JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2005; **18:** 572–577
DOI: 10.1002/poc.915

A missed turning point for theory in organic chemistry: molecular orbitals at Montpellier in 1950

Jerome A. Berson*

Department of Chemistry, Yale University, 225 Prospect Street, P.O. Box 208107, New Haven, Connecticut 06517-3401, USA

Received 9 November 2004; revised 11 January 2005; accepted 21 January 2005

ABSTRACT: Michael Dewar's attempt to introduce physical organic chemists to molecular orbital ideas began with his book *The Electronic Theory of Organic Chemistry* (1949) and his lectures at the Montpellier Colloquium (1950). Influential members of the community resisted these efforts for a number of reasons, which included Dewar's inability to communicate his ideas to chemists in need of instruction and also a series of apparent errors in working out the experimental details of his mechanistic proposals. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: history of chemistry; molecular orbital theory; benzidine rearrangement; carbonium ion rearrangements; Diels–Alder reaction

INTRODUCTION

The *Colloque International sur les Réarrangements Moléculaires et l'Inversion de Walden* took place in Montpellier, France, during 24–29 April 1950. Organized by Professor M. Mousseron of the university in that city, and supported by the Centre National de la Recherche Scientifique (CNRS) and the Rockefeller Foundation, this meeting seems to have been one of the first concerted attempts in France to bring together an internationally representative group of organic and theoretical chemists in the field of physical organic chemistry. Although a list of attendees at the conference was not provided in the proceedings published in *Bulletin de la Société Chimique de France*, I speculate that Christopher Ingold, probably the most famous physical organic chemist in Britain, or even in all of Europe for that matter, was not present. His name is not on any of the papers presented, nor does it appear among those of the participants in the discussions after each lecture, where his forceful personality would have been expected to express itself. In addition to a number of French chemists, the speakers included both Americans (Paul D. Bartlett and Saul Winstein) and Britons (Michael J. S. Dewar, Edward D. Hughes, Joseph Kenyon, Charles W. Shoppee and Hugh Felkin, who was British but by then already working in France).

It seems likely that French chemists were motivated to hold the conference in order to bring themselves into closer contact with modern trends in the field. According to Nye,[1]

> 'Students of French Chemistry after the Second World War were to feel that they had lost step with the progress in theoretical chemistry elsewhere, especially in the understanding of organic reaction mechanisms and in the application of quantum mechanics to chemical problems.'

Although the presentations at the colloquium described a wide range of experimental studies, our attention here is turned to two of the more theoretical lectures by Michael J. S. Dewar (for a biographical note, see Ref. 2). As examples of didactic strategies used at the time to enlighten organic chemists about the utility of quantum mechanics, these lectures are relevant to the theme of the present cluster of papers.

The intensity of focus on this issue at Montpellier perhaps can best be appreciated from the lively discussions that followed Dewar's lectures. We must be grateful to the conference organizers for publishing not only the lectures themselves but also the text of these post-lecture comments, passages which reveal the immediate responses of the attendees, at least of the more outspoken ones.

Dewar himself was an eager participant in these discussions, but so also were two American giants of physical organic chemistry, Paul Bartlett and Saul Winstein. Dewar was soon to find himself under heavy fire from these two sources.

In the 1930s, two approximations to the solution of the Schrödinger equation for molecules proved eventually to be of special significance for organic chemistry: the molecular orbital (MO) theory and the valence bond (VB) theory, the latter specifically as truncated by Pauling and Wheland and named the 'theory of resonance.'

Although neither approximation could be considered more 'correct,' for many years resonance theory was by

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**Correspondence to:* J. A. Berson, Department of Chemistry, Yale University, 225 Prospect Street, P.O. Box 208107, New Haven, Connecticut 06517-3401, USA.
E-mail: jerome.berson@yale.edu

far the more popular. (An interesting discussion of the contention between adherents of MO vs. VB theory was given by Hoffmann *et al.*[3] See also ref. 4, Chapter 3.) A major reason was that resonance theory used a formalism in which the approximate solutions were obtained by a mathematical superposition of wavefunctions or, as they were called, 'contributing structures.' These had a property that was very attractive to organic chemists, namely they could be represented by simple drawings that superficially seemed to resemble exactly the conventional organic structures derived from the structural theory. Molecular orbital theorists, on the other hand, made extensive use of equations and matrices rather than any graphic notation. In the minds of most organic chemists, this put up a major barrier to acceptance of MO theory, because organic chemists grew up learning how to draw molecular structures, not how to manipulate matrices. Their whole conceptualization of chemistry was founded on the bed-rock of the structural theory.

It is advisable to keep in mind that the argument between MO theory and resonance theory involved a choice between two major approximations. Under the circumstances of the time (about 1930–70), quantitative calculations of the type in use today simply were not possible. Chemists had to wait for years until the development of increased computing power and the solution of a number of technical problems had been achieved. In the meantime, those organic chemists who were eager to apply quantum chemical ideas to guide their work took recourse in one of the two approximations, usually resonance theory. The virtual exclusion of MO theory from the toolkit of organic chemists therefore amounted to an intellectual impoverishment, since the two theories in their approximate forms disagreed in some significant predictive tests.

Dewar's work of the 1940s and 1950s on MO theory succeeded that of Erich Hückel, who pioneered the field in the 1930s. The opportunity for rapid and broad application of Hückel's MO theory shortly after its appearance was missed for reasons discussed elsewhere.[4] It is curious that the adoption of methods based on Dewar's efforts also was delayed. Why this was so does not seem to have been examined in any detail. The present paper will try to show that certain poignant events of the Montpellier Colloquium were instrumental in determining that outcome.

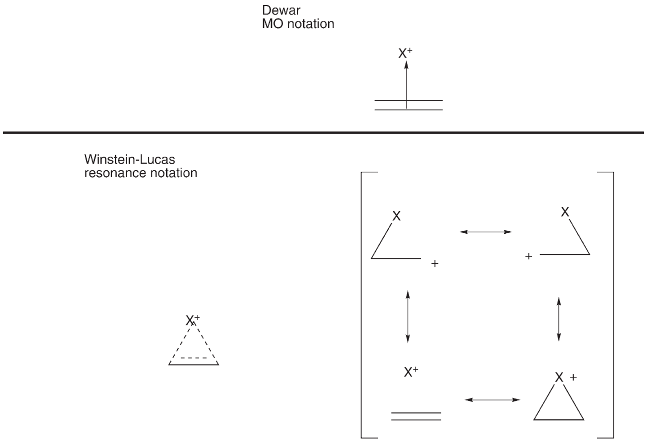
MICHAEL JAMES STEUART DEWAR

Figure 1. Michael J. S. Dewar (1918–97). Reproduced with permission of Columbia University Press

Dewar (Fig. 1) had studied quantum mechanics with Charles Coulson at Oxford and then became a researcher in the laboratory of the famous organic chemist Robert Robinson. He eventually was to become a prominent figure in organic chemistry in his own right, but in 1950, at the age of only 32, he had yet to reach that status. Nevertheless, he already had developed a considerable reputation for his success in deducing the structure of the mold metabolite stipitatic acid from experiments by other chemists.

DEWAR'S ADVOCACY OF MO THEORY

Dewar's book entitled *The Electronic Theory of Organic Chemistry* appeared a year before the Colloquium. Note: not *AN* Electronic Theory, but *THE* Electronic Theory. In it, Dewar proposed to demonstrate that the explanatory power of MO theory in the interpretation of the properties and reactions of organic compounds was equal to, and in a number of cases superior to, that of the then dominant resonance theory. The youthful bravado thus implied in his title and exhibited elsewhere in his writings was a characteristic aspect of his style. Some older chemists no doubt found presumptuous the lack of modesty implied in such a direct attack on existing concepts. However, others welcomed his brashness as stimulating, even though (full disclosure) many of us did not really understand the origin of his ideas. The reason we did not understand was simple: we had been educated in the prevailing paradigm of resonance theory and were completely unfamiliar with MO theory.



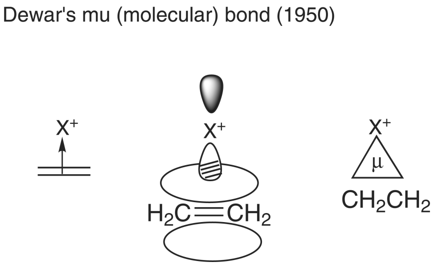
Scheme 1

Both of Dewar's lectures concerned carbon skeletal rearrangements. One dealt with hydrocarbons and the other with diarylhydrazines, of which benzidine is the parent compound. In both, Dewar invoked a new kind of cationic species which he called a π-complex (Scheme 1).

Such rearrangements commonly had been described at the time, notably by Winstein and Lucas, as passing through carbonium ions, with a 'bridged' ion formulated as a resonance hybrid serving as an intermediate or a transition state, as shown in Scheme 2. Dewar nevertheless proposed π-complexes as more satisfactory alternatives.

Dewar's initial presentation apparently encountered some skepticism, largely, I think, because the true significance of the π-complex formula could not be readily expressed in the framework of resonance theory. Scheme 2 shows an attempt that he made in his second lecture at the colloquium and elsewhere to describe the π-complex more completely.

In this formulation, the complex appears as the result of overlap between a p-orbital on the bridging atom and the bonding π-orbital of an olefin, to give, Dewar explains, a 'molecular bond' or 'mu bond,' which covers both the bridging atom and the two olefinic carbons. Someone unfamiliar with MO theory would have had great difficulty in deciphering just what were the underlying physical implications of this. Critically, Dewar omitted to mention the elementary concept that he had in mind the overlap of an *empty* p-orbital and a *filled* π-orbital. In 1950, most organic chemists could not readily deduce the implications of that. Hence the omission was a pedagogically damaging oversight, as we shall see.


Dewar's mu (molecular) bond (1950)

Scheme 2

Dewar's paper met with a chilly reception from some important attendees at the Colloquium. A rather dismissive comment came from the brilliant and influential Saul Winstein (Fig. 2). Winstein's objection,[5] made in the discussion after Dewar's second lecture, went straight to the heart of the π-complex idea:

> 'I find troublesome Dewar's statement that our [that is, Winstein and Lucas's] formulation of the ethylene bromonium ion involves a ring and his doesn't. All that is meant by a 3-ring is a triangular arrangement of three atoms.'

In other words, what is the difference between the two species?

The clear implication of Winstein's remarks here and elsewhere is that Dewar's π-complex is a superfluous *notation*, just a variant way of saying the same thing that Winstein had said earlier, which has no implications beyond those of the bridged ion.

Figure 2. Saul Winstein (1912–69). Reproduced with permission of Columbia University Press

Dewar's response was loaded with significance but apparently made no impact on Winstein:

> 'Equivalent valence bond descriptions of π-complexes can of course be given. Thus the simple π-complex can be represented as the hybrid. As it stands, this description is unsatisfactory since it does not explain why π-complexes are formed from olefins with acceptors, and not with radicals or anions.'

Here we come to a crucial turning point. Dewar was giving a reason why he considered the π-complex structure to be preferable to the bridged ion structure. Resonance theory would predict that if cations (or, more generally, Lewis acids) form complexes with olefins, so too should anions or Lewis bases. At this point, that is as far as he goes. His argument, however, still lacks punch: what is the exact *physical reason why* anions and olefins do not form complexes? Clearly, Winstein was not perturbed or persuaded, nor was he sufficiently interested to press Dewar for an answer. He continued to use resonance notation rather than π-complex notation. I speculate that under the surface of Winstein's resistance was the conviction that the two representations were indistinguishable by any experiment.

Dewar also came under fire at the Montpellier Colloquium from Paul Bartlett (Fig. 3), who was one of the most thoughtful physical organic chemists. In the discussion period, using unrestrainedly disparaging terms, such as those a tough teacher might use to scold a callow student, Bartlett sharply criticized Dewar's π-complex analyses of hydrocarbon rearrangements and of benzidine rearrangements.

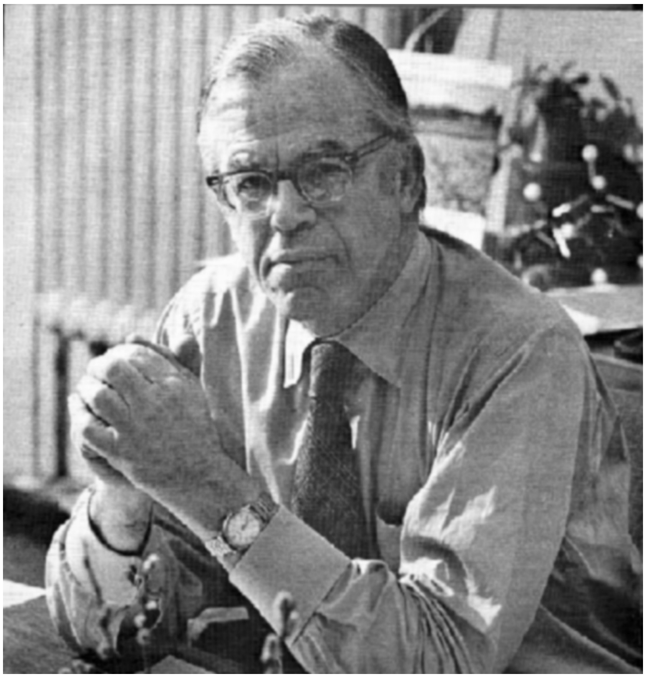


Figure 3. Paul D. Bartlett (1907–97). Reproduced with permission of J. M. McBride

The alkane rearrangements Dewar chose as the topic of his first lecture were extremely complex systems in which the action of strong Lewis acids such as aluminum bromide on added small amounts of alkene or alkyl halide were believed to initiate the formation of carbonium ions. Bartlett's comment[6] after Dewar's lecture was caustic:

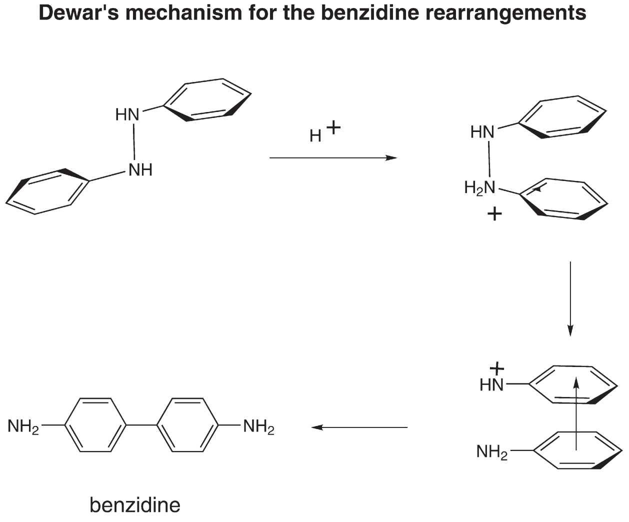
> 'The existing data on the composition of paraffin alkylates, including much work from oil companies which remains to be published, are far in advance of our readiness to interpret them. Chemists wanting to contribute to this field will do well to attack the basic problem of the nature of the carbonium ion, or the ionic complex, in paraffinic media . . . We are totally ignorant of the state of the carbonium ion in paraffinic solution, and even of whether it exists there at all or not.'

Similarly, Dewar's mechanism for the benzidine rearrangements (Scheme 3) became a source of skepticism. It involves protonation of one of the nitrogens, followed by formation of a π-complex, in which the two aniline moieties can slide over each other and position themselves for the formation of a new p,p′-bond.

Perhaps the most devastating criticism came in Bartlett's laconic comment on this proposal:

> 'The mechanism of benzidine rerarrangement as formulated by Dr Dewar calls for kinetics of the first-order with respect to hydrogen ion . . . [R]ecent work by [George] Hammond [and Henry Shine] establishes the reaction as being of the *second* order with respect to hydrogen ion.'

Ironically, years later events were to show that the reactions of 1,2-diarylhydrazines in acidic media are extraordinarily complex and that, under some conditions, the benzidine rearrangement kinetics indeed could also be first order in hydrogen ion. The later developments of



Scheme 3

the benzidine story are given, for example, in an excellent review by Shine in the *Journal of Physical Organic Chemistry.*[7] However, at the Montpellier Colloquium, the participants could not help but gain the impression that Dewar had made a blunder by not even determining the kinetics.

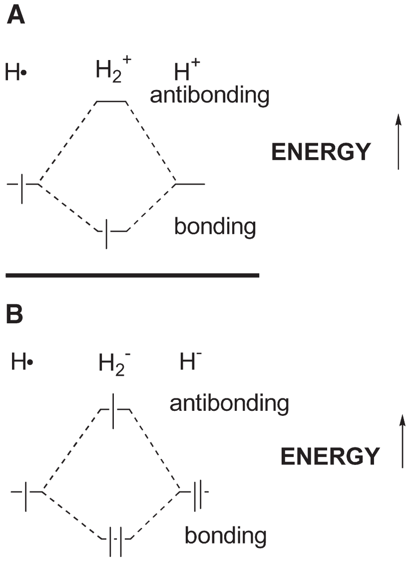
In 1952, two years after the colloquium, Dewar strove to make a general case for π-complexes and, in a larger sense, for the MO method itself, as against resonance hybrids and the resonance theory. These arguments appeared in a series of six back-to-back papers in the *Journal of the American Chemical Society* under the general title 'A Molecular Orbital Theory of Organic Chemistry.'[8] There he surveyed the standard reaction types of the field: substitution, elimination, cycloaddition and so forth, using extensions of the MO perturbational methods developed earlier by Coulson and others.

Unfortunately, in the introductory article of the series, he used a highly formalized and mathematicized presentation. It seems to me that Dewar aimed at an audience that included not only the community of organic chemists but also the quantum mechanicians, prominent among whom was his former mentor Coulson.

Dewar's presentation could be seen as a misguided attempt to display his theoretical virtuosity. He was striving to demonstrate that although he was considered an organic chemist, he had impressive qualifications as a theoretician. Thus, in broad panorama a typical page from the first paper of the series seemed to consist of a impenetrable thicket of equations and matrices. Whatever the reaction of the quantum mechanics community, most organic chemists of the era who swept their eyes over this forbidding sight soon passed on to more welcoming territory. Perhaps a few of us then may have learned something about MO theory in one or another class in graduate school, but that exposure did not equip us to plunge into the arcana of Dewar's arguments. Moreover, Dewar had not made clear why we should bother. What was it about even qualitative perturbational MO thinking that made it more useful, more flexible than resonance theory?

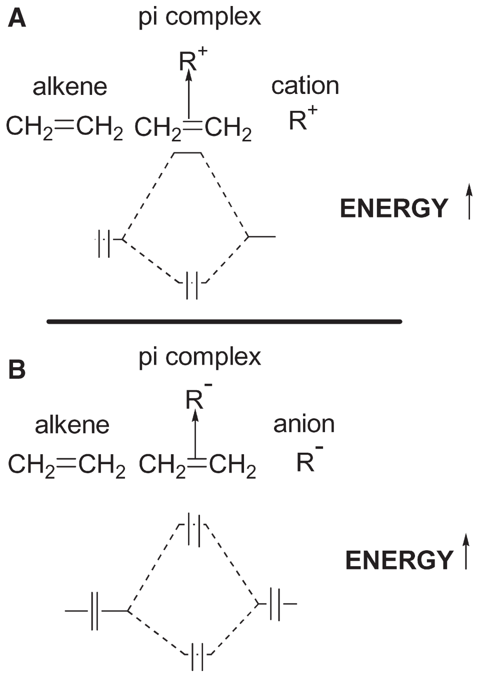
Dewar certainly could have been more persuasive about this had he displayed a couple of simple diagrams to show the energy perturbations resulting from orbital interactions. Lennard-Jones had used such representations in the 1920s and 30s, for example, in explaining why the H_2^+ ion is energetically favorable [Scheme 4(A)] but the H_2^- ion is not [Scheme 4(B)]. Dewar *could* have used exactly the same kind of diagrammatic perturbational argument to explain why cations but not anions form π-complexes [Scheme 5(A) and (B), respectively].

Such diagrams reappeared in abundance many years later in the orbital symmetry and frontier orbital theories. The heart of those theories is the interaction of a *filled* HOMO with an *unfilled* LUMO, just as Dewar had postulated but failed to emphasize clearly. I believe that these diagrams would have had a telling pedagogical impact had Dewar presented them at Montpellier. They would have provided a *physical basis* for Dewar's idea of a mu bond in the π-complexes.



Scheme 4

It is striking that even in Dewar's 1969 revision of his 1949 book on the electronic theory of organic chemistry, no such graphical displays were given. It was not until 1975, when a third Dewar book appeared, entitled 'The PMO (Perturbational Molecular Orbital) Theory of Organic Chemistry' and co-authored with Ralph Dougherty, that at last Dewar's presentation reached that point. By that time, the pedagogy of MO theory for organic chemists had developed greatly, in textbooks and publications by the Pullmans, by Daudel, by Roberts, by Streitwieser and by others.



Scheme 5

CONCLUSIONS

Why did organic chemists initially resist Dewar's ideas? One reason was his unfortunate choice of the exceptionally complex benzidine rearrangement as a showcase for π-complexes in the aromatic rearrangements. Similar incidents occurred (although not at the Montpellier Conference) in collisions with Robert Burns Woodward, another pillar of the establishment. The first was over the mechanism of the dienone–phenol rearrangement.[9] In 1953, Woodward and Singh reported an ingenious stereochemical test for π-complexes in the dienone–phenol rearrangement and concluded that they were not involved. A little later, Woodward and Katz[10] made a sharp rejoinder to a Dewar proposal[11] on the mechanism of the Diels–Alder reaction. Dewar had suggested that the reaction was concerted rather than two step or two phase as Woodward and Katz had proposed earlier. In essence, Dewar argued that a mechanism in which only one new C—C bond is formed in the transition state could not explain the much greater dienophilic reactivity of the unsaturated dicarbonyl compound maleic anhydride as compared with unsaturated monocarbonyl compounds, since then the second carbonyl group of maleic anhydride would not be in a position to enhance the rate. Woodward and Katz seized upon a large gap in Dewar's argument, namely that it did not compare the rates of monocarbonylated alkenes and of maleic anhydride in *radical* addition reactions, which surely do take place one bond at a time. Woodward and Katz then pointed out that in fact maleic anhydride is also much more reactive in that comparison, a finding that effectively overthrew Dewar's proposal. Although this had nothing directly to do with π-complexes, the result was to undercut further Dewar's credibility. With these thrusts, Woodward thus joined Winstein and Bartlett in the line-up of important chemists arrayed against Dewar's ideas, which unsurprisingly, then found few supporters in the community at large.

A second problem, or perhaps another aspect of the same problem, was inherent in Dewar's personality. Conversations with others who were close to him confirm my impression that, as an organic chemist, Dewar was truly proud and rather possessive of his knowledge of theory, which surpassed that of most of us. By declining to make the effort to transmit that knowledge in a form accessible to experimental organic chemists, he maintained his position of superiority, but what we needed more in the early 1950s was a teacher, not an icon. I believe that Dewar's deficiency in communication, on an international stage at Montpellier, was a major factor in delaying the development of an MO consciousness among organic chemists for at least a decade.

Acknowledgment

I thank Professor Ralph Dougherty for helpful correspondence.

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