^{13}C Nuclear Magnetic Resonance Spectra of Bis-phosphonates

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Summary The appearance of ^{13}C n.m.r. spectra of certain bis-phosphonates varies with concentration due to intermolecular effects of neighbouring P–O bonds.

IT has recently been shown that ^{13}C n.m.r. should provide an applicable technique for determining the stereochemistry of bis-phosphine metal complexes.[1] This proposal was questioned in a recent communication and some examples were given.[2]

Both investigations have shown that the appearance of the ^{13}C n.m.r. spectra varies with changes in the coupling constants relative to each other. The spectra are of the AA'X-type ($^{13}C = X$), and this spin system has been analysed as a border case of the ABX system where $\nu_A = \nu_B$.[3] The X part normally consists of a triplet if $|^2J_{PP'}|$ is large: The spectral pattern may change to a doublet when $|^2J_{PP'}|$ approaches zero provided that $J_{CP} \gg J_{CP'}$, otherwise two doublets are observed.[3]

By contrast the ^{13}C n.m.r. spectra of certain bis-phosphonates (see Table) where the metal atom is formally replaced by a CH_2-grouping showed quintets. This pattern reflects another case of the AA'X system in which the combination lines are of sufficient intensity to be observed, which has also been found for other ^{13}C-PP systems.[4] Dilution with C_6H_6 or C_6H_{12} effects a change in spectral form; the central line, No. 11 (using the notation in ref. 3) losing intensity whereas the outer lines show a gain in intensity. At 10% concentration observation is made of a clean

TABLE. ^{13}C N.m.r. data

		^{13}C Chemical shifts[a] (p.p.m.) and coupling constants (Hz)						
		C(bridge)	Me		MeO	CH_2O		CHO
$(MeO)_2P(O)CH_2P(O)(OMe)_2$	neat	105·9			75·6			
		^1J(134·3)			q(6·1; 12·2)[b]			
	ca. 10%				q(6·6; 10·2)			
$(EtO)_2P(O)CH_2P(O)(OEt)_2$	neat	103·4	112·2			66·3		
		^1J(134·4)	q(6·4; 12·7)			q(5·9; 12·0)		
	ca. 50%					q(5·9; 10·0)		
	ca. 25%					q(5·9; 9·3)		
	ca. 10%		d(6·6)[b]			d(5·9)		
$(Pr^iO)_2P(O)CH_2P(O)$-$(OPr^i)_2$	neat	100·1	104·4	104·7				58·0
		^1J(136·7)	q(3·7)[c]	q(5·6; 10·3)				q(6·1; 11·2)
	ca. 10%		d(3·7)	d(5·9)				d(6·1)
$(EtO)_2P(O)CHP(O)(OEt)_2$	neat	67·3	84·7	84·8		65·9	66·5	
|		^1J(139·4)	t(6·1)[b]	t(6·1)		t(6·4)	t(6·8)	
NMe_2	*ca.* 10%		t(6·1)	t(6·3)		t(6·1)	t(6·8)	

[a] Relative to internal C_6H_6 (upfield). [b] Splitting refers to ($2N = J_{CP} + J_{CP'}$, and between combination lines). [c] Not measured. [d] $\delta(CH_3N) = 112{\cdot}0$; $^3J_{CP} = 4{\cdot}9$.

doublet for the ethyl and isopropyl ester. However, at this concentration the methyl ester still shows quintet structure with a central line of half the intensity of that observed for the neat liquid.

From spectra simulations we have found that the coupling constant $J_{PP'}$ shows a wide variation (5—0·5 Hz) on going from the neat liquid to a diluted solution. We suggest, therefore, that $J_{PP'}$ varies with concentration due to intermolecular effects of neighbouring P–O bonds. It has been concluded from proton spectra that the value of $J_{PP'}$ is negligible (<1 Hz) for the P–CH_2–P grouping.[5] Since these values have been derived from measurements in solution at only one concentration this does not interfere with our conclusion.

In the case of the amino-substituted bis-phosphonate we observe, for both sets of magnetically nonequivalent carbon groups, triplets in the neat liquid which do not change their appearance on dilution up to 10%. Measurements on this compound and the ethyl ester have recently been carried out but no details on the ester group were given.[6]

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[1] B. E. Mann, B. L. Shaw, and R. E. Steinbank, *J.C.S. Chem. Comm.*, 1972, **151**.
[2] D. E. Axelson and C. E. Holloway, *J.C.S. Chem. Comm.*, 1973, **455**.
[3] R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, **39**, 216.
[4] R. K. Harris and S. Aime, personal communication; M. Fild, unpublished results.
[5] R. K. Harris, J. R. Woplin, K. Issleib, and R. Lindner, *J. Magnetic Resonance*, 1972, **7**, 291.
[6] H. Gross, B. Costisella, L. Brennecke, and G. Engelhardt, *J. Prakt. Chemie*, 1972, **314**, 969.