Supplementary Material for

**Crystal structure of rilpivirine hydrochloride, N6H19C22Cl**

Petr Buikin,1,2 Alexander Korlyukov,1 Roman Svetogorov,3 Nadezhda Bakuleva,3 Roman Novikov,4 and Anna Vologzhanina1,a)

*1 A. N. Nesmeyanov Institute of Organoelement Compounds RAS, Vavilova str. 28, 119334 Moscow, Russia*

*2 Institute of General and Inorganic Chemistry RAS, Leninsky Prosp. 31,119991, Moscow, Russia.*

*3 Kurchatov Institute, National Research Center, Pl. Akad. Kurchatova 1, 123182 Moscow, Russia*

*4 N. D. Zelinsky Institute of Organic Chemistry, RAS. Leninsky Prosp. 47, 119991 Moscow, R*ussia.



**Figure S1.** Unit cells of the optimized (blue) and refined (model I, red) models.



a



b



c

**Figure S2.** XRD patterns of **I (a), II and III**. Red and blue lines correspond to the calculated profile and experimental pattern respectively. The bottom trace shows the difference curve.



**Figure S3.** Theoretical XRD pattern for **IV** for CuKα-radiation.



**Figure S4.** 35Cl Hahn-Echo solid-state NMR spectrum (14 kHz MAS) of powder Rilpivirin-HCl.

**Table S1.** Characteristic peak positions and intensities for sample **II** (λ = 0.75 Å)

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| H | K | L | *d*obs (Å) | *d*calc (Å) | *∆d* | *2θ*obs (°) | *2θ*calc (°) | *∆2θ* | *I/I*o |
| 1 | 1 | 0 | 10.7026 | 10.8500 | 0.1474 | 4.0159 | 3.9600 | -0.0559 | 0.77 |
| 1 | -1 | -1 | 9.8463 | 9.8400 | -0.0063 | 4.3653 | 4.3700 | 0.0047 | 0.81 |
| 2 | 0 | 0 | 9.1604 | 9.1500 | -0.0104 | 4.6923 | 4.7000 | 0.0077 | 1.00 |
| 1 | 1 | 1 | 8.2209 | 8.2000 | -0.0209 | 5.2290 | 5.2400 | 0.0110 | 0.78 |
| 0 | 0 | 2 | 8.0840 | 8.0800 | -0.0040 | 5.3176 | 5.3200 | 0.0024 | 0.87 |
| 2 | 0 | -2 | 7.4013 | 7.3900 | -0.0113 | 5.8085 | 5.8200 | 0.0115 | 0.73 |
| 0 | 2 | 0 | 6.5933 | 6.5800 | -0.0133 | 6.5210 | 6.5300 | 0.0090 | 0.85 |
| 0 | 2 | 1 | 6.1052 | 6.1000 | -0.0052 | 7.0430 | 7.0500 | 0.0070 | 0.80 |
| 1 | 1 | 2 | 5.9220 | 5.9100 | -0.0120 | 7.2611 | 7.2700 | 0.0089 | 0.99 |
| 3 | 1 | 0 | 5.5415 | 5.5300 | -0.0115 | 7.7604 | 7.7700 | 0.0096 | 0.68 |
| 2 | -2 | -1 | 5.4023 | 5.4000 | -0.0023 | 7.9607 | 7.9700 | 0.0093 | 0.76 |
| 2 | 2 | 0 | 5.3513 | 5.3500 | -0.0013 | 8.0367 | 8.0400 | 0.0033 | 0.77 |
| 1 | -1 | -3 | 5.2388 | 5.2400 | 0.0012 | 8.2097 | 8.2100 | 0.0003 | 0.68 |
| 0 | 2 | 2 | 5.1094 | 5.1100 | 0.0006 | 8.4179 | 8.4200 | 0.0021 | 0.64 |
| 2 | -2 | -2 | 4.9232 | 4.9200 | -0.0031 | 8.7370 | 8.7400 | 0.0030 | 0.67 |
| 3 | 1 | 1 | 4.8161 | 4.8100 | -0.0061 | 8.9315 | 8.9500 | 0.0185 | 0.67 |
| 3 | -1 | -3 | 4.6213 | 4.6200 | -0.0013 | 9.3090 | 9.3200 | 0.0111 | 0.63 |
| 4 | 0 | 0 | 4.5802 | 4.5800 | -0.0002 | 9.3926 | 9.3900 | -0.0026 | 0.63 |
| 1 | 1 | 3 | 4.4774 | 4.4800 | 0.0026 | 9.6088 | 9.6100 | 0.0012 | 0.57 |
| 2 | 0 | -4 | 4.2564 | 4.2500 | -0.0064 | 10.1090 | 10.1200 | 0.0110 | 0.69 |
| 1 | -3 | -1 | 4.2137 | 4.2100 | -0.0037 | 10.2116 | 10.2100 | -0.0016 | 0.72 |
| 0 | 2 | 3 | 4.1727 | 4.1700 | -0.0027 | 10.3122 | 10.3200 | 0.0078 | 0.72 |
| 0 | 0 | 4 | 4.0420 | 4.0400 | -0.0020 | 10.6467 | 10.6500 | 0.0033 | 1.00 |
| 4 | -2 | -1 | 3.9063 | 3.9100 | 0.0037 | 11.0175 | 11.0200 | 0.0025 | 0.60 |
| 3 | -1 | -4 | 3.8668 | 3.8600 | -0.0068 | 11.1306 | 11.1400 | 0.0094 | 0.58 |
| 4 | 2 | 0 | 3.7617 | 3.7600 | -0.0017 | 11.4427 | 11.4500 | 0.0073 | 0.50 |
| 5 | -1 | -1 | 3.7049 | 3.0000 | -0.7049 | 11.6186 | 11.6300 | 0.0115 | 0.47 |
| 1 | 3 | 2 | 3.6632 | 3.6600 | -0.0032 | 11.7513 | 11.7600 | 0.0087 | 0.70 |
| 3 | 3 | 0 | 3.5675 | 3.5700 | 0.0025 | 12.0675 | 12.0700 | 0.0025 | 0.62 |
| 3 | -3 | -2 | 3.5261 | 3.5200 | -0.0061 | 12.2098 | 12.2200 | 0.0102 | 0.62 |
| 2 | 2 | 3 | 3.4753 | 3.4700 | -0.0053 | 12.3890 | 12.4000 | 0.0111 | 0.63 |
| 3 | 1 | 3 | 3.3872 | 3.3900 | 0.0029 | 12.7128 | 12.7200 | 0.0072 | 0.39 |
| 3 | 3 | 1 | 3.3498 | 3.3500 | 0.0002 | 12.8553 | 12.8600 | 0.0047 | 0.53 |
| 1 | -1 | -5 | 3.2763 | 3.2800 | 0.0037 | 13.1449 | 13.1500 | 0.0051 | 0.46 |

**Table S2.** Characteristic peak positions and intensities for sample **IV** (λ = 0.75 Å)

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| H | K | L | *d*obs (Å) | *d*calc (Å) | *∆d* | *2θ*obs (°) | *2θ*calc (°) | *∆2θ* | *I/I*o |
| 1 | -1 | -1 | 9.8036 | 9.8000 | -0.0036 | 4.3843 | 4.3800 | -0.0043 | 0.50 |
| 2 | 0 | 0 | 9.1651 | 9.1600 | -0.0051 | 4.6899 | 4.7000 | 0.0101 | 0.82 |
| 1 | 1 | 1 | 8.1938 | 8.1900 | -0.0038 | 5.2463 | 5.2500 | 0.0037 | 0.47 |
| 0 | 0 | 2 | 8.0674 | 8.0700 | 0.0026 | 5.3285 | 5.3300 | 0.0015 | 0.60 |
| 0 | 2 | 0 | 6.5472 | 6.5400 | -0.0072 | 6.5670 | 6.5700 | 0.0030 | 0.61 |
| 0 | 2 | 1 | 6.0667 | 6.0600 | -0.0067 | 7.0877 | 7.0900 | 0.0023 | 0.59 |
| 1 | 1 | 2 | 5.9066 | 5.9000 | -0.0066 | 7.2802 | 7.2900 | 0.0098 | 0.81 |
| 3 | 1 | 0 | 5.5370 | 5.5400 | 0.0030 | 7.7669 | 7.7600 | -0.0069 | 0.43 |
| 2 | -2 | -1 | 5.3772 | 5.3800 | 0.0028 | 7.9980 | 8.0000 | 0.0020 | 0.56 |
| 2 | 2 | 0 | 5.3275 | 5.3300 | 0.0025 | 8.0728 | 8.0700 | -0.0027 | 0.57 |
| 1 | -1 | -3 | 5.2239 | 5.2200 | -0.0039 | 8.2331 | 8.2300 | -0.0031 | 0.45 |
| 0 | 2 | 2 | 5.0837 | 5.0800 | -0.0037 | 8.4606 | 8.4600 | -0.0006 | 0.41 |
| 2 | -2 | -2 | 4.9018 | 4.9000 | -0.0018 | 8.7751 | 8.7800 | 0.0049 | 0.48 |
| 3 | 1 | 1 | 4.8116 | 4.7900 | -0.0216 | 8.9400 | 8.9800 | 0.0400 | 0.49 |
| 3 | -1 | -3 | 4.6135 | 4.6100 | -0.0035 | 9.3248 | 9.3300 | 0.0053 | 0.47 |
| 4 | 0 | 0 | 4.5826 | 4.5800 | -0.0026 | 9.3877 | 9.3900 | 0.0023 | 0.63 |
| 1 | 1 | 3 | 4.4670 | 4.4700 | 0.0030 | 9.6312 | 9.6300 | -0.0012 | 0.39 |
| 2 | 0 | -4 | 4.2484 | 4.2500 | 0.0016 | 10.1280 | 10.1300 | 0.0021 | 0.56 |
| 1 | -3 | -1 | 4.1863 | 4.1900 | 0.0037 | 10.2788 | 10.2800 | 0.0012 | 0.59 |
| 0 | 2 | 3 | 4.1559 | 4.1600 | 0.0042 | 10.3542 | 10.3600 | 0.0058 | 0.61 |
| 0 | 0 | 4 | 4.0420 | 4.0300 | -0.0120 | 10.6467 | 10.6700 | 0.0233 | 1.00 |
| 4 | -2 | -1 | 3.8981 | 3.9000 | 0.0019 | 11.0408 | 11.0400 | -0.0008 | 0.52 |
| 3 | -1 | -4 | 3.8594 | 3.8600 | 0.0006 | 11.1520 | 11.1500 | -0.0020 | 0.49 |
| 4 | 2 | 0 | 3.7543 | 3.7500 | -0.0043 | 11.4651 | 11.4600 | -0.0051 | 0.38 |
| 5 | -1 | -1 | 3.7049 | 3.7000 | -0.0049 | 11.6186 | 11.6200 | 0.0014 | 0.33 |
| 1 | 3 | 2 | 3.6437 | 3.6400 | -0.0037 | 11.8144 | 11.8200 | 0.0056 | 0.62 |
| 3 | 3 | 0 | 3.5517 | 3.5500 | -0.0017 | 12.1217 | 12.1200 | -0.0017 | 0.53 |
| 3 | -3 | -2 | 3.5100 | 3.5100 | 0.0000 | 12.2663 | 12.2700 | 0.0038 | 0.59 |
| 2 | 2 | 3 | 3.4653 | 3.4600 | -0.0053 | 12.4249 | 12.4300 | 0.0051 | 0.57 |
| 3 | 1 | 3 | 3.3827 | 3.3800 | -0.0027 | 12.7298 | 12.7300 | 0.0002 | 0.27 |
| 3 | 3 | 1 | 3.3361 | 3.3400 | 0.0039 | 12.9082 | 12.9100 | 0.0018 | 0.46 |
| 1 | -1 | -5 | 3.2684 | 3.2700 | 0.0017 | 13.1769 | 13.1800 | 0.0031 | 0.41 |

Atomic coordinates of the optimized model

CELL 0.71075 19.430542 13.094307 17.102518 90 109.393692 90

LATT 7

SYMM -X,+Y,0.5-Z

Cl2 0.39352 0.15220 0.34729

N8 0.21437 0.50969 0.45734

N11 0.12136 0.50352 0.51697

N24 0.19848 0.59550 0.33595

N28 0.64558 0.35317 0.36761

N37 0.22971 0.41657 0.57857

N47 0.53189 0.13362 0.61798

C3 0.18935 0.47761 0.51573

C16 0.07601 0.55953 0.45350

C24 0.09788 0.59123 0.38966

C32 0.17048 0.56582 0.39398

C40 0.27145 0.56859 0.34189

C42 0.28304 0.47680 0.30511

C50 0.35444 0.44799 0.31529

C64 0.41381 0.50929 0.36027

C72 0.40000 0.60160 0.39411

C80 0.32921 0.63255 0.38633

C82 0.22001 0.40997 0.25889

C96 0.31624 0.72887 0.42668

C101 0.48887 0.48123 0.37175

C108 0.51171 0.38859 0.35487

C116 0.58535 0.37012 0.36305

C125 0.29468 0.36577 0.58518

C133 0.33360 0.32346 0.66297

C141 0.39525 0.26458 0.67331

C149 0.41968 0.24704 0.60563

C157 0.38191 0.29151 0.52827

C165 0.32042 0.35063 0.51819

C173 0.48149 0.18469 0.61360

H3 0.10419 0.47401 0.56373

H16 0.02234 0.57746 0.45656

H24 0.06138 0.63471 0.33855

H32 0.16411 0.62546 0.28043

H34 0.36336 0.37700 0.28688

H48 0.44574 0.64986 0.42873

H50 0.17733 0.45216 0.21135

H58 0.19373 0.37823 0.30141

H66 0.23839 0.34626 0.22935

H80 0.31397 0.71200 0.48881

H88 0.26451 0.76568 0.39176

H96 0.36108 0.78276 0.43374

H102 0.52985 0.54077 0.39613

H108 0.47422 0.32410 0.33396

H117 0.20341 0.39404 0.61947

H125 0.31478 0.33670 0.71550

H133 0.42397 0.23102 0.73362

H141 0.39972 0.27697 0.47512

H149 0.29189 0.38462 0.45837

**Table S3**. Calculated and experimental chemical shifts for sample **IV**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Atom label | ISO c.s., ppm | Standard value, ppm | δcalc, ppm | δexp, ppm | δcalccorr, ppm |
| N4 | 226.7 | 16.4 | 210.2 | 201.4 | 212.4 |
| N6 | 156.3 | 16.4 | 139.8 | 132.3 | 139.1 |
| N10 | 151.3 | 16.4 | 134.8 | 126.4 | 132.9 |
| N22 | 297.0 | 16.4 | 280.5 | 262.5 | 277.2 |
| N23 | 137.5 | 16.4 | 121.0 | 111.4 | 117.0 |
| N31 | 291.5 | 16.4 | 275.1 | 258.3 | 272.7 |
| C5 | 182.5 | 32.1 | 150.4 | 162.7 | 171.4 |
| C7 | 180.8 | 32.1 | 148.7 | 145.0 | 152.6 |
| C8 | 135.7 | 32.1 | 103.6 | 99.7 | 104.6 |
| C9 | 194.2 | 32.1 | 162.1 | 150.4 | 158.3 |
| C11 | 178.0 | 32.1 | 145.9 | 138.5 | 145.7 |
| C16 | 175.8 | 32.1 | 143.7 | 137.4 | 144.6 |
| C15 | 164.1 | 32.1 | 132.0 | 131.6 | 138.4 |
| C14 | 169.9 | 32.1 | 137.8 | 132.8 | 139.7 |
| C13 | 169.3 | 32.1 | 137.2 | 128.9 | 135.5 |
| C12 | 178.3 | 32.1 | 146.2 | 137.0 | 144.1 |
| C18 | 53.7 | 32.1 | 21.6 | 18.3 | 18.3 |
| C17 | 50.3 | 32.1 | 18.3 | 19.7 | 19.8 |
| C19 | 19.4 | 32.1 | 159.3 | 148.6 | 156.4 |
| C20 | 131.8 | 32.1 | 99.7 | 97.2 | 101.9 |
| C21 | 161.7 | 32.1 | 129.6 | 118.3 | 124.3 |
| C24 | 177.5 | 32.1 | 145.5 | 141.7 | 149.1 |
| C25 | 156.9 | 32.1 | 124.8 | 120.5 | 126.6 |
| C26 | 170.3 | 32.1 | 138.3 | 131.6 | 138.4 |
| C27 | 138.0 | 32.1 | 105.9 | 104.4 | 109.6 |
| C28 | 172.8 | 32.1 | 140.8 | 131.6 | 138.4 |
| C29 | 156.0 | 32.1 | 124.0 | 120.5 | 126.6 |
| C30 | 163.5 | 32.1 | 131.4 | 118.3 | 124.3 |

ISO c.s. – calculated isotropic chemical shift

Standard value – the value of ISO c.s. calculated for 13C (orthorhombic SiMe4) and 15N (crystalline ammonia)

δcalc – chemical shift calculated as ISO c.s. - Standard value

δexp – experimental value of chemical shift

δcalccorr – the values of δcalc corrected with linear regression (Fig. S5)



**Figure S5**. δexp *vs* δcalc plot.