SUPPLEMENTARY DATA

One-pot synthesis of N-phosphorylmethyl pyrrolidines via acid-catalyzed cyclization/Friedel-Crafts reaction

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X-Ray data

Crystals of compounds 6b and 7b, suitable for single crystal X-ray diffraction analysis, were obtained by slow evaporation from DMSO (6b)/ water (7b). The X-ray diffraction data for the crystals of 6b and 7b were collected using graphite monochromated radiation on a Smart Apex II and a Kappa Apex II automatic diffractometers respectively. The structures were solved by direct methods using the 'SHELX 97\(^1\) and refined by full-matrix least-squares using the 'SHELXL-2017/1 program. All the non-hydrogen atoms were refined with anisotropic atomic displacement parameters. All figures were made using the program OLEX2\(^2\). Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center (CCDC 1843120 (7b) and CCDC 18748002 (6b)) and can be obtained free of charge from via www.ccdc.cam.ac.uk/data_request/cif.

The main geometrical parameters of molecule 6b are ordinary, the geometry of the molecule is shown in (Figure 1). Conformation of the molecule is stabilized by intramolecular hydrogen bond O-H...N type, and crystal structure is formed by intermolecular hydrogen bonds O-H...O type (Figure 2).

![Figure 1](image1.png)

**Figure 1** The molecular structure of compound 6b in crystal. Ellipsoids are shown with 50% probability

![Figure 2](image2.png)

**Figure 2** System of H-bonds in crystal of compound 6b

Crystallographic data for 6b: (C\(_{16}\)H\(_{26}\)NO\(_5\)P): M = 343.35, monoclinic, space group P2\(_1\)/n, a = 7.5349(6), b = 12.3083(9), c = 19.0584(13) Å, β=93.559(4)˚; V = 1764.1(2) Å\(^3\); Z = 4; \(\rho\text{calc} = 1.293 \text{ g cm}^{-3}\), \(\mu\text{(Mo -K\(_\alpha\))} = 0.180\text{ mm}^{-1}\), \(F(000) = 736\), 40372 reflections collected (\(±h, ±k, ±l\)), 5424 independent (\(R\text{int} = 0.040\)), 3378 observed (I
X-ray investigations of compounds 7b has shown that this compound crystallizes with two molecules of the primary substance and one water molecule in the independent part of the unit cell. The conformation of independent molecules is the same, the geometrical parameters (bond lengths, bond and torsion angles in molecules) is the same within the experimental errors, and have values that are within standard for each type of chemical bonds. Therefore, in Figure 1, we present the geometry of one of the independent molecules of compound 7b. (Figure 3). The crystal packing of compound 7b is formed by classical N-H...O and O-H...O hydrogen bonds and additionally stabilized by C-H...O interactions (Table 1, Figure ).

![Figure 3](image1.png)

**Figure 3** The molecular structure of compound 7b in crystal. Ellipsoids are shown with 50% probability.

![Figure 4](image2.png)

**Figure 4** System of H-bonds in crystal of compound 7b

<table>
<thead>
<tr>
<th>H-bond</th>
<th>D - H</th>
<th>H...A</th>
<th>D...A</th>
<th>D - H...A</th>
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</thead>
<tbody>
<tr>
<td>6b</td>
<td></td>
<td></td>
<td>0.25</td>
<td>3.47</td>
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<tr>
<td>H-bond</td>
<td>D - H</td>
<td>H...A</td>
<td>D...A</td>
<td>D - H...A</td>
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<tr>
<td>----------------</td>
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<td>----------</td>
</tr>
<tr>
<td>N3A-H3A...O13A</td>
<td>0.84(4)</td>
<td>1.95(4)</td>
<td>2.704(7)</td>
<td>149(4)</td>
</tr>
<tr>
<td>N3B-H3B...O13B</td>
<td>0.91(5)</td>
<td>2.04(5)</td>
<td>2.809(7)</td>
<td>141(5)</td>
</tr>
<tr>
<td>O11A-H11A...O2B</td>
<td>0.82</td>
<td>1.79</td>
<td>2.594(7)</td>
<td>166</td>
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<tr>
<td>O11B-H11B...O1A</td>
<td>0.71(7)</td>
<td>2.00(6)</td>
<td>2.635(7)</td>
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<tr>
<td>O13A-H13A...O4</td>
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<tr>
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<tr>
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<td>1.97(6)</td>
<td>2.770(7)</td>
<td>156(6)</td>
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<tr>
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<td>1.75(9)</td>
<td>2.633(8)</td>
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<tr>
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<td>3.508(8)</td>
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<tr>
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<td>2.775(8)</td>
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<td>2.36</td>
<td>2.796(8)</td>
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<tr>
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<td>2.54</td>
<td>3.483(8)</td>
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</table>

**7b**

<p>| | | | | |</p>
<table>
<thead>
<tr>
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<td>O(11)-H(11)...O(1)</td>
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<td>2.01</td>
<td>2.736(2)</td>
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<td>C(14)-H(14A)...O(11)</td>
<td>0.96</td>
<td>2.32</td>
<td>2.782(3)</td>
<td>109</td>
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</table>

Crystallographic data for 7b: (2(C14H22NO5P), H2O): M = 648.61, triclinic, space group P-1, a = 8.552(8), b = 10.588(11), c = 18.684(19)Å, α=78.127(14), β=80.050(14), γ=74.060(14)°; V = 1580(3) Å³; Z = 2; ρcalc = 1.364 g cm⁻³, μ(MoKα) = 0.198 mm⁻¹, F(000) = 692, 12360 reflections collected (±h, ±k, ±l), 6090 independent (Rint = 0.1382), 1919 observed (I > 2σ(I)) reflections, 412 refined parameters, R₁ value 0.0724, wR2 = 0.2574, goodness of fit 0.92, maximum and minimum residual electron densities 0.383 and -0.263 eÅ³.

**References**

Copies of NMR spectra

Figure 1 $^1$H NMR spectrum of compound 4a, CDCl$_3$
Figure 3 $^{13}$C NMR (DEPT) spectrum of compound 4a, CDCl$_3$
Figure 4 $^{31}$P NMR spectrum of compound 4a
Figure 5 $^1$H NMR spectrum of compound 4b, $d_6$-acetone
Figure 6 $^1$H NMR spectrum of compound 6b, $d_6$-DMSO
Figure 7: $^{31}$P NMR spectrum of compound 6b, $d_6$-DMSO
Figure 8 $^{31}$P NMR spectrum of compound 4c, CDCl$_3$
Figure 9. $^{13}$C NMR spectrum of compound 4c, D$_2$O
Figure 10 $^{13}$C NMR (DEPT) spectrum of compound 4c, CDCl$_3$.
Figure 11 \(^{31}\text{P}\) spectrum of compound \(4\text{c}\), CDCl\(_3\)
Figure 12 $^1$H NMR spectrum of compound 5, $d_6$-DMSO
Figure 13 $^{13}$C NMR spectrum of compound 5, $d_6$-DMSO
Figure 14: $^{13}$C NMR (DEPT) spectrum of compound 5, $d_6$-DMSO
Figure 15 $^{31}$P NMR spectrum of compound 5, $d_6$-DMSO
Figure 16 $^1$H NMR spectrum of compound 7a, D$_2$O
Figure 17 $^{13}$C NMR spectrum of compound 7a, D$_2$O
Figure 18 $^{13}$C NMR spectrum of compound 7a, D$_2$O
Figure 19 \(^1\text{H} \) NMR spectrum of compound 7b, D\(_2\)O
Figure 20 $^{13}$C NMR spectrum of compound 7b, $d_6$-DMSO
Figure 21 $^{31}$P NMR spectrum of compound 7b, $d_6$-DMSO
Figure 22 $^1$H NMR spectrum of compound 7c, D$_2$O
Figure 23 $^{13}$C NMR spectrum of compound 7c, D$_2$O
Figure 24 $^{31}$P NMR spectrum of compound 7c, D$_2$O