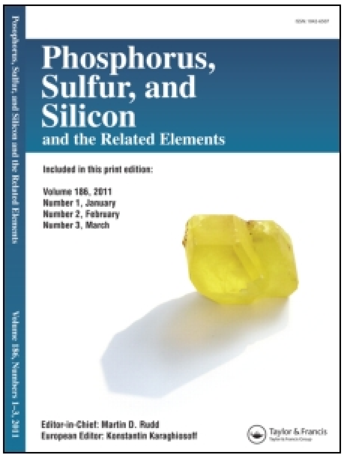

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THE SOLID-STATE NMR OF P–S AND P–Se COMPOUNDS – AN IMPORTANT TOOL FOR THE STRUCTURE INVESTIGATION

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Abstract The efficiency of the solid-state NMR spectroscopy is demonstrated on various examples of P-S and P-Se compounds. Experimentally determined ^{31}P nuclear magnetic shielding values are discussed on the base of IGLO calculations.

INTRODUCTION

The fast development of NMR instrumentation made it possible that the applied spectroscopist nowadays uses solid-state NMR spectroscopy as an important tool for the structure investigation. In many cases this method provides information comparable or complementary to those of the X-ray structure analysis. As most of the nuclear spin interactions in solids are tensor quantities special requirements concerning measurement [high-power dipolar decoupling, cross-polarisation (CP), magic angle spinning (MAS)] and spectra interpretation have to be met.

In the examples discussed below only two of the nuclear spin interactions - the chemical shift and the dipolar interaction - differ considerably from those in solution. The scalar interaction is negligible since for all compounds the indirect spin-spin coupling constant (J_{PP}) is less than 50 Hz. Quadrupolar interactions are not present.

The chemical shift is different along various directions. Solid-state NMR spectroscopy yields the three principal values of the shielding tensor. The orientation of the shielding tensor in the molecular coordinate system is principally available from single-crystal NMR experiments, quantum mechanical calculations and in some favourable cases from dipolar spectroscopy. The microsymmetry around the investigated nucleus can provide partial information.

RESULTS

The ^{31}P solid-state NMR spectroscopy under CP-MAS conditions is preferably used e.g. for the investigation of compounds being practically insoluble, the determination of the number of crystallographically independent molecules in a unit cell and the determination of the number of chemically nonequivalent phosphorus atoms in a molecule.

On the example of the well-known LAWESSON reagent, 2,4-bis(*p*-methoxyphenyl)-2,4-dithioxo-1,3,2,4-dithiadiphosphetane the existence of different modifications and the influence of short intermolecular S--S distances on the ^{31}P nuclear magnetic shielding tensor is shown.[1] The LAWESSON reagent can either crystallise as solvate or in form of solvent-free crystals.[2] Although, the presence of solvent molecules in the lattice has a negligible influence on the molecular structure, isotropic chemical shift δ_{iso} and the principal tensor component σ_{33} are remarkably different (27 and 70 ppm, resp.) for the both forms. Considering the crystal packing it becomes obvious that shorter intermolecular S--S distances in the solvent-free lattice account for this result.

Solution NMR investigations of perthiophosphonic acid anhydrides have the disadvantage that under these conditions dynamic processes may proceed.[3,4] To determine the composition of the solid product (monomer or dimer, *cis* or *trans* isomer) ^{31}P CP MAS spectra are well qualified. Both, monomer and dimer, have a shielding anisotropy of several hundred ppm, but they differ in the isotropic chemical shift δ_{iso} and the principal values σ_{11} and σ_{33} by the order of 300 ppm.[4] The distinction of the configuration isomers is possible since the *cis* isomer can never possess a centre of symmetry and hence, a more complex MAS spectrum results.

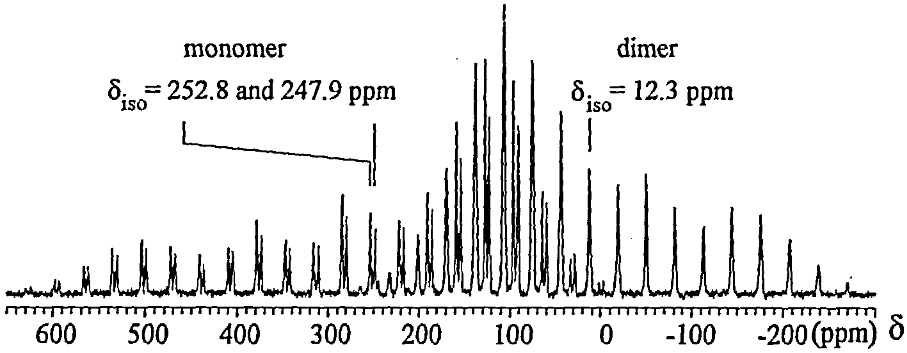

FIGURE 1 ^{31}P CP MAS spectrum of a monomer/dimer mixture of $[(CF_3)_2C_6H_3PS_2]_n$.

In Figure 1 the ^{31}P CP MAS spectrum of a monomer/dimer mixture of the perthiophosphonic acid anhydride $[(CF_3)_2C_6H_3PS_2]_n$ is shown. According to the number of sideband systems it follows that the unit cell of the monomer contains two crystallographically independent molecules whereas in the unit cell of the dimer only crystallographically equivalent molecules with equivalent P atoms are present. The small frequency-dependent splitting of the sideband system of the dimer is in agreement with the *cis* configuration of this isomer (see Figure 2).

The dipole-dipole interaction of two P nuclei in a molecule can be used to determine the orientation of the principal axes system of the shielding tensor with respect to the dipolar vector.[5] The analysis of static powder spectra as demonstrated on the example of a new, recently isolated four-membered ring compound, 2,4-bis(2,4,6-tri-isopropylphenyl)-1-oxa-3-thia-2,4-diphosphetane, yields data being in good agreement with the results of quantum mechanical calculations[6] applying the IGLO method.[7] Numerous calculations of the nuclear magnetic shielding tensor[8] of different four-coordinated P–S compounds with one P=S double bond have shown that in all cases principal axis *3* which corresponds to the most shielded component is directed nearly along the P=S bond (see Figure 2).

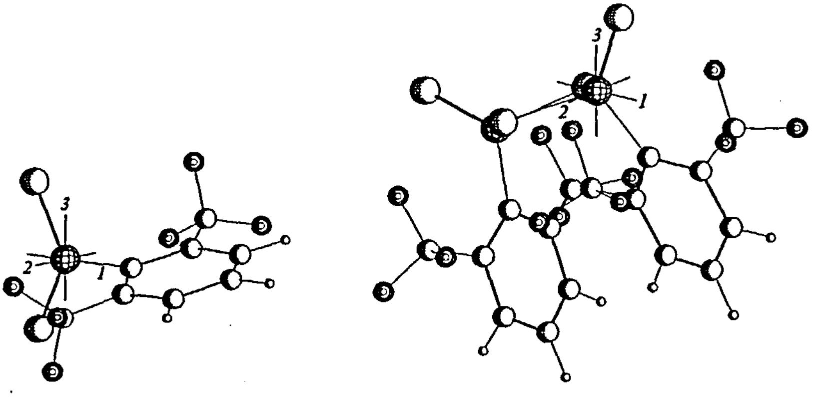

FIGURE 2 Molecular structure and orientation of the principal axes of the ^{31}P shielding tensor for monomer (left) and dimer (right) of $[(CF_3)_2C_6H_3PS_2]_n$.

Using the ovaloid presentation[9] for the shielding tensor (see Figure 3) it can be shown very descriptively how the shielding changes along various directions. Here, the distance between the origin and any point on the surface represents the shielding value in the given direction and hence, the principal values σ_{ii} are reflected by the section of the corresponding axis *i*.

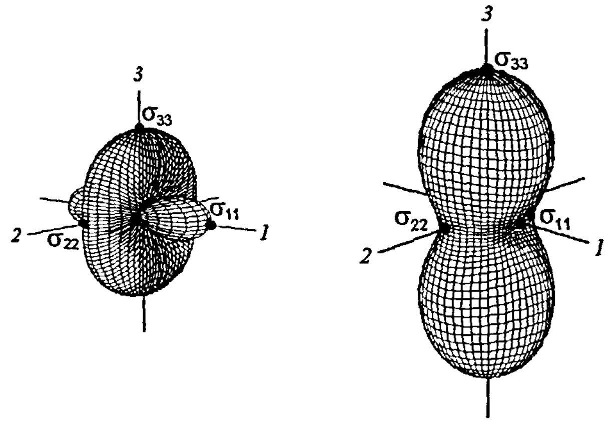

FIGURE 3 Graphical presentation of the ^{31}P shielding tensor for monomer (left) and dimer (right) of $[(CF_3)_2C_6H_3PS_2]_n$.

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