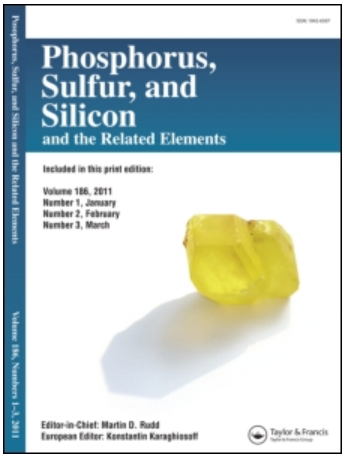

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THE ^{31}P-CHEMICAL SHIFT OF DIPHOSPHENES

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THE ^{31}P-CHEMICAL SHIFT OF DIPHOSPHENES

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Including recent examples the phosphorus-31 chemical shift range of (*E*)-diphosphenes extends from δ = 192 to 816. For a given substituent at P_A the chemical shift δ_A decreases when the substituent at P_B changes from electron accepting to electron donating. The smallest δ_A values (and also the smallest coupling constants $^1J_{AB}$) are found for diphosphenes with an ylide substituent at P_B, the largest δ_A value is found for a disilyl diphosphene.

Keywords: ^{31}P NMR; diphosphenes; substituent effects; ylide substituents

Since the early days of ^{31}P NMR spectroscopy the observed chemical shifts have been correlated with the influence of substituents. For this purpose diphosphenes seem to be a particularly suitable object due to their wide range of chemical shifts[1–5] and as there is the influence of only two substituents to be considered. The chemical shifts of two-coordinate phosphorus[1] extend from δ^{31}P = 954 to −363 and largely reflect its phosphenium or phosphide character. Within this range the shifts of *E*-diphosphenes are found at the low field end typically between δ = 500 and 700. A ten year old compilation of chemical shifts of two-coordinate phosphorus compounds[1] lists 27 diphosphenes, a chapter on diphosphenes in a book from 1990[3] gives the data of 36 examples. Their number has considerably increased since then and new examples with extreme shifts to low[6] and high[7,8] field prompt us to update this list.

Tables I to IV present groups of diphosphenes $R^1P_A = P_BR^2$ (*E*-isomers only) each of which with a constant R^1. Within a group the immediate surrounding of P_A thus remains the same and δ_A solely reflects the influence of the different β-substituents R^2.

In the group of P_A-trifluoromethylphenyl-substituted diphosphenes (Table I) the shift δ_A clearly depends on the nature of R^2: For aryl derivatives δ_A = 445

Dedicated to the memory of Leonid Markovskii.

TABLE I ^{31}P NMR Data of (*E*)-diphosphenes $R^1-P_A=P_B-R^2$ with R^1 = substituted phenyl groups (Flu: fluorenyl, Tmp: tetramethylpiperidyl); coupling constants *J* in Hz.

R^1	R^2	δ_A	δ_B	$^1J_{AB}$	Lit.
2,4,6-$(F_3C)_3C_6H_2$	2,4,6-$(F_3C)_3C_6H_2$	474			13
	2,4,6-^{t}Bu$_3C_6H_2$	417.7	537.3	567.6	3
	2,4,6-$Me_3C_6H_2$(9-Flu)N	254.0	478.4	531.7	14
	^{c}Hex$_2$N	224.5	470.2	538.9	15
2,6-$(F_3C)_2C_6H_3$	2,6-$(F_3C)_2C_6H_3$	477			16
	2,4,6-^{t}Bu$_3C_6H_2$	422.1	533.0	574.3	3
	$(Me_3Si)_2N$	373.7	539.9	577.4	15
	Tmp	287.8	482.3	570.6	15
	^{c}Hex$_2$N	228.7	471.3	538	15
2,6-^{t}Bu$_2C_6H_3$	2,6-^{t}Bu$_2C_6H_3$	488.7	3		
2,4,6-^{t}Bu$_3C_6H_2$	^{t}Bu$_2$HP$^+$TfO$^-$	647	310	574	17
	$Ph_3P^+BPh_4^-$, TfO^-,PF_6^-	641	334	580	17
	$(Et_2N)_3P^+TfO^-$	621	382	588	17
	^{t}Bu$_2$P	599	485	575	17
	2,4,6-^{t}Bu$_3C_6H_2$PH	553	495	567	17
	$Me_5C_5(CO)_2Fe$	554	715	594	1
	$Me_5C_5(CO)_2Ru$	552	677	597	17
	TmpH$^+$TfO$^-$	550	435	604	17
	^{i}Pr$_2$HN$^+$TfO$^-$	544	433	596	17
	^{c}Hex$_2$HN$^+$TfO$^-$	536	439	594	17
	2,4,6-$(F_3C)_3C_6H_2$	537.3	417.7	567.6	3
	2,6-$(F_3C)_2C_6H_3$	533.0	422.1	574.3	3
	$(Me_3Si)_3C$	533.1	530.0	620	2
	^{t}Bu	524.1	531.9	576	18
	2,4-^{t}Bu$_2C_6H_3$[a]	517.0	480.1	583.5	3
	2-^{t}Bu-3,4,5,6-Me_4C_6[a]	512	478	580	3
	$(Me_3Si)_3Si$	501.2	610.6	598.0	18
	$(Me_3Si)_2CH$	495	508	575	1
	2,4,6-^{t}Bu$_3C_6H_2$	492.4			3
	2,4,6-^{t}Pn$_3C_6H_2$	491.2	489.9	582.9	3
2,4,6-^{t}Bu$_3C_6H_2$	Me_5C_5[a]	491.1	484.6	584	3
	Me_3Si	487	628	575	1
	2-Me-4,6-^{t}Bu$_2C_6H_2$	480.1	517.0	583.5	1
	$(CO)_3Cr$-2,4,6-^{t}Bu$_3C_6H_2$	479	503	591	1
	2,4-^{t}Bu-6-MeOCH$_2C_6H_2$[a]	473.9	517.9	583	19
	Cl	473.4	522.4	598	18
	2,3,4-Me_3-6-^{t}BuC$_6$H	470	535	572	1
	2,4,6-$Me_3C_6H_2$	467.6	540.4	573.3	1
	Me	467.5	543	573.7	18
	2,4,6-^{i}Pr$_3C_6H_2$	463	541	571	1
	Br	458	532	586	17
	Ph_3Si	457.7	641.9	588.7	20
	Ph	455.5	525.5	548.7	1
	2,4-^{t}Bu$_2$-6-MeOC$_6H_2$	448.5	502.8	562.0	21
	^{t}BuS	448.1	468	549.3	18
	2,4,6-(MeO)$_3C_6H_2$[a]	435.0	520	546	22
	I	431	560	574	17
	2,4,6-^{t}Bu$_3C_6H_2$P(Me_3SiO)C	414.6	394.3	510	23
	$(Me_3Si)_2N$	409.3	501.5	584.2	15
	^{t}BuO	397.6	524.3	573.7	18
	^{t}Bu(Me_3Si)N	354	476	586	1

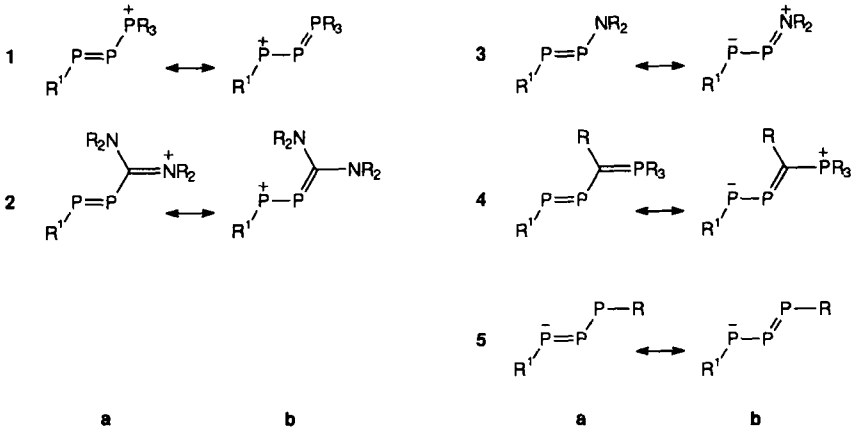
TABLE I *continued*

R^1	R^2	δ_A	δ_B	$^1J_{AB}$	*Lit.*
	Tmp	332.1	455	574.9	17
	2,4,6-^{t}Bu$_3$C$_6$H$_2$NH	314	455	537	18
	(Me$_3$Si)$_3$N$_2$	311	481	551.6	14
	^{i}Pr$_2$N	276.4	446.9	537.0	18
	^{c}Hex$_2$N	270.2	448.8	543.5	15
	2,4,6-^{t}Bu$_3$C$_6$H$_2$P$^-$Li$^+$	208	548	524	24
2,4,6-^{t}Pn$_3$C$_6$H$_2$	2,4,6-^{t}Pn$_3$C$_6$H$_2$	490.8	3		
2,4-^{t}Bu-6-Me$_2$NC$_6$H$_2$	2,4-^{t}Bu-6-Me$_2$NC$_6$H$_2$	428.2	25		
2,3,4-Me$_3$-6-^{t}BuC$_6$H	2,3,4-Me$_3$-6-^{t}BuC$_6$H	509.8	26		

[a] $\delta_{A,B}$ tentatively assigned, not assigned in the reference.

$\pm$ 30, for secondary amino derivatives δ_A = 225 $\pm$ 30 is found. The upfield shift effected by the amino substituents obviously has to do with its donor capability (as expressed by resonance formula **3b**). Consequently it is much smaller for a bis(trimethylsilyl)amino than for a dialkylamino substituent.

By far the largest choice of R^2 is available for diphosphenes with R^1 = 2,4,6-^{t}Bu$_3$C$_6$H$_2$ (Table I). The chemical shift δ_A decreases (moves to higher field) in the R^2-order $R_3P^+ > R_2P$, $L_nM > R_3N^+ > R_3C >$ Ar, R_3Si, Hal > RS > RO, R_2N. This order obviously corresponds to a change from electron-accepting to electron-donating substituents as expressed by the resonance formulae **1b** and **3b** for the two limiting cases (Scheme 1). The P_A shift difference for R^2 =



a **b** **a** **b**

Examples of diphosphenes with pronounced electron-accepting substituents R^2

Examples of diphosphenes with pronounced electron-donating substituents R^2

SCHEME 1

alkylsubstituted aryl (δ_A = 490 ± 30) and R^2 = secondary amino group (δ_A = 300 ± 30) is similar to that mentioned above. An analogous (although smaller) substituent effect is known on the ^{13}C chemical shift of the β-carbon atoms of alkenes.[9] The influence of electron-donating substituents is shown again by a more detailed look at the P_B-aryl substituted examples: δ_A decreases in the order CF_3-substituted phenyl > alkylsubstituted phenyl > unsubstituted phenyl > methoxyphenyl for R^2.

In case of the P_B-halodiphosphenes with R^1 = 2,4,6-^{t}Bu$_3$C$_6$H$_2$ the ^{31}P chemical shift δ_A decreases with decreasing electronegativity of the halogen atom acting as R^2: Cl > Br > I. This is in contrast to the effect of halosubstituents in alkenes where $\delta^{13}C$ of the β-atom increases in the order F < Cl < Br < I.[9]

The lowest δ_A value of Table I is found with a phosphido substituent R^2 *i.e.* for the terminal phosphorus atoms of a triphosphaallylic anion (triphosphenide ion) of type **5**.

The shielding of *tert.*butyl substituted P_A (Table II) again increases from R^2 = aryl to R^2 = amino group although the shift difference ($\Delta\delta_A$ = 150) is smaller than in case of the aryl derivatives.

TABLE II ^{31}P NMR Data of (*E*)-diphosphenes $R^1-P_A=P_B-R^2$ with R^1 = unsubstituted and substituted alkyl groups and amidino groups (Tmp: tetramethylpiperidyl); coupling constants *J* in Hz.

R^1	R^2	δ_A	δ_B	$^1J_{AB}$	*Lit.*
Me_5C_5	$(Me_3Si)_3C$	522.2	545.8	635	3
	Me_5C_5	504.0			3
	$(Me_3Si)_2CH$	492.6	522.8	599	3
	2,4,6-^{t}Bu$_3$C$_6$H$_2$	484.6	491.1	584	3
	$(Me_3Si)_2N$	478.3	546.2	632	3
	^{t}Bu(Me$_3$Si)N[a]	440.1	529.1	640	3
^{t}Bu	$(Me_3Si)_3C$	533	530	619	1
	2,4,6-^{t}Bu$_3$C$_6$H$_2$	531.9	524.7	576	18
	Tmp	383	508	611	1
$Me_3SiO(F_3C)_2C$	$Me_3SiO(F_3C)_2C$	539.8			27
$Cl_3Si(Me_3Si)_2C$	$Cl_3Si(Me_3Si)_2C$	578.2			28
$Cl_3Ge(Me_3Si)_2C$	$Cl_3Ge(Me_3Si)_2C$	553.7			28
$(Me_3Si)_2CH$	Me_5C_5	522.8	492.6	599	3
	$(Me_3Si)_2CH$	517			3
	2,4,6-^{t}BuC$_6$H$_2$	508	495	575	1
$(Me_3Si)_3C$	$(Me_3Si)_3C$	599.6			3
	Me_5C_5	545.8	522.2	635	3
	Me_3Si	544.1	686.8	633.2	20
	2,4,6-^{t}Bu$_3$C$_6$H$_2$	533	530	620	13
	^{t}Bu	530	533	619	1
	Ph_3Si	511.8	711.4	633.1	20
$(Et_2N)_2C^+TfO^-$	Tmp	210	465	525	29
	^{c}Hex$_2$N	210	465	525	30
	^{i}Pr$_2$N[a]	200	493.5	520	29

[a] $\delta_{A,B}$ tentatively assigned, not assigned in the reference.

In contrast to the examples discussed so far the chemical shift δ_A of amino-substituted phosphorus (Table III) is relatively constant ($\Delta\delta_A$ = 70 at the most) and the influence of aryl and amino substituents R^2 is often found to be in the reversed order. Even amidinio substituents R^2 which according to formula **2b** should load some phosphenium charge onto P_A are not of great influence.

The chemical shift δ_A for R^1 = $(^iPr_2N)_2P$ (Table IV) extends again over the wide range of $\Delta\delta_A$ = 257 from aryl to amino groups as substituents R^2. For these diphosphenes a significant correlation of δ_A with the π-donating ability of R^2 has been noted:[10] While the arrangement of R^2 = $(Me_2{}^tBuSi)_2N$ in respect to the diphosphene π-system is almost orthogonal, R^2 = $^iPr_2N$ adopts a coplanar conformation and leads to an increased shielding of P_A.

The widest range of the chemical shifts δ_A is found for the triphenylsilyl- and trialkylsilyl- substitued phosphorus (Table IV). It contains the highest value of δ_A, contributed by a disilyldiphosphene, and also the lowest value of δ_A, contributed by a silyl-ylidyldiphosphene. The shift difference $\Delta\delta_A$ = 420 between

TABLE III ^{31}P NMR Data of (*E*)-diphosphenes $R^1-P_A=P_B-R^2$ with R^1 = amino and phosphino groups (Tmp: tetramethylpiperidyl); coupling constants *J* in Hz.

R^1	R^2	δ_A	δ_B	$^1J_{AB}$	*Lit.*
2,3,4,5-Me_4C_4N	2,3,4,5-Me_4C_4N	454			31
Tmp	^{t}Bu	508	383	611	1
	$(^iPr_2N)_2P$	496.5	320.1	574	10
	2,6-$(F_3C)_2C_6H_3$	482.3	287.8	570.6	15
	Tmp	471			1
	$(Et_2N)_2C^+TfO^-$	465	210	525	29
	2,4,6-$^tBu_3C_6H_2$	455	332.1	574.9	17
$^cHex_2N$	2,6-$(F_3C)_2C_6H_3$	471.3	228.7	538	15
	2,4,6-$(F_3C)_3C_6H_2$	470.2	224.5	538.9	15
	$(Et_2N)_2C^+TfO^-$	465	210	525	30
	2,4,6-$^tBu_3C_6H_2$	448.8	270.2	543.5	15
$(Me_2{}^tBu)_2N$	$(^iPr_2N)_2P$	577.6	442.9	602	10
	$(Me_2{}^tBuSi)_2N$	561			1
^{t}Bu$(Me_3Si)N$	Me_5C_5[a]	529.1	440.1	640	3
	$(Me_3Si)_2N$	507	544	670	1
	^{t}Bu$(Me_3Si)N$	499			1
^{t}Bu$(Me_2{}^tBuSi)N$	^{t}Bu$(Me_2{}^tBuSi)N$	495.7			32
$(Me_3Si)_2N$	$(Me_3Si)_2N$	572			3
	Me_5C_5	546.2	478.3	632	3
	^{t}Bu$(Me_3Si)N$	544	507	670	1
	2,6-$(F_3C)_2C_6H_3$	539.9	373.7	577.4	15
	2,4,6-$^tBu_3C_6H_2$	501.5	409.3	584.2	15
$(Me_2{}^tBuSi)_2N$	$(^iPr_2N)_2P$	577.6	442.9	602	10
	$(Me_2{}^tBuSi)_2N$	561			33
$(Me_3Si)_3N_2$	Me_3Si[a]	542	210.3	540	34
	$(Me_3Si)_3N_2(Cl)P$	529.9	292.2	524	34
	$(^iPr_2N)_2P$	522.3	298.7	522	10
	2,4,6-$^tBu_3C_6H_2$	481	311	551.6	14

[a] $\delta_{A,B}$ tentatively assigned, not assigned in the reference.

TABLE IV ^{31}P NMR Data of (*E*)-diphosphenes $R^1-P_A=P_B-R^2$ with R^1 = phosphino and silyl groups (Tmp: tetramethylpiperidyl); coupling constants *J* in Hz.

R^1	R^2	δ_A	δ_B	$^1J_{AB}$	Lit.
$(^iPr_2N)_2P$	2,4,6-$Me_3C_6H_2$	502.7	554.0	574	10
	$(Me_2{}^tBuSi)_2N$	442.9	577.6	602	10
	2,4,6-$Me_3C_6H_2NH$	407.4	544.0	570	10
	2,4,6-$Me_3C_6H_2O$	386.2	590.2	564	10
	Tmp	320.1	496.5	574	10
	$(Me_3Si)_3N_2$	298.7	522.3	522	10
	$^iPr_2N$	245.7	483.9	534	10
Me_3Si	$(Me_3Si)_3C$	686.9	544.1	633.2	20
	2,4,6-$^tBu_3C_6H_2$	628	487	575	5
	$(Me_3Si)_3N_2$	210.3	542	540	34
	$Ph_3P(Me_3Si)C$	232.6	556.1	536.7	7
	$Ph_3P(2,6\text{-}Cl_2C_6H_3)C$	191.8	488.7	510.7	7
$^tBu_3Si$	$^tBu_3Si$	816.1			6
	$^tBu_3SiP^-Na^+$	212.5	732.5	552.6	8
Ph_3Si	$(Me_3Si)_3C$	711.4	511.8	633.1	20
	2,4,6-$^tBu_3C_6H_2$	641.9	457.7	588.7	20

the examples with R^2 = aryl (δ_A = 635 ± 10) and those with R^2 = triphenylphosphonium ylidyl groups (δ_A = 215 ± 20) is much larger than the differences $\Delta\delta_A$ = 150 to 250 between examples with R^2 = aryl and R^2 = amino group as mentioned above. It demonstrates that an ylide group is a more powerful electron donor (expressed in resonance formula **4b**) than an amino group. This has recently also been demonstrated by the structure and dissociation behaviour of halophosphines.[11]

Another way to discuss the phosphorus chemical shifts of diphosphenes is to look for the difference $\delta_A - \delta_B$. This difference naturally reflects the "dissimilarity" of the substituents R^1 and R^2 and as a consequence the polarity of the PP bond. Large absolute differences $\|\delta_A - \delta_B\|$ close to or beyond 300 are found for diphosphenes for which polar resonance formulas such as in Scheme 1 are of importance, *i.e.* for diphosphenes with strong electron-accepting substituents such as Ph_3P^+ (type **1**, Table I) or $(Et_2N)_2C^+$ (type **2**, Tables II, III)

TABLE V ^{31}P NMR Data of (*Z*)-diphosphenes $R^1-P_A=P_B-R^2$ (Ad = adamantyl); coupling constants *J* in Hz.

R^1	R^2	δ_A	δ_B	$^1J_{AB}$	Lit.
2,4,6-$^tBu_3C_6H_2$	2,4,6-$^tBu_3C_6H_2$	367.8			35
	2,4,6-$^tPn_3C_6H_2$[a]	368.7	367.3	581.2	35
	^tBuNH[a]	214	377	526.0	36
	Et_3CNH[a]	212.3	379.0	527.2	36
	1-AdNH[a]	213	375	524.5	36
	2,4,6-$^tPr_3C_6H_2NH$[a]	209.3	379.7	523	20
	$^cHex_2N$	153.1	335.5	591.6	15
$^tBu_3SiP^-Na^+$	$^tBu_3SiP^-Na^+$	403.0		502.6	37

[a] $\delta_{A,B}$ tentatively assigned, not assigned in the reference.

or with strong electron-donating substituents such as $(Me_3Si)_3N_2$ (type **3**, Tables III, IV) or $Ph_3P{=}CR$ (type **4**, Table IV). Even larger differences are found for triphosphenides $(^tBu_3C_6H_2)P_3^-$ and $(^tBu_3Si)_2P_3^-$ of type **5** (Tables I, IV).

The ^{31}P chemical shifts of acyclic (*Z*)-diphosphenes (Table V)[12] are generally smaller than those of the corresponding (*E*)-diphosphenes. The dependence of δ_A from the substituent R^2 is very similar in both isomers.

The PP coupling constants of diphosphenes range from 503 to 670 Hz and are large as compared to $^1J_{PP}$ of other types of compounds.[1] Polar diphosphenes, such as the ylide substituted (Table IV), tend to somewhat smaller coupling constants.

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