# PROTOBRANCHING REBUTTED

Gronert[1] has published a scathing criticism of the concept of "protobranching" (see my previous blog post) put forth by Schleyer, Houk and Ma2 – SHM for short. As a review, protobranching is the term coined by SHM for attractive 1,3-interactions in alkanes. They argue that these attractive 1,3-interactions are the reason for the energetic stability of the branched alkanes over the straight-chain alkanes. Their argument largely rests on the fact that Reaction 1 is exothermic by 2.8 kcal mol$^{-1}$.

$$2\ CH_2CH_3 \rightarrow CH_4 + CH_3CH_2CH_3 \qquad \text{Reaction 1}$$

Gronert's arguments are many and I will discuss only some of them. First, he notes that choosing ethane and methane as the reference molecules leads to *all* alkanes being stabilized. The stabilization energy of *n*-heptane is 5.7 kcal mol$^{-1}$ and that of *n*-heptane is 14.1 kcal mol$^{-1}$; is this a difference that is meaningful? Under the protobranching method, the stabilization energies of norbornane and *n*-heptane are quite similar (13.8 and 14.1 kcal mol$^{-1}$, respectively) – does that mean they are equally strained? Similarly, protobranching leads to an extraordinary prediction for the resonance energy of benzene: 69 kcal mol$^{-1}$. (I find these arguments quite compelling – the use of protobranching extenuates to magnitude of many chemical effects like ring strain, π-conjugation and resonance energy to the point that they become unusable.)

Gronert notes that the C-C-C angle in propane is larger than 109.5°, suggestive of a repulsive force, and one that is in fact much larger than suggested by SHM. The "attractive interaction" is not reproduced in intermolecular models. He points out the SHM attribute the attractive 1,3-interaction in alkenes to hyperconjugation and not to protobranching, and further notes that SHM correct for the strength of the C-H bond in ethyne but not for the $C_{sp}$-C bond in propyne, nor do they make any such corrections for the alkenes.

But Gronert's main complaint rests on the fact that there is simply no evidence for an attractive 1,3-interaction. All previous suggestions for this have been refuted by many others over the past 30 years. SHM's main support rests on the ability to fit the thermodynamic trends, but Gronert points out that many other possibilities exist for doing so, including a repulsive model. There is ample evidence to support a repulsive interaction. It seems to me that Schleyer, Houk and Ma have their work cut out for them to carefully rebut Gronert's arguments.

Source: http://comporgchem.com/blog/?p=143