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Abstract

Ab initio calculations of the phosphorus ^{31}P NMR chemical shielding (CSA) tensor as a function of molecular geometry are reported. The CSA surface as a function of the bridging P-O-P bond angle and the O=P-O-P torsional angle were evaluated, allowing changes in the principal components, and the isotropic value to be correlated with specific geometry variations. Preliminary results on the changes in ^{31}P CSA tensors due to phosphate ring formation were also investigated.

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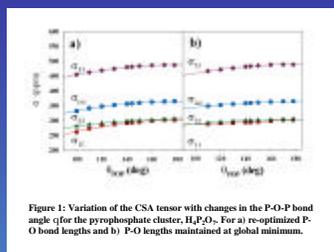
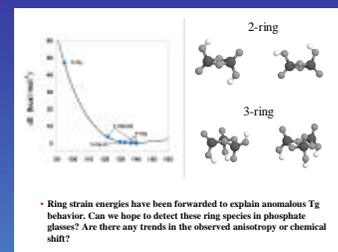
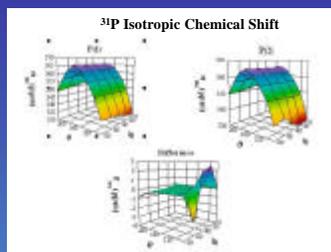


Figure 1: Variation of the CSA tensor with changes in the P-O-P bond angle α for the pyrophosphate cluster, $\text{H}_4\text{P}_2\text{O}_7$. For a) re-optimized P-O bond lengths and b) P-O lengths maintained at global minimum.



Ring strain energies have been forwarded to explain anomalous Tg behavior. Can we hope to detect these ring species in phosphate glasses? Are there any trends in the observed anisotropy or chemical shift?

Computational Details

The ^{31}P chemical shift anisotropy (CSA) tensors were calculated using the parallel version of the GAUSSIAN 98 software package on a multi-node DEC Alpha workstation. The gauge-including atomic orbital (GIAO) method at both the Hartree-Fock (HF) and density functional theory (DFT) level were employed for the calculation of the CSA tensors. All geometry optimizations used the DFT B3LYP hybrid functional, while the NMR shieldings were obtained using HF methods, both at the 6-311++G(2d,2p) level. Additional details can be obtained in [1].

[1]. T. M. Alam, Chapter 22 in *Modeling NMR Chemical Shifts* (1999) Facelli and de Dios Ed., ACS Series #732.

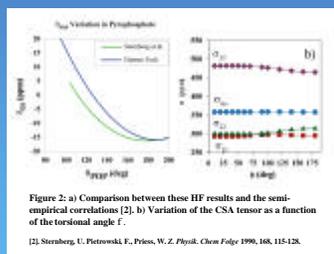
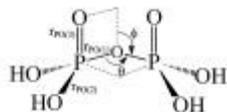
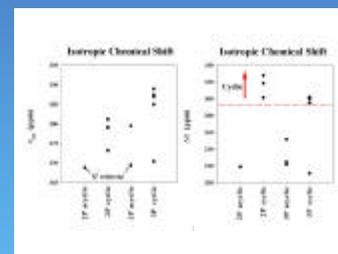
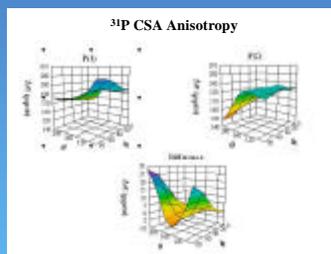


Figure 2: a) Comparison between these HF results and the semi-empirical correlations [2]. b) Variation of the CSA tensor as a function of the torsional angle ϕ .

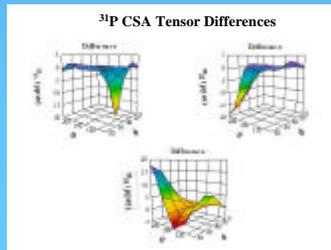
[2]. Sternberg, U., Pietrowski, F., Pries, W. Z. *Physik. Chem. Folge* 1990, 108, 115-128.



Can evaluate the ^{31}P CSA NMR tensor as a function of both bridging angle α and the torsional angle ϕ using *ab initio* techniques.

CSA Shielding Surfaces

- Isotropic chemical shift variation has largest gradient as a function of the P-O-P bond angle (α) compared to variation in the torsional angle (ϕ).
- Absolute variation in isotropic chemical shift larger than the variation observed for the CSA anisotropy.
- Inequivalent P sites are better resolved through differences in the CSA anisotropy.
- Anisotropy variation and differences dominated by changes in the c_{33} element (near P=O bond direction).



Summary

- *Ab Initio* NMR shielding calculations suggest that variations in the CSA tensor are dominated by changes in the P-O-P bond angle.
- In some instances differences in the ^{31}P anisotropy can be used to distinguish phosphorus sites not resolvable by isotropic chemical shifts.
- The ^{31}P anisotropy is significantly higher for cyclic phosphate systems than acyclic systems.
- These distinct differences in the CSA tensor for ring systems result from changes in the P-O-P bond angle. With increasing ring size, the ring strain, and these CSA tensor differences diminish.