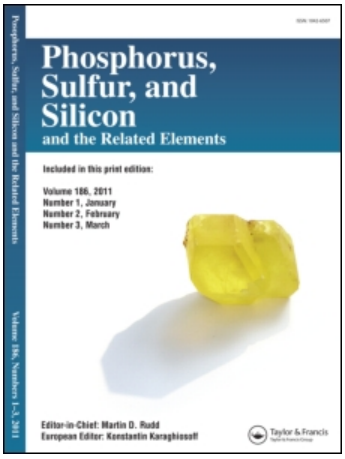

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A THEORETICAL STUDY ON CORRELATION BETWEEN THE STRUCTURES AND ^{31}P NMR CHEMICAL SHIFTS OF DICOORDINATED PHOSPHENIUM CATIONS

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A THEORETICAL STUDY ON CORRELATION BETWEEN THE STRUCTURES AND ^{31}P NMR CHEMICAL SHIFTS OF DICOORDINATED PHOSPHENIUM CATIONS

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MNDO calculations are performed for studying correlation between the electronic and geometrical structures and ^{31}P NMR chemical shifts of dicoordinated phosphenium cations. A simple relationship is introduced to elucidate the ^{31}P NMR chemical shifts of the cations from the calculated net atomic charges of the related atoms, Wiberg bond orders between the phosphorus atom and the atoms attached to it, and the bond angle at the phosphorus. The agreement of the calculated numerical results with the experimental data shows that the relationship obtained in this paper is satisfactory for the prediction of the ^{31}P NMR chemical shifts of the dicoordinated phosphenium cations.

Keywords: ^{31}P NMR chemical shift; Dicoordinated phosphenium cations; MNDO calculation; Net atomic charge; Wiberg bond order

1. INTRODUCTION

As pointed out by Parry and his co-workers[1,2], ^{31}P NMR spectroscopy is an ideal tool both for the identification of the dicoordinated phosphenium cations and for the elucidation of subsequent reactions. As a result of the presence of a formal positive charge at the dicoordinated phosphorus center, the dicoordinated phosphenium cations have specially designated ^{31}P NMR characteristics. Their ^{31}P chemical shifts are rather deshielded and fall in the range +110.0 to 513.2ppm. Many researchers have contributed to this field.[1-31] Niecke and

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Gudat et al. have studied the correlation between the excitation energies and the ^{31}P NMR chemical shifts of other low valent phosphorus compounds.[32,33] However, because the structure effects of the ^{31}P NMR chemical shifts of the dicoordinated phosphenium cations are very complicated, until now no one has presented a qualified generalized relationship between their ^{31}P NMR chemical shifts and the structures. Cowley[4] and Sanchez[6] interpreted the change of ^{31}P NMR chemical shift on the basis of conjugation effect of substituents attached to the phosphorus center. For example, the downfield shift which is observed when the R_2N group is replaced by a Cl atom can be explained by the inferior conjugating ability of the latter. Moreover, the observation that $[(Me_2N)\ (t\text{-}Bu)P]^+$ possesses the most deshielded ^{31}P chemical shift can be ascribed to the inability of the t-Bu to π-donate. However, this kind of explanation is not enough for understanding the ^{31}P chemical shifts of the recently synthesized dicoordinated phosphenium cations featuring with a S-P-N bond.[7-10] For example, the value[7] of the ^{31}P chemical shift of $[(n\text{-}PrS)\ (Me_2N)P]^+$ is larger than that[2] of $[(Cl)\ (Me_2N)P]^+$, whereas the organic chemist's point of view tells us that the conjugating ability of an RS group should be more powerful than that of a Cl.[34] It follows that the ^{31}P chemical shifts of the dicoordinated phosphenium cations not only correlate with conjugation effect, but also with electronic effects, steric effect, and other possible factors. In this paper, we attempt to employ a molecular orbital method to study the structure effects of the ^{31}P NMR chemical shifts of the dicoordinated phosphenium cations. Utilizing the calculated results for the geometrical and electronic structures and the ^{31}P NMR chemical shifts published in the literature, we try to summarize the main factors of determining and influencing the ^{31}P NMR chemical shifts and find a useful relationship which can be applied to the prediction of the ^{31}P NMR chemical shifts of the dicoordinated phosphenium cations.

2. CALCULATION METHOD

In the present study, we have accumulated 69 dicoordinated phosphenium cations for which the experimental ^{31}P NMR chemical shifts have been reported in the literature. In these cations, the atoms attached to the dicoordinated phosphorus center are N, S, C or Cl. Their structures and formulae are given in Table I, and the observed ^{31}P NMR chemical shifts are listed in Table III. To our knowledge, the crystal structures have been reported for only a few dicoordinated phosphenium cations. Hence, in order to carry out our theoretical study on these cations, as a first step, the geometries of the 69 cations must be optimized at a common level of reliability. Of course, ab initio calculations at a suitable level

TABLE I The calculated net atomic charges of the dicoordinated phosphorus and the atoms attached to the phosphorus center, the Wiberg bond orders between the phosphorus and the substituents and the bond angle at the phosphorus

No.	Cation[a]	Net atomic charge			Bond order		Bond angle
		Q_P	Q_X	Q_Y	B_{PX}	B_{PY}	X-P-Y
1	$[(Me_2N)_2P]^+$	0.9569	-0.5351	-0.5351	1.2701	1.2701	117.8
2	$[(Et_2N)_2P]^+$	0.9302	-0.5173	-0.5174	1.2697	1.2695	120.5
3	$[(i\text{-}Pr_2N)_2P]^+$	0.8821	-0.4899	-0.4898	1.2787	1.2787	125.3
4	$[(Et_2N)(Me_2N)P]^+$	0.9425	-0.5148	-0.5370	1.2861	1.2541	119.2
5	$[((Me_3Si)_2N)_2P]^+$	0.9178	-0.9935	-0.9935	1.2868	1.2871	128.6
6	$[(Me_2N)(i\text{-}Pr_2N)P]^+$	0.9166	-0.4881	-0.5352	1.3035	1.2459	121.8
7	$[(Me_2N)((Me_3Si)_2N)P]^+$	0.9343	-1.0424	-0.4990	1.2220	1.3194	115.9
8	$[(Me_2N)((t\text{-}BuMe_2Si)_2N)P]^+$	0.9400	-1.0705	-0.4785	1.1514	1.3584	116.4
9	$[MeNCH_2CH_2N(Me)P]^+$	0.9820	-0.5353	-0.5354	1.2663	1.2663	115.3
10	$[PhNCH_2CH_2N(Ph)P]^+$	0.9759	-0.4606	-0.4610	1.2600	1.2584	115.1
11	$[MeNCH_2C(Me_2)CH_2N(Me)P]^+$	0.9544	-0.5307	-0.5289	1.2680	1.2678	107.9
12	[MeNBMeNMeBMeNMeP]$^+$	0.9104	-0.4606	-0.4594	1.2671	1.2678	126.0
13	[MeNBMeNMeNMeP]$^+$	0.8285	-0.4374	-0.3237	1.2010	1.2984	112.2
14	$[TmsNSiCl_2N(Tms)P]^+$	0.9725	-1.0188	-1.0178	1.2864	1.2908	89.2
15	$[TmsNAl^-(Cl_2)N(Tms)P]^+$	0.7466	-0.8632	-0.8631	1.3522	1.3532	94.0
16	$[TmsNAl^-Cl_3(Tms_2N)P]^+$	0.7574	-1.0436	-0.7302	1.0470	1.6353	118.8
17	$[MeN\text{-}o\text{-}C_6H_4\text{-}NMeP]^+$	0.7687	-0.3751	-0.3748	1.2247	1.2247	96.5
18	$[t\text{-}BuNPCl(Bu)P]^+$	1.0120	-0.6864	-0.6873	1.2343	1.2339	98.4
19	$[t\text{-}BuNP(NMe_2)N(Bu)P]^+$	0.9304	-0.6786	-0.6796	1.2712	1.2662	98.3
20	$[(i\text{-}Pr_2N(Cl)P^+{=}N)(i\text{-}Pr_2N)P]^+$	1.1155	-0.4632	-0.8420	1.4327	0.9985	114.1
21	$[(Me_2N(Cl)P^+{=}N)(Me_2N)P]^+$	1.1816	-0.5133	-0.8273	1.4060	0.9921	111.5
22	$[((Me_2N)_3P{=}N)(Me_2N)P]^+$	1.0601	-0.5990	-1.0444	1.0627	1.4252	112.6

TABLE I (continued)

No.	Cation[a]	Net atomic charge			Bond order		Bond angle
		Q_P	Q_X	Q_Y	B_{PX}	B_{PY}	X-P-Y
23	$[((Me_2N)_3P{=}N)(i\text{-}Pr_2N)P]^+$	1.0360	-0.5633	-1.0487	1.0842	1.4122	115.0
24	$[(Et_2N)(EtS)P]^+$	0.5974	-0.3931	0.0113	1.4659	1.2644	110.6
25	$[(Et_2N)(n\text{-}PrS)P]^+$	0.5964	-0.3937	0.0098	1.4636	1.2676	110.6
26	$[(Et_2N)(i\text{-}PrS)P]^+$	0.5980	-0.3961	0.0045	1.4577	1.2713	110.2
27	$[(Et_2N)(n\text{-}C_6H_{13}S)P]^+$	0.5958	-0.3942	0.0099	1.4624	1.2689	110.6
28	$[(Et_2N)(n\text{-}C_8H_{17}S)P]^+$	0.5956	-0.3942	0.0103	1.4621	1.2693	110.6
29	$[(Et_2N)(n\text{-}C_{12}H_{25}S)P]^+$	0.5955	-0.3941	0.0105	1.4620	1.2694	110.6
30	$[(i\text{-}Pr_2N)(EtS)P]^+$	0.5700	-0.3673	0.0127	1.4850	1.2573	112.4
31	$[(i\text{-}Pr_2N)(n\text{-}PrS)P]^+$	0.5663	-0.3678	0.0115	1.4836	1.2603	112.5
32	$[(i\text{-}Pr_2N)(i\text{-}PrS)P]^+$	0.5658	-0.3704	0.0101	1.4790	1.2644	112.4
33	$[(i\text{-}Pr_2N)(Sec\text{-}BuS)P]^+$	0.5663	-0.3713	0.0033	1.4761	1.2664	112.4
34	$[(i\text{-}Pr_2N)(n\text{-}C_6H_{13}S)P]^+$	0.5662	-0.3687	0.0117	1.4833	1.2609	112.6
35	$[(i\text{-}Pr_2N)(n\text{-}C_8H_{17}S)P]^+$	0.5658	-0.3688	0.0119	1.4832	1.2611	112.6
36	$[(i\text{-}Pr_2N)(n\text{-}C_{12}H_{25}S)P]^+$	0.5654	-0.3689	0.0120	1.4834	1.2612	112.4
37	$[\overline{CH_2CH_2CH_2CH_2CH_2N})(n\text{-}PrS)P]^+$	0.6058	-0.3918	0.0047	1.4609	1.2605	110.3
38	$[(Me_2N)(n\text{-}PrS)P]^+$	0.6119	-0.4163	0.0156	1.4428	1.2883	109.3
39	$[(n\text{-}Bu_2N)(n\text{-}PrS)P]^+$	0.5943	-0.3929	0.0098	1.4681	1.2629	110.6
40	$[(i\text{-}Bu_2N)(n\text{-}PrS)P]^+$	0.5361	-0.3516	0.0134	1.5019	1.2407	118.3
41	[(t-BuNTms)(n-PrS)P]$^+$	0.5587	-0.5937	-0.0185	1.5287	1.2431	113.4
42	$[\overline{N(Ph)N{=}C(SMe)SP}]^+$	0.3951	-0.1159	0.3323	1.2942	1.2176	94.2
43	$[\overline{NHN{=}C(SMe)SP}]^+$	0.5249	-0.2281	0.3391	1.3230	1.2739	94.7
44	$[\overline{N(Ph)N{=}C(R)SP}]^+$	0.3952	-0.1307	0.3032	1.2973	1.2244	94.5
45	$[\overline{N(Ph)N{=}C(R')SP}]^+$	0.4452	-0.1666	0.2882	1.2998	1.2777	94.6
46	$[\overline{N(Ph)N{=}C(Et)SP}]^+$	0.4497	-0.1528	0.2908	1.2933	1.2562	94.7

TABLE I (continued)

No.	Cation[a]	Net atomic charge			Bond order		Bond angle
		Q_P	Q_X	Q_Y	B_{PX}	B_{PY}	X-P-Y
47	[N(Ph)N=C(Bz)SP]$^+$	0.4833	-0.1753	0.2813	1.3066	1.2782	95.0
48	[N(Ph)N=C(Ph)SP]$^+$	0.4338	-0.1511	0.2738	1.3008	1.2510	95.0
49	[N(Ph)N=C(p-MeOC$_6$H$_4$)SP]$^+$	0.4321	-0.1576	0.2709	1.3053	1.2515	94.8
50	[N(Ph)N=C(p-BrC$_6$H$_4$)SP]$^+$	0.4831	-0.1793	0.2886	1.3102	1.2869	94.6
51	[N(i-Pr)N=C(Ph)SP]$^+$	0.4476	-0.2376	0.2883	1.3252	1.2695	94.7
52	[NH-o-C$_6$H$_4$-SP]$^+$	0.5375	-0.3047	0.3334	1.2984	1.3258	98.2
53	[N(Ph)CH$_2$CH$_2$SP]$^+$	0.6866	-0.3717	0.1119	1.4108	1.2784	120.5
54	[N(p-Me-C$_6$H$_4$)CH$_2$CH$_2$SP]$^+$	0.6887	-0.3728	0.1141	1.4143	1.2780	120.6
55	[N(p-OMe-C$_6$H$_4$)CH$_2$CH$_2$SP]$^+$	0.6642	-0.3510	0.1099	1.4184	1.2615	120.3
56	[N(p-OEt-C$_6$H$_4$)CH$_2$CH$_2$SP]$^+$	0.6686	-0.3516	0.1073	1.4209	1.2610	120.5
57	[N(p-Cl-C$_6$H$_4$)CH$_2$CH$_2$SP]$^+$	0.6933	-0.3805	0.1215	1.4028	1.2880	120.5
58	[N(p-Br-C$_6$H$_4$)CH$_2$CH$_2$SP]$^+$	0.6933	-0.3785	0.1196	1.4040	1.2860	120.5
59	[N(n-Pr)CH$_2$CH$_2$SP]$^+$	0.6787	-0.4516	0.1372	1.4077	1.2952	120.0
60	[MeNNHC(Me)=CHP]$^+$	0.7148	-0.3310	-0.3787	1.1306	1.4411	112.3
61	[MeNNHC=C(CH$_2$)$_3$P]$^+$	0.7377	-0.3515	-0.4128	1.0847	1.4643	113.3
62	[MeNNHC(Me)=C(Me)P]$^+$	0.7042	-0.3263	-0.3935	1.1394	1.4142	112.2
63	[NHN(Me)C(Me)=CHP]$^+$	0.7328	-0.3106	-0.3881	1.1320	1.4417	115.1
64	[NHN(Me)C=C(CH$_2$)$_3$P]$^+$	0.7512	-0.3273	-0.4188	1.0908	1.4610	115.7
65	[MeNN(Me)C(Me)=CHP]$^+$	0.6896	-0.3341	-0.3750	1.1354	1.4457	113.7
66	[MeNNHC(Me)=C(SMe)P]$^+$	0.7185	-0.3196	-0.4955	1.1454	1.3465	112.1
67	[MeNNHC(Me)=C(SPh)P]$^+$	0.7358	-0.3324	-0.5326	1.1347	1.3826	111.7
68	[(Me$_2$N)(Cl)P]$^+$	0.9452	-0.4518	-0.1413	1.5182	1.0820	110.7
69	[(i-Pr$_2$N)(Cl)P]$^+$	0.8945	-0.4044	-0.1531	1.5566	1.0623	113.9

[a] R represents the -α-Furan group and R' represents the -α-naphthalene group.

with an extended basis set could give most reliable theoretical results. However, the CPU time would be very expensive if all of the geometries of the 69 cations listed in Table I would be optimized by use of the ab initio calculations. A practical choice for studying this problem is the use of a reliable semiempirical molecular orbital method. As we know, the MNDO method[35] was employed to optimize the geometries of several kinds of dicoordinated phosphenium cations listed in Table I. The geometries optimized by using the MNDO method are in good agreement with the experimental results.[4,15] The only problem is that no crystal structure data are available for the dicoordinated phosphenium cations containing an S-P-N bond. For this special kind of cation, we can not compare the optimized geometry with the crystal structure; we can only compare the geometry optimized by using the MNDO method with that obtained by using ab initio calculations at a suitable level. For this purpose, we have applied both the MNDO method and the ab initio molecular orbital method at RHF/6-31G** level to the geometry optimization of cation 43 listed in Table I. This cation is the smallest one of the systems featuring an S-P-N bond. The P-N and P-S bond lengths optimized by the MNDO are 1.596Å and 1.948Å, respectively. The P-N and P-S bond lengths optimized at the ab initio RHF/6-31G** level are 1.622Å and 2.025Å, respectively. The differences between the two kinds of calculated results for other geometrical parameters are all smaller than those for P-S and for P-N bond lengths. The two kinds of calculations have also been carried out for the optimization of the geometry of the three-coordinated phosphorus compound formed from the cation 43 plus a Cl^- anion. After the cation 43 forms a bond with a Cl^- anion, the P-N and P-S bond lengths become 1.655Å and 1.993Å, respectively (the MNDO results), and 1.686Å and 2.099Å, respectively (ab initio RHF/6-31G** results). Hence, after the cation 43 forms a bond with a Cl^- anion, the MNDO calculation results indicate that the P-N and P-S bond lengths increase 0.059Å and 0.045Å, respectively, and the ab initio calculation results reveal that the P-N and P-S bond lengths increase 0.064Å and 0.074Å, respectively. The detailed optimized results will be published elsewhere.[36] All the optimized results show that the geometries optimized by the MNDO calculations are in good agreement with those optimized at the ab initio RHF/6-31G** level, especially for the relative lengths of each kind of bonds. It follows that the MNDO method is feasible for studying all kinds of the cations listed in Table I. Therefore, in this paper, we employ the MNDO method to study the 69 dicoordinated phosphenium cations.

The equilibrium geometries of the 69 dicoordinated phosphenium cations are fully optimized by use of the MNDO calculation with the analytical energy gradient technique and the parameters presented in literature.[35] Considering that the electron density of the phosphorus center is undoubtedly the most direct fac-

tor in determining the ^{31}P chemical shift and that the substituent effects can also influence the ^{31}P chemical shift to a great extent, the electronic structure calculations are carried out using the optimized equilibrium geometries.

3. RELATIONSHIP AND CALCULATED RESULTS

In Table I we present calculated results for: (1) the net atomic charges at the phosphorus center [denoted by Q_P]; (2) the net charge [Q_X and Q_Y] on each of the substituents [X and Y] bonded directly to phosphorus; (3) the Wiberg bond order [B_{PX} and B_{PY}] between the phosphorus and each of the substituents bonded directly to phosphorus; and (4) the bond angle [θ_{XPY}] at the central phosphorus atom. Values for each of these parameters change as the substituents on phosphorus are changed [see Table I]. In this study it was difficult to get a satisfactory generalized correlation of the ^{31}P chemical shift using only the net atomic charges, bond order values, and bond angle values as variables. Therefore, some tentative treatments to the calculated results must be done in order to get the suitable parameters for our theoretical analysis. The four quantities Q_X, Q_Y, B_{PX} and B_{PY} can merge into two parameters, one is Q_X+Q_Y denoted by Q_{XY} and another is $(Z_X+M_X-Z_N)B_{PX}+(Z_Y+M_Y-Z_N)B_{PY}$ denoted by B_{XY}. The parameter B_{XY} is adopted in order to eliminate the effects brought by the differences of the different kinds of substituents. In expression of parameter B_{XY}, M_X and M_Y are the numbers of atoms attached to X and Y atoms, respectively, and Z_X, Z_Y and Z_N are the atomic numbers of X, Y and N atoms, respectively. In addition, for the 18-23th dicoordinated phosphenium cations which have a non-dicoordinated phosphorus atom besides the phosphorus center, it is found from the calculated results that the non-dicoordinated phosphorus atoms in the molecular systems all have also very high positive net atomic charges, and the change of the net charge of the non-dicoordinated phosphorus atom is sensitive to its chemical enviroment (from +0.9192 to +1.4257). When the distances between two phosphorus atoms in these systems are in the range 2.5-3.0Å, there probably exists strong interaction between the two phosphorus atoms. So the effect of the non-dicoordinated phosphorus should also be considered, and a new parameter representing the change of the net charge of non-dicoordinated phosphorus atom, denoted by Q_{PP}, is introduced. Q_{PP} is defined as the net atomic charge of the non-dicoordinated phosphorus atom minus 1.30 which is a value between the maximum and the minimum net charges of the six non-dicoordinated phosphorus atoms listed in Table II. For the other dicoordinated phosphenium cations which has a four-membered ring involving the dicoordinated

phosphorus atom, the net charge of the atom at the opposite site of the phosphorus are much smaller, and therefore the interaction between this atom and the phosphorus atom is not important, although the distance between them is not very long, too.

TABLE II The net atomic charges for the non-dicoodinated phosphorus atom in the 18-23th dicoordinated phosphenium cations

No.	*18*	*19*	*20*	*21*	*22*	*23*
Q	0.9192	0.9569	1.0107	1.0258	1.4380	1.4257

In this way, we may propose the following relationship:

$$\delta^{31}P = C_1Q_P + C_2Q_{XY} + C_3B_{XY} + C_4\,\theta_{XPY} + C_5Q_{PP} + C_0 \quad (1)$$

It should be noted that for the dicoordinated phosphenium cations not containing the non-dicoordinated phosphenium atom, the value of parameter Q_{PP} in Eq. (1) is zero. For all of the dicoordinated phosphenium cations listed in Table 1, by use of Eq. (1) and the least square process we get the following explicit form:

$$\delta^{31}{}_P = -235.86\,Q_P - 173.46\,Q_{XY} + 19.59\,B_{XY} + 2.97\,\theta_{XPY} - 240.8\,Q_{PP} - 190.65 \quad (2)$$

with a correlation coefficient of 0.984 and a standard deviation of 14.75ppm. The $\delta^{31}P$ values predicted by Eq. (2) for all of the cations studied in this paper are listed in Table III, together with the experimental data.

4. DISCUSSION AND CONCLUSION

It can be concluded from the relationship, Eq. (2), that the magnitude of the ^{31}P NMR chemical shift of the dicoordinated phosphenium cation is not only determined by the net atomic charge at the dicoordinated phophorus center, but also influenced by the net charges of the atoms bonding with the phosphorus center, the bond orders between the phosphorus and the substituents and the bond angle at the phosphorus. All these calculated quantities determine the environment of the phosphorus nucleus, and, therefore, determine its magnetic shielding. As one can see from Table III, on the whole, the calculated ^{31}P NMR chemical shifts reflect general trends in experimental values. However, for some cations the difference between the calculated and experimental chemical shifts is significantly larger than the difference for others. This may be due to the limitation of the MNDO approximation. Nevertheless, the calculated results adequately reflect

some important trends, e.g., the ^{31}P chemical shifts in $[i\text{-}Pr_2N\text{-}P\text{-}Y]^+$ increase with the substituent Y in the series: NMe_2 (6), $N(i\text{-}Pr)_2$ (3), Cl (69) and S(i-Pr) (32). The ^{31}P chemical shifts in $[Me_2N\text{-}P\text{-}Y]^+$ increase with Y in the series: NMe_2 (1), NEt_2 (4), $N(i\text{-}Pr)_2$ (6), Cl (68), $N(Me_3Si)_2$ (7), S(n-Pr) (38). The ^{31}P chemical shift in $[i\text{-}Pr_2N\text{-}P\text{-}Y]^+$ are always larger than that in $[Me_2N\text{-}P\text{-}Y]^+$, when the substituent Y in them is fixed, such as NMe_2, $N(i\text{-}Pr)_2$ or Cl. It follows that the relationship Eq. (2) obtained in this paper is satisfatory for calculating the ^{31}P NMR chemical shifts of the dicoordinated phosphenium cations from the MNDO calculation results.

TABLE III The experimental and calculated ^{31}P NMR chemical shifts(ppm) for the dicoordinated phosphenium cations[a]

No.	*Calc.*	*Expt.*	*Ref.b*	*No.*	*Calc.*	*Expt.*	*Ref.b*
1	268.3	264.0	2,11	36	430.6	437.2	10
2	276.4	263.0	13,14	37	418.6	418.7	10
3	293.6	313.0	15	38	421.5	430.6	10
4	272.7	266.0	16	39	422.4	428.1	10
5	470.6	450.3	17	40	448.4	431.5	10
6	282.1	290.0	15	41	478.2	443.1	10
7	349.8	354.3	17	42	296.7	261.9	10
8	349.4	370.1	17	43	299.7	269.7	10
9	254.6	264.0	18	44	307.0	312.1	10
10	228.8	254.0	19	45	315.8	318.0	10
11	237.4	222.0	20	46	307.2	321.0	10
12	277.3	302.0	21	47	311.3	322.7	10
13	226.0	228.0	21	48	313.8	318.9	10
14	349.5	343.0	22	49	315.6	320.1	10
15	448.8	450.0	22	50	311.6	331.9	10
16	370.8	379.0	22	51	327.6	328.6	10
17	188.6	212.0	23	52	331.2	306.0	26
18	337.8	365.7	17	53	408.6	406.4	10
19	349.1	334.5	24	54	408.4	402.6	10
20	324.0	311.3	19,25	55	406.9	411.8	10

No.	*Calc.*	*Expt.*	*Ref.b*	*No.*	*Calc.*	*Expt.*	*Ref.b*
21	301.2	293.5	19,25	56	407.0	406.2	10
22	291.7	289.0	16	57	408.5	411.2	10
23	302.5	304.0	16	58	408.1	402.6	10
24	421.7	427.9	10	59	421.9	443.2	10
25	422.8	426.6	10	60	220.2	230.7	27
26	423.0	426.6	10	61	225.4	209.3	27
27	423.2	427.5	10	62	223.6	237.7	28
28	423.3	427.6	10	63	222.5	211.0	29
29	423.3	427.4	10	64	226.5	195.2	29
30	428.3	437.9	10	65	230.7	230.3	30
31	430.4	437.8	10	66	234.2	220.0	31
32	431.5	435.0	10	67	238.3	231.1	31
33	433.0	435.2	10	68	340.3	325.0	2
34	430.9	438.0	10	69	353.6	334.0	12
35	431.0	437.4	10				

[a] The ^{31}P chemical shift referenced to 85% H_3PO_4(external).
[b] References from which the experimental values come.

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