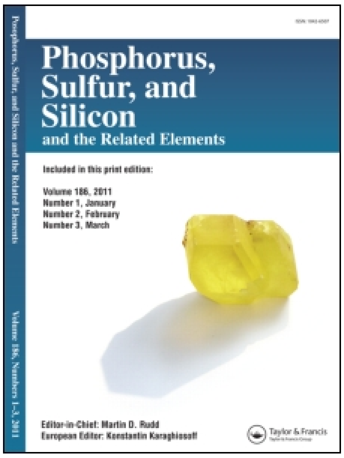


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CHARACTERIZATION OF AN UNUSUAL IODO-γ^5P-AZONIUM IODIDE INVOLVING A COVALENT γ^5P—I BOND BY SOLID STATE N.M.R. SPECTROSCOPY

David C. Apperley[a]; Robin K. Harri[a]; Thomas Kaukorat[b]; Reinhard Schmutzler[b]
[a] Department of Chemistry, The University Science Laboratories, South Road, Durham, ENGLAND [b] Institut für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig, Federal Republic of Germany

To cite this Article Apperley, David C. , Harri, Robin K. , Kaukorat, Thomas and Schmutzler, Reinhard(1990) 'CHARACTERIZATION OF AN UNUSUAL IODO-γ^5P-AZONIUM IODIDE INVOLVING A COVALENT γ^5P—I BOND BY SOLID STATE N.M.R. SPECTROSCOPY', Phosphorus, Sulfur, and Silicon and the Related Elements, 54: 1, 227 — 229

To link to this Article: DOI: 10.1080/10426509008042144

URL: http://dx.doi.org/10.1080/10426509008042144

Phosphorus, Sulfur, and Silicon, 1990, Vol. 54, pp. 227–229
Reprints available directly from the publisher
Photocopying permitted by license only

Communication

CHARACTERIZATION OF AN UNUSUAL IODO-λ^5P-AZONIUM IODIDE INVOLVING A COVALENT λ^5P—I BOND BY SOLID STATE N.M.R. SPECTROSCOPY

DAVID C. APPERLEY and ROBIN K. HARRIS
Department of Chemistry, The University Science Laboratories, South Road,
Durham DH1 3LE, ENGLAND

and

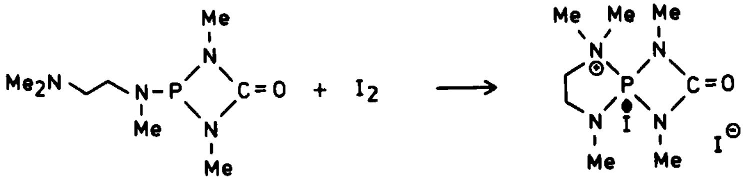
THOMAS KAUKORAT and REINHARD SCHMUTZLER*
Institut für Anorganische und Analytische Chemie der Technischen Universität,
Hagenring 30, D-3300 Braunschweig, Federal Republic of Germany

(Received May 1, 1990)

An unusual iodophosphorane, **2** was unambiguously identified as involving a λ^5P—I bond, by solid state ^{13}C-, ^{15}N- and ^{31}P-n.m.r. spectroscopy.

Key words: 4-Iodo-2-oxo-1.3.5.5.8-pentamethyl-1.3.8-triaza-5-azonia-4λ^5-phosphaspiro[3.4]octanyl-iodide, solid state n.m.r. spectroscopy.

Phosphoranes, involving iodine covalently bonded to five-coordinate (λ^5) phosphorus have only recently been reported.[1] Previous claims, regarding λ^5P—I bonded systems[2] proved to be incorrect.[3] Based on electrical conductivity measurements the identity of these species as λ^4P (phosphonium) iodides was established.[4,5] We have recently reported an unusual compound **2** which was obtained in the reaction of the phosphadiazetidinone, **1** with an equimolar amount of iodine in petroleum ether (Equation 1).



(1)

1 2

Compound **2** was precipitated as a brownish solid in 95% yield. It was proposed to be the novel iodophosphorane iodide, **2** solely on the basis of its mass and elemental analysis. N.m.r. spectra of **2** could not be recorded either because of its lack of solubility or due to its instability in common organic solvents, e.g. CH_2Cl_2, $CHCl_3$, CH_3CN; **2** was found to decompose in solution with formation of iodine.[6]

In this note we wish to report new information on the structure of **2**. According to solid state n.m.r. spectra (^{13}C, ^{15}N and ^{31}P) the identity of **2** has unambiguously been established. The δ(P) value of **2** (−109.2 ppm), at rather low frequency, falls into the region typical of the authentic iodophosphorane reported in Reference 1. The δ(P) values in halospirophosphoranes are well known to increase with increasing size of the halogen. A broadening of the ^{31}P n.m.r. resonance of **2** is suggested to be caused by the quadrupole moment of the iodine atom bonded to λ^5P.

In the ^{13}C n.m.r. spectrum of **2** a broad resonance area between 20 to 60 ppm, and a single line at δ 156.5 ppm are seen. In the 20 to 60 ppm region five individual signals are evident. From a comparison of these n.m.r. data with those of some cyclic halophosphoranes related to **2**[8] the solid state ^{13}C n.m.r. signals for **2** are assigned as follows,

δ 32.1 ppm $[(NCH_3)_2C(:O)]$
δ 43.5 ppm $[N(CH_3)P]$
δ 46.5 ppm $[(CH_3)_2NCH_2]$
δ 51.0 ppm $[CH_2N(CH_3)P]$
δ 54.1 ppm $[CH_2N(CH_3)_2]$
δ 156.5 ppm $[C(:O)]$

Four signals are observed in the solid state ^{15}N n.m.r. spectrum of **2** (Figure 1). It is suggested that the *N,N'*-dimethylurea group is attached in axial-equatorial positions, based on the observation of two different ^{15}N n.m.r. signals, at δ −252 and −260 ppm; the axial-equatorial attachment of the *N,N'*-dimethylurea group renders the two nitrogen atoms nonequivalent. However, such nonequivalence might arise simply as a result of crystallographic effects. Two further ^{15}N resonances, at −303 and −321 ppm, are assigned to the two nitrogen atoms in the five-membered ring originating from the intramolecular co-ordination between the nitrogen atom of the NMe_2-group and phosphorus in **2**. Coupling constants between phosphorus and nitrogen cannot be observed because all resonances are broader than for typical solution spectra.

The above solid state n.m.r. data, together with the elemental analysis, unambiguously serve to establish the structure and identity of **2**. Besides 4-iodo-

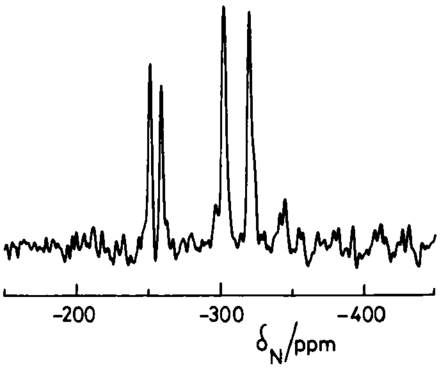


FIGURE 1. Nitrogen-15 CPMAS spectrum of 2 under the conditions described in the text.

tetramethyl-1.3.5.7-tetraaza-4λ^5-phosphaspiro[3.3]heptane-2.6-dione[1] **2** constitutes, to our knowledge, only the second example of a well established iodophosphorane, involving a covalent λ^5P—I bond.

EXPERIMENTAL

The solid state NMR spectra were obtained using a Varian VXR 300 spectrometer fitted with Doty MAS probes. Spectra were obtained at 30.41, 75.43 and 121.42 MHz for ^{15}N, ^{13}C and ^{31}P, respectively, using ambient probe temperature. The techniques of high-power proton decoupling, cross polarization (CP) and magic-angle spinning were employed, though CP was omitted for the ^{31}P spectrum. A 7 mm o.d. rotor was used for the ^{13}C and ^{15}N spectra, whereas the ^{31}P spectrum was obtained using a 5 mm o.d. rotor.

Spectrometer operating conditions were as follows:

	^{15}N	^{13}C	^{31}P
Contact time/ms	5.0	2.5	—
Relaxation delay/s	1.0	1.0	60.0
Number of transients	56400	2000	100
Spinning speed/Hz	4470	4480	8910

A 90° pulse (5.5 μs) was used for ^{31}P, and flip-back was employed for ^{15}N and ^{13}C.

The spectra were referenced to the signals for tetramethylsilane (^{13}C), 85% phosphoric acid (^{31}P) and the nitrate signal of ammonium nitrate (^{15}N), in each case using the high-frequency-positive convention.

ACKNOWLEDGEMENT

We are indebted to Fonds der Chemischen Industrie, Frankfurt am Main, for support.

REFERENCES

1. J. Breker, P. G. Jones, and R. Schmutzler, *Angew. Chem.*, **100**, 1620 (1988); *Angew. Chem. Int. Edit. Engl.*, **27**, 1562 (1988).
2. V. D. Romanenko, V. O. Tovstenko and L. N. Markovskii, *Zhur. Obshch. Khim.*, **49**, 1907 (1979).
3. A. Skowronska, M. Pakulski, J. Michalski, D. Cooper, S. Trippett, *Tetrahedron Lett.*, 1725 (1980).
4. K. Issleib and W. Seidel, *Z. Anorg. Allg. Chem.*, **288**, 201 (1959).
5. A. D. Beveridge, G. S. Harris, and F. Inglis, *J. Chem. Soc. (A)*, 1520 (1966).
6. T. Kaukorat and R. Schmutzler, *Z. Naturf.*, **44b**, 481 (1989).
7. J. Breker, Dr. rer. nat. *Thesis, Braunschweig* (1988).
8. T. Kaukorat and R. Schmutzler, unpublished.