ^{19}F chemical shifts (relative to $CFCl_3$) of (a) $(NPF_2)_n$, (b) PFX, (c) PF_2 nearest to PFX, and (d) remote PF_2 groups in $N_nP_nF_{2n-1}(p\text{-}FC_6H_4)$.

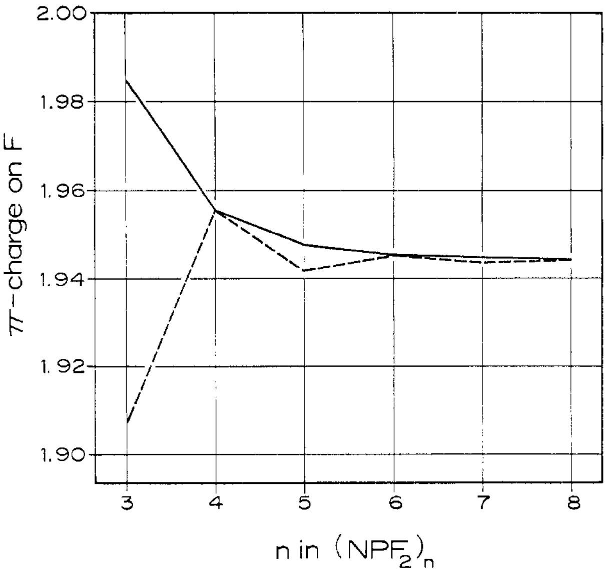

Figure 2.—Calculated π charge on fluorine in $(NPF_2)_n$ (HMO calculations, $\alpha_F = \alpha_N$, $\alpha_N = \alpha_P + \beta_{PN}$, $\beta_{PN} = \beta_{PF}$): solid line, heteromorphic interactions; dashed line, homomorphic interactions.

The results of Figure 1 show that the influence of a substituent on a fluorine shift extends for at least four bonds, though as stated, the type of electronic interaction cannot be decided. The spectra of the fluoroaryl groups are more informative. The sensitivity of the shielding of fluorine to small changes in molecular environment is well known, and for many groups the interpretation of the fluorine chemical shifts of m-fluorophenyl and p-fluorophenyl derivatives in terms of π-electron densities has been justified theoretically[23–25] and the shielding parameters correlated[26] with the Taft reactivity parameters σ_I and σ_R^0. More recently,[27] it has been found that there is a good correlation between σ_R^0 and $\Sigma\Delta q(\pi)$, as obtained from CNDO/2 calculations, so verifying that σ_R^0 is a measure of π-charge transfer and hence of conjugative interactions. The parameters have also been shown to be applicable to substitution at a phosphorus center.[22] The ^{19}F chemical shifts of the fluorophenyl parts of the new compounds are given in Table III. By comparison with the shifts of fluorobenzene (δ^F 113.3 ppm) and pentafluorobenzene ($\delta^F_{o,m,p}$ 138.7, 162.6, 154.3 ppm) it can

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TABLE III
^{19}F CHEMICAL SHIFTS[a] OF (MONOFLUOROPHENYL)- AND (PENTAFLUOROPHENYL)FLUOROPHOSPHONITRILES[b]

	δ^F_p	δ^F_m	δ^F_o	$-(\delta^F_p - \delta^F_m)$
$N_3P_3F_5(FC_6H_4)$	102.7	110.0	...	7.3
$N_4P_4F_7(FC_6H_4)$	102.9	110.1	...	7.2
$N_5P_5F_9(FC_6H_4)$	103.1	110.0	...	6.9
$N_6P_6F_{11}(FC_6H_4)$	103.2	110.0	...	6.8
$N_7P_7F_{13}(FC_6H_4)$	103.3	110.0	...	6.7
$N_8P_8F_{15}(FC_6H_4)$	103.3	110.0	...	6.7
$N_3P_3F_5(C_6F_5)$	143.8	159.1	132.1	15.3
$N_4P_4F_7(C_6F_5)$	144.6	159.3	132.1	14.7
$N_5P_5F_9(C_6F_5)$	143.3	159.4	131.9	16.1
$N_6P_6F_{11}(C_6F_5)$	144.4	159.4	131.7	15.0
$N_7P_7F_{13}(C_6F_5)$	144.4	159.4	131.6	15.0
$N_8P_8F_{16}(C_6F_5)$	144.4	159.4	131.0	15.0

[a] In ppm relative to CCl_3F (internal standard). [b] J'_{24} (the apparent coupling constant between the ortho and para fluorine atoms in the pentafluorophenyl derivatives) was found to be in the range 7.3–7.7 Hz but could not be determined accurately owing to long-range effects.

TABLE IV
SHIELDING PARAMETERS[a] AND TAFT INDUCTIVE AND RESONANCE PARAMETERS

	Substituent									
	CH_3	NMe_2	BF_2[b]	PF_2	CF_3	Br	CN	F	$N_nP_nF_{2n-1}$[c]	NO_2
m-FC_6H_4	+1.15	−0.08	−0.54	−2.11	−2.12	−2.55	−2.78	−3.10	−3.28	−3.38
p-FC_6H_4	+5.45	+15.77	−9.59	−8.30	−5.10	+2.25	−9.07	+6.40	−10.22	−9.38
σ_I[d]	−0.08	+0.10	+0.16	+0.38	+0.38	+0.44	+0.48	+0.52	+0.55	+0.56
σ_R^0[e]	−0.15	−0.54	+0.31	+0.21	+0.10	−0.16	+0.21	−0.32	+0.24	+0.20

[a] Shifts relative to fluorobenzene; except where stated, the data are from ref 26 and refer to dilute solution. [b] P. Heffley, unpublished results for CH_2Cl_2 solution, quoted in ref 22. [c] This work, mean of six compounds. [d] $\sigma_I = 0.1409(0.6 - \int_H^{m\text{-}x})$. [e] $\sigma_{R^0} = 0.0339 \cdot (\int_H^{m\text{-}x} - \int_H^{p\text{-}x})$.

TABLE V
SHIELDING PARAMETERS OF PENTAFLUOROPHENYL DERIVATIVES

	Substituent X						
	CH_3	PF_2	Br	BF_2	CF_3	CN	$N_nP_nF_{2n-1}$[a,b]
$\int_H^{m\text{-}x}$	+1.7	−0.5	−1.6	−2.2	−2.2	−3.5	−3.2
$\int_H^{p\text{-}x}$	+5.0	−6.9	+0.75	−11.3	−6.54	−10.9	−10.15
Ref	28, 29, 33, 35	34	28, 33, 34, 35	36	28, 29, 33, 35	28, 29, 33, 35	This work

[a] Mean values; $n = 3$–8. [b] Mean $J_{24} = 7.4$ Hz; taken in conjunction with δ^F_p through the Graham plot (Figure 5, ref 29); this figure indicates strong π withdrawal, similar to that of a cyano group.

be seen that the fluorophosphonitrilic ring withdraws electron density from the fluoroaryl ring at all positions. In Table IV, the shielding parameters and the derived inductive and resonance constants of the fluorophosphonitrilic rings, averaged over all ring sizes, are compared with those of other groups, arranged in order of increasing σ_I.

It can be seen that inductive withdrawal by a fluorophosphonitrilic group is of the same order as that of a cyano or nitro group or fluorine itself. Conjugative withdrawal is also large, being comparable with that of the cyano, nitro, and PF_2 groups, but exceeded, as might be expected, by that of the BF_2 group and also by that of the PF_4 group ($\sigma_I = 0.45$, $\sigma_R^0 = 0.32$). These measurements therefore classify the fluorophosphonitrilic groups in relation to other possible substituents in a benzene ring.

Similar conclusions can be drawn from a study of the pentafluorophenyl derivatives, which have been extensively used for the assessment of electronic interactions, especially π interactions.[25,28-31] Equations relating shielding parameters and the Taft constants σ_I and σ_R^0 have been derived,[28,29] and the results frequently agree with those obtained from monofluorophenyl derivatives. However, the theory is less good, partly because of "ortho effects,"[25,32] and the empirical justification[28,29] is at present less detailed. We therefore prefer to rely on a direct comparison of shielding parameters, and the empirical observation that the joint variation of δ_p^F and J'_{24} (the ortho–para coupling constant) depends mainly on resonance interactions.[29] Shielding parameters, again in order of increasing withdrawal, are given in Table V,[28,29,33-36] and it will be seen that, although the order of the individual substituents is different, the fluorophosphonitrilic substituents are again closely similar to the cyano group, in withdrawing electrons strongly both inductively and conjugatively. The π-electron effect, as indicated by $\int_H^{p\text{-}X}$, is again less than that of the BF_2 group, and both effects are less than those of the $P(O)F_2$ group, for which the meta and para shielding parameters are −5.0 and −14.1 ppm, respectively.[30]

Although these results show that the fluorophosphonitrilic ring is conjugated with the fluorophenyl group, there remains the question, especially in view of the last quoted result, of how far the interaction extends within the phosphonitrilic ring. The individual chemical shifts are of possible importance here. The meta shifts (Table III) vary very little with ring size, either in the monofluorophenyl or the pentafluorophenyl series, and it is not perhaps to be expected that inductive effects would vary much with ring size. On the other hand, the para shifts of the monofluorophenyl derivatives increase steadily with ring size, though again the range is not great, 0.6 ppm, corresponding to 0.02 in σ_R^0. The para shifts of the pentafluorophenyl derivatives cover a larger range (1.4 ppm), and the alternation of $-(\delta^F_p - \delta^F_m)$ with increasing ring size, although not large, is experimentally significant. The

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alternation is good evidence that conjugation extends beyond the first phosphorus atom and is explicable in terms of conjugation of the fluorophenyl group with the homomorphic π system in the phosphonitrile, transfer of charge from the para position being greatest to fluorophosphonitrilic rings containing $4m + 2$ π electrons, *i.e.*, the N_3P_3 and N_5P_5 rings.[37] The different behavior of the monofluorophenyl derivatives may be a result of different steric requirements, and further work is needed to find out. In both series, the ring size variation is small, suggesting that the strong conjugation indicated by the mean chemical shifts relays negative charge principally to the phenyl-substituted phosphorus atom.

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[37] Delocalization effects are attenuated rapidly with increase of ring size on account of the different electronegativities of phosphorus and nitrogen.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY,
TALLAHASSEE, FLORIDA 32306

Variable-Temperature Proton Nuclear Magnetic Resonance Spectra of Borazine and Borazine-^{10}B

BY EDWARD K. MELLON,* BEATRICE M. COKER, AND PATRICK B. DILLON[1]

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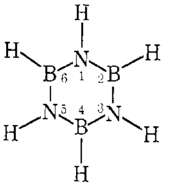
Variable-temperature proton nmr spectra of borazine and borazine-^{10}B are analyzed for chemical shifts, coupling constants, and line widths. The line width data suggest that the broadening is due to a combination of quadrupolar relaxation resulting from the high-spin nuclei present and long-range spin coupling. Three models, including one involving computer simulation of spectra with large constant intrinsic line widths, are tested for applicability for estimating the spin–lattice relaxation times T_{1B} and T_{1N} using Arrhenius plots. The preferred model yields estimates of 1.95 kcal/mol for the average activation energy for molecular reorientation of borazine and 3.6 and 1.5 MHz for the effective quadrupole coupling constants of ^{11}B and ^{14}N, respectively.

Introduction

The proton nmr spectrum of borazine, **1**, consists of broad lines,[2,3] whose number is determined by spin–spin coupling between pairs of nuclei consisting of one proton and one high-spin nucleus, the high-spin nuclei present in appreciable abundance being ^{10}B ($I = 3$, 18.8%), ^{11}B ($I = {}^3/_2$, 81.2%), and ^{14}N ($I = 1$, 99.6%). Line broadening in the proton nmr spectrum of borazine results in part from a relaxation effect involving the nuclear quadrupole moments of the high-spin nuclei. In favorable cases such broadening can be analyzed to yield estimates of nuclear quadrupole coupling constants and activation energies for molecular reorientation.



1

Pople[4] has presented a theoretical treatment of the quadrupolar relaxation of protons spin coupled to ^{14}N nuclei and subsequent theoretical work has dealt with protons coupled to nuclei with $I = {}^3/_2$ through ${}^7/_2$, and $I = {}^9/_2$.[5] The quadrupolar relaxation model has been used in a discussion of the proton nmr spectra of lithium borohydride, trimethylamine–borane-^{10}B, and *N*-tri(methyl-d_3)borazine-^{10}B[6] and in the analysis of the ^{19}F nmr spectra of BF_3 and ClO_3F.[5] The variable-temperature ^{19}F nmr spectra of NbF_6^- indicate that quadrupolar relaxation is the dominant mechanism at low temperatures while chemical exchange predominates at temperatures above 87°.[5]

In this paper the temperature dependences of the proton nmr spectra of borazine and of borazine-^{10}B are analyzed in terms of quadrupole broadening and of intrinsic line widths arising from long-range spin coupling. In addition, computer-simulated spectra involving quadrupolar broadening in the presence of appreciable constant intrinsic line widths for $I = 1$ and $I = {}^3/_2$ are presented.

Experimental Section

Borazine of normal isotopic content was prepared by the sodium borohydride reduction of tri-*B*-chloroborazine.[7] The product was suitable for chemical shift and coupling constant determinations and for dilution studies but contained impurities which could not be removed by repeated trap-to-trap distillation and which exhibited absorptions near the two high-field components of the ^{11}B quartet. Consequently, the borazine sample (containing 2

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