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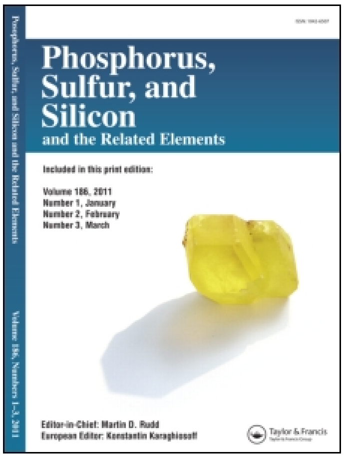

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The Solid State NMR Studies of Static and Dynamic Properties of Phosphoroorganic Disulfides

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The Solid State NMR Studies of Static and Dynamic Properties of Phosphoroorganic Disulfides.

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Abstract

The ^{31}P high resolution solid state NMR spectroscopy has been used to establish the relationship between the molecular structure and shielding parameters for series of dithiophosphoroorganic disulfides. One and two dimensional ^{13}C experiments were performed in order to investigate the dynamics of alkyl/aryl groups attached to phosphorus.

Introduction

The phosphorus-sulfur systems have been attractive for investigators for many decades, however, only very recently have been used as models for solid state NMR studies[1]. These investigations have been mainly carried out for series of inorganic phosphorus sulfides[2]. In this paper, we wish to report the first attempt to correlate of ^{31}P shielding parameters with molecular structure as well as the studies of dynamic properties of the dithiophosphoroorganic disulfides in the solid.

Results and Discussion

The high resolution ^{31}P solid state NMR spectra for series of dithiophosphoroorganic disulfides were performed employing the cross polarization, magic angle sample spinning technique (CP MASS). In the spectrum, each sample shows a number of spinning sidebands due to large anisotropy. The principal elements of the chemical shift tensor were calculated[3] from spinning sidebands intensities employing the graphical method of Berger and Herzfeld[4].

From our results, the relationship between the shielding parameters defined according to commonly used notation[3] and S=P-S angles is apparent. Figure 1a displays the correlation of S=P-S angle to anisotropy parameter $\Delta\delta$. Figure 1b shows similar relationship between S=P-S angle and asymmetry parameter η. Both relationships provide evidence that as in case of phosphates the shielding parameters reflect the changes of local environment for dithiophosphates.

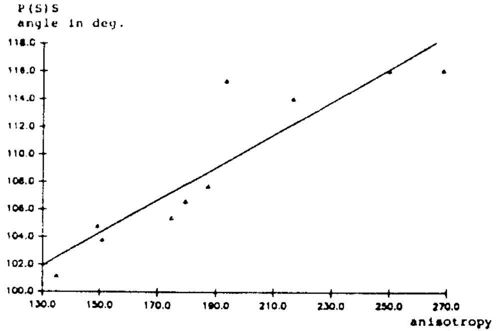

Figure 1a

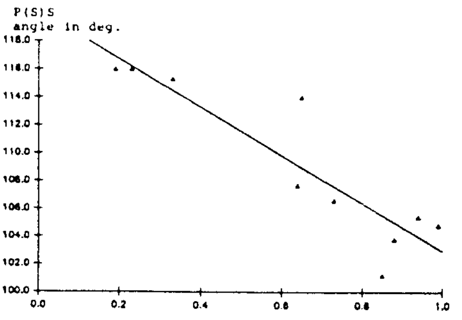

Figure 1b

In previous paper, we reported the studies of dynamics of methoxy groups attached to phosphorus employing the broad-line deuterium NMR spectroscopy as a probe[5]. It has been found that the t-butyl groups of bis[t-butyl phenylthiophosphinyl] disulfide undergo similar dynamic processes. Careful inspection of ^{13}C CP MASS spectrum for disulfide suggests that t-Bu groups are in fast exchange regime in the solid state, hence the crystallographically distinguishable methyl groups are observed as single degenerate resonance.

The one and two dimensional spin diffusion experiments with mixing time ranging from 1 to 50s suggest that, contrary to t-butyl group the aromatic groups do not undergo the dynamic processes.

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