Spectroscopy 15 (2001) 27–32
IOS Press


# $^{13}C$ and $^{15}N$ NMR shieldings of 1,2,4-diazaphospholes in the solid state and in solution

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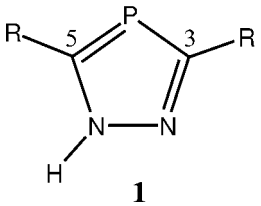
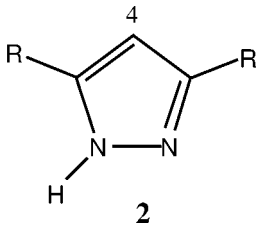
**Abstract.** The solid state $^{13}C$ and $^{15}N$ CPMAS NMR spectra of 3,5-di-*tert*-butyl-1,2,4-diazaphosphole **4** and 3,5-diphenyl-1,2,4-diazaphosphole **5** have been recorded. The X-ray structure of the first compound was already known (it is a cyclic dimer with localized N–H protons) while the structure of the second cannot be determined due to the difficulty to grow suitable single crystals. NMR results pointed out that **4** is a "classical" compound while **5** is probably a tetramer showing Intermolecular Solid-State Proton Transfer (ISSPT). GIAO/ab initio calculations have been carried out to estimate the absolute $^{1}H$, $^{13}C$ and $^{15}N$ shieldings. The agreement with the experimental chemical shifts is good enough to assign the signals of carbons C-3 and C-5.

## 1. Introduction

1,2,4-Diazaphospholes **1** are related to pyrazoles **2** since they can be considered 4-phosphapyrazoles.




**1**




**2**

This relationship has far-reaching structural consequences. Of two 1*H*-1,2,4-diazaphospholes: **3** (**1**, R = H) and **4** (**1**, R = Bu$^t$) the structure is known from X-ray analysis: **3** crystallizes forming helical chains (catemers) and **4** forming cyclic dimers [1]. The corresponding pyrazoles, pyrazole itself **6** (**2**, R = H) [2–4] and 3,5-di-*tert*-butylpyrazole **7** (**2**, R = Bu$^t$) [5] crystallize using the same patterns. Since 3,5-diphenylpyrazole **8** (**2**, R = $C_6H_5$) crystallizes in cyclic tetramers [6] we decided to explore the structure of 3,5-diphenyl-1,2,4-diazaphosphole **5** (**1**, R = $C_6H_5$) [1] in order to extend the comparison.

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Table 1
$^{13}C$ and $^{15}N$ NMR chemical shifts [ppm] and coupling constants [Hz] of 1*H*-1,2,4-diazaphospholes **1** in $CDCl_3$ (or $CH_2Cl_2$, compound **5**) solution

| | Average C-3,5 | R | | Average N-1,2 |
|---|---|---|---|---|
| **3** | 158.9 | – | | 105.5 |
| (R = H) | $^1J_{CH} = 181.2$ Hz | | | $^2J_{NH} = 6.7$ |
| | $^1J_{CP} = 60.0$ Hz | | | |
| | $^3J_{CP} = 5.1$ Hz | | | |
| **4** | 189.7 | 35.2 (C) | 31.9 (Me) | |
| (R = $Bu^t$)[a] | $^1J_{CP} = 60.8$ | $^2J_{CP} = 14.7$ | $^3J_{CP} = 6.6$ | |
| **5** | 177.0 | | | |
| (R = Ph)[b] | $^1J_{CP} = 53.4$ | 134.5 ($C_i$) | 126.3 ($C_o$) | |
| | | $^2J_{CP} = 18.6$ | $^3J_{CP} = 9.8$ | |
| | | 129.2 ($C_m$) | 129.1 ($C_p$) | |

[a] $\delta\,^{31}P = 67.6$ ppm ($CDCl_3$, this work). [b] $\delta\,^{31}P = 74.3$ ($CH_2Cl_2$ [7]), $\delta\,^{31}P = 76.0$ ppm ($CDCl_3$, this work).

As we could not obtain crystals of **5** suitable for X-ray analysis, we decided to investigate the structure of 1*H*-1,2,4-diazaphospholes **3**, **4** and **5** using solid state NMR spectroscopy. For comparison, the not yet published $^{13}C$ NMR data of these compounds in solution [7] are collected in Table 1. Generally only averaged signals for C-3,5 and N-1,2 are observed in the spectra of the *N*-unsubstituted 1,2,4-diazaphospholes as well as in the spectra of the *N*-unsubstituted pyrazoles. While, however, by using $Me_2SO$ or $(Me_2N)_3PO$ as a solvent, separate signals for C-3 and C-5 could be achieved for pyrazole (**2**, R = H) [8–10] and 3,5-dimethylpyrazole (**2**, R = Me) [11], this is not the case for the diazaphosphole **3** [7].

## 2. Experimental

Compounds **3**–**5** have been described previously [1,7]. CPMAS NMR experiments: the solid state $^{13}C$ and $^{15}N$ NMR spectra were obtained at 300 K on a Bruker AC-200 spectrometer operating at 50.32 MHz ($^{13}C$) and 20.28 MHz ($^{15}N$) under cross polarization (CP) and magic angle spinning (MAS) conditions, using a 7 mm Bruker DAB 7 probehead that achieves rotational frequencies of about 3.5–4.5 kHz. Samples (approximately 200 mg of material) were carefully packed in $ZrO_2$ rotors. The standard CPMAS pulse sequence was applied with $^1H$-90° pulse width of 7 $\mu$s for $^{13}C$ and of 10.5 $\mu$s for $^{15}N$; 1 ms contact pulses and 5 s repetition time, the spectral width being of 15 000–17 000 Hz. The chemical shifts are given in ppm from TMS for $^1H$ and $^{13}C$ and external nitromethane for $^{15}N$ NMR spectra. $^{31}P$ chemical shifts are given from external 85% $H_3PO_4$ in water.

## 3. Computational details

All the calculations have been carried out with the *Gaussian 98* package [12]. The molecules studied have been optimized using the 6–31G* basis set and the Becke3LYP method [13,14], as implemented in *Gaussian 98*. For the geometry optimization, the planarity of diazaphosphole ring has been imposed whenever possible. The calculations of the absolute shieldings, $\sigma_{calc}$, have been performed using the GIAO perturbation method [15].

## 4. Results and discussion: NMR spectroscopy

The results we have obtained with compounds **4** and **5** are reported in Table 2, together with those of compound **3** from [7]. It has not been possible to observe the $^{15}N$ NMR signals of compound **5**, even after 76 000 scans (corresponding to 63 h). The chemical shifts of the corresponding pyrazoles have been added for comparative purposes.

It is interesting to compare these $^{13}C$ NMR data with those of the corresponding *N*-methyl derivatives **9**, **10**, **11** and *N*-phenyl derivatives **12**, **13**, **14** reported in Table 3.

Table 2

$^{13}C$ and $^{15}N$ CPMAS NMR chemical shifts [ppm] and coupling constants [Hz] of 1*H*-1,2,4-diazaphospholes **1** and 1*H*-pyrazoles **2**

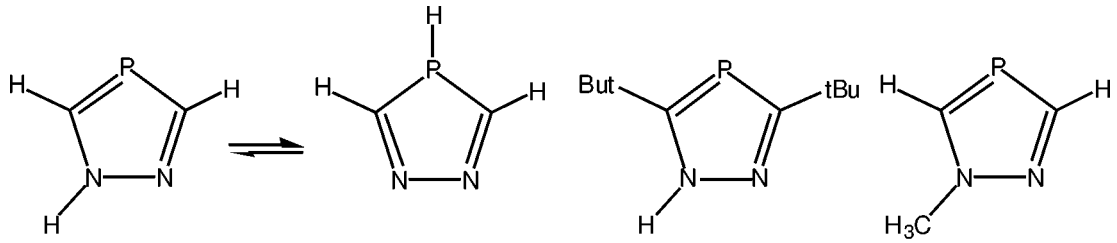
| Comp. | C-3 | C-5 | R | N-1 | N-2 |
|---|---|---|---|---|---|
| **3** | 165.8 | 159.4 | – | | |
| (R = H) [7] | | $^1J_{CP} = 65.2$ | | | |
| **6** | 138.7 | 107.0 | – | −167.8 | −90.5 |
| (R = H) [16,17] | | | | | |
| **4** | 191.5 | 188.5 | 35.0 (C) | −161.4 | −63.7 |
| (R = $Bu^t$) | | | 32.3 (Me) | $^2J_{NP} = 48$ | $^2J_{NP} = 48$ |
| **7** | 160.7 | 152.9 | 32.7 (C) | −178.1 | −96.8 |
| (R = $Bu^t$) [16,17] | | | 31.3 (Me) | | |
| **5** | 176.4 | 175.3 | 133.4 ($C_i$) | N.o.[a] | |
| (R = $C_6H_5$) | | | 134.8 ($C_i$) | | |
| | | | 125.2 ($C_o$) | | |
| | | | 128.6 ($C_m$, $C_p$) | | |
| **8** | 146.9 | 139.0 | N.o.[a] ($C_i$) | −175.0 | −102.0 |
| (R = $C_6H_5$) [16,17] | | | 127.0 ($C_o$, $C_m$, $C_p$) | | |

[a]Not observed.

Table 3

$^{13}C$ NMR chemical shifts [ppm] and $^{13}C$–$^{31}P$ coupling constants [Hz] of 1-substituted 1,2,4-diazaphospholes in $CDCl_3$ solution [7]

| | $R^1$ | $R^3$ | $R^5$ | C-3 | C-5 | $R^1$ | $R^3$ | $R^5$ |
|---|---|---|---|---|---|---|---|---|
| **9** | $CH_3$ | H | H | 163.7 | 156.8 | – | | |
| | | | | $^1J = 62.5$ | $^1J = 54.4$ | | | |
| **10** | $CH_3$ | $Bu^t$ | $Bu^t$ | 188.3 | 185.9 | 42.1 | 35.6 (C) | 34.6 (C) |
| | | | | $^1J = 59.2$ | $^1J = 54.9$ | $^3J = 1.2$ | $^2J = 16.5$ | $^2J = 14.7$ |
| | | | | | | | 31.1 ($CH_3$) | 31.9 ($CH_3$) |
| | | | | | | | $^3J = 10.4$ | $^3J = 6.7$ |
| **11** | $CH_3$ | Ph | Ph | 177.5 | 175.5 | 40.1 | 137.0 ($C_i$) | 133.2 ($C_i$) |
| | | | | $^1J = 56.4$ | $^1J = 49.1$ | $^3J = 1.5$ | $^2J = 19.8$ | $^2J = 18.3$ |
| **12** | Ph | H | H | 164.4 | 154.1 | – | | |
| | | | | $^1J = 63.3$ | $^1J = 54.3$ | | | |
| **13** | Ph | $Bu^t$ | $Bu^t$ | 179 | 183 | 130.7 ($C_i$) | 31.2 ($CH_3$) | 33.2 ($CH_3$) |
| | | | | $^1J = 60$ | $^1J = 55$ | $^3J = 5.5$ | $^3J = 11.9$ | $^3J = 6.7$ |
| **14** | Ph | Ph | Ph | 177.5 | 175.4 | 141.2 ($C_i$) | 135.0 ($C_i$) | 132.6 ($C_i$) |
| | | | | $^1J = 57.2$ | $^1J = 49.1$ | | $^2J = 19.8$ | $^2J = 18.3$ |




In each of the series, the chemical shifts of the ring carbon atoms depend, in a similar way, of the substituents R and tend to lower field in the order R = H, Ph, Bu$^t$. While in the NMR spectra of compounds **3**–**5** in solution (as mentioned above) only averaged signals are found for C-3,5 and N-1,2 (Table 1), individual signals are found in their solid state NMR spectra. In these spectra, the C-3/C-5 shift difference is largest in case R = H. The same is found in the solution spectra of compounds **9**–**11** and **12**–**14**. The two signals can be assigned unequivocally in case of compound **9**. As only the signal at higher field shows a coupling to the protons of the *N*-methyl group it is assigned to C-5. This signal also shows the somewhat smaller $^1J_{CP}$. For the other mentioned 1,2,4-diazaphospholes (with **13** as the only exception) also the signal with the smaller coupling constant $^1J_{CP}$ and the smaller chemical shift $\delta$ $^{13}$C is assigned to C-5. This assignment is in accord with that for pyrazoles, where also the signal of C-3 is found at lower field than that of C-5.

The assignment of N1 and N2 in compound **4** is based on the homology with chemical shifts of the pair pyrazole **6** and 3,5-di-*tert*-butylpyrazole **7** (see Table 2 [17]).

## 5. Results and discussion: GIAO calculations

We have calculated the absolute shieldings of the structures represented above. It is clear that 1,2,4-diazaphospholes are N(1)*H* tautomers and not P(4)*H* tautomers; nevertheless, we wanted to know the energy gap between both tautomers and also if the chemical shifts are very different.

The first point is easily answered: the difference in energy is 190 kJ mol$^{-1}$, a value considerable who precludes any attempt of observing **3′** in the gas phase or even in solution (the respective dipole moments are **3**, 2.53 D and **3′**, 4.94 D).

The calculated absolute shieldings, $\sigma$ in ppm, are reported in Table 4.

We have compared these values to the experimental values, when available. We have used the calculated $\sigma$ values for the three references ($^1$H-TMS: 31.97; $^{13}$C-TMS: 189.69; $^{15}$N-MeNO$_2$: $-117.75$ ppm) and we have mixed the values in solution, averaged for **3** and **4**, with the CPMAS values. We have treated all the values, 18, in a single equation:

$$\delta_{exp} = (32.5 \pm 1.3) - (1.01 \pm 0.01)\sigma_{calc} + (160.2 \pm 1.8)[^{13}C] - (151.2 \pm 2.0)[^{15}N], \quad r^2 = 0.999. \quad (1)$$

The equation is excellent, not only because $r^2$ is very high but, more important, because the slope is close to 1. [$^{13}$C] and [$^{15}$N] are indicative variables, which are 0 for the $^1$H and 1 when the other nuclei are considered (the corresponding data matrix is called a matrix of presence/absence). The intercept is close to the value for $^1$H-TMS and the two other slopes are close to the differences between the references ($189.69-31.97 = 157.72$ and $-117.75-31.97 = -149.72$). The equation is simple to use. For instance, in Table 4, the absolute shieldings of carbons C-3 and C-5 are 30.30 and 36.48 ppm. Assuming that the

Table 4
$^{1}H$, $^{13}C$, $^{15}N$ and $^{31}P$ absolute shieldings [ppm] as calculated by GIAO/B3LYP

| | N–H (or P–H) | C(3)–H | C(5)–H | $^{31}P$ | C-3 | C-5 | N-1 | N-2 |
|---|---|---|---|---|---|---|---|---|
| **3** | 22.28 | 23.52 | 23.77 | 274.11 | 29.52 | 38.24 | 48.38 | −71.11 |
| **3′** | 23.68 | 23.83 | 23.83 | 363.81 | 68.77 | 68.77 | −114.82 | −114.82 |
| **4** | 22.95 | –[a] | –[b] | 285.57 | 1.34 | 7.06 | 57.80 | −61.73 |
| **9** | –[c] | 23.75 | 23.86 | 257.96 | 30.30 | 36.48 | 37.61 | −83.25 |

[a] $Bu^t$-3: C: 151.14, Me: 157.33, H: 30.77; [b] $Bu^t$-5: C: 154.06, Me: 158.50, H: 30.74; [c] N-$CH_3$: $^{1}H$ 28.20, $^{13}C$ 149.44.

slope of $\sigma_{calc}$ is 1, the use of Eq. (1) yields, for C-3: $32.5 - 30.30 + 160.2 = 162.4$ ($\delta_{exp} = 163.7$ ppm, Table 3) and for C-5: $32.5 - 36.48 + 160.2 = 156.2$ ($\delta_{exp} = 156.8$ ppm, Table 3).

The above equation predicts for the symmetrical compound **3′** a signal at $\delta = 123.4$ ppm for the carbon and $\delta = -2.8$ ppm for the nitrogen, very different from those measured for **3**. Finally, the calculations confirm that the assignment of carbons C-3 and C-5 in **9** were correct.

In the case of compound **4** we can compare the shielding of P-4 (285.6 ppm, Table 4) and the experimental chemical shift (67.6 ppm, Table 1). The difference, 353.2 ppm, is close to the experimental absolute shielding of 85% $H_3PO_4$ in water (328.4 ppm [18]).

## 6. Conclusions

The conclusion of this study is that compound **4** behaves "classically", i.e., the proton of the dimer is localized and no intermolecular solid state proton transfer (ISSPT [19]) occurs. On the other hand, compound **5** presents a "dynamic" behavior in the solid state (ISSPT), therefore is not a catemer being probably a tetramer like **7**. The dynamic disorder of compound **5** explains why no $^{15}N$ signal was observed for this compound (Table 2): a broad signal is very difficult to observe without $^{15}N$ labelling.

Finally, we want to point out that the understanding of dynamic properties of crystals involving proton transfer along the hydrogen bond needs necessarily the use of solid state NMR spectroscopy, if possible combined with X-ray crystallography. But even in those cases where monocrystals of sufficient size cannot be obtained (case of compound **5**), CPMAS NMR spectroscopy could provide with a sufficiently accurate description of the compounds under study.

## Acknowledgements

This work has been financially supported by the Spanish DGI/MCT (project numbers PB96-0001-C03 and BQU 2000-0252) and to the "Comunidad de Madrid" (project number 07N/0001/1999) of Spain. Thanks are due to Dr. Angelika Sebald, Universität Bayreuth, for the $^{13}C$ CPMAS NMR spectrum of **3**.

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