1236. *The Relative Signs of the Spin–Spin Coupling Constants* J(^{195}Pt–CH$_3$) *and* J(^{195}Pt–CH$_2$) *in Triethylplatinum Chloride Tetramer*

By S. F. A. Kettle

The proton magnetic resonance (p.m.r.) spectra of diethyl mercury,[1] triethyl phosphorus, tetraethyl tin, and tetraethyl lead [2] show that the sign of the spin-spin coupling constants J_{XA} and J_{XB} are opposite (X is an isotope of the central atom with spin $\frac{1}{2}$ and A and B are methyl and methylene protons, respectively). In all of these cases the spectra were complex and a detailed analysis was necessary. We now report that the p.m.r. spectrum of triethylplatinum chloride,[3] recorded in a solution in carbon tetrachloride on a Varian A60 spectrometer, similarly shows that $J(^{195}\text{Pt–A})$ and $J(^{195}\text{Pt–B})$ have opposite signs. In contrast to the other spectra, that of $(\text{PtEt}_3\text{Cl})_4$ is simple, interactions being confined to one region of the spectrum. The spectrum is shown in Figure 1 and shows methylene group resonances centred at $\tau = 7{\cdot}77$ and methyl group resonances centred at $\tau = 9{\cdot}25$. The hyperfine splitting of these peaks gives $J(\text{CH}_2\text{–CH}_3) = 7{\cdot}5$ c./sec. The platinum isotope ^{195}Pt (spin $\frac{1}{2}$, natural abundance 35·3%) would be expected to split the methylene and methyl resonances symmetrically. This pattern is found but in the central region, where the ^{195}Pt isotope-shifted CH$_2$ and CH$_3$ group resonances are expected to be superimposed, an A_3B_2 spectrum is observed. From the complete spectrum it is found that $J(^{195}\text{Pt–CH}_3) = 72{\cdot}0$ c./sec. and $J(^{195}\text{Pt–CH}_2) = 86{\cdot}0$ c./sec. It follows that δ for the A_3B_2 system is 10 c./sec. and $J(\text{CH}_2{\cdot}\text{CH}_3)/\delta = 0{\cdot}75$. Figure 2 shows the spectrum of the A_3B_2 region, recorded at a slower scanning rate, compared with the predicted peak positions and intensities taken from Corio's Tables.[4] There is excellent agreement. The peak labelled I in Figure 1 is assigned to an impurity, and is seen to be much reduced in intensity in Figure 2,[5] which is the spectrum of a solution made from a large, washed, single crystal of the compound.

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[1] P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, 1959, **31**, 1430.
[2] P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, 1961, **34**, 1049.
[3] S. F. A. Kettle, *J.*, 1965, 5737.
[4] P. L. Corio, *Chem. Rev.*, 1960, **60**, 363.
[5] The compounds $(\text{CH}_3\text{PtI})_4$ and $(\text{CH}_3\text{PtCl})_4$ also usually show impurity bands. I am indebted to Dr. J. A. S. Smith for a discussion on this point.

From these observations it follows that (*a*) the ^{195}Pt nuclear spin orientation must be identical for the interacting methylene and methyl resonances; otherwise a superimposition spectrum would have been obtained; (*b*) $J(^{195}\text{Pt–CH}_2)$ and $J(^{195}\text{Pt–CH}_3)$ must have opposite sign, for again the spectrum would have been a superimposition. These is no need in this case to apply the criteria of Narasimhan and Rogers,[1] although there are also satisfied: *viz.* $|\delta'|$, $|\delta''| = 69{,}89 \geqslant J_{AB} = 7{\cdot}5$ c./sec. By exploiting the variation of chemical shifts with solvent and with field strength it may be possible to simplify the spectra of other A_3B_2X compounds; several cases appear favourable [6] in addition to those studied by Narasimhan and Rogers.[1,2]

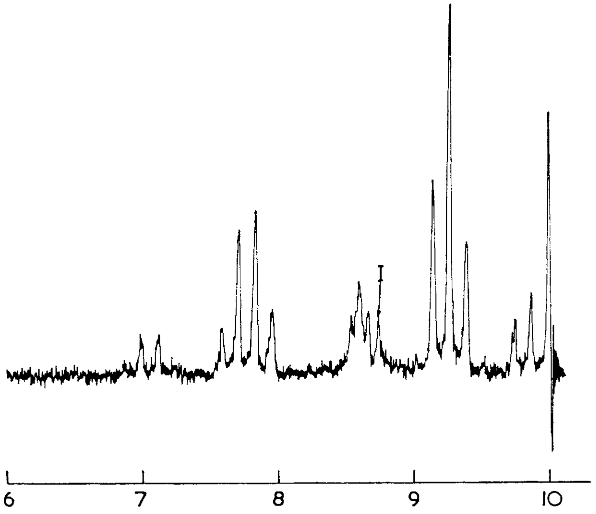

FIGURE 1

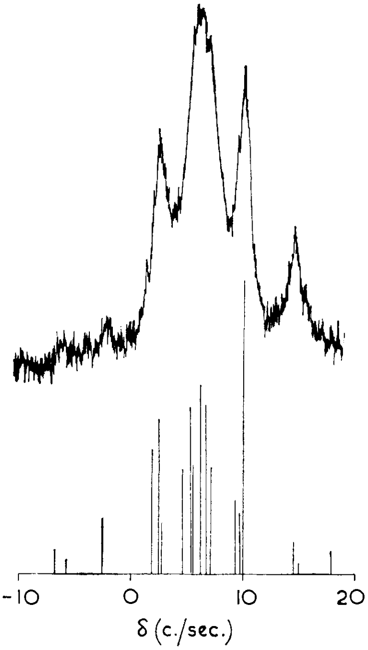

FIGURE 2

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[6] G. J. Bene, E. Duval, A. Finaz, G. Hochstrasser, and S. Koide, *Physics Letters*, 1963, **7**, 34.