

# Entropic factors also contribute to the high melting points of polyhedral alkanes

**To the Editor** — In a 2011 Article, Shaik, Alvarez and co-authors reported a computational study of dihydrogen C–H...H–C interactions in dimers of linear, branched and polyhedral alkanes<sup>1</sup>. They found that the intermolecular interactions between isolated pairs of polyhedral alkanes are significantly stronger than those between linear alkanes with the same number of carbon atoms, and the discussion of these results included the question “Why do polyhedranes have higher melting points than linear alkanes of similar size?” The purpose of this Correspondence is to mention that the melting point of a solid is also influenced by the entropy change on melting, according to  $T_m = \Delta H_m / \Delta S_m$ . The reported discussion based on calculated intermolecular interaction energies and the expected number of nearest neighbours in a crystal structure addresses only  $\Delta H_m$ , which cannot alone account for trends in melting points.

It is suggested here that Fig. 1b in the Article from Shaik, Alvarez and co-authors (which shows the melting points of *n*-alkanes, cycloalkanes and polyhedranes as a function of the number of carbon atoms) is substantially

influenced by entropic factors. One contribution to  $\Delta S_m$  is the change in rotational freedom as molecules are released from the solid to the liquid. According to statistical thermodynamics, rotational entropy is dependent on the number of distinguishable molecular orientations, which is governed by the molecular symmetry. Molecules with higher symmetry number ( $\sigma$ ) have fewer distinguishable orientations, and their rotational entropy in the liquid is reduced by  $R \ln \sigma$  compared with an equivalent asymmetrical case<sup>2</sup>. Thus,  $\Delta S_m$  is smaller for a more symmetrical molecule, and the melting point is increased compared with an asymmetrical molecule with comparable  $\Delta H_m$ . The point symmetry groups of the linear alkanes ( $C_nH_{2n+2}$ ) are  $C_{2h}$  or  $C_{2v}$  for even and odd *n*, respectively, both giving  $\sigma = 2$ . The polyhedranes considered are cubane ( $O_h$ ,  $\sigma = 24$ ), adamantane ( $T_d$ ,  $\sigma = 12$ ), octahedrane ( $D_{3d}$ ,  $\sigma = 6$ ), congressane ( $D_{3d}$ ,  $\sigma = 6$ ), pagodane ( $D_{2h}$ ,  $\sigma = 4$ ), dodecahedrane ( $I_h$ ,  $\sigma = 60$ ) and cyclohexamantane ( $D_{3d}$ ,  $\sigma = 6$ ), all of which have  $\sigma > 2$ . It is notable that the molecule with the highest symmetry number, dodecahedrane ( $C_{20}H_{20}$ ), has by far the highest melting point.

It is also possible for entropy to be increased in the solid prior to melting through molecular motion. Again, this reduces  $\Delta S_m$  and contributes to an increased melting point. Molecular motion in the solid state has been studied for the alkanes, and plastic phases (where the molecules are essentially free to rotate around fixed lattice points) are experimentally established for the high-symmetry molecules cubane<sup>3</sup>, adamantane<sup>4</sup> and dodecahedrane<sup>5</sup>. These dynamic effects can also be expected to contribute to the differences in melting points seen for the polyhedranes compared with the linear alkanes. □

## References

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## Reply to ‘Entropic factors also contribute to the high melting points of polyhedral alkanes’

**Shaik and Alvarez *et al.* reply** — Andrew Bond proposes<sup>1</sup> that to explain the high melting points of polyhedral alkanes compared with linear or cyclic alkanes of the same size, besides the intermolecular interaction energies<sup>2</sup>, the symmetry-determined rotational entropy change should be taken into account, as the melting point  $T_m$  results from a balance of the enthalpic and entropic changes,  $T_m = \Delta H_m / \Delta S_m$ . He adds that molecules with higher symmetry number ( $\sigma$ ) have a smaller number of distinguishable orientations, hence their rotational entropy in the liquid phase is smaller, resulting in a smaller  $\Delta S_m$  contribution and higher melting temperatures.

The aim of our recent work on the homopolar intermolecular C–H...H–C interactions<sup>2,3</sup> was to use gas-phase

computations to find out if, and why, those non-covalent interactions are stronger for polyhedranes than for open-chain and cyclic alkanes. We concluded that our calculated interaction energies and the experimental melting points follow similar trends. We further commented that the enthalpies associated with the formation of a solid from independent molecules depends on the number and topology of the nearest-neighbour interactions, and that the higher symmetry of the polyhedranes results in a large number of nearest neighbours that produce amazingly robust networks with high melting points. We agree with Bond that the entropic factor must be considered if an understanding of the high melting points of polyhedranes at the quantitative or even semi-quantitative level is desired, but we think that the trends

in melting points cannot be rationalized if trends in interaction energies are not taken into account.

That the symmetry criterion is not sufficient for understanding the trends in melting points among the polyhedranes can be seen by comparing the highly symmetric cubane ( $\sigma = 24$ ), which has a melting point of 403 K, with other alkanes with lower symmetry numbers, such as octahedrane, congressane, pagodane and cyclohexamantane with melting points (383, 541, 516 and 587 K, respectively) that are either marginally lower or even higher than that of cubane. Moreover, methane and adamantane, both with tetrahedral symmetry, are expected to have similar rotational entropy changes upon melting, yet their melting points are as different as night and day (91 and 587 K, respectively),