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Structure-Basicity Relations among Phosphate and Phosphite Esters. CNDO/2 and Protonation Studies

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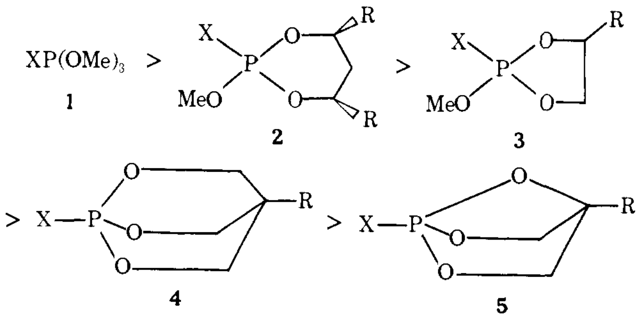
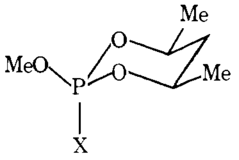
Abstract: Protonation in $HFSO_3$ at −50 °C of the phosphite triesters 1^{III}-5^{III} revealed a steady increase in $^1J_{PH}$ (826-928 Hz) upon increased constraint of the alkoxy groups. CNDO/2 calculations showed a concomitant rise in the positive charge on phosphorus and the phosphorus-bound hydrogen in the protonated species, but no trend was observed in the P hybridization. A plot of the cube of the sum of these charges vs. $^1J_{PH}$ (correlation coefficient 0.92) suggests that the charge contribution is probably dominant in the Fermi contact term. These results are consistent with stereochemically dependent orbital effects proposed earlier. A similar rise in the calculated negative charges at the ring oxygens of the phosphate analogues 1^V-4^V along with smaller differences in the protonation energies of the phosphoryl oxygen on constraint parallels the decreased hydrogen bonding tendency of the phosphoryl oxygen as shown by phenol shift experiments. A minor reversal in basicity of the first two members of the phosphite series is indicated by the BH stretching frequency trend of the BH_3 adducts 1^A-5^A and is rationalized in terms of the greater polarizing power of the proton than BH_3.

Substantial spectroscopic and chemical evidence has been put forth within the last 2 years which suggests a decreasing trend in the basicity of the phosphorus and the phosphoryl oxygen upon molecular constraint in phosphite and phosphate triesters, respectively,[2] **1** > **2** > **3** > **4** > **5**. The rationale which has been given for this progression entails a consideration of changing orbital orientations[2,3] (particularly those of the ester oxygen p lone pairs with respect to X) which can give rise to orbital repulsions.[3a] In addition, a "hinge effect" resulting from ester oxygen hybridization changes induced by increased strain in the rings has been invoked.[2,3b]



X = lone pair (LP) or oxygen
R = H or alkyl

It has also been noted that the conformation which obtains for the second member of the above series is chair, with the X moiety in the equatorial position.[2b,3] If this system is forced by ring substitution to direct the X group axial, spectroscopic studies reveal that the order of basicities is **2a** > **2b** toward $Mo(CO)_4$ where X = LP and toward a proton where X = O.[2b,3]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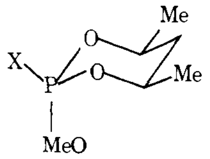

2b

The threefold purpose of the present investigation was to ascertain if calculations of the atomic charges of pertinent atoms in these systems would reflect the above basicity orders, to protonate the phosphorus of the phosphite esters in a strong acid medium to ascertain if the calculational parameters of the

Table I. Selected Bond Angles (deg) and Lengths (Å) Used in the CNDO/2 Calculations[a]

	POC	OPO	PO	P=O	CO
1$^{\mathrm{III}}$	119	103	1.62		1.46
2a$^{\mathrm{III}}$, **2b**$^{\mathrm{III}}$	113	99	1.62		1.46
3$^{\mathrm{III}}$	112[b]	95[b]	1.62[b]		1.46
	118[c]	101[c]	1.62[c]		
4$^{\mathrm{III}}$	114[d]	103[d]	1.62		1.46
5$^{\mathrm{III}}$	112[e]	98	1.62		1.46
	113[f]				
1$^{\mathrm{V}}$	121	104	1.56	1.47	1.47
2a$^{\mathrm{V}}$, **2b**$^{\mathrm{V}}$	121[b]	107[b]	1.57[b]	1.48	1.44
	118[c]	104[c]	1.59[c]		
3$^{\mathrm{V}}$	119[b]	99[b]	1.57[b]	1.44	1.43
	112[c]	108[c]	1.57[c]		
4$^{\mathrm{V}}$	115	104	1.57	1.46	1.45

[a] The CCC bond angle was taken to be tetrahedral and the C-C bond length was assumed to be 1.54 Å throughout. [b] Endocyclic. [c] Exocyclic. [d] The relatively small error in the POC and OPO angles compared to the values observed after the calculation was completed (118 and 100°, respectively) are not expected to alter the overall trend since these calculations are rather insensitive to 2-3° bond angle changes. [e] POC(methine). [f] POC(methylene).

protonated species could be correlated with the observed $^1J_{\mathrm{PH}}$ values, and to determine the relative basicities of **2a** and **2b** with respect to X-P(OMe)$_3$.

CNDO/2 Calculations

The calculations were carried out with a standard program[4] and the percentages of s character were evaluated with a population analysis described earlier.[5] Structural parameters (Table I) used for O=P(OMe)$_3$ (**1**$^{\mathrm{V}}$) and **2b**$^{\mathrm{V}}$ were those obtained for $O{=}P(OCH_2Ph)_2OH$[6] and $O{=}P(OCH_2CH_2CH_2O)(OPh)$,[7] respectively, while x-ray diffraction data for $O{=}P(OCH_2CH_2O)(OMe)$ (**3**$^{\mathrm{V}}$)[8] and $O{=}P(OCH_2)_3CMe$ (**4**$^{\mathrm{V}}$)[9] have been reported. Calculations on **2a** were executed with the opposite conformer of **2b**$^{\mathrm{V}}$. Bond angles and distances for phosphite **3**$^{\mathrm{III}}$ were those of meso-hydrobenzoin phosphite[10] and the distances encountered in the latter were also employed for the remaining phosphite esters. Structural parameters used for **5**$^{\mathrm{III}}$ were those of $P(OCH_2)_3CCH_2Br$[11] suitably altered (Table I) to accommodate the loss of a bridging CH$_2$ group. The bond angles used for phosphites **1**$^{\mathrm{III}}$, **2a**$^{\mathrm{III}}$, and **2b**$^{\mathrm{III}}$ were the same as those of the corresponding phosphates except for the POC and OPO bond angles in Table I which were optimally adjusted in the ring compounds to accommodate bond distance changes from the pentavalent to the trivalent species. Calculations for the protonated phosphites were carried out using the structural parameters employed for the phosphites with a P-H distance of 1.54 Å.[12]

Experimental Section

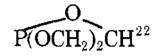
Materials. Part of the fluorosulfuric acid was a kind gift from Research Organic/Inorganic Chemical Corp. while the remainder was purchased from Aldrich Chemical Corp. The fluorosulfuric acid was always distilled before use (bp = 50 °C) as were the trimethyl phosphite and phosphate. Compounds **1**$^{\mathrm{A}}$[13] (where superscript A designates the BH$_3$ adduct), **2a**$^{\mathrm{III}}$ (R = Me),[14] **2a**$^{\mathrm{V}}$ (R = Me),[13] **2b**$^{\mathrm{III}}$ (R = Me),[15] **2b**$^{\mathrm{V}}$ (R = Me),[15] **2b**$^{\mathrm{A}}$ (R = Me),[16] **3**$^{\mathrm{III}}$ (R = Me),[15] **3**$^{\mathrm{V}}$ (R = H),[18] **3**$^{\mathrm{A}}$ (R = H),[18] **4**$^{\mathrm{III}}$ (R = Me),[19] and **4**$^{\mathrm{V}}$ (R = *n*-Pent)[20] were prepared according to literature procedures.

The adduct **2a**$^{\mathrm{A}}$, while previously obtained in a mixture with **2b**$^{\mathrm{A}}$, was prepared isomerically pure according to ^{1}H NMR spectroscopy. Using a general approach described previously[13] with the modification that the reaction vessel was kept between 0 and 5 °C, distillation of the residue at 85-90 °C at 0.1 mm after normal workup gave an 81% yield of a colorless liquid (^{1}H NMR spectrum neat; CH_3, δ 1.29 d, $^3J_{\mathrm{HH}} = 6.0$; CH_2, δ 1.85 m; CH_3O, δ 3.59 d, $^3J_{\mathrm{PH}} = 11.2$; CH, δ 4.54 m). A mass spectrum gave a parent ion corresponding to the correct mass (178).

Adduct **4**$^{\mathrm{A}}$ (R = Et) was prepared following the general method described before[13] and melted with decomposition from 132 to 134 °C (^{1}H NMR spectrum in CDCl$_3$; CH_2, 4.3 d, $^3J_{\mathrm{PH}} = 4.5$; CH_3CH_2, δ 1.1 A$_3$B$_2$ pattern).

The trialcohol 2-methylglycerol needed for compound **5**$^{\mathrm{III}}$ was synthesized from 2-methyl-2-propen-1-ol following a procedure used to hydroxylate cyclohexene[21] with the modification that acetone was used for the extraction (^{1}H NMR spectrum in CD$_3$CN; CH_3, δ 1.07 s, OH, δ 3.25 m; CH_2, δ 3.42 m).

Phosphite **5**$^{\mathrm{III}}$ was prepared analogously to



$$\overset{\frown O \frown}{P(OCH_2)_2CH}$$ [22]

in 73% crude yield which on purification with a second distillation had a boiling point from 46 to 48 °C at 5.6 mm (^{1}H NMR spectrum in CDCl$_3$; CH_3, δ 1.62 s, CH_2, δ 3.55 m). The peak at *m/e* 134 in the mass spectrum corresponded to the parent ion mass of the desired compound.

Phosphate **5**$^{\mathrm{V}}$ was made by oxidizing **5**$^{\mathrm{III}}$ with N$_2$O$_4$ following a procedure described earlier[15] except that CH$_2$Cl$_2$ was the solvent. After removal of the solvent and excess N$_2$O$_4$ under vacuum at room temperature, the residue was redissolved in CH$_2$Cl$_2$ and diethyl ether added to the cloud point. The yield of colorless material (mp 92-94 °C) on cooling to −78 °C was 90% (^{1}H NMR spectrum in CDCl$_3$; CH_3, δ 1.65 s; CH_2, δ 4.3 m). A peak at *m/e* 150 in the mass spectrum corresponded to the parent ion of the desired compound.

Adduct **5**$^{\mathrm{A}}$ was prepared in nearly quantitative yield by slowly adding the stoichiometric amount of 1.0 M diborane in THF to a THF solution of **5**$^{\mathrm{III}}$ kept at room temperature. Evaporation of the THF under vacuum left a viscous liquid which decomposed violently producing flames upon attempted vacuum distillation. Fortunately the adduct is sufficiently pure since its ^{1}H NMR spectrum revealed only the expected singlet CH_3 resonance at δ 1.69 and a multiplet for the CH_2 absorptions at δ 4.0. A mass spectrum of this adduct run as a solid (no heat applied) revealed a peak at *m/e* 148 corresponding to the molecular weight of the parent ion.

Spectroscopy. Undecoupled ^{31}P resonances were recorded with a Bruker HX-90 spectrometer operating at 36.44 MHz in the Fourier mode. The HFSO$_3$ solution provided the ^{19}F signal required for lock stabilization. Samples for the protonation studies were prepared by cooling 2 mL of HFSO$_3$ to −78 °C in a 10-mm (o.d.) NMR tube and allowing the phosphite (liquid, solid, or frozen) to flow down the side of the tube in small amounts (ca. 20 mg per addition) until about 200 mg of solute had been added. Vigorous shaking along with alternate warming (−40 °C) and cooling (−78 °C) served to effect solution. *Severe decomposition or small explosions occurred if localized areas of heating were allowed to intensify around undissolved phosphite.* The ^{31}P signal of 85% H$_3$PO$_4$ was used as the external standard even though slight broadening occurs at −50 °C.

Routine ^{1}H NMR spectra were obtained on either a Varian A-60 or a Hitachi Perkin-Elmer R20-B spectrometer operating at 60 MHz. An Atlas CH-4 mass spectrometer provided the low resolution mass spectra. Infrared spectra were obtained on a Beckman IR-4250 spectrometer using the 2851.5-cm^{-1} band of polystyrene as a calibration. A 0.015 M phenol solution was used to prepare solutions of 1.2×10^{-3}, 6.0×10^{-3}, 1.5×10^{-2}, 4.00×10^{-2}, and 10.00×10^{-2} M in each of the phosphates.

Results and Discussion

In Table II are listed the calculated net charges (ρ) on phosphorus and oxygen, the energy difference upon protonation of phosphorus ($\Delta E_{\mathrm{H^+}}(\mathrm{P})$), a measure of the number of lone pair electrons on phosphorus (LP), and the percent s character in the phosphorus lone pair for phosphite esters **1**$^{\mathrm{III}}$ to **5**$^{\mathrm{III}}$. LP is calculated by subtracting the total of the overlap populations[5] of the phosphorus valence orbitals from the total electron density on the phosphorus atom. An indication of the basicity trend can be obtained from the calculated results by noting that as ρ_{P} increases upon constraint of the molecular angles, LP decreases as expected. Thus, the decrease in the absolute values of the differences in these parameters from **1**$^{\mathrm{III}}$ to **5**$^{\mathrm{III}}$ also follows the decreasing basicity of phosphorus.

Table II. CNDO/2 Parameters for Phosphite Esters

	ρ_P	$(\rho_P)^3$	ρ_O	LP	LP − ρ_P	ΔE_{H^+}(P), au	% s
1^{III}	0.361	0.047	−0.246	2.152	1.791	−0.3776	38.3
2a^{III} [a]	0.371	0.051	−0.256	2.150	1.779	−0.3560	38.3
2b^{III} [a]	0.395	0.061	−0.264	2.138	1.743	−0.3530	38.4
3^{III} [a]	0.392	0.059	−0.265	2.139	1.747	−0.3373	38.3
4^{III} [b]	0.409	0.068	−0.285	2.127	1.718	−0.3641	37.6
5^{III} [b]	0.477	0.109	−0.302[c] −0.276[d]	2.088	1.611	−0.3132	39.7

[a] Calculations were done for R = H. [b] R = Me. [c] OCMe. [d] OCH_2.

Table III. CNDO/2 and ^{31}P Parameters for Protonated Phosphite Esters

	ρ_{P^+}	$(\rho_{P^+})^3$	ρ_{H^+}	$(\rho_{H^+})^3 \times 10^{-3}$	$^1J_{PH}$[c,d] (±1 Hz)	$^3J_{PH}$[f] (±1 Hz)	$\delta^{31}P$[e] (±0.2 ppm)
1^{III}	0.696	0.337	0.0218	0.0104	826.2	12.0 dec[g]	−24.4
2a^{III} [a]	0.698	0.340	0.0502	0.1265	850.6	12.8 q[h]	−18.2
2b^{III} [a]	0.717	0.369	0.0756	0.4321	865.0	12.8 q[h]	−17.3
3^{III} [a]	0.721	0.375	0.0766	0.4495	890.4	12.8 sep[i]	−44.7
4^{III} [b]	0.738	0.402	0.0797	0.5063	899.2[e]	4.5 sep	−32.2
5^{III} [a]	0.822	0.555	0.1110	1.3676	928.8	[j]	−46.1

[a] Calculations were done for R = H whereas the protonation data were obtained on the R = Me analogue. [b] R = Me. [c] For protonated species at −50 °C. [d] Doublet in all cases. [e] Compares favorably with the previously published value (898 ± Hz) obtained from the H NMR spectrum at −55 °C (L. J. Vande Griend and J. G. Verkade, *Phosphorus*, **3**, 13 (1973). [f] dec = decet, qd = quartet, sep = septet. [g] Eight out of ten lines observed. [h] $^3J_{POCH_3}$. [i] $^3J_{POCH_3} = {}^3J_{POCH_2} = {}^3J_{POCH}$. [j] Insufficient resolution to resolve fine structure due to this coupling.

In Table III are shown the calculated phosphorus and phosphorus-bound proton charges in the protonated forms of **1**^{III}–**5**^{III}, and the $^1J_{PH}$ values obtained from the ^{31}P NMR signals in $HFSO_3$. Since the one-bond PH coupling should depend mainly on the Fermi contact term,[23] the upward trend of this coupling with molecular constraint would be consistent with an increase in phosphorus lone pair s character and/or an augmentation of the effective nuclear charge on this atom. To the extent that the calculations are reliable, it appears that the change in ρ_P is more influential than the percent s character of phosphorus in the P–H link since there is no discernible trend in the latter values (Table II). Because the Fermi term relates $^1J_{PH}$ directly to the cube of the effective nuclear charge,[24] the plots in Figure 1 of $^1J_{PH}$ vs. the $(\rho_{P^+})^3$ taken from Table III are of interest to examine. The correlation coefficient of 0.93 for both plots, exclusive of the point for protonated **5**^{III}, drops to 0.86 and 0.91, respectively, for the $(\rho_{P^+})^3$ and $(\rho_{H^+})^3$ graphs when this point is included. These decreases may be indicative of the importance of some unobvious factor associated with (i) the highly strained cage, (ii) the assumptions made in the calculations, or (iii) the extrapolation of the coupling theory of $^1J_{CH}$ to $^1J_{PH}$. On the other hand, it is reasonable to suppose that the effect of charge on $^1J_{PH}$ should be composed of the sum of the charges on the coupling nuclei. The correlation coefficient of 0.92 for $(\rho_{P^+} + \rho_{H^+})^3$ vs. $^1J_{PH}$ for all six points is quite reasonable considering the crudeness of the calculations and the possible presence of other contributions to the coupling.

Another experimental measure of the basicity of phosphites **1**^{III}–**5**^{III} is the B–H stretching frequency of their borane adducts **1**^{A}–**5**^{A} which are recorded in Table IV. For such systems, an increase in ν(BH) is expected to be accompanied by a decrease in basicity owing to greater s character in the B–H links.[25,26] In contrast to the order of basicities obtained from the protonation studies (**1**^{III} > **2a**^{III} > **2b**^{III} > **3**^{III} > **4**^{III} > **5**^{III}), **1**^{III} and **2a**^{III} are reversed in order, according to the ν(BH) values exhibited by their borane adducts **1**^{A} and **2a**^{A}. It is conceivable that the more polarizing proton induces greater enlargement of the OPO angles than does a BH_3 group. Consequently, the ring POC angles would diminish resulting in more sp^3 character of the oxygen and less π donation to phosphorus. The lack of corroboration of the order of basicity toward adduct formation given by the calculations of the parent phosphites may, in part, be ascribed to the absence of structural parameters for compounds such as **2a**^{III}. Thus the agreement of the calculations with the protonation results may be coincidental in the case of **1**^{III} and **2a**^{III}.

The general decrease in the magnitude of ΔE_{H^+}(P) (**4**^{III} being an exception) with basicity is expected since protonation of a poor Lewis base will not result in as large an energy difference as the same process with a better one. The general rise in negative charge on the ring oxygens (ρ_O) from **1**^{III} to **5**^{III} is also reasonable since constraint is expected to reduce orbital

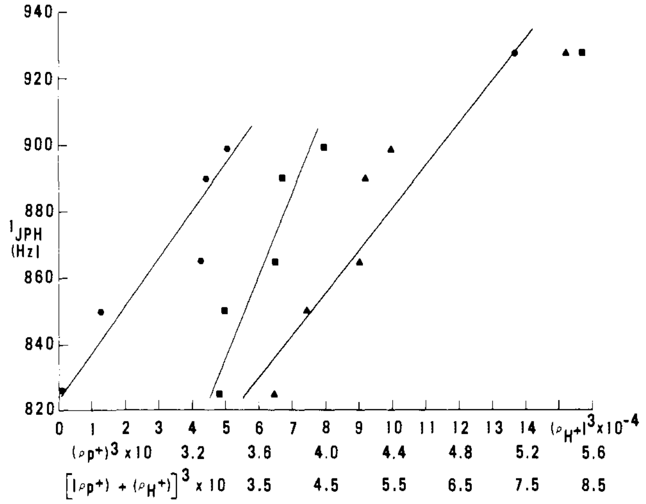


Figure 1. Plots of $^1J_{PH}$ vs. the cube of the calculated positive charge on the proton (●) and the phosphorus atom (■) for the protonated forms of phosphites **1**^{III}–**5**^{III}. The symbols ▲ represent a plot of the cube of the sums of these charges vs. $^1J_{PH}$.

Table IV. Infrared and ^{31}P NMR Data for Phosphite Ester Borane Adducts

	ν(BH) bands^a			δ^{31}P	$^1J_{\mathrm{P^{11}B}}$
	Asymm	Symm	Wt av	(±0.2 ppm)	(±1 Hz)^e
$\mathbf{1}^{\mathrm{A}}$	2397.5	2352.0	2382.3	−117.1 −118^f	103.2 97.2^f
$\mathbf{2a}^{\mathrm{A}\ b}$	2392.5	2342.0	2375.7	−109.6	108.0
$\mathbf{2b}^{\mathrm{A}\ b}$	2410.0	2354.0	2391.3	−108.5	103.2
$\mathbf{3}^{\mathrm{A}\ c}$	2412.0	2354.0	2392.7	−127.4	94.0
$\mathbf{4}^{\mathrm{A}\ d}$	2421.5	2363.5	2402.2	−97.6	91.4
$\mathbf{5}^{\mathrm{A}\ b}$	2432.5	2365.5	2410.2	−126.8	63.3

[a] Precise to ±0.5 cm^{-1}. All the spectra were taken in CCl_4 and compare favorably with those in ref 18 where the same solvent was used. [b] R = Me. [c] R = H. [d] R = Et. [e] Except for $\mathbf{2b}^{\mathrm{A}}$ and $\mathbf{5}^{\mathrm{A}}$ (±2 Hz). [f] Reference 3b.

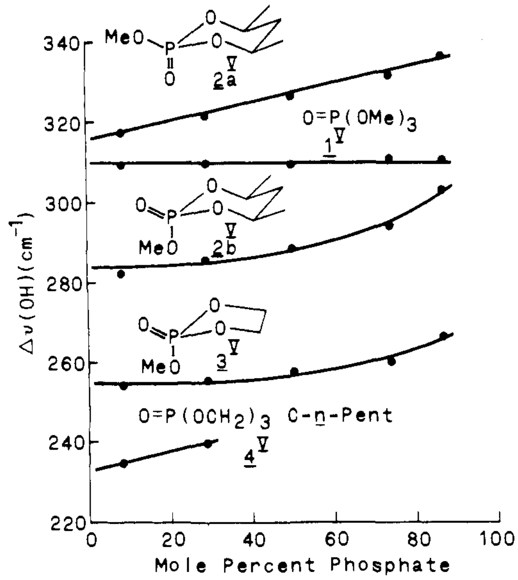


Figure 2. Plot of $\Delta\nu$(OH) for phenol vs. mole percent of phosphates $\mathbf{1}^{\mathrm{V}}$–$\mathbf{4}^{\mathrm{V}}$ in CCl_4.

repulsion effects[3a] as well as π delocalization from these atoms to phosphorus.[2,3b] While protonation of the ester oxygens undoubtedly occurs in $HFSO_3$, exchange processes rapid on the NMR time scale prevent observation of these resonances. It is reasonable to suppose, however, that protonation of the oxygens will not affect the trend in $^1J_{\mathrm{PH}}$ nor the correlation of $^1J_{\mathrm{PH}}$ with calculated parameters since the rise in this coupling on decreasing phosphorus basicity from $\mathbf{1}^{\mathrm{III}}$ to $\mathbf{5}^{\mathrm{III}}$ is complementary to increasing oxygen basicity.

In Table V appear the relevant parameters of the CNDO/2 calculation for the phosphates $\mathbf{1}^{\mathrm{V}}$–$\mathbf{5}^{\mathrm{V}}$ along with their phosphoryl group stretching frequencies (ρ(P=O)) and phenol shifts ($\Delta\nu$(OH)) obtained by extrapolation of the plot in Figure 2 to infinite dilution. From the near identity of the two ν(P=O) values for both $\mathbf{1}^{\mathrm{V}}$ and $\mathbf{2a}^{\mathrm{V}}$,[27] it is clear that the phosphoryl oxygen basicities are probably very nearly the same and this is reflected in the relative closeness of their extrapolated values of $\Delta\nu$(OH). While the calculated values of $\rho_{=\mathrm{O}}$ for these two phosphates are rather different, their $\Delta E_{\mathrm{H^+}}$ parameters are close. It should again be noted, however, that the assumed structural parameters for $\mathbf{2a}^{\mathrm{V}}$ may well be too inaccurate to permit comparison of the resultant $\rho_{=\mathrm{O}}$ and $\Delta E_{\mathrm{H^+}}$ values to those of $\mathbf{1}^{\mathrm{V}}$.

As was the case with the phosphite esters, negative charge is calculated to accumulate on the ring oxygens of the phosphates on constraint (ρ_{O} in Table V). The rise in the negative value of $\Delta E_{\mathrm{H^+}}$(O) is also consonant with the expected increase in basicity of these atoms. Interestingly, the smaller negative charge and the smaller energy of protonation of the ring oxygens compared to the phosphoryl oxygens ($\Delta E_{\mathrm{H^+}}$(=O)) in the phosphate esters may be associated with a small shoulder on the high energy side of the ν(OH) peak arising from the P=O bond. However, no trend in $\Delta\nu$(OH) for the new absorption could be discerned.

Phosphinic and phosphonic acids are known to undergo fluorination reactions in $HFSO_3$, eventually producing PF_3 and OPF_3, after the formation of a variety of intermediate fluorophosphorus compounds.[28] In the series of phosphites $\mathbf{1}^{\mathrm{III}}$–$\mathbf{5}^{\mathrm{III}}$, it was found that fluorination reactions were sufficiently slow at −50 °C to obtain adequate ^{31}P NMR data on the protonated species. Evidence for the absence of detectable fluorination in our experiments is the absence of any $^1J_{\mathrm{PF}}$ couplings which would have been immediately apparent owing to their large size (>1000 Hz). It was noted, for instance, that $\mathbf{3}^{\mathrm{III}}$ (R = H) was fluorinated too rapidly to be employed, giving rise to the ^{31}P quartet resonance (δ ^{31}P −104.0, $^1J_{\mathrm{PF}}$ = 1402) associated with PF_3 even at −50 °C whereas $\mathbf{3}^{\mathrm{III}}$ (R = Me) was stable.[28] Furthermore $\mathbf{4}^{\mathrm{III}}$ (R = Me) kept at −78 °C for 2 days showed the presence of OPF_3 (δ ^{31}P +37.7, $^1J_{\mathrm{PF}}$ = 1057.6) in addition to PF_3. Finally, $\mathbf{5}^{\mathrm{III}}$ (R = Me) was almost completely difluorinated when the temperature was allowed to rise to −20 °C as shown by the doublet ($^1J_{\mathrm{PH}}$ = 937) of triplets ($^1J_{\mathrm{PF}}$ = 1139.0) for the ^{31}P resonance (δ −0.1). The absence of any detectable $^3J_{\mathrm{PH}}$ coupling in this spectrum suggests that the $H^+PF_2OCMe(CH_2OSO_2F)_2$ cation may be formed.

Table V. CNDO/2 Parameters and Infrared Data for Phosphates

	$\rho_{=\mathrm{O}}$	ρ_{O}	$\Delta E_{\mathrm{H^+}}$(=O)	$\Delta E_{\mathrm{H^+}}$(O), au	$\Delta\nu$(OH), cm^{-1}	ν(P=O),^{j} cm^{-1}
$\mathbf{1}^{\mathrm{V}}$	−0.431	−0.202	−0.5003	−0.3008	310^f	1274,1290^k
$\mathbf{2a}^{\mathrm{V}\ a}$	−0.377	−0.232	−0.5028	−0.3610	316	1271,1289^k
$\mathbf{2b}^{\mathrm{V}\ a}$	−0.343	−0.232	−0.5047	−0.3668	284	1304^l
$\mathbf{3}^{\mathrm{V}\ b}$	−0.354	−0.238	−0.4921	−0.3645	255^g	1302^m
$\mathbf{4}^{\mathrm{V}\ c}$	−0.316	−0.245	−0.4890	−0.3709	233^h	1327^n
$\mathbf{5}^{\mathrm{V}\ d,e}$					i	1346,1354

[a] Calculations were done for R = H whereas the phenol shift data were obtained for R = Me. [b] R = H. [c] Calculations were done for R = Me whereas $\Delta\nu$(OH) data were taken for R = *n*-Pent which was more soluble. [d] R = Me. [e] Calculations involving the structural data obtained in ref 11 led to nonconvergence, presumably owing to the substantial nonbonded interactions in this highly strained molecule. [f] Compares favorably to 315 cm^{-1} obtained by G. Aksnes and T. Gramstad, *Acta Chem. Scand.*, **14,** 1485 (1960) and 304 cm^{-1} observed in ref 18. [g] Compares favorably with 257 ± 2 cm^{-1} observed in ref 18. [h] Compares favorably with 230 ± 5 cm^{-1} observed in ref 18. [i] Insoluble. [j] Observed in CCl_4 except for $\mathbf{2a}^{\mathrm{V}}$ (C_6H_6), $\mathbf{4}^{\mathrm{V}}$ ($CHCl_3$) and $\mathbf{5}^{\mathrm{V}}$ (CH_2Cl_2). [k] D. W. White, G. K. McEwen, R. D. Bertrand, and J. G. Verkade, *J. Chem. Soc. B*, 1454 (1971). [l] J. A. Mosbo, Ph.D. Thesis, Iowa State University, 1973. [m] L. J. Vande Griend, D. W. White, J. G. Verkade, *Phosphorus*, **3,** 13 (1973). [n] Established from ^{18}O experiments (L. J. Vande Griend and J. G. Verkade, to be published).

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Carbon-13 Relaxation Study of Stereoregular Poly(methyl methacrylate) in Solution

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Abstract: Carbon-13 spin–lattice relaxation times (T_1) have been determined for pyridine and for CDCl$_3$ solutions of both predominantly isotactic and predominantly syndiotactic poly(methyl methacrylate), PMMA, at 38 and 100 °C. The T_1's of both backbone and side-chain carbons are longer in the isotactic chain configuration. The relative T_1 data for both quaternary and methylene backbone carbons suggest the isotactic chain skeleton is more flexible than that of the syndiotactic polymer. In addition, spin–spin relaxation data (T_2) and ^{13}C{^{1}H} nuclear Overhauser enhancements for the CH$_2$ carbon indicate that backbone motion in the PMMA systems is characterized by a distribution of correlation times. Both Cole–Cole and log χ^2 distributions were found to provide reasonable fits of the experimental data; however, a broader distribution was required to fit the syndiotactic results than the isotactic results. Finally, the T_1 results for the α-methyl carbons in the different stereoforms of the polymer suggest that the constraint to methyl internal rotation in the isotactic chain is less than in the syndiotactic chain.

Introduction

Recently, Hatada and co-workers[1] have reported a dependence of the proton spin–lattice relaxation times, T_1, of poly(methyl methacrylate), PMMA, on the polymer chain configuration. From their study, the relaxation times of the various protons of the repeat unit were found to be (1) shorter in a highly syndiotactic PMMA relative to a highly isotactic PMMA, and (2) shorter in a syndiotactic triad relative to isotactic triad in atactic PMMA. Thus, differential relaxation times were found for the case of two stereoregular polymers and for the case of local regions of stereoregularity (stereochemical triads) in a nonstereoregular polymer.

Hatada et al.[1] suggest that, unlike the proton results, the corresponding carbon-13 relaxation times in PMMA should be *independent* of chain configuration. Evidence cited for this conclusion includes the results that (1) in *o*-dichlorobenzene solutions of polystyrene, the T_1 results are the same for the atactic and isotactic polymers;[2] and (2) in atactic polyacrylonitrile, poly(vinyl chloride), and poly(vinyl alcohol),[3] the methine carbon resonances corresponding to syndiotactic, heterotactic, and isotactic stereochemical triads have equal T_1 values. The physical basis cited for the equivalency of the C-13 T_1 values is that[1] "the mechanism of ^{13}C relaxation is mainly a dipole–dipole interaction between the carbon and the directly bonded protons". There is of course ample evidence to support this relaxation mechanism for carbons with attached hydrogens;[4–6] however, this alone does not preclude differences in ^{13}C T_1 occurring between different stereoforms of the same polymer. Indeed, such differences can arise in two ways: (1) from differences in the chain segmental motion between stereoregular polymers or between regions of stereoregularity in an atactic polymer; and (2) from differences in preferred conformations between the stereoforms which lead to different "average distances" for the interaction of a carbon with a proton of a neighboring repeat unit. This latter mode is largely precluded for a carbon with a directly attached proton,[7] the