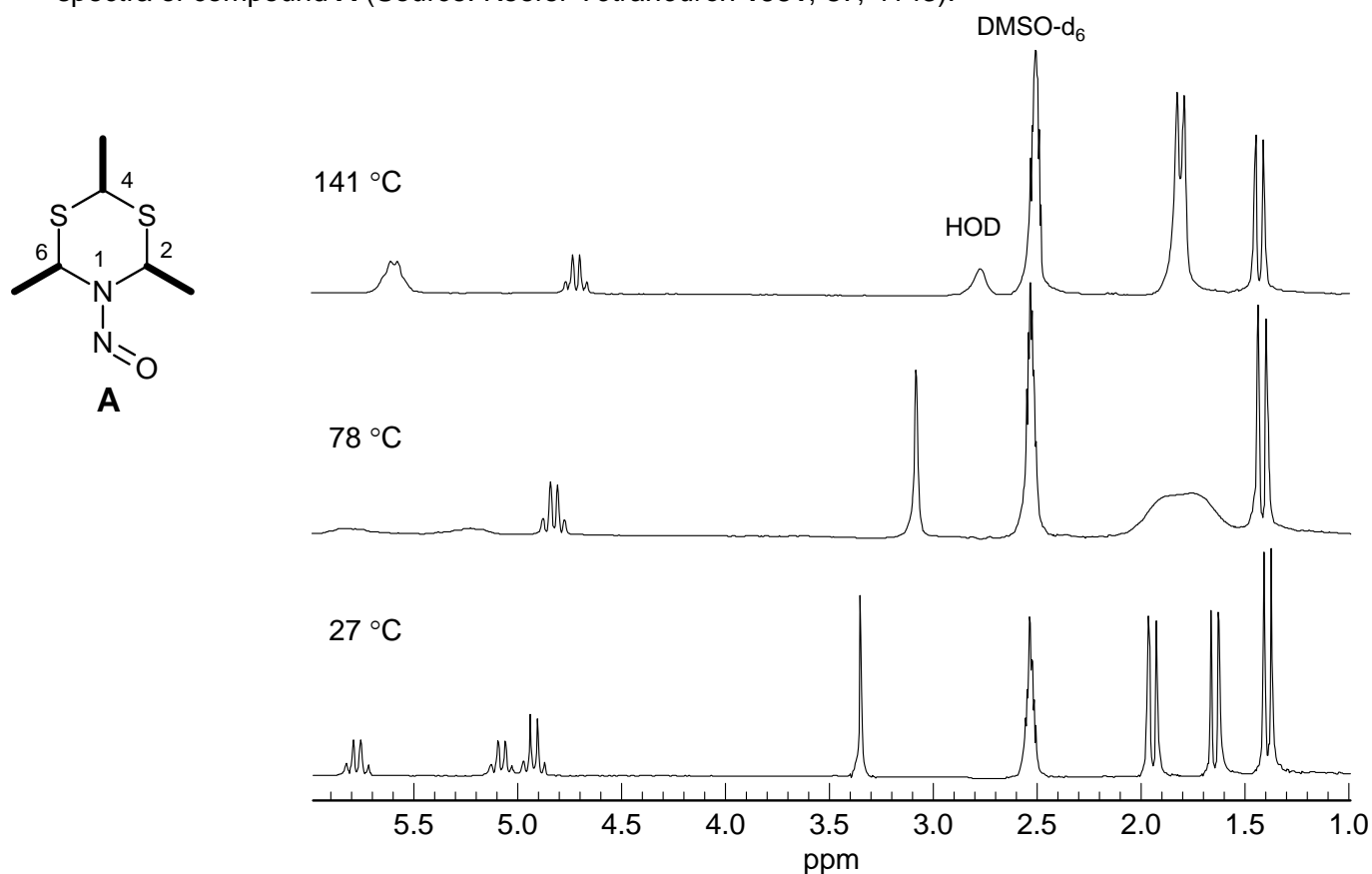


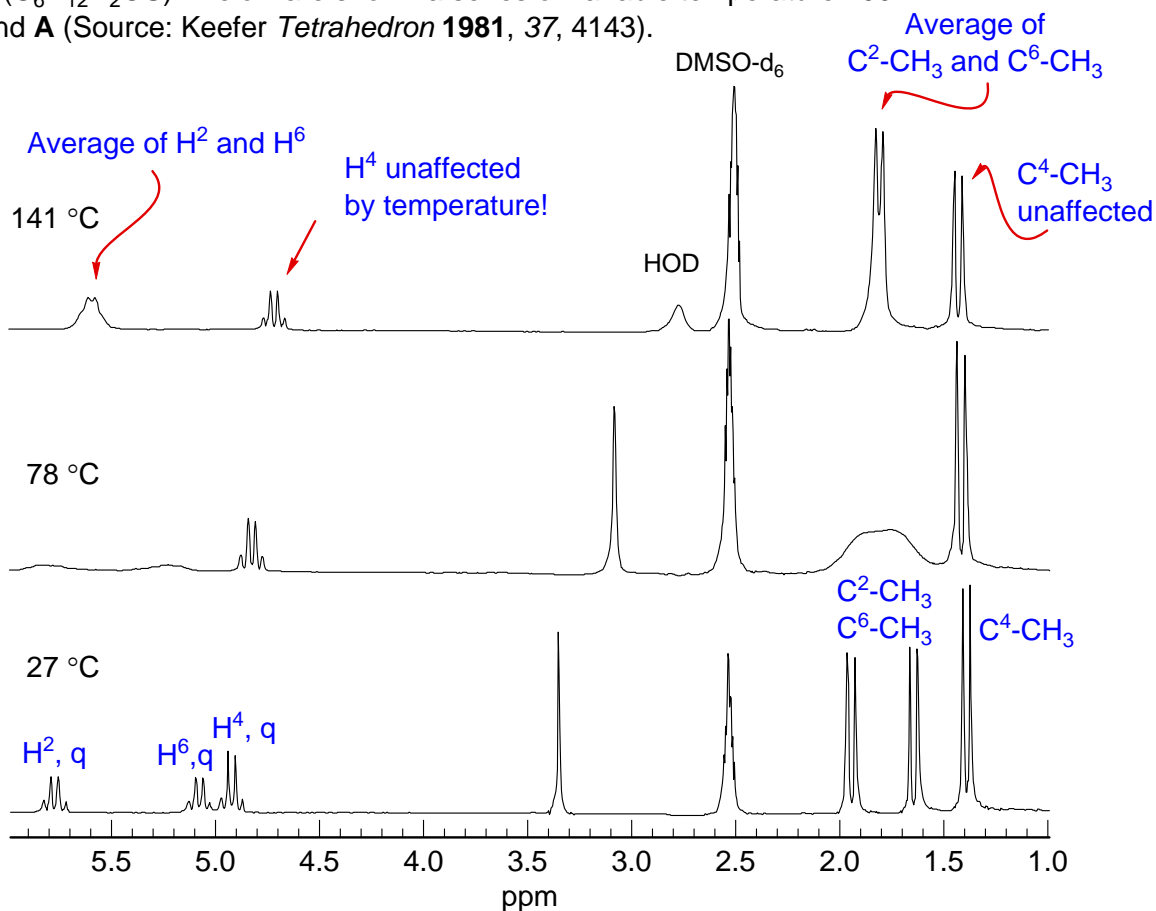
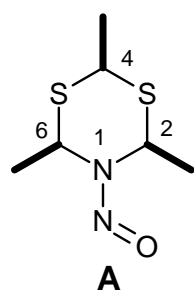
**Problem R-05N** ( $C_6H_{12}N_2OS$ ). Below are shown a series of variable temperature 200 MHz  $^1H$  NMR spectra of compound **A** (Source: Keefer *Tetrahedron* **1981**, 37, 4143).



(a) Identify the process that is causing the changes in the NMR spectra (show structures and/or conformational drawings).

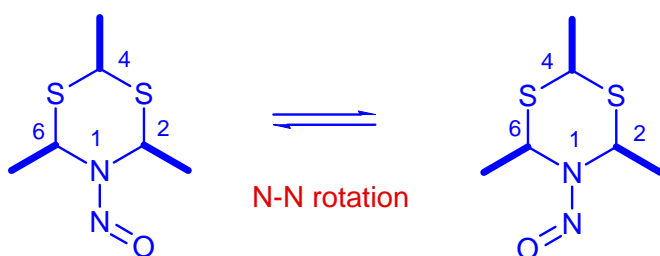
(b) On the spectrum, assign as many of the signals as possible, using the numbering system shown on the structure. Do not attempt to measure coupling constants (they are all basically 7 Hz), but do report multiplicities.

**Problem R-05N** ( $C_6H_{12}N_2OS$ ). Below are shown a series of variable temperature 200 MHz  $^1H$  NMR spectra of compound **A** (Source: Keefer *Tetrahedron* **1981**, 37, 4143).

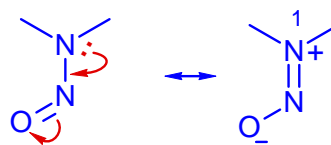


(a) Identify the process that is causing the changes in the NMR spectra (show structures and/or conformational drawings).

At low temperature the left and right portions of the molecule are different ( $CH$  and  $CH_3$  at  $C^2$  and  $C^6$ )

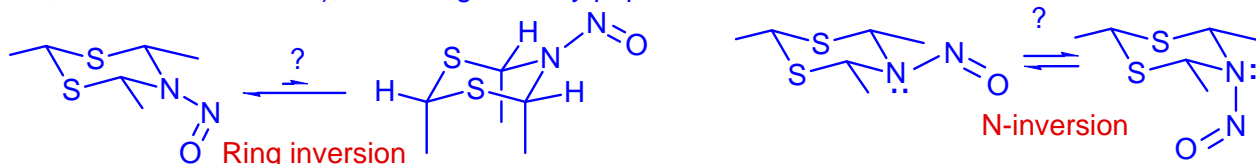


Restricted rotation around N-N bond, due to partial double bond character



(b) On the spectrum, assign as many of the signals as possible, using the numbering system shown on the structure. Do not attempt to measure coupling constants (they are all basically 7 Hz), but do report multiplicities.

Ring inversion is not a possible explanation: the ring flip isomer would be MUCH higher in energy (3 axial met with 1,3 diaxial interactions), so not significantly populated.



A nitrogen inversion process would require that the two isomers be present in a 1:1 ratio, and that at low temperature there would be 4 CH protons in a 1:1:2:2 ratio, and 4  $CH_3$  groups, also in a 1:1:2:2 ratio (we see only 3, in a 1:1:1 ratio), thus a lot of coincidences would have to occur for this explanation.