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Textbooks and tensions that shaped physical organic chemistry in its formative years

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ABSTRACT: By the 1930s, physical organic chemistry had become sufficiently established in American and British universities to produce a market for textbooks in the field. Between 1937 and 1949, five textbooks appeared from UK and US authors; these set the framework for their successors for some years after. A close examination of these five reveals dissension about some major issues that often arise when a new subdiscipline is seeking a place in the sun: the nature of the audience; the basic theoretical framework; the standard nomenclature and formats for representation; and the identity of the 'founding fathers.' Copyright © 2005 John Wiley & Sons, Ltd.

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Radical changes in existing disciplines and the birth of new disciplines are subjects of great interest among those who study the evolution of the sciences. For example, studies of the so-called Chemical Revolution constitute a virtual industry within the history of chemistry,[1] and the attention paid recently to the history of quantum chemistry shows that more contemporary developments also command attention.[2] The creation of physical organic chemistry as a major sub-discipline is no less worthy of consideration.

Such accounts can hold as much interest for chemists as for those who examine the field from other perspectives. I myself have found that reading them has taught me much about how physical organic chemistry assumed the shape it has today (for the history of physical organic chemistry, see Ref. 3). Inquiring about our past may enable us to gain a greater control over our present.

In order to start an inquiry into its origins, one must ask how one knows that a field actually came into existence, and when. One clear indication is the appearance of university courses devoted to it, which in turn stimulate the writing of textbooks. The introduction of a recent volume concerned with chemistry textbooks asserted that, 'The task of stabilizing a body of knowledge, when that knowledge is in a dynamic state, and the tendency in many textbooks to conceal the controversies that ultimately made them possible, surely invite deeper analysis.'[4] In this paper, I examine a selection of early textbooks of physical organic chemistry to reveal issues that arose during a crucial period when the subject was finding a niche in some British and US university curricula. (The term 'physical organic chemistry' only came into existence in 1940 with the publication of Hammett's book by that name. It then gained increasing currency, especially in the Anglophone world.)

Although there had been seminal research in organic reaction mechanisms as far back as the turn of the 20th century, particularly by the English chemist Arthur Lapworth,[5] the topic only began to flourish after World War I. Between 1919 and 1936, several monographs devoted to organic chemical theory and reaction mechanisms appeared in German and English, but none of them was intended as a textbook for students.[6] Thus, they addressed the practitioner at least as much or more than the beginner and would therefore have been problematic for classroom use.

The first true textbook specifically intended for undergraduate and graduate students was published in 1937,[7] and the following 12-year period, 1937–49, was very important in setting the parameters for future texts. Four years later, C. K. Ingold published his commanding overview of the field.[8] No subsequent textbook could possibly ignore it even if that meant no more than reacting against its perceived shortcomings. I have analyzed the five books published in English during that 12-year period that qualified as physical organic textbooks. The virtues and defects of these pioneering works would have a decisive effect on the format and content of all their successors.

Table lists the books in publication order together with some relevant information: authors' nationality and discipline area; their professional honors; and the percentage of the text devoted to discussions of mechanisms. What these books all had in common was that they sought

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Table 1. Physical organic textbooks in English, 1937–1949, showing authors' doctoral field, institutional affiliation and honors, dates and length of 1st and 2nd editions and mechanistic content

Title, author(s) (UK or US; PhD)	Academic affiliation of author(s)	Honors[a]	1st ed 2nd ed	Pages	Mechanism content (%)
Modern Theories of Organic Chemistry, Herbert B. Watson (UK; organic)	City of Cardiff Technical College, Wales		1937 1941	218 267	71
Physical Organic Chemistry: Reaction Rates, Equilibria, and Mechanisms, Louis P. Hammett (US; physical)	Columbia University, New York	NAS	1940 1970	404 420	67
The Theory of Organic Chemistry: an Advanced Course, Gerald E. K. Branch (US; physical/organic) and Melvin Calvin (US; physical/inorganic)	University of California, Berkeley	Nobel Prize (1961); NAS	1941	523	20
Electronic Interpretations of Organic Chemistry, A. Edward Remick (US; organic)	Wayne (State) University, Detroit		1943 1949	474 600	53
The Electronic Theory of Organic Chemistry, Michael J. S. Dewar (UK, organic)	Queen Mary College, London	FRS; NAS	1949	324	75

[a] NAS, National Academy of Sciences; FRS, Fellow of the Royal Society.

to ground the new discipline in transition-state theory and quantum mechanics. However, they also displayed significant differences, and a comparison among them suggests some interesting conclusions. For example, there seems to be little correlation between the scientific eminence of the authors and the success of their books, if we judge success by the printing or not of a second edition. (Clearly, better indicators would be, *inter alia*, adoption statistics, referee reports and relevant publishers' and authors' correspondence. Reviews might also be helpful, although the preferences of individual reviewers will weigh heavily since the number of reviews is generally small.

The appearance of three texts in as many years by American authors gives strong evidence of the growing presence of physical organic chemistry in US chemistry departments in the early 1940s. And the modest size (at least by current standards) of these volumes is in keeping with the modest state of the field *vis-à-vis* more traditional areas of organic chemistry, such as natural product and synthetic chemistry—a situation that would change markedly in the coming decade.

A word about 'mechanistic content' is in order. Since physical organic chemistry lies on the border between physical chemistry and organic chemistry, it could in theory have attracted its adherents from either or both its parent fields. (In P. D. Bartlett's review[9] of Hammett's *Physical Organic Chemistry*, he notes that Hammett (a physical chemist) 'writes like a physical chemist in that the discussions are quantitative and are developed algebraically.... He writes like an organic chemist in that no general statement is found very far from its supporting evidence.') In fact, virtually all the researchers and students have been drawn from organic chemistry. A crude but not inaccurate generalization is that most organic chemists are primarily interested in reactions. Since mechanisms are about reactions, the portion of a book devoted to discussions of mechanisms provides a rough index of how well the text would appeal to organic chemists. This conclusion is lent some support by the observation that Branch and Calvin's work, the most 'physical' and abstract of the five, never appeared in a second edition, although one was planned.

A closer look at the structural content of these five volumes reveals some additional areas of substantial difference, resulting from different conceptions not only of content and pedagogy but also of how the subject should be grounded. When a field is still developing and its boundaries and core content are still fluid, a number of central issues remain contentious:

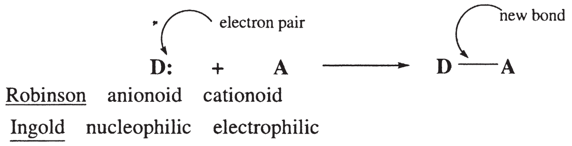
- What should be the discipline's theoretical base, its standard vocabulary and its accepted forms of representation?
- What is the relative importance of the various topic areas?
- Who is/are to be acknowledged as the leader(s) of the field?
- Do national differences and traditions substantially affect the subject's development?

Our specimens provide us with a window on to all these issues.

Consider the issue of nationality. Although chemists from several countries made crucial contributions to what would become physical organic chemistry, the UK was its principal incubator. (The absence of an important French contribution is discussed in Ref. 3a, pp. 139–162. Although there were several first-rank investigators of reaction mechanisms in Germany, traditional topics such as synthesis and natural product chemistry were dominant. Furthermore, there was a wide gulf between physical and organic chemists in Germany, and the

Germans were slow to adopt the Lewis theory of valence.[10]) In fact, during the 1930s and 1940s, the phrase 'the English School' was routinely encountered in American texts and journal articles. That tag arose because two English chemists, Robert Robinson[11] and Christopher Ingold,[12] independently began to lay a theoretical groundwork for the field in the 1920s. (Martin Saltzman has evaluated Robinson's contributions in detail,[13] and appreciations and critiques of Ingold's approach can be found in Refs. 14 and 15.)

They concentrated on that large class of reactions that were eventually designated as 'polar.' Ingold and Robinson each recognized that the reactants, infinitely diverse as they appeared to be, could nonetheless be divided into just two classes: electron pair acceptors (A) and electron pair donors (D). With this insight they were able to demonstrate that a plethora of reactions amounted to nothing more than instances of a single pattern [Eqn (1)].



(1)

Robinson called the two classes of reactants anionoid and cationoid, by analogy with the anions and cations of classical chemistry. Ingold, however, was an astute practitioner of what might be called the Lavoisier strategy: seize the nomenclature and hearts and minds will follow.[16] He therefore chose to coin two neologisms to describe these reagents, nucleophilic and electrophilic, which were just the advanced guard of his nomenclatural blitz. (A large fraction of the terms we routinely use to designate reaction types such as S_N1, S_N2, $E1$ and $E2$, were coined by Ingold.[17]) Ingold had sound reasons for choosing these terms, since nucleophiles and electrophiles do not necessarily carry charges, whereas anions and cations always do. However, I believe that his intentions went further, as I shall explain shortly.

Robinson and Ingold differed on much more than nomenclature; in fact, they were at odds over nothing less than who should be credited with formulating the modern electronic theory of organic chemistry. This bitter dispute, which can only be glimpsed indirectly in the early textbooks, was carried on even after the death of both protagonists by certain of their partisans.[18]

Opposition to the Ingold nomenclature was often blunt and not confined to the UK. In a 1938 laudatory review of Watson's book, Paul Bartlett, a junior faculty member at Harvard who would become the dean of American physical organic chemists, touched on this issue: 'In the electronic interpretation of organic reactions certain English chemists have been pioneers. Their views might originally have been more cordially received in this country if presented inductively and in terms whose meanings are well known.'[19]

Ingold also anticipated the version of quantum mechanics that provided most organic chemists with their first basic theoretical framework. Just before the advent of wave mechanics, Ingold showed how the structural formulas of classical organic chemistry could be combined to represent molecules that did not behave classically—benzene was the standard exemplar. He called this phenomenon mesomerism.[20] A few years later, Linus Pauling devised a quantum mechanical treatment of molecules, the resonance method, that provided a theoretical justification for mesomerism. (Ingold had been anticipated by the German chemist Fritz Arndt[21], who used the term 'intermediate state.' Like many others, Arndt eventually capitulated and adopted Ingold's mesomerism.) Pauling's first papers on resonance appeared in 1931, and the theory was expanded and illustrated in a book.[22]

For several decades thereafter, mesomerism/resonance became the reigning theoretical paradigm in physical organic chemistry, as reflected in the textbooks (Table 2). For instance, resonance was explicitly endorsed by Watson, who claimed that its rival, the molecular orbital method, 'cannot be described as a wave-mechanical theory of valency'.[7] Since Watson's research was closely allied with Ingold's and Ingold had read most of Watson's manuscript, the Watson text could be seen as a definitive statement of doctrine from that corner.

Ingold's nomenclature did not, however, enjoy such general acceptance. Of the three American textbooks, only Remick's embraced Ingold's terminology. Branch and Calvin explained their avoidance of it in this way: 'The language of the new theories of organic chemistry have not had time to become uniform. The same ideas are expressed in different words by different authorities. C. K. Ingold, whose contributions to electronic structural theory are second to none, has developed a language to express his ideas. We have taken scant recognition of this language, and have even taken liberties with it. Actually, we are in very close agreement with Prof. Ingold's theories.'[23] Hammett, whose book had more references to Ingold's papers than to his own, simply ignored the nomenclature.

What inspired such resistance, even among Ingold's American admirers? Perhaps some of them found Ingold a bit overweening and balked at adopting his language as a form of protest. (A reviewer of Ref. 8 noted that 'although the author writes with experience and authority, his style may arouse some controversy. The privilege of writing solely from one point of view has been assumed and past dissenters have been dealt with firmly and neatly, although occasionally with intuitive rather than logical arguments;' review of[24]) There may, however, have been a more substantive issue. Whatever his desire to promote himself, Ingold was much more concerned with promoting physical organic chemistry *and establishing its claim to be an independent sub-discipline*. One means of accomplishing that goal would be to endow the subject

Table 2. Nomenclatural and theoretical choices among the chosen textbooks: the books are categorized as to their general orientation, quantitative or qualitative

Title	Author(s)	Ingold nomenclature	Major quantum chemical method	Quantitative or qualitative	Mechanistic content (%)
Modern Theories of Organic Chemistry	H. B. Watson	Yes	Resonance	Qualitative	71
Physical Organic Chemistry: Reaction Rates, Equilibria, and Mechanisms	L. P. Hammett	No	Resonance	Quantitative	67
The Theory of Organic Chemistry: an Advanced Course	G. E. K. Branch and M. Calvin	No	Resonance	Quantitative	20
Electronic Interpretations of Organic Chemistry	A. E. Remick	Yes	Resonance	Qualitative	53
The Electronic Theory of Organic Chemistry	M. J. S. Dewar	Few	Molecular orbital	Qualitative	75

with its own distinct language. But by no means all of the early adherents of physical organic chemistry shared Ingold's vision. Even Paul Bartlett, the outstanding American physical organic chemist of the 20th century and one uniquely qualified by temperament and experience to give a balanced assessment of the field, told an interviewer that he just considered himself 'an organic chemist interested in mechanisms' and did not 'see the need for a definition of physical organic chemistry' (Paul D. Bartlett, interview with Leon Gortler, 18 July 1978, Center for the History of Physics, American Institute of Physics, College Park, MD, USA). I believe that these divergent views about the status of physical organic chemistry were one of the main causes of dissension about the most effective ways of representing its concepts.

Other aspects of these textbooks are noteworthy. The subtitle of Branch and Calvin's book suggests that the subject was sufficiently entrenched by 1941 to warrant an advanced level course. That conclusion may have been premature: a planned second edition was never published. It is possible that the book's relative paucity of mechanisms and its abstract and generalized treatment of them did not find favor with its intended audience. Bartlett's 1942 review of this book was quite appreciative,[24] and in replying to a 1947 request from Prentice-Hall for suggestions concerning a possible revision of Branch and Calvin, Bartlett praised the utility of its data tables. Nonetheless, he also noted that the text was 'heavy on the structural side and light on the side of mechanisms,' and 'that the more philosophical parts of the book are the less successful' among the students {Barlett to Blaisdell, 7 January 1948, Bartlett Papers, Harvard University Archives, HUG (FP) 10.6, Box 2, Folder B (October 1947–January 1948)]. While hardly definitive, this evaluation supports the proposal that the book's market was more modest than that of its competitors.

Both Hammett's and Branch and Calvin's volumes are highly quantitative and would probably have stretched the mathematical resources of many organic chemists. Remick's, by contrast, is comparable to Watson's in its orientation and lower level of difficulty. Remick's intention to 'give the student such knowledge as is necessary to follow future developments in the field by reading the research literature' led him to introduce 'the symbolism and the language of the English school . . . despite the fact that they are not popular in this country at this time.'[26]

Remick also followed Watson in beginning with an historical introduction that traces the origin of some basic concepts back to about 1800s. But he adds something extra—an extended discussion of the work of several pre-quantum era American organic theorists, including that of his teacher, Julius Stieglitz. These men are only cursorily mentioned in Watson's book. Even committed American followers of 'the English school' such as Remick were concerned that the contributions of those outside that school should not be slighted. That fear was apparently not unfounded, as Remick made clear in a 1958 review of an introductory English text of organic electronic theory: 'I would stoutly defend Dr. Baker's right to decide which subject matter is to be included in his book and which is to be ignored. But I would also stoutly maintain that the prospective reader of the book has the right to know which subjects, of those pertinent to the field covered, are omitted. With this in mind, it might be mentioned that, with the sole exceptions of the contributions made by Lewis and Pauling to theories of atomic and molecular structure, no mention is made of any basic electronic principles contributed by Americans.'[27] (The book in question was Ref. 28.)

Michael J. S. Dewar's book also had several agendas. Dewar was a student of Robinson's, and Robinson had originally intended to be his co-author. As it happens, Robinson wrote only the Foreword, which opens with a shot across the bow: 'During the last twenty-five years the writer has had constantly in mind the desirability of a fuller exposition of what may be termed the Lapworth–Robinson system of organic chemical theory . . . .'[29] Ingold's name is conspicuous by its absence. Dewar was fully behind this campaign to revive and support Robinson's claim to being a founding father of physical organic chemistry.[18] In addition, Dewar cast doubt on the main theoretical prop of Ingold's system, the resonance method, which he found 'most unsuitable from the organic chemist's point of view since it involves a new symbolism and a novel and uncongenial outlook. (A cursory examination of the literature shows how difficult it is for chemists to distinguish between resonance and tautomerism.)' Dewar maintained that the molecular orbital method, by contrast, 'provides a picture of molecular structure closely akin to that of classical organic chemistry,' and that is the theoretical approach he promoted [Ref. 29, ix–x].

Alas, neither of Dewar's aims met with success. Reviving Robinson's reputation as a theorist proved to be a quixotic quest; his postwar lectures on theoretical and mechanistic organic chemistry were quietly derided by many knowledgeable people. And although Dewar's advocacy of the molecular orbital method over the resonance approach was fundamentally sound, he had not found an effective way of doing what he claimed he would—presenting the MO method clearly in a non-mathematical manner. ('The hope of better things which this statement [Ref. 29, ix–x] raises is, in the reviewer's opinion, not fulfilled in the book; for no general operational superiority is demonstrated for the rather nebulous notation of molecular orbitals as an instrument of correlation and prediction, in comparison to the well-developed qualitative resonance scheme.'[30]) That would await the publication in the early 1960s of Streitwieser's *Molecular Orbital Theory for Organic Chemists* and Roberts' small paperback, *Notes on Molecular Orbital Calculations*.[31]

In 1953, Ingold published *his* magnum opus, *Structure and Mechanism in Organic Chemistry.*[8] More than 800 pages long and filled with both historical and technical detail, it testified to a magisterial command of the field that few if any could match. It was, in the words of Roberts, 'one of the few great books of organic chemistry.'[24] This work confirmed Ingold's status as one of—if not the—creators of physical organic chemistry.

It was also completely unsuitable as a textbook. Interestingly, the truly successful textbooks were for the most part *not* written by the major research figures in the field. There were further incongruities. Robinson eventually won the Nobel Prize, but not for his work on reaction mechanisms, whereas Ingold never won the prize, and nor did any of the other heroic early figures. Finally, Ingold's *Structure and Mechanism* was the outgrowth of a series of lectures he delivered at Cornell in 1950. The venue had a certain ironic appropriateness, for by the 1950s the center of gravity in physical organic chemistry had shifted westward across the Atlantic.

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