Dynamic Polarisation of Phosphorus-31 Nuclei at 12,500 Gauss

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THAT the nuclear–electron Overhauser effect can be used to enhance greatly nuclear magnetic resonance signals has been amply demonstrated for proton and fluorine nuclei.[1,2] More recently the technique has been applied, at 3300 gauss, to observe carbon-13 nuclei in natural abundance.[3–5] With protons the sign of the enhancement is usually negative[1,2] but with ^{19}F and ^{13}C nuclei both positive and negative enhancements have been observed. Quantitative experiments have shown that the negative proton enhancements may be interpreted in terms of a dipolar interaction between the nuclei and the unpaired radical electron.[1,2] On the other hand, the fluorine enhancements may be interpreted in terms of combined scalar and dipolar interactions.[1]

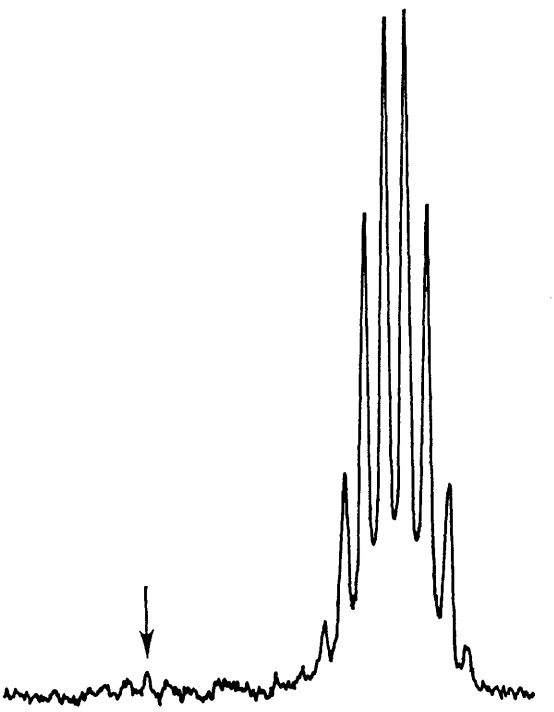
We have investigated, qualitatively, at 12,500 gauss, the enhancements of several solutions of

^{31}P compounds containing the tri-t-butylphenoxy-radical (T.T.B.P.). The Table shows the sign and magnitude of the enhancements observed for several representative compounds. The Figure illustrates the enhancement obtained using a 3 mm. diameter non-spinning sample of trimethyl phosphite.

TABLE. *The sign and magnitude of the enhancement for solutions of several ^{31}P compounds containing the T.T.B.P. radical*

Compound	Maximum observed enhancement
$(MeO)_3P$	+50
$(EtO)_3P$	+30
*Ph_3P	+20
†Ph_2ClP	+15
†$(PhO)_3P$	+15
$(MeO)_3PO$	0
$(EtO)_3PO$	0
Ph_2ClPO	+1
*$(PhO)_3PO$	0
$(EtO)_3PS$	+3
$(EtO)_2P(O)H$	+5

* Solution in CCl_4.
† Chemical reaction with radical and enhancement observed immediately after addition of T.T.B.P. in CCl_4.



FIGURE

The enhancement of the ^{31}P resonance of a solution of $P(OMe)_3$ containing 10^{-3} moles $l.^{-1}$ T.T.B.P. radical. The arrow indicates the unenhanced signal. The enhancement shown is +35 times.

If these enhancements are partially due to a scalar interaction between the phosphorus nucleus and the free electron of the radical, then the free electron must have a finite density at the nucleus. It may then be that the enhancements observed with the tervalent phosphorus compounds are larger than those of the quinquevalent phosphorus compounds because the lone pair of electrons on the tervalent phosphorus contains some 3*s* wave-function character and thus provides a direct mechanism for the scalar interaction.

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