The Disputed Charge Account

Chemists recently resurrected an age-old and famous fight over where the positive charge lies on a certain seven-carbon molecule

By LINDA GARMON

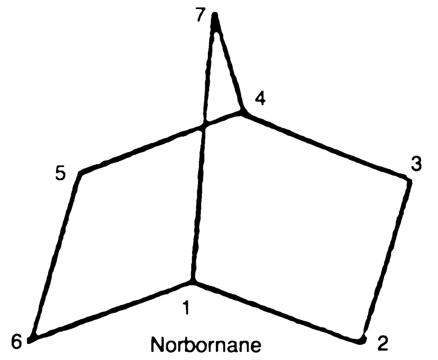
It's between rounds in one of the longest-lasting and most impassioned battles in contemporary chemistry: the fight over where the positive charge lies on a certain seven-carbon ion, or charged molecule.

In one corner stand the vast majority of participants in the fight, who believe that the positive charge is simultaneously "smeared" over, or shared by, several atoms of that molecule. Having just dealt a few sizable blows, this group says the fight now should be called in its favor. In the other corner stand the mere handful of remaining participants, who either cling to the notion that the positive charge behaves more conventionally, belonging to only one atom at a time, or at least insist that there is not yet enough evidence to support the "smeared" idea. Though it is the general consensus of the chemistry community that this minority opinion has been scientifically pummeled, its most vociferous proponent, a Nobel-Prize winning chemist, shows no signs of throwing in the towel.

While there have been several other "chemistry controversies that also...were carried forth because virtually only one of their participants would not give up," says one observer, there really have been no others quite like this debate over the positively charged molecule, or cation, called the 2-norbornyl cation (nôr-bôr′-n'l kat′-ī-ən). In some ways, it ranks among the worst of chemistry debates: Its strained, often brutal discourse, for example, led at least one prominent chemist early on to quit doing research related to the issue because he "didn't like the stress involved." But in other ways, it ranks among the best: It has depended on—and in some cases, redefined — the state of the art in several research fields. In addition, the heart of the issue — how the positive charge is distributed on the 2-norbornyl cation — "is not a negligible question," says George A. Olah, champion of the smeared theory.

The skeletal norbornyl structure "is found in many of nature's terpenes [chemicals found in plant oils]," Olah says. Moreover, the norbornyl cation is an ionic intermediate—a charged link between the neutral starting materials and neutral end products of various chemical reactions; and some of its chemical cousins are ionic intermediates in major petrochemical reactions, says Olah, of the University of Southern California in Los Angeles. Understanding the precise behavior of the 2-norbornyl cation eventually could have implications for research on both terpenes and major industrial processes.

The attempt to understand the precise behavior of the 2-norbornyl cation can be traced back to work reported in 1949 by the late Saul Winstein of the University of California at Los Angeles. Winstein was studying a chemical reaction that can start with either of two versions of the same compound: One, called the *exo*-norbornyl starting material, has a group of atoms (labeled "A" in the diagram on p. 107) substituted for a hydrogen at the carbon-2 position of norbornane in such a manner that it lies slightly above the plane formed by carbons 2, 3, 5 and 6. The other version, called the *endo*-starting material, also has the same group of atoms attached at the carbon-2 position, but this time the group pokes down below the plane.



The 2-norbornyl cation belongs to the norbornane family. "Norbornane" — which can be depicted in a sketch that resembles a roof with a steeple —is the nickname for bicyclo[2.2.1] heptane: "bicyclo," because the compound contains two rings; "heptane," because it contains seven carbon atoms; and "[2.2.1]," because the number of carbons between bridgeheads (the shared carbons, or carbon-1 and carbon-4) is two (carbon-2 and carbon-3), two (carbon-5 and carbon-6) and one (carbon-7). There are two hydrogen atoms attached to each of the carbons at positions 2, 3, 5, 6 and 7 and one hydrogen each at carbons 1 and 4. (For the sake of simplicity, hydrogens generally are excluded from diagrams of carbon compounds.) The 2-norbornyl cation is an intermediate in a reaction whose starting material has a group of atoms substituted for one of the hydrogens attached at the carbon-2 position of norbornane.

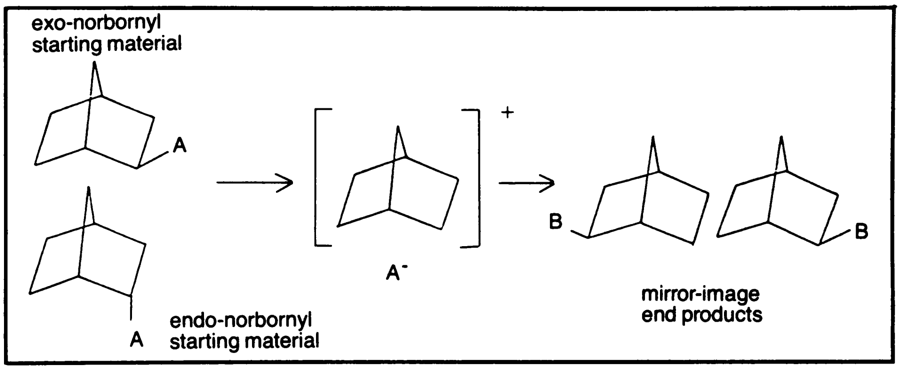
When placed in an appropriate solution, both *exo*- and *endo*-A leave their parent compounds, stealing the two electrons they shared with carbon 2. This transforms the starting material into the electron-deficient intermediate: the 2-norbornyl cation. But this positively charged intermediate lives for only a few fleeting moments, because another (negatively charged) group of atoms, B, rapidly attacks it, taking the place of A. Then, the reaction—called solvolysis—is over.

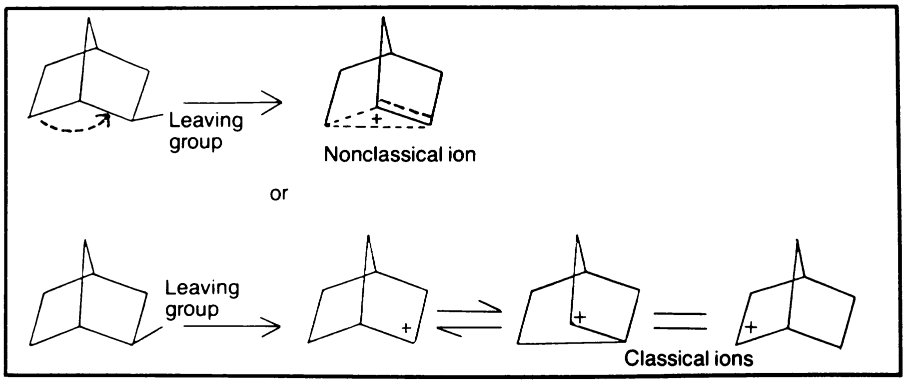
While conducting such solvolysis experiments, Winstein discovered three curious phenomena. First, the *exo*-norbornyl starting material reacts about 400 times faster than the *endo*-version. Second, whether the reaction begins with *endo*- or *exo*-norbornyl compounds, only end products that have the new B group attached in an *exo*-(above-the-plane) fashion are formed. And finally, the reaction yields not only the expected end product with B attached at the carbon-2 position, but also that product's nonsuperimposable mirror image. (Chemical mirror images have the same spatial relationship as do the left and right hand.)

To explain these curious findings, Winstein theorized that while A is leaving, the carbon-6 atom — which already bonds (shares electrons with) two carbons and two hydrogens — somehow manages to also partially bond to carbon 2. (Carbon usually only bonds to four neighbors.) This extra bond, he suggested, stabilizes the 2-norbornyl cation; helps to "push out" A; and smears the positive charge of the (electron deficient) carbon-2 atom over three carbons of the ion. The geometry of the *exo*-norbornyl starting material is conducive to smoothly forming such a smeared ion in one step, Winstein said, while the more awkward *endo*-version must first slowly form the conventional, or classical, ion — with the positive charge only on carbon 2—and then rapidly convert to the more stable nonclassical, or smeared, ion.

This theory explains why the *exo*-norbornyl starting material reacts more quickly than its *endo*-counterpart. And because the *exo*- and *endo*-versions ultimately react via the same 2-norbornyl cation intermediate — one whose smeared positive charge makes "*exo*-attack" by B

This is how it all started: Winstein observed that regardless of whether he used the exo- *or* endo-*starting material, the reaction would yield mirror-image* exo-*norbornyl end products. Winstein also noticed that the* exo-*norbornyl starting material reacted much more swiftly than the* endo-*version. ("A" and "B" represent groups of atoms attached to the norbornyl structure.)*





Where does the positive charge lie on the 2-norbornyl cation? Is it smeared over several carbons (the nonclassical ion), or does it hop back and forth from the original electron-deficient carbon to an adjacent carbon (the pair of classical ions)? Note that the two lower right structures are equivalent but oriented in space differently.

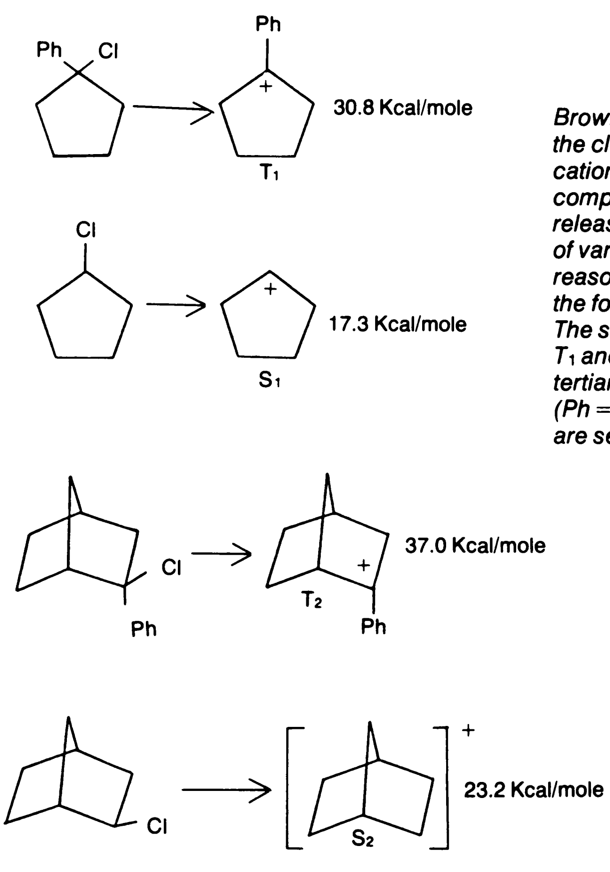
equally easy at two different positions — the theory also explains why both starting materials yield the same mirror-image end products in the reaction.

This nonclassical view of the 2-norbornyl cation seemed to be generally accepted until 1962, when Herbert C. Brown — who won the 1979 Nobel Prize in Chemistry for research not directly related to this issue — provided an alternative explanation of the curious solvolysis phenomena. Brown, of Purdue University in Lafayette, Ind., suggested that the 2-norbornyl cation intermediate is not a smeared ion, but rather two distinct ions — with the positive charge at either carbon 1 or carbon 2 — in equilibrium with each other. (Suppose you found it equally enjoyable to spend time in two distinct locations that were separated by only a small hill; if there were no other factors but your enjoyment to consider, you probably would spend equal amounts of time at each location, since it would take only minimal energy to go back and forth. This is analogous to the behavior of the proposed equilibrating ions.)

Each ion is open to attack from above the plane by B, so the mirror-image end products form. And the *exo*-starting material reacts more swiftly, Brown suggested, simply because the "*endo*-attached" leaving-group A, which lies in a fold of the parent compound, takes longer to escape.

In proposing this classical ion theory, Brown's major contention was not that the nonclassical theory was necessarily wrong, but rather that it had been too readily accepted on the basis of too little evidence. And, more than 20 years later, this is what Brown continues to argue.

Brown recently confronted Olah, his long-time opponent in the 2-norbornyl cation controversy, in the latest of a series of seminars to specifically address this issue: a petroleum chemistry symposium at the spring American Chemical Society (ACS) meeting in Seattle, Wash. Before a standing-room only crowd of about 300 chemists, Brown reported that thermochemical data — expressed as the kilocalories of heat either given off or absorbed during chemical reactions — do not support the nonclassical cation theory.

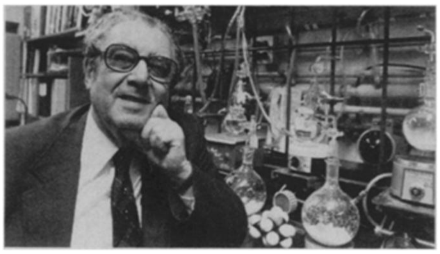


Brown sees evidence for the classical 2-norbornyl cation theory when he compares the energy released upon formation of various ions. (His reasoning is detailed on the following page.) The structures labeled T_1 and T_2 fall into the tertiary ion category ($Ph = C_6H_5$); S_1 and S_2 are secondary ions.

According to that theory, such an ion is so energetically favorable—that is, stable—that even the *endo*-norbornyl starting material, which initially forms a classical ion, prefers to rearrange to it. If such an ion exists, it should be 8 kilocalories more stable (less energetic) than its classical counterpart, Brown calculated, using the "Goering-Schewene" diagram—a graph of the energy of a chemical reaction versus the progress of that reaction. In other words, Brown predicts that upon formation, the nonclassical 2-norbornyl cation should give off 8 more kilocalories of heat per mole than does its classical counterpart. (A mole is the gram-weight of a substance that contains 6.02 x 10^{23} units—molecules, atoms or ions, for example—of that substance.)

According to the nonclassical cation theory, once the *endo*-norbornyl cation forms, it rearranges to the more stable nonclassical ion in little more than one molecular vibration (1 x 10^{-12} second). In such a short time period, it is not possible to detect whether Brown's predicted difference in heat evolution between classical and nonclassical ions exists. So, in order to see if the 2-norbornyl cation passes his "8 kilocalorie test," Brown drew inferences from thermochemical data—obtained by Edward M. Arnett of Duke University in Durham, N.C.—on a variety of ions.

B rown: The nonclassical theory is not necessarily wrong, but it has been too readily accepted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The ions can be classified according to how many carbon atoms are attached to the carbon that lost some of its electrons. The 2-norbornyl cation, with two carbons bonded to carbon 2, is a secondary ion; its tertiary relative has three carbons bonded to that carbon. Arnett has found that a particular tertiary ion, called "1-phenylcyclopentylchloride" (T_1 in diagram on page 107), gives off 14 more kilocalories of heat per mole upon formation than does cyclopentylchloride (S_1), the corresponding secondary ion in that same chemical family.

Arnett also has found that when a tertiary chemical cousin (T_2) of the 2-norbornyl cation is formed, it gives off 37 kilocalories of heat per mole. Extrapolating from the cyclopentylchloride data (with the 14-kilocalorie difference between tertiary and secondary ion heat evolution), Brown reasoned that upon formation, the (secondary) 2-norbornyl cation (S_2) should give off 23 (37 — 14) kilocalories per mole if it is a classical ion and 31 (subtract 14 from 37, but then add those 8 kilocalories that Brown predicts must be released for extra stability) if it is a nonclassical ion.

Arnett's data show that the 2-norbornyl cation gives off 23.2 kilocalories of heat per mole upon formation. "This supports the formation of a classical cation," he reported at the ACS meeting.

Brown's interpretation of Arnett's data in this manner has met with significant opposition: Arnett himself disagrees with it. In establishing the "8-kilocalories test" and then showing that the 2-norbornyl cation does not pass it, Brown "to a certain extent has set up a straw man and then knocked it down," Arnett told SCIENCE NEWS. "I think it's a numbers game," he says, "and I know of no data in the literature on ... ion energetics that support his picture of how those data can be analyzed." For example, says Arnett, to truly determine whether the 2-norbornyl cation has an "extra" stability, "then you should compare it not with tertiary ions, but with other secondary ions." And when Arnett does just that, he does see evidence for an extra-stable, nonclassical 2-norbornyl cation.

"I've come reluctantly to that conclusion," Arnett says, "because I feel a fair amount of the arguments given years ago to support the nonclassical formulation of the ion really weren't very strong." But, says Arnett, the evidence accumulated in the last several years — including his thermochemical data and analytical results reported by chemists, including Olah—points to a nonclassical ion.

Olah is such a staunch supporter of the nonclassical 2-norbornyl cation theory that he believes it should no longer be branded "nonclassical." It is only nonclassical "in the sense that organic chemists [who study certain carbon compounds] are most familiar with bonds involving two electrons between two carbons," he says. But the type of bond proposed for the 2-norbornyl cation — a two-electrons-among-three-carbon bond — does occur in many compounds in other areas of chemistry, such as organometallics (metal-containing carbon compounds). The nonclassical 2-norbornyl cation theory "is just a realization that this type of bonding also plays a major role in organic chemistry," Olah says.

Olah pioneered the development in the 1960s of methods to capture, or keep from further reacting, ionic intermediates such as the 2-norbornyl cation. This paved the way for structural probes of the ions by analytical techniques such as nuclear magnetic resonance (NMR). When a molecular sample is probed by NMR, it is placed within the bore of a magnet, where the magnetic atomic nuclei in that sample — those with an uneven number of protons or neutrons — align themselves "with" the magnetic field. Low energy radio waves that are absorbed by the nuclei, causing them to align "against" the magnetic field, then are applied. The types of energies absorbed are "fingerprint" data that are recorded on spectral printouts as peaks that identify types of bonds between atoms in the molecular sample.

At the ACS seminar, Olah reported that analyses of such NMR spectra "unequivocally" show that the 2-norbornyl cation is a nonclassical ion. Olah has observed, for example, a significant spectral shift of peaks when a known "ordinary" classical carbon ion, the cyclopentyl cation, forms from its parent compound. But when the 2-norbornyl cation forms from its norbornane parent, says Olah, such a significant shift of peaks is missing; in fact, the resulting spectrum more closely resembles certain features of NMR spectra of compounds containing "higher-coordinate carbons" ("nonclassical" carbon atoms, or ones simultaneously bonded to more than four neighbors).

The 2-norbornyl cation structure also has been probed by a revolutionary NMR technique developed by Philip C. Myhre of Harvey Mudd College in Claremont, Calif., and Costantino S. Yannoni and colleagues of IBM Research Laboratory in San Jose. Myhre and colleagues have obtained the lowest-temperature NMR spectra ever reported in the United States. (Japanese researchers T. Terao and colleagues of Japan's Kyoto University report in the Aug. 15, 1982 JOURNAL OF CHEMICAL PHYSICS comparably low-temperature NMR research.) Specifically, the California researchers have obtained spectra for the 2-norbornyl cation cooled to near absolute zero (-273°C). The researchers say they owe their success to the design of a system that keeps the helium gas—which is used for cooling—from interfering with the radio waves that are applied to the sample being probed. Says Yannoni, the successful low-temperature NMR probe was a "brute force" attempt to capture a classical 2-norbornyl cation—if it exists.

Imagine again those two equally enjoyable locations separated by a small hill. Now imagine that the surrounding temperature is so drastically lowered that you "freeze" in one of the two locations. This is analogous to what Myhre and colleagues attempted to do with the low-temperature NMR—to observe a spectrum of a "frozen" classical ion. Such a spectrum would differ markedly from a printout obtained at higher temperatures — at which the two classical 2-norbornyl ions are presumably equilibrating with each other.

But Myhre—who will report his findings in October at the Pacific Conference on Chemistry and Spectroscopy in Pasadena, Calif.—could not find those expected differences in his low-temperature NMR probe of the 2-norbornyl cation. At temperatures as low as 5 degrees above absolute zero (−268°C), the norbornyl spectra indicate a smeared positive charge, he will report.

Yannoni is a bit more reluctant to draw that same conclusion. There is a slight possibility, he explains, that classical 2-norbornyl ions could continue to equilibrate at super-cool temperatures due to a phenomenon called tunneling. Once more, imagine those two locations separated by a hill. Tunneling is analogous to burrowing right through the hill, instead of going over it (SN: 4/2/83, p. 213). The chemical community seems to view with skepticism the concept of light-particle (such as electron) tunneling and to not at all consider that anything heavier can tunnel, Yannoni says. While research reported by Barry K. Carpenter of Cornell University in Ithaca, N.Y., in the March 23 Journal of the American Chemical Society showed that heavy-atom tunneling may be possible, the prospects for something as heavy as the 2-norbornyl cation still are extremely tenuous. Nonetheless, Yannoni is withholding judgement on the 2-norbornyl cation controversy until the matter of tunneling is further investigated.

A third group investigating the 2-norbornyl cation with NMR is Martin Saunders and colleagues of Yale University in New Haven, Conn. In research reported in the June 1 Journal of the American Chemical Society, the Yale researchers looked at what changes occur in an NMR spectrum of the controversial cation when an isotope (a form of a given element that has a different mass) is introduced.

When two molecules rapidly equilibrate, the atoms involved in that conversion give an "averaged" peak on an NMR printout. Nine years ago, Saunders and colleagues discovered how to perturb this phenomenon. They found that if you took that rapidly equilibrating structure and introduced deuterium (an isotope of hydrogen), then a very large spectral split appeared; a single averaged peak became two peaks. "In the absence of deuterium," Saunders says, "the molecules rapidly go back and forth between two structures that are exactly energetically equivalent." When deuterium is substituted for hydrogen, it disrupts that energy equivalence, and that translates to a split peak on the NMR printout.

Using this analytical method — called isotopic perturbation — Saunders and co-workers observed very clear splits on the spectra of systems that are known "equilibraters." However, when they applied the method to the analysis of the 2-norbornyl cation, no such splitting appeared. "We concluded that the cation is a single, non-equilibrating nonclassical structure," Saunders says.

Brown's reaction to the use of any of these NMR data by advocates of the nonclassical theory is the same: It is a "smoke-screen," he says, over the real issue.

The real 2-norbornyl cation question, according to Brown, is, "What is responsible for the different *endo-exo* rates of reaction in norbornyl solvolysis?" Subjecting the 2-norbornyl cation to super-cooled conditions—or any "unnatural" condition necessary for NMR probes—does not address this question, he says. But, counters Arnett, "There's no way you can make the direct measurements of an *endo*-versus-*exo* ion" to answer the solvolysis question"; and anyway, he says, it's no longer the crux of the matter. The real question, says Arnett, is, "What does the 2-norbornyl cation structure look like?" And this question *can* be addressed with NMR data.

And therein lies the major reason why the 2-norbornyl cation controversy has been surfacing in journals and at meetings for more than 20 years; Brown wants to stick to the solvolysis data, while the vast majority of other participants want to look at the "big norbornyl picture." Brown, says Olah, is like an "old general [trying to limit the fighting] in a modern-day war to cavalry attacks."

Olah and many other expounders of the nonclassical cation theory agree that Brown's role as gadfly was extremely valuable in the early stages of the controversy. Researchers were inappropriately applying the notion of a nonclassical cation to explain too many chemical phenomena. In addition, Brown's inexhaustible provocation "spurred us on to the limits of our scientific capabilities," Yannoni says.

Now, however, many chemists believe that Brown's gadfly role has outlived its usefulness. Some go so far as to say that had Brown not been so insistent on maintaining that role, he would have been awarded his Nobel Prize sooner.

"Above my desk," says Saunders, "I have literally two feet of paper — all of which was received from H. C. Brown, all of which was written on this particular controversy. The man will not give up."

Meanwhile, Olah is trying out a new strategy for ending the 2-norbornyl cation fight: He's getting out of the ring. "I don't intend to do anything more on the norbornyl-cation matter," he says. "It's an old traveling show, a rehash of stuff we've heard many times over."

"Frankly," says Olah, "I believe there is nothing further to be discussed, and I suggest that if any further discussions of this topic do take place, that they be in the [ACS] Division of the History of Chemistry." ☐

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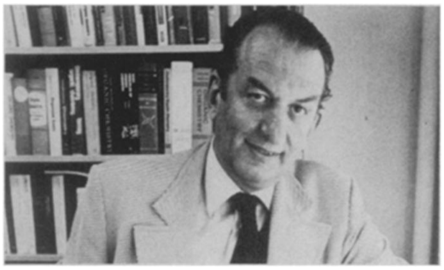

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