

“WHAT’S IN A NAME?” FROM DESIGNATION TO DENUNCIATION — THE NONCLASSICAL CATION CONTROVERSY*

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In July, 1939 Christopher L. Wilson, a member of the Hughes-Ingold group at University College, London (UCL), published a paper on the rearrangement in chloroform of the terpene derivative, camphene hydrochloride (1). This reaction belongs to the class of so-called Wagner-Meerwein rearrangements, which are characterized by a change in the carbon-carbon bond skeleton as reactants are transformed into products. These rearrangements had long puzzled and fascinated organic chemists, since they represented a challenge to classical structural theory, which rested upon the postulate of skeletal invariance. For the UCL group, rearrangements provided a highly visible test of their electronic theories of organic chemistry. Twenty-six pages of Ingold's classic *Structure and Mechanism in Organic Chemistry* are devoted to Wagner-Meerwein rearrangements (2). The title of Wilson's paper announced it as Part I of a series on the "Use of Isotopes in Chemical Reactions." The imminent outbreak of WW II seems to have precluded the appearance of further papers in the series.

From this seedling sprang a mighty cactus of contention; among its thorny spines were "some of the most powerful minds and personalities in organic chemistry (3, 4)." Whatever the status of the disputed ions, the invective they evoked was assuredly classical. The principal naysayer, H. C. Brown, seems to have been the main target of the more barbed comments. In one celebrated example he was accused by J. D. Roberts of preparing to "trample some wonderful and complex little flowers with his muddy boots (5, 6)." Lest one conclude that Brown was more sinned against than sinning, his antagonists claimed to have been provoked to these

outbursts by Brown's obduracy and duplicity (7)—all in all, not a pretty picture, one that the gentlemanly Paul Bartlett of Harvard took to be symptomatic of "abnormal psychology (8)." In their judicious review of the entire episode Arnett and co-workers even raised the question of whether it constituted an instance of "pathological science (3)." Furthermore, this topic seems to have limitless potential for generating contention. As recently as 1989 a paper on the archetypal nonclassical ion, norbornyl cation (9), ended with an editor's note indicating profound disagreement among its referees. Two separate rebuttals and a counter-rebuttal appeared a year later (10).

Is there anything to be gained by an examination of this controversy, other than titillation from watching "some of the most powerful minds" (and largest egos) in organic chemistry fighting among themselves in fierce and often undignified fashion? The response is unquestionably yes. Writing in a 1965 collection of major contributions to the dispute, Bartlett praised the increased knowledge of valence theory and solvolysis mechanisms that the controversy had afforded (11). From the historical standpoint, I believe that an analysis of this episode can contribute to our understanding of many significant issues:

- the impact of new experimental techniques on the study of reaction mechanisms
- the shifting status among major subdisciplines within organic chemistry
- the role of Cold War funding in the evolution of post-World War II chemistry

the relationship of alternate theoretical formalisms to differing representations of molecules and the conflicts that arise when new forms of representation are introduced

In this paper I concentrate on the last of these issues; I hope to treat others in subsequent publications.

Wilson's results and his associated interpretation of them are as follows. Under the catalytic influence of hydrogen chloride, camphene hydrochloride ionizes with unexpected rapidity and also rearranges, producing only one of two possible isomeric rearrangement products (Fig. 1). The speed with which the starting material lost chloride ion suggested to Wilson that the organic cation, the camphenyl ion, must be unusually stable. It also seemed highly likely that the rearrangement took place following ionization, after which the rearranged cation recaptured chloride ion to give isobornyl chloride. The entire process was reversible, with equilibrium favoring isobornyl chloride. Wilson sought an explanatory mechanism that was in

harmony with two signal findings: the ionization of camphene hydrochloride was much faster than anticipated (kinetic anomaly), and only isobornyl chloride was formed, although its isomer, bornyl chloride, was the more stable of the two (stereochemical anomaly). Figure 1 shows a "classical" mechanism for the rearrangement. However, this mechanism explains *neither* the kinetic nor the stereochemical anomaly. The first anomaly can be accounted for by assuming that chloride ion loss and carbon skeleton rearrangement are *concerted*; that is, the C-6/C-2 bond is formed simultaneously with cleavage of the C-2/Cl bond, thus bypassing free camphenyl ion altogether. Such an *assisted* ionization would indeed result in an accelerated rate of ion-

ization (2). However, even this modified classical scheme cannot accommodate the stereochemical results.

Wilson's ingenious but tentative solution to this dilemma was to propose that C-6 became only *partly* bonded to C-2, while remaining partly bonded to C-1 as well (Fig. 2a). In this bridged cation the positive charge would then be divided between C-1 and C-2. Moreover, the electron pair originally binding C-6 to C-1 would now be shared among or *delocalized* over three centers—C-1, C-2 and C-6. Wilson proposed this delocalized cation not as a fleeting transition state but rather as a reaction intermediate, long-lived on the molecular time scale. The partial bonding between C-6 and C-1 would preclude nucleophilic attack on C-1 from the *endo*

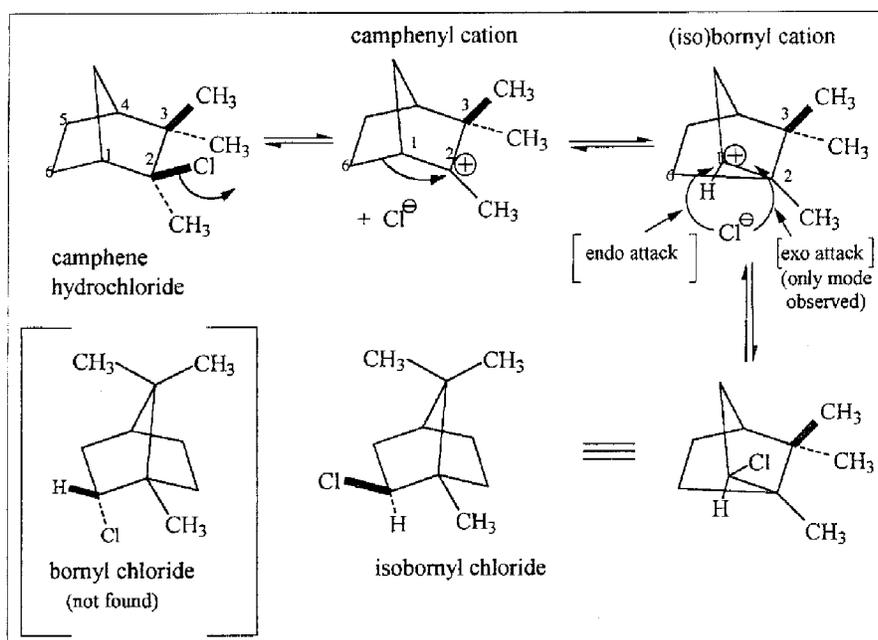


Figure 1. Classical mechanism

Lavoisier gambit—seize the nomenclature and hearts and minds will follow—Ingold in 1951 named these species **synartetic** ions (12).

The novelty of Wilson's explanation lay in the idea that the s electrons of the C-1/C-6 bond could be delocalized over more than two centers. The division of bonding electrons into two types, s and p, had been worked out several years earlier by the theoretician Erich Hückel (13). By treating the s electrons like the localized electron pairs of classical Lewis theory, while allowing the p electrons to be delocalized over more than two nuclei, the Hückel theory nicely rationalized the well established reactivity differences between single and

endo direction, thus explaining the anomalous formation of only one product stereoisomer. The proposed intermediate would thus be neither a camphenyl nor an isobornyl ion but rather a *mesomeric* ion, i.e., a *resonance hybrid* of the two. Ever mindful of what we might call the

multiple bonds. The theoretically sophisticated knew that the *s/p* division was but *one* possible representation of multiple bonds, and that a strict boundary between localized and delocalized electrons was illusory. However, since the thesis of a qualitative difference between *s* and *p* electrons helped make sense of a raft of chemical and spectroscopic data, it came to be accepted as an accurate description of the actual state of affairs.

Incorporating the *s/p* dichotomy within the already very successful conventions for drawing molecular structures was not easy, and representing electron delocalization was particularly tricky. In the case of benzene it required *at least* two Lewis structures (resonance structures), both of which were fictional. The properties of the real benzene molecule are such that a single Lewis structure is inadequate to express them, and resonance theory is one way of dealing with that inadequacy without abandoning classical molecular representations (14, 15).

Wilson was proposing analogously that there was only one organic ion involved in the camphene hydrochloride rearrangement, that the ion was easily formed because it was resonance stabilized, and that this stabilization required the delocalization of a pair of *s* electrons (Fig. 2a). Wilson's proposal occupied a mere line in his paper and was only put forward as a possibility, but its initial reception was apparently cool (16, 17). In addition to struggling with the correct structure of the ionic intermediate, Wilson also had to decide how to represent it. Literally pushed off to the side of the paragraph, the representation he chose was unusual (Fig. 2a). Double brackets were not very common and in this case rather unclear as well. This ambiguous representation, coupled with Wilson's statement (1), that "it is *possible* that [the intermediate ion] is mesomeric between [the camphenyl] and the corresponding isobornyl structures," (emphasis added) gives his presentation a very tentative air.

Subsequent to Wilson's publication, a half dozen or more papers about bridged ions appeared that sought to extend the *s* delocalization concept to carbonium ions in general (18). Although the bridged ion thesis was gaining favor, the authors of these papers reported no new experimental work and many of them overlooked Wilson's contribution. One might have concluded, a decade after its publication, that Wilson's hypothesis had produced but a small ripple in the rising tide of physical organic research. In the mind of Saul Winstein, however, it had produced much more than a ripple. Both

Winstein and the Wilson paper arrived at Harvard at about the same time in the fall of 1939. Winstein was taking up a National Research Council fellowship in Bartlett's laboratory, fresh from doctoral and postdoctoral work with Howard Lucas at Caltech, where he studied metal ion-alkene complexes and neighboring group participation, both subjects with close affinities to the Wagner-Meerwein rearrangement (19, 20). Winstein apparently first read Wilson's piece on September 22, 1939. In the course of the following three weeks he wrote out no fewer than 33 pages of notes on this paper and the antecedent literature, including derivations of the kinetic equations and verification of the calculations. He even went so far as to check the Eastman catalog for the prices of camphene, borneol, and other compounds necessary to continue the project (21). It seems fair to conclude that Winstein was not only deeply impressed by the Wilson paper but was making definite plans to pursue his own investigations in the area.

He did not act on this plan for almost a decade. However, starting in 1949 at UCLA, Winstein began publishing solvolytic studies of a simplified version of Wilson's molecule that retained its most important structural feature, the strained bicyclic ring system (Fig. 2b) (22). He mustered an assortment of kinetic, stereochemical, and theoretical tools to establish the reality of cationic intermediates with delocalized *s* electrons. In concurrent investigations at MIT and then at Caltech, Roberts used ^{14}C labeling to uncover the full complexity of the rearrangements taking place in norbornyl and other cations. Winstein thought the array of evidence strongly supported a delocalized structure for the norbornyl cation but, nonetheless, was cautious in terms of extending both the concept and the terminology. He observed that (22b):

[t]he evidence for an unclassical (*sic*) structure for the norbornyl cation lends credence to the earlier suggestion of Christopher Wilson of a possible mesomeric cation from camphene hydrochloride. Such a formulation, while again not required by any one result, takes account the most simply of products and reactivities....The number of known cases of carbonium ions the stereochemistry of whose reactions is best accounted for, under some circumstances, by so-called non-classical structures, is still small....Thus it remains to be seen how general this situation may become.

It was Roberts, struggling with the "chimerical" cyclopropylmethyl cation, who had coined the term **nonclassical** (23) as a successful alternative to Ingold's

synartetic – “earthly English [...] preferable to graceful Greek,” in Bartlett’s felicitous phrase (although Bartlett made it abundantly clear that he found “nonclassical” very infelicitous) (24). There were in fact many organic ions and radicals alleged to be “nonclassical.” Indeed, in the eyes of critics this wholesale baptism was a symptom of the imprecision and trendiness of the concept. However, critics and advocates alike have agreed that the 2-norbornyl cation is the crucial case, and this discussion will concentrate on the initial phase of the controversy over this species.

Opposition to the notion of s-electron delocalization appeared in the form of an alternative, more “classical” explanation for the kinetic and stereochemical behavior of presumed nonclassical ions. Starting in 1944 at Wayne State and continuing at Purdue, Brown began to investigate the role of steric effects on organic reactivity. Steric effects are very classical in that they depend only on the size and relative position of nonbonded atoms in the same molecule and may be treated independently of the nature of the bonding. Brown had become disturbed by the widespread explanatory power granted to the electronic theory, as a result of which “many phenomena which today are recognized as resulting from steric forces were attributed to the operation of purely electronic factors....attention to the role of steric effects in organic chemistry sank to a very low ebb (25).” Beginning with very modest means, Brown embarked on a lifelong effort to give steric effects their due.

It was not long before Brown and Ingold came into conflict over Brown’s theory of steric strain (5). In essence, the theory holds that the course of a reaction can be profoundly affected by crowding in the reactants, products and/or intermediates. Camphene hydrochloride is just such a crowded reactant (Fig. 1), and the loss

of chloride during ionization would partly relieve that crowding. Thus, the unusually high reactivity of camphene hydrochloride could be explained by the relief of ground state steric strain, without the invocation of any special

electronic effect. By the time Brown publicly challenged the nonclassical ion hypothesis during a Chemical Society meeting in 1962 at Sheffield, England, the focus of the battle had become the norbornyl system (25). The two positional isomers of 2-norbornyl chloride, *exo* and *endo*, differed in reactivity by a factor of several hundred. To Winstein this clearly signaled that loss of chloride from the *exo* isomer led to a single organic ion stabilized by s-delocalization (22).

Brown’s counterproposal was that the reactivity of the *exo* isomer was normal and that of the *endo* isomer retarded by steric effects. In Brown’s model *endo* ionization would

lead to an increase in steric congestion, whereas *exo* ionization would not. Furthermore, Brown insisted that the rearrangement could be accounted for by an equilibrium between two distinct, “classical” organic cations rather than requiring a single, delocalized cation (Fig. 2b)(26).

Brown’s opposition to nonclassical ions puzzled as well as provoked many of his opponents. In the research that ultimately earned him the 1979 Nobel Prize, Brown explored the organic chemistry of diborane, B_2H_6 . This

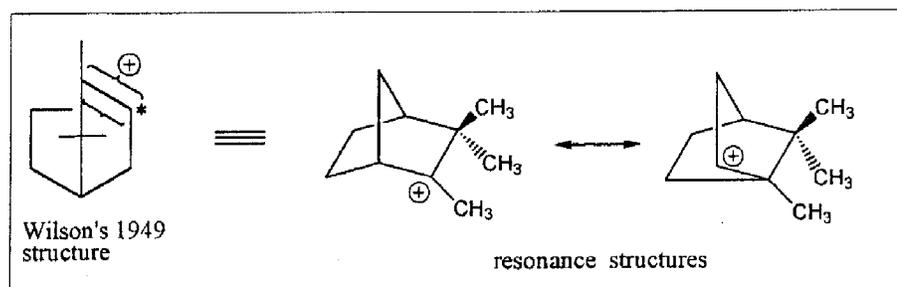


Figure 2a. Intermediates in the rearrangement of Camphene Hydrochloride

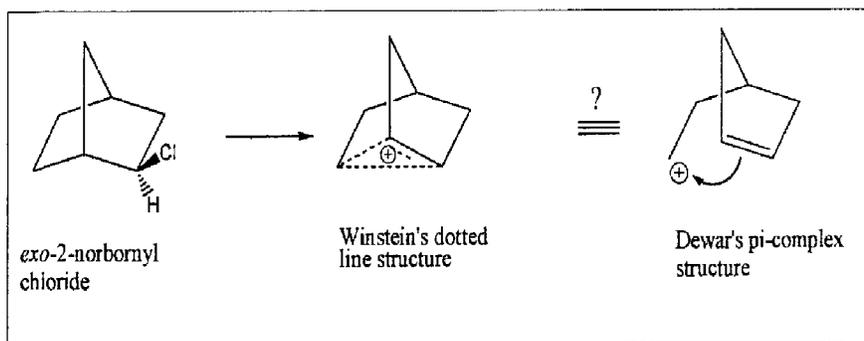


Figure 2b. Winstein and Dewar’s structures for the intermediate from Solvolysis of *exo*-2-Norbornyl Chloride

compound had long posed a structural conundrum, one that was finally solved by assigning it a pair of two-electron three-center B-H-B bonds. In other words, diborane exhibited just the kind of s-electron delocalization that Brown refused to recognize in nonclassical carbocations. In response to charges of inconsistency, Brown pointed out that diborane exhibited its delocalized structure only in the gas phase, while in solution where most nonclassical ion chemistry was being studied, diborane reverted to more "normal" modes of bonding (25). He also asserted that he was not opposed in principle to the concept of s-delocalization; the experimental data just did not support it. Brown likes to invoke Occam's Razor and to claim that "Nature is simple (27)." One might, however, see the problem as not how simple nature is but how subtle.

Brown's inability to accept the nonclassical ion hypothesis was rooted in the intertwined strands of his entire scientific career. In order to quantify steric effects, Brown studied a variety of equilibria among Lewis acids and bases. The results led him to the general conclusion that, while Lewis acids formed strong complexes with donors of the n-class and weaker complexes with members of the p-class, "donor-acceptor interaction has never been demonstrated for saturated alkanes or cycloalkanes, such as would be involved in the extension of participation to the proposed s-class (28)." In addition, Brown and his coworkers had formulated an important extension of the Hammett equation (29), itself based in "classical" resonance theory, which rested on a strict division between s- and p-electrons (30). Thus, one important issue at stake was the viability of the venerable and successful classical system of representing molecular structure. The system had managed to incorporate the Lewis electron pair bond and its numerous implications. It even accommodated resonance theory, although that development came perilously close to stretching the system to its limit. Further erosion of the distinction between s- and p-electrons could be seen as possibly undermining one of the most compact and powerful qualitative tools available to the organic chemist.

Brown was heavily outnumbered in this fight; several commentators likened him to "Horatio at the bridge (31)." Poised against him was an international coalition consisting of Hughes, Ingold, Dewar, Bartlett, Roberts, Cram, and Winstein, soon to be joined by a number of equal and lesser luminaries. But within the allied camp there were differences that were themselves of great significance. For if the physical organic "estab-

lishment" (32) shared ideas about structure and reactivity that were much more indebted to quantum mechanics than were Brown's, there remained the troublesome fact that there was more than one way to harness quantum mechanics to chemical ends.

Nye has described in detail how two rival paths formed and diverged in the 1930s (15): valence bond (VB) theory, with which resonance theory is closely allied, and molecular orbital (MO) theory. While there was more than a little sniping between the principal players over which approach led to "true understanding," for many chemists the crucial issues were more pragmatic: how well the methodology accorded with long established chemical concepts, and how effectively the calculations produced theoretical parameters of interest and reproduced important experimental measurements. The VB/resonance approach had a clear advantage with respect to the first criterion. Pauling insisted that resonance theory had purely chemical roots, and he was as well its very persuasive advocate. In that respect he far outshone Robert Mulliken, the champion of molecular orbital theory (33). When it came to the second consideration the outcome was considerably less clear and depended on the nature of the molecules under study, the properties being examined, and the skill and ingenuity of the theoretician.

Although hardly lacking in theoretical sophistication, the Hughes-Ingold group was quite committed to resonance terminology. Saltzman has described how Ingold's development of mesomerism actually anticipated many resonance concepts (34). The smooth blending of Ingold mesomerism and the Pauling/Wheland resonance made that commitment perhaps inevitable (35):

The inception of the theory of mesomerism slightly preceded (1926) the discovery...of the fundamental significance of quantal resonance for the formation of covalent bonding (1927). However, during the following years, it became evident that quantal resonance has a closely similar significance for that modification of covalent bonds which is described in the theory of mesomerism..

At least one of Ingold's admirers, the author of an influential textbook, seemed to harbor doubts about the utility of MO theory for most chemists (36).

It is certainly not the case that MO theory lacked adherents in the UK. The British theoreticians Christopher Longuet-Higgins and Charles Coulson (37) were pioneers in applying quantum mechanics to chemical problems. One of their younger colleagues who very

strongly believed in the power of MO methods in organic chemistry was Michael J. S. Dewar (38), but he was on the "wrong" (i.e., Robinson's) side of the Robinson-Ingold dispute (39). As a result the relations between Dewar and Ingold were cool at best, and often worse (40). Dewar eventually migrated to the US, having already had a major impact on leading edge American physical organic chemists, who were chafing at the limitations of resonance theory.

Because of its qualitative aspect and its use of classical structural representations, resonance theory is very appealing. Once the rules for manipulating these formulas have been mastered, one is able to rationalize a large body of experimental data with amazing ease. Yet, as one presses the technique, it becomes necessary to keep adding *ad hoc* rules and hypotheses to explain, for example, why benzene is aromatic but cyclobutadiene is antiaromatic, or why cyclopropenyl cation is isolable but cyclopropenyl anion is not. MO theory can rationalize these differences without resorting to *ad hoc* hypotheses (41).

For Winstein and Roberts, then, as for Brown, the 2-norbornyl cation was a hook on which to hang a much larger agenda. The Californians were intent on alerting organic chemists to the benefits of abandoning resonance for molecular orbital theory. Roberts has described how difficult it actually was to use the seductively simple resonance approach (42):

And there were others...who didn't understand what Pauling was talking about, particularly with benzene. Pauling would say, 'Well, you've got two resonance forms of benzene, and they're nearly the same.' And he said, 'If they're nearly the same, they're both important, the molecules are a composite of the two forms, and will not be like either form.' Nobody could understand the reality of the separate structures, and Pauling's book wasn't much help on this.

Thus, the nonclassical ion controversy was not only about the scope of electronic theories in organic chemistry; it also concerned the claimed *superiority* of one of the two prevailing theories. While resonance is a very useful tool for the *explanation* of experimental findings, MO theory is in many ways more effective for **exploration** of potentially new phenomena. After Andrew Streitwieser arrived in Roberts' laboratory as a postdoctoral fellow concentrating on MO calculations, he and Roberts proceeded to have a "wild time.... One or the other of us would draw some new structure. I remember doing things that hadn't been contemplated before.... Anything that we could do, we would do (33)."

Winstein's conceptions of homoallylic resonance and homoaromaticity demonstrated the power of MO theory quite dramatically (43).

In the US enthusiasm for MO theory was an integral part of a general sense that American physical organic chemistry had come of age and was at least the equal of that of the English school. No one questioned Ingold's singular role in bringing the field to center stage worldwide (44). At the same time, his often imperious manner did not sit too well with the ex-colonials (45). Ingold's practice of aggressively coining and promoting his own systems of nomenclature was particularly effective at raising hackles on this side of the Atlantic (46):

In the electronic interpretation of organic reactions certain English chemists have been pioneers. Their views might originally have been more cordially received in [the US] if presented inductively and in terms whose meanings are well known.

Beyond resenting Ingold's linguistic hegemony, many Americans felt that his views had become dogmatic on some issues and impervious to revision (47). Within this context Roberts' assessment of the significance of Ingold's achievements is perhaps not quite so startling (48):

The thing that depressed me about physical organic chemistry and the Ingold work was that it was terribly important in a way, and yet it really didn't do much for organic chemistry.

The reasons for Roberts' reservations become clearer when he lays out his vision of a characteristically American style of physical organic chemistry (49):

Bartlett set a new style for physical organic chemists. Physical organic chemistry was going big in Britain...[b]ut they were working on compounds you could get off the shelf. They never made anything special; they did not utilize the special characteristic of organic chemistry, which allows you to tailor make molecules to prove particular kinds of concepts.

Of the many conclusions that might be gleaned from revisiting the nonclassical ion controversy, one is very familiar. Struggles among chemists over competing representations are often protracted and intense. Since at least the time of Lavoisier, chemists have known that symbols do not merely describe preexisting entities but rather help create and shape them. Ingold's commanding position in physical organic chemistry is due in part to his astute recognition of that fact (50). The ways in which chemical bonds are *represented* are as much a matter of contention as theories that specify how they

are constituted (51). Thus, even when the protagonists agree on major conceptual issues, such as the superiority of MO over VB methods, there is ample room for dispute over representational issues. In this instance as well, nonclassical ions served as lightning rods. Dewar suggested in 1946 that carbonium ions undergoing rearrangement could be represented as p-complexes and further elaborated this proposal in his 1949 textbook (52). Thus, for Dewar, Winstein's claims for the nonclassical nature of the norbornyl cation did not constitute "a major contribution to chemical theory;" Winstein was merely confirming Dewar's prior proposals. According to Dewar, Winstein's hostility toward p-complexes was not only ungenerous to a junior colleague (53):

[it] had unfortunate consequences for organic chemistry, because the large majority of 'nonclassical carbocations' are, in fact, p-complexes and their chemistry can be interpreted much more simply and effectively on this basis than it can in terms of the obscure 'dotted line' representation that Winstein introduced... (Fig. 2b).

Not surprisingly, Winstein had reservations about Dewar's motives and methods. After praising Dewar's "skillful qualitative discussion of the wave-mechanical basis of chemical bonding, especially from the molecular orbital viewpoint," Winstein complained about the book's "novel interpretations, novelty often being achieved by mere substitution of new language for existing explanations and employing a 'p-complex' interpretation for everything conceivable (54, 55)."

Arguments about the superiority of one notational convention over another are often motivated by personal pique and priority claims. Nonetheless, different conventions can lead to different outcomes. A graduate student attending a seminar on the nonclassical ion problem was inspired to conceive a very important experimental approach to the problem because he had seen Streitwieser's then recently published three-dimensional MO structure for the 2-norbornyl cation (56).

Introducing a planned series of articles on "The Nonclassical Ion Problem," the editor of *Chemical and Engineering News* wrote (57):

[t]o someone not expert in carbonium ion chemistry, the nonclassical ion problem may seem largely one of notation.... But the root of the problem goes much deeper than notation and nomenclature, or the topic could surely not have absorbed so much of the energies of some of the leading physical organic chemists for more than 15 years.

Precisely so. Speaking of his student Robert Mazur's work on the "chimerical" cyclopropylmethyl cation, Roberts put his finger on one of those deep problems (58):

It was especially important as the opening of the Pandora's box of an extraordinarily difficult and subtle problem—a problem concerned in an important way with what we mean when we write chemical structures on paper.

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26. H. C. Brown, *The Nonclassical Ion Problem*, with comments by P. v. R. Schleyer, Plenum Publishing, New York, 1977, Ch. 6, 8.
27. That these themes constitute a leitmotif for Brown is attested to by numbers of his graduate students and postdoctoral fellows: *Remembering HCB: A Collection of Memoirs by Colleagues and Former Students of Herbert C. Brown*, Dept. of Chemistry, Purdue University, 1978.
28. H. C. Brown, "The Nonclassical Ion Problem," *Chem. Eng. News*, Feb. 13, 1967, 87-97.
29. L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 1940, 184-207.
30. H. C. Brown and L. M. Stock, "A Quantitative Treatment of Directive Effects in Aromatic Substitution," *Adv. Phys. Org. Chem.*, **1963**, 1, 35-154.
31. That precise characterization is used by both Roberts (Ref. 7, p 89) and Brock (Ref. 4).
32. Both Brown and others have referred to Brown's feeling of exclusion from the bicoastal American physical organic network: H. C. Brown, interview with L. Gortler, June 7, 1982; Ref. 7, p 250.
33. According to Roberts, "...if Pauling had really pushed the molecular orbital theory, and Mulliken had pushed resonance, I just sort of have the feeling that we may never have heard much about resonance" J. D. Roberts,

- interviews with L. Gortler, January, 1979 and January, 1981.
34. M. D. Saltzman, "C. K. Ingold's Development of the Concept of Mesomerism," *Bull. Hist. Chem.*, **1996**, *19*, 25-32.
35. Ref. 2, p 82.
36. "Both the electron pair method and the molecular orbital method are approximations, and the exact truth probably lies intermediate between them. The latter cannot be described as a wave-mechanical theory of valency, however, and the conception of the 2-electron bond as originally put forward by G. N. Lewis still provides the most useful picture of the molecule for the purpose of interpreting chemical phenomena" (H. B. Watson, *Modern Theories of Organic Chemistry*, Oxford University Press, Oxford, 1937, 14; emphasis added). In the second edition (1941) the underlined phrase was replaced by a more neutral one.
37. C. A. Coulson, *Valence*, Oxford University Press, Oxford, 1952.
38. M. J. S. Dewar, *The Electronic Theory of Organic Chemistry*, Oxford University Press, Oxford, 1949.
39. M. D. Saltzman, "The Robinson-Ingold Controversy: Precedence in the Electronic Theory of Organic Reactions," *J. Chem. Educ.*, **1980**, *57*, 484-488.
40. M. J. S. Dewar, "Some Comments on 'A Semiempirical Life,'" *Chem. Intell.*, **1997**, *3* (1), 34-39; K. J. Laidler, K. T. Leffek, and J. Shorter, "Some Comments on 'Some Comments on 'A Semiempirical Life,'" an Article by Michael Dewar," *Chem. Intell.*, **1997**, *3* (4), 55-57.
41. J. D. Roberts, *Notes on Molecular Orbital Calculations*, Benjamin, New York, 1961.
42. J. D. Roberts, interview with Rachel Prud'homme, 1987, Caltech Archives, Pasadena, CA, 47. See related comments in Ref. 38, p 15.
43. S. Winstein, "Nonclassical Ions and Homoaromaticity," *Quart. Rev. Chem. Soc.*, **1969**, *23*, 141-176.
44. Winstein expressed great pride in "join[ing] Ingold and Hammett on the list of recipients" of the American Chemical Society Norris Award (letter to C. R. Hauser, April 13, 1967, Winstein Collection, UCLA, Box 2).
45. Davenport very aptly chose the title, "C. K. Ingold: Master and Mandarin of Physical Organic Chemistry," for his retrospective survey of Ingold's accomplishments (*Bull. Hist. Chem.*, **1996**, *19*, 1-98).
46. P. D. Bartlett, review of Watson (Ref. 36): *J. Am. Chem. Soc.*, **1938**, *60*, 2278.
47. Hearing that Ingold had been ignoring one of his important discoveries, the special salt effect, Winstein observed that "a good many Americans think he has been an ass in his recent papers on ion pairs and solvolysis. In fact, I'm building up to murder him" (letter to E. F. Jenny, January 13, 1958, Winstein Collection, UCLA, Box 2).
48. Ref. 33, p 94.
49. Ref. 42, p 32
50. Ref. 15, pp 269-271.
51. B. T. Sutcliffe, "The Development of the Idea of a Chemical Bond," *Int. J. Quantum Chem.*, **1996**, *58*, 645-655.
52. Ref. 38, pp 211-213.
53. M. J. Dewar, *A Semiempirical Life*, American Chemical Society, Washington DC, 1992, 46-47.
54. S. Winstein, review of Dewar (Ref. 38): *Chem. Eng. News*, **1949**, *27*, 3440.
55. The early evolution of different representations for the 2-norbornyl cation is described by G. D. Sargeant, "The 2-Norbornyl Cation," in G. A. Olah and P. v. R. Schleyer, Ed., *Carbonium Ions*, Wiley-Interscience, New York, 1972, Vol. III, 1103-1106.
56. This intriguing story and much else relating to the non-classical ion controversy may be found in B. P. Coppola, "Deeper Beneath the Surface of the Chemical Article: Richard G. Lawton and the Norbornyl Cation Problem," *Chem. Intell.*, **1998**, *4* (2), 40-49.
57. Ref. 28, p 87.
58. Ref. 7, p 64.

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