

Aleksandr Mikhailovich Butlerov and chemical structure: Tribute to a scientist and to a 150-year old concept

István Hargittai

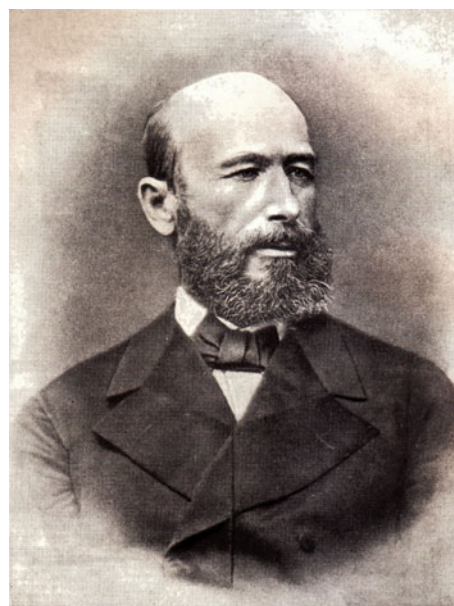
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Abstract In a pioneering move, one hundred and fifty years ago the Russian organic chemist Aleksandr Butlerov (1828–1886) coined the term “chemical structure.” He called for basing our understanding of the chemical composition of substances on the concepts of atomicity and structure.

Keywords Aleksandr Butlerov · Chemical structure · Stereochemistry

In the 1850s and 1860s, excellent chemists worked on elucidating the composition of organic substances, such as August Kekulé, Hermann Kolbe, Archibald Couper, and others. Concepts such as valence in general and the tetravalence of the carbon atom in particular were born. It was felt intuitively that there should be a correlation between the chemical properties of organic compounds and the distribution of bonds between their atoms. However, it was not yet possible to understand and, accordingly, to depict this correlation properly.

From this background is it only possible to appreciate the importance of Aleksandr Butlerov’s (Fig. 1) presentation one hundred and fifty years ago this year at the meeting of the chemistry division of the 36th congress of the German physicians and scientists. The title of his presentation on September 19, 1861, was “Einiges über die chemische Structur der Körper,” which was then printed in



A handwritten signature in dark ink, which appears to read "A. M. Butlerov". The signature is written in a cursive style with a large, sweeping flourish at the end.

Fig. 1 Aleksandr Mikhailovich Butlerov (1828–1886). The portrait is from Ref. [1]

the German journal *Zeitschrift für Chemie und Pharmacie* [2] (Fig. 2). Note the spelling of „Structur” which is „Struktur” in today’s German. Butlerov at the time was professor at Kazan University and his paper was reprinted next year in Russian translation in the journal of Kazan University [3]. Figure 3 shows the first page of this paper in which the asterisked footnote refers to the original German publication.

I. Hargittai (✉)

Materials Structure and Modeling Research Group of the Hungarian Academy of Sciences and Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, PO Box 91, 1521 Budapest, Hungary
e-mail: istvan.hargittai@gmail.com

(a) Einiges über die chemische Structur der Körper.

Von Prof. Dr. A. Butlerow.

(Vorgetragen in der chemischen Section der 36. Versammlung deutscher Naturforscher und Aerzte zu Speyer am 19. Septbr.)

Bei dem gegenwärtigen Zustande der Chemie, wo wir in den Besitz einer Masse ebenso unerwarteter als interessanter Thatsachen gekommen sind, lässt es sich ziemlich allgemein fühlen, dass die theoretische Seite unserer Wissenschaft ihrer thatsächlichen Entwicklung nicht genug entspricht.

In der That, die jetzt fast allgemein angenommene typische Betrachtungsweise, obgleich sie erst vor wenigen Jahren entstanden, und für die Entwicklung der Chemie ungemein fruchtbar gewesen ist, genügt uns doch kaum.

Es sind sogar in der neuesten Zeit einige Thatsachen entdeckt worden, welche viel mehr für die Wahrheit mancher älteren Ansichten sprechen. In der That spricht die Bildung der von Wurtz neu entdeckten Oxyäthylbasen zu Gunsten der Ansicht von Berzelius, welcher die Alkaloide als copulirte Ammoniake betrachtete, und die Aethylen-theorie der Aethylverbindungen erscheint bis zu einem gewissen Grade richtig, wenn man der Bildung des Alkohol's aus Aethylen und Wasser, der Bildung des Jodäthyl's aus Aethylen und Jodwasserstoff u. s. w. gedenkt.

Die Sache ist so, dass die Mehrzahl der älteren und, ebenso die neue Ansicht, nur einem gewissen Kreis von Thatsachen angemessen sind, und zwar denen, auf welche sie sich hauptsächlich stützen.

Dieser Kreis ist natürlicherweise viel grösser für die neue An-

Zeitschrift f. Chemie. 1861.

36

(b)

560 Butlerow, Einiges über die chemische Structur der Körper.

da man aber gewohnt ist, unter denselben diese Letztere zu verstehen und da ihre vollkommene Entwicklung nur auf Kosten von sehr vielem Raume möglich ist, so erscheinen sie kaum passend.

Ich bin weit entfernt von dem Gedanken, dass ich hier eine neue Theorie vorschlage, vielmehr glaube ich, solche Ideen auszudrücken, welche sehr vielen Chemikern gehören. Ich muss sogar bemerken, dass der Anschauung und den Formeln von Couper, dessen zu absolute und zu exclusive Schlüsse ich zur Zeit bestritt, ein ähnlicher aber nicht hinreichend klar aufgefasster und ausgedrückter Gedanke zu Grunde lag. Im Vorstehenden wollte ich nur aussprechen, dass es Zeit wäre, die Idee der Atomigkeit und der chemischen Structur in allen Fällen und ganz frei von der typischen Anschauung, als Grundlage für die Betrachtung der chemischen Constitution anzuwenden und dass dieselbe ein Mittel, der jetzigen unbehaglichen Lage der Chemie abzuhelfen, an die Hand zu geben scheint.

Fig. 2 Opening (a) and closing (b) pages of Butlerov's 1861 paper in the German journal [2]

The term „khimicheskoe stroenie” in Russian and „chemische Struktur” in German means chemical structure and was probably used for the first time. It did not go into general usage very soon, and the term stereochemistry became more popular after it had been coined in 1890 by Victor Meyer to describe the relative three-dimensional positions of the atoms in the molecule [4]. Even in Butlerov's native Russian, „struktura” and „stroenie” are used alternatively, and the word „stroenie” has a connotation of being related with the building industry. This

О ХИМИЧЕСКОМЪ СТРОЕНИИ ВЕЩЕСТВЪ *)

ПРОФ. ХИМИИ А. БУТЛЕРОВА.

Нынѣ, послѣ открытія массы неожиданныхъ и важныхъ фактовъ, почти все сознають, что теоретическая сторона химіи не соответствуетъ ея фактическому развитію. Теорія типовъ, принятая теперь большинствомъ, начинаеть оказываться недостаточною; несмотря на то, что она возникла еще недавно и много сдѣлала для развитія химіи, нѣкоторые изъ фактовъ, открытыхъ въ новѣйшее время, подтверждаютъ даже справедливость прежнихъ воззрѣній: образованіе окислѣнныхъ щелочей открытыхъ Вюрцомъ, говоритъ въ пользу взгляда Берцеліуса, принимавшаго алкалоиды за парныя соединенія амміака, а эвильная теорія эвильныхъ соединений является справедливою до известной степени, если принять во вниманіе образованіе алкоголя изъ эвильна и воды, іодистаго эвильна изъ эвильна и іодоводорода и проч.

Дѣло въ томъ, что большинство старыхъ воззрѣній, также какъ и новыя справедливы лишь для опредѣленного круга фактовъ, и преимущественно для тѣхъ, которые легли въ ихъ основаніе.

*) Статья эта была уже напечатана въ Zeitschrift f. Chemie und Pharmacie 1861. p. 549. (Einiges über die chemische Structur der Körper.), но такъ, какъ она, вмѣстѣ съ слѣдующей статьей, составляетъ приложение къ отчету о заграничной поездкѣ проф. Булѣрова, помѣщенному во II-мъ отдѣлѣ этого выпуска и при томъ объ эти статьи имѣютъ неоспоримую солидарность, то редакция и сочла необходимымъ съ одобренія факультета помѣстить въ Ученыхъ Запискахъ статью уже напечатанную въ заграничномъ изданіи.

Учен. Зап. 1862 г. отд. 1.

1

Fig. 3 Opening page of the Russian version of Butlerov's German paper in which he introduced the term “chemical structure” [3]

connotation though subtracts nothing from its being appropriate for chemical nomenclature since, knowingly or not, Butlerov introduced a term that was supposed to stress the three-dimensional nature of chemical entities. Incidentally, the bonds in Butlerov's paper linked groups of atoms rather than atoms. In this connection we note that even in the 1930s, when electronic theory of bonding was already in the vogue, the arrows in chemical texts, supposed to be indicating electron movements in chemical transformations, were often placed wherever it served the printers' convenience rather than expressing meaningful chemistry.

The tetrahedral arrangement of chemical structures goes back to Louis Pasteur who had to suppose it in order to account for dissymmetry and the optical activity of substances. There was another, little known pioneer of the tetrahedral bond arrangement of carbon, Emanuel Paternò. He published his ideas in an obscure Sicilian journal in 1869 [5]. From what he wrote though it is possible to derive what we call today conformational isomerism [6].

The year of the birth of stereochemistry, however, is considered to be 1874. The basic concepts were proposed by J. H. van 't Hoff and J. A. Le Bel, and in 1875 van 't Hoff published a booklet La Chimie dans l'Espace (Chemistry in Space). Van 't Hoff's and Le Bel's ideas were not readily accepted. The most vocal of their

opponents was Hermann Kolbe whose vitriolic words illustrate the barrier the concept of three-dimensional chemistry had to overcome [Ref. 4, p. 93]:

...A Dr. J. H. Van 't Hoff, of the Veterinarian College, Utrecht, appears to have no taste for exact chemical research. He finds it a less arduous task to mount his Pegasus (evidently borrowed from the Veterinary College) and to soar to his Chemical Parnassus, there to reveal in his *La Chimie dans l'Espace* how he finds the atoms situated in the world's space.

It is not possible, even cursorily, to criticize this paper, since its fanciful nonsense carefully avoids any basis of fact, and is quite unintelligible, to the calm investigator...

Butlerov did not participate in the controversy. When he gave his lecture in 1861, he did not even claim credit for any new thoughts. Rather, in the conclusion of his paper he stressed that he was expressing ideas that had occurred to many of his colleagues, and he mentioned in particular Couper. Butlerov added that the ideas he was presenting had not yet been expressed with sufficient clarity. In the last sentence of his paper he stresses that „it is time to base our understanding about the chemical composition of substances on the concepts of atomicity and chemical structure...” [translated from the Russian original, Ref. 1, p. 74].

Recently, David E. Lewis reviewed the significance of Butlerov's contribution to the science of organic structures accompanied by a brief description of his career [7]. Butlerov's complete works have appeared in a monumental series of four volumes in Russian, the first volume being referred to in our Ref. [1]. In the subsequent volumes, his organic chemistry text book was reproduced (Vol. 2), along with his science-popularizing works, correspondence, reviews, and other writings (Vol. 3), and, finally, treatises concerning agriculture and other studies not related to chemistry (Vol. 4).

Butlerov's activities in organic chemistry beyond the structural aspects were also significant (see e.g., [8]), but the evaluation of his oeuvre has been clouded with interference from politics. In the Soviet Union, he was at times considered as the founder of the science of organic chemistry, and his memory was kept alive (Figs. 4, 5, 6). In contrast, in the West, his contributions were often underestimated. The blatant actions to politicize his chemistry occurred most conspicuously during the big controversy about the theory of resonance in the Soviet Union in the early 1950s. Butlerov explicitly stated that each compound had one chemical structure and only one. The critics of the theory of resonance used Butlerov's teaching to discard the possibility of resonance structures as it would allow two or



Fig. 4 Butlerov's statue in Kazan, courtesy of Boris Solomonov, Kazan



Fig. 5 Butlerov's statue in front of the Chemistry Department, Moscow State University (photograph by the author)



Fig. 6 Soviet stamp issued in 1951, at the height of the Soviet resonance controversy, and it says, “A. M. Butlerov, great Russian chemist creator of the theory of chemical structure of organic compounds”

more structures to coexist. Had this been part of a sober scientific discussion it could have been considered a reasonable argument.

Unfortunately, in the early 1950s, this grew into an ideological and even nationalistic controversy with grave consequences for the proponents of the theory of resonance. The critics of the theory of resonance contrasted Butlerov’s true Russian values with the cosmopolitan views of those who had bowed slavishly to Western values, etc. The proponents of the theory of resonance had to exercise humiliating self-criticism and lost their jobs [9]. The minutes of a meeting in Moscow on June 11–14, 1951, were published in a 440-page hardbound volume [10]. Four hundred and fifty chemists, physicists, and philosophers attended the meeting, including the top chemists from all over the Soviet Union. There was a report on “The status of chemical structure theory in organic chemistry” compiled by a special commission of the Chemistry Division of the

Soviet Academy of Sciences. It was followed by forty-three oral contributions. The report consisted of eight chapters and the first was titled “Butlerov’s teachings and their role in the development of chemistry.”

Linus Pauling was among the Western scientists attacked in the Soviet resonance controversy, and he seemed rather puzzled by these attacks and even after many years appeared as if he had misunderstood the situation in Soviet Union in the 1950s [11]. Today, we should not let the unprincipled past misuse of Butlerov’s teachings mask the values of his pivotal contributions to organic chemistry as well as to structural chemistry.

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