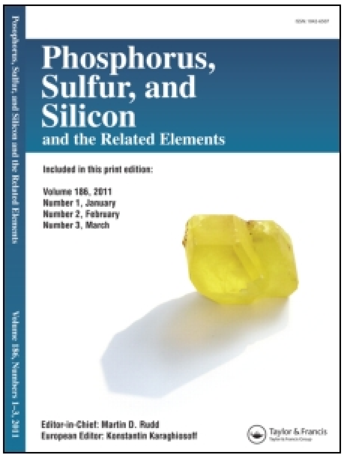

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Bonding in Alkyltriarylphosphonium Salts

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To cite this Article Singh, Gurdial(1987) 'Bonding in Alkyltriarylphosphonium Salts', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 279 — 282

To link to this Article: DOI: 10.1080/03086648708080576

URL: http://dx.doi.org/10.1080/03086648708080576

Phosphorus and Sulfur, 1987, Vol. 30, pp. 279–282
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BONDING IN ALKYLTRIARYLPHOSPHONIUM SALTS

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Abstract ^{31}P, ^{13}C, and ^{1}H NMR data of $(\underline{p}\text{-}XC_6H_4)_3\overset{+}{P}R\ I^-$ where R = Me, Me_3CCH_2 or Me_3SiCH_2 and X = H, Me, OMe or NMe_2 are reported and discussed in terms of hyperconjugative pπ-dπ bonding involving the α C-H or C-Si bonds and the direct β atom (H or Si) with the 3d orbitals of phosphorus.

Although several NMR studies of phosphonium salts have been reported,[1] their ^{31}P chemical shifts and coupling constants $^{1}J_{PC}$ and $^{2}J_{PH}$ have not been fully explained in terms of bonding around phosphorus. Grim et al.[2] studied the effect of alkyl substituents on ^{31}P chemical shifts of alkyltriphenylphosphonium salts and found that as substitution on the α carbon increased: Me, Et, i-Pr, and t-Bu, the phosphorus shielding decreased which is opposite to what is expected from the alkyl inductive effect. But when substitution occurs at the β carbon, R = Et, n-Pr, i-Bu, and neo-Pent (TABLE I), ^{31}P shielding increases with alkyl polar substituent constants.

Hyperconjugative pπ-dπ bonding in phosphonium salts implies ylid as one of the contributing resonance structures. Both phosphorus[3] and α carbon[4,5] are generally more shielded in ylids vs. those of their phosphonium salts, which suggests that hyperconjugation in phosphonium salts should also provide shielding to phosphorus and α carbon. A plot of the α carbon chemical shifts of alkylphosphonium salts vs. those of carbon directly bonded in H-R alkanes[6] is shown in FIGURE 1. The < 1.0 slope of the correlation shows that the deshielding effect of quaternary phosphorus on α carbon decreases with the branching of the alkyl groups presumably due to increase in hyperconjugative pπ-dπ bonding with more substitution on α or β carbons. The isopropyl carbon is more shielded because its secondary structure can form more effective π bonding with phosphorus. The _t_-butyl carbon, on the other hand, is deshielded either due to the absence of hyperconjugative π bonding or the steric hindrance as suggested by Schweizer and coworkers.[1]

Based on hyperconjugative π bonding alone, the ^{31}P chemical shifts of phosphonium salts would be expected to fall, at least roughly, in the same order as of their ylids. On the contrary, their ^{31}P shifts diverge from those of their ylids as substitution on α or β carbon increases.[3] We attribute it to the direct interaction of β H with the 3_d_ orbitals of phosphorus. Further, it may be noted that phosphorus is very strongly deshielded in trimethylsilymethylphosphonium salts vs. neopentyl compounds (TABLE II) in spite of the fact that Me_3SiCH_2 is more electron donating than Me_3CCH_2. It is probably due to β Si interacting with phosphorus. In other words, hyperconjugative π bonding and direct β atom (H or Si) interaction with the 3_d_ orbitals of P are occurring simultaneously.

Phosphorus and directly bonded aromatic carbon are more shielded with electron donating substituents on the phenyl rings: NMe_2>OMe>Me>H. However, the alkyl α carbon gets more deshielded indicating the presence of incipient ylid whose contribution increases as X = H>Me>OMe>NMe_2. With electron donating substituents on the phenyl rings, the _d_ orbitals of phosphorus become more diffuse and thus reduce hyperconjugative π bonding. It also reduces the β atom interaction with P changing its hybridization more toward _sp^3_ vs. _sp^3d_ and thus

TABLE I NMR data of $(C_6H_5)_3\overset{+}{P}R\ I^-$

R	$\delta_{^{31}P}$ ppm	$\delta_{C_{Alk}}$ ppm	$^1J_{PC_{Alk}}$ Hz
CH_3	22.7^a	11.5	57.4
CH_2CH_3	26.7^a	17.0^c	51.6^c
$CH(CH_3)_2$^{b}	30.9^a	21.5^c	47.0^c
$C(CH_3)_3$	34.7^a	35.3^c	42.5^c
$CH_2CH_2CH_3$	24.1^a	24.17	48.2
$CH_2CH(CH_3)_2$	23.5	30.83	46.5
$CH_2C(CH_3)_3$	20.0	35.6	44.5

[a] From ref 2. [b] Phosphonium bromide.
[c] From ref 1.

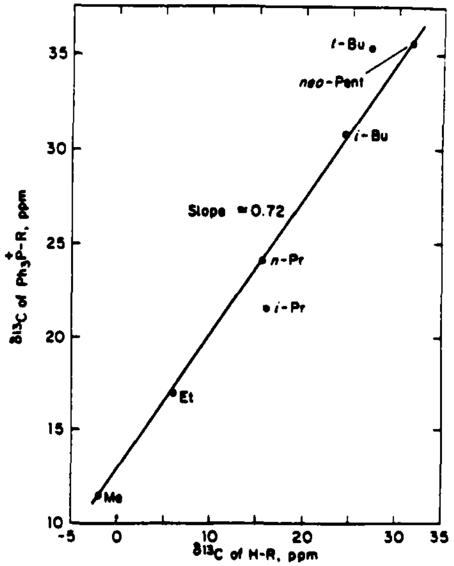

FIGURE 1

Table II. ^{31}P, ^1H, and ^{13}C NMR data of $(p\text{-}XC_6H_4)_3\overset{+}{P}R\ I^-$

			CH_3 or CH_2					
R	X	$\delta_{^{31}P}$ ppm	δ_H ppm	$^2J_{PH}$ Hz	$\delta_{C_{ALK}}$ ppm	$^1J_{PC}$ Hz	$\delta_{C_{Ar}}$ ppm	$^1J_{PC}$ Hz
CH_3	H	22.10	3.16	13.2	11.52	57.4	118.69	88.5
	CH_3	20.85	3.01	13.2	11.69	58.3	115.66	90.8
	OCH_3	19.37	2.92	13.1	12.34	59.6	109.78	97.0
	$N(CH_3)_2$	16.49	2.54	13.0	12.27	62.0	102.98	101.3
$CH_2C(CH_3)_3$	H	19.95	3.82	12.9	35.56	44.5	120.25	84.5
	CH_3	18.95	3.63	12.9	35.44	46.6	116.28	86.6
	OCH_3	17.67	3.50	12.8	36.01	49.5	110.02	91.3
	$N(CH_3)_2$	15.12	3.02	12.8	36.64	52.7	102.70	97.6
$CH_2Si(CH_3)_3$	H	24.85	3.14	18.4	10.15	44.7	120.86	86.4
	CH_3	23.68	2.97	18.2	10.46	44.6	117.86	90.1
	OCH_3	22.11	2.88	18.1	11.27	47.6	111.82	95.2
	$N(CH_3)_2$	19.17	2.37	17.7	11.71	50.0	104.80	100.5

explain the increase in $^{1}J_{PC}$ with more electron donating substituents on the phenyl rings.

The β H interaction with phosphorus would provide a dual pathway for their coupling, $^{2}J_{PH}$. Presumably, the two-bond P-C-H coupling is negative and the P-H coupling is positive,[8] which will result in reducing the actually observed coupling. The $^{2}J_{PH}$ in trimethylsilylmethylphosphonium salts is much larger (~ 18 Hz) than in the neopentyl compounds (~ 12.8 Hz). Actually, they are the largest couplings observed for any phosphonium salt of $Ph_3\overset{+}{P}CH_2R$ structure.[9] It could be due to the Si being involved in the direct interaction with phosphorus leaving the geminal coupling to occur essentially via the P-C-H bonding system.

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