Applicability of the Karplus Relation to $^{31}PCC^{13}C$ Coupling Constants

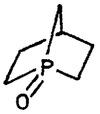
By Ronald B. Wetzel and George L. Kenyon*

(*Department of Chemistry, University of California, Berkeley, California* 94720)

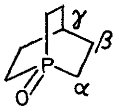
Summary Observation of an unusually large J ($^{31}PCC^{13}C$) value (47 Hz) for coupling between the bridgehead atoms of the newly synthesized phosphine oxide (**2**) has led to the suggestion that Karplus relation may apply to the correlation of J ($^{31}PCC^{13}C$) values.

The extensive studies of ^{31}P–^{13}C coupling constants in phosphine oxides of relatively fixed geometries recently reported by Gray and Cremer[1] have prompted us to report here and comment on some of the more striking ^{13}C-n.m.r. parameters of phosphine oxides (**1**) and (**2**). Phosphine oxide (**2**)[2] was synthesised by an analogous method to that already reported[3] for (**1**), and was characterized by elemental analysis and spectral data.

Natural abundance ^{13}C-n.m.r. spectra of (**2**) were determined at both 14 and 24 kG using pulsed Fourier transform techniques and proton noise coupling. The spectra each showed three doublets centred at $+20\cdot9$ p.p.m. (3 α-carbons), $+23\cdot2$ p.p.m. (1 γ-carbon) and $+27\cdot4$ p.p.m. (3 β-carbons) from the carbons of $SiMe_4$;† the ^{31}P–^{13}C coupling constants (confirmed by measurement at the two different field frequencies) for the three doublets were 63, 47, and 5 Hz, respectively. Thus the ^{31}P–^{13}C coupling constants for the α- and β-carbons are within 1 Hz of the values found



(1)



(2)

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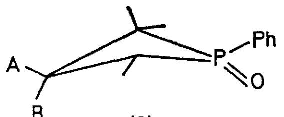
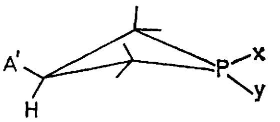
† A positive shift value represents a higher frequency shift or deshielding of the carbon atom, relative to the carbons of Me_4Si. This sign convention was adopted to coincide with that of Gray and Cremer,[1] and is the opposite of that used in ref. 3. Thus the shift values for the carbons of compound (**1**) quoted in ref. 3 should now be positive in sign.

for the corresponding carbons of (**1**)[3] and are also consistent with similar J (${}^{31}\mathrm{P}{}^{13}\mathrm{C}$) and J (${}^{31}\mathrm{P}\mathrm{C}{}^{13}\mathrm{C}$) values reported by Gray and Cremer.[1]

Recent studies indicate that the dihedral angular dependence of J (${}^{1}\mathrm{HCC}{}^{1}\mathrm{H}$) values postulated by Karplus[4,5] holds for J (${}^{31}\mathrm{PCC}{}^{1}\mathrm{H}$) values as well.[3,6,7] Our results imply that, other factors (see below) being equal, the Karplus relation may also be applicable to ${}^{31}\mathrm{PCC}{}^{13}\mathrm{C}$ coupling. The ${}^{31}\mathrm{P}$–${}^{13}\mathrm{C}$ coupling constants between the bridgehead atoms in (**1**) and (**2**) are 35 and 47 Hz, respectively, the largest J (${}^{31}\mathrm{PCC}{}^{13}\mathrm{C}$) values yet reported. Assuming a completely eclipsed, rigid structure for compound (**2**),‡ the dihedral angle between the bridgehead atoms, along any of the equivalent three J (${}^{31}\mathrm{PCC}{}^{13}\mathrm{C}$) coupling paths, is 0°, one of the two maxima for J values predicted by the Karplus relation.[4,5] Assuming the vicinal J (${}^{31}\mathrm{PCC}{}^{13}\mathrm{C}$) paths for coupling between the bridgehead atoms dominate over the geminal J (${}^{31}\mathrm{PC}{}^{13}\mathrm{C}$) path in compound (**1**), then the large J value of 35 Hz can likewise be accounted for, since the dihedral angles for these vicinal paths are also both 0°.



(3)



Series (4a): x = Me, CH$_2$Ph, Bu^t, Ph
y = =O

Series (4b): x = =O
y = Me, CH$_2$Ph, Bu^t, Ph

Results of Gray and Cremer lend support to this hypothesis. For example, in the phosphetan (**3**) a J (${}^{31}\mathrm{PCC}{}^{13}\mathrm{C}$) value of only 1·6 Hz was found for coupling between phosphorus and methyl carbon B, whereas the corresponding J (${}^{31}\mathrm{PCC}{}^{13}\mathrm{C}$) value to methyl carbon A was 24·9 Hz. Inspection of molecular models, carefully constructed in accord with *X*-ray diffraction data available for similar phosphetans,[8] indicates that the relevant dihedral angle to B is *ca.* 90°, the Karplus minimum, while the dihedral angle to A is *ca.* 140°, an angle where an intermediate J value is predicted.

The data of Gray and Cremer indicate, however, that the Karplus relation may be inadequate as the sole stereochemical criterion for correlating J (${}^{31}\mathrm{PCC}{}^{13}\mathrm{C}$) values. As Gray and Cremer have pointed out, there is a significant effect on these vicinal J values by the orientation (in a *cis,trans* sense) of the carbon relative to the phosphoryl oxygen substituent. In the phosphetan series (**4a**) and (**4b**), for example, J (${}^{31}\mathrm{PCC}{}^{13}\mathrm{C}$) values for coupling of phosphorus to methyl carbon A′ range from 12·6 to 16·9 Hz when the phosphoryl oxygen is in position y (series **4a**) and from 21·2 to 23·1 Hz when the phosphoryl oxygen is in position x (series **4b**).

We thank both the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the U.S. Public Health Service for support and Dr. D. M. Wilson, Dr. D. T. Browne, and Mr. Stephen Kent for ${}^{13}\mathrm{C}$-n.m.r. measurements.

(*Received, 5th February* 1973; *Com.* 155.)

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‡ A molecular model of compound (**1**) shows it to be highly rigid. Compound (**2**), however, displays a twisting mode along the axis connecting the bridgehead atoms and so the adjacent pairs of methylene hydrogens may not be completely eclipsed.

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