Supplementary Materials

Dramatic slowing down of the conformational equilibrium in the silyl derivative of glucose in the vicinity of the glass transition

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1. Materials

1,2,3,4,6-penta-O-(trimethylsilyl)-D-glucopyranose, S-GLU (composition: 41:1 α:β anomeric mixture, distinguished according to ^{1}H NMR), was synthesized using the modified procedure adapted on the base of the literature.[1] In our case, S-GLU was prepared from D-glucose in the reaction with trimethylsilyl chloride in the presence of triethyl-amine and imidazole in dry dichloromethane. The reaction was carried out overnight at room temperature. The solution was washed in water, dried over $MgSO_4$ and purified by column chromatography on silica gel providing the product with a 98% yield. ^{1}H NMR (CDCl$_3$, 600 MHz) δ 5.00 (d, 1H, J=3 Hz, H-1α), 4.45 (d, 1H, J = 7.8 Hz, H-1β). ^{13}C NMR (CDCl$_3$, 150 MHz) δ 98.35 C-1β, 94.07 C-1α (data not shown).
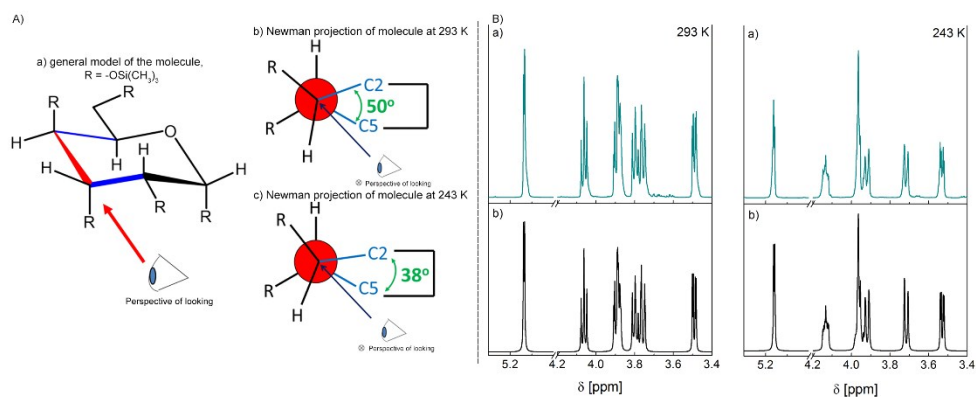

Figure S1 A) Visualization of the intra-molecular reorganization at *T*=293 K and *T*=243 K. a) image of per-*O*-silylated glucose with highlighting the bonds (blue, red), which are subjected to torsion movement. b) and c) represent the Newman projection at *T*=293 K and *T*=243 K, respectively, with torsion angles between carbon atoms C2-

C3-C4-C5. B) NMR spectra collected, respectively, at T=293 K (left panel) and at T=243 K (right panel): a) represents the simulation data, b) real spectrum.

2. Experimental part: Theoretical computations

Quantum mechanical calculations were applied to resolve the problem of band assignments in the Raman spectra to the certain vibrations during the experiment. Density functional theory (DFT) level calculations were done in the gas phase[2–4] using B3LYP functional[5–7] and standard split-valence basis sets 6-31G(d). Gaussian09 software package was used for the optimization of the geometry of molecular structures.[8] The optimized structures were taken as input files for vibrational harmonic calculations. All conformers had positive harmonic vibrations proving a true energy minimum. The theoretical methods overestimate vibrational frequencies due to neglecting the anharmonicity, incomplete incorporation of the electron correlation and the use of finite basis sets in the theoretical treatment. Therefore, the spectra were adjusted by a scale factor of 0.967.[9] Theoretical Raman intensities (I_i) were obtained from the calculated Raman scattering activities (S_i) taken into account experimental temperatures based on the expression:

$$I_i = \frac{10^{-12}(v_0 - v_i)^4 S_i}{v_i B_i},$$

(S1)

where B_i is a temperature factor, which accounts for the intensity contribution of excited vibrational states and is represented by the Boltzmann distribution:

$$B_i = 1 - \exp\left[\frac{(-hv_i c)}{(kT)}\right],$$

(S2)

where h, k, c, and T are Planck and Boltzmann constants, speed of light and temperature in Kelvin, respectively; v_0 is the frequency of the laser excitation line ($v_0 = 1/\lambda_0$ where λ_0 is the laser wavelength), v_i is the frequency of normal mode.

3. Results

3.1. The NMR analysis of conformational changes of S-GLU

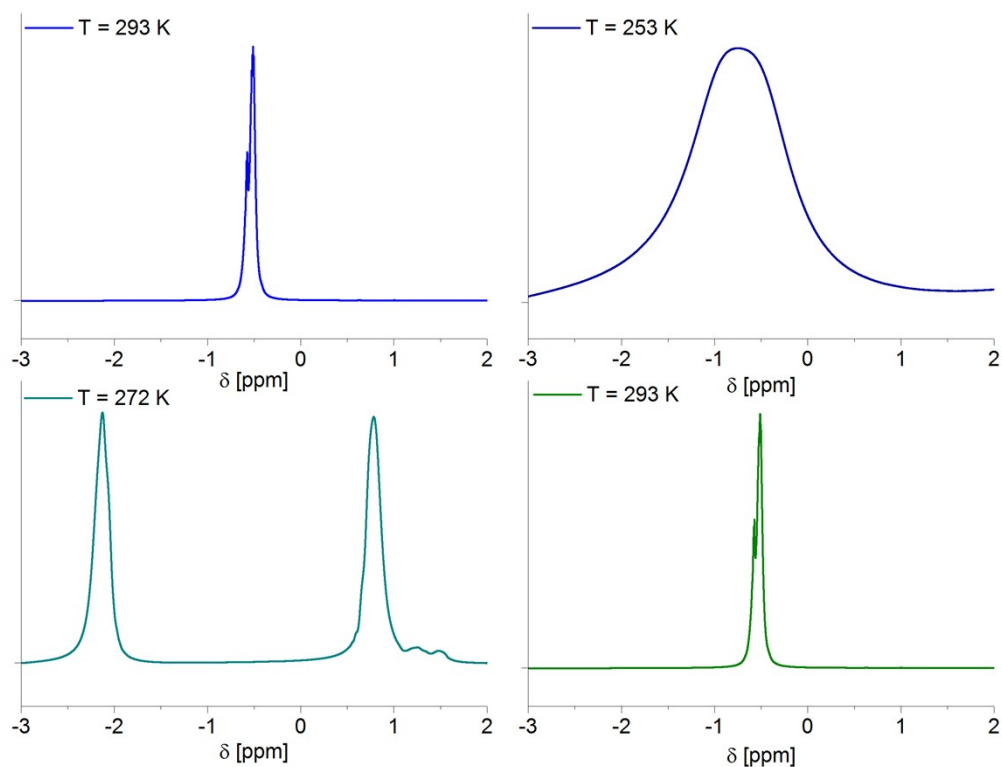The graphical representation of NMR data discussed in the main text:

Figure S2. NMR spectra collected at $T = 293$ K, upon cooling to $T = 253$ K, heating up to $T = 273$ K and further heating to the ambient temperature, $T = 293$ K.

3.2. Theoretical analysis of conformational changes of S-GLU

Theoretical calculations were carried out for different conformational systems of S-GLU to predict possible and most probably molecular configuration. As a result, the twist-boat conformers have shown that the greater ring deformation, the more diversified might be a spatial arrangement of trimethylsilyl groups leading to a separation of Raman bands in a very specific way. One can add that for one of twist boat conformer ($^2S_0$), four bands around 598, 608, 619, 628 cm^{-1} have been found (Figure 2 in the main text). Unfortunately, such band configuration is in low agreement with the position of the experimentally measured ones, indicating a lack of this conformer in a real system. It is probably an effect of the random functional group distribution implying low molecular stability, which leads to the very quick

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transformation of such conformer to more stable boat conformation. In turn, in the other twist-boat configurations, $^1S_5$ and $^3S_1$, one well-visible band centered around 625 cm^{-1} and relatively low line-width value, as well as two close-lying band maxima at 618, 624 cm^{-1} related to a specific ring configuration with more less symmetrically, and out-of-ring plane functional group arrangement are observed. This configuration enforces vibration at the same time, practically all –Si-(CH$_3$)$_3$ groups. It is worth to note that twist-boat and boat conformers may exist both in alpha and beta configurations. However, according to the theoretical data, it is hardly possible to unambiguously distinguish both isomers from each other. According to literature, the twist-boat conformations are usually in dynamic equilibrium with the boat conformations, which co-exist together due to a similar energy minimum (data not shown). Boat isomers in this consideration seem to be more ring-ordered implying the trimethylsilyl spatial rearrangement, which modifies the theoretical band layout visible on the spectrum. In this context, two forms, $^{2,5}B$ and $^{0,3}B$, are characterized by similar band arrangement to twist-boat isomers ($^1S_5$ and $^3S_1$), but with position of the main bands red-shifted about ~10 cm^{-1} and one $^{1,4}B$ form more less corresponded to the spectrum of $^2S_0$ form with bands blue-shifted about ~15 cm^{-1} (Figure 2 in the main text). It is probably associated with the ring-ordering, which enforces the specific spatial methyl-silyl group's re-orientation. Similar band arrangement ensures that twist-boat and boat conformers are usually treated as a unity. Theoretical prediction also suggests the existence of other molecular conformations as half-chair or envelope but due to very high tension in the ring, those forms are very unstable and transform very quickly to the other molecular configuration. Hence, they are not considered in more detail in this paper. In turn, the most stable, practically free of torsional strain are chair $^1C_4$ and $^4C_1$ conformations. In this consideration, $^1C_4$ seems to be energetically unfavored because of adverse van der Waals interactions of the ring substituent. In turn, specific chair conformation of pyranose rings with a dihedral angle of 60° between adjacent silyl moieties, enforces the great stability of the $^4C_1$ conformer. Those configurations in modified glucose imply the specific spatial arrangement of the methyl-silyl units at which some of the substituents are co-planar with pyranose ring, while other ones are oriented out-of-plane and symmetrically to each other designated by the ring. This ensures very weak van der Waals repulsion interactions, which generate a clearly visible band splitting observable on the theoretical spectrum with maxima at 590, 618 cm^{-1} ($^4C_1$) and 611, 621 cm^{-1} ($^1C_4$).

Moreover, the lower centered band may be assigned to the out-of-plane units, while the band at higher wavenumber originates from co-planar trimethylsilyl units. Crucial is to note that the position of theoretical bands for $^4C_1$ or $^1C_4$ conformers might in some degree of probability reproduce the experimental band position and its relative intensity, as well. However, the position of bands for chair isomers are very similar and in a real experiment, both conformers may be difficult to distinguish from each other. A similar effect may be linked to beta forms, which also may exist in the system, but due to the limitation of the theoretical calculations and experimental data, there is not possible to distinguish alpha and beta forms from each other. Therefore, both chair isomers ought to be treated as the unity similar to a boat and twist-boat analysis mentioned before. An analogous effect has been previously observed in cyclohexane.

3.3. Experimental *vs* theoretical analysis

According to the theoretical analysis of the individual conformers we can assume that the position of negative bands at around 600 and 620 cm^{-1} might correspond to the signal of boat (e.g. $^{2,5}B$ and/or $^{0,3}B$) and twist-boat (e.g. $^1S_5$ and/or $^3S_1$) conformers, while the position of the maxima at 609 and 626 cm^{-1} in some probability may be assigned to $^1C_4$ and $^4C_1$ form, respectively (Figure 4). It might suggest the conversion of twist-boat into $^4C_1$, boat into $^1C_4$ or interconversion of $^1C_4$ into $^1C_4$ due to ring-flipping process.
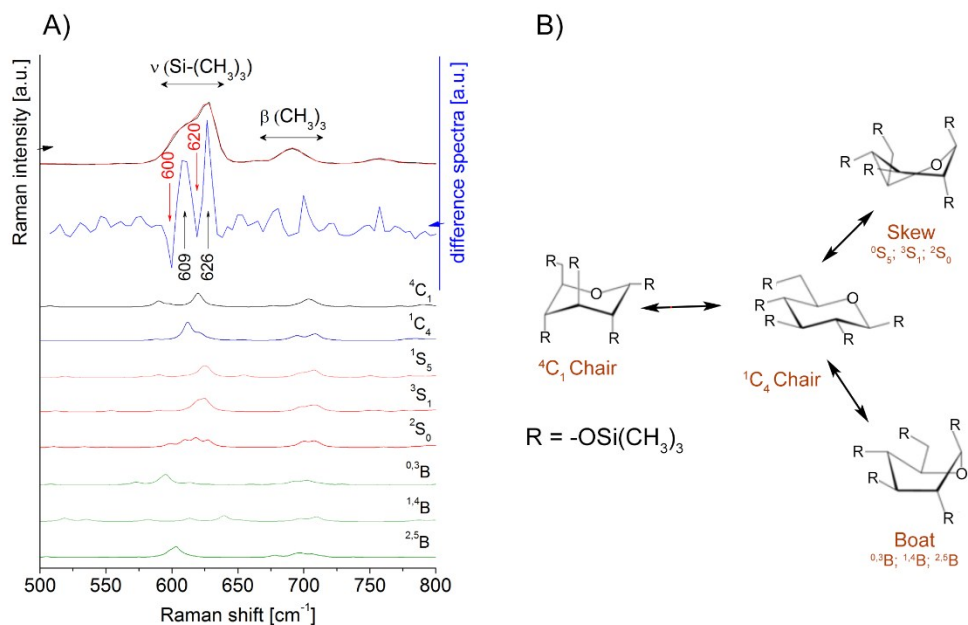
Figure S3. A) Raman spectra collected at the beginning (black spectrum) and at the end (red spectrum) of the isothermal measurements with difference spectrum (blue spectrum) of the region 500 - 800 cm^{-1}. The difference spectrum illustrates two maxima (black arrows) and minima (red arrows) indicating the direction of the transformation. The lower part of the figure presents recalculated theoretical spectra of different conformers (chair: $^1C_4$, $^4C_1$, twist-boats: $^1S_5$, $^3S_1$, $^2S_0$ and boats: $^{0,3}B$, $^{1,4}B$, $^{2,5}B$). Theoretical data corresponds to the experimental data collected at $T = 243$ K. B) Graphical illustration of possible conformational changes.

4. References

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