

Structure of 3(5)-[(4-diphenylphosphinoyl)phenyl]pyrazole in the solid state (X-ray and CPMAS NMR) and in solution (NMR): tautomerism and hydrogen bonds

Rosa M. Claramunt,^{a,*} Concepción López,^a José Elguero,^b Arnold L. Rheingold,^c
Lev N. Zakharov,^c and Swiatoslaw Trofimenko^{c,*}

^a *Departamento de Química Orgánica y Biología, Facultad de Ciencias, UNED,
Senda del Rey 9, E-28040 Madrid, Spain*

^b *Instituto de Química Médica, CSIC, Juan de la Cierva 3, E-28006 Madrid, Spain*

^c *Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716-2522,
USA*

E-mails: rclaramunt@ccia.uned.es; trofimen@udel.edu

Dedicated to Professor Edmundo A. Rúveda on his 70th anniversary
Dedicated to Professor Roberto A. Rossi on his 60th anniversary
(received 30 Jun 03; accepted 03 Sep 03; published on the web 09 Sep 03)

Abstract

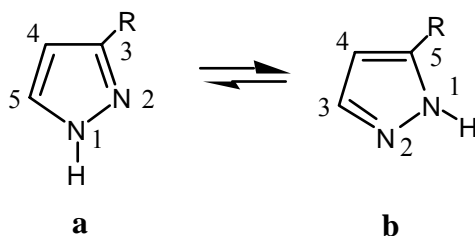
The structure of 3(5)-[(4-diphenylphosphinoyl)phenyl]pyrazole has been determined by X-ray crystallography. The compound crystallizes from DMF as the 1*H*-3-substituted tautomer (monoclinic, space group *P2₁/c*). The complete characterization by means of ¹³C, ³¹P and ¹⁵N CPMAS NMR allowed us to confirm that at the solid state only such tautomer is found, with strong intermolecular hydrogen bonds between the pyrazole-NH donor and the phosphine oxide group acceptor. At 300 K in DMSO-*d*₆ solution, the two tautomers were detected in a ratio 3-tautomer *versus* 5-tautomer of 86:14. According to DFT calculations (B3LYP/6-31G** + ZPE), the 3-[(4-diphenylphosphinoyl)phenyl]-1*H*-pyrazole tautomer is more stable by about 3.8 kJ mol⁻¹.

Keywords: Pyrazoles, X-ray, CPMAS NMR, supramolecular architectures, theoretical calculations

Introduction

Our research on supramolecular architectures formed by NH-azoles in the solid state,¹⁻¹⁰ and most particularly pyrazoles,²⁻⁶ led us to try to establish several rules capable of predicting annular tautomerism, which nitrogen bears the proton, and the network formed by the intermolecular N-H...N hydrogen bonds.

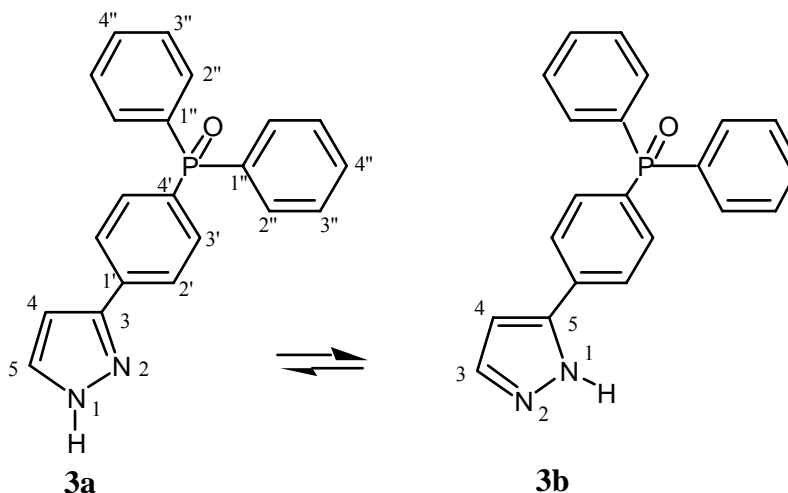
Concerning tautomerism, we have found that in 3(5)-substituted pyrazoles alkyl groups prefer to occupy position 5 (tautomer **b**), while aryl groups seem to prefer position 3 (tautomer **a**). The secondary structure, resulting from the hydrogen bonds between molecules in the crystal, leads to the formation of dimers or tetramers in alkyl substituted pyrazoles and trimers or catemers for the aryl ones. In general the substituent at position 4 plays a minor role by pushing away the adjacent substituents (buttressing effect).



Scheme 1

We have found a few number of exceptions: the 3(5)-(1-adamantyl)pyrazole (**1**) where the simultaneous presence of both tautomers **a** and **b** in the crystal gives rise to a catemer,² and the 3(5)-phenylpyrazole (**2**) where it is possible to isolate the two independent tautomers in the solid state, the most stable one 5-phenyl-1*H*-pyrazole (**2b**) forming a catemer of order 2,⁵ and the 3-phenyl-1*H*-pyrazole (**2a**) hexamers.⁶

In order to advance in the understanding of the problem, we decided to study the case of the 3(5)-[(4-diphenylphosphinoyl)phenyl]pyrazole (**3**).



Scheme 2

Pyrazoles bearing phosphorus substituents are uncommon and in most of them the P atom is directly linked to one of the pyrazole ring carbon atoms: C(4)-P(=O)R₂,¹¹ C(4)-P(=O)(OEt)₂,¹² C(4)-P(=O)Ph₂,^{13,14} C(4)-PX₂ (X = Cl, Br),¹⁵⁻¹⁷ C(5)-PR₂.¹⁸

Results and Discussion

NMR spectroscopy in solution and in solid state

When the ^1H NMR spectra of compound **3** was recorded in DMSO- d_6 solution the two tautomers were detected as proved by the two pyrazole-NH signals appearing at 13.50 ppm and 13.05 ppm with a relative intensity of 14/86. Concerning the other proton signals we have been able to assign those corresponding to the major tautomer **3a** at 7.82 (bs, H5) and 6.79 (d, $^3J = 2.2$, H4), 7.97 (d, $^3J = 6.1$, H2'), 7.62 (d, $^3J = 6.1$, H3'), 7.61 (m, H2''), 7.59 (m, H3'') and 7.55 (tt, H4'', $^3J = 7.4$, $^4J = 2.4$), by means of the ^1H - ^1H homonuclear-shift-correlation-spectra gs-COSY, and 2D-inverse-proton-detected heteronuclear-shift-correlation spectra gs-HMQC and gs-HMBC.¹⁹ The coupling constants were measured directly on the spectra and ^1H - ^{31}P coupling constants, similar to those reported for triarylphosphine oxides ($^3J_{\text{ortho}} = 11$ Hz, $^4J_{\text{meta}} = 2\text{--}3.5$ Hz)²⁰ were not determined due to the complexity of the aromatic part. For the minor tautomer **3b** only the signal at 7.83 (bs, H3) could be clearly observed, besides the aforementioned NH signal at 13.50 ppm.

The ^{31}P NMR spectrum of **3** in DMSO- d_6 shows two signals, corresponding to both tautomers in the same ratio of 86/14 at 26.73 ppm for **3a** and 26.47 ppm for **3b**, were observed. The ^{13}C NMR in the same solvent confirmed that the major tautomer is **3a**, the chemical shift values for the pyrazole carbon atoms being 149.05 (quaternary, C3), 130.21 (ddd, $^1J = 190.0$, $^2J = ^2J = 8.4$, C5), 102.56 (dd, $^1J = 170.6$, $^2J = 8.4$, C4). The assignment of C5 and C4, has been made not only on the basis of the chemical shift difference but also in the magnitude of the 1J coupling constant values and the 2D inverse proton detected heteronuclear correlation spectra gs-HMQC (^1H - ^{13}C), gs-HMBC (^1H - ^{13}C) and gs-HMBC (^1H - ^{15}N). Concerning the carbon atoms of the diphenylphosphinoyl group the assignment is: 137.26 (C1'), 125.24 [C2', $^3J(^{31}\text{P}) = 12.2$], 131.98 [C3', $^2J(^{31}\text{P}) = 9.9$], 130.96 [C4', $^1J(^{31}\text{P}) = 100.0$], 133.35 [C1'', $^1J(^{31}\text{P}) = 101.0$], 131.51 [C2'', $^2J(^{31}\text{P}) = 9.9$], 128.77 [C3'', $^3J(^{31}\text{P}) = 12.2$], 128.77 [C4'', $^4J(^{31}\text{P}) = 2.9$]. ^{13}C - ^1H aryl carbons coupling constants have standard values.²¹ The pyrazole carbon signals corresponding to the minor tautomer **3b** appear at 140.31 (dd, $^1J = 182.5$, C3), 103.60 (dd, C4, $^1J = 173.3$) and 140.69 (quaternary, C5). The coupling constants measured on the pyrazole carbons are similar to those reported for other pyrazoles.²² The only remarkable result was the observation of two 8.4 Hz couplings in the C5 carbon of tautomer **3a**. One of them is a 2J coupling with H-4,²² but the other must be a 2J coupling with the NH. These last couplings are almost never observed, the only previous report concerns 3-azidoindazole: on C7a –the equivalent of C5– a $^2J = 7.9$ Hz was measured.²³

When we recorded the ^{15}N CPMAS NMR only two sharp signals at -165.5 ppm for the -NH-nitrogen (-170.5 in DMSO- d_6) and -79.3 ppm for the imino =N– one were observed, pointing out to the presence of a single tautomer in the solid state. This result was confirmed by the ^{31}P CPMAS NMR spectrum where a signal at 35.05 ppm was obtained and by the chemical shift values in ^{13}C CPMAS NMR, of the most representative carbon atoms: 147.0 (quaternary, C3), 130.4 (C5), 104.5 (C4), 138.3 (C1'), 134.4 (C4'') and 124.1 and 124.8 (two different C2'). In Figure 1 the full ^{13}C CPMAS spectrum of 3-[(4-diphenylphosphinoyl)phenyl]-1H-pyrazole (**3a**) is shown, and it can be observed that carbons C3', C4', C1'', C2'' and C3'' lie in the range of

126.8-132.5 ppm and it has not been possible to determine the chemical shift values neither with the help of the NQS (non quaternary carbon suppression) nor the SCP CPMAS experiments (only the CH carbon atoms are observed), due to the dipolar couplings with ^{31}P .

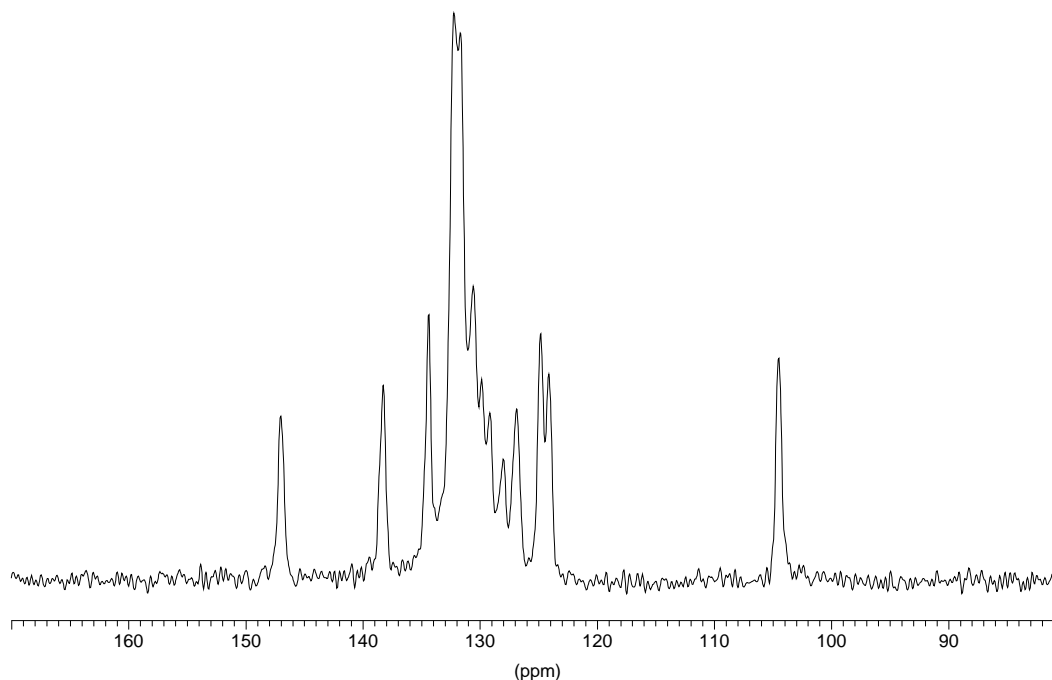


Figure 1. ^{13}C CPMAS spectrum of 3-[(4-diphenylphosphinoyl)phenyl]-1*H*-pyrazole (**3a**).

X-Ray crystal and molecular structure

The values of the bond lengths and positions of the H atoms found by X-ray diffraction study indicate that in solid state the compound **3** exist as **3a** (Fig. 2). In the crystal structure the molecules **3a** form an infinite chain by N(2)-H(2N)···O(1) H-bonds which are joint by weak C(20)-H(20)···N(1) interactions (Fig. 3, crystallographic numbering).

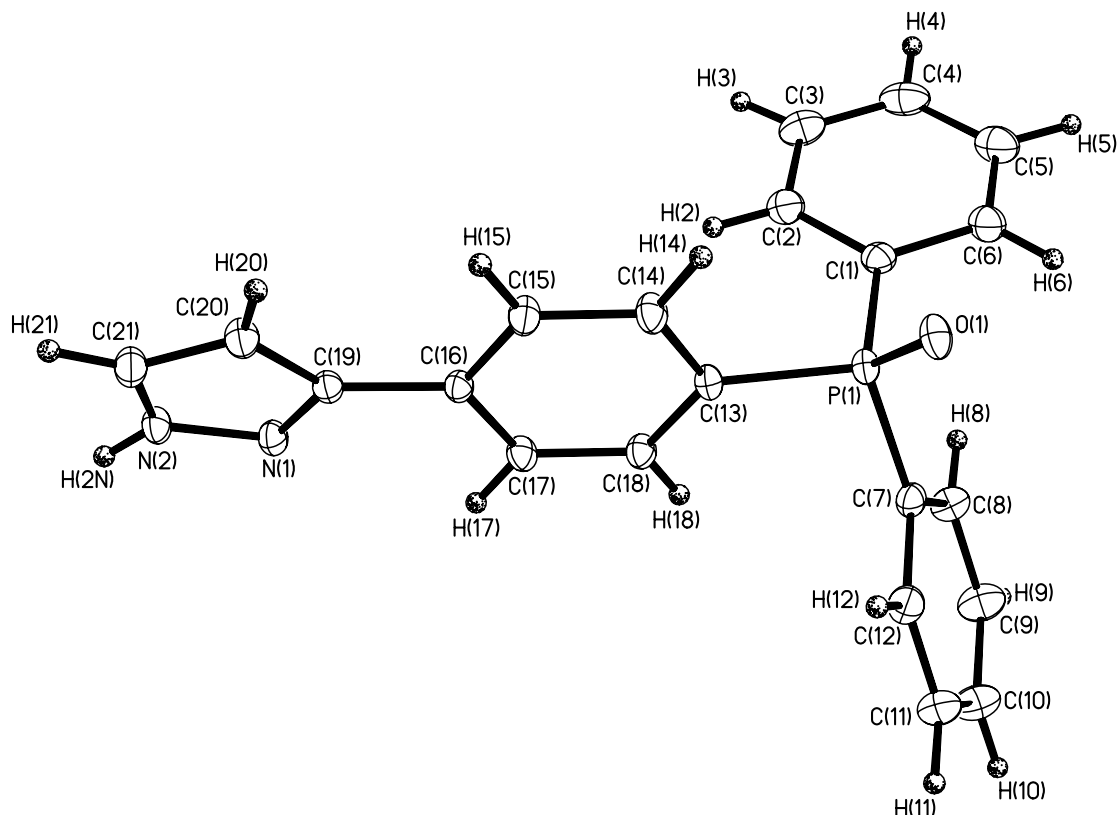


Figure 2. ORTEP plot of the molecular structure of 3-[(4-diphenylphosphinoyl)phenyl]-1*H*-pyrazole (**3a**). Selected bond distances (Å) and angles (°): P(1)-O(1) 1.4918(15), P(1)-C(1) 1.799(2), P(1)-C(7) 1.975(2), P(1)-C(13) 1.794(2), C(19)-N(1) 1.340(3), N(1)-N(2) 1.347(2), N(2)-C(21) 1.337(3), C(19)-C(20) 1.404(3), C(20)-C(21) 1.362(3), N(2)-H(2N) 0.91(3); O(1)-P(1)-C(1) 112.51(10), O(1)-P(1)-C(7) 112.59(9), O(1)-P(1)-C(13) 111.39(9), C(1)-P(1)-C(7) 107.59(10), C(1)-P(1)-C(13) 106.18(10), C(7)-P(1)-C(13) 106.16(10), C(16)-C(19)-N(1) 120.6(2), C(16)-C(19)-C(20) 128.3(2), C(19)-N(1)-N(2) 104.1(2), N(1)-N(2)-C(21) 112.8(2), N(2)-C(21)-C(20) 107.3(2), C(19)-C(20)-C(21) 104.8(2).

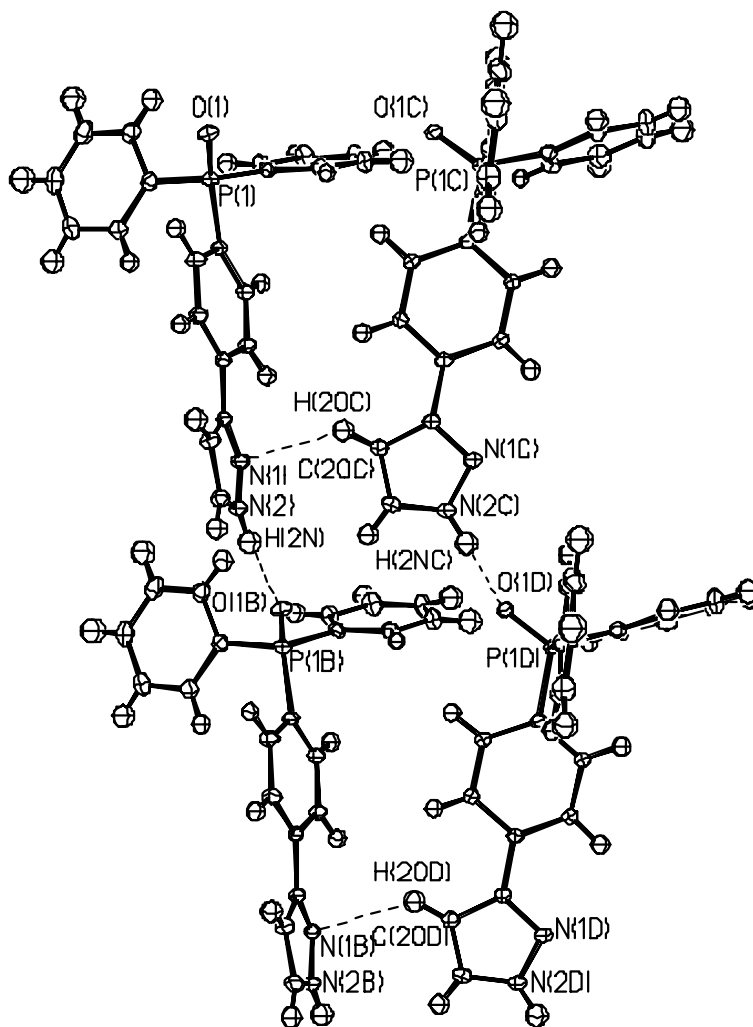


Figure 3. View of a fragment of the crystal structure of **3a**. Parameters of the H-bond: O(1B)···N(2) 2.745(2) Å, O(1B)···H(2N) 1.84(3) Å, N(2)-H(2N) 0.91(3) Å; N(2)-H(2N)···O(1B) 172(3)°. The N(1)···C(20C) distance is 3.313(3) Å.

Theoretical calculations

Both tautomers of 3(5)-[(4-diphenylphosphinoyl)phenyl]pyrazole (**3**) have been fully optimized and characterized as minima (no imaginary frequencies) using different theoretical approaches (Table 1).

Table 1. Theoretical calculations on both tautomers of compound **3** (energies in hartree if not otherwise indicated)

Method	Tautomer 3a	Tautomer 3b	Difference (kJ mol ⁻¹)
AM1	74.31 kcal mol ⁻¹ $\mu = 5.80$ D	73.54 kcal mol ⁻¹ $\mu = 4.74$ D	3.22
HF/6-31G*	-1329.63187 $\mu = 5.75$ D	-1329.63077 $\mu = 4.77$ D	2.89
HF/6-31G**	-1329.66519 $\mu = 5.72$ D	-1329.66397 $\mu = 4.76$ D	3.20
B3LYP/6-31G**	-1336.59095 $\mu = 5.38$ D	-1336.58958 $\mu = 4.07$ D	3.60
ZPE correction	207.62 kcal mol ⁻¹	207.67 kcal mol ⁻¹	0.23
B3LYP/6-31G** + ZPE			3.83

All methods yield very similar results, including AM1, which gives confidence of the results obtained. At the highest level, the difference is 3.83 kJ mol⁻¹ in favor of the 1*H*-3-substituted tautomer **3a**. This difference in energy corresponds to $K = 4.64$, that is to 82% of **3a** and 18% of **3b**. Since in solution we have determined an 86/14 ratio, the agreement is excellent considering that the highest dipole moment of **3a** would increase its stability in polar solvents.

Conclusions

Concerning tautomerism, 3(5)-[(4-diphenylphosphinoyl)phenyl]pyrazole exists in the solid state as the 3-substituted tautomer **3a**, the same that is predominant in DMSO solution (86%). This result is to be compared with 3(5)-phenylpyrazole (**2**) (compound **3** can be considered a 4'-diphenylphosphinoyl derivative of **2**). 3(5)-Phenylpyrazole exists in HMPA-d₁₈:acetone-d₆ as a 72/28 mixture of **2a** and **2b**,²⁴ while in pure HMPA-d₁₈ the proportions are 65/35.⁵ We have measured the equilibrium constant of **2** in DMSO-d₆ and found a 70/30 ratio of tautomers **a/b**. Therefore, the *para* substitution has slightly increased the percentage of the 3-substituted tautomer, probably due to its electron withdrawing effect.

The model for the secondary structure in crystals of NH-pyrazoles was established for NH-pyrazoles lacking better hydrogen bond acceptors (HBA) than N-2.¹ In the case of **3** there is a strong HB between N1-H1 and O=P leading to catemers. It is well known that the phosphine oxides are excellent HBA.^{25,26}

Experimental Section

General Procedures. The starting material, 4-(diphenylphosphino)acetophenone, was prepared by the literature method.²⁷ It was converted to 3(5)-(4-diphenylphosphine)pyrazole by the method used for converting acetophenone to 3(5)-phenylpyrazole.²⁸ The crude product was characterized only by NMR [7.72 doublet (2H, 3-phenylene), 7.57 (1 H, d, H-5), 7.34 (12 H, phenyl groups plus phenylene doublet), 6.59 (1H, d, H-4) ppm], and was oxidized to 3(5)-(4-diphenylphosphinoylphenyl)pyrazole **3** by dissolving it in acetone, and treating this solution dropwise with an excess of 10% solution of hydrogen peroxide. Evaporation of the solution gave the product in over-all yield of 43 %, which was purified by recrystallization from anisole. M.p. 252-254 °C, main IR peaks: 3148, 3035, 2956, 2913, 1604, 1436, 1171, 1116, 841, 741, 695, 585 (doublet) cm⁻¹. Calcd. for C₂₁H₁₇N₂OP: C 73.3, H 4.94, N 8.14. Found: C 74.5, H 5.12, N 7.98 %. Crystals of 3(5)-[(4-diphenylphosphinoyl)phenyl]pyrazole (**3**), m.p. 251.8 °C (DMF) by DSC with a Seiko 220C calorimeter with a heating rate of 10 °C min⁻¹.

NMR measurements

NMR spectra were recorded on a Bruker DRX 400 (9.4 Tesla, 400.13 MHz for ¹H, 100.62 MHz for ¹³C, for ³¹P and 40.56 MHz for ¹⁵N) spectrometer. Chemical shifts (δ in ppm) are given from internal solvent CDCl₃ 7.26 for ¹H and 77.0 for ¹³C, and for ³¹P and ¹⁵N NMR, 85% H₃PO₄ and nitromethane were used as external standards. 2D gs-COSY (¹H-¹H) and 2D inverse proton detected heteronuclear shift correlation spectra, gs-HMQC (¹H-¹³C), gs-HMBC (¹H-¹³C) and gs-HMBC (¹H-¹⁵N), were obtained using the standard pulse sequences.¹⁹

Solid state ¹³C (100.73 MHz), ³¹P (162.16 MHz) and ¹⁵N (40.60 MHz) CPMAS NMR spectra have been obtained on a Bruker WB 400 spectrometer at 300 K using a 4 mm DVT probehead. Samples were carefully packed in a 4-mm diameter cylindrical zirconia rotors with Kel-F end-caps and the standard CPMAS with the TPPM decoupling pulse sequence was used. ¹³C spectra were originally referenced to a glycine sample and then the chemical shifts were recalculated to the Me₄Si (for the carbonyl atom δ (glycine) = 176.1 ppm), ³¹P spectra to (NH₄)₂HPO₄ and converted to solution 85% H₃PO₄ using the relationship: $\delta^{31}\text{P}(85\% \text{H}_3\text{PO}_4) = \delta^{31}\text{P}[(\text{NH}_4)_2\text{HPO}_4] + 1.6 \text{ ppm}$ and ¹⁵N spectra to ¹⁵NH₄Cl and then converted to nitromethane scale using the relationship: $\delta^{15}\text{N}(\text{nitromethane}) = \delta^{15}\text{N}(\text{ammonium chloride}) - 338.1 \text{ ppm}$.

The typical acquisition parameters for ¹³C CPMAS were: spectral width, 40 kHz, acquisition time, 30 ms; contact time, 2 ms; and spin rate, 12 kHz. To assign *in the solid state* the carbon signals we run the NQS (Non-Quaternary Suppression) experiments by conventional cross-polarization with the difference that before the acquisition the decoupler is switched off for a very short time of 25 μs ²⁹ and by examination of short contact time, 200 μs (SCP CPMAS)³⁰ C-H subspectra (in this experiment only protonated carbon atoms are observed).

For ³¹P CPMAS the acquisition conditions were: spectral width, 100 kHz, acquisition time, 40 ms; contact time, 2 ms; and spin rate, 10 kHz. For natural abundance ¹⁵N were: spectral width, 40 kHz, acquisition time, 35 ms; spin rate 6 kHz, contact time for spin lock, 2 ms; and relaxation delay, 5 s.

X-Ray crystallography

A summary of the crystal data, data collection and refinement procedures is given in Table 2. Data were collected with a Bruker SMART APEX CCD diffractometer using graphite-monochromated MoK α -radiation ($\lambda = 0.7173 \text{ \AA}$). Crystals were obtained from dimethylformamide and mounted with Paratone N mineral oil on a diffractometer in the cold stream. Corrections for absorption were applied using SADABS. The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters, and the positions of the H atoms were found on the F-map and refined.

Table 2. Crystal data and structure refinement for **3a**

Empirical formula	C ₂₁ H ₁₇ N ₂ OP	
Formula weight	344.34	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	$a = 11.3276(8) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 18.3713(14) \text{ \AA}$	$\beta = 100.4670(10)^\circ$
	$c = 8.7248(6) \text{ \AA}$	$\gamma = 90^\circ$
Volume	1785.4(2) Å ³	
Z	4	
Density (calculated)	1.281 Mg m ⁻³	
Absorption coefficient	0.164 mm ⁻¹	
F(000)	720	
Crystal size	0.20 x 0.15 x 0.10 mm	
θ range for data collection	2.14 to 28.30°	
Index ranges	-14 ≤ h ≤ 14, -24 ≤ k ≤ 18, -11 ≤ l ≤ 9	
Reflections collected	11269 [R _{int} =0.319]	
Absorption correction	SADABS (T _{min} =0.9679, T _{max} =0.9837)	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4193 / 0 / 294	
Goodness-of-fit on F ²	0.766	
Final R indices [I > 2σ(I)]	R ₁ ^a = 0.0540, wR ₂ ^b = 0.1438	
R indices (all data)	R ₁ ^a = 0.0732, wR ₂ ^b = 0.1631	
Largest diff. peak and hole	0.481 and -0.239 e.Å ⁻³	

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}; w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP], P = [2F_c^2 + \max(F_o, 0)] / 3.$$

All software is contained in the SHELXTL (5.1) library (G. M. Sheldrick, Bruker AXS, Madison, WI, USA). Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as deposition No. CCDC-206683. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ UK (fax: +44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

Theoretical calculations

The optimization of the structures of the two tautomers was carried out at the different levels: semiempirical AM1, ab initio Hartree Fock (HF/6-31G* and HF/6-31G**) and density functional (B3LYP/6-31G**), as shown in Table 1, by using the Windows Titan 1.0.5 package from Wavefunction Inc.

Acknowledgements

Financial support was provided by the Spanish DGI/MCYT (Project no. BQU2000-0252).

References

1. Foces-Foces, C.; Alkorta, I.; Elguero, J. *Acta Crystallogr. Sect. B* **2000**, *56*, 1018.
2. Claramunt, R. M.; Santa María, M. D.; Forfar, I.; Aguilar Parrilla, F.; Minguet-Bonvehí, M.; Klein, O.; Limbach, H.-H.; Foces-Foces, C.; Llamas Saiz, A. L.; Elguero, J. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1867.
3. Claramunt, R. M.; López, C.; García, M. A.; Pierrot, M.; Giorgi, M.; Elguero, J. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2049.
4. Trofimenko, S.; Rheingold, A. L.; Liable-Sands, L. M.; Claramunt, R. M.; López, C.; Santa María, M. D.; Elguero, J. *New. J. Chem.* **2001**, *25*, 819.
5. García, M. A.; López, C.; Claramunt, R. M.; Kenz, A.; Pierrot, M.; Elguero, J. *Helv. Chim. Acta* **2002**, *85*, 2763.
6. Haghiri, A.; Lerner, H.-W.; Wagner, M.; Bats, J. W. *Acta Crystallogr. Sect. E* **2002**, *58*, 1378.
7. Claramunt, R. M.; Santa María M. D.; Infantes, L.; Cano, F. H.; Elguero, J. *J. Chem. Soc., Perkin Trans. 2* **2002**, 564.
8. Sánchez-Migallón, A.; de la Hoz, A.; López, C.; Claramunt, R. M.; Infantes, L.; Motherwell, S.; Shankland, K.; Nowell, H.; Alkorta, I.; Elguero, J. *Helv. Chim. Acta* **2003**, *86*, 1026.
9. García, M. A.; López, C.; Peters, O.; Claramunt, R. M.; Klein, O.; Schagen, D.; Limbach, H.-H.; Foces-Foces, C.; Elguero, J. *Magn. Reson. Chem.* **2000**, *38*, 604.
10. Claramunt, R. M.; López, C.; García, M. A.; Otero, M. D.; Torres, M. R.; Pinilla, E.; Alarcón, S. H.; Alkorta, I.; Elguero, J. *New. J. Chem.* **2001**, *25*, 1061.
11. Akacha, A. B.; Ayed, N.; Baccar, B.; Charrier, C. *Phosphorus Sulfur* **1988**, *40*, 63.

12. Aboujaoude, E. E.; Collignon, N.; Savignac, P. *Phosphorus Sulfur* **1987**, *31*, 231.
13. Polozov, A. M.; Khotinen, A. V. *Dokl. Akad. Nauk.* **1993**, 328, 464.
14. Kingsley, S.; Chandrasekhar, V.; Incarvito, C. D.; Lam, M. K.; Rheingold, A. L. *Inorg. Chem.* **2001**, *40*, 5890.
15. Tolmachev, A. A.; Sviridon, A. I.; Kostyuk, A. N.; Kozlov, E. S. *Zh. Obshch. Khim.* **1992**, *62*, 2395.
16. Tolmachev, A. A.; Sviridon, A. I.; Kostyuk, A. N.; Pinchuk, A. M. *Heteroat. Chem.* **1995**, *6*, 449.
17. Tolmachev, A. A.; Konovets, A. I.; Kostyuk, A. N.; Pinchuk, A. M. *Top. Heterocycl. Syst.: Synth. React. Prop.* **1996**, *1*, 239 [*Chem. Abstr.* **1997**, *127*, 318989].
18. Antiñolo, A.; Carrillo-Hermosilla, F.; Díez-Barra, E.; Fernández-Baeza, J.; Fernández-López, M.; Lara-Sánchez, A.; Moreno, A.; Otero, A.; Rodríguez, A. M.; Tejada, J. *J. Chem. Soc., Dalton Trans.* **1998**, 3737.
19. Braun, S.; Kalinowski, H.-O.; Berger, S. *150 and more Basic NMR Experiments*, Wiley-VCH: Weinheim, 1998.
20. Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* 2nd Edn. Pergamon: Oxford, 1969.
21. Berger, S.; Braun, S.; Kalinowski, H.-O. *NMR Spectroscopy of the Non-metallic Elements*, Wiley: New York, 1997.
22. Begtrup, M.; Boyer, G.; Cabildo, P.; Cativiela, C.; Claramunt, R. M.; Elguero, J.; García, J. I.; Toiron, C.; Vedsø, P. *Magn. Reson. Chem.* **1993**, *31*, 107.
23. Fruchier, A.; Alcalde, E.; Elguero, J. *Org. Magn. Reson.* **1977**, *9*, 235.
24. Aguilar-Parrilla, F.; Cativiela, C.; Diaz de Villegas, M. D.; Elguero, J.; Foces-Foces, C.; García, J. I.; Cano, F. H.; Limbach, H.-H.; Smith, J. A.; Toiron, C. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1737.
25. Llamas-Saiz, A. L.; Foces-Foces, C.; Elguero, J.; Molina, P.; Vidal, A. *Chem. Commun.* **1991**, 1694 and references therein.
26. Alkorta, I.; Elguero, J. *J. Phys. Chem. A* **1999**, *103*, 272.
27. Schiemenz, G. P.; Kaack, H. *Liebigs Ann. Chem.* **1973**, 1494.
28. Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507.
29. Opella, S. J.; Frey, D. M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5855.
30. Wu, X.; Burns, S. T.; Zilm, K. W. *J. Magn. Reson. A* **1994**, *111*, 29.