Several days ago I offered a solution to the assignment of the bridgehead carbons to (1\*R\*,2\*S\*,4\*R\*)-2-bromo-2-methylbicyclo[2.2.2]octane \*\*1\*\*. During the middle of the night I realized that the method was faulty because the solution would not accommodate the (1\*S\*,2\*R\*,4\*S\*) enantiomer \*\*3\*\* but would rather predict (1\*R\*,2\*R\*,4\*R\*) which clearly is a diastereomer. The shortcoming lay in not applying, in a heirarchical sense, [CIP rule 4b (RR/SS>RS/SR) over rule 5 (R/S)][1].<br>

Focusing on bromide \*\*1\*\*, the configuration of C<sub>2</sub> is "S" with Br>C<sub>1</sub>>C<sub>3</sub>>C<sub>9</sub>. Structure \*\*2\*\* is structure \*\*1\*\* from a different perspective to which we will refer during the ensuing discussion. To determine the configurations of the bridgehead carbons, C<sub>1</sub> and C<sub>4</sub>, a digraph is the method of choice. In the "Digraph of C<sub>1</sub>" one starts at the non-duplicate atom C<sub>1</sub> and traces the six possible paths back to duplicate atoms C<sub>(1)</sub> that are each attached to three phantom atoms of atomic number zero. The vertical chain has the top priority while the hydrogen (not shown) at C<sub>1</sub> has the lowest priority. The two horizontal chains are mirror images and they must be assigned to the second and third priorities. In these chains C<sub>2</sub> has been predetermined as having the \*S\*-configuration. Locate C<sub>4</sub> in the left chain. It has the \*R\*-configuration because C<sub>3</sub>>C<sub>8</sub>>C<sub>5</sub>. Locate these atoms in structure \*\*2\*\* and convince yourself. [I use my hands. Point your right thumb from C<sub>4</sub> to H and your fingers will point from C<sub>3</sub> to C<sub>8</sub> to C<sub>5</sub>]. In the right hand chain C<sub>4</sub> has the \*S\*-configuration because C<sub>3</sub>>C<sub>5</sub>>C<sub>8</sub>. Check these priorities in structure \*\*2\*\*.<br>

Now the left hand chain is designated as RS and the right hand chain as SS. Since RR/SS>RS/SR, the order of carbon atoms attached to non-duplicate C<sub>1</sub> is C<sub>2</sub>>C<sub>6</sub>>C<sub>7</sub>. Locate these atoms in structure \*\*2\*\* and convince yourself that C<sub>1</sub> does indeed have the \*R\*-configuration!

Now that you are versed in the method, the priorities around non-duplicate C<sub>4</sub> is C<sub>3</sub>>C<sub>8</sub>>C<sub>5</sub> because C<sub>3</sub>-chain>SS>RS>H. C<sub>4</sub> also is of the \*R\*-configuration! <\*continued\*>

<img src="https://i.stack.imgur.com/c8HVW.jpg" height="400"><br>

The digraphs below confirm the assignments to the enantiomer \*\*3\*\* (\*\*4\*\*), (1\*S\*,2\*R\*,4\*S\*)-2-bromo-2-methylbicyclo[2.2.2]octane. I'll leave the analysis to the reader.

<img src="https://i.stack.imgur.com/dJif8.jpg" height="400"><br>

 [1]: http://ursula.chem.yale.edu/~chem220/chem220js/STUDYAIDS/isomers/CIP%20rules%20NEW.html