Supporting information available: It contains the molecular electron scattering intensity curves (see Figures S1–S2), the details of the GED experiments (Table S1), experimental interatomic distances, mean square amplitudes and vibrational corrections (Tables S2–S3) and experimental Cartesian coordinates of gauche and anti conformers in the gas-phase (Tables S4–S5).

Figure S1. Total intensity curves and additive background lines of CH$_2$CISCN for short and long nozzle-to-plate distances

Figure S2. Experimental (circles) and model (lines) molecular intensity curves of CH$_2$CISCN for short and long nozzle-to-plate distances. Difference curves are shown at the bottom

Table S1. Details of the GED experiments

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CH$_2$CISCN</th>
</tr>
</thead>
</table>

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Camera setting | Short | Long
---|---|---
Nozzle-to-plate distance, mm | 250.0 | 500.0
Accelerating voltage, kV | 60 | 60
Fast electrons current, $\mu$A | 0.16 | 0.07
Electron wavelength, Å | 0.048478 | 0.048423
Nozzle temperature, K | 338 | 336
Sample gas pressure, mbar | $3.7 \times 10^{-6}$ | $1.9 \times 10^{-5}$
Residual gas pressure, mbar | $2.0 \times 10^{-7}$ | $6.6 \times 10^{-7}$
Exposure time, s | 38 | 24
Used $s$ range, Å$^{-1}$ | 6.4 – 32.2 | 2.2 – 17.4
Number of inflection points | 5 | 3

*a Average value for the parameter is given.
*b Determined from $C_6H_6$ diffraction patterns measured in the same experiment.
*c During of the measurement.
*d Number of inflection points on the background line.

Table S2. Experimental interatomic distances, mean square amplitudes and vibrational corrections to equilibrium geometry of CH$_2$CISCN, gauche conformer

<table>
<thead>
<tr>
<th>Atom 1</th>
<th>Atom 2</th>
<th>$r_a$</th>
<th>$l_{exp}$</th>
<th>corr</th>
<th>group</th>
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<tbody>
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<td>0.030532</td>
<td>−0.003900</td>
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<tr>
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<td>0.040859</td>
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<tr>
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<tr>
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</table>
All values are in Å; corrections were calculated using SHRINK program from B3LYP/6-31G(d) harmonic and cubic force fields. The amplitudes were refined in groups by multiplying on scale factors (one per group), which were treated as independent parameters. Threefold standard deviations for the scale factors in groups 1 – 5 were 0.060, 0.141, 0.056, 0.194 and 0.138, respectively.

Table S3. Experimental interatomic distances, mean square amplitudes and vibrational corrections to equilibrium geometry of CH$_2$CICSN, anti conformer

<table>
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<tr>
<th>Atom 1</th>
<th>Atom 2</th>
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<th>$\xi_{exp}$</th>
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* All values are in Å; corrections were calculated using SHRINK program from B3LYP/6-31G(d) harmonic and cubic force fields. For the definition of groups and further information see caption of Table S1.
Table S4. Experimental (GED) Cartesian coordinates of CH$_2$ClSCN, gauche conformer (Å)

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<thead>
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<th>N</th>
<th>At</th>
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<th>Mass</th>
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<th>y</th>
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Table S5. Experimental (GED) Cartesian coordinates of CH$_2$ClSCN, anti conformer (Å)

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<th>At</th>
<th>An</th>
<th>Mass</th>
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<th>y</th>
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