CORRESPONDENCE

The 2-Norbornyl Cation Revisited

I read the two letters by Dewar and by Olah in the recent issue with considerable interest and amusement.[1,2] While I agree with almost all of Dewar's comments, it is fascinating to compare the positions taken by these authors with the original position for the 2-norbornyl cation. The difference provides an excellent case history for the psychology of scientists.

The 2-norbornyl cation was originally presented to me as the least ambiguously known case for a nonclassical ion.[3] It was then the position that σ-bridging between C-2 (the cationic center) and C-6 (the transannular carbon) was very powerful, so powerful as to distort the structure from the unsymmetrical one of the classical form to a new symmetrical one, designated the nonclassical structure. The large stabilization postulated to be provided by σ-bridging in the transition state for solvolysis of the exo isomer and its absence in the endo isomer provided the generally accepted explanation for the high exo/endo rate ratio. The symmetrical structure for the intermediate provided the explanation for the racemization accompanying the solvolysis of optically active 2-norbornyl derivatives.

The magnitude of this stabilization was considered to be huge. Calculated values for nonclassical stabilization of 50 kcal/mol[4] and 39 kcal/mol[5] were accepted without question.[6]

Goering demonstrated that there must be a difference in the energies of the exo and endo transition states of 6.0 kcal/mol to account for the high exo/endo rate ratios observed in solvolysis.[7] This provides a firm experimental basis for the magnitude of the proposed nonclassical stabilization—6.0 kcal/mol in the solvolytic transition state for the exo and ~8 kcal/mol for the fully developed cation.

Comparisons of the heats of ionization of tertiary benzylic chlorides vs. the corresponding secondary in three representative systems (Cp = cyclopentyl and Nb = norbornyl), $PhMe_2CCl/2\text{-}PrCl$, 1-PhCpCl/CpCl, 2-Ph-*exo*-NbCl/*exo*-NbCl, fail to show any significant difference between the three systems.[3] There is no evidence for a stabilization of 8.0 kcal/mol in secondary 2-norbornyl, not present in the highly stabilized classical[6] 2-phenyl-2-norbornyl cation.

Small stabilizations of 1–2 kcal/mol cannot be ruled out. They are within the uncertainties of the data. But, to retain perspective, such stabilizations are comparable to weak van der Waals interactions. The data clearly establish the absence of 6 kcal/mol of stabilization in the transition state and 8 kcal/mol in the fully developed cation. Therefore, the stabilization originally postulated to account for the high exo:endo rate ratio cannot be confirmed experimentally.

As pointed out by Dewar[1] and Kramer,[8] Olah's own ESCA spectra[9] support a nonsymmetrical structure for the 2-norbornyl cation.

Both Dewar[1] and Olah[2] now conclude that the 2-norbornyl cation is not symmetrical. But they argue that because the cation is "delocalized" it should be considered nonclassical. But *all* carbonium ions are delocalized. The high stability of the *tert*-butyl cation was attributed to delocalization (hyperconjugation) as long ago as 1943.[10] Such "delocalization" has never been considered to be a synonym for "nonclassical".

The fact is that the large stabilization required by the original explanation is not found experimentally.[3] The symmetry required by the nonclassical structure is ruled out by the ESCA results.[9] If authors wish to continue using the term for a species which has neither the large stabilization nor the symmetry of the original proposed structure, we cannot stop them. However, we can enjoy the spectacle.

Herbert C. Brown

Purdue University

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Happiness Is a Legitimate Research Project

Contrary to popular belief the quest for legitimacy, so important in the humanities and the social and political sciences, does not stop at the door of the chemistry lab.

In fact, a cursory check of the opening sentences of chemical research papers reveals two schools of thought, the we-are-doing-something-nobody-else-does legitimation (i.e., "Virtually nothing is known about X; thus we decided to investigate X...") and the we-are-doing-the-same-thing-as-everybody-else legitimation (i.e., "The current increased interest in Y prompts us to report...").

It is intriguing to speculate whether these extremes touch, i.e., if just about any research project could be accommodated within these two categories, or whether there is a third category. Probably a chemist who wrote an opening sentence going like "In our desire to add to the meager, but steady trickle of papers concerning Z we wish to report..." would be made to wash his mouth with soap by irate taxpayers and/or referees.

Alexander Senning

Aarhus University
Denmark

The Nuclear Warfare Chain Letter II

While catching up on back issues of *Accounts* recently, I came across Dr. Bunnett's editorial on the nuclear warfare chain letter.[1] It brought to mind a somewhat analogous effort 37 years ago that is still relevant to the times.

Albert Einstein and a number of other prominent Americans published a letter[2] warning about a notorious mideast terrorist, also described as a fascist and a racist, who had formed a political party and was seeking American support. Within a few decades, the constituency of this terrorist, which was explicitly compared by Einstein

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