Steric Hindrance in Pentafluorophenyl Compounds of Group IV Elements

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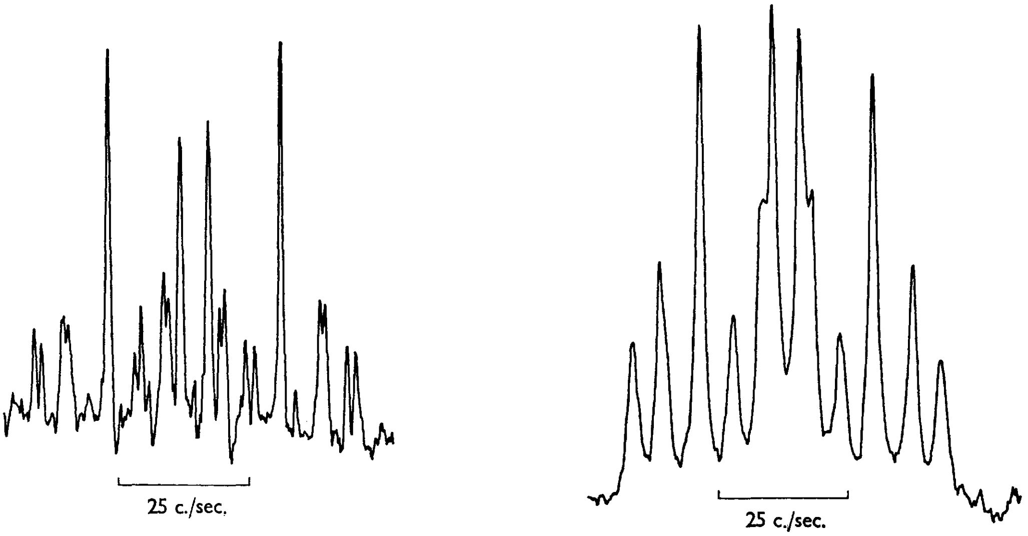
THE ^{19}F n.m.r. spectra of a number of Group IV pentafluorophenyl compounds have been examined[1] as saturated solutions in carbon tetrachloride using a Varian HA-60 spectrometer. A pronounced variation in resolution was evident depending on the number of pentafluorophenyl groups attached to the Group IV atom.

The spectra of these compounds correspond to an AA'PXX' spin system[2] the analysis of which depends on the ability to resolve the two outer doublets of the AA' part of the spectrum.

The appearance of *meta*-fluorine part of the ^{19}F spectrum for the compounds $Ph_3GeC_6F_5$ and $Ph_2Ge(C_6F_5)_2$ is shown in the Figure. It can be seen that while the outer doublets are readily resolvable in the case of the monopentafluorophenylgermanium compound, each of these doublets merge into a single broad band in the case of the bispentafluorophenyl compound. Increasing the number of pentafluorophenyl groups at the expense of phenyl groups leads to a further loss of resolution.

It is believed that the broadening of the spectral lines is due to the large pentafluorophenyl groups causing a restriction of the intramolecular motion. This steric hindrance prevents an averaging out of the dipole–dipole interactions resulting in a broadening of the spectral lines.

Assuming this to be the case then increasing the temperature of the bispentafluorophenyl



(a) (b)

The ^{19}F *n.m.r. spectrum at* 56·44 *Mc./sec.* (HA) *of the* meta-*fluorine nuclei of* (a) $C_6F_5GePh_3$ *and* (b) $(C_6F_5)_2GePh_2$.

compound should lead to a narrowing of the spectral lines. Because of the volatility of the solvent it was possible to raise the temperature to only 70° when no increase in resolution was observed.

The compounds $Ph_2Sn(C_6F_5)_2$ and $Me_2Sn(C_6F_5)_2$ were also examined and it was seen that while line broadening is present in the diphenyltin derivative, the spectrum of bis(pentafluorophenyl)-dimethyltin was readily resolvable. All the trispentafluorophenyl Group IV compounds examined were unresolvable irrespective of the other substituent or the Group IV atom and all the tetrakispentafluorophenyl compounds, from silicon to lead, were also unresolvable.

It would appear therefore that steric hindrance is only completely absent in the monopentafluorophenyl compounds.

Hydrogen resonance spectra obtained at 60 Mc./sec. were insufficiently well resolved for any definite conclusions to be reached. However, Chivers and David[3] have observed two bands having an intensity ratio of 2 : 1 for the ^{1}H resonance spectrum of $C_6Cl_5SnMe_3$ at low temperatures, attributed to hindered rotation of the pentachlorophenyl group.

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[1] K. W. Jolley and L. H. Sutcliffe, unpublished work.

[2] J. Lee and K. G. Orrell, *J. Chem. Soc.*, 1965, 582.

[3] T. Chivers and B. David, Paper presented at the 3rd International Symposium on Organometallic Chemistry, Munich, September, 1967.