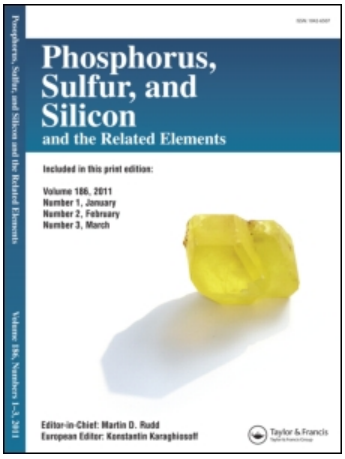

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CRYSTAL STRUCTURE, SOLID-STATE NMR STUDIES AND IGLO CALCULATIONS OF 1-HYDROXYCYCLOHEXANEPHOSPHONIC ACID

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CRYSTAL STRUCTURE, SOLID-STATE NMR STUDIES AND IGLO CALCULATIONS OF 1-HYDROXYCYCLOHEXANEPHOSPHONIC ACID

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Dedicated to Professor Gisbert Großmann on the occasion of his 65th birthday

(Received February 27, 1996)

X-ray diffraction of 1-hydroxycyclohexanephosphonic acid, $C_6H_{13}O_4P$, gives the following crystal data: orthorhombic, $P2_12_12_1$ (no. 19), a = 6.558(1), b = 7.644(2), c = 16.271(1) Å, V = 815.65 Å^3, Z = 4, and D_x = 1.467 g/cm^3. The molecular structure shows a chair conformation of the cyclohexane ring with the phosphonate group in equatorial position. The asymmetric unit consists of the formula unit. Solid-state ^{31}P CP MAS NMR spectroscopy of different crystallization fractions of the title compound gives two sets of principal values of the nuclear magnetic shielding tensor caused by different modifications of the acid. According to IGLO caculations the most shielded component is almost along the P=O bond. The results are compared with the principal values of some other C_6 phosphonic acids.

Key words: 1-Hydroxycyclohexanephosphonic acid, crystal structure, NMR, chemical shift anisotropy, IGLO calculations, phosphonic acids.

INTRODUCTION

Solid-state NMR investigations of inorganic phosphates have shown that a sensitive correlation between principal values of the ^{31}P nuclear magnetic shielding tensor and structure data occurs.[1] Despite of the large importance of phosphonic acids and their wide industrial application only few papers report solid-state NMR data of this class of compounds. The investigation of a series of aminophosphonic acids by Harris *et al.*[2] has shown that the phosphorus spectra of simple aminoalkylphosphonic acids are remarkably similar and solid-state and solution-state chemical shifts are comparable. Anisotropy values range in magnitude from 53 to 82 ppm for the investigated aminophosphonic acids and are similar to those given for a series of phosphonic acids (46 to 82 ppm)[3] but smaller than for phosphonic acid diesters (145–195 ppm).[4] The orientation of the ^{31}P shielding tensor has been determined either by NMR investigation of a single crystal[5,6] or quantum mechanical calculations applying the PCILO method.[7]

In this paper we present the crystal structure and solid-state NMR data of 1-

TABLE I

Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of 1-hydroxycyclohexanephosphonic acid. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
P(1)	0.18671(6)	0.25579(6)	0.23002(3)	0.0220(1)
O(1)	-0.0159(2)	0.3033(2)	0.2658(1)	0.0289(3)
O(2)	0.3444(2)	0.2478(3)	0.3002(1)	0.0369(4)
O(3)	0.1858(3	0.0819(2)	0.1813(1)	0.0362(4)
C(1)	0.2694(3)	0.4175(2)	0.1546(1)	0.0198(3)
C(2)	0.0965(3)	0.4519(2)	0.0934(1)	0.0259(4)
C(3)	0.1603(4)	0.5765(3)	0.0248(1)	0.0335(5)
C(4)	0.3483(4)	0.5081(3)	-0.0196(1)	0.0347(5)
C(5)	0.5235(3)	0.4809(3)	0.0401(1)	0.0293(4)
C(6)	0.4640(3)	0.3576(2)	0.1103(1)	0.0255(4)
O(4)	0.3179(2)	0.5736(2)	0.2004(1)	0.0257(3)

hydroxycyclohexanephosphonic acid. The results of the NMR investigations (chemical shift anisotropy and principal values of the nuclear magnetic shielding tensor) are compared with those of other phosphonic acids of equal number of C atoms but different constitutions to show if differences between cyclic and acyclic compounds and saturated and unsaturated compounds occur.

In order to determine the orientation of the principal axis system in the molecular framework, quantum mechanical calculations of the nuclear magnetic shielding tensors of isolated molecules were performed using the IGLO method.[8]

RESULTS AND DISCUSSION

Crystal and Molecular Structure of $C_6H_{13}O_4P$

1-Hydroxycyclohexanephosphonic acid crystallizes in the orthorhombic space group $P2_12_12_1$ (no. 19). The unit cell consists of four molecules with one molecule per unique volume as an independent unit. Atomic coordinates and equivalent isotropic displacement parameters are reported in Table I, molecular structure and atomic labeling are shown in Figure 1.

The molecule displays a chair conformation of the cyclohexane ring with the phosphonate group in equatorial position. In Table II bond lengths and bond angles are compiled. Each molecule realizes six intermolecular hydrogen bonds to four other molecules (see Figure 2). The oxygen atoms of the P=O group and 1-hydroxy group participate in two hydrogen bonds. Each molecule is linked with two other molecules by two different hydrogen bonds (O···O distances 2.553 and 2.704 Å, O—H···O angles 174 and 170°) and with further two molecules by only one hydrogen bond (2.584 Å, 157°) forming a layer structure along the crystallographic axes a and b. The shortest intermolecular phosphorus-phosphorus distances are 4.586 Å. Thus, only weak dipolar P-P interactions are to expect.

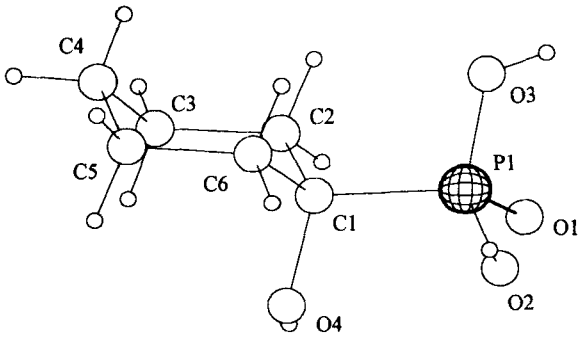

FIGURE 1 Molecular structure of 1-hydroxycyclohexanephosphonic acid.

TABLE II
Selected bond lengths (Å) and angles (°) of 1-hydroxycyclohexanephosphonic acid

P(1) – O(1)	1.495	P(1) – O(2)	1.542
P(1) – O(3)	1.548	P(1) – C(1)	1.825
C(1) – C(2)	1.532	C(2) – C(3)	1.521
C(3) – C(4)	1.519	C(4) – C(5)	1.519
C(5) – C(6)	1.532	C(6) – C(1)	1.535
C(1) – O(4)	1.443		
O(1) – P(1) – O(2)	108.5	O(2) – P(1) – O(3)	110.3
O(2) – P(1) – C(1)	109.0	O(1) – P(1) – O(3)	113.9
O(1) – P(1) – C(1)	111.2	O(3) – P(1) – C(1)	103.8
C(4) – C(5) – C(6)	111.6	C(3) – C(4) – C(5)	110.8
C(1) – C(2) – C(3)	112.3	C(5) – C(6) – C(1)	112.2
C(2) – C(3) – C(4)	111.2	P(1) – C(1) – O(4)	106.1
P(1) – C(1) – C(2)	109.5	P(1) – C(1) – C(6)	111.1
O(4) – C(1) – C(2)	110.9	O(4) – C(1) – C(6)	107.8
C(6) – C(1) – C(2)	111.2		

^{31}P *Solution and Solid-State NMR*

The ^{31}P NMR data of solution and solid-state experiments of different phosphonic acids and the results of IGLO calculations are reported in Table III, a typical ^{31}P CP MAS spectrum is shown in Figure 3. All compounds investigated are characterized by rather similar isotropic chemical shift values in solution and in solid state and by small chemical shift anisotropies ($\Omega = \delta_{11} - \delta_{33}$).

Except for the title compound the CP MAS spectra show only one spinning sideband system. Accordingly, the asymmetric unit should consist of the formula unit. This is in agreement with the known structure of benzenephosphonic acid.[9] For different crystallization fractions of the title compound two spinning sideband systems of changing intensity ratios are observed while in aqueous solutions of the same samples only one ^{31}P NMR signal is measured. Different reasons may account for this result obtained for polycrystalline samples: (i) the presence of racemate crystals

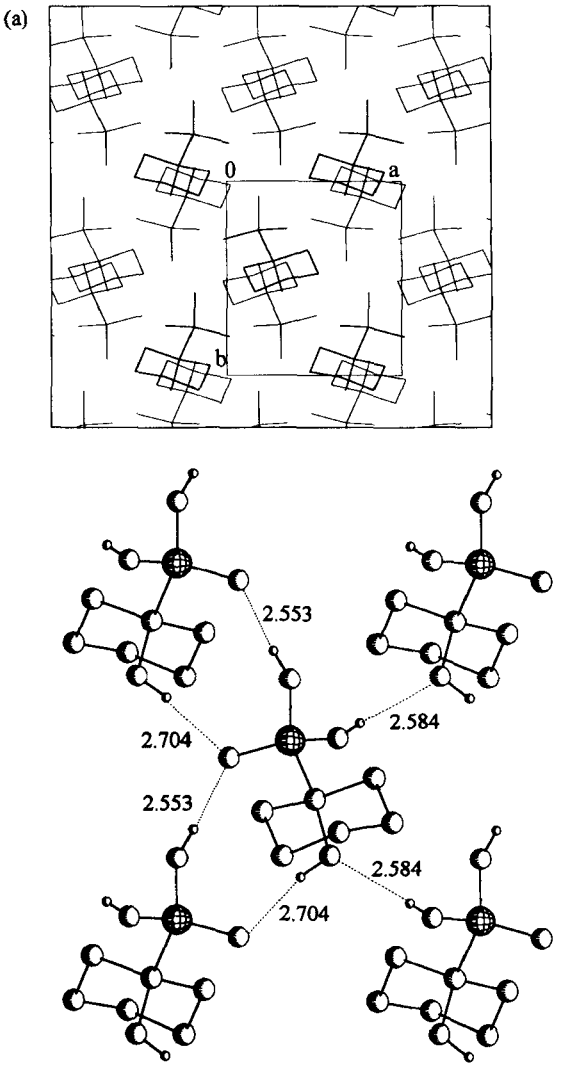

FIGURE 2 Molecular packing of 1-hydroxycyclohexanephosphonic acid: (a) view along the crystallographic axis c, (b) fragment showing all hydrogen bonds of one molecule. For more clarity the most H atoms are omitted.

besides the crystals of the polar space group or (ii) the presence of a hydrate besides the solvent-free crystals. X-ray diffraction investigations of a powder sample (main component δ_{iso} 24.4 ppm) well agree with the diffractogram calculated from the known structure data. The differences of the experimental values δ_{iso} and δ_{ii} for both modifications are of the same order of magnitude as for the other investigated phosphonic acids.

Isotropic chemical shifts in solution and solid state of the compounds under investigation differ by less than 10 ppm reflecting the different interactions between the molecules in the lattice and between phosphonic acid and the solvent water. In aqueous solution the acids dissociate establishing a protolysis equilibrium including

TABLE III

^{31}P NMR solution and solid-state data and results of IGLO calculations of phosphonic acids

phosphonic acid	δ_{sol}	δ_{iso}	δ_{11}	δ_{22}	δ_{33}
n-hexyl	31.2 (0.5 M)	37.0	64	43	4
cyclohexyl	32.6 (0.2 M)	40.0	59	51	8
cyclohex-1-enyl	19.0 (0.5 M)	22.3	62	23	-17
phenyl	16.8 (1.5 M)	21	71	24	-31
phenyl [a]		21	69	22	-28
phenyl (IGLO)		-7.5	71	30	-124
1-hydroxy-cyclohexyl	26.0	27.6	66	31	-14
		24.4	64	48	-38
1-hydroxy-cyclohexyl (IGLO)		1.7	70	50	-115
trans-cyclohexyl-1,2-di [b]		35.8	66	52	-10

[a] Ref. 3

[b] Ref. 23

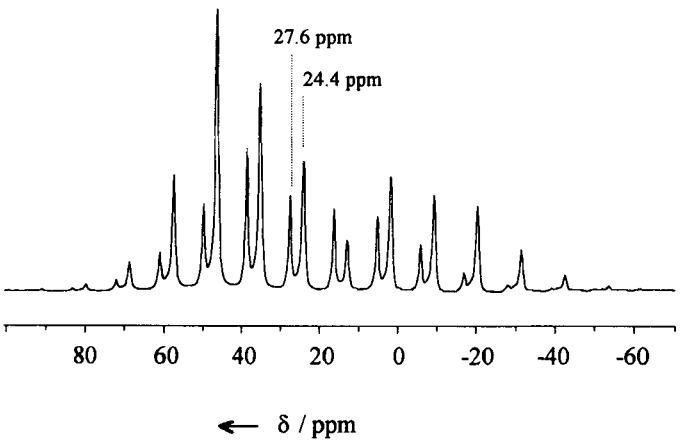

FIGURE 3 ^{31}P CP MAS NMR spectrum of 1-hydroxycyclohexanephosphonic acid at 121.5 MHz.

the phosphonate anions, mainly RP(O)(OH)(O$^-$). The chemical shift of this anion is smaller than δ(P) of the acid.

The principal values δ_{ii} and the anisotropy of *n*-hexanephosphonic acid and cyclohexanephosphonic acid are rather similar. For the latter compound a nearly axially symmetric tensor is observed. It is in agreement with the fact that in this compound the C_{3v} symmetry of a PO_4^{-3} group is less disturbed than in phosphonic acids with double bonds or substituents at the α-C atom.

IGLO calculations performed with the molecular geometries taken from the crystal structures of 1-hydroxycyclohexanephosphonic acid and benzenephosphonic acid[9] show for both compounds a good agreement between the calculated principal values

δ_{11} and δ_{22} and the experimental data (see Table III). δ_{33} is calculated to be stronger shielded by ca. 100 ppm. The reason for such a large deviation is the difference between the objects under investigation. In the quantum mechanical calculations an isolated molecule with non-moving nuclei is considered while in the NMR experiment an ensemble of molecules in a solid-state phase is studied. For our example it becomes obvious that the crystal packing mainly affected by hydrogen bonds influences the chemical shift of the phosphorus atoms.

The IGLO calculations provide not only the principal values but also the orientation of the ^{31}P shielding tensor in both calculated molecules. In agreement with other papers[6,7] the most shielded component (the corresponding axis is 3) is almost directed along the shortest P—O bond. If one considers that deshielding contributions to a given δ_{ii} depend on the electronic structure in a plane perpendicular to the principal axis i, the comparably large variations of δ_{33} in connection with changes at the α-C atom can be understood. Depending on the organic substuents the principal axes 1 and 2 may change their orientations.

EXPERIMENTAL

Preparation: The phosphonic acids were synthesized as described by Clayton and Jensen[10] (cyclohexanephosphonic acid), Fay and Lankelma[11] (1-hydroxycyclohexanephosphonic acid and cyclohex-1-enephosphonic acid), Tavs[12] (benzenephosphonic acid) and Kosolapoff[13] (hexanephosphonic acid). Identity and purity were confirmed by ^{31}P and ^{13}C NMR spectroscopy.[14]

Crystal structure analysis. Crystal data: $C_6H_{13}O_4P$, M_r = 130.135, orthorhombic, $P2_12_12_1$, a = 6.558(1), b = 7.644(2), c = 16.271(1) Å, V = 815.65 Å^3, Z = 4, D_x = 1.467 Mg m^{-3}, λ(Mo Kα) = 0.71069 Å, T = 294 K.

Data collection and reduction: A single crystal suitable for X-ray diffraction was placed in a glass capillary and measured on an Enraf-Nonius four-circle CAD4 diffractometer. Cell constants were determined using the automatic search routine of the CAD4 diffractometer (centring and indexing 25 reflections in the range 2θ = 11–24°). A total number of 1958 reflections has been measured (2θ max = 63.9°) and lead to 1872 unique data.

Structure solution and refinement: The structure was solved by direct methods with SHELXS-86[15] and refined on F^2 using the program SHELXL-93.[16] H atoms were located by difference electron density synthesis and refined as isotropic free atoms. The weighting scheme was $w^{-1} = [\sigma^2(F_o^2) + (0.046P)^2 + 0\ P]$, with $P = (F_o^2 + 2F_c^2)/3$. The final wR(F^2) for 1573 reflections [$F_o > 4\sigma(F_o)$] was 0.0796, with a conventional R(F) of 0.0323, for 152 parameters, the Flack x parameter = 0.071 (0.122) indicates the correct structure. Final atomic coordinates are given in Table I, with selected bond lengths and angles in Table II.

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material can be obtained on quoting the full literature citation and the reference number CSD 405005.

^{31}P NMR spectroscopy: The solid-state NMR spectra were recorded using a Bruker MSL 300 at 121.5 MHz and the solution NMR spectra on a Bruker WH 90 DS at 36.44 MHz. The ^{31}P chemical shifts are relative to 85% phosphoric acid (solutions) or hydroxyapatite (δ_{iso} 2.8). For the determination of the anisotropy parameters ^{31}P CP MAS spectra were measured at spinning frequencies of 0.8–2.0 kHz using cross polarization with a pulse sequence containing two contact pulses.[17] The spinning sideband systems were computed by means of the program WIN-MAS of Jeschke.[18] The standard deviations of the principal values of the chemical shift tensors caused by phase and basis line correction are 2 ppm while the systematical deviations are estimated to 5 ppm. The principal values of the shielding tensors were transformed into shift values using the relation[19] $\delta_{ii} = 328$ ppm $- \sigma_{ii}$ and have been labeled according to the convention $\sigma_{33} \geq \sigma_{22} \geq \sigma_{11}$ or $\delta_{33} \leq \delta_{22} \leq \delta_{11}$, resp.

IGLO calculation: The calculations were performed with coordinates from the X-ray diffraction studies. In a first step the electronic ground state was calculated with the TURBOMOLE package.[20] The ^{31}P shielding tensors were calculated with the direct IGLO program (DIGLO)[21] using the following Huzinaga basis sets[22] (3s) contracted to [2 1] for H, (9s 5p 1d) contracted to [51111, 2111, 1] for C and O, (11s 7p 2d) contracted to [5111111, 211111, 11] for P. As d exponents were used 1.40; 0.35 for P and 1.0 for C and O.

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