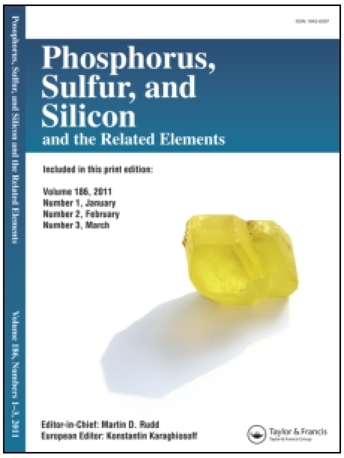

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SUBSTITUENT EFFECTS ON THE ^{31}P, ^{13}C, AND ^{1}H NMR CHEMICAL SHIFTS OF SUBSTITUTED DIPHENYL 1-PHENYLAMINO-1-PHENYLMETHANEPHOSPHONATES AND THEIR ANIONS

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SUBSTITUENT EFFECTS ON THE ^{31}P, ^{13}C, AND ^{1}H NMR CHEMICAL SHIFTS OF SUBSTITUTED DIPHENYL 1-PHENYLAMINO-1-PHENYLMETHANEPHOSPHONATES AND THEIR ANIONS

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For a series of thirty-five novel diphenyl 1-phenylamino-1-phenylmethanephosphonates, substituted in the meta and para positions on the anilino and/or aryl ring, ^{31}P chemical shifts show a good linear correlation with Hammett σ_n and Taft σ^0 parameters, the ^{31}P nucleus being better shielded in the case of electron withdrawing substituents. The same pattern is observed for the phosphonate anions, except when para phenyl substituents can interact with the phosphorus atom by direct resonance. This inverse relationship is due to a field effect of the substituent dipole which polarizes π-electron clouds in the molecule. A corresponding shift in π-electron density is likewise observed for ^{13}C resonances of the two diastereotopic phenoxy groups, the phenylamino and phenyl moieties. Vicinal CH-NH coupling is shown to be dependent on the rate of NH proton exchange as influenced by resonance, temperature and solvent effects.

INTRODUCTION

A series of papers from this laboratory has demonstrated the usefulness of α-heterosubstituted methanephosphonates and their carbanions in synthesizing enamines, amidines, substituted vinyl chlorides, acetylenes, diacetylenes, indols, benzofurans, silylenol ethers, deoxybenzoins, anilides, substituted ferrocenes, and most recently quinolines.[1] While generating the anions derived of diesters of 1-(substituted phenylamino)-1-(substituted phenyl)methanephosphonates a large substituent effect on the acid strength and yield in Horner–Emmons type reactions of such phosphonates was noticed.[1b] Due to the importance of understanding the electron distribution within molecules in predicting chemical behavior, the relation between NMR chemical shifts and substituent parameters such as Hammett and Taft σ values has been used as a probe. As the applications

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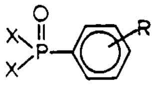
† Correspondence author; this is part 15 of "Synthesis with α-Heterosubstituted Phosphate Carbanions". Part 14, D. Burkhouse and H. Zimmer *Synthesis*, 330 (1984). Presented in part at "Organophosphorus Symposium"; Bonn, Federal Republic of Germany, August 31–September 6, 1986.

of ^{31}P NMR have expanded, a number of investigators have attempted these types of correlations with ^{31}P NMR chemical shifts, to develop a more unified theoretical foundation of electron density and bonding in phosphorus containing compounds.[2–11] In studies of the series of compounds (**1–4**) containing different R substituents on the meta and para positions of the phenyl moiety, it was observed that electron withdrawing substituents lead to an upfield shift of the ^{31}P chemical shift.[2,3,6,11] In contrast, deshielding and a down field shift is normally found in similar carbon compounds. Explanations have usually invoked changes in $d\pi-p\pi$ bond order leading to an increased contribution of the P=O resonance structure.[2–5] Subsequent work with aryl N-aryliminotriphenylphosphoranes,[5,7,10,12] **5**, and diphenyl phosphinate,[9] **6**, found a normal relationship between ^{31}P chemical shift and the electron withdrawing ability of R. In each case Hammett and/or Taft σ parameters were used as the measure of substituent electron withdrawal. In all cases but one the results were explained on the basis of changes in the $d\pi-p\pi$ bonding involving direct resonance of the hetero atom with the phosphorus. Pomerantz[10] alone proposes an alternative mechanism in which the heteroatom lone electron pair is in resonance with the aromatic ring.

In this investigation we have demonstrated that the ^{31}P chemical shifts of a series of thirty five diphenyl α-heterosubstituted phosphonates, **7**, and their anions correlate well with both Hammett σ_n and Taft σ^0 values. In both cases an increase in the electron-withdrawing ability of the substituent on either the aryl or anilino moiety leads to an upfield shift of the ^{31}P signal, implying an increase in the shielding of the phosphorus atom.

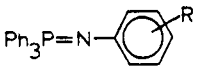
Absolute assignment of the ^{13}C spectra of the same phosphonates in $CDCl_3$ and DMSO illustrates the extent of substituent effect throughout the molecule. Substituents act as dipoles that shift the π cloud electron density in all aryl rings and the P=O bond by a field effect.

Proton NMR is used to examine the basicity and the rate of exchange of the hydrogen of the NH-group. It is shown that the exchange rate is influenced by substituent effects, solvent effects, and temperature.



Compounds 1 - 4

X = F, Cl, OH, OEt
R = various groups



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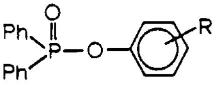
R = various groups



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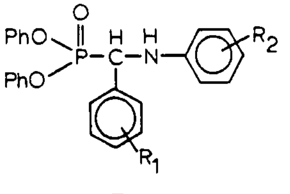
R = MeO, Me, H, F, Br, CH_3OH, CF_3, CN, NO_2



7

R = H; m,p-Br; m,p-OMe; m,p-NO_2; m,p-CN

RESULTS AND DISCUSSION

^{31}P-*Shifts; Neutral Species*

A series of thirty five diphenyl α-heterosubstituted phosphonates, **7**, were prepared that varied in the aryl and arylamino substituents. Both meta and para substituents were used, the only restriction being that in the case of a substituent being positioned on both rings, that both be either meta or para. The measured ^{31}P chemical shifts are given in Table I.

A least squares fit of these ^{31}P chemical shifts with the corresponding Hammett σ_m or σ_p values exhibited a linear relationship with a sample correlation coefficient, *r*, of 0.950 (Figure 1). This linear relationship can be described by the equation:

$$\delta^{31}P = 16.2 - 1.56\Sigma\sigma$$

Several previous studies reported a better correlation with Taft constants.[2a,9] Similarly, a least squares analysis of the data in this study with Taft σ^0 parameters was slightly improved, with a correlation coefficient of 0.976 (Figure 2). This linear relationship can be described the the equation:

$$\delta^{31}P = 16.3 - 1.70\Sigma\sigma^0$$

The greater the electron-withdrawing ability of the substituent, the further upfield the ^{31}P signal was shifted. The data in this study also indicated that the substituent effect was nearly identical whether a given substituent was on the aryl or the anilino moiety, whether dissimilar substituents were on both rings or whether meta or para substituted anilino or aryl moieties were present. In all cases, the same linear relationship was verified by a *t*-test of the above mentioned subsets. The slopes and intercepts were indistinguishable within 95% confidence limits. Hammett and Taft σ^0 values were found to be additive over the range of the substituents tested. The effect is consistent in DMSO and $CDCl_3$, with DMSO chemical shifts 0.6 ppm average downfield from that measured in $CDCl_3$ (Figure 3). A plot of the twenty-two δ ^{31}P values measured in $CDCl_3$ versus Taft σ^0 parameters (not shown) has a correlation coefficient of 0.986 ($s_y = 0.175$, $s_{coef} = 0.0424$).

The physical significance of these linear relationships might be interpreted in terms of resonance structures **7a** and **7b**. It has been suggested that the state of d-orbital occupancy and, hence, the degree of dπ-pπ bonding, may be a major factor in influencing ^{31}P chemical shifts.[9] Electron withdrawing substituents in either the R_1 or R_2 position appear to favor the predominance of resonance structure **7a** over resonance structure **7b** by enhancing the degree of dπ-pπ bonding. This increase in phosphorus d orbital occupancy would lead to increase

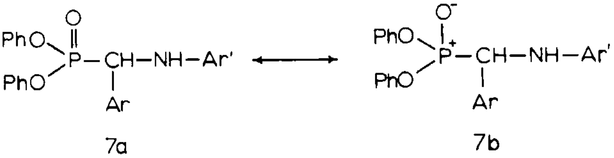


TABLE I

	R_1	R_2	$\delta\ ^{31}P$ DMSO($CDCl_3$)	Anion $\delta\ ^{31}P$	σ p.m.	σ^0		R_1	R_2	$\delta\ ^{31}P$ DMSO($CDCl_3$)	$\delta\ ^{31}P$	σ p.m.	σ^0
7.1	H	H	16.29 (15.76)	10.08	0	0	**7.19**	m-OMe	m-OMe	16.11 (15.59)	9.80	0.24	0.12
7.2	H	m-Br	15.82 (15.09)	9.61	0.39	0.38	**7.20**	p-Br	p-NO_2	14.03 (13.50)	7.72	1.03	1.12
7.3	H	p-Br	15.92 (15.24)	9.70	0.23	0.29	**7.21**	P-Br	P-OMe	15.82 (15.11)	9.61	0.04	0.10
7.4	H	m-NO_2	15.45 (14.69)	9.14	0.71	0.70	**7.22**	m-Br	m-NO_2	14.79	8.19	1.10	1.08
7.5	H	p-NO_2	14.79 (14.19)	8.57	0.78	0.83	**7.23**	m-Br	m-OMe	15.54	9.04	0.51	0.42
7.6	H	m-OMe	16.29 (15.61)	10.08	0.12	0.06	**7.24**	p-NO_2	p-Br	14.32	18.08	1.03	1.12
7.7	H	p-OMe	16.58 (15.99)	10.45	0.27	0.15	**7.25**	p-NO_2	p-OMe	14.98	18.18	0.51	0.66
7.8	m-Br	H	15.54 (14.73)	9.13	0.39	0.38	**7.26**	m-NO_2	m-Br	14.50	8.01	1.10	1.08
7.9	p-Br	H	15.54 (14.88)	9.32	0.23	0.29	**7.27**	m-NO_2	m-OMe	14.98	8.57	0.83	0.76
7.10	m-NO_2	H	14.98 (13.88)	8.66	0.71	0.70	**7.28**	p-OMe	p-NO_2	14.98 (14.36)	8.95	0.51	0.66
7.11	p-NO_2	H	14.79 (13.77)	18.08	0.78	0.83	**7.29**	p-OMe	p-Br	16.20	10.17	0.04	0.10
7.12	m-OMe	H	16.20 (15.63)	10.08	0.12	0.06	**7.30**	m-OMe	m-NO_2	15.35	9.04	0.83	0.76
7.13	p-OMe	H	16.58 (16.03)	10.74	0.27	0.15	**7.31**	m-OMe	m-Br	15.73	9.42	0.51	0.42
7.14	p-NO_2	p-NO_2	13.28 (12.45)	17.42	1.65	1.66	**7.32**	H	p-CN	15.26	—	0.69	0.66
7.15	m-NO_2	m-NO_2	14.22 (12.95)	7.82	1.42	1.40	**7.33**	p-CN	H	14.98	—	0.69	0.66
7.16	p-Br	p-Br	15.07 (14.44)	8.85	0.46	0.52	**7.34**	p-CN	p-CN	14.10	—	1.36	1.32
7.17	m-Br	m-Br	15.07 (14.19)	8.57	0.78	0.76	**7.35**	p-NO_2	p-CN	13.66	—	1.47	1.49
7.18	p-OMe	p-OMe	16.77 (16.20)	10.83	0.54	0.30							

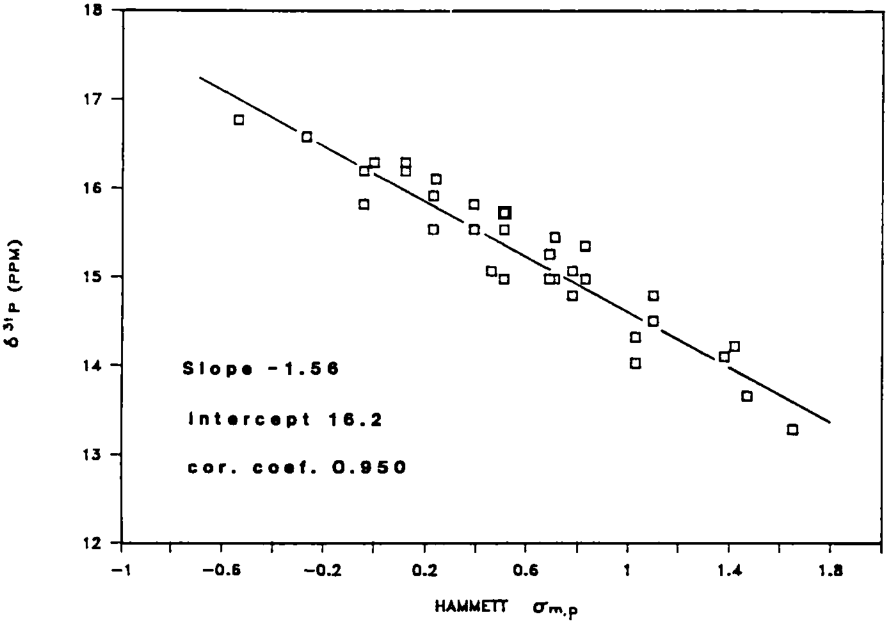


FIGURE 1 Plot of ^{31}P chemical shifts (0.3 M solution in DMSO) of the neutralphosphonates **7.1–7.25** versus Hammett σp, m values (N = 35, Standard err of Y est (s_y) = 0.2714, Standard err of coef (s_{coef}) = 0.08937).

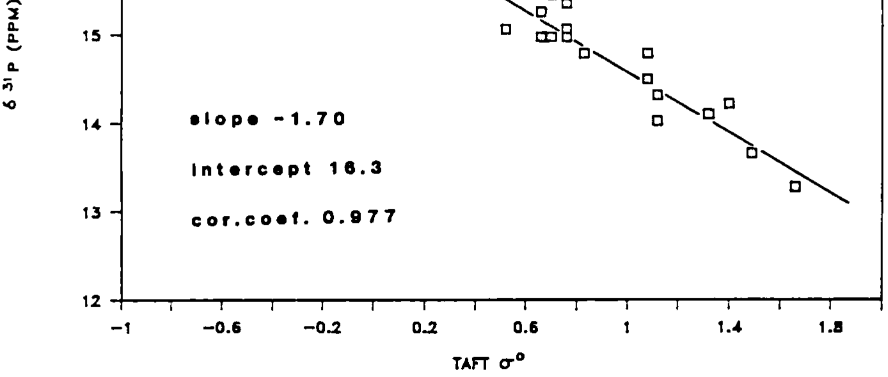


FIGURE 2 Plot of ^{31}P chemical shifts (0.3 M solution in DMSO) of the neutral phosphonates **7.1–7.35** versus Taft σ^0 values (N = 35, s_y = 0.1871, s_{Coef} = 0.06511).

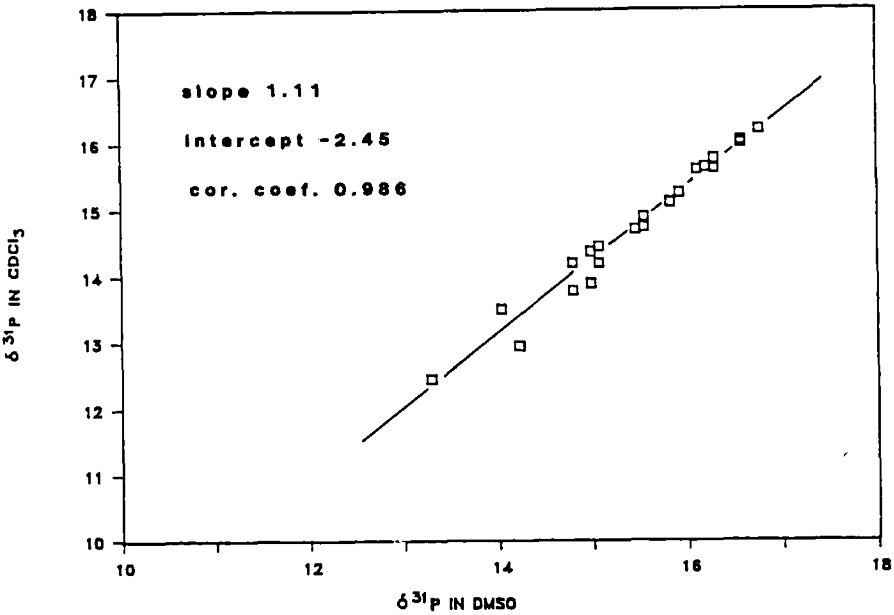


FIGURE 3 Plot of ^{31}P chemical shifts of neutral phosphonates **7.1–7.21**, **7.28** in $CDCl_3$ versus ^{31}P chemical shifts is DMSO ($N = 22$, $s_y = 0.1749$, $s_{coef} = 0.04236$).

in the P—O bond order and a corresponding upfield shift. The predominance of this effect over the normally expected effect of electron withdrawing substituents was demonstrated by previous researchers examining compounds in which the substituent bearing moiety was bonded directly to the phosphorus.[2,3,6,11] In the present investigation, the first evidence is presented that this effect can be observed through up to 3 bonds from the phenyl ring, including a C—N bond of the anilino moiety. The effect of the substituent must be due to an inductive or field effect since the phosphorus atom is separated by two or three single bonds from the respective phenyl rings. In earlier reports compounds of type **5** and **6**, involving a heteroatom adjacent to the phosphorus were examined[5,7,9,10,12] and a "normal" relationship between the Hammett–Taft σ values and ^{31}P NMR chemical shift was observed. In these compounds, in contrast to the ones investigated in the present study however, a direct resonance interaction with the phosphorus atom is operative; thus, a "normal" relationship was to be expected.

Although the two substituted rings are not the same distance from the P atom, and one is bonded to a heteroatom, the electrical effects exerted by substituents of either ring or the P atom are not statistically distinguishable at 95% confidence limits. Possibly the contribution of the heteroatom lone pair to the dipole of the substituted anilino moiety produces a slightly more effective field effect that compensates for its marginally greater distance from the P atom than the aryl moiety.

^{31}P-Shifts Anions

The ^{31}P NMR chemical shifts of the anions of the diphenyl α-heterosubstituted phosphanates examined in this investigation also showed a clear correlation with

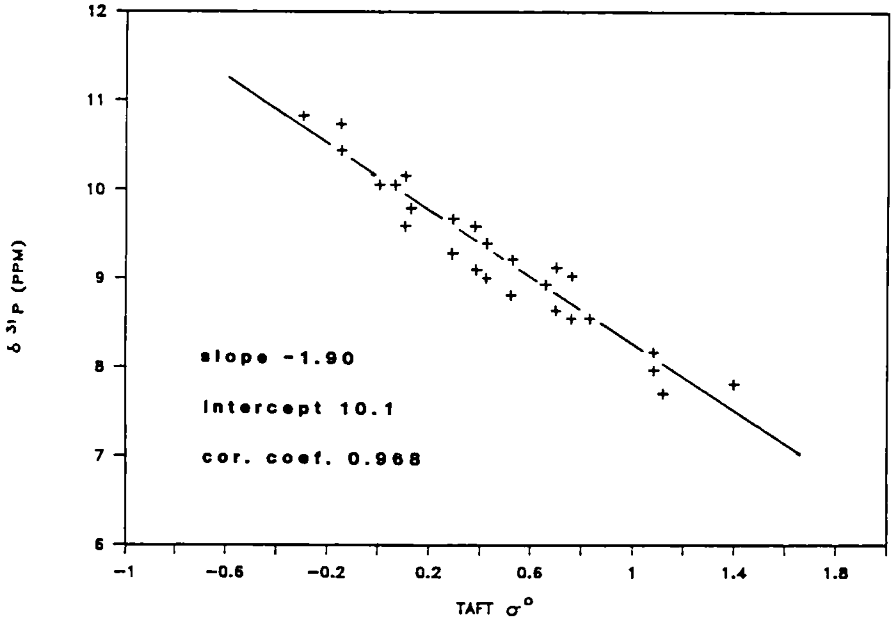
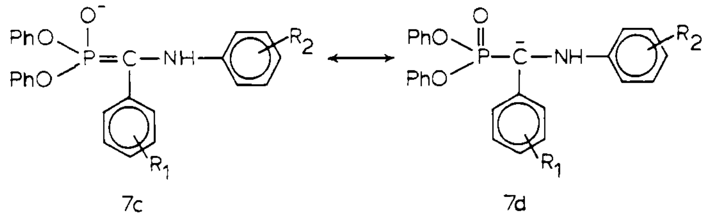


FIGURE 4 Plot of ^{31}P chemical shifts (0.3 M solution in DMSO) of the phosphonate anions **7.1–0.10**, **7.12**, **7.13**, **7.15–7.23**, **7.26–7.31** versus Taft σ^0 parameters ($N = 27$, $s_y = 0.2187$, $s_{coef} = 0.09824$). The 1-(4-nitrophenyl) derivatives are graphed in Figure 5.

the electron withdrawing properties of the R_1 and R_2 substituents. The best fit again was obtained with Taft σ^0 parameters (Figure 4) and can be expressed by the equation:

$$\delta\,^{31}P = 10.13 - 1.90\Sigma\sigma^0 \quad (r = 0.968)$$

Electron withdrawing substituents produced an upfield shift in the ^{31}P shifts in a pattern nearly identical to that of the corresponding neutral species. All ^{31}P chemical shifts of the anions, with a few notable exceptions, were also shifted upfield from that of the parent compounds (Figure 5). Every compound having a para-nitro substituent on the aryl ring, however, had anion ^{31}P δ values shifted downfield from that of the neutral phosphonates. This seems readily explainable by the ability of the p-nitro group to give rise to additional resonance structures and bear much of the negative charge; thus, decreasing the electron density around the P-atom. In the majority of the anions derived of the investigated phosphonates, the dominant contributing resonance structure appears to be **7c** or **d**, indicating an increase of the electron density around the phosphorus atom



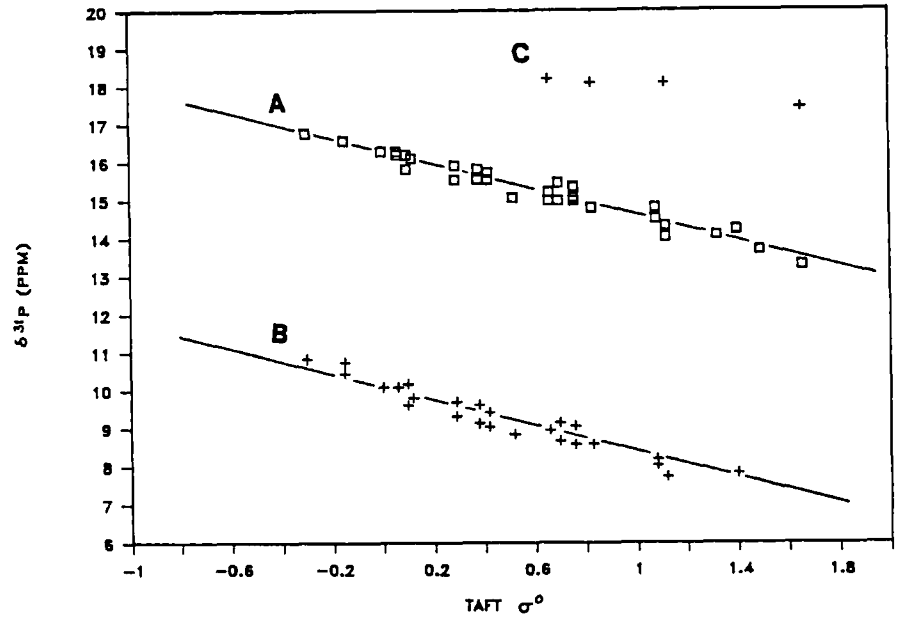
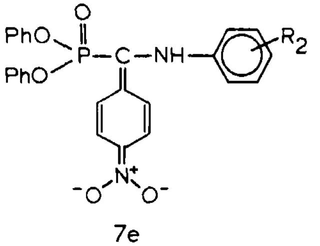


FIGURE 5 Plot of ^{31}P chemical shifts (0.3 M solution in DMSO) of the neutral phosphonates (A) and the corresponding anions [(B) for all anions except the 1-(4-nitrophenyl) derivatives (C)] versus Taft σ^0 parameters.

resulting in an upfield shift. The presence of the p-nitro substituent on the aryl ring is responsible for a contributing resonance structure **7e**, and consequently a deshielding of the phosphorus atom occurs with a concomitant downfield shift. Thus, when direct resonance with the phosphorus atom is possible, an electron withdrawing aryl substituent causes the phosphorus atom to be deshielded. This is opposite to the effect which is observed when only an inductive or field effect is operative.



7e

^{13}C-*Shifts*

Absolute assignment of the ^{13}C spectra in $CDCl_3$ and DMSO provided a view of the substituent effect on electron density throughout the molecule (Figure 6). Aryl and anilino substituents appear to act as dipoles that shift the π electron clouds by a field effect. The powerful NO_2 dipole induces a polarization that results in a deshielding of all para, and to a lesser extent, meta aryl carbon atoms. The ipso and ortho positions experience a concomitant increase in shielding. Thus, the electron density of the π cloud is shifted toward the nitro group bearing moiety (Figure 7).

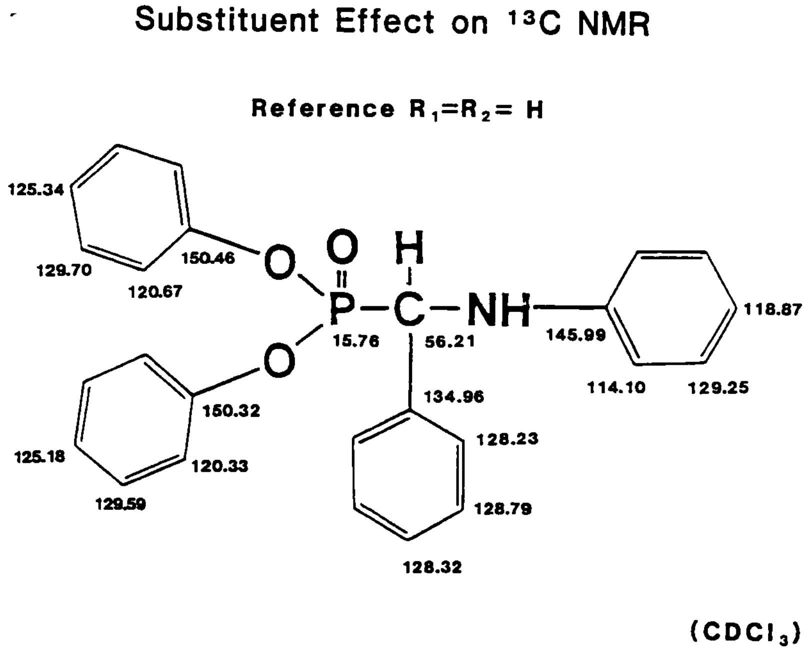


FIGURE 6 ^{13}C chemical shifts of reference nonsubstituted phosphonate **7.1** (0.1 M solution in $CDCl_3$).

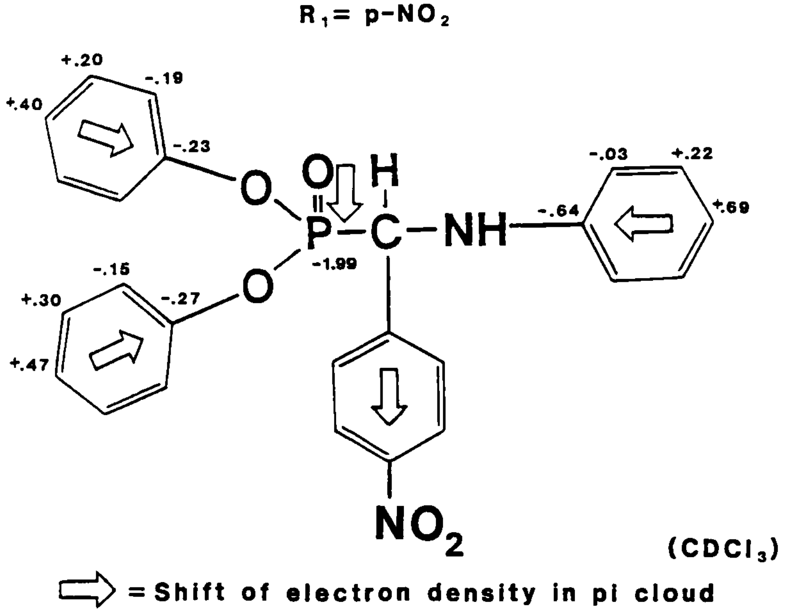


FIGURE 7 Changes in ^{13}C and ^{31}P NMR chemical shifts when $R_1 = p\text{-}NO_2$ relative to the non substituted phosphonate **7.1** ($R_1 = R_2 = H$).

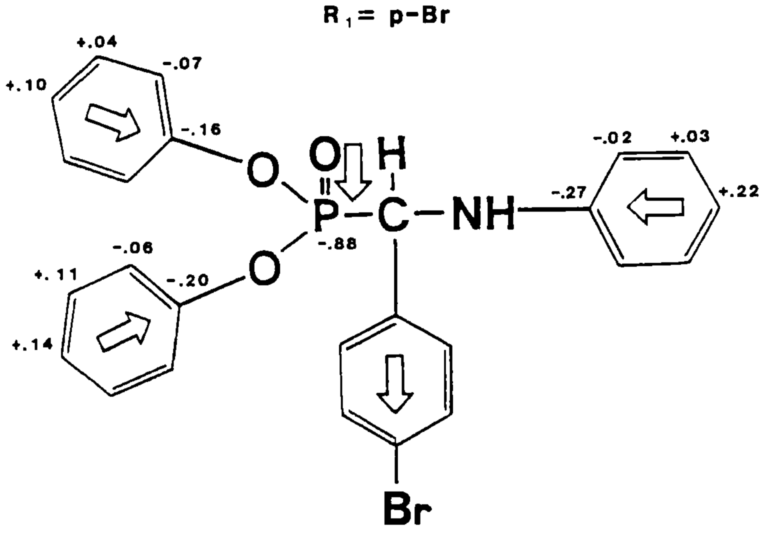


FIGURE 8 Changes in ^{13}C and ^{31}P chemical shifts when R_1 = p-Br relative to the nonsubstituted phosphonate.

While the change in ^{13}C chemical shift is in all cases less than one ppm, the effect is much more pronounced on the ^{31}P chemical shift. The difference is easily explained since the P=O double bond is closer to the dipole bearing moiety and the $d\pi$–$p\pi$ bonding involved is more easily distorted than the electron density in the phenyl rings. Thus, it can be assumed that the polarization caused by the substituent is shifting the P=O π-electron cloud in a manner analogous to that determined in the aryl rings. This accounts for the increased shielding of the

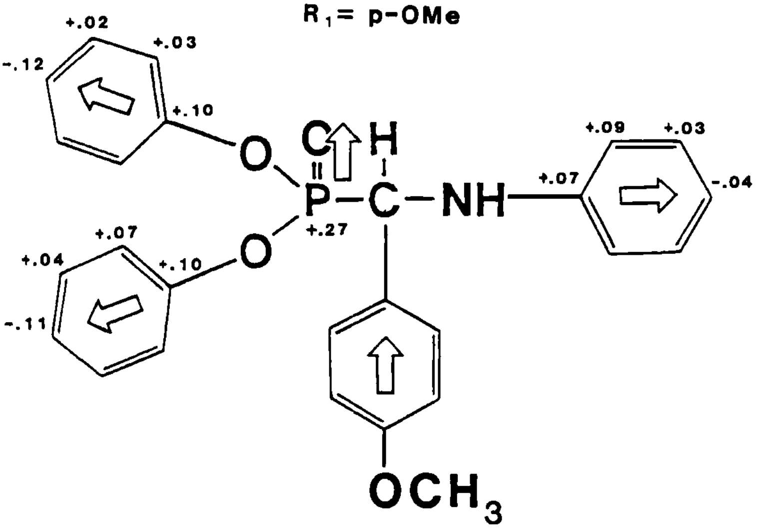


FIGURE 9 Changes in ^{13}C and ^{31}P chemical shifts when R_1 = p-OMe relative to the nonsubstituted phosphonate.

phosphorus atom when an electron withdrawing substituent, such as P-NO_2, is present.

Substitution by a bromine atom produces a similar but much attenuated polarization (Figure 8) with the π clouds also shifted toward the substituent. The opposite effect is witnessed when the p-OME substituent is present. (Figure 9) The M+ effect of the methoxy group decreases shielding at the ipso and ortho positions while increasing the shielding at the meta and para positions. The aryl π clouds are thus shifted away from the substituent. The evidence of this polarization of all π clouds in the molecule clearly argues for a field rather than inductive effect. Substituent effects are slightly greater in the more polar DMSO than in $CDCl_3$.

The ^{13}C data consistantly indicate that the two phenoxy groups are diastereotopic. Corresponding phenoxy carbon signals vary by as much as 0.40 ppm. This non-equivalence is also visible in the high resolution proton NMR spectra. The data on hand so far do not permit assignment of the observed shift differences to a specfic phenoxy group.

^1H-Shifts

Proton NMR was used to examine differences in the basicity and rate of exchange of the NH proton. Temperature, solvent and substituent effects are all influential. In $CDCl_3$, vicinal ^3J(CH–NH) coupling is normally not witnessed due to rapid NH proton exchange. At ambient temperature it is observed only with strong -M substituents on the anilino ring, e.g. p-NO_2 and p-CN groups, that can participate in a direct resonance interaction with the amine group nitrogen atom lone pair electrons (Figure 10). Removal of electron density from the nitrogen atom in this

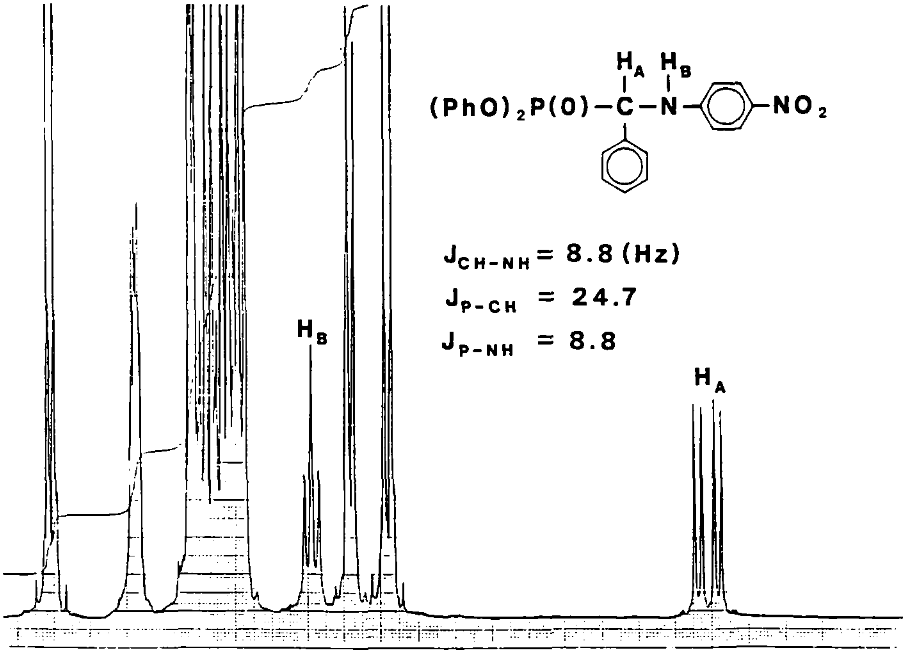


FIGURE 10 Vicinal CH—NH coupling when $R_2 = p\text{-}NO_2$ ($CDCl_3$).

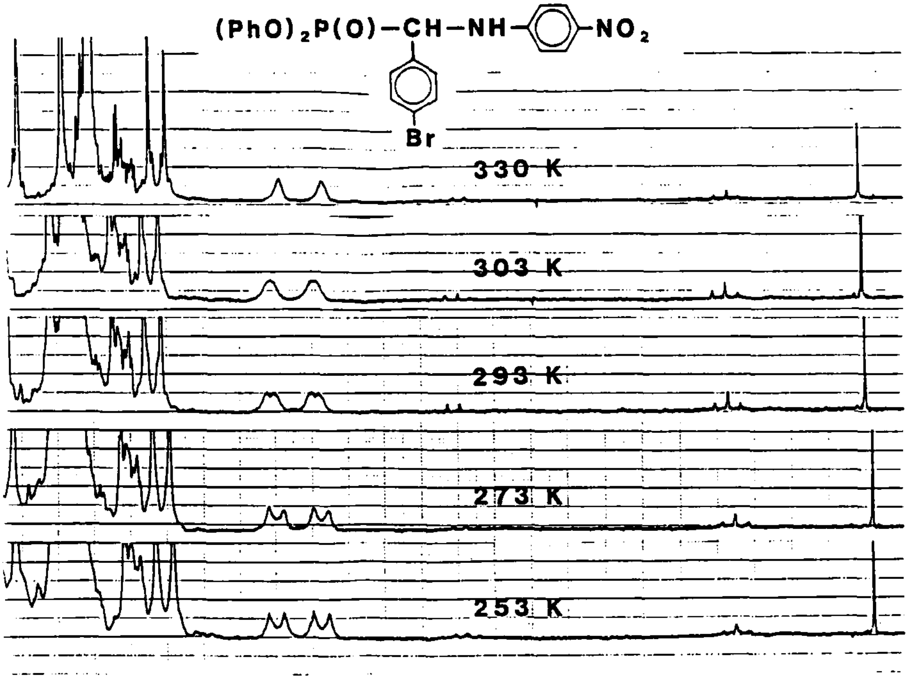


FIGURE 11 Loss of CH—NH coupling at high temperature when $R_2 = p\text{-}NO_2$ ($CDCl_3$).

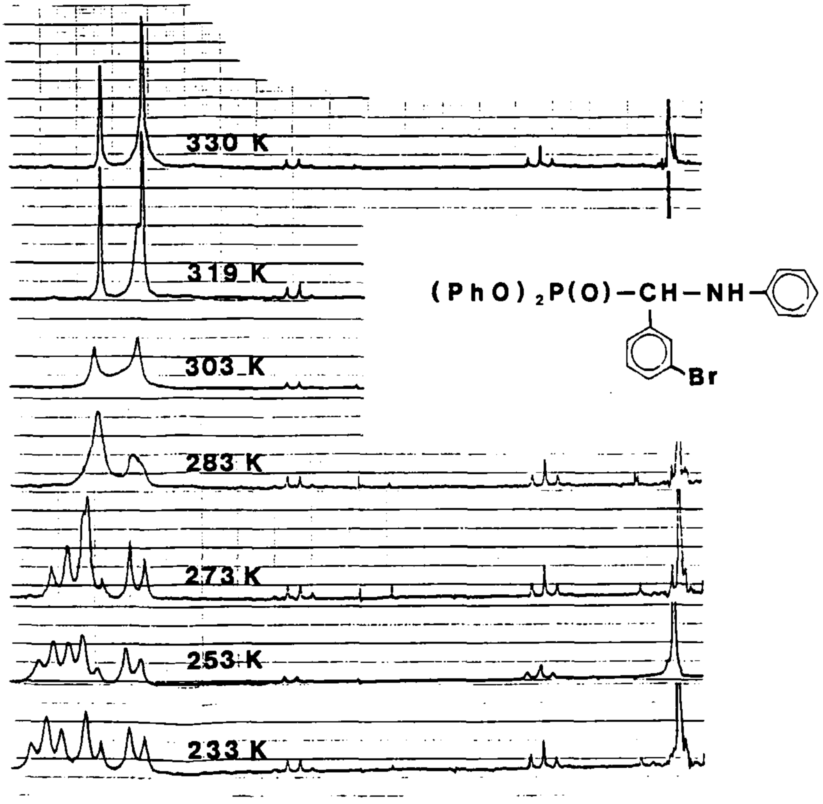


FIGURE 12 CH—NH coupling at low temperature when $R \neq M^-$ substituent ($CDCl_3$).

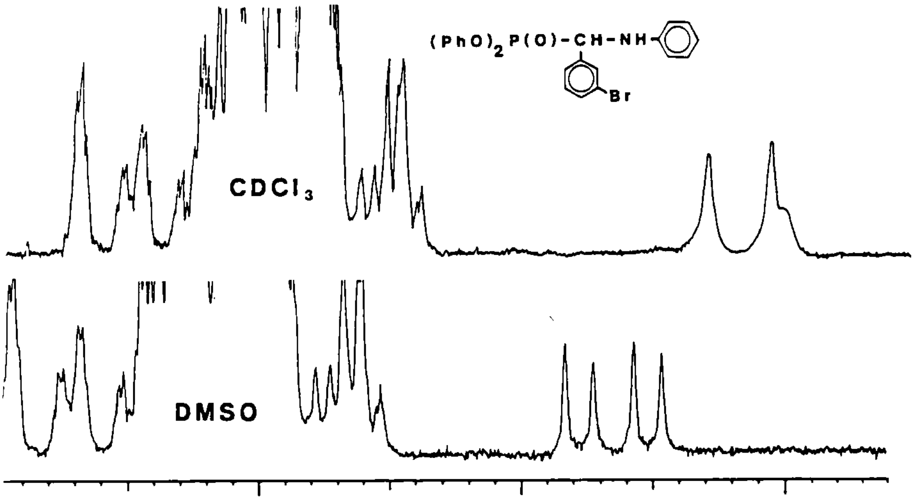


FIGURE 13 Vicinal CH—NH coupling in $CDCl_3$ versus DMSO.

manner reduces its basicity and slows the rate of exchange. The NH signal now appears as a triplet since the $^3J_{CH-NH}$ coupling constant is nearly equal to that of the $^3J_{P-CH}$ in the examples studied. The NH signal is also shifted downfield relative to that in non-coupling situations. This would further support the assumption of a reduction in basicity of the nitrogen.

The coupling witnessed at ambient temperature in appropriately substituted phosphonates can be eliminated by increased temperature (Figure 11).

In a few cases NH exchange can be frozen out at lower temperatures in the absence of a substituent involved in resonance with the lone pair of electrons of the nitrogen atom (Figure 12). This effect appears again to be caused by a decrease in the rate of NH exchange rather than a change in the quadrupolar relaxation of the nitrogen. The N-H coupling constants are typically much larger than those measured in this investigation.[13] Coupling in $CDCl_3$ was never observed with an electron-donating substituent on the anilino moiety regardless of temperature.

The exchange rate in DMSO varies significantly from that in $CDCl_3$ previously discussed. DMSO's ability to hydrogen bond with the anilino NH-group causes vicinal CN-NH coupling regardless of anilino substitution (Figure 13).

EXPERIMENTAL

The substituted diphenyl 1-phenylamino-1-phenylmethane phosphonates, **7.1–7.35**, were prepared in a one-pot reaction by the method outlined by Zimmer and Seemuth.[14] An equal molar benzene solution of the appropriate benzaldehyde and aniline was refluxed for 2 hrs in a flask equipped with a Dean–Stark trap to form the Schiff base. After cooling and treatment with 1 equivalent of diphenyl phosphite the solution was refluxed an additional 1 hr beyond the cessation of water generation. The benzene was removed by rotary evaporation at reduced pressure, 100 ml of anhydrous diethylether was added and the mixture kept at 0°C overnight to facilitate crystal formation. Para substituted phosphonates usually crystallized while some meta substituted phosphonates separated as an oil. If an oil was obtained it usually was dissolved in hot ethanol from which it crystallized upon cooling. The crude product was recrystallized twice from ethanol. Yields were generally between 60 to 80%.

Diphenyl 1-phenylamino-1-phenylmethanephosphonate, (**7.1**), mp 156–157°C; Anal. Calcd. for $C_{25}H_{22}PNO_3$:C, 72.3; H, 5.3; N, 3.4. Found: C, 71.8; H, 5.4, N, 4.0. *Diphenyl 1-(3-bromophenylamino)-1-phenylmethanephosphonate,* (**7.2**), mp 151–152°C; Anal. Calcd. for $C_{25}H_{21}PNO_3Br$:C, 60.7; H, 4.3. Found: C, 60.9; H, 4.5. *Diphenyl 1-(4-bromophenylamino)-1-phenylmethanephosphonate,* (**7.3**), mp 183–184°C; Anal. Calcd. for $C_{25}H_{21}PNO_3BR$:C, 60.7; H, 4.3. Found: C, 6.9; H, 4.5. *Diphenyl* 1-(3-*nitrophenylamino*)-1-*phenylmethanephosphonate*, (**7.4**), mp 150°C; Anal. Calcd. for $C_{25}H_{21}PN_2O_5$:C, 65.2; H, 4.6. Found: C, 65.1; H, 4.7. *Diphenyl 1-(4-nitrophenylamino)-1-phenylmethanephosphonate*, (**7.5**), mp 165–66°C; Anal. Calcd. for $C_{25}H_{21}PN_2O_5$:2C, 65.2; H, 4.6. Found: C, 65.2; H, 4.7. *Diphenyl 1-(3-methoxyphenylamino)-1-methanephosphonate,* (**7.6**), mp 141°C; Anal. Calcd. for $C_{26}H_{24}PNO_4$:C, 70.1; H, 5.4. Found: C, 70.2; H, 5.4. *Diphenyl 1-(4-methoxyphenylamino)-1-methanephosphonate,* (**7.7**), mp 155°C; Anal. Calcd. for $C_{26}H_{24}PNO_4$:C, 70.1; H, 5.4; N, 3.1. Found: C, 69.5; H, 5.6; N, 3.1. *Diphenyl 1-phenylamino-1-(3-bromophenyl)methanephosphonate*, (**7.8**), mp 130°C; Anal. Calcd. for $C_{25}H_{21}PNO_3Br$:C, 60.7; H, 4.3. Found: C, 60.5; H, 4.5. *Diphenyl 1-phenylamino-1-(4-bromophenyl)methanephosphonate*, (**7.9**), mp 148–149°C; Anal. Calcd. for $C_{25}H_{21}PNO_3Br$:C, 60.7; H, 4.3. Found: C, 60.9; H, 4.4. *Diphenyl 1-phenylamino-1-(3-nitrophenyl)methanephosphonate*, (**7.10**), mp 135°C; Anal. Calcd. for $C_{25}H_{21}PN_2O_5$:C, 65.2; H, 4.6. Found: C, 65.3; H, 4.9. *Diphenyl 1-phenylamino-1-(4-nitrophenyl)methanephosphonate*, (**7.11**), mp 161–162°C; Anal. Calcd. for $C_{25}H_{21}PN_2O_5$:C, 65.2; H, 4.6; N, 6.1. Found: C, 65.2; H, 4.4; N, 6.3. *Diphenyl 1-phenylamino-1-(3-methoxyphenyl)methanephosphonate*, (**7.12**), mp 136–137°C; Anal. Calcd. for $C_{26}H_{24}PNO_4$:C, 70.1; H, 5.4. Found: C, 70.2; H, 5.6. *Diphenyl 1-phenylamino-1-(4-methoxyphenyl)methanephosphonate*, (**7.13**), mp 139–140°C; Anal. Calcd. for $C_{26}H_{24}PNO_4$:C, 70.1; H, 5.4; N, 3.4. Found: C, 70.1; H, 5.6; N, 3.2. *Diphenyl 1-(4-nitrophenylamino)-1-(4-nitrophenyl)methanphosphonate*, (**7.14**), mp 191–193°C; Anal. Calcd. for $C_{25}H_{20}PN_3O_7$:C, 59.4; H, 4.0; N, 8.3. Found: C, 58.9; H, 4.1; N, 8.5. *Diphenyl 1-(3-nitrophenylamino)-1-(3-nitrophenyl)methanephosphonate*, (**7.15**), mp 125–126°C; Anal. Calcd. for $C_{25}H_{20}PN_3O_7$:C, 59.4; H, 4.0. Found: C, 59.2; H, 4.06. *Diphenyl 1-(4-bromophenylamino)-1-(4-bromophenyl)methanephosphonate*, (**7.16**), mp 160–162°C; Anal. Calcd. for $C_{25}H_{20}PNO_3Br_2$:C, 52.4; H, 3.5. Found: C, 52.2, H, 3.7. *Diphenyl 1-(3-bromophenylamino)-1-(3-bromophenyl)methanephosphonate*, (**7.17**), mp 131°C; Anal. Calcd. for $C_{22}H_{20}PNO_3Br_2$:C, 52.4; H, 3.5. Found: C, 52.5; H, 3.6. *Diphenyl 1-(4-methoxyphenylamino)-1-(4-methoxyphenyl)methanephosphonate*, (**7.18**), mp 124–125°C; Anal. Calcd. for $C_{27}H_{26}PNO_5$:C, 68.2; H, 5.5; N, 3.0. Found: C, 68.4; H, 5.6; N, 3.0. *Diphenyl 1-(3-methoxyphenylamino)-1-(3-methoxyphenyl)methanephosphonate*, (**7.19**), mp 120°C; Anal. Calcd. for $C_{27}H_{26}PNO_5$:C, 68.2; H, 5.5. Found: C, 68.2; H, 5.5. *Diphenyl 1-(4-nitrophenylamino)-1-(4-bromophenyl)methanephosphonate*, (**7.20**), mp 184–185°C; Anal. Calcd. for $C_{25}H_{20}PN_2O_5Br$:C, 55.7; H, 3.7. Found: C, 55.7; H, 3.8. *Diphenyl 1-(4-methoxyphenylamino)-1-(4-bromophenyl)methanephosphonate,* (**7.21**), mp 123°C; Anal. Calcd. for $C_{26}H_{23}PNO_4Br$:C, 59.6; H, 4.4. Found: C, 59.5; H, 4.7. *Diphenyl 1-(3-nitrophenylamino(-1-(3-bromophenyl)methanephosphonate*, (**7.22**) mp 168°C; Anal. Calcd. for $C_{25}H_{20}PN_2O_5Br$:C, 55.7; H, 3.7. Found: C, 55.6; H, 3.8. *Diphenyl 1-(3-methoxyphenylamino)-1-(3-bromophenyl)methanephosphonate*, (**7.23**), mp 124°C; Anal. Calcd. for $C_{26}H_{23}PNO_4Br$:C, 59.6; H, 4.4. Found: C, 59.6; H, 4.3. *Diphenyl 1-(4-bromophenylamino)-1-(4-nitrophenyl)methanephosphonate*, (**7.24**) mp 169–170°C; Anal. Calcd. for $C_{25}H_{20}PN_2O_5Br$:C, 55.7; H, 3.7. Found: C, 55.9; H, 4.0 *Diphenyl 1-(4-methoxyphenylamino)-1-(4-nitrophenyl)methanephosphonate*, (**7.25**), mp 111–112°C; Anal. Calcd. for $C_{26}H_{23}PN_2O_5$:C, 63.7; H, 4.7; N, 5.7. Found: C, 63.7; H, 4.7; N, 5.9. *Diphenyl 1-(3-bromophenylamino)-1-(3-nitrophenyl)methanephosphonate*, (**7.26**) mp 132°C; Anal. Calcd. for $C_{25}H_{20}PN_2O_5Br$:C, 55.7; H, 3.7. Found: C, 55.7; H, 3.8. *Diphenyl 1-(3-methoxyphenylamino)-1-(3-nitrophenyl)methanephosphonate*, (**7.27**), mp 168–170°C; Anal. Calcd. for $C_{26}H_{23}PN_2O_6$:C, 63.7; H, 4.7. Found: C, 63.6; H, 4.8 *Diphenyl 1-(4-nitrophenylamino)-1-(4-methoxyphenyl)methanephosphonate*, (**7.28**), mp 197–198°C; Anal. Calcd. for $C_{26}H_{23}PN_2O_6$:C, 63.7; H, 4.7; N, 5.7. Found: C, 63.6; H, 4.8; N, 5.8. *Diphenyl 1-(4-bromophenylamino)-1-(4-methoxyphenyl)methanephosphonate*, (**7.29**) mp 150°C; Anal. Calcd. for $C_{26}H_{23}PNO_4Br$:C, 59.6; H, 4.4. Found: C, 59.8; H, 4.4. *Diphenyl 1-(3-nitrophenylamino)-1-(3-methoxyphenyl)methanephosphonate*, (**7.30**), mp 160°C; Anal. Calcd. for $C_{26}H_{23}PN_2O_6$:C, 63.7; H, 4.7. Found: C, 63.4; H, 4.8. *Diphenyl 1-(3-bromophenylamino)-1-(3-methoxyphenyl)methanephosphonate*, (**7.31**), mp 117–119°C; Anal. Calcd. for $C_{26}H_{23}PNO_4Br$: C, 59.6; H, 4.4. Found: C, 59.4; H, 4.5. *Diphenyl 1-(4-cyanophenylamino)-1-phenylmethanephosphonate*, (**7.32**), mp 161°C, Anal. Calcd. for $C_{26}H_{21}PN_2O_3$:C, 70.9; H, 4.8. Found: C, 70.7; H, 4.9. *Diphenyl 1-(phenylamino)-1-(4-cyanophenyl)methanephosphonate*, (**7.33**) mp 161°C, Anal. Calcd. for $C_{26}H_{21}PN_2O_3$:C, 70.9; H, 4.8. Found: C, 71.0; H, 5.0. *Diphenyl 1-(4-cyanophenylamino)-1-(4-cyanophenyl)methanephosphonate*, (**7.34**), mp 185°C; Anal. Calcd. for $C_{27}H_{20}PN_3O_3$:C, 69.7; H, 4.3. Found: C, 69.8; H, 4.6. *Diphenyl*

1-(4-cyanophenylamino)-1-(4-nitrophenyl)methanephosphonate, (**7.35**), mp 159°C; Anal. Calcd. for $C_{26}H_{20}PN_3O_5$: C, 64.3; H, 4.1. Found: C, 64.3; H, 4.1.

The ^{31}P spectra in DMSO were determined at 304 K on a WP-60 spectrometer operating at 24.3 MHz. A 5 mm sample tube was used with a 2 mm lock tube of C_6D_6 fixed concentrically in the large tube; 85% H_3PO_4 was used as an external standard. A 0.30 M solution of a phosphonate dissolved in DMSO was used except where the concentration was limited by solubility. A concentration study was performed that showed ^{31}P chemical shift to vary less than 0.03 ppm over a 10-fold concentration range. All reported chemical shifts used were values for the 0.30 M solution. No attempt was made to extrapolate back to infinite dilution.

Anions were generated by adding 1 equivalent of 0.50 M LDA in Et_2O to the appropriate DMSO sample solution dropwise in the 5 mm sample tube under argon before the addition of the lock tube. Measurements were performed 3 times with no change in chemical shift of the anionic solution noted over a 3 hr period.

The ^{13}C spectra where determined on a Bruker 300 and WP-90 spectrometer in $CDCl_3$ and a Jeol FX-100 in DMSO. Tetramethysilane was used as an internal standard with 1% phosphonate solutions.

The ^1H spectra were determined at 304 K on a WP-60 and Bruker 300 spectrometer $CDCl_3$. Again 1% phosphonate solutions with an internal TMS standard were employed. Temperature studies were performed on the WP-60 instrument.

A Lotus 1-2-3 linear least squares program was employed to analyze the data for the best fit for the relationship $\delta\ ^{31}P = m\Sigma\sigma + b$. The program also supplied graphs, standard deviations and correlation values.[15] Taft σ^0 values[16] and Hammett σ_n values[15] were used. Elemental analysis of all compounds gave values within 0.4% of the calculated ones.

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