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A Stable Cyclotriphosphine

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During the past several years, a large number of papers have appeared in the literature concerning various aspects of cyclopolyphosphine $(RP)_n$ chemistry, including, *e.g.*, synthesis [1], electrochemical studies [2], alkali metal reductions [3], and PES investigations [4]. Of particular interest and importance have been studies attempting to clarify the ring size of cyclopolyphosphines in solution and to deliniate the factors which dictate the ring size during synthesis. Much confusion over ring size existed in the early cyclopolyphosphine chemistry because of the difficulties associated with molecular weight determinations: ebullioscopic, isopiestic, and cryoscopic solution measurements, mass spectrometry, and vibrational spectroscopy all have lead to erroneous assignments of the size of the ring in certain cyclopolyphosphines. It has been recently shown that the ^{31}P NMR chemical shift of a cyclopolyphosphine $(RP)_n$ can be used to unequivocally assign the value of n, the ring size [5]. For alkylcyclopolyphosphines, the determinative factors in ring size seems to be a subtle interplay between ring

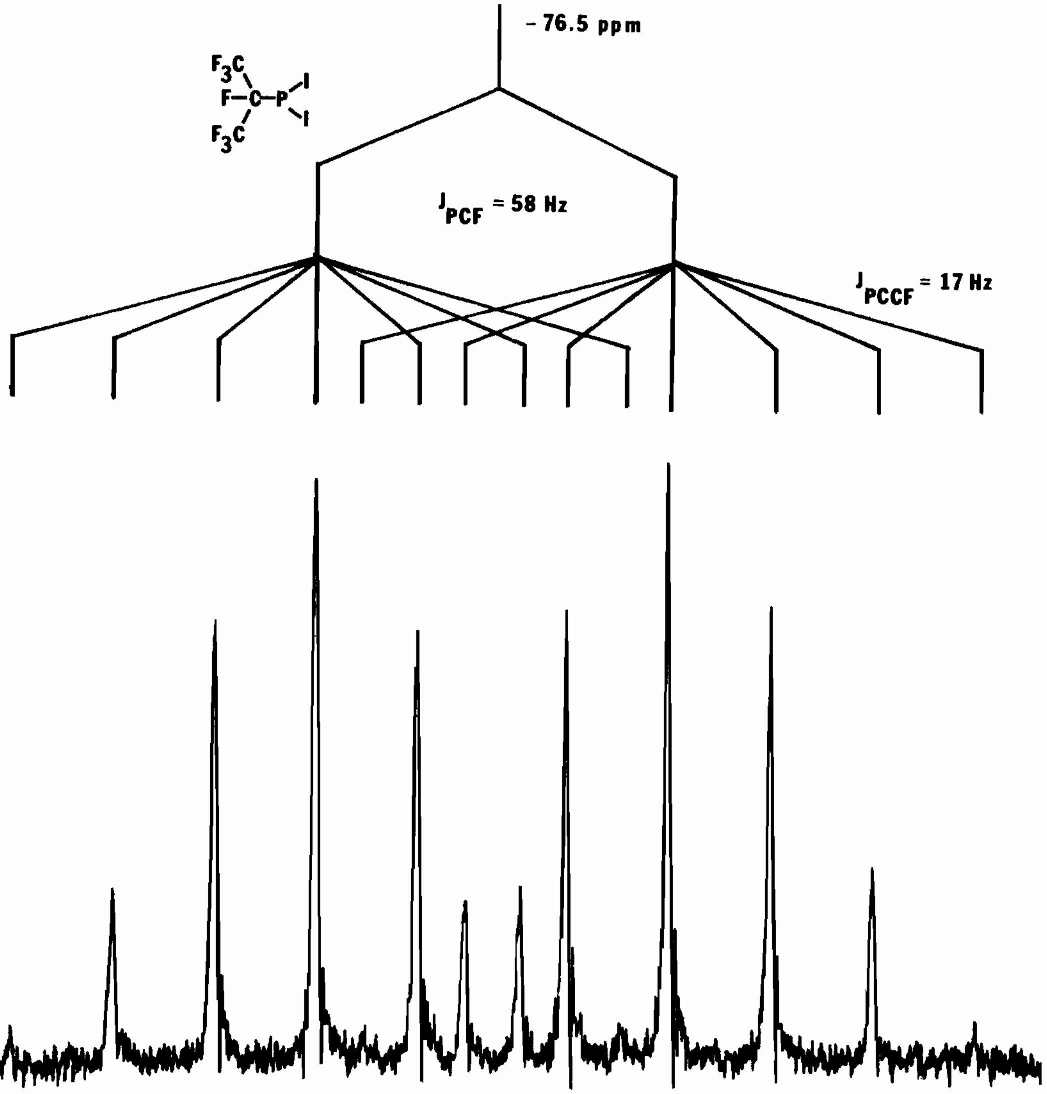

Figure 1. ^{31}P NMR spectrum of $i\text{-}C_3F_7PI_2$. Chemical shift is downfield (deshielded) from external H_3PO_4.

strain and R group–R group repulsions, with the former favoring five-membered rings and the latter favoring four-membered rings (where the pendant organic groups can symmetrically alternate with the phosphorus lone electron pairs around the ring). However, for highly electronegative substituents such as perfluoroalkyls, the situation appears to be more complex [5]; for the cyclopolyphosphines $(RP)_n$ where $R = CF_3$, $n = 4$ and 5, for $R = C_2F_5$, $n = 3$ and 4; and for $R = n\text{-}C_3F_7$, $n = 3$ and 4. Before any rationalization can be made concerning the forces that dictate the ring size for the perfluoroalkylcyclopolyphosphines, be they kinetic or thermodynamic, first more compounds must be synthesized and characterized. Towards this end we undertook the synthesis of heptafluoroisopropylcyclopolyphosphine, $(i\text{-}C_3F_7P)_n$. This compound seemed to be particularly important inasmuch as the isopropyl group was the "crossover" group in the alkylcyclophosphines between four- and five-membered rings [5].

Results and Discussion

The compound $i\text{-}C_3F_7PI_2$, which was used to synthesize the heptafluoroisopropylcyclopolyphosphine, was prepared by the bomb reaction of $i\text{-}C_3F_7I$ with red phosphorus [6]. Characterization of $i\text{-}C_3F_7PI_2$ was accomplished by the ^{19}F and ^{31}P NMR spectroscopy (Figure 1), a gas phase molecular weight determination, and infrared spectroscopy.

The coupling reaction of $i\text{-}C_3F_7PI_2$ with Hg yielded a clear liquid (0.75 Torr at 25 °C) which solidified at 20 °C. A ^{31}P NMR spectrum (Figure 2) yielded a complex pattern centered at *ca.* 130 ppm upfield from H_3PO_4 (it was not possible to broadband ^{19}F decouple, since the perfluoroisopropyl resonances occurred over a 10,000 Hz range). The ultraviolet spectrum (gas phase) was a broad absorption beginning at about 200 nm with a slight shoulder at 260 nm, followed by increased absorption until the cut-off, as is characteristic for polyphosphines [1b]. Infrared absorptions were characteristic of the perfluoroisopropyl group, and were very similar, as expected, to the infrared spectrum of $i\text{-}C_3F_7PI_2$. The gas-phase molecular weight of the cyclopolyphosphine was 571.

All of the above data confirm the formation of a trimeric cyclopolyphosphine $(i\text{-}C_3F_7P)_3$. Only the three-membered ring was formed, and no conversion to any other ring size was noted when the compound was stored at ambient temperature over extended time periods. Particularly demonstrative of the trimeric nature of the ring is the extremely high field chemical shift, which has been shown to be definitive for the assessment of three-membered cyclopolyphosphines [5]. Thus, *tris*-heptafluoroisopropylcyclotriphosphine is the first known stable cyclotriphosphine (for example, $[C_2F_5P]_3$ converts to $[C_2F_5P]_4$ at room temperature). The reasons why a three-membered ring, which not only has considerable ring strain but also has R group–R group and lone pair–lone pair repulsions, should be kinetically and apparently thermodynamically favored are not clear.

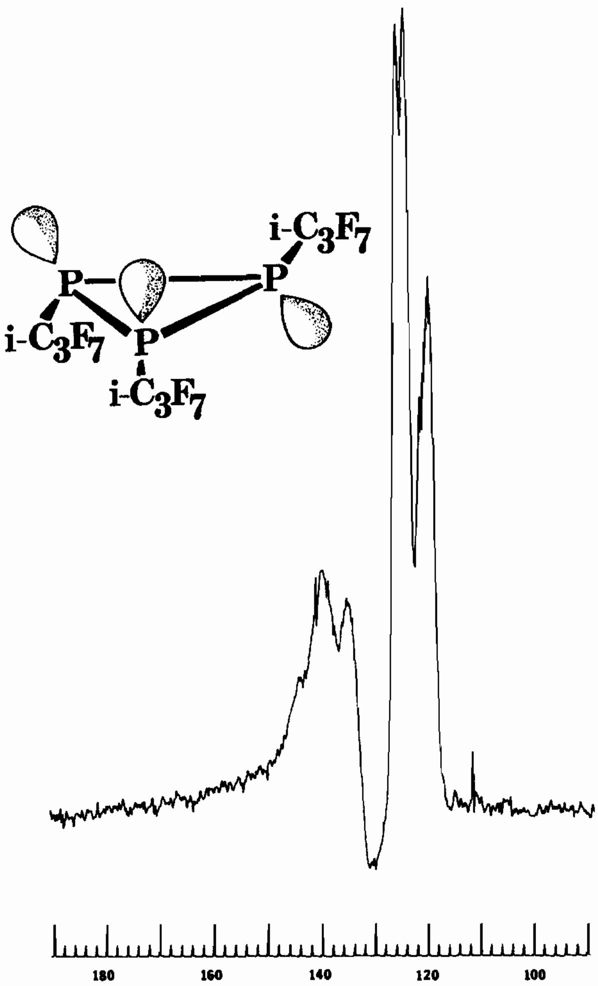

Figure 2. ^{31}P NMR spectrum of $(i\text{-}C_3F_7P)_3$. Chemical shifts are in ppm upfield (shielded) from external H_3PO_4.

Experimental

All compound manipulations were carried out under high-vacuum line or inert atmosphere techniques. NMR spectra were recorded on either a Varian Model XL-100-15 or a Bruker HFX-90 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer.

The reaction of $i\text{-}C_3F_7I$ with P_4 in a stainless steel bomb for 40 h at 220 °C afforded a 10% yield of $i\text{-}C_3F_7PI_2$. The compound $i\text{-}C_3F_7PI_2$ is a yellow liquid with a melting point of about 0 °C which was trapped in a bromobenzene slush. The pure compound has a vapor pressure of about 3 Torr at 25 °C. A vapor phase molecular weight determination yielded a value of 445 (calcd 454). ^{19}F and ^{31}P (Figure 1) further confirmed the identity of the compound.

The reaction of i-$C_3F_7PI_2$ with Hg was quantitative, yielding (i-$C_3F_7P)_3$. The compound is a clear liquid which melts at 20 °C with a vapor pressure of 0.75 Torr at 25 °C. A vapor phase molecular weight determination gave a value of 571 (calcd 600). The compound was further characterized by ^{19}F and ^{31}P (Figure 2) NMR, ultraviolet and infrared spectroscopy. Infrared peaks were (cm^{-1}): 1270(s), 1240(s), 1160(m), 950(w), and 900(w).

Acknowledgements

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