Temperature Dependent Geminal P–P Coupling Constants

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Summary The geminal P–P coupling constant increases by more than 90 Hz. as the temperature is decreased from 0 to –120° in PF_2SPF_2; equally large *percentage* variations in $^2J_{PP}$ have been observed in bis(phosphino)silanes and germanes.

WE have observed substantial temperature variations of the $^2J_{PP}$ coupling constant in μ-sulphatobis(difluorophosphine), PF_2SPF_2 (I), bis(phosphino)dimethylgermane, $Me_2Ge(PH_2)_2$ (II), and bis(phosphino)dimethylsilane, $Me_2Si(PH_2)_2$ (III). In each case the coupling constant changes by over 25% in a temperature range of about 100°.

N.m.r. spectra were recorded on a Varian HA-100 spectrometer using the internal lock frequency sweep mode. The spectra were interpreted as AA'XX'X''X''' systems following the procedures of Harris[1] and Lynden-Bell.[2] The X portion of each spectrum is symmetrical about its midpoint. The upfield half of the spectrum for (I) is shown in the Figure. The integrated area of the large peak at 640 Hz. is 16 times larger than the area of any of the other 16 peaks shown in the Figure. The $^2J_{PP}$ is given by the difference between the average frequency of the lowfield and highfield sextets in the upfield half of the spectrum, and increases from 302 Hz. at –1° to 335 Hz. at –42°, 361 Hz. at –70°, and 393 Hz. at –120°. This change in $^2J_{PP}$ is almost fifty times larger than the largest previously observed variation of a geminal coupling with temperature. Ramey and Brey found $^2J_{FF}$ on C-3 in 1-chloroperfluoroprop-2-ene increased from 54·9 Hz. at –90° to 56·9 Hz. at 58°.[3] The percentage variation of $^2J_{PP}$ in (II) and (III) is as large as for (I), but the PP coupling is an order of magnitude smaller and the absolute value of the coupling decreases as the temperature is lowered. In (II), $^2J_{PP}$ decreases from 1·4 Hz. at 40° to 0·6 Hz. at –30°. Below –30° it was not possible to resolve the separate lines in the spectrum. In (III), $^2J_{PP}$ decreases from 10 Hz. at 30° to 6 Hz. at –80°.

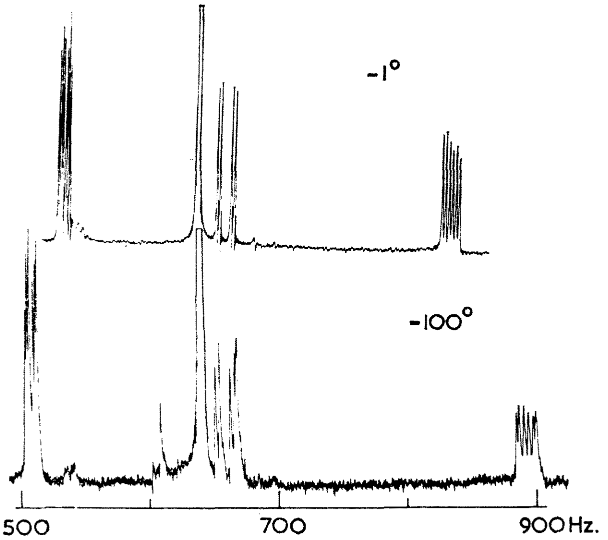

FIGURE. *Fluorine upfield half-spectrum of* PF_2SPF_2. *The two additional peaks in the* –100° *spectrum are spinning sidebands of the large* 640 *Hz. peak.*

Studies of (I) in $CFCl_3$ and (III) in tetramethylsilane show little variation of the coupling constant with concentration. Thus it appears that intermolecular association is not responsible for the observed changes. Changes of the coupling constant due to changes in the P–M–P bond angle in excited vibrational states of the molecule[3] or a dependence of the coupling constant on internal rotation about the P–M bond, where M = S, Ge, or Si are possibilities. Other determinations of the temperature variations of $^2J_{PP}$ are necessary for a reasonable explanation of this phenomenon.

Compound (I) was synthesized following the procedure of Bokerman;[4] the syntheses of (II) and (III) will be reported separately.[5]

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