Five- to Nine-bond ^{31}P–^{31}P Spin Coupling Constants in Derivatives of Benzene and Naphthalene

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Summary The 1,5-, 1,6-, 2,7-, and 2,6-isomers of bis(diethoxyphosphinoylmethyl)naphthalene show interbenzylic ^{31}P–^{31}P spin coupling constants over seven, eight, and nine bonds, respectively, which are primarily determined by π-electron contributions.

Spin coupling constants involving a ^{31}P nucleus are usually rather large[1] because of the high effective nuclear charge of ^{31}P compared to most other 'common' magnetic nuclei. Consequently, one expects to detect spin coupling between two phosphorus atoms even if they are separated by a considerable distance, yet $^4J_{PP}$ is the longest-range coupling reported in the literature.[1] The present communication describes ^{31}P–^{31}P couplings of considerable magnitude over a large number of bonds.

From the second-order nature of the proton-decoupled ^{13}C n.m.r. spectra of the bis(phosphinoylmethyl)benzenes (**1a**)—(**1c**) we concluded[2] that there exist sizeable J_{PP} couplings over five, six, and seven bonds, respectively,† and we have now studied the diphosphonates (**2a**)—(**2e**) which exhibit interbenzylic J_{PP} over up to nine bonds (Table). For the symmetrical molecules, J_{PP} was derived by two independent methods: (a) by observation of the outer ^{13}C satellites in the ^{31}P spectra ($^1J_{PC}$ *ca.* 137 Hz) from which

Table

^{31}P–^{31}P Spin coupling constants[a] in (**1**) and (**2**)

	(**1a**)	(**1b**)	(**1c**)	(**2a**)	(**2b**)	(**2c**)	(**2d**)	(**2e**)
$^nJ_{PP}$[b]	9·0(5)	3·1(6)	7·8(7)	1·4(7)	1·8(8)	1·4(8)	4·0(9)	5·3(5)

[a] Given in Hz, accuracy ±0·2 Hz, $(CD_3)_2CO$ (**1**) or $CDCl_3$ (**2**) solutions. [b] Number of bonds separating the coupled nuclei given in parentheses.

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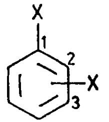
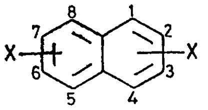
† By analogy with the corresponding J_{HH} (M. Barfield and B. Chakrabarti, *Chem. Rev.*, 1969, **69**, 757) these J_{PP} are termed 'interbenzylic' coupling constants.

J_{PP} can be measured directly and (b) by analysis of the five-line[3] ester $^{13}CH_2$–{^1H} and $^{13}CH_3$–{^1H} spectra which represent the X parts of AA′X spectra and from which $J_{AA'}$ can be derived, because J_{AX} and $J_{AX'}$ are known from the related monophosphonates.[2] In the unsymmetrical compound (**2b**), $^8J_{PP}$ is taken directly from the ^{31}P–{^1H} spectrum which shows an AB pattern.



(1)



(2)

X = –CH_2 P(O)(OET)$_2$

a; 1,2-isomer
b; 1,3-isomer
c; 1,4-isomer

a; 1,5-isomer
b; 1,6-isomer
c; 2,7-isomer
d; 2,6-isomer
e; 2,3-isomer

The large magnitudes of the interbenzylic J_{PP}, in particular $^9J_{PP} = 4{\cdot}0$ Hz, point to considerable π-electron contribution to these couplings. In the preferred conformations[4] of the present benzyl-type phosphonates the C–P bonds lie parallel to the adjacent carbon p_z orbitals. This geometry is most favourable for σ–π exchange polarization which transmits the coupling information to the aromatic π-system and it is responsible for the large magnitude of the observed J_{PP}.

It is interesting to note the large decrease of $^5J_{PP}$ as the mobile bond order of the intervening aromatic bond is decreased; compare (**1a**) with (**2e**).

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[1] G. Mavel, in 'Annual Reports on NMR Spectroscopy,' ed. E. F. Mooney, Vol. 5B, Academic Press, London, 1973, p. 1; R. Grinter, in 'Specialist Periodical Reports; Nuclear Magnetic Resonance,' Senior Reporter R. K. Harris, Vols. 1—5, The Chemical Society, 1972—1976, ch. 2.

[2] L. Ernst, *Org. Magnetic Resonance*, 1977, **9**, 35.

[3] M. Fild and W. Althoff, *J.C.S. Chem. Comm.*, 1973, 933.

[4] *Cf. e.g.* K. Chum, J. B. Rowbotham, and T. Schaefer, *Canad. J. Chem.*, 1974, **52**, 3489.