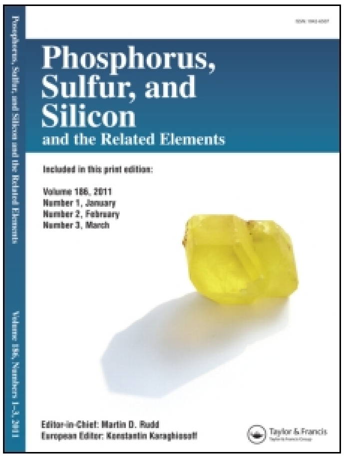
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

STRUCTURAL STUDY OF CARBANIONIC SPECIES FROM BIS(DIETHOXYPHOSPHONYL)-METHANE BY IR, RAMAN AND ^{1}H, ^{31}P, ^{13}C NMR SPECTROSCOPIES

T. Bottin-strzalko[a]; J. Corset[b]; F. Froment[b]; M. J. Pouet[c]; J. Seyden-penne[a]; M. P. Simonnin[c]
[a] Laboratoire des Réactions Sélectives sur Supports, UA 478 du CNRS, Université Paris-Sud, Orsay Cedex, France [b] Laboratoire de Spectrochimie Infrarouge et Raman, CNRS, Thiais, France [c] U.A. 403 du CNRS, Ecole Nationale Supérieure de Chimie de Paris, Paris Cedex, France

To cite this Article Bottin-strzalko, T. , Corset, J. , Froment, F. , Pouet, M. J. , Seyden-penne, J. and Simonnin, M. P.(1985) 'STRUCTURAL STUDY OF CARBANIONIC SPECIES FROM BIS(DIETHOXYPHOSPHONYL)-METHANE BY IR, RAMAN AND ^{1}H, ^{31}P, ^{13}C NMR SPECTROSCOPIES', Phosphorus, Sulfur, and Silicon and the Related Elements, 22: 2, 217 — 223

To link to this Article: DOI: 10.1080/03086648508073450
URL: http://dx.doi.org/10.1080/03086648508073450

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus and Sulfur, 1985, Vol. 22, pp. 217–223
0308-664X/85/2202–0217/$15.00/0

© 1985 Gordon and Breach, Science Publishers, Inc.
and OPA Ltd. Printed in the United Kingdom

STRUCTURAL STUDY OF CARBANIONIC SPECIES FROM BIS(DIETHOXYPHOSPHONYL)-METHANE BY IR, RAMAN AND ^{1}H, ^{31}P, ^{13}C NMR SPECTROSCOPIES

T. BOTTIN-STRZALKO,* J. CORSET,** F. FROMENT,**
M. J. POUET,*** J. SEYDEN-PENNE* and M. P. SIMONNIN***

**Laboratoire des Réactions Sélectives sur Supports, UA 478 du CNRS,*
Université Paris-Sud, Bât. 410, 91405 Orsay Cedex, France
***Laboratoire de Spectrochimie Infrarouge et Raman, CNRS,*
2 rue Henri Dunant, 94320 Thiais, France
****U.A. 403 du CNRS, Ecole Nationale Supérieure de Chimie de Paris,*
11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

(Received July 16, 1984; in final form October 2, 1984)

Downloaded At: 08:43 30 January 2011

An IR and Raman study of the lithium associated carbanionic species **1** formed from bis(diethoxyphosphonyl)-methane in the solid state and in THF solution, as well as the IR and ^{1}H, ^{31}P, ^{13}C NMR study of the potassium associated one in pyridine and dimethylsulfoxide are reported. A chelated symmetrical structure exists in the solid state and in associating medium. The central carbon is planar or nearly so from the NMR data. However, the negative value of $^2J_{PH}$ in the anionic species raises the problem of estimating the various factors involved in the two bond coupling constants.

INTRODUCTION

Recent studies have shown that bisphosphonates can be used as heavy metal extractants.[1] Although their carbanions can give unusual complexes[2] with $[Pt_2Cl_4(PR_3)_2]$ there are only incomplete spectroscopic studies of these species.[3–6] Within a general study of the structure of carbanionic species α to a phosphoryl group,[7–9] we extend our previous approach to the carbanionic species **1** formed from bis(diethoxyphosphonyl)-methane **2**. From the symmetrical structure of these species, one can expect strong chelating properties.

$[(EtO)_2P(O)CHP(O)(OEt)_2]^-M^+$ — **1a** M = Li; **1b** M = K

$(EtO)_2P(O)CH_2P(O)(OEt)_2$ — **2**

The IR and Raman spectra of **2** and the IR spectra of **1a** were studied in the solid state and in tetrahydrofurane (THF) solution and of **1b** in pyridine solution. The ^{1}H, ^{31}P and ^{13}C NMR study of **1b** was performed in pyridine and dimethylsulfoxide (DMSO).

RESULTS

IR and Raman spectra

The spectra of **1a**, **1b** and of **2** are in Figure 1. The various assignments rely on the following arguments:

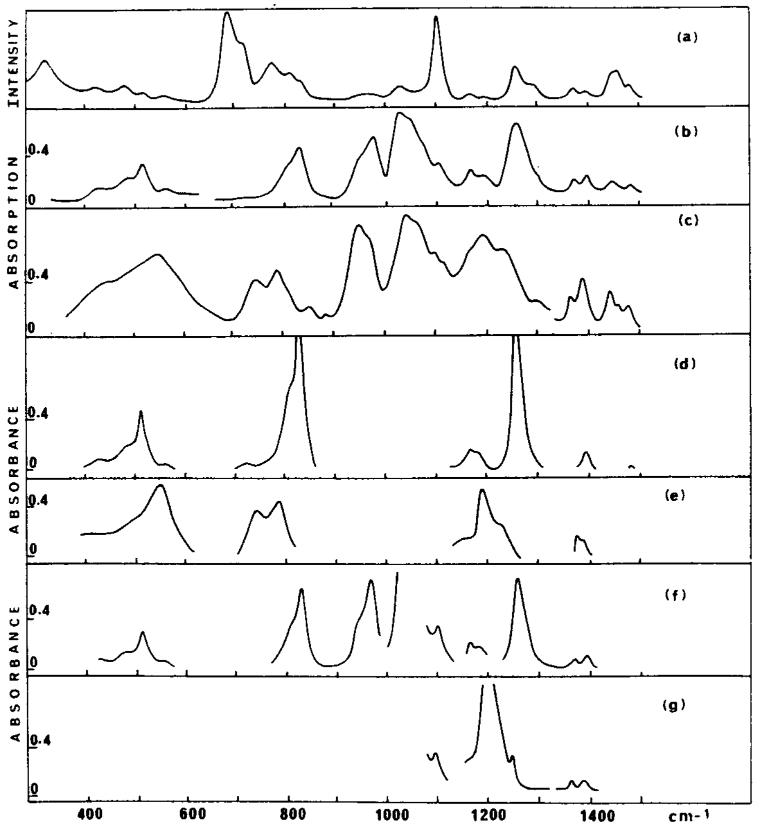


FIGURE 1 Raman (a) and infrared (b, c, d, e, f, g) spectra of bis(diethoxyphosphonyl)-methane **2** and of its carbanionic species **1**, Li^+ **1**, K^+. (a, b): pure liquide of **2**; (c): carbanionic species **1**, Li^+ in solid state; (d): solution in THF of **2** (0.4 M/l); (e): solution in THF of carbanionic species **1**, Li^+ (0.4 M/l); (f): solution in pyridine of **2** (0.4 M/l); (g): solution in pyridine of carbanionic species **1**, K^+ (0.5 M/l). The cell thickness for solutions is 0.0043 cm from 400 to 1100 cm^{-1} and 0.0030 cm from 1100 to 1500 cm^{-1}.

Neat bisphosphonate **2**. Due to the numerous rotational conformations of the molecule, its structure is probably poorly symmetrical; it can be estimated by comparison with the calculated favoured conformations of methyl phosphonates **3**.[10] In the case of **2**, the two phosphoryl groups can lie in different planes, the ethoxy moieties being in different conformations (trans or gauche). Thus, it is not possible to assign to this molecule a precise conformation at room temperature. Some attributions can be made by comparison with those deduced from the spectra of **3** and its various isotopically labelled analogs,[11] taking into account the expected

Downloaded At: 08:43 30 January 2011

TABLE I

Raman and infrared vibrations modes frequencies and assignments of bis(diethoxyphosphonyl)-methane **2** and its carbanionic species: **1a** and **1b**

	Pure liquid		Solid state	THF solutions		Pyridine solutions	
Assignments[a]	**2** (R)	**2** (IR)	**1a** (IR)	**2** (IR)	**1a** (IR)	**2** (IR)	**1b** (IR)
δ (CH_2) Et	1478 w	1479 w		1480 w			
δ_a' (CH_3)	1457 m	1457 sh					
δ_a (CH_3)	1446 sh	1444 m					
w (CH_2) Et	1394 m	1393 m		1392 m	1385 sh	1392 m	1387 m
δ_s (CH_3)	1369 m	1368 m			1376 m	1368 m	1362 m
ν (P → O)	1286 w	1295 sh	1291 sh				
	1253 m	1257 s		1261 s		1259 s	
ν (P $\overline{\cdots}$ O)			1226 s		1228 m		1247 m
			1191 s		1193 s		1206 s
r (CH_3)		1189 w		1179 m		1183 m	
	1168 w	1165 m		1168 m		1165 m	1166 m
			1112 w				
r (CH_3)	1099 s	1099 m	1095 w			1099 m	1099 m
		1069 sh					
ν_a (PO–C)		1048 s	sh				
ν_s (PO–C)	1024 w	1027 s	1040 s				
ν (C–C) Et		973 s	968 sh			972 s	
	951 w	942 sh	949 s			941 sh	
			882 w				
ν_a (PO_2)	828 m	829 s	850 w	828 s			
r (CH_2)	811 m	807 sh		811 sh			
ν_s (PO_2)	776 m						
ν_a (PCP)	719 sh		790 m		789 m		
ν_s (PCP)	694 s		747 m		745 m		
	556 w	559 w		562 w			
δ (OPO)	512 w	517 m	551 m	515 m	554 m		
and	481 w	487 sh		486 *m*			
δ (OPC)	424 w	428 w	423 sh	423 w			
	326 m	335 w					
	252 m	260 w					

[a] ν (elongations), δ (deformations), w (wagging) and r (rocking) values are given in cm^{-1}; intensities are indicated by sh: shoulder, w: weak, m: medium, s: strong.

Downloaded At: 08:43 30 January 2011

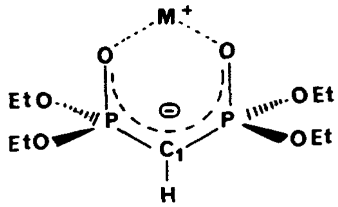
vibrations of an EtO group.[12] These assignments in terms of group frequencies are given in Table I.

A few points are worthy of comment: The ν (P → O) modes were assigned to the band and to the shoulder at 1257 and 1295 cm^{-1} in IR and 1253 and 1286 cm^{-1} in Raman; the slight difference between IR and Raman frequencies suggest some coupling between the two P → O groups. The two shoulders at 1295 and 1286 could be due to a Fermi resonance with a combination (517 and 776), as they disappear in the spectra recorded in THF and pyridine solution. The Raman intense band at 694 and shoulder at 719 cm^{-1} were tentatively assigned to the modes ν_s (PCP) and ν_a (PCP) respectively, as a single intense Raman band is observed in this region for other phosphonates $(EtO)_2P(O)CH_2A$ (A = $COCH_3$, $COOCH_3$, CH_2CN, CH_2Ph).[13] It is to be noted that Richard[14] who studied the IR spectrum of bis(di-*n*-hexylphosphinyl)-methane, has assigned the band at 718 cm^{-1} to the P—C_6H_{11} vibration and the broad band around 800 cm^{-1} to the P—C—P bridge.

To our opinion the Raman frequency at 811 cm^{-1} and the IR shoulder at 807 cm^{-1} are rather due to a CH$_2$ rocking mode.

The region below 550 cm^{-1} is difficult to assign in the absence of calculated normal mode vibrations.[13]

Lithium and potassium associated carbanions **1**. The IR spectrum of **1a** in the solid state exhibited two strong bands at 1191 and 1226 cm^{-1} which were assigned to the ν (P $\overset{\cdot\cdot}{-}$ O) mode of a species in which the Li$^+$ is directly interacting with the two phosphoryl oxygen atoms, forming thus a chelate **4** where the anionic charge is delocalized over five atoms (OPCPO).



4

This structural proposal was strengthened by the IR results obtained in THF solution (M$^+$= Li$^+$): ν (P $\overset{\cdot\cdot}{-}$ O) bands were observed at 1193 and 1228 cm^{-1}, the eventual solvation of the Li$^+$ cation affecting poorly the anion-cation interaction. On the other hand, the K$^+$ associated species in pyridine showed these two bands at 1206 and 1247 cm^{-1}: the averaged frequency decrease, when going from the neutral precursor **2** to the anionic species **1**, is thus 67 cm^{-1} when M$^+$= Li$^+$ and 50 cm^{-1} when M$^+$= K$^+$. These figures are very close to those previously observed with the related ester (EtO)$_2$P(O)CH$_2$COOMe **5**.[8] The existence of two ν (P $\overset{\cdot\cdot}{-}$ O) bands in the anionic species could be assigned, as in the neutral molecule **2**, to a dipolar coupling between two modes; however, such a multiplicity has been observed in the spectrum of **5**.[8] This can be due either to a Fermi resonance with a harmonic or combination, or to the existence of different species in solution. The presence of hexamers for the Na$^+$ associated carbanion **1** has been indeed deduced from cryoscopic determinations in benzene solution.[3]

The medium intensity bands at 747 and 790 cm^{-1} in the IR of the solid can be assigned to the vibrations ν_s (P—C—P) and ν_a (P—C—P): the averaged ν (P—C) frequency shows a high frequency shift of 60 cm^{-1}, suggesting a P—C bond shortening in **1** related to the neutral precursor **2**.

NMR spectra

The different data for **1b** and for the neutral precursor **2** are in Table II. Our results in pyridine are in good agreement with the previously published data for **2**[2,3,5] and for **1b** in C$_6$H$_6$ (^{1}H and ^{31}P NMR).[4]

The main features when going from the neutral precursor **2** to the anionic species are (a) a great increase in $^1J_{PC}$ and $^1J_{CH}$; (b) a high field chemical shift of C$_1$; (c) a low field shift of ^{31}P. The solvent change affects significantly δ_{H_1} and only slightly the $^1J_{PC}$ and $^1J_{CH}$ coupling constants.

Downloaded At: 08:43 30 January 2011

Downloaded At: 08:43 30 January 2011

TABLE II

NMR data[a] of bis(diethoxyphosphonyl)-methane **2** and anionic species **1b** (solvent: dimethyl sulfoxide and pyridine)

Compounds (solvent)	$\delta_{^{31}P}$	δ_{H_1}	$\delta_{\bar{H}_{2'}}$	$\delta_{H_{3'}}$	δ_{C_1}	$\delta_{C_{2'}}$	$\delta_{C_{3'}}$	$^2J_{PH_1}$	$^1J_{PC_1}$	$^1J_{C_1H_1}$
2 (DMSO)	19.0	2.63	4.03	1.23	23.7_4	61.6_1	16.0_7	-21.0_3[c]	133.1[b,c]	125.2[b]
2 (Py)	19.0	2.88	4.24	1.26	25.6_7	62.3_8	16.4_4	-20.9_0	134.5[b]	124.5
1b (DMSO)	40.1	0.35	3.76	1.13	9.6_4	58.4_8	16.4_2	-5.8_5[c]	214.5[c]	143.8
1b (Py)	41.0	1.06	4.07	1.27	9.6_2	59.9_9	16.73	-5.8_5	212.9	145.1

[a] $\delta_{^1H}$ and $\delta_{^{13}C}$ in ppm from internal Me_4Si. $\delta_{^{31}P}$ in ppm relative to external H_3PO_4 (85%). Positive δ values are in the direction of increasing frequency. J values in Hertz.

[b] From ^1H $\{^{31}P\}$ experiments, $^1J_{PC_1}$ and $^1J_{C_1H_1}$ bear the same sign i.e. $^1J_{PC_1}$ is positive.

[c] From ^{13}C $\{^1H\}$ off-resonance experiments, $^1J_{PC_1}$ and $^2J_{PH_1}$ are of opposite signs i.e. $^2J_{PH_1}$ is negative.[18]

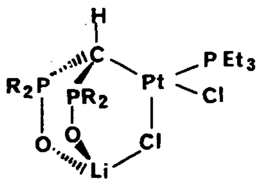
DISCUSSION

From the IR spectra, it appears that the Li^+ and the K^+ associated anionic species **1** adopt a chelate structure **4**, the anion-cation interaction being stronger in the former case than in the latter, as expected. The NMR data for **1b** in pyridine are consistent with such a symmetrical chelate structure as the $P(OEt)_2$ groups are equivalent. A similar equivalence is observed in the spectra in DMSO solution which could correspond either to a single symmetrical chelate or to a rapid interconversion between species of different geometries. Furthermore from the $^1J_{PC_1}$ and $^1J_{C_1H_1}$ values, the central anionic carbon is planar or nearly so,[7-9] as previously proposed for **1** ($M^+ = Na^+$) in CCl_4 solution.[3] INDO-SCPT calculations of $^1J_{PC_1}$ and $^1J_{C_1H_1}$ values, performed with the assumption of a planar carbon, are in fair agreement with the experimental data.[15] The slight discrepancy between the calculated $^1J_{PC_1}$ (201 Hz) and the experimental value (214 Hz) cannot be explained by any pyramidalization of the carbanionic center, as this would have induced a decrease in $^1J_{PC}$ instead of an increase as observed.

From literature data,[16,17] it appears that the sign of $^2J_{PH}$ depends upon the hybridization of the central carbon: when C_1 is sp^3, $^2J_{PH}$ is negative while it becomes positive when C_1 is sp^2. Indeed, positive $^2J_{PH}$ have been observed in all the previously studied anionic species $[(EtO)_2P(O)CHA]^-M^+$ (A = CN, Ph, COOMe, COMe). This is not the case for **1b** as $^2J_{PH}$ is small but negative, although C_1 can be considered as planar from the experimental and calculated $^1J_{PC}$ and $^1J_{CH}$ values. Such a discrepancy sets the unsolved problem of the estimation of the various factors affecting the signs and the magnitude of two bond coupling constants.

The increased shieldings of C_1 and H_1 as well as the deshielding of ^{31}P when going from the neutral precursor **2** to the anionic species **1** is in agreement with a P^+—C^- polarisation of the carbon phosphorus bond, as deduced from infrared intensities data.

Finally, a comparison can be done between **1a, b** and the platinum complex **6** (R = OEt) obtained from **1a** and $[Pt_2Cl_4(PEt_3)_2]$. The structure of this complex is proposed by analogy with **6** (R = Ph), the structure of which has been determined by X-ray crystallography.[2]



6 — R = EtO
— R = Ph

The averaged decrease in ν ($P \rightarrow O$) from **2** to **6** (91 cm^{-1}) and from **2** to **1a** (67 cm^{-1}) suggests a larger decrease of the $P \overset{-}{\cdots} O$ force constant in the former case than in the latter. While the ^{31}P chemical shift are similarly deshielded related to **2**, in **6** (35.7 ppm) and in **1b** (41 ppm), the $^2J_{PH}$ values are quite different (**6** (−21.5 Hz), **1** (−5.8 Hz)) as expected for a change in hybridization from sp^3 in **6** and **2** (−21 Hz) to sp^2 in **1b**. Both IR and NMR results confirm that the charge delocalization in the

Downloaded At: 08:43 30 January 2011

$C(PO)_2Li$ cycle is lessened when going from the planar **1** (i.e. **4**) to the boat form **6**. The anionic charge being probably more localized on the two oxygen atoms in **6**.

EXPERIMENTAL PART

The experimental conditions are the same as in the reference 8.

ACKNOWLEDGMENT

We thank Professor G. Sturtz for providing bis(diethoxyphosphonyl)-methane.

BIBLIOGRAPHY

1. J. L. M. Martin and M. J. F. Leroy, *J. Chem. Res. Synop.*, 88 (1978).
2. J. Browning, G. W. Bushnell and K. R. Dixon, *Inorg. Chem.*, **20**, 3912 (1981).
3. J. D. Baldeschwieler, F. A. Cotton, B. D. Nageswara Rao and R. A. Schunn, *J. Amer. Chem. Soc.*, **84**, 4454 (1962).
4. F. A. Cotton and R. A. Schunn, *J. Amer. Chem. Soc.*, **85**, 2394 (1963).
5. M. Fild and W. Althoff, *Chem. Comm.*, 1973, 933.
6. J. J. Brophy and M. J. Gallagher, *Austr. J. Chem.*, **20**, 503 (1967).
7. T. Bottin-Strzalko, J. Seyden-Penne, M. J. Pouet and M. P. Simonnin, *J. Org. Chem.*, **43**, 4346 (1978).
8. T. Bottin-Strzalko, J. Corset, F. Froment, M. J. Pouet, J. Seyden-Penne and M. P. Simonnin, *J. Org. Chem.*, **45**, 1270 (1980).
9. T. Bottin-Strzalko, G. Etemad-Moghadam, J. Seyden-Penne, M. J. Pouet and M. P. Simonnin, *Nouv. J. Chim.*, **7**, 155 (1983).
10. B. J. Van Der Veken and M. A. Herman, *Mol. Struct.*, **42**, 161 (1977).
11. B. J. Van Der Veken and M. A. Herman, *Phosphorus and Sulfur*, **10**, 357 (1981).
12. J. P. Perchard, *J. Mol. Struct.*, **6**, 457 (1970).
13. J. Corset and R. M. Moravie, to be published.
14. J. J. Richard, K. E. Burke, J. W. O'Laughlin and C. V. Banks, *J. Amer. Chem. Soc.*, **83**, 1722 (1961).
15. G. A. Webb, M. P. Simonnin, J. Seyden-Penne and T. Bottin-Strzalko, *Org. Magn. Res.*, accepted.
16. (a) H. Schmidbaur, W. Buchner and D. Scheutzow, *Chem. Ber.*, **106**, 1251 (1973); (b) W. McFarlane, *Proc. Roy. Soc. London, Ser. A*, **306**, 185 (1968).
17. (a) R. M. Le Quan and M. P. Simonnin, *Bull. Soc. Chim. Fr.*, **1973**, 2365; (b) M. P. Simonnin and C. Charrier, *Org. Magn. Res.*, **1**, 27 (1969).
18. H. J. Jacobsen, T. Bundgaard and R. S. Hansen, *Mol. Phys.*, **23**, 197 (1972).

Downloaded At: 08:43 30 January 2011