Kekulé Escapes, Popper Notwithstanding**

Jerome A. Berson*

1. Does the Philosophy of Science Teach Us How to Do Science?

In ancient Greece, during the age of Aristotle (384–322 B.C.) and Plato (427–347 B.C.), the disciplines of science and philosophy overlapped, often in the work of the same individual. Beginning at the time of Francis Bacon (1561–1626), if not earlier, some philosophers of science have pressed upon us sets of guidelines on how science should be done, and in some cases, have attempted to show that the events, discoveries, theories, and controversies of science—in short, the components of the history of science—correspond to such guidelines. Some authors of elementary science textbooks, often not working scientists themselves, have codified various versions of these guidelines into what they teach as "the scientific method."

At least partly in response to the imperatives of specialization, the fields separated over the centuries, and scientists, despite such notable exceptions as Descartes, Mach, Bohr, and Einstein, became increasingly ignorant of philosophy. Relationships between the practitioners have now become remote. Indeed, some highly visible and influential scientists[1, 2] express active hostility toward the enterprise of philosophy, especially toward the philosophy of science. Even those working scientists who do not reject philosophical contributions as a matter of principle, nevertheless give little thought to an activity that once commanded the deep concern of our remote predecessors.

I would argue that, in spite of Weinberg, Feynman, and other skeptics of philosophy, those of us in the community who recognize our own ignorance might want to learn enough about that field to make reasoned decisions about what modern philosophers of science tell us, and to make up our own minds on its relevance to the work of science itself. Perhaps we will conclude that the philosophers are wasting our time and their own, but on the other hand, perhaps we will learn something that may be helpful in our own work. This will require that we familiarize ourselves, at least to some extent, with the major themes in the philosophy of science. The present article, necessarily limited in scope, cannot claim to provide a broad view. Instead, it should be seen as a preliminary scrutiny of the interaction of one philosophically derived guideline with the events of actual scientific discovery.

2. Popper Prohibits Ad-Hoc Rescue of Refuted Theories.

I daresay that of the modern philosophers of science, Sir Karl Popper is among the very few whose names are at all familiar to most chemists. In a famous book, *The Logic of Scientific Discovery*, first published in 1934[3] and followed by a later companion volume,[4] Popper developed a set of rules for close logical analysis of criteria for the acceptability of theories and of the steps scientists should take to test their validity. The dominant theme of Popper's scientific philosophy is that progress can be made only by a series of *conjectures and refutations.* According to Popper, because no theory can ever be *proven* correct, the major work of the experimentalist is to *falsify*, that is, to prove incorrect, the conjectures of the theorist. We must defer even a cursory examination of these highly influential and highly controversial ideas to a later study, but it may be instructive to examine here one corollary of the method of falsification.

Popper[3] set down the restriction that, once promulgated, a theory could not be changed in response to experiments that seemed to disagree with it. As a direct consequence of the falsfication strategy, this prohibition can be seen simply as fair play, for one cannot hope to land a telling blow on a target that will not stand still. He scorned the "strategems", especially the *auxiliary hypotheses*, that theoreticians sometimes use to save a theory that appears to be threatened by a seemingly contradictory finding.

> "As regards auxiliary hypotheses, we propose to lay down the rule that only those are acceptable whose introduction does not diminish the degree of falsifiability or testability of the system in question, but, on the contrary, increases it.… An example of an unsatisfactory hypothesis would be [one] which had no falsifiable consequences but merely served to restore the agreement between theory and experiment."

We examine now a famous (and famously fruitful) instance of the rescue of a theory. As we shall see, the intellectual construct put forward for this purpose violated this stricture on auxiliary hypotheses.

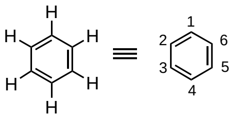
---

[*] Prof. Dr. J. A. Berson
Department of Chemistry, Yale University
225 Prospect Street, P.O. Box 208107
New Haven, CT 06520-8107 (USA)
Fax: (+1) 203-432-6144
E-mail: jerome.berson@yale.edu

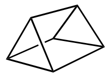
[**] I thank R. Hoffmann, J. M. McBride, and J. S. Siegel for helpful suggestions.

3. Kekulé's Benzene.

In 1865, August Kekulé proposed the cyclohexatriene structure for benzene (molecular formula C_6H_6).[5, 6] In his original publications Kekulé did not actually write down the formula shown as **1**,[7, 8] but there is no doubt that is what he had in mind. In his verbal description,[6] the structure was conceptually generated by cyclization of an open-chain 1,3,5-hexatriene to a symmetrical six-membered carbon ring with each carbon atom attached to a hydrogen atom. Additionally, the hydrogen atoms were explicitly assumed to be equivalent.



1 **1**



2

Our inquiry focuses on one of the main lines of argument used then to test the theory, namely the concordance of the number of known distinguishable isomers of multiply substituted benzene with the number predicted by the theory.

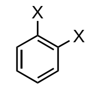
4. Ladenburg's Objection.

Although the initial reaction of the chemical community to Kekulé's theory was quite favorable, by 1869 a serious criticism of the Kekulé's formula had emerged in a discussion by Albert Ladenburg, who had been a laboratory assistant to Kekulé at Ghent. This criticism appeared in the paper[9] in which Ladenburg proposed the prismatic structure **2** for benzene as an alternative to Kekulé's cyclohexatriene structure. The opening passage of his paper succinctly summarizes the problem:

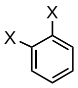
> "Several years ago I already had the opportunity to point out to Mr. Kekulé that the … graphical formula which he had assigned to benzene does not suffice for the hypothesis, since in it [the] 1.2 and 1.6 [bonds] are not equivalent…"

Thus, the Kekulé structure leads to a difficulty when the molecule is *ortho*-substituted with groups other than H, since now there should be two structural isomers (**3a** and **3b**). Only one *ortho* isomer had ever been observed, regardless of the method of synthesis.

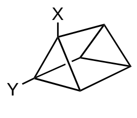
Ladenburg's prismatic structure **2** does not suffer this deficiency. Today we notice, however, that the prismatic structure with two *nonequivalent ortho* substituents, would lead again to two isomers (**4a** and **4b**), but these are enantiomers (nonsuperimposable mirror images) rather than structural isomers. The nature of enantiomerism was not recognized until five years later, with the advent of Van't Hoff and Le Bel's theory of stereochemistry. Indeed, Van't Hoff himself[10] pointed out the flaw in Ladenburg's theory soon after.



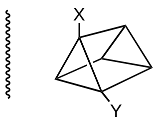
3a



3b



4a



4b

Even though the prismatic structure thus had its own difficulties, Ladenburg's objection to Kekulé's structure did not depend upon whether the prismatic structure was correct. He had pointed out a very serious obstacle to Kekulé's theory. In fact, his arguments potentially represented a refutation of it.

5. Kekulé's Auxiliary Hypothesis.

It took three years for Kekulé to respond to this challenge.[11] Significantly, he did not bring into play a number of escape mechanisms he might have used. These included the possibility that the properties of the two isomers called for by his original theory were so similar that the compounds were experimentally indistinguishable. Also, the whole method of isomer numbers, which organic chemists often used for want of a better procedure, was logically vulnerable because the apparent nonexistence of isomers in a number greater than that predicted by the theory is a negative criterion, that is, one could not be sure that further isomers might not be found sometime in the future.

Instead, Kekulé put forward a completely new and unprecedented hypothesis which significantly modified his theory. This hypothesis was later formulated by others as a fast oscillation of the bonds in benzene, so that each double bond became single, and each single bond became double. It is of great interest, as Gero[12] has pointed out, that Kekulé's proposal in the new modification of his cyclohexatriene theory was not really an oscillation of bonds. We can describe Kekulé's modifying argument only briefly here. It put forward a new theory of the actual bonding forces in benzene, which he believed to be controlled by the rates of collisions of the atoms within the molecule with each other, occurring not randomly, but according to an arbitrary and invariant assigned sequence. He advanced this crucial idea without derivation from existing theory or experiment. The proposal was a breathtakingly daring (but of course erroneous) rationale for the entire physical basis of valence. Its operative consequences *in terms of the experimental tests available in 1872* were the same as that of the bond-switching formulation to which it was later simplified.

Kekulé's new argument amounts to the assertion that he wrote double and single bonds in benzene to keep track of the tetravalence of carbon, not to represent their actual nature. The actual bonds in benzene are assumed not to be like the familiar single and double bonds of the aliphatic compounds. Instead, all the C–C bonds of benzene are *equivalent*. He suggested that the best explanation at the time for this new type of bonding was given by his collision theory.[13]

The revised theory thus consists of three parts: 1) benzene is cyclohexatriene; 2) despite that, the molecule is regularly hexagonal, with all C–C bonds equal and specifically with $C_1–C_2 = C_1–C_6$; 3) the *explanation* of the apparent incompatibility of points 1 and 2 is given by the auxiliary hypothesis of the collision theory. It will be noted that the second hypothesis is itself more vulnerable to the method of isomer numbers than the first, since an experimental finding of two *ortho* isomers would disprove the second hypothesis but merely confirm the first. However, the vulnerability of the second hypothesis is inherent and is not increased by the merely explanatory rescuing hypothesis of the collison theory. The revision of Kekulé's benzene theory thus violates Popper's requirement that "only those [auxiliary hypotheses] are acceptable whose introduction does not diminish the degree of falsifiability or testability of the system in question, but, on the contrary, increases it."

Kekulé's brilliant strategem not only had no theoretical justification at the time but would not find any for another sixty years, until the advent of the quantum mechanical concept of delocalization in the 1930s. It was simply a device for salvaging the cyclohexatriene structure. Walter Hückel[14] called it a "hypothesis of embarrassment."

The history of organic chemistry shows that even though this theory was not really understood by most organic chemists of the 19th century, it was applied nearly everywhere. The tremendous flowering of synthesis and the discovery of an abundance of new reactions and structures during that time all took place in an atmosphere of growing conviction that, *for whatever reason*, the C_1-C_2 and C_1-C_6 bonds of benzene were structurally equivalent, as Kekulé had said. Even Ladenburg eventually agreed that the Kekulé structure probably was superior to the prism or other alternatives that had been proposed.

6. Theory Confronts Experiment in a Specific Time Period.

In Kekulé's time such techniques as X-ray crystal structure analysis, electron diffraction, vibrational (IR and Raman) spectroscopy, and NMR spectroscopy, which today provide direct information about molecular symmetry and actual bond lengths and convince the modern chemist that the hypothesis of equivalent C–C bonds in benzene is true, lay decades in the future. By Popper's rules, Kekulé's benzene theory should have been abandoned forthwith as invalid on the grounds of its unfalsifiability.

Popper's demand for expanded testability of any theory rescued by an ad-hoc hypothesis does not take into account the historical context of the moment when the hypothesis was put forward. How soon should we discard such a theory? Is it not possible that at a future time, as happened in the benzene case, predictions made or implied by the theory may become testable?

7. Conclusions

The issue of whether a theory is logically testable can hardly be of great concern to the working chemist. In our daily encounters with nature we are guided by all kinds of theories, some tested by experiment, some logically testable but not yet tested, *and some not testable by any procedure known or conceivable at the time*. The progress of chemical research cannot be reasonably expected to stand still until enough time has passed for the means finally to emerge that can test a theory by the falsification protocol. Thus, our decision on whether to continue to use the theory must be based upon pragmatic considerations: Does it predict new phenomena or rationalize a body of information?

That Kekulé's theory eventually was shown to be testable was of no help to the chemists of the late 19th century. In fact, had the organic chemical community applied Popper's requirement and abandoned Kekulé's benzene formula, much of the development of the subject in that period would have been retarded. Because the "no ad-hoc rescues" rule is central to the falsification strategy, such cases reveal reasons why we should resist attempts to force our research efforts onto this Procrustean bed.

---

[1] "Scientist at Work: Steven Weinberg": J. Glanz, *New York Times*, New York, **2000**, January 25, p. F1.

[2] R. Feynman (Ed.: J. Robbins), Perseus Books, Cambridge, MA, **1999**, pp. 195–196. I heard these remarks directly from Feynman in a conversation at lunch, Caltech Athenaeum, 1959.

[3] K. R. Popper, *The Logic of Scientific Discovery*, Routledge, London, **1959**, translated by the author together with J. Freed and L. Freed from *Logik der Forschung*, Springer, Vienna, **1935** (reprinted 1992).

[4] K. R. Popper, *Conjectures and Refutations: The Growth of Scientific Knowledge*, Routledge and Kegan Paul, London, **1993** (reprinted from the revised fifth edition of 1989, original edition 1963).

[5] A. Kekulé, *Bull. Soc. Chim. Fr.* **1865**, *Nouvelle Serie 3*, 98.

[6] A. Kekulé, *Ann. Chem. Pharm.* **1866**, *137*, 129.

[7] A. J. Rocke, *Ann. Sci.* **1985**, *42*, 355, and references therein.

[8] S. G. Brush, *Stud. Hist. Philos. Sci.* **1999**, *30*, 21, and references therein.

[9] A. Ladenburg, *Ber. Dtsch. Chem. Ges.* **1869**, *2*, 140.

[10] J. H. Van't Hoff, *Ber. Dtsch. Chem. Ges.* **1876**, *9*, 1881.

[11] A. Kekulé, *Ann. Chem. Pharm.* **1872**, *162*, 77.

[12] A. Gero, *J. Chem. Educ.* **1954**, *31*, 201.

[13] For an instructive modern discussion of why the C–C bond lengths in benzene are all equivalent, see P. Hiberty, D. Danovich, A. Shurki, S. Shaik, *J. Am. Chem. Soc.* **1995**, *117*, 7760, and references therein.

[14] W. Hückel, in *Theoretical Principles of Organic Chemistry, Vol. 1*, Elsevier, Amsterdam, **1954**, p. 642.

1433-7851/00/3917-3047 $ 17.50+.50/0