

DIVERSIONS AND DIGRESSIONS

Koerner, Dewar and the Structure of Pyridine

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As Leonard Dobbin remarked half a century ago, there has been much confusion in the literature concerning the discovery of the structure of the most important heterocyclic aromatic compound, pyridine (1). A hitherto unpublished letter throws some additional light on the question, and supports James Dewar's claim to be earlier than the German-Italian chemist Guglielmo Koerner (Wilhelm Körner) in suggesting a formula for pyridine analogous to that of benzene.

The first to *publish* such a structure was clearly Koerner, in April 1869 in an extremely obscure Italian journal, the *Giornale di scienze naturali ed economiche*, published by the Palermo Academy of Sciences. Koerner sent this short article to the Palermo Academy only after the footnote in which the pyridine formula was proposed failed to appear in the original French version, published in the *Comptes rendus* of the Paris Academie des Sciences (2). Some scholars have suggested that the structure must have appeared too speculative to the cautious French editors; it is unlikely that Koerner himself suppressed the passage (3). The structural hypothesis would undoubtedly have remained virtually unknown to northern European chemists, had not Koerner - apparently - sent private communications of the pyridine hexagon concept to a number of colleagues. In the next few years Koerner's structure was mentioned, but without reference to a particular literature citation, by several prominent chemists (4).

In June 1870 James Dewar read a paper before the Royal Society of Edinburgh containing the same hypothesis; it was



James Dewar (1842 - 1923)



Guglielmo Koerner (1839 - 1925)

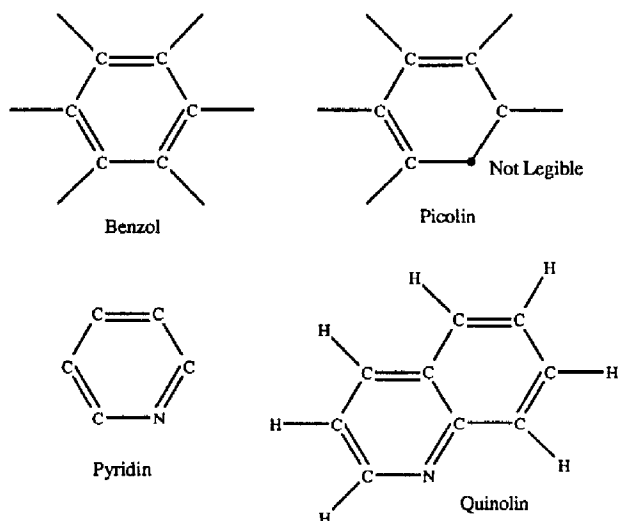
first published in January 1871 (5). He did not cite Koerner's Italian article, even though he had either a reprint or an exact transcript of it in his possession. Dewar's publication became widely disseminated, and for decades afterward it was thought that, while Koerner was the first to privately propose the idea of a pyridine hexagon, Dewar had been the first to publish it (6). A few textbook authors and historians from the 1880's onward, however, discovered Koerner's Italian publication, and gradually the news spread; the last author to assert that Koerner had never published the hypothesis was Edvard Hjelt (7).

But Dobbin showed that the situation is even more interesting: Dewar always believed that Koerner had stolen the discovery from him. Dewar and Koerner had been fellow students in August Kekulé's laboratory in Ghent in the summer of 1867 and were great friends at that time. Dewar later claimed (privately) that he had the concept even before that summer, that he had told both Kekulé and Koerner of his hypothesis, and that he was appalled when he learned of Koerner's publication. He also suggested that the hypothesis could be inferred from the contents of a paper he published in 1868. He never made a public priority claim, partly at least because he still felt friendship toward Koerner (8).

Dewar's assertion that he had revealed his thoughts on pyridine to Kekulé and Koerner is supported by a hitherto unpublished letter from Dewar to Kekulé, dated 1 June 1869, and preserved in the *August Kekulé Sammlung* at the Institut für Organische Chemie of the Technische Hochschule in Darmstadt (9). Dewar wrote, in part:

Since I had the pleasure of working under your superintendence on the Pyridine Series of Bases, I have succeeded in proving the close relationship between these nitrogenous hydrocarbons and the benzol derivatives. You recollect my idea in Ghent was that Picolin was

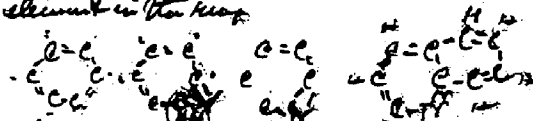
Benzol in which the N functions as a triatomic element in the ring[:]



If you don't remember [-] Koerner does [-] as lately I find this idea (nearly) "que je m'avais faite" (10) [presented] to the Palermo Academy. At the British Association [annual meeting] last year I communicated a paper on the Coal Tar Bases. Unfortunately a serious accident I had with my knee joint has prevented me from continuing the investigation for the present, but this will appear in a complete form shortly (11). I exhibited a fairly crystallized acid produced by the oxidation of Picoline[:] Dicarboxypyridenic or Pyridin Phthalic [acid]. This shows clearly the close relationship suspected between the two series. In the published abstract, I go the length of saying "I believe the bases will be produced by the action of HCN on C_2H_2 at high temperatures" (12). Now if Koerner is so confoundedly sharp in giving us new ideas in *footnotes*, why did he not go a little further and say the Pyridin bases have the same relation to the Quinolin bases as the Benzin has to the Naphthalin series? This is a very small matter but coming from a friend, I don't like it.

In short, it seems probable that Dewar did indeed conceive the pyridine structure first, and Koerner may well have imbibed the notion from Dewar, perhaps even without conscious recognition of the processes. Koerner and Dewar had been, according to Dewar's friend Henry Armstrong, a "wild pair" during that summer in Kekulé's lab; they "became associated in all sorts of devilry - Koerner being a great practical joker and Dewar a wild young Scot" (13). It was Koerner, not Dewar, who made a reputation in organic, and particularly aromatic chemistry. Indeed, Koerner became a brilliant theoretician as well as "a laboratory worker of supreme ability," to use Armstrong's words. It was Koerner who first developed, between 1869 and 1874, an absolute method of determining the structures of positional aromatic isomers - a magnificent achievement. Considering Koerner's high character and his close friendship with Dewar, it is difficult to believe that he

de la Pyridine par J. Dewar. J'en ai eu l'idée
 le jour où j'étais à l'école de chimie à Berlin
 dans un laboratoire de chimie organique. C'est là
 que j'ai vu la structure de la pyridine. J'en ai eu l'idée
 le jour où j'étais à l'école de chimie à Berlin.
 Je l'ai vu dans un livre de chimie organique.
 Je l'ai vu dans un livre de chimie organique.



Benzol Picolin Pyridin Quinolin
 J'ai vu la structure de la pyridine dans un
 livre de chimie organique. J'en ai eu l'idée
 le jour où j'étais à l'école de chimie à Berlin.
 Je l'ai vu dans un livre de chimie organique.
 Je l'ai vu dans un livre de chimie organique.
 Je l'ai vu dans un livre de chimie organique.
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 Je l'ai vu dans un livre de chimie organique.

The page of Dewar's letter showing the structure of benzene and his proposed structures for picoline, pyridine and quinoline

consciously stole Dewar's ideas. It is also a testament to Dewar's character that, despite having strong suspicions of Koerner's plagiarism, he maintained his friendship and never made a public priority claim. It was this diffidence on the part of both men that partially explains the continuing confusion in the literature on this question.

References and Notes

1. L. Dobbin, "The Story of the Formula for Pyridine," *J. Chem. Educ.*, 1934, 11, 596-600.
2. G. Koerner, "Synthese d'une base isomere a la toluidine," *Comptes rendus hebdomadaires des séances de l'Académie des Sciences*, 1869 (5 April), 68, 824; "Synthese d'une base..." *Giornale*

di scienze naturali ed economiche, Palermo, 1869 (15 April), 5, 111-114. Koerner was then working in Stanislaw Cannizzaro's laboratory in Palermo. I wish to thank Professor Leonello Paoloni of the University of Palermo for sending me a photocopy of the Italian article.

3. G. Koerner, *Ueber die Bestimmung des chemischen Ortes bei den aromatischen Substanzen*, ed. G. Bruni and B. L. Vanzetti (*Ostwalds Klassiker der exakten Wissenschaften*, No. 174, Leipzig, 1910), p. 131.

4. For example, by A. Baeyer, *Annalen der Chemie*, **1870**, 155, 282, 321; by C. Schorlemmer, *J. Chem. Soc.*, **1871**, 24, 145n.; by W. Koenigs, *Ber. Deutsch. Chem. Ges.*, **1879**, 12, 453; and by Dewar, as early as June 1869 (see letter published here). Several near-contemporary sources assert that Koerner sent "Privatmittheilungen" to friends; see reference 1 for citations.

5. J. Dewar, "On the Oxidation Products of Picoline," *Proc. Roy. Soc. Edinburgh*, **1872** (read on 6 June 1870), 7, 192-193; *ibid.*, *Trans. Roy. Soc. Edinburgh*, **1872**, 26, 189-96. Both of these articles were first published in 1872, but a reprint appeared in *Chemical News*, **1871** (27 January), 23, 38-41.

6. For example, A. Ladenburg, *Ber. Deutsch. Chem. Ges.*, **1883**, 16, 2063; E. von Meyer, *History of Chemistry*, Macmillan, London, 1891, p. 331; E. Hjelt, *Geschichte der Organischen Chemie*, Vieweg, Brunswick, 1916, pp. 326-27.

7. The first writer actually to cite the Italian journal was G. Schultz, *Chemie des Steinkohlentheers*, 2nd ed., Vol. 1, Vieweg, Brunswick, 1886, pp. 427-28. For other examples, see reference 1.

8. This paragraph summarized in reference 1.

9. I am grateful to Professor K. Hafner for permission to use this collection in May 1975, and for permission to publish this letter.

10. This is Koerner's wording in the critical pyridine footnote; Dewar evidently had received a reprint or detailed communication from Koerner within six weeks after publication of the Italian article.

11. J. Dewar, "On the Coal-Tar Bases," *Rep. Brit. Assoc. Adv. Sci.*, **1868**, 38, 35-36. The "complete form" is "On the Oxidation Products of Picoline," read to the Edinburgh Royal Society one year after this letter was written.

12. "Dicarbopyridenic" acid is of course pyridinedicarboxylic acid. I cannot see that the hexagonal structure of pyridine is even implied by Dewar's quotation from his 1868 paper.

13. H. E. Armstrong, "James Dewar," *J. Chem. Soc.*, **1928**, 130, 1066-76, on p. 1069; *idem*, *James Dewar*, Benn, London, 1924, pp. 6, 17.

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OLD CHEMISTRIES

Mystery Editors of Early American Chemistry Texts

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American chemistry, like its culture and commerce, was dominated by European influence until the latter half of the 19th century. More than half of the chemistry books published in America prior to 1850 were American editions of European works (1). The most widely used European works included Chaptal's *Elements of Chemistry* (1796 to 1813), Henry's *Epitome of Chemistry* and *Elements of Experimental Chemistry* (1802 to 1831), Marcet's *Conversations on Chemistry* (1806 to 1850), Brande's *Manual of Chemistry* (1821 to 1839), Turner's *Elements of Chemistry* (1830 to 1874) and Fowne's *Manual of Elementary Chemistry* (1845 to 1878). Even so-called "American authored" chemistry books were largely abstracts or mosaics of European works - chiefly British. Indeed, most early American chemical writers described themselves as "compilers" rather than authors.

Before the time of international copyright agreements, American publishers found it cheaper and less risky to reprint a foreign issue than to import it or to use an untried American work. Some of these reprints were unaltered copies, while others had American chemists as editors. The editor was responsible for proofreading and evaluating the text. He added footnotes, appendices, or an American preface or frontispiece. The editor was usually listed on the title page and signed his additions with "Ed" or the initial of his surname.

A few of the earliest 19th century American chemists preferred to keep their editorship anonymous. Three such volumes attributed notes to "an American gentleman", "a professor of chemistry in this country" and "an American professor of chemistry." Another three texts made no mention of an editor, but contained initialed American footnotes or other obvious American additions.

The following describes these six anonymously edited chemistry books and seeks to identify each "mystery chemist" editor.

A New System of Chemistry (1800)

In 1800, a collection of articles pirated from the *Supplement to the Third Edition of the Encyclopaedia Britannica* was issued by publisher Thomas Dobson in Philadelphia under the title *A New System of Chemistry ...* (2). The title page did not list author, editor, or source, but American footnotes signed "T.P.S." were added to the 197 page section on chemistry. The additional articles (Mineralogy, Animal and Vegetable Substances, and Dyeing Substances) did not contain "T.P.S." footnotes.

The date and initials leave little doubt that this American editor was Thomas Peters Smith (1777-1802), a promising