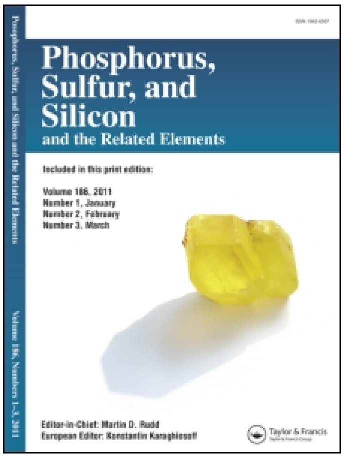

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Substituent Effects on ^{31}P and ^{13}C Chemical Shifts of Substituted Diphenyl 1-anilino-1-arylmethanephosphonates and Their Anions

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SUBSTITUENT EFFECTS ON ^{31}P AND ^{13}C CHEMICAL SHIFTS OF SUBSTITUTED DIPHENYL 1-ANILINO-1-ARYLMETHANEPHOSPHONATES AND THEIR ANIONS

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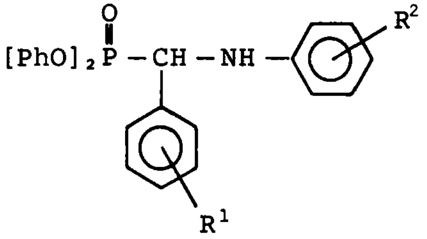
Abstract For a series of 31 novel diphenyl 1-anilino-1-arylmethanephosphonates, substituted in the meta and para position of the anilino and/or the aryl ring, ^{31}P chemical shifts show good linear correlation with Taft's σ° parameters, the ^{31}P nucleus appearing better shielded in the case of electron-withdrawing substituents. This inverse relationship is due to a field effect of the substituent dipole which polarizes π-electron clouds in the molecule, resulting in a higher P=O double bond order, and thence better ^{31}P shielding. A corresponding shift of π-electron density is likewise observed for the ^{13}C resonances of the two diastereotopic phenoxy and the anilino or aryl rings, respectively, where -M and -I substituents cause a downfield shift of para and meta, and an upfield shift of ortho and ipso carbon resonances.

A series of 31 diphenyl 1-arylamino 1-aryl methanephosphonates were prepared by the method of Zimmer and Seemuth,[1] with different meta and para substituents in the aryl and anilino ring, the only restriction being that in disubstituted derivatives both groups be either meta or para.



R^1, R^2 = H
m,p-Br
m,p-OCH_3
m,p-NO_2

^{31}P resonances in this series are shifted more and more upfield as the electron-withdrawing potential of the substituents increases. Such an inverse correlation has likewise been observed for benzenephosphonic acid derivatives with different meta and para substituents, and explained in terms of varying P=O $p_\pi d_\pi$ bond order.[2]

For all 31 1-anilino-1-arylmethanephosphonates, ^{31}P chemical shifts show good linear correlation with Hammett $\sigma_{m,p}$, and even better with Taft $\sigma°$ parameters over the whole range of substituents, OCH_3 to NO_2; σ values are additive for disubstituted compounds (see Figure 1). The 3.5 ppm variation in $\delta(^{31}P)$ must be due to an inductive or field effect since resonance interaction between the substituted π system and the P=O group is not possible.

Thus, in the 1-(4-nitrophenyl) derivative, the powerful NO_2 dipole induces a corresponding polarization in all the π-electron clouds of the molecule: phenoxy, anilino, and P=O. The respective shift in π-electron density results in a deshielding of all para and, to a lesser extent, meta aryl carbon atoms, and a concomitant high-field shift of all ortho and ipso carbon resonances (see Figure 2). Since the P=O double bond is (a) closer to the dipole, and (b) more "receptive", the effect

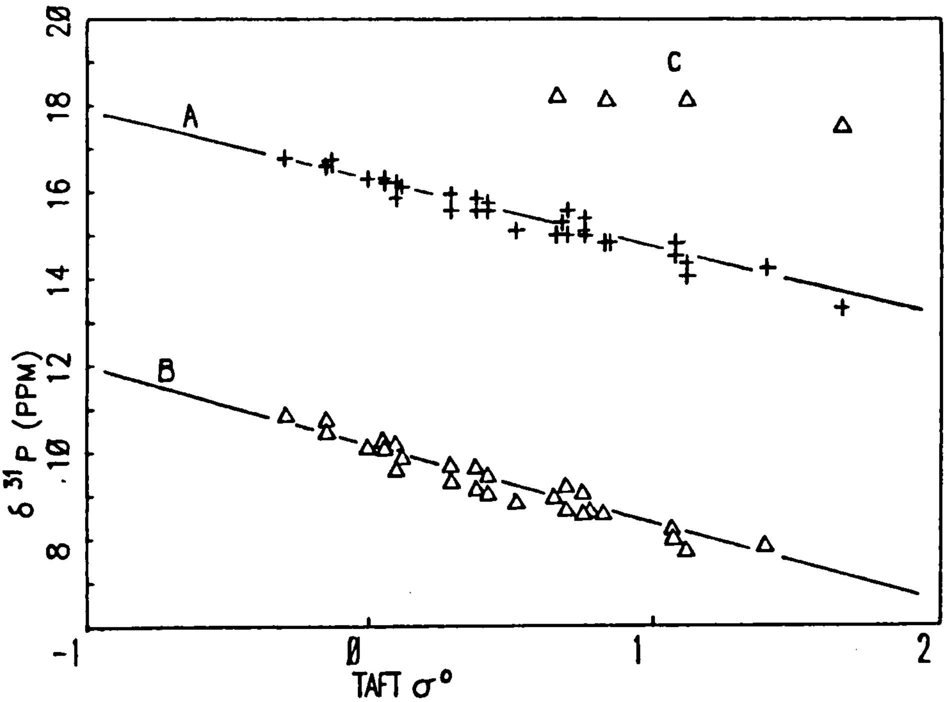


FIGURE 1 Plot of ^{31}P chemical shifts (0.3 M solution in DMSO-d_6) of the neutral phosphonates (A) and the corresponding anions (B; for the 1-(4-nitrophenyl) derivatives, C) versus Taft σ° parameters .

(in ppm) is more pronounced in ^{31}P than in ^{13}C resonances. Polarization appears much attenuated in the p-bromo compound, and is reversed in the case of a p-methoxy substituent where the +M effect of the OCH_3 group polarizes the aryl π cloud in the opposite direction.

The corresponding anions were generated by adding 1 equivalent of 0.5 M LDA to DMSO solutions of the respective neutral phosphonates. ^{31}P chemical shifts for the anions also correlate well with the electron-withdrawing potential of R^1,R^2, the best fit again being obtained with Taft σ° parameters. They are shifted upfield 5-6 ppm from the values for the neutral compounds - with the notable exception of the p-NO_2-aryl derivatives (see

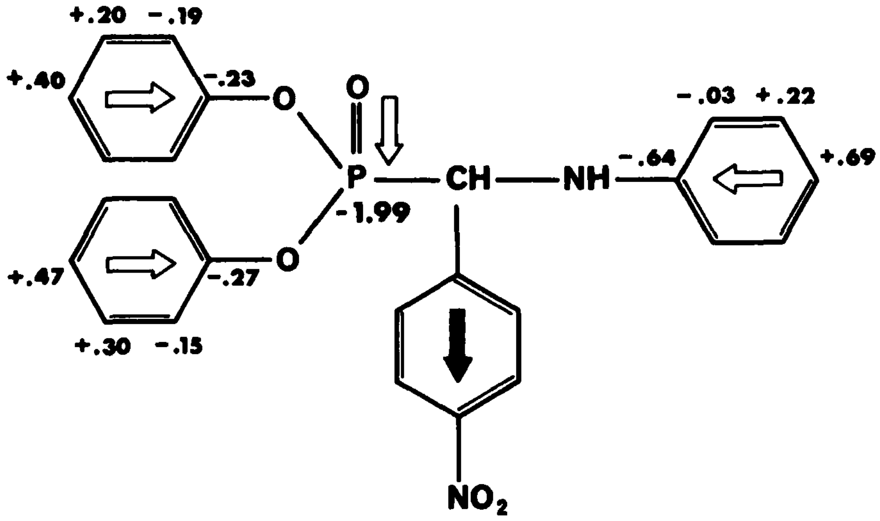


FIGURE 2 ^{31}P and ^{13}C differential shifts (Δδ) for diphenyl 1-anilino-1-(4-nitrophenyl)methanephosphonate relative to the unsubstituted compound ($R^{1/2}$ =H).

Figure 1, C). Here, the nitro rather than the P=O group will accomodate much of the negative charge.

In $CDCl_3$, vicinal $^3J(CH,NH)$ coupling normally is washed out by rapid NH proton exchange. At ambient temperature, it is observed only with strong -M substituents on the anilino moiety, e.g. p-NO_2, p-CN, which reduce the basicity of the NH lone pair by resonance interaction. In a few cases, but never with derivatives bearing electron-donating substituents, NH exchange can be frozen out at lower temperatures. In the more polar solvent DMSO, on the other hand, CH,NH coupling is always visible.

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