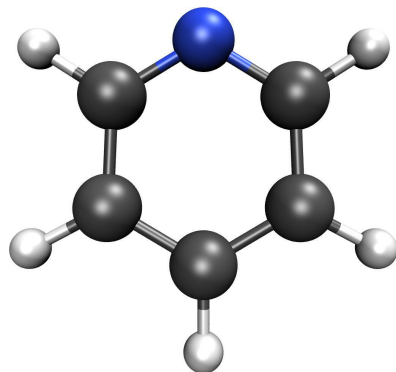# Si
Silico

# A Report On The Calculation Of The Optimised Structure, Vibrational Frequencies And Excited States Of Pyridine At The PBE0/6-31G** Level

osl - 24th June 2022

## Abstract

The calculation of optimised structure, vibrational frequencies and excited states for the system 'Pyridine' is presented, accompanied by automated analysis and image generation provided by the Silico software package. The calculations were performed using the Turbomole software package(s) at the PBE0/6-31G** level of theory. The total self-consistent field (SCF) energy of the system was found to be -6748.46 eV after 9 steps. The highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) were calculated to be -7.17 and -0.47 eV respectively, corresponding to a HOMO-LUMO band gap of 6.71 eV. The permanent dipole moment (PDM) was calculated to be 2.20 D. The most intense vibrational frequencies were calculated to be at 722, 1028, 1494, 1668 and 3206 $cm^{-1}$, and there were zero negative frequencies.

**Table 1:** *Summary of overall calculation metadata. [a]: The date and time at which the calculation was completed. [b]: Total combined duration in real-time (wall-time) for all components of the calculation. [c]: Temperature used for thermochemistry analysis. [b]: Pressure used for thermochemistry analysis.*

| Calculation no. | Date[a] | Duration[b] | Success (Converged) | Computational package | Level of theory | Calculations | Wavefunction | Multiplicity | T[c] / K | p[d] / atm |
|---|---|---|---|---|---|---|---|---|---|---|
| Combined | 24/06/2022 12:28:25 | 58 s | True (True) | Turbomole (7.5.0) | PBE0/6-31G** | Optimisation, Frequencies, Excited States | restricted | 1 (singlet) | N/A | N/A |
| 1 | 24/06/2022 12:20:46 | 33 s | True (True) | Turbomole (7.5.0) | PBE0/6-31G** | Optimisation, Frequencies | restricted | 1 (singlet) | N/A | N/A |
| 2 | 24/06/2022 12:24:30 | 13 s | True (N/A) | Turbomole (7.5.0) | PBE0/6-31G** | Excited States | restricted | 1 (singlet) | N/A | N/A |
| 3 | 24/06/2022 12:28:25 | 10 s | True (N/A) | Turbomole (7.5.0) | PBE0/6-31G** | Excited States | restricted | 1 (singlet) | N/A | N/A |

## Summary Of Results

### Scf Energy

**Table 2:** *Summary of SCF energy properties.*

| | |
|---|---|
| **No. of steps** | 9 |
| **Final energy** | -6748.4564 eV |
| **Final energy** | -651,127 kJ·mol$^{-1}$ |

### Geometry

**Table 3:** *Summary of geometry properties.*

| | |
|---|---|
| **Formula** | $C_5NH_5$ |
| **Molar mass** | 79.0999 g·mol$^{-1}$ |
| **Alignment method** | Minimal |
| **X extension** | 4.31 Å |
| **Y extension** | 3.88 Å |
| **Z extension** | 0.00 Å |
| **Linearity ratio** | 0.10 |
| **Planarity ratio** | 1.00 |

### Molecular Orbitals

**Table 4:** *Summary of HOMO & LUMO properties.*

| | |
|---|---|
| **E$_{HOMO,LUMO}$** | 6.71 eV |
| **E$_{HOMO}$** | -7.17 eV |
| **E$_{LUMO}$** | -0.47 eV |

### Permanent Dipole Moment

**Table 5:** *Summary of the permanent dipole moment properties.*

| | |
|---|---|
| **Total** | 2.20 D |
| **X axis angle** | 89.98 ° |
| **XY plane angle** | 0.01 ° |

### Vibrations

**Table 6:** *Summary of the properties of the calculated vibration frequencies.*

| | |
|---|---|
| **No. frequencies** | 27 |
| **Simulated peaks** | 722, 1028, 1494, 1668 and 3206 ... cm$^{-1}$ |
| **No. negative frequencies** | 0 |
| **Negative frequencies** | N/A |

## Methodology

### Metadata

This report was generated from the combined results of three individual calculations. The individual metadatas for each separate calculation are presented in the following sections, and the overall calculation was performed using the **Turbomole (7.5.0)** program, the **DFT** method with the **PBE0** functional and the **6-31G**** basis set. It was completed on the **24th June 2022** after a total duration of **58 s** and **finished successfully**. The base multiplicity of the system under study was **1 (singlet)**.

Finally, a **restricted wavefunction** was used, resulting in a single set of doubly occupied orbitals. The full calculation metadata is tabulated in table 1.

The calculation of the optimised structure and vibrational frequencies was performed using the **Turbomole (7.5.0)** program, the **DFT** method with the **PBE0** functional and the **6-31G\*\*** basis set. It was completed on the **24th June 2022** after a total duration of **33 s** and **finished successfully**. The base multiplicity of the system under study was **1 (singlet)**. Finally, a **restricted wavefunction** was used, resulting in a single set of doubly occupied orbitals.

The calculation of the excited states was performed using the **Turbomole (7.5.0)** program, the **DFT** method with the **PBE0** functional and the **6-31G\*\*** basis set. It was completed on the **24th June 2022** after a total duration of **13 s** and **finished successfully**. The base multiplicity of the system under study was **1 (singlet)**. Finally, a **restricted wavefunction** was used, resulting in a single set of doubly occupied orbitals.

The calculation of the excited states was performed using the **Turbomole (7.5.0)** program, the **DFT** method with the **PBE0** functional and the **6-31G\*\*** basis set. It was completed on the **24th June 2022** after a total duration of **10 s** and **finished successfully**. The base multiplicity of the system under study was **1 (singlet)**. Finally, a **restricted wavefunction** was used, resulting in a single set of doubly occupied orbitals.

### Analysis

The report presented here was generated using the Silico software package. This toolset relies upon a number of third-party applications and libraries which should be cited appropriately in derivative works. In particular, the calculation results described within were parsed by the cclib library.[1] Scientific constants which were used, among other things, for the interconversion of scientific units were provided by SciPy.[2] Three-dimensional plots of atom positions and calculated densities, including molecular orbitals, were rendered using Visual Molecular Dynamics (VMD)[3] and the Tachyon ray-tracer.[4] Finally, two-dimensional graphs were plotted using the MatPlotlib library,[5] while this report itself was prepared using the Mako template library[6] and the Weasyprint library[7], the latter of which was responsible for generation of the PDF file.

## Discussion

### Total SCF Energy

The total energy of the system was calculated at the **self-consistent field (SCF)** level, corresponding to the energy calculated by the density-functional theory (DFT) method, over a total of nine steps, the results of which are displayed in figure 1. The energy calculated by the final step was -6748.46 eV, corresponding to -651,127 KJmol$^{-1}$. A plot of the total SCF electron density is shown in figure 2.
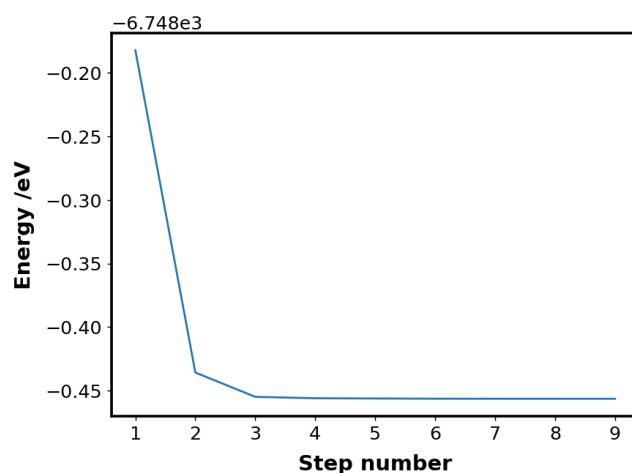


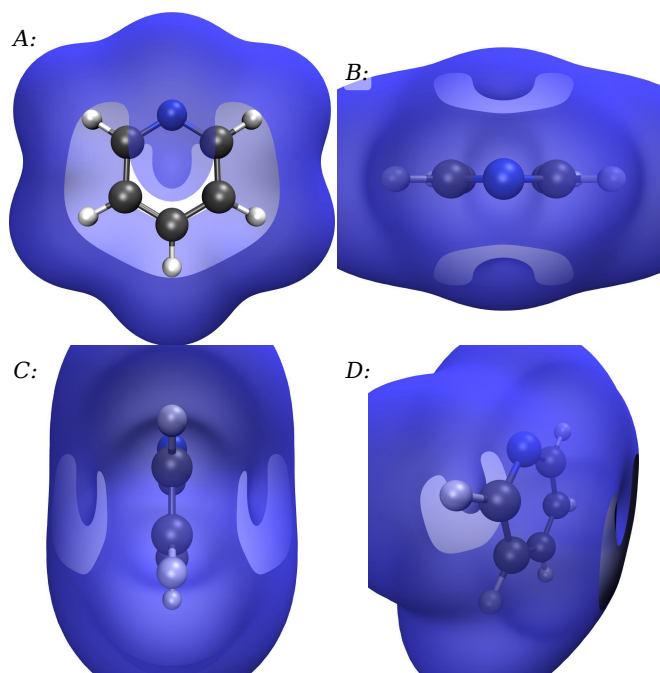**Figure 1:** *Graph of calculated energies at the self-consistent field (SCF) level.*



**Figure 2:** *Plot of the total SCF electron density, plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

### Geometry

The **empirical formula** of the studied system was $C_5NH_5$, corresponding to a **molecular mass** of 79.10 gmol$^{-1}$. The molecular geometry was aligned to the cartesian (X, Y and Z) axes by the **Minimal (MIN)** method. Using this method, the **extent of the molecular system** in the X, Y and Z axes ($L_X$, $L_Y$ and $L_Z$, corresponding to the molecular width, length and height respectively) was determined to be 4.31, 3.88 and 0.00 Å respectively. These extensions give rise to a **molecular linearity ratio** ($1-(L_Y/L_X)$) and **planarity ratio** ($1-(L_X/L_Y)$) of 0.10 and 1.00 respectively.

### Permanent Dipole Moment

The calculated **permanent dipole moment** was 2.20 D, with a vector (x,y,z) of -0.00, -2.20, -0.00 D. The angle between the dipole moment vector and the x-axis was 89.98 °, while the angle between the dipole moment and the xy-plane was 0.01 °. A plot of the permanent dipole moment is shown in figure 3.
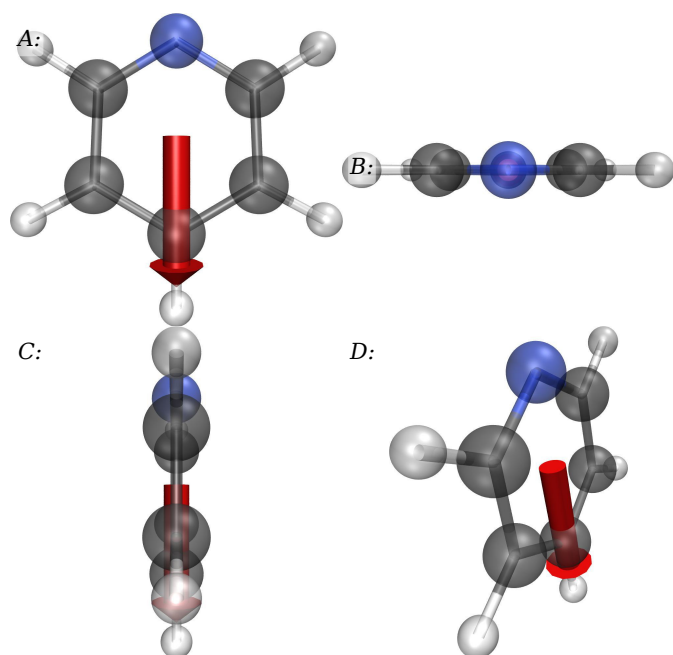
**Figure 3:** *The permanent dipole moment (red arrow) plotted against the aligned molecular geometry with a scale of 1 Å = 1.0 D. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

## Molecular Orbitals

In total, 109 doubly occupied molecular orbitals were calculated, divided into 21 occupied orbitals and 88 unoccupied (or virtual) orbitals. The calculated energies of the **HOMO and LUMO** were -7.17 and -0.47 eV respectively, corresponding to a **HOMO-LUMO band gap** of 6.71 eV (figure 7). Plots of the orbital density for the HOMO and LUMO are shown in figures 4-5 respectively, while the orbital overlap between the HOMO and LUMO is shown in figure 6.
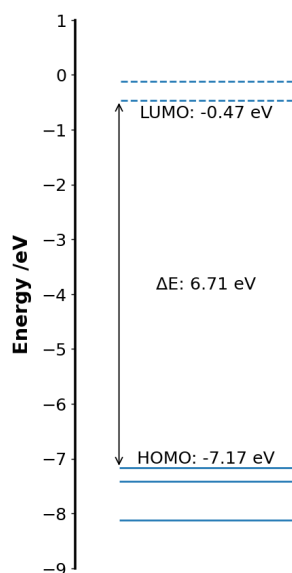




**Figure 4:** *Orbital density plots of the HOMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*



**Figure 5:** *Orbital density plots of the LUMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

**Figure 7:** *Graph of the calculated molecular orbital energies in close proximity to the HOMO-LUMO gap. Solid lines: occupied orbitals, dashed lines: virtual orbitals.*
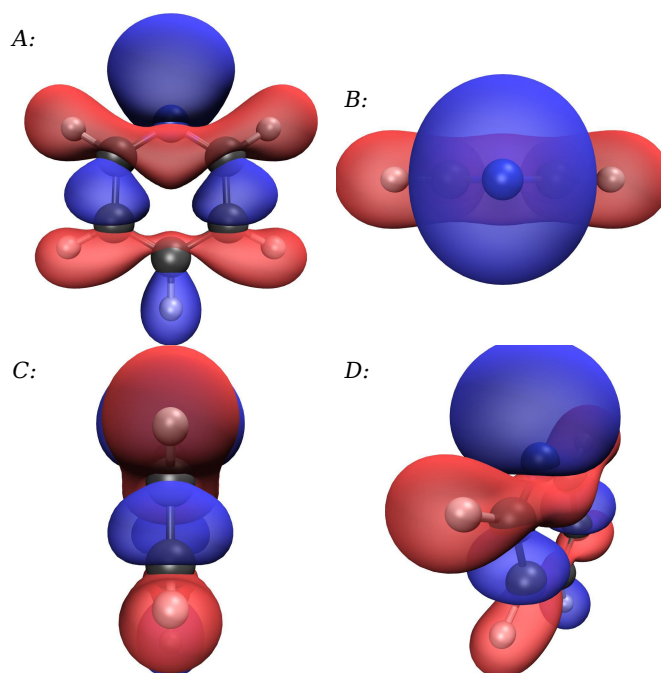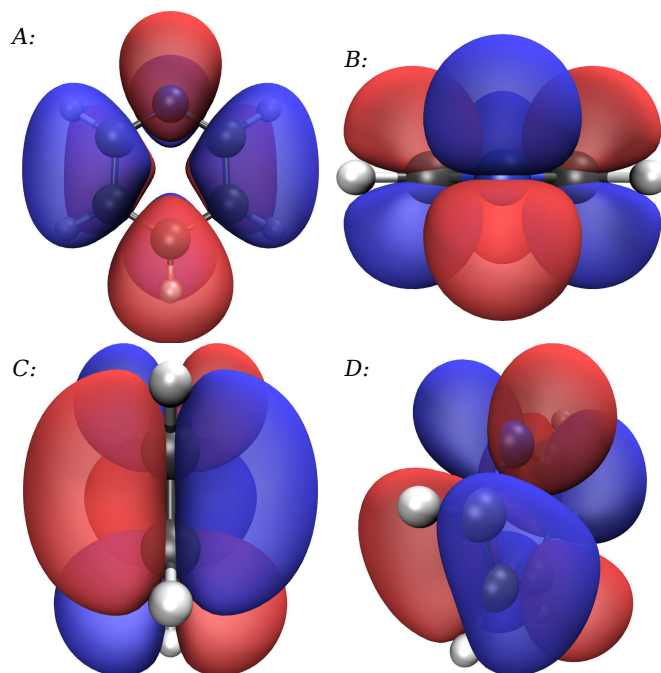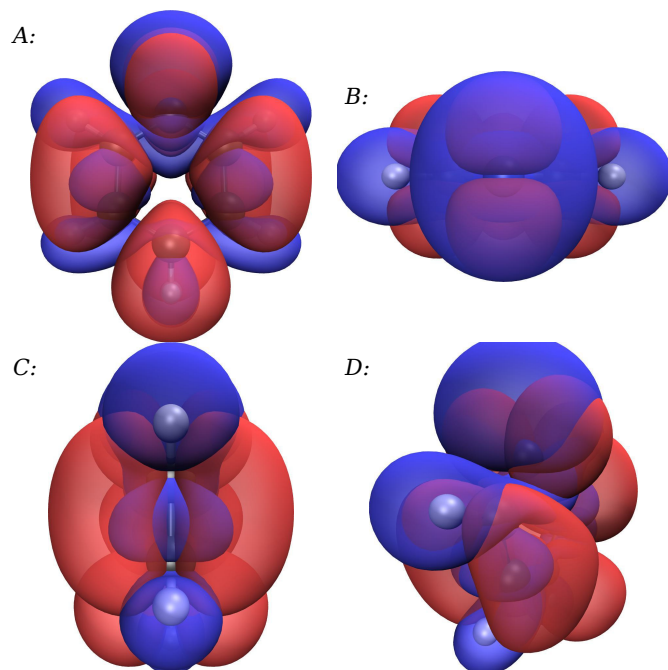
A:

B:

C:

D:



***Figure 6:*** *Orbital density plots of the HOMO (blue) and LUMO (red), plotted simultaneously with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

## Vibrational Frequencies

The energies of a total of 27 vibrational transitions were calculated and vibrational absorption peaks were simulated using a gaussian function with full-width at half maximum (FHWM) of 80 cm$^{-1}$. From this analysis the **five most intense vibrational peaks** were found at 722, 1028, 1494, 1668 and 3206 cm$^{-1}$. The full simulated vibrational frequency spectrum is shown in figure 8. Finally there were zero **calculated negative frequencies**.
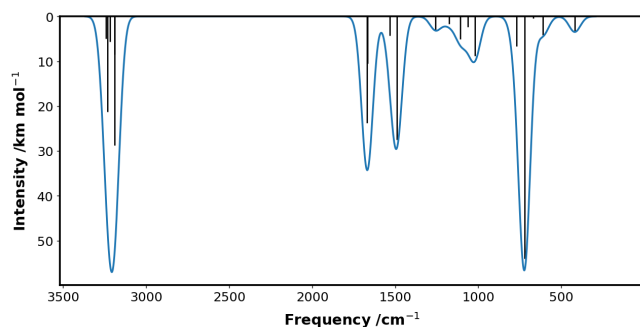


***Figure 8:*** *Graph of simulated vibrational spectrum. Calculated vibrational frequencies are shown as vetical black bars while simulated peaks with a gaussian function with FHWM: 80 cm$^{-1}$ are shown as a blue line. Peaks can be found at: 418, 722, 1028, 1253, 1494, 1668 and 3206 cm$^{-1}$.*

# Tables Of Results

## Atom Coordinates

*Table 7: Coordinates of the atoms of the system under study, as aligned to the cartesian axes by the Minimal method.*

| Element | X Coord /Å | Y Coord /Å | Z Coord /Å |
|---|---|---|---|
| C | -1.1374880 | 0.6846500 | -0.0000203 |
| C | -1.1954410 | -0.7066373 | 0.0000749 |
| C | -0.0004716 | -1.4179164 | 0.0000717 |
| C | 1.1949723 | -0.7074353 | -0.0001501 |
| C | 1.1379485 | 0.6838900 | 0.0000885 |
| N | 0.0004626 | 1.3802168 | 0.0001982 |
| H | -2.0551243 | 1.2706886 | -0.0005978 |
| H | -2.1544681 | -1.2150527 | 0.0001467 |
| H | -0.0008321 | -2.5041577 | 0.0003545 |
| H | 2.1536570 | -1.2164949 | -0.0006432 |
| H | 2.0559747 | 1.2693189 | 0.0002970 |

## Molecular Orbitals

*Table 8: Energies of the calculated molecular orbitals.*

| Level | Label | Symmetry | Energy /eV |
|---|---|---|---|
| 37 | LUMO+15 | A | 15.0342 |
| 36 | LUMO+14 | A | 14.5841 |
| 35 | LUMO+13 | A | 12.7701 |
| 34 | LUMO+12 | A | 12.6778 |
| 33 | LUMO+11 | A | 9.0193 |
| 32 | LUMO+10 | A | 8.9991 |
| 31 | LUMO+9 | A | 8.2736 |
| 30 | LUMO+8 | A | 6.8258 |
| 29 | LUMO+7 | A | 5.1991 |
| 28 | LUMO+6 | A | 5.1849 |
| 27 | LUMO+5 | A | 4.5869 |
| 26 | LUMO+4 | A | 4.2866 |
| 25 | LUMO+3 | A | 4.1186 |
| 24 | LUMO+2 | A | 2.8373 |
| 23 | LUMO+1 | A | -0.1198 |
| 22 | **LUMO** | **A** | **-0.4664** |
| 21 | **HOMO** | **A** | **-7.1729** |
| 20 | HOMO-1 | A | -7.4192 |
| 19 | HOMO-2 | A | -8.1232 |
| 18 | HOMO-3 | A | -10.1396 |
| 17 | HOMO-4 | A | -11.1930 |
| 16 | HOMO-5 | A | -11.2837 |
| 15 | HOMO-6 | A | -11.9543 |
| 14 | HOMO-7 | A | -13.1334 |
| 13 | HOMO-8 | A | -13.4087 |
| 12 | HOMO-9 | A | -14.7906 |
| 11 | HOMO-10 | A | -17.5660 |
| 10 | HOMO-11 | A | -17.6204 |
| 9 | HOMO-12 | A | -21.3179 |
| 8 | HOMO-13 | A | -22.5352 |
| 7 | HOMO-14 | A | -26.3512 |
| 6 | HOMO-15 | A | -278.7372 |

## Vibrational Frequencies

*Table 9: Energies of the calculated vibrational frequencies.*

| Number | Symmetry | Frequency /cm$^{-1}$ | Intensity /km mol$^{-1}$ |
|---|---|---|---|
| 1 | A | 383.7300 | 0.0000 |
| 2 | A | 418.8300 | 3.4700 |
| 3 | A | 610.8100 | 4.1300 |
| 4 | A | 669.5500 | 0.4300 |
| 5 | A | 720.8700 | 53.9400 |
| 6 | A | 769.0500 | 6.6100 |
| 7 | A | 903.1900 | 0.0000 |
| 8 | A | 964.8600 | 0.0000 |
| 9 | A | 1006.5300 | 0.0000 |
| 10 | A | 1019.4400 | 8.7800 |
| 11 | A | 1019.6600 | 0.0100 |
| 12 | A | 1063.0900 | 2.3400 |
| 13 | A | 1094.9400 | 0.0300 |
| 14 | A | 1107.3800 | 5.0600 |
| 15 | A | 1176.8300 | 1.7100 |
| 16 | A | 1256.6600 | 3.0700 |
| 17 | A | 1347.6300 | 0.0200 |
| 18 | A | 1387.9500 | 0.0000 |
| 19 | A | 1491.3400 | 27.4400 |
| 20 | A | 1533.3700 | 4.3300 |
| 21 | A | 1666.2100 | 10.5600 |
| 22 | A | 1669.7000 | 23.7500 |
| 23 | A | 3189.0900 | 28.7200 |
| 24 | A | 3191.5700 | 8.4800 |
| 25 | A | 3216.3200 | 5.6200 |
| 26 | A | 3232.9100 | 21.2400 |
| 27 | A | 3240.5600 | 4.9800 |

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