

**(C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)[BPO<sub>4</sub>F<sub>2</sub>] – Structural Relations between [BPO<sub>4</sub>F<sub>2</sub>]<sup>2-</sup> and [Si<sub>2</sub>O<sub>6</sub>]<sup>4-</sup>**Ya-Xi Huang, Gerd Schäfer<sup>1)</sup>, Horst Borrmann, Jing-Tai Zhao<sup>1)</sup>, and Rüdiger Kniep\*

Dresden, Max-Planck-Institut für Chemische Physik fester Stoffe

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**(C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)[BPO<sub>4</sub>F<sub>2</sub>] – Strukturbeziehungen zwischen [BPO<sub>4</sub>F<sub>2</sub>]<sup>2-</sup> und [Si<sub>2</sub>O<sub>6</sub>]<sup>4-</sup>**

**Abstract.** Colourless crystals of (C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)[BPO<sub>4</sub>F<sub>2</sub>] were prepared from mixture of ethylenediamine, H<sub>3</sub>BO<sub>3</sub>, BF<sub>3</sub> · C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub> and HCl under mild hydrothermal conditions (220 °C). The crystal structure was determined by single crystal methods (triclinic, *P* $\bar{1}$  (no. 2), *a* = 451.85(5) pm, *b* = 710.20(8) pm, *c* = 1210.2(2) pm,  $\alpha$  = 86.08(1)°,  $\beta$  = 88.52(2)°,  $\gamma$  = 71.74(1)°, *Z* = 2) and contains

infinite tetrahedral zweier-single-chains  $\frac{1}{2}\{\text{[BPO}_4\text{F}_2\text{]}^{2-}\}$  which are isoelectronic (48e<sup>-</sup>) with the polyanions  $\frac{1}{2}\{\text{[Si}_2\text{O}_6\text{]}^{4-}\}$  of the pyroxene family.

**Keywords:** Borophosphate, Fluorine substitution, Templates

A large family of silicate minerals contains single-chain tetrahedral anions [1] as a main structural feature. Among these, the pyroxene-type structures are characterized by unbranched zweier-single-chains (e.g. Diopside, (CaMg)[Si<sub>2</sub>O<sub>6</sub>] [2]). This structural motif is also known for a variety of non-silicates (e.g. Mg[GeO<sub>3</sub>] [3], Rb[PO<sub>3</sub>] [4] and NH<sub>4</sub>[VO<sub>3</sub>] [5]). The rather young class of borophosphates already shows a rich structural chemistry, which also includes infinite tetrahedral chain structures [6]. These are known as loop-branched and open-branched arrangements and there is only one example for an unbranched chain: the vierer-single chain  $\frac{1}{2}\{\text{[B}_2\text{P}_2\text{O}_7(\text{OH})_5\text{]}^{3-}\}$  in the crystal structure of Fe[B<sub>2</sub>P<sub>2</sub>O<sub>7</sub>(OH)<sub>5</sub>] [7]. In the course of our recent investigations in templated borophosphates we obtained the title compound, (C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)[BPO<sub>4</sub>F<sub>2</sub>], which now exhibits an infinite and unbranched tetrahedral zweier-single chain. The pyroxene-analogue periodicity is obviously stabilized by partial and ordered replacement of oxygen against fluorine. (C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)[BPO<sub>4</sub>F<sub>2</sub>] was prepared under mild hydrothermal conditions from a mixture of 0.81 g (13.5 mmol) ethylenediamine (Merck, 99%), 1.12 g (18.1 mmol) H<sub>3</sub>BO<sub>3</sub> (Alfa, 99.9%), 2.04 g (18.1 mmol) BF<sub>3</sub> · C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> (Alfa) and 2.08 g (18.1 mmol) 85% H<sub>3</sub>PO<sub>4</sub> (Merck, p.a.) by adding 10 ml of deionized water and stirring at 100 °C. Meanwhile, 0.7 ml of 37% HCl (Merck, p.a.) were slowly added, leading to a highly viscous red-orange coloured gel with a pH-value of 3. The gel was held at 220 °C for three days under autogenous pressure in a Teflon-lined stainless steel autoclave (Berghof, *V* = 25 ml, degree of filling ≈ 30%). The solid reac-

tion product was filtered, washed with deionized water and dried at 60 °C. The title compound can also be prepared in absence of H<sub>3</sub>BO<sub>3</sub> (molar ratio ethylenediamine : BF<sub>3</sub> · C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> : H<sub>3</sub>PO<sub>4</sub> = 0.75 : 2 : 1) at 170 °C within three to five days reaction time.

Phase purity for the reaction products was controlled first using X-ray powder diffraction (HUBER Image Foil Guinier Camera G670, CuK<sub>α1</sub>-radiation, germanium monochromator). Boron and phosphorus were analysed using ICP-AES (VARIAN Vista, radial observation), while a hot extraction method was applied for carbon (LECO C200 carbon analyser) and nitrogen (LECO TC-436 DR, furnace: EF 500), respectively (obs.(e.s.d.)/calc.) mass-%: C 11.82(4) / 11.67; N 15.5(16) / 13.61; B 5.37(3) / 5.25; P 14.73(4) / 15.04. The fluoride content was determined semi-quantitatively using a fluoride sensitive electrode (Microprocessor-Hochleistungs-pH-Ionen-Meter, pMX 3000/ION, Wissenschaftlich-Technische Werkstätten GmbH) (obs.(e.s.d.)/calc.) mass-%: F 16.9(2) / 18.3. The presence of all elements except for boron and hydrogen were also confirmed by EDX measurements (Philips XL 30 with software package EDAX, sample covered with gold). The compound is stable in air up to a temperature of 330 °C (NETZSCH STA 409 EP; heating rate 5 °C/min.)

The crystal structure of (C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)[BPO<sub>4</sub>F<sub>2</sub>] was determined by using a colourless prismatic crystal (0.12 × 0.03 × 0.02 mm<sup>3</sup>). Single crystal data were collected on a RIGAKU AFC7 four-circle diffractometer. The structure was solved by direct methods and refined with the full-matrix least-squares technique [8]. Atomic coordinates and equivalent/isotropic displacement parameters are given in Table 1. Displacement parameters and bond lengths (Table 2) are consistent with an ordered distribution of O and F. This observation is in agreement with the <sup>19</sup>F NMR MAS-Spectrum (Bruker AV 400 WB) which reveals two resonance peaks at -141.6 ppm and -143.8 ppm with an intensity ratio about 1:1 for the two crystallographically inequivalent fluorine-sites [9].

The crystal structure of (C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)[BPO<sub>4</sub>F<sub>2</sub>] contains infinite chains  $\frac{1}{2}\{\text{[BPO}_4\text{F}_2\text{]}^{2-}\}$  which are built from alternating PO<sub>4</sub>- and BO<sub>2</sub>F<sub>2</sub>-tetrahedra sharing common oxygen corners (Figure 1b). The chains can be classified as unbranched zweier-single chains [1]. They are isoelectronic (48e<sup>-</sup> systems) to the zweier-single silicate chains  $\frac{1}{2}\{\text{[Si}_2\text{O}_6\text{]}^{4-}\}$  (Figure 1a) which are characteristic for the pyroxene family (e.g. Diopside, (CaMg)[Si<sub>2</sub>O<sub>6</sub>], [2]). The essential

\* Prof. Dr. Rüdiger Kniep  
Max-Planck-Institut für Chemische Physik fester Stoffe  
Nöthnitzer Straße 40  
D-01187 Dresden, Germany  
Phone: 49 ((0)351)-4646-3000  
Fax: 49 ((0)351)-4646-3002  
e-mail: kniep@cpfs.mpg.de

<sup>1)</sup> Present address:  
G. Schäfer: Institut für Neue Materialien, Saarbrücken (Germany)  
J.-T. Zhao: Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai (P. R. China)

**Table 1** (C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)[BPO<sub>4</sub>F<sub>2</sub>]: Atomic coordinates and equivalent/isotropic displacement parameters /10<sup>-4</sup> pm<sup>2</sup>, e.s.d.'s are given in parentheses.

Atom	Site	x	y	z	U <sub>eq</sub> / U <sub>iso</sub>
P1	2 i	0.3076(2)	0.29327(15)	0.73839(9)	0.0220(3)
B1	2 i	0.6952(10)	0.5095(7)	0.7758(4)	0.0268(10)
O1	2 i	0.9579(6)	0.3291(4)	0.7712(2)	0.0238(6)
O2	2 i	0.3329(6)	0.3221(4)	0.6137(2)	0.0292(7)
O3	2 i	0.4038(6)	0.4592(4)	0.7929(2)	0.0270(7)
O4	2 i	0.4836(6)	0.0890(4)	0.7850(2)	0.0303(7)
F1	2 i	0.7194(6)	0.6195(4)	0.8634(2)	0.0467(8)
F2	2 i	0.6765(6)	0.6270(4)	0.6764(2)	0.0476(8)
N1	2 i	0.0702(8)	0.8874(5)	0.8622(3)	0.0252(8)
H1	2 i	0.114(10)	0.761(7)	0.841(4)	0.037(13)*
H2	2 i	-0.117(10)	0.954(6)	0.832(3)	0.021(10)*
H3	2 i	0.238(13)	0.940(8)	0.838(4)	0.062(16)*
C1	2 i	0.0478(11)	0.8935(6)	0.9842(3)	0.0290(9)
H4	2 i	-0.104(10)	0.824(7)	1.012(4)	0.040(13)*
H5	2 i	0.245(12)	0.817(7)	1.014(4)	0.052(15)*
N2	2 i	0.8598(9)	0.2779(5)	0.4907(3)	0.0266(8)
H6	2 i	0.667(12)	0.301(7)	0.540(4)	0.052(15)*
H7	2 i	1.032(12)	0.288(7)	0.532(4)	0.052(15)*
H8	2 i	0.804(11)	0.380(8)	0.430(4)	0.057(15)*
C2	2 i	0.0382(10)	0.9254(6)	0.5497(3)	0.0287(9)
H9	2 i	-0.150(9)	0.945(6)	0.600(3)	0.022(10)*
H10	2 i	0.206(10)	0.940(6)	0.591(3)	0.031(11)*

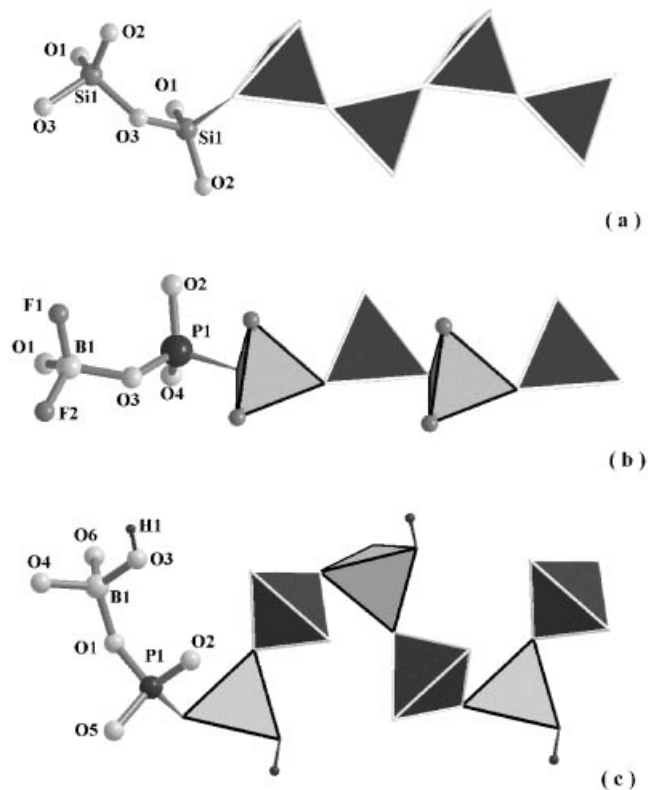
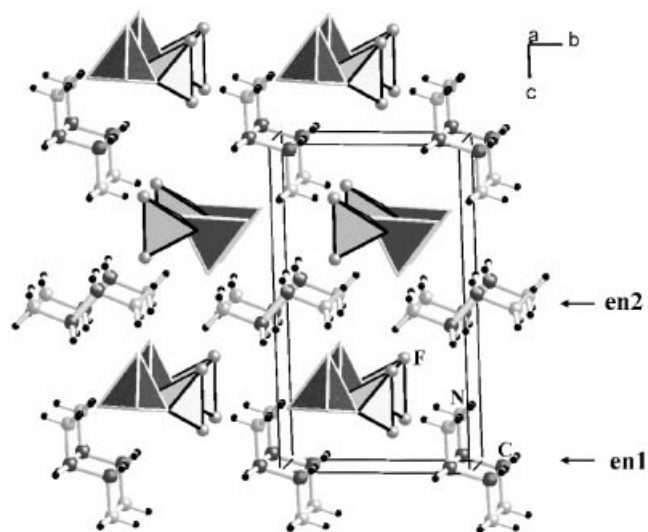
\* Refined with isotropic displacement parameters.

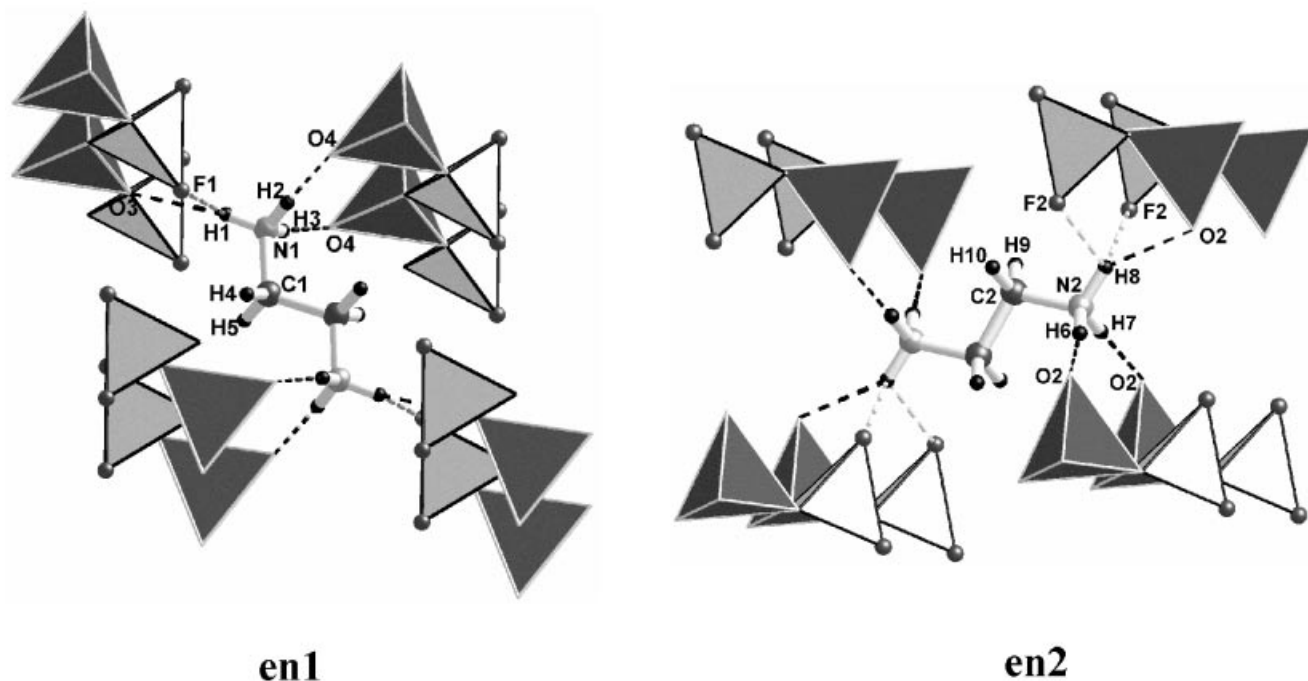
**Table 2** (C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)[BPO<sub>4</sub>F<sub>2</sub>]: Selected interatomic distances /pm and angles /°, e.s.d.'s are given in parentheses.

P1–O4	149.8(3)	O4–P1–O2	114.21(17)	O2–P1–O3	108.71(16)
O2	151.5(3)	O4–P1–O1	106.47(15)	O1–P1–O3	105.46(14)
O1	156.5(3)	O2–P1–O1	109.13(15)		
O3	156.6(3)	O4–P1–O3	112.44(16)		
B1–O1	145.1(5)	O1–B1–O3	109.9(3)	O1–B1–F1	111.8(3)
O3	147.5(5)	O1–B1–F2	109.9(4)	O3–B1–F1	106.7(3)
F1	138.5(5)	O3–B1–F2	109.4(3)		
F2	140.4(5)	F1–B1–F2	109.0(4)		
		B1–O3–P1	127.7(3)	B1–O1–P1	131.9(2)
C1–C1	151.1(8)	N1–C1–C1	109.8(4)		
N1	147.9(5)				
C2–C2	151.8(8)	N2–C2–C2	108.6(4)		
N2	148.5(5)				

Hydrogen bonds			Angles /°		
N1–H1	91(5)	N1...O3	310	N1–H1...O3	158
		N1...F1	283	N1–H1...F1	117
N1–H2	90(4)	N1...O4	274	N1–H1...O4	174
N1–H3	98(6)	N1...O4	280	N1–H1...O4	167
N2–H6	102(5)	N2...O2	272	N2–H6...O2	174
N2–H7	96(5)	N2...O2	274	N2–H7...O2	175
N2–H8	97(6)	N2...O2	291	N2–H8...O2	146
		N2...F2	308	N2–H8...F2	112

structural difference between the zweier-single chains (Figures 1a and 1b) results from the relative orientation (conformation) of adjacent tetrahedra along the chains: In looking along the Si1...Si1 (B1...P1)-directions, adjacent tetrahedra are in an almost eclipsed (staggered) arrangement. By this (staggered) conformation, the terminal fluorine (F1, F2)- and the terminal oxygen (O2, O4)-positions of adjacent tetrahedra in the borophosphate chain reach F...O distances  $\geq 317.3(1)$  pm (F1...O2). Bond angles at the bridging oxygen sites within the chains are 132.5° (pyroxene, Figure 1a), 127.7(3)° (B1–O3–P1) and 131.9(2)° (P1–O1–B1) for the title compound (Figure 1b). Similar values for angles at the bridging oxygen positions are observed in the unbranched vierer-single

**Fig. 1** (a) Part of the unbranched zweier-single chain  $\frac{1}{2}\{\text{Si}_2\text{O}_6\}^{4-}$  in the crystal structure of (CaMg)[Si<sub>2</sub>O<sub>6</sub>] [2]. Ball and stick together with polyhedral presentation. (b) Part of the unbranched zweier-single chain  $\frac{1}{2}\{\text{BPO}_4\text{F}_2\}^{2-}$  in the crystal structure of (C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)[BPO<sub>4</sub>F<sub>2</sub>]. Dark grey tetrahedra: PO<sub>4</sub>, light grey tetrahedra: BO<sub>2</sub>F<sub>2</sub>. (c) Part of the unbranched vierer-single chain  $\frac{1}{2}\{\text{B}_2\text{P}_2\text{O}_7(\text{OH})_3\}^{3-}$  in the crystal structure of Fe[B<sub>2</sub>P<sub>2</sub>O<sub>7</sub>(OH)<sub>3</sub>] [7]. Dark grey tetrahedra: PO<sub>4</sub>, light grey tetrahedra: BO<sub>4</sub>, black spheres: Hydrogen.**Fig. 2** Crystal structure of (C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)[BPO<sub>4</sub>F<sub>2</sub>] viewed along [100]. The two crystallographically inequivalent (C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)<sup>2+</sup> ions are denoted as en1 and en2, respectively (dark grey tetrahedra: PO<sub>4</sub>, light grey tetrahedra: BO<sub>2</sub>F<sub>2</sub>).



**Fig. 3** Hydrogen bonds N–H···O and N–H···F between C<sub>2</sub>H<sub>10</sub>N<sub>2</sub><sup>2+</sup> (**en1** and **en2**) and the zweier-single  $\frac{1}{2}$ {[BPO<sub>4</sub>F<sub>2</sub>]<sup>2-</sup>}. N–H···O hydrogen bonds are shown as black dotted lines and N–H···F hydrogen bonds as grey dotted lines. For interatomic distances see Table 2.

chain  $\frac{1}{2}$ {[B<sub>2</sub>P<sub>2</sub>O<sub>7</sub>(OH)<sub>5</sub>]<sup>3-</sup>} [7] given in Figure 1c : 135.2(3)° (B1–O1–P1) and 130.3(2)° (P1–O6–B1).

The arrangement of anionic chains  $\frac{1}{2}$ {[BPO<sub>4</sub>F<sub>2</sub>]<sup>2-</sup>} running parallel along [100] in the crystal structure of the title compound is shown in Figure 2. (C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)<sup>2+</sup> ions (denoted as **en1** and **en2**) interconnect the chains via N–H···O and N–H···F hydrogen bridges [10]. The systems of hydrogen bridges which fix the diprotonated **en1**- and **en2**- molecules between neighbouring polyhedral chains are given in Figure 3. Concerning the distances N···F and N···O (see Table 2) the hydrogen bridges can be classified as “moderate strong” [10].

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[8] Crystal structure analysis of (C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)[BPO<sub>4</sub>F<sub>2</sub>]: colourless prismatic crystal (0.12 × 0.03 × 0.02 mm<sup>3</sup>); Crystal system: triclinic; Space group: *P* $\bar{1}$  (no. 2); *a* = 451.85(5) pm, *b* = 710.20(8) pm, *c* = 1210.2(2) pm,  $\alpha$  = 86.08(1)°,  $\beta$  = 88.52(2)°,  $\gamma$  = 71.74(1)°; *Z* = 2; *d*<sub>calc.</sub> = 1.859 g/cm<sup>3</sup>;  $\mu_{\text{MoK}\alpha}$  = 0.39 mm<sup>-1</sup>; *T* = 295 K; Data collection: RIGACU AFC7 CCD (MoK $\alpha$ -radiation, graphite monochromator);  $\phi/\omega$ -scan; 3442 collected data and 1386 unique data; *R*<sub>int</sub> = 0.035; Solution of the crystal structure: SHELXS-97-2, Direct methods; Structure refinement: SHELXL-97-2; *R*<sub>1</sub> = 0.059, *wR*<sub>2</sub> = 0.105 (*I* > 2 $\sigma$ (*I*)), GOOF = 1.144; Residual electron density: 0.294/–0.393 e<sup>-</sup> · 10<sup>-6</sup> pm<sup>-3</sup>; b) G. M. Sheldrick, SHELXS 97-2, Program for the solution of crystal structures, Göttingen, 1997; c) G. M. Sheldrick, SHELXL 97-2, Program for the refinement of crystal structures, Göttingen, 1997; d) Further details on the crystal structure may be obtained from the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 172711. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: fileserv@ccdc.cam.ac.uk).

[9] The NMR experiment was performed with a Bruker AV 400WB spectrometer. The <sup>19</sup>F MAS NMR spectrum was acquired at a spinning rate of 35 kHz (2.5 mm rotor) under the following conditions: no decoupling referenced to trifluoroacetic acid (–78.5 ppm); a simple one pulse acquisition was used with a <sup>19</sup>F  $\pi/2$  pulse of 3  $\mu$ s, an acquisition time of 16 ms, a dead time delay of 4.5  $\mu$ s, and a recycle delay of 10 s; resonance frequency of 376.5 MHz. A total of 64 scans was accumulated. For results see text.

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