Tetrahedron Vol. 33, pp. 1075 to 1079 Pergamon Press 1977 Printed in Great Britain

A ^{19}F NMR STUDY OF ELECTRONIC EFFECTS IN IMINOPHOSPHORANES AND IN THEIR METHYL IODIDE SALTS

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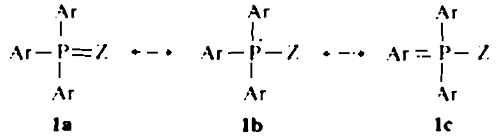
(*Received in the USA* 28 *June* 1976; *Received in the UK for publication* 11 *November* 1976)

Abstract—^{19}F NMR shifts have been obtained for the iminophosphoranes $(FC_6H_4)_n(C_6H_5)_{3-n}PNC_6H_4X$ (n = 1, 3) and $(XC_6H_4)_3PNC_6H_4F$ and for their methyl iodide salts. The data for the iminophosphoranes indicate the presence of a polar P=N bond, considerable electron delocalization from nitrogen to the attached aryl ring, and a modest degree of aryl-phosphorus conjugative interaction. In the salts the delocalization of the electron pair of nitrogen is largely curtailed.

Because the phosphorus atom is able to expand its octet, the system, Ar_3PZ, **1**, can, in principle, exist as a hybrid of three resonance contributing structures, **1a**, **1b**, **1c**, two of which involve d_π–p_π orbital overlap between phosphorus and an adjacent electron-rich center:



$$\mathrm{Ar_3P{=}Z \longleftrightarrow Ar_3P{-}Z \longleftrightarrow Ar{=}P(Ar)_2{-}Z}$$

1a **1b** **1c**

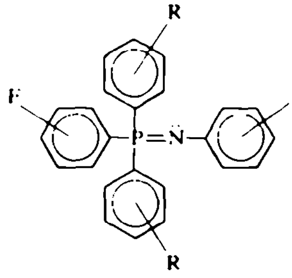
Studies of the electronic properties of methylene ylids ($Z = -\bar{C}H_2$) and phosphine oxides ($Z = -\bar{O}:$) by Johnson[1] and Taft,[2] using ^{19}F NMR spectroscopy, have indicated a substantial contribution from structure **1a** but little from structure **1c** in these systems. No comparable investigation of the isoelectronic iminophosphorane system ($Z = -\bar{N}-Ar$) has been made, although limited studies of trends in substituent effects on the nucleophilicity and basicity of this system suggest similar conclusions regarding its electron distribution.

The objective of this work is a detailed study of the nature of electronic effects in the iminophosphoranes, using the ^{19}F nucleus as probe because of its demonstrated high sensitivity to electronic perturbations in aromatic systems. The ^{19}F chemical shifts of the iminophosphoranes, **Ia**, **Ib**, **IIa**, **IIb**, as well as those of their derivative methyl iodide salts, **IIIa**, **IIIb**, **IVa** and **IVb**, were determined. Because of their ionic nature, the electron distribution of the latter is expected to be substantially different from that of the parent iminophosphoranes.

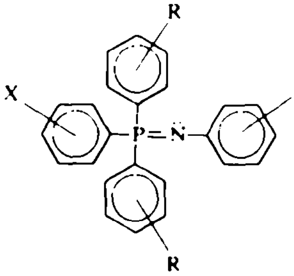
RESULTS

The iminophosphoranes, **Ia**, **Ib**, **IIa** and **IIb**, and their methyl iodide salts, **IIIa**, **IIIb**, **IVa** and **IVb**, prepared for this study, are new compounds which were identified by means of their integrated PMR spectra.

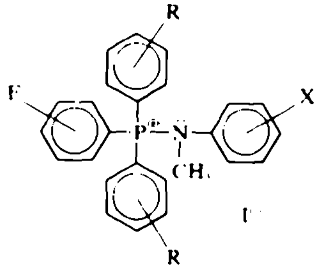
The ^{19}F chemical shift of each iminophosphorane,



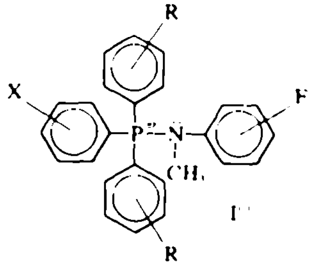
Ia: R = H
b: R = F



IIa: R = H
b: R = X



IIIa: R = H
b: R = F



IVa: R = H
b: R = X

determined in deuterochloroform at a 0.74 molal concentration using 1,1,2,2-tetrachlorotetrafluorocyclobutane (TCTFCB; 0.05 M) as internal reference, was converted to the fluorobenzene scale using:

δ(relative to TCTFCB) - 0.20 ppm = δ(relative to C_6H_5F). These corrected shifts are summarized in Tables 1 and 2. Here $\delta(mF_nX)$ and $\delta(pF_nX)$ are the shifts of the *meta*- and *para*-fluoro-X-substituted iminophosphoranes, **Ia** (n = 1) and **Ib** (n = 3); $\Delta\delta(pF_nX-mF_nX)$ is the shift difference between corresponding *para*- and *meta*-fluoro-X-substituted compounds, **I**. Similarly, $\delta(X_nFm)$ and $\delta(X_nFp)$ are the shifts of the *meta*- and *para*-fluoro-X-substituted iminophosphoranes, **IIa** (n = 1) and **IIb** (n = 3) and $\Delta\delta(X_nFp-X_nFm)$ is their respective *para–meta* shift difference.

The ^{19}F shifts of selected samples of iminophosphoranes (0.074 m), subjected to a 20-fold dilution, were found to be reproducible within experimental error. It was, therefore, assumed that the shifts of all iminophosphoranes were concentration independent.

The ^{19}F shifts of the methyl iodide salts, **III** and **IV**, (0.074 m in $CDCl_3$), measured relative to TCTFCB (0.05 M) and referenced to fluorobenzene, are listed in Tables 3 and 4. Although the ^{19}F resonance of most salts exhibited a significant, non-linear concentration dependence, the overall trends demonstrated by the 0.074 molal samples were preserved at all concentrations.

Correlation of substituent electronic effects. The ^{19}F shifts of the iminophosphoranes, **I** and **IIb**, could be correlated satisfactorily with Taft's dual substituent

Table 1. ^{19}F chemical shifts[a,b] of N-(X-phenyl)iminofluorophenyldiphenylphosphoranes, **Ia**, and N-(X-phenyl)iminotrifluorophenylphosphoranes, **Ib**

	$FC_6H_4(C_6H_5)_2P{=}NC_6H_4X$ (**Ia**)			$(FC_6H_4)_3P{=}NC_6H_4X$ (**Ib**)		
Substituent, X	$\delta(mF_1X)$	$\delta(pF_1X)$	$\Delta\delta(pF_1X-mF_1X)$	$\delta(mF_3X)$	$\delta(pF_3X)$	$\Delta\delta(pF_3X-mF_3X)$
p-OCH_3	2.20	5.77	3.57	2.90	6.40	3.50
p-CH_3	2.19	5.76	3.57	2.91	6.42	3.51
H	2.27	—	—	3.00	6.57	3.57
p-F	2.38	6.09	3.71	3.15	6.79	3.64
m-F	2.52	6.30	3.78	3.26	7.05	3.79
p-Cl	2.53	6.32	3.79	3.26	7.03	3.77
p-CF_3	—	—	—	3.48	7.35	3.87
p-CN	3.03	7.17	4.14	3.76	7.89	4.13
p-NO_2	3.26	7.58	4.32	3.98	8.29	4.31
2,4,6-$(NO_2)_3$	3.55	8.25	4.70	4.34	9.04	4.70

[a] Values are in ppm relative to fluorobenzene.
[b] Positive values indicate ^{19}F shifts downfield from fluorobenzene.

Table 2. ^{19}F chemical shifts[a,b] of N-(Fluorophenyl)imino(X-phenyl)diphenylphosphoranes, **IIa**, and N-(Fluorophenyl)iminotri(X-phenyl)phosphoranes, **IIb**

	$XC_6H_4(C_6H_5)_2P{=}NC_6H_4F$ (**IIa**)			$(XC_6H_4)_3P{=}NC_6H_4F$ (**IIb**)		
Substituent, X	$\delta(X_1Fm)$	$\delta(X_1Fp)$	$\Delta\delta(X_1Fp-X_1Fm)$	$\delta(X_3Fm)$	$\delta(X_3Fp)$	$\Delta\delta(X_3Fp-X_3Fm)$
p-OCH_3	—	—	—	-1.77	-15.53	-13.76
p-CH_3	—	—	—	-1.85	-15.52	-13.67
H	—	—	—	-1.69	-15.05	-13.36
p-F	-1.53	-14.67	-13.14	-1.17	-14.17	13.00
m-F	-1.51	-14.61	-13.10	-1.16	—	—
p-Cl	—	—	—	-1.05	-13.86	-12.81

[a] Values are in ppm relative to fluorobenzene.
[b] Negative values indicate ^{19}F shifts upfield from fluorobenzene.

Table 3. ^{19}F chemical shifts[a] of N-methyl-N-(X-phenyl)iminofluorophenyldiphenylphosphonium iodides, **IIIa**, and N-methyl-N-(X-phenyl)iminotrifluorophenylphosphonium iodides, **IIIb**

	$FC_6H_4(C_6H_5)_2\overset{\oplus}{P}N(CH_3)C_6H_4X, \overset{(-)}{I}$ (**IIIa**)			$(FC_6H_4)_3\overset{\oplus}{P}N(CH_3)C_6H_4X, \overset{(-)}{I}$ (**IIIb**)		
Substituents, X	$\delta(mF_1X^+)$	$\delta(pF_1X^+)$	$\Delta\delta(pF_1X^+-mF_1X^+)$	$\delta(mF_3X^+)$	$\delta(pF_3X^+)$	$\Delta\delta(pF_3X^+-mF_3X^+)$
p-CH_3	6.14	14.10	7.96	6.90	14.56	7.66
p-OCH_3	6.16	14.05	7.89	6.89	14.54	7.65
H	6.19	14.15	7.96	6.90	14.71	7.81
p-F	6.35	14.30	7.95	7.16	14.95	7.79
m-F	6.46	14.53	8.07	7.18	15.06	7.88
p-Cl	6.47	14.48	8.01	7.26	15.09	7.83
p-CF_3	—	—	—	7.37	15.33	7.96
p-CN	6.93	15.04	8.11	7.62	15.65	8.03
p-NO_2	6.98	15.15	8.17	7.68	15.79	8.11

[a] See footnotes a and b, Table 1.

Table 4. ^{19}F chemical shifts[a] of N-methyl-N-(fluorophenyl)imino(X-phenyl)diphenylphosphonium iodides, **IVa**, and N-methyl-N-(fluorophenyl)iminotri(X-phenyl)phosphonium iodides, **IVb**

Substituent, X	$X\overset{(+)}{C_6H_4(C_6H_5)_2PN}(CH_3)C_6H_4F, I^{(-)}$ (**IVa**) δ(X,Fm$^+$)	δ(X,Fp$^+$)	$\Delta\delta$(X,Fp$^+$–X,Fm$^+$)	$(XC_6H_4)_3\overset{(+)}{P}N(CH_3)C_6H_4F, I^{(-)}$ (**IVb**) δ(X,Fm$^+$)	δ(X,Fp$^+$)	$\Delta\delta$(X,Fp$^+$–X,Fm$^+$)
p-OCH$_3$	—	—	—	3.41	0.84	−2.57
p-CH$_3$	—	—	—	3.46	1.06	−2.40
H	—	—	—	3.72	1.44	2.28
p-F	3.82	1.56	−2.26	4.13	1.97	−2.16
p-Cl	—	—	—	4.36	2.23	−2.13
m-F	3.98	1.81	−2.17	4.46	2.54	−1.92

[a] See footnotes a and b, Table 1.

parameter (DSP) equation,[4] utilizing the σ_R and σ_R scales, respectively:

$$\delta(\mathrm{mF_nX}) = \rho(\sigma_I + \lambda\sigma_R) + \delta(\mathrm{mF_nX})_{X=H} \quad 1a$$

$$\Delta\delta(\mathrm{pF_nX{-}mF_nX}) = \rho(\sigma_I + \lambda\sigma_R) + \Delta\delta(\mathrm{pF_nX{-}mF_nX})_{X=H} \quad 1b$$

$$\delta(\mathrm{X_1Fm}) = \rho(\sigma_I + \lambda\sigma_R) + \delta(\mathrm{X_1Fm})_{X=H} \quad 2a$$

$$\Delta\delta(\mathrm{X_1Fp{-}X_1Fm}) = \rho(\sigma_I + \lambda\sigma_R) + \Delta\delta(\mathrm{X_1Fp{-}X_1Fm})_{X=H}. \quad 2b$$

Here σ_I and σ_R (or σ_R) are the inductive and resonance potentials, respectively, of the substituent, X. The coefficient, ρ, is a measure of the susceptibility of the ^{19}F shift parameter to the overall electronic effects of X, and λ reflects the relative importance of resonance versus inductive potentials of the substituent in these correlations. The values of ρ and λ, determined by the double regression technique for best linear fit of experimental data to the correlation line of eqns (1) and (2), are summarized in Table 5, together with the number of substituents (n) in each set, the correlation coefficient (r), and the root-mean-square deviation (rms).

The parameters of the methyl iodide salts, **III** and **IV**, could also be correlated with the DSP equation (Table 5), although the resulting values of the coefficients have less significance in view of the concentration dependence of the chemical shifts. The order of magnitude of ρ and λ is, however, invariant with concentration.

DISCUSSION

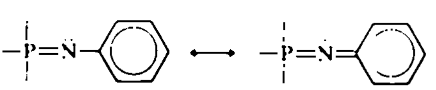
When the fluorobenzene ring is attached to the phosphorus atom of the PN bond in the iminophosphorane system, the fluorine atom is deshielded, relative to fluorobenzene itself, as indicated by the positive values of δ(mF$_n$X) and δ(pF$_n$X) of compounds **I** (Table 1). With the fluorobenzene ring at the nitrogen atom, electron density is furnished to the ring and the fluorine atom becomes shielded (negative values of δ(X$_n$Fm) and δ(X$_n$Fp); compounds **II**, Table 2). In particular, since a substituent, X, in *meta*-X-fluorobenzene exerts primarily its field effect on the ^{19}F chemical shift, the relative extent of deshielding and shielding of the fluorine nucleus in the (m)F–C_6H_4–P and N–C_6H_4–F(m) moieties of **I** and **II** reflects the degree of polarization of the P=N bond. Thus, the effect of the quaternary phosphorus, which is comparable to that of a -CN substituent (δ((m)FC$_6$H$_4$CN) = 2.78 ppm), and the effect of nitrogen in the N–C_6H_4F(m) system, which approaches in magnitude that of oxygen in the phenoxide anion ($\delta(\bar{O}{-}C_6H_4{-}F(m)) = -1.63$ ppm), indicate a polar P=N bond with considerable negative charge at the nitrogen atom.

Table 5. Correlation of ^{19}F chemical shifts with the DSP equations, 1a,b and 2a,b

Compound	Shift Parameter	ρ	λ	r[a]	rms[b]	n[c]	Scale
Ia	δ(mF$_1$X)	0.881	0.9	0.999	0.02	7	σ_R
	$\Delta\delta$(pF$_1$X–mF$_1$X)	0.607	0.9	0.998	0.02	6	σ_R
Ib	δ(mF$_3$X)	0.941	0.8	0.999	0.02	8	σ_R
	$\Delta\delta$(pF$_3$X–mF$_3$X)	0.659	0.9	0.999	0.02	7[d]	σ_R
IIb	δ(X$_3$Fm)	1.859 (0.620)[e]	0.5	0.999	0.01	6[f]	σ_R
	$\Delta\delta$(X$_3$Fp–X$_3$Fm)	2.100 (0.700)[e]	0.7	0.997	0.03	5	σ_R
IIIa	δ(mF$_1$X$^+$)	0.841	0.7	0.996	0.03	7	σ_R
	$\Delta\delta$(pF$_1$X$^+$–mF$_1$X$^+$)	0.140	1.5	0.983	0.02	7	σ_R
IIIb	δ(mF$_3$X$^+$)	0.831	0.6	0.989	0.04	8	σ_R
	$\Delta\delta$(pF$_3$X$^+$–mF$_3$X$^+$)	0.336	1.0	0.982	0.03	8	σ_R
IVb	δ(X$_3$Fm$^+$)	2.120 (0.707)[e]	0.7	0.999	0.02	6	σ_R
	$\Delta\delta$(X$_3$Fp$^+$–X$_3$Fm$^+$)	0.864 (0.288)[e]	0.9	0.994	0.02	4	σ_R

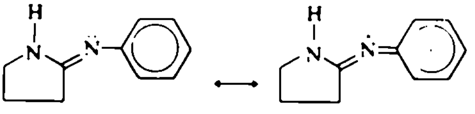
[a] Correlation coefficient.
[b] Root-mean-square deviation.
[c] Number of substituents.
[d] Data for X = CF$_3$ omitted in the correlation (0.09 ppm below the correlation line).
[e] Value of ρ per substituted phenyl ring.
[f] Shift for **IIa**, X = F included.

The extent of conjugative interaction between nitrogen and the attached phenyl ring, and between phosphorus and its phenyl rings, is reflected by the magnitudes of the *para-meta* shift differences, $\Delta\delta(X_nFp-X_nFm)$, of compounds **II** and $\Delta\delta(pF_nX-mF_nX)$ of compounds **I**, respectively. The large negative values of the parameter for the $N-C_6H_4-F$ system (**II**) imply considerable electron delocalization from nitrogen into the benzene ring. The extent of this conjugative interaction, however, is much less than it is in the phenoxide anion, despite the negative charge density at nitrogen ($\Delta\delta(X_nFp-X_nFm) = -12.81$ to -13.76 ppm compared to -17.6 ppm for $\bar{O}-C_6H_4F$), and resembles the degree of electron delocalization in anilines ($\Delta\delta(Fp-Fm) = -13.8$ ppm for $NH_2C_6H_4F$). This result suggests major contributions from resonance structures **2a** and **2b**:



2a **2b**

Conjugation of this type, which implies a significant degree of sp-hybridization of the nitrogen atom, has been postulated by Jackman[4] for the structurally similar 2-iminopyrrolidine system, **3**:

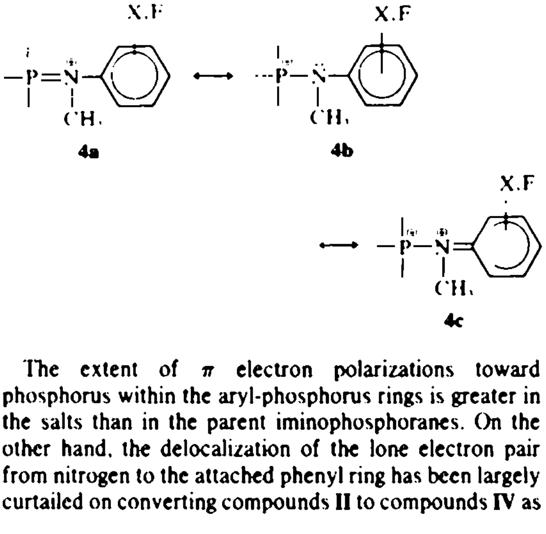


3a **3b**

The positive values of $\Delta\delta(pF_nX-mF_nX)$ for compounds **I** and the non-zero values of λ in the correlations of $\delta(X_5Fm)$ and of $\Delta\delta(X_5Fp-X_5Fm)$ with the DSP equation, 2, suggest the presence of conjugative pi electron polarizations within the phenyl rings, Ar-P, toward the phosphorus atom. The modest size of the *para-meta* shift difference of compounds **I** attests to the moderate nature of these conjugative interactions. Indeed, the substituent effect in Ar-P is predominantly of inductive origin. Thus, a change from phenyl to fluorophenyl substitution at phosphorus (**IIa**, X = H to **IIb**, X = F) results in deshielding of the fluorine nucleus in the $N-C_6H_4-F$ moiety, indicating a net increase in positive charge at the phosphorus atom.

The polarizability of the multiple bond between nitrogen and phosphorus can be determined[1] by the effect of increased fluorination of the phosphorus-phenyl rings (**Ia** to **Ib**) on the *para-meta* shift differences, $\Delta\delta(pF_nX-mF_nX)$. Polarization of π electrons of the PN bond toward phosphorus, resulting from increased positive charge at that atom, is expected to inhibit competitive π electron polarizations within the P-phenyl rings and lead to a reduction in the values of the *para-meta* shift differences: $\Delta\delta(pF_5X-mF_5X) - \Delta\delta(pF_1X-mF_1X) < 0$. The data in Table 6 show that the change in these shift differences with the indicated structural change is negligible. Thus the extent of phosphorus-nitrogen multiple bonding is approximately constant in the iminophosphoranes, a situation which is paralleled in the isoelectronic phosphine oxides and methylene ylids.†

On converting the iminophosphoranes, **I** and **II**, to the derivative methyl iodide salts, **III** and **IV**, large downfield shifts of all ^{19}F resonances are observed (Tables 3 and 4), a consequence of the increased positive charge at phosphorus and nitrogen in the hybrid of resonance structures **4**:



4a **4b**

4c

The extent of π electron polarizations toward phosphorus within the aryl-phosphorus rings is greater in the salts than in the parent iminophosphoranes. On the other hand, the delocalization of the lone electron pair from nitrogen to the attached phenyl ring has been largely curtailed on converting compounds **II** to compounds **IV** as

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†Johnson's claim of a polarizable P=C bond in the methylene ylids is based on an error in the treatment of his data.

Table 6. Changes in chemical shift parameters with changes in structure: **Ia** to **Ib**, **IIIa** to **IIIb**

	$\delta(mF_5X) - \delta(mF_1X)$		$\Delta\delta(pF_5X-mF_5X) - \Delta\delta(pF_1X-mF_1X)$		$\delta(mF_5X^+) - \delta(mF_1X^+)$	$\Delta\delta(pF_5X^+-mF_5X^+) - \Delta\delta(pF_1X^+-mF_1X^+)$
Substituent, X	Observed	Calculated	Observed	Calculated	Observed	Observed
p-NH_2	—	0.73	—	−0.07	—	—
p-$N(CH_3)_2$	—	0.72	—	−0.07	—	—
p-OCH_3	0.70	0.75	0.07	−0.07	0.73	0.24
p-CH_3	0.72	0.70	−0.06	−0.06	0.76	0.30
H	0.73	0.71	—	−0.06	0.71	−0.15
p-F	0.77	0.75	0.07	−0.06	0.81	−0.16
m-F	0.74	—	0.01	—	0.72	0.19
p-Cl	0.73	0.74	−0.02	0.04	0.79	−0.18
p-CN	0.73	0.72	−0.01	−0.02	0.69	−0.08
p-NO_2	0.72	0.72	0.01	0.01	0.70	−0.06
2,4,6-$(NO_2)_3$	0.79	—	0.00	—	—	—

*Calculated using eqn 1 and appropriate values of ρ and λ from Table 5.

reflected by the dramatic reduction (*ca.* 11 ppm) in the magnitudes of the *para–meta* shift differences, $\Delta\delta(X_3Fp-X_3Fm)$ to $\Delta\delta(X_3Fp^*-X_3Fm^*)$. This result is not surprising in view of the unfavorable structure **4c**.

The effect of increased fluorination of phenyl rings attached to phosphorus (**IIIa** to **IIIb**) is a reduction in the magnitudes of the *para–meta* shift differences, $\Delta\delta(pF_5X^*-mF_5X^*)$ (Table 6), a result which implies increased p_π–d_π back-bonding between nitrogen and phosphorus (structure **4a**) with increasing electron demand at the latter. The extent of this multiple bonding, which varies with each salt, appears to be dependent on the degree of competitive electron demand by substituents, X, in the $N(CH_3)C_6H_4X$ moiety.

Although the susceptibility, ρ, of all *meta*-fluoro shifts to electronic effects of X in the iminophosphoranes, **I** and **II**, is not greatly altered on methylation at nitrogen (**III** and **IV**), the response of conjugative effects in Ar–P and in N–Ar to substituent electronic effects is largely reduced on salt formation. This trend may parallel the reduction in p_π–d_π overlap of phosphorus and nitrogen resulting from this structural change.

EXPERIMENTAL

The iminophosphoranes were synthesized according to the methods of Staudinger[6] and Horner.[7] The methyl iodide salts were derived from the iminophosphoranes by refluxing the latter with excess methyl iodide in acetonitrile for twelve hours, then precipitating the crude salts from hot ethanol solution with ether.

The ^{19}F NMR chemical shifts were determined at 27 ± 1°C using a JEOL PS-100 FT spectrometer operating at 93.65 MHz. Repetitive determinations of shifts gave a reproducibility within 0.04 ppm or better.

REFERENCES

[1] A. W. Johnson and H. L. Jones, *J. Am. Chem. Soc.* **90**, 5232 (1968).

[2] L. W. Rashyk, R. W. Taft and W. A. Sheppard, *Ibid.* **90**, 5236 (1968).

[3] A. W. Johnson and S. C. K. Wong, *Can. J. Chem.* **44**, 2793 (1966).

[4] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson and G. T. Davis, *J. Am. Chem. Soc.* **85**, 709 (1963); *Ibid.* **85**, 3146 (1963).

[5] L. M. Jackman and T. Jen, *Ibid.* **97**, 2811 (1975).

[6] H. Staudinger and J. Meyer, *Helv. Chim. Acta* **2**, 635 (1919).

[7] L. Horner and H. Oediger, *Ann. Chem.* **627**, 142 (1959).