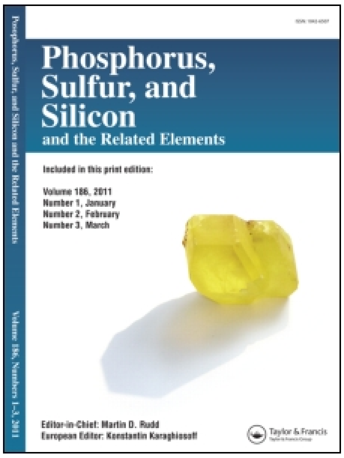

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Dithiadiphosphetanes. NMR Studies in Solution and Solid State

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DITHIADIPHOSPHETANES.
NMR STUDIES IN SOLUTION AND SOLID STATE

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Abstract Solid state NMR spectra and solution spectra of dithiadiphosphetanes $[RP(S)S]_2$ are compared and discussed with respect to configuration and conformation of these compounds.

INTRODUCTION

Single crystal X-ray studies have shown that dithiadiphosphetanes $[RP(S)S]_2$ where R = methyl,[1] *tert*-butyl,[2] phenyl[3] and 2,4,6-trimethyl-phenyl[4] crystallize in trans-configuration. There is only one crystal structure of a cis-dithiadiphosphetane known, the 1,8-naphthyl bridged compound.[5] In solution several dithiadiphosphetanes isomerize and trans- and cis-isomer exist in an equilibrium.[6] In the case of 2,4-diisopropyl-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane we observed a different course of this isomerization reaction and therefore we assume that this compound crystallizes in cis-configuration.[7]

Here we report some solid state NMR spectra and compare with NMR data of dissolved dithiadiphosphetanes.

RESULTS AND DISCUSSION

^{31}P NMR investigations of dissolved dithiadiphosphetanes show that in the 4-membered P_2S_2 ring the P nuclei are much stronger shielded than in other compounds of the same constitution. The reason is the geometry of the ring (bond angles and bond lengths) which causes relatively short interatomic distances between the ring P atoms. Comparing the δ_P-values of trans- and cis-isomer the conclusion may be drawn that always the cis-isomer has the smaller chemical shift. The reason could be a further decrease of the interatomic P-P distance due to puckering of the P_2S_2 ring in cis-configuration.

^{31}P solid state NMR spectra of dithiadiphosphetanes are characterized by a large anisoropy ($\Delta\delta$) of the chemical shift. Depending on the symmetry of the molecules in the lattice one or two side band systems are observed in the ^{31}P CP-MAS spectrum. In the first case the asymmetric unit consists of a molecule half, in the second case of the whole molecule with the two P atoms. The number of side band systems does not allow a conclusion concerning cis- or trans-configuration of the investigated compound.

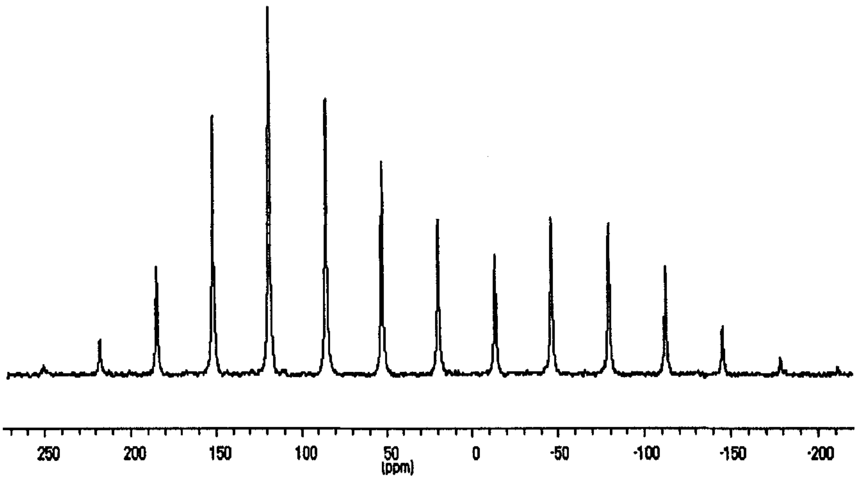

FIGURE 1 ^{31}P CP-MAS spectrum of $[MeP(S)S]_2$ at a spinning rate of 4 kHz.

In all compounds the ^{31}P isotropic chemical shift of the solid (δ_{iso}) is greater than of the dissolved compounds. This difference is great in compounds with small organic substituents, whereas dithiadiphosphetanes with bulky organic substituents show very similar isotropic chemical shifts. These differences can be attributed to a different strong influence of the solvent on the P_2S_2 ring.

^{31}P CP-MAS studies of several probes of 2,4-Bis-(4-methoxy-phenyl)-2,4-di-thioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane yield to different isotropic chemical shift values. According to ^{13}C CP-MAS spectra similar isotropic chemical shifts of solid and dissolved compound are observed in such cases where the dithiadiphosphetane contains a stoichiometric amount of the organic solvent used for the recrystallization of the sample (e.g. benzene, toluene, *o*-dichlorobenzene). If the 4-methoxy-phenyl compound crystallizes without insertion of solvent molecules in the lattice δ_{iso} is about 27 ppm higher than the ^{31}P chemical shift of the same compound in solution.

TABLE I ^{31}P shielding parameters of dithiadiphosphetanes $[RP(S)S]_2$

R	δ_{sol} (ppm) trans	δ_{sol} (ppm) cis	δ_{iso} (ppm)	$\Delta\delta$ (ppm)	δ_{iso}- δ_{sol} (ppm)
Me	23.7	14.2	52.6	317	28.9
iso-Pr	52.0	44.5	52.2	415	7.7
			50.6	422	6.1
tert-Bu	61.4	-	63.0	443	1.6
cyclo-Hex	48.7	41.3	53.2	417	4.5
Ph	18.5	16.3	30.7	405	12.2
4-MeO-Ph[a]	17.1	-	22.2	446	5.1
4-MeO-Ph[b]	17.1	-	43.8	370	26.7
1,8-Naphthyl	-	18.0	30.2	307	12.2
			22.8	323	4.8

[a] recrystallized from benzene

[b] recrystallized from tetrachloromethane

Some infomation concerning the conformation of the substituent R is gained by ^{13}C CP-MAS spectroscopy. Thus, appearance of 6 aromatic C signals in the case of a 2,4-diaryl-dithiadiphosphetane with only one ^{31}P sideband system reflects an asymmetric arrangement of the aryl substituent with respect to the C-P=S plane. The reason can be either an arrangement of the phenyl ring being not exactly perpendicular to the C-P=S plane or an asymmetric arrangement of a substituent at the phenyl ring with respect to this plane.

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