

Johann Friedrich Wilhelm Adolf von Baeyer

A Pioneer of Synthetic Organic Chemistry

Gopalpur Nagendrappa

Important discoveries in chemistry most certainly contribute to the industrial and economic developments and indirectly direct the course of history. A majority of Baeyer's research findings are of this kind. In the pursuit of synthesising a variety of organic compounds for more than half a century, Baeyer became the first chemist who can be considered as classical synthetic organic chemist. He did groundbreaking research in sixteen different areas of organic chemistry, such as dyes, hydroaromatic compounds, polyacetylenes, uric acid and related compounds, natural products. Baeyer's strain theory is a common textbook topic at the UG level. His work on hydroaromatic compounds strongly supported Kekule's benzene structure. For this and the work on dyes, he was awarded the 1905 Nobel Prize in Chemistry.

Introduction

Organic synthesis is the science as well as the art of putting together simpler molecules step-by-step in order to get a molecule of previously determined more complex structure. The methodology had a humble beginning around the mid-nineteenth century and has reached a stage where it has become possible to make molecules of mind-boggling complexity.

Starting with alizarine and then indigo, the two important dyes that used to be extracted from plant sources, Baeyer and his associates were able to first systematically determine their structures and synthesise them by rationally planned multistep reactions. The methodology they used may seem to be primitive now, but that was a great achievement then, and the fundamental principle of the method is followed even today. During its initial period, organic synthetic chemistry was significantly enriched by the pioneering and multifaceted activity of Baeyer's school,



G Nagendrappa was a Professor of Organic Chemistry at Bangalore University, and Head of the Department of Medicinal Chemistry, Sri Ramachandra (Medical) University, Chennai. He is currently in Jain University, Bangalore. He continues to teach and do research. His work is in the area of organosilicon chemistry, synthetic and mechanistic organic chemistry, and clay-catalysed organic reactions (Green Chemistry).

Keywords

Baeyer, dyes, alizarin, indigo, strain theory, benzene structure, phthalein dyes, acetylenes.

Even as a boy Baeyer had a keen interest in chemistry. At the age of twelve years he discovered a double salt of copper which was found to be $\text{CuNa}_2(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$.

Baeyer's fascination for the blue indigo was so much that he bought a lump of the brilliant dye to celebrate his 13th birthday.

which nourished not only good chemistry but great chemists, who contributed immensely to the advancement of organic chemistry subsequently. Here is a very brief account of Baeyer's life and some of his achievements.

Early Life and Education

Adolf Baeyer was born in Berlin on October 31, 1835, to Johann Jacob Baeyer and Eugenie Hitzig, both of whom belonged to highly respected and well-known families. Johann Jacob Baeyer served as lieutenant-general in the Prussian army and also taught in the army school. He was a famous geodesist who started the European system of geodetic measurement and became the Director of Berlin Geodetical Institute. Eugenie's father, Julius Eduard Hitzig, was a jurist and distinguished himself in literature too. Hitzigs were Jews, but Eugenie converted to Evangelical Christianity. (However, Jewish records show that Adolf von Baeyer was the first Jew to get the Nobel Prize). Adolf was the fourth of the five children of Johann Jacob and Eugenie Baeyer. The older siblings were Clara, Emma and Eduard, and the younger was Jeanette, born respectively in 1826, 1831, 1832 and 1839.

Adolf completed his school education at Friedrich Wilhelm Gymnasium in Berlin, and then joined the University of Berlin in 1853. Even as a boy he had a keen interest in chemistry. At the age of twelve years he discovered a double salt of copper which was found to be $\text{CuNa}_2(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$. His fascination for the blue indigo was so much that he bought a lump of the brilliant dye to celebrate his 13th birthday. However, when he joined Berlin University he took physics and mathematics as subjects of his study. After three semesters at the university he had to go for compulsory military service in the Prussian army for a year. When he returned to his studies in 1856 he went back to his old love, chemistry, and headed to Heidelberg to train under Robert Bunsen. After one semester, he worked there in the private laboratory of August Kekule. While in Heidelberg with Bunsen and Kekule, he did his thesis work on methyl chloride and its arsenical or cacodyl compounds (e.g., $\text{Me}_2\text{As}-\text{AsMe}_2$). Based on



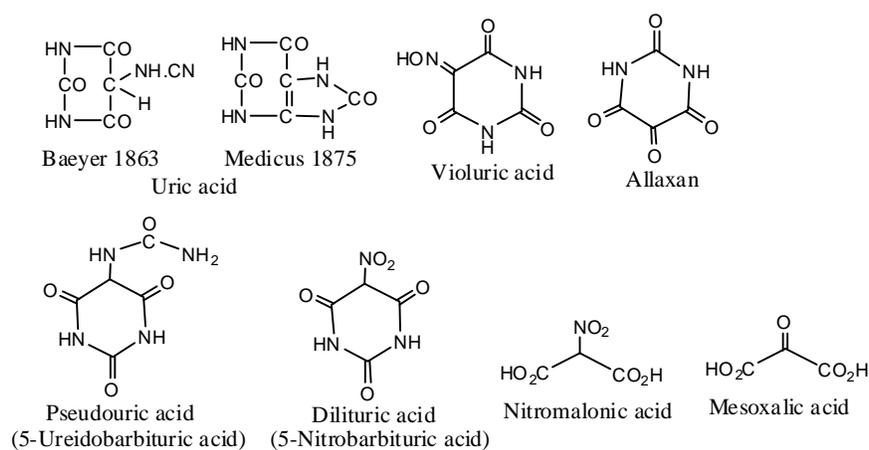
this work, written in Latin, Baeyer was awarded the doctorate degree in 1858 by the University of Berlin. Since he did not get an academic appointment soon after, Bayer followed Kekule to the University of Ghent in Belgium, where the latter was appointed as Professor in the same year. At Ghent, Baeyer started his work on finding the constitution of uric acid (*Box 1*).

Box 1.

Uric acid has a long history. It was discovered by Karl Wilhelm Scheele in 1776 in bladder stone and human urine. He studied some of its properties. It is a major constituent of excrement of birds and reptiles, but mammals excrete it rarely. Though healthy human urine has hardly any of this substance, gout patients' urine contains it in significant amounts. It forms in the body as a metabolic product of proteins and purines in nucleic acids. Because of its importance in animals and humans, a lot of work has been done on its chemical, physiological, pathological and other biological aspects.

From Scheele to Friedrich Wöhler and Justus von Liebig many chemists studied its properties and reactions. Liebig and Mitscherlich independently determined its molecular formula as $C_5H_4N_4O_3$ in 1834. Between 1834 and 1838, they subjected uric acid to many reactions.

Baeyer's work on uric acid and related compounds – pseudouric acid, hyaluric acid, violuric acid, dilituric acid and their salts, violautin (a complex derivative of barbituric acid), and allaxan bromide, allaxan derivatives, nitromalonic acid, mesoxalic acid and some of their derivatives – during the first half of the 1860s gave some clue to its constitution. Several structures were proposed for uric acid in 1870s (soon after Kekule's structural theory was proposed). The structure proposed by L. Medicus in 1875 was confirmed by E. Fischer in 1882.



Baeyer used the structural theory in his research to solve the molecular structures and later provided solid experimental support to the theory, particularly to Kekule's benzene structure.

Back to Berlin – a Long Teaching and Research Career Starts

Baeyer presented his uric acid work at Berlin University in 1860 by which he earned the eligibility to teach there. As a result, Berlin University appointed him as a Privat Dozent (similar to an assistant professor) at a constituent institution, the Gewerbe Akademie¹. The Akademie provided Baeyer a big laboratory, but he was given very little remuneration and inadequate funds for the laboratory. However, he was quite happy to be in the Akademie, because at that time the University of Berlin did not have a proper chemical laboratory.

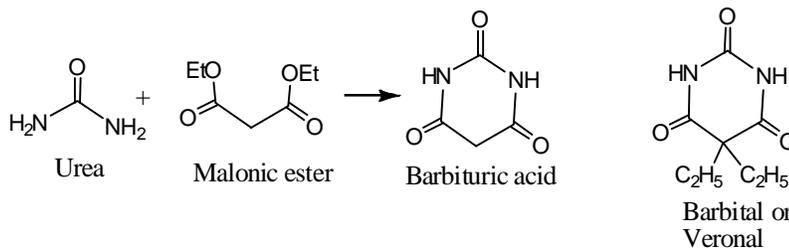
Baeyer's association with Kekule had greatly benefited him in terms of getting to know firsthand the latter's ideas on the structural theory from its initial stage. Baeyer used the structural theory in his research to solve the molecular structures and later provided solid experimental support to the theory, particularly to Kekule's benzene structure. Though Kekule was older and Baeyer's doctoral thesis adviser, the two had a very cordial and friendly relationship throughout their lifetime.

¹ Trade Academy or the Berlin College of Vocational Studies, which was later renamed as Charlottenburg Technische Hochschule, and now has become the Technical University of Berlin

In Gewerbe Akademie, Baeyer continued to work on the problems he was engaged in earlier. The experience he had gained from the studies on uric acid enabled him in 1864 to develop the

Box 2.

Barbituric acid is the parent compound of a class of more than 2000 medicinal compounds called 'barbiturates'. The first barbiturate of medicinal application was 'barbital' synthesised by Emil Fischer and von Mering. It is a long-acting sedative. It was tested on a dog, which slept peacefully for many hours. It was marketed under the name 'Veronal', named by von Mering after the city of Verona in Italy, because he considered it as the most peaceful place in the world.



Box 2. continued

Box 2. continued

As for the origin of the name 'barbituric acid', there are many stories. But the most credible one seems to be the following. The day on which the compound was prepared happened to be Saint Barbara Feast Day. Baeyer was celebrating his discovery of the new compound in a pub, where a guest suggested to him to use the name of the saint. Thus combining Barbara with urea, Baeyer coined the word 'barbituric' and ended it with 'acid'.

There are other interesting stories, which are most likely made up. One such is this. At the time when Baeyer synthesised barbituric acid, he had a girlfriend named Barbara after whom he named the compound. Yet another, quite a queer one, is that the urea used for the synthesis of the compound was extracted from the urine of a local bar maid named Barbara.

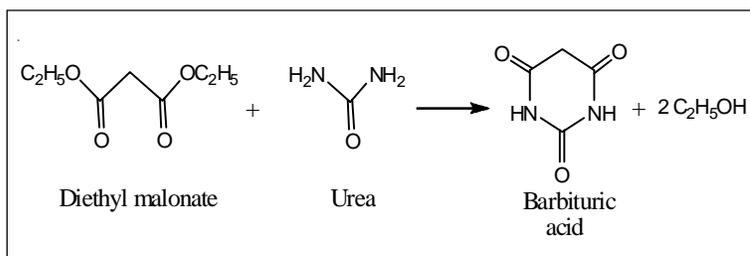
synthesis of barbituric acid (*Box 2*) by condensing diethyl malonate with urea (*Scheme 1*). (It should be remembered that the structures written here were unknown in this form then.)

In 1865, Baeyer started his life's most important work, namely the determination of indigo structure (more about this later), which held his attention for nearly two decades. He proposed its correct structure finally in 1883. Thereafter, he continued to take interest in making its commercial production possible.

In 1866, impressed by the success of young Baeyer, August Wilhelm Hofmann, who was then Professor and Director of the chemistry laboratory in Berlin University, recommended him for Professor's position. Baeyer was promoted, but was not given financial benefits. Though Baeyer felt unhappy about this, it did not detract him from his hard work. By 1869 he converted indigo into indole through a series of reactions. Thus, he discovered indole, one of the most important heterocyclic compounds.

In 1867, he took a leading role in establishing the Deutsche

By 1869 he converted indigo into indole through a series of reactions. Thus, he discovered indole, one of the most important heterocyclic compounds.



Scheme 1. Baeyer's barbituric acid synthesis.

Chemische Gesellschaft zu Berlin, the oldest forerunner of the present day Gesellschaft Deutscher Chemiker (Society of German Chemists). The first President of the Society was AW Hofmann and the Secretary was Baeyer.

² The University was named after the Prussian ruler Kaiser Wilhelm. It has a long history starting from the 16th century under German rule. It changed hands several times between France and Germany, and presently it is the second largest university in France.

³ See *Resonance*, Vol.16, pp.606–618, 2011.

⁴ See *Resonance*, Vol.18, pp.397–417, 2013.

In 1872, the University of Strassburg² (Strasbourg in French) was re-established under Prussian rule after the Franco–German war of 1870–71 ended and Strassburg was ceded to Germany. Baeyer was offered the position of Chair of Organic Chemistry there, and he gladly accepted it. There he continued to work on uric acid derivatives, nitroso compounds, indigo, and also started research on phthalein dyes and phenol-formaldehyde reactions. Otto Fischer and Emil Fischer³ joined him as PhD students. Baeyer stayed in Strassburg only for three years and moved to the University of Munich in 1875 to succeed Justus von Liebig⁴, an eminent and influential chemist, who had passed away in 1873. He was associated with Munich University for the next 43 years until he retired in 1915 at the age of 80 years, just 2 years before he died on August 20, 1917. During this period he completed his most important work on the elucidation of the structure of indigo and its synthesis, proposed the strain theory of ring compounds, worked on the C- and N-nitroso compounds and acetylenes, provided a great deal of experimental evidence for Kekule's benzene theory, discovered oxidation of ketones with peracids (Baeyer–Villiger reaction), continued his collaboration with the BASF chemical company by which he greatly contributed to the development of the German dye industry, and received, apart from other honours, the Nobel Prize in 1905.

Marriage and Family

Baeyer was associated with Munich University for the next 43 years until he retired.

Baeyer married Adelheid Bendemann in 1868. They had four children: Eugenie (Baeyer's mother's namesake), Franz, Hans Emil Ritter and Otto, born respectively in 1869, 1870, 1875 and 1877. Eugenie married the well-known organic chemist Oskar Piloty. Piloty had joined Baeyer for his PhD, but later worked and obtained the degree under Emil Fischer at Berlin (*Box 3*). Franz died at the age of 10. Hans Emil Ritter von Baeyer studied



Box 3.

Oskar Piloty (1866–1915) fell in love with Eugenie while working as a doctoral student of Baeyer. The story is that as Baeyer did not like the affair, he failed Piloty in an examination and Piloty had to leave. However, Piloty joined Emil Fischer and obtained his PhD degree at the University of Würzburg and married Eugenie. He moved to the University of Berlin with Fischer. In 1900, Baeyer offered Piloty a position in his department in Munich, which Piloty accepted, although Fischer offered him a better position in Berlin. Piloty had to go for compulsory military service during World War I. He was killed in 1915 during a fight at the battle of Champagne in the Western Front. His research work was in the field of natural products, particularly on the structure of haemoglobin.

medicine and became Professor of Orthopaedics and Physician-in-Chief at the University of Heidelberg. In 1930, he was the President of the German Society for Orthopaedics. In 1933, he was dismissed by the Nazi government, because of his Jewish ancestry. (Adolf von Baeyer's mother as well as his wife were of Jewish descent and he is listed as the first among the 191 Jews who have won the Nobel Prize, which amounts to about 22% of all Nobel Prize winners worldwide between 1901 and 2013, while the Jews constitute just about 0.2% of the world population). Otto von Baeyer became Professor of Physics at the Agricultural University in Berlin.

Awards and Honours

The impact of Baeyer's work in different areas of organic chemistry on contemporary and later research and German chemical industry was enormous. The methodology he developed for determining the structures of a large number of organic molecules was highly systematic, and the crowning glory was solving the structure and the synthesis of the so-called 'king of dyes', indigo, (which was considered at that time as a tough task) accomplished with great skill, perseverance and hard work. It was the first natural product molecule whose structure was solved systematically by degradative reactions followed by analysing the products formed, which culminated in developing several logical routes by him and others for its synthesis. The procedure became a model for natural products studies. The development of industrial production

Bayer is listed as the first among the 191 Jews who have won the Nobel Prize, which amounts to about 22% of all Nobel Prize winners worldwide between 1901 and 2013,

The impact of Baeyer's work in different areas of organic chemistry on contemporary and later research and German chemical industry was enormous.



Indigo had a special implication for Indian agriculture, and the economic, social and political setting in the early part of the 20th century.

⁵ See *Resonance*, Vol.8, No.3, pp.42–48, 2003.

⁶ One of the giant chemical industries of Germany, Bayer AG, thrived under Duisburg's leadership

Baeyer's research activity spanned almost sixty years of the eighty-two years of his life.

of synthetic indigo had a special implication for Indian agriculture, and the economic, social and political setting in the early part of the 20th century⁵.

These accomplishments naturally attracted recognition by the academic, scientific and industrial community and Baeyer was honoured with awards, prizes and in other ways. In 1905, he was given the Nobel Prize “in recognition of his service in the advancement of organic chemistry and the chemical industry, through his work on organic dyes and hydroaromatic compounds”. The accolades had started pouring in much earlier. In 1881, the Royal Society of London honoured him with the prestigious Davy Medal. In 1884, he was elected foreign honorary member of the American Academy of Arts and Sciences. On his 50th birthday (in 1885) Bayer, like his predecessor Justus von Liebig, was bestowed with the status of hereditary nobility by the Bavarian ruler, and since then his family name got the prefix of honour ‘von’. In 1891, the Bavarian government conferred him with its highest civilian award ‘Order of Maximilian’. Likewise, in 1894, the Prussian government granted ‘Order pour le Merite’. Baeyer's students celebrated his 70th birthday and the occasion was commemorated by the publication of two volumes of *Collected Works (Gesammelte Werke)*, a collection of his research papers classified in sixteen groups (more on this later). On his 75th birthday, an endowment was created in his honour by Carl Duisburg, who, once Baeyer's assistant in Munich, became one of the outstanding industrial chemists of the 20th century⁶. With the proceeds of this endowment, the Society of German Chemists presents the Adolf von Baeyer Medal once in 2–3 years to a distinguished organic chemist.

Baeyer's Scientific Achievements

Baeyer's research activity spanned almost sixty years of the eighty-two years of his life, though the last ten years were not quite productive, as he published only two of his 305 papers in this period. The range of topics he worked on is amazingly varied and spread over many different classes of organic compounds.



The two volumes of the *Collected Works* brought out at his 70th birthday celebrations together consisted of sixteen different areas of research: (1) Organic arsenic compounds, (2) Uric acid group, (3) Indigo – indigo researches, (4) Pyrrole and pyrrole bases, (5) Condensation reactions, (6) Phthaleins, (7) Hydroaromatic compounds and structure of benzene, (8) Terpenes, (9) Nitroso compounds, (10) Furfural, (11) Acetylene compounds and strain, (12) Peroxides, (13) Basic properties of oxygen and oxonium salts, (14) Dibenzalacetone and triphenylmethane, (15) Aromatic series, and (16) Aliphatic series. Most of them were of fundamental importance in advancing the progress of organic chemistry. Although each one of these topics became significant, the ones that made the greatest impact on the contemporary chemistry include indigo, hydroaromatic compounds and strain theory of ring compounds.

Before Baeyer started his work on indigo, his major research activity during 1860–1865 was in the area of uric acid and related compounds. The analysis of the components and characteristics of urine had engaged the attention of scientists and medical men since a long time. From the time Walter Scheele isolated it from kidney stones, many leading chemists worked on various aspects of its properties, reactions and structure. (More on this in *Box 1*.)

Work on Dyes

Baeyer's research work on indigo has special significance to India, because the synthetic indigo completely eliminated the cultivation of indigo plants which had provided livelihood to a large number of farmers, labourers and traders. The shift from natural to the synthetic dye brought misery not only to these communities, but it also led to a minor social and political upheaval in a large part of Bihar and Bengal in the early part of the 20th century. The sordid events brought Mahatma Gandhi on the scene to resolve through negotiations the conflict that had ensued between the farmers and the landlords who had leased land to cultivate indigo crop. Gandhiji's intervention was initially prevented by the British rulers, but they quickly relented

The sordid events brought Mahatma Gandhi on the scene to resolve through negotiations the conflict that had ensued between the farmers and the landlords who had leased land to cultivate indigo crop.

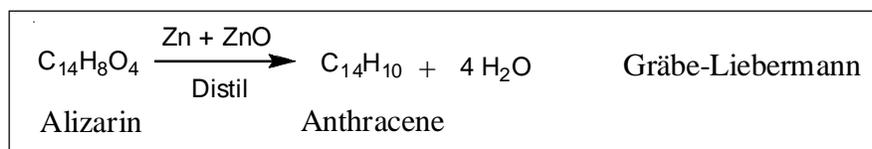


Indigo characterises the magnificence of Adolf von Baeyer's research work and is integral to the story of his life.

⁷ See *Resonance*, Vol.16, pp.1168–1175, 2011; Vol.17, pp.1022–1033, 2012.

In 1868, Baeyer's group reduced alizarin to anthracene by its dry distillation with zinc dust, a procedure discovered by Baeyer while reducing anthraquinone to anthracene.

Scheme 2. Reduction of alizarin to anthracene.

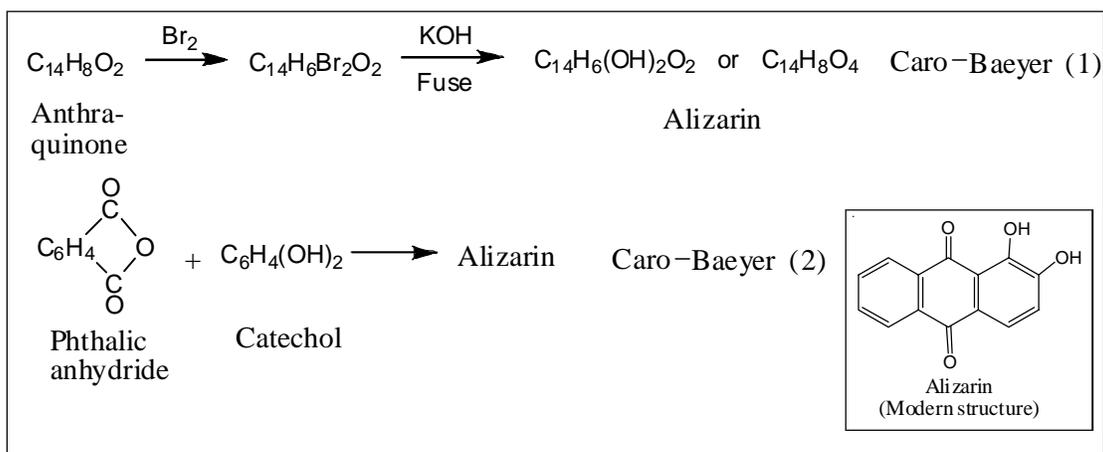


when they realised that they could not handle the consequences of the firm stand he had taken to resolve the issue. It was the first instance of the Mahatma's involvement with the civil disobedience as part of the Indian independence movement. More on this subject and chemistry aspect can be found in earlier *Resonance* articles⁷. Synthetic indigo had impact on commercial interests, history and of course chemistry. It characterises the magnificence of Adolf von Baeyer's research work and is integral to the story of his life. Therefore, a perspective of indigo chemistry is presented here.

Alizarin

Baeyer started his research on indigo in 1865. The blue-coloured indigo and the red-coloured alizarin were then the two most important dyes in use; these were isolated from plant sources. Indigo was produced mainly from *Indigofera tinctoria* and a relatively small quantity from *Isatis tinctoria* (woad plant) in Europe. Alizarin was extracted from the roots of madder plant (*Rubia tinctorum*, the common madder; *Rubia peregrine*, the wild madder; and *Rubia cordifolia*, the Indian madder, Manjistha, used even at the time of Mohenjo-daro). The common madder was the main source of alizarin and was grown largely in France. Carl Liebermann, who had obtained his PhD in 1865 under Baeyer, and Carl Gräbe, who had received his PhD from Heidelberg under the supervision of Bunsen, were in Baeyer's group. In 1868, they reduced alizarin to anthracene by its dry distillation with zinc dust (*Scheme 2*), a procedure discovered by Baeyer while reducing anthraquinone to anthracene. It was an exciting revelation to know that the beautiful red dye is a simple dihydroxy derivative of anthracene.

The fledgling chemical company, Badische Anilin and Soda Fabrik, saw the commercial possibility in it and supported the

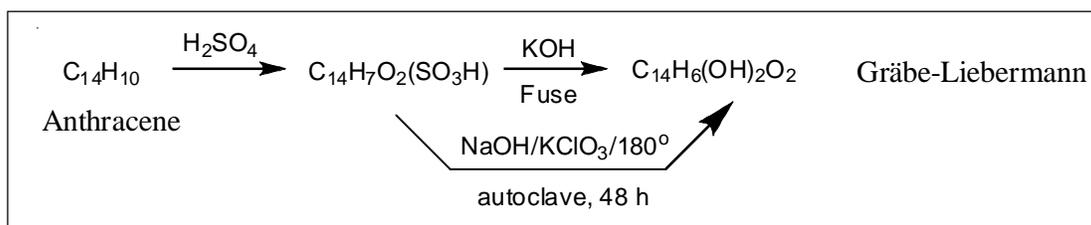


research. Heinrich Caro (1834–1910), the head of chemical research at BASF from 1868, and Baeyer, who knew Caro from an earlier time, together determined the position of the two hydroxyl groups by degradative and synthetic methods. They accomplished the synthesis by two routes (*Scheme 3*). In the first one carried out in 1869, they brominated anthraquinone to its dibromo-derivative, which they fused with potassium hydroxide to get the dye, (see equation (1)). They were lucky to have obtained the right isomer from among the ten possible ones. In the other method, they condensed phthalic anhydride with catechol and obtained alizarin, (see equation (2)). However, these two methods were not commercially competitive with the natural dye.

Scheme 3. Baeyer–Caro synthesis of alizarin.

Since several other reactions of anthraquinone were already known, it was not difficult for Gräbe and Liebermann to devise alizarin synthesis starting from it, which was made by oxidising anthracene, a product of coal tar distillation that had no useful application till then. For industrial synthesis a method was developed by Gräbe and Liebermann, consisting of a combined sulphonation-oxidation of anthracene to anthraquinone sulphonic acid, which was then fused with KOH to alizarin (*Scheme 4*).

This method was found to be commercially viable. Gräbe and Liebermann got the patent for the synthesis and BASF bought the manufacturing rights. BASF was fortunate to apply for patent just one day before William Henry Perkin did, who had indepen-



Scheme 4. Gräbe–Liebermann industrial synthesis of alizarin.

⁸ See *Resonance*, Vol.15, pp.779–793, 2010.

Bayer's contribution to the field of phthalein dyes is quite significant: his studies on phenolphthalein, resorophthalein and related colouring compounds centred on their synthesis, application and understanding the relationship between their colour and constitution.

dently developed a synthetic method for alizarin⁸.

This was the first successful attempt at synthesising a natural product after systematically determining its structure. (The then recently proposed Kekule theory of benzene structure helped in solving the alizarin structure, though proper ring structures were still not written freely at that time). Within a very short time artificial alizarin replaced the natural dye and BASF could make huge profits by marketing it all over the world (except in the United Kingdom, where Perkin had the patent right).

Before the manufacture of the artificial alizarin, France was the main source of madder root. The availability of a cheaper and better quality artificial dye rendered its natural source, the madder root unwanted. France, which had earned \$ 5 million in 1868 from madder products, could earn only \$ 300,000 three years later and within the next five years, the earning had practically stopped. This case of alizarin business of France presaged the fate of the Indian indigo business about three decades later, when again Baeyer succeeded in solving the structure of indigo finally in 1883, and its commercial manufacture by BASF was achieved towards the end of the 19th century.

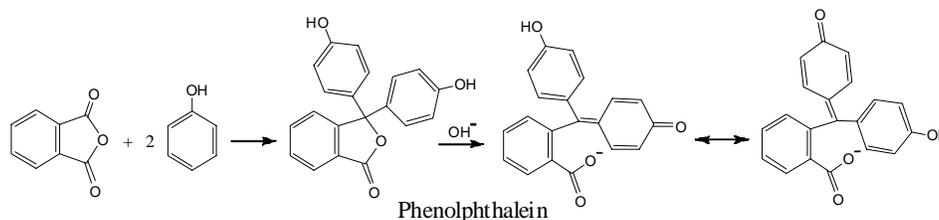
Phthalein Dyes

With the success of alizarin synthesis, Baeyer's relationship with BASF became closer and his interest in the chemistry of dyes continued. His contribution to the field of phthalein dyes is quite significant: his studies on phenolphthalein, resorophthalein (*Box 4*) and related colouring compounds centred on their synthesis, application and understanding the relationship between their colour and constitution. The most important piece of



Box 4

Phthaleins, a large group of triphenylmethane dyes, are synthesised by condensing phthalic anhydride with phenols. Phenolphthalein is one such dye commonly used as an indicator in acid–base titrations, because it changes colour sharply from colourlessness in acidic medium to pink in alkaline solution. It is also used in crime detection as in exposing bribery and identifying blood in stains.



Similarly, resorcinol, cresols or any other phenol forms the corresponding phthalein. The reaction of resorcinol with phthalic anhydride gives an orange-red solid which is soluble in water and alcohol. The solution is of yellow-green fluorescent colour and hence the dye is called fluorescein. The dye has application in microscopy, as dye laser, in detecting blood in stains and as fluorescent tracer.



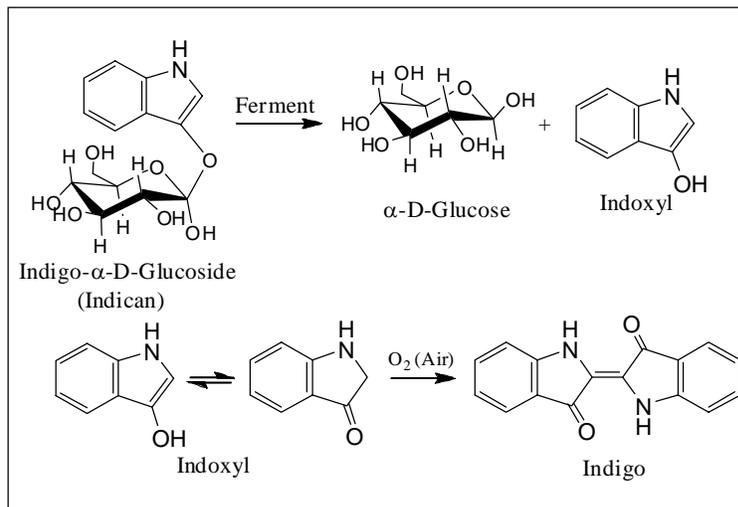
In 1961, a plumber in Chicago used fluorescein to find out which one of the city waste drain pipes was polluting the Chicago River. The plumber's act gave the idea to the manager of the plumbing company to dump fluorescein dye into the river to turn it green for Saint Patrick's Day, because green colour is associated with the Saint. Since then this practice is observed every year as part of the celebrations and the Chicago River flows with green water with yellow fluorescence for some time on that day.

Baeyer's work in the area of dyes has been the determination of the structure and synthesis of blue indigo. This is considered as one of the important achievements of 19th century organic chemistry.

Indigo

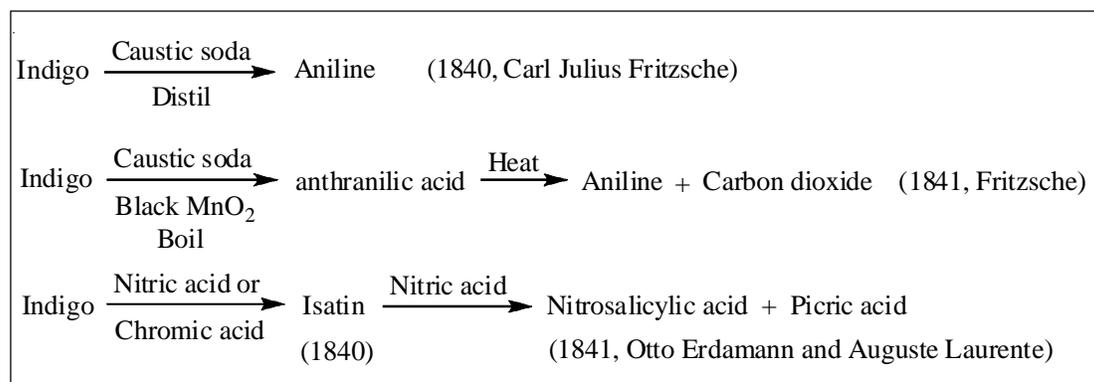
Indigo, also called indigotin and indigo blue, is found in indigofera plants in the form of glycoside of indoxyl, called indican. When these plants are boiled with water and the mixture is allowed to ferment, indican is released and further converted into indoxyl and then to indigo by air oxidation (*Scheme 5*).

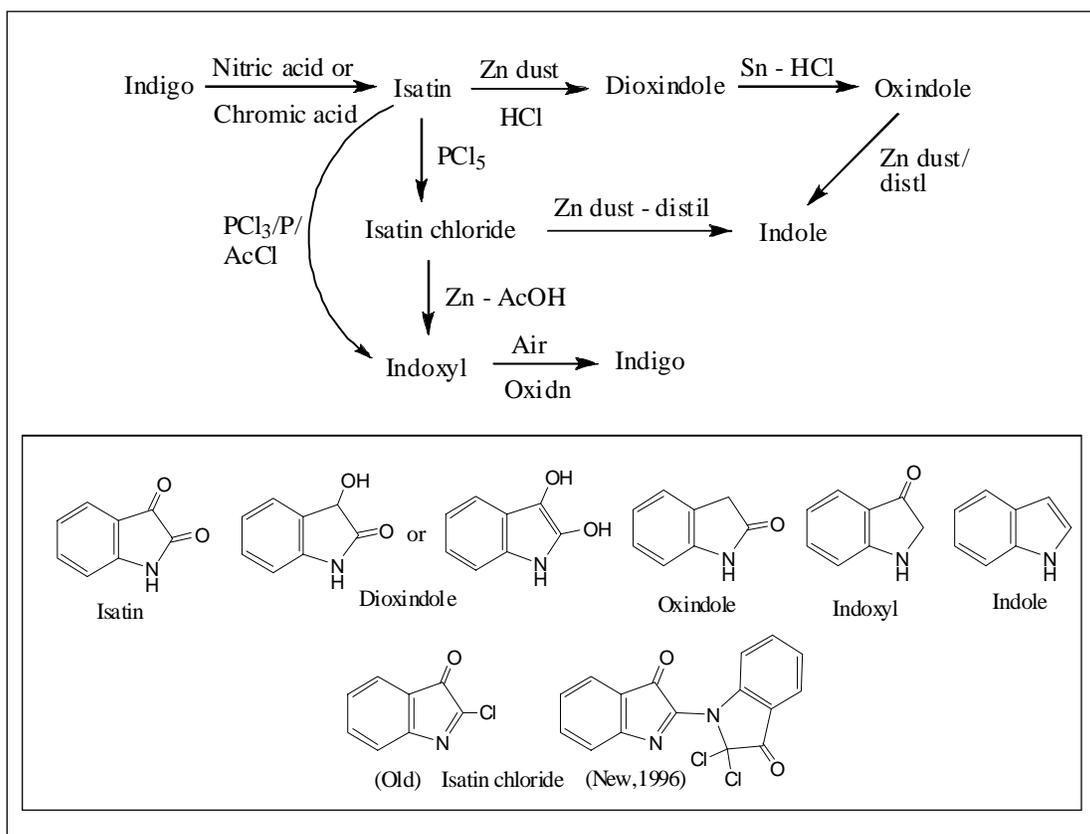
Indigo, also called indigotin and indigo blue, is found in indigofera plants in the form of glycoside of indoxyl, called indican.

Scheme 5. Indigo from natural source, indicant.

Carl Fritzsche distilled indigo with caustic soda and obtained aniline (Spanish: *Anil*, Arabic: *An-nil*, Sanskrit: *Nila* for indigo plant and also dye).

Walter Crum had obtained pure indigo by sublimation. In 1840, Carl Fritzsche distilled indigo with caustic soda and obtained aniline (Spanish: *Anil*, Arabic: *An-nil*, Sanskrit: *Nila* for indigo plant and also dye). In 1841, Fritzsche obtained anthranilic acid on boiling indigo with caustic soda and black manganese dioxide. In the same year Otto Erdmann and Auguste Laurent independently oxidised indigo with nitric acid and chromic acid and isolated isatin, which with more nitric acid yielded nitrosalicylic acid and picric acid (*Scheme 6*).

Scheme 6. Indigo reactions known before Baeyer's work.



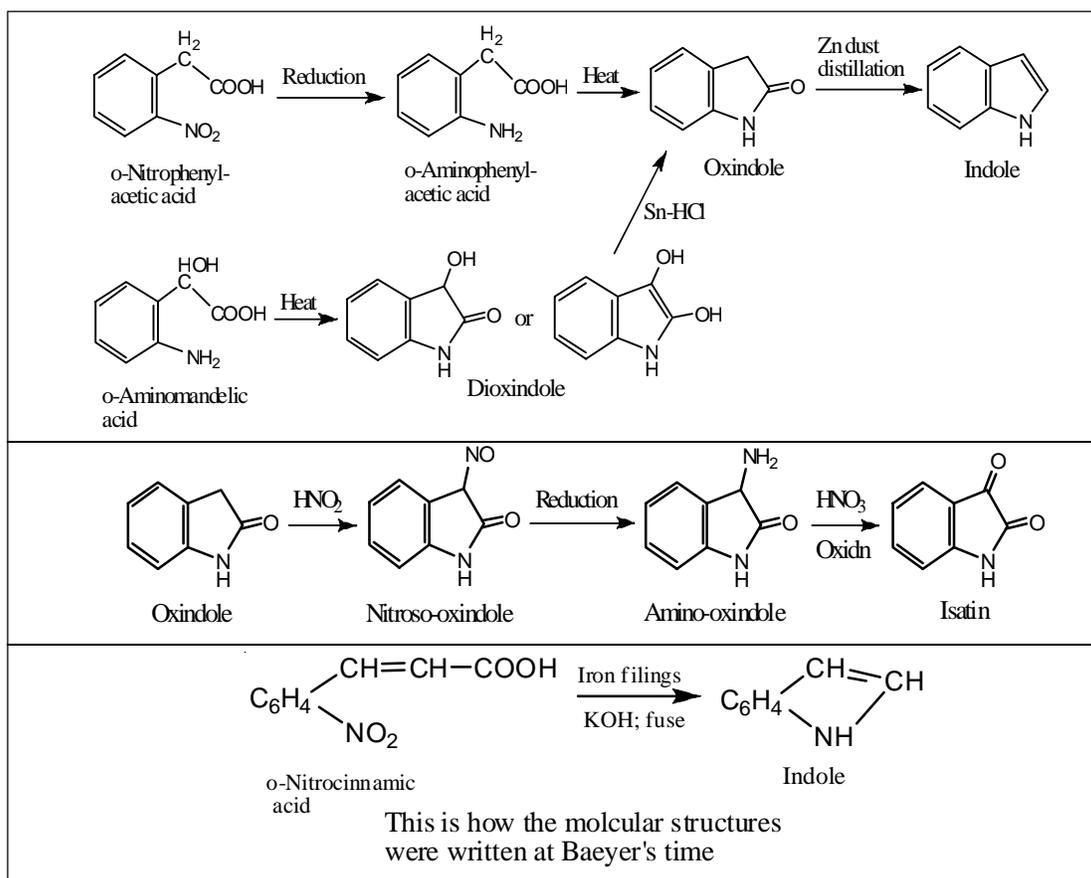
determined its vapour density, he revised the molecular formula to $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$.

Baeyer started his research on indigo in 1865 with the earlier work of others as the backdrop. He perhaps did not need the correct molecular formula for his earlier work (before 1878), but once it was found, it certainly did help him in solving its structure. Between 1865 and 1869, he investigated the conversion of indigo into various products and succeeded in carrying out its partial synthesis. Some of these transformations are presented in *Scheme 7*.

In the process of determining the structure of indigo, Baeyer discovered indole, of which he considered indigo to be a derivative. (Later indole was found to be the parent heterocyclic structural unit in a large number of natural products, including alkaloids, amino acid tryptophan, plant growth hormone indole-3-acetic

Scheme 7. Some indigo reactions carried out by Baeyer. Inset: Modern structures of the products appearing in *Scheme 7*.

Between 1865 and 1869, he investigated the conversion of indigo into various products and succeeded in carrying out its partial synthesis.



Scheme 8 (top). Baeyer's indole synthesis.

Scheme 9 (center). Conversion of oxindole to isatin.

Scheme 10 (bottom). Baeyer–Emmerling indole synthesis.

The relationship of indole to benzene was demonstrated in 1869 by Baeyer and Emmerling by preparing indole starting from *o*-nitrocinnamic acid.

acid and others). He established the structural identities of these compounds by carefully planned syntheses (*Scheme 8*).

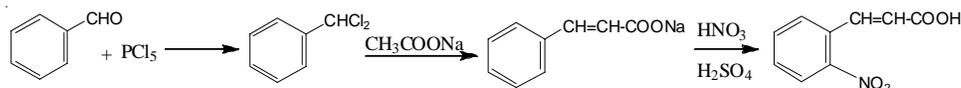
Baeyer and Knop converted oxindole to nitroso-oxindole by reacting it with nitrous acid. This was reduced and the amino derivative was oxidised to isatin (*Scheme 9*).

From these conversions Baeyer recognised close relationship between these compounds by their empirical formulae: indigo = C_8H_5NO , isatin = $C_8H_5NO_2$, dioxindole = $C_8H_7NO_2$ and indole = C_8H_7N .

The relationship of indole to benzene was demonstrated in 1869 by Baeyer and Emmerling by preparing indole starting from *o*-nitrocinnamic acid (*Scheme 10*). Baeyer gave the formula of indole as shown in the scheme.

Box 5.

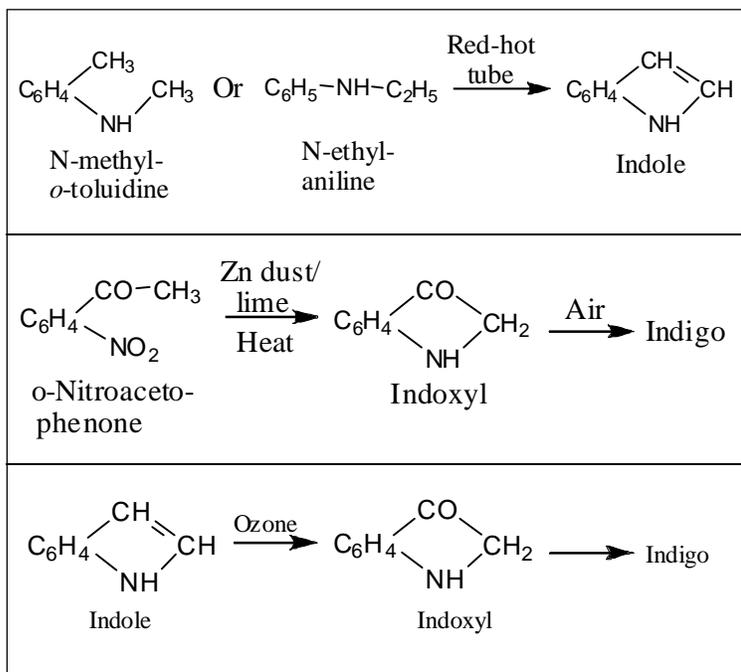
Baeyer prepared sodium cinnamate and then converted it to 2-nitrocinnamic acid by the following route.



It should be noted that Perkin had not yet discovered the condensation of aromatic aldehydes with acetic anhydride and sodium acetate to produce α,β -unsaturated carboxylic acids. Hence, Baeyer used a slightly circuitous method given above.

Baeyer and Caro obtained indole, in 1877, by passing N-methyl-*o*-toluidine or N-ethylaniline through red hot tube (*Scheme 11*).

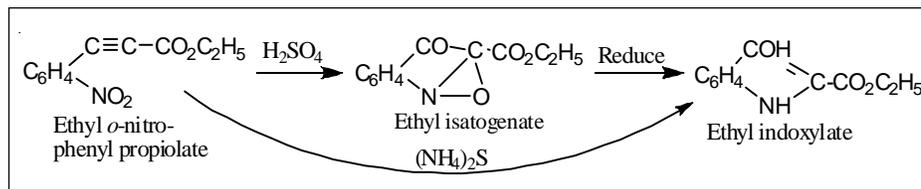
In 1870, Emmerling and Engler succeeded in getting trace amounts of indigo by strongly heating a mixture of *o*-nitroacetophenone, zinc dust and lime (*Scheme 12*). However, it was not reproducible. Five years later, in 1875, Marcell Nencki showed that indole yields small quantities of indigo when treated with ozone (*Scheme 13*).



Scheme 11 (top). Baeyer–Caro indole synthesis.

Scheme 12 (center). Emmerling–Engler indigo synthesis.

Scheme 13 (bottom). Nencki indigo synthesis.

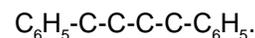


In 1881, Baeyer prepared indoxyl by hydrolysis-decarboxylation of ethyl indoxylate obtained by treating ethyl *o*-nitrophenylpropiolate with conc. H₂SO₄, followed by reduction of the intermediate (*Scheme 17*).

Scheme 17. Baeyer's synthesis of ethyl indoxylate from which he made indoxyl. (The structures and nomenclature are Baeyer's.)

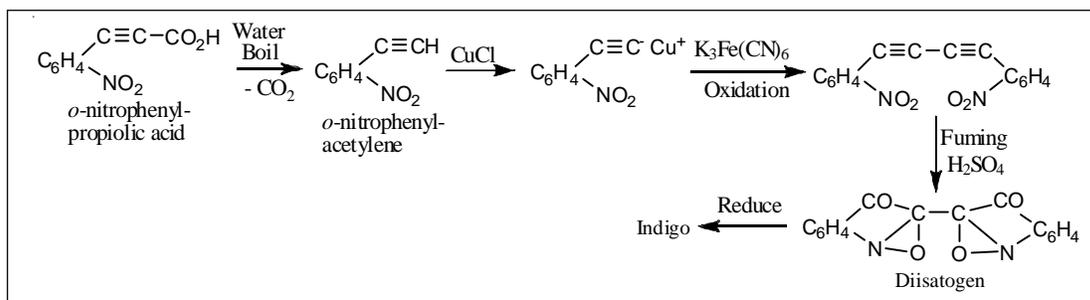
In 1878, E von Sommaruga determined the vapour density of indigo, from which it became clear that the molecular formula of indigo should not be C₈H₅NO, but it should be doubled to C₁₆H₁₀N₂O₂. This fresh evidence pointed to the fact that indigo should constitute not one unit, but two units of indoxyl or isatin or indole in its structure, and these two units must be linked through two carbon atoms. In order to provide proof for this linkage, Baeyer carried out the following sequence of reactions in 1882 (*Scheme 18*).

Baeyer concluded that the carbon atoms in indigo are linked as follows:



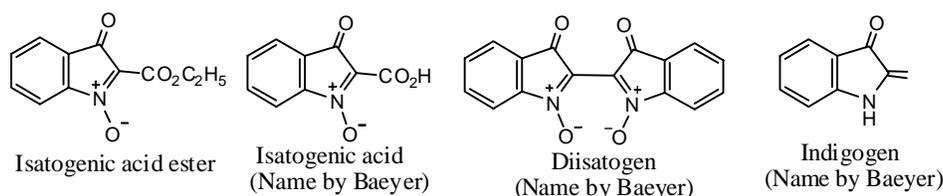
From this observation Baeyer concluded that the carbon atoms in indigo are linked as follows: C₆H₅-C-C-C-C-C₆H₅. This evidence and the fact that indoxyl readily gives indigo indicated that indigo has two nitrogen atoms, because indoxyl has one, perhaps as an imino function. However, chemists of that time, including Baeyer, were confused about the location of one of the hydrogen atoms, because indoxyl showed reactions of phenol and also ketone. The reason for this confusion was that the phenomenon of keto-enol tautomerism was not yet known then and that enolic

Scheme 18. Baeyer's synthetic proof for the C-C link of two indoxyl units in indigo. (The structures and nomenclature are Baeyer's; see Box 6).



Box 6.

This structure for diisatogen was a purely speculative one proposed by Baeyer at that time based on its elemental analysis and the method of its synthesis followed by its conversion to indoxylic acid ester. Its actual modern structure and other related structures are given below.



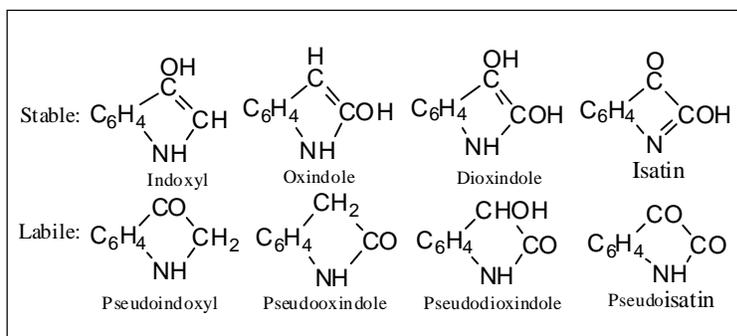
and ketonic forms were independently stable compounds. In fact, they believed that indoxyl, oxindole, isatin and dioxindole existed only in the enolic form and their ketonic forms are labile and unstable, and therefore called them psuedoindoxyl, psuedooxindole, psuedoisatin and psuedodioxindole. These structures are given in *Figure 1*.

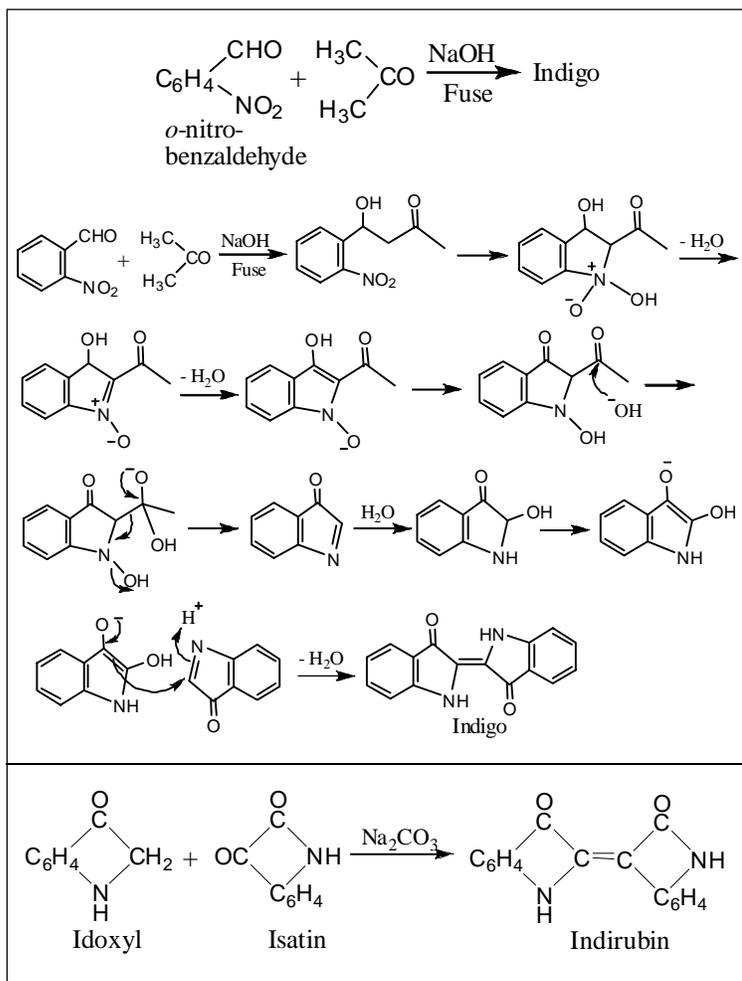
An additional clue for the indigo structure came from its closely related compound indirubin.

Apart from the work described above, a lot more evidence was gathered through the synthesis of intermediates, their derivatives and indigo itself by Baeyer and Viggo Dawson, in 1882 by fusing a mixture of *o*-nitrobenzaldehyde and acetone with NaOH. (*Scheme 19*).

An additional clue for the indigo structure came from its closely related compound indirubin. Edward Schunck isolated indirubin in 1879 from the crude natural indigo obtained from woad. It was found to be an isomer of indigo and exhibited similar properties.

Figure 1. Products of indigo. (The structures and names are according to Baeyer)



**Scheme 19 (top).**

Baeyer–Drawson synthesis of indigo and its modern mechanism.

Scheme 20 (bottom).

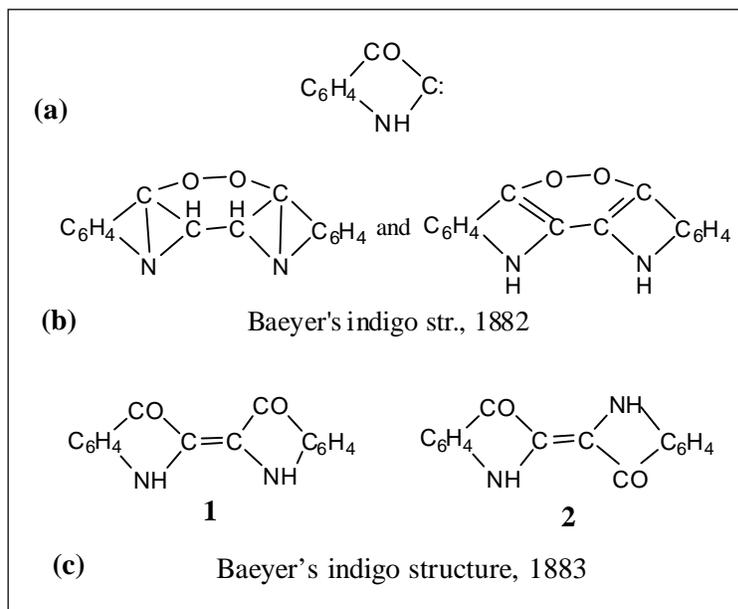
Baeyer's synthesis of indirubin.

Baeyer was able to synthesise it by reacting indoxyl with isatin in the presence of sodium carbonate in alcohol solution (*Scheme 20*).

He reasoned that in this reaction the condensation takes place at the β -carbon as the α -carbon is unreactive in such reactions; therefore, if indirubin has the above constitution, its isomer indigo must have link at the α -carbon, i.e., it is a product of the coupling of two units of the divalent moiety given in *Figure 2a*.

Based on all these pieces of evidence, Baeyer proposed the structures for indigo in 1882 (*Figure 2b*).

Figure 2.



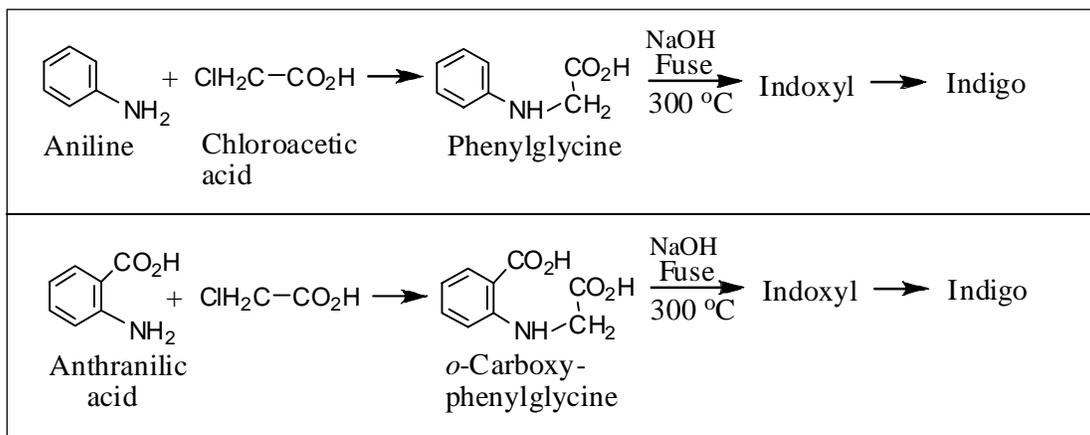
But finally, in 1883, he gave structure **1** for indigo, which is now accepted as the correct structure. However, its geometric isomeric structure **2** is more stable and is usually represented by it (Figure 2c).

Industrial Indigo

BASF tried to commercialise the indigo syntheses developed by Baeyer. However, they were not viable, because the indigo so produced was more expensive than the natural dye. But the dye was so precious that BASF intensified the research efforts to develop an economically competitive process, particularly after the correct structure of the compound was identified, which made it easier to plan appropriate synthetic routes. Even then, it took a few years to find success and when it was achieved, it was a moment of triumph for organic chemistry and a turning point in its history.

In 1890, Carl Heumann of Zurich University developed the method given in *Scheme 21*. The yield was low, and therefore, it could not be commercialised. Three years later, he discovered

It took a few years to find success and when it was achieved, it was a moment of triumph for organic chemistry and a turning point in its history.



another method with a slight modification of the previous one, which started with anthranilic acid instead of aniline (*Scheme 22*).

This vastly improved the yield of indigo and was adopted for industrial manufacture, and the commercial production started in 1897 by BASF and Hoechst.

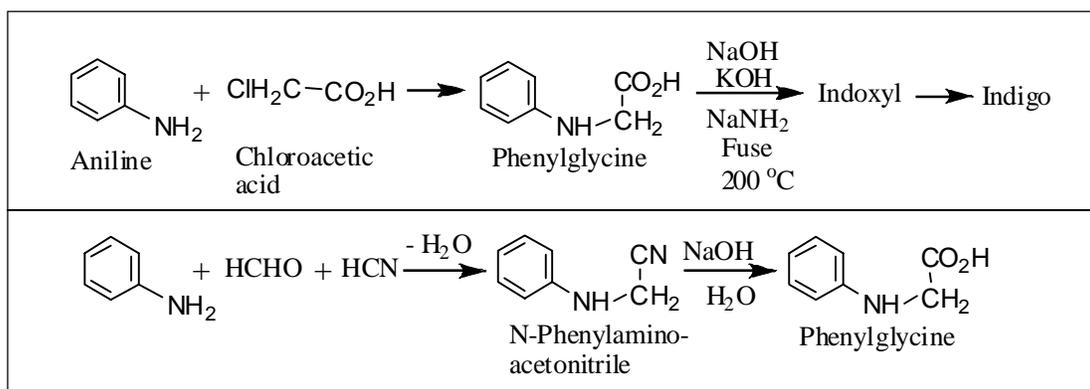
This method was economically competitive, because anthranilic acid could be made cheaply from naphthalene, then a waste product of coal tar processing. The economic production of anthranilic acid was made possible through an accidental discovery of oxidation of anthracene to phthalic anhydride by Eugene Sapper of BASF, when he accidentally broke the mercury thermometer he was using for stirring naphthalene and sulphuric acid reaction mixture. This whole story, which had some effect on Indian history, has been told in an earlier issue of *Resonance* (Vol.8, No3, pp.42–48, 2003). Since phthalic anhydride was required both for indigo and phthalein dyes, the accidental discovery was important for the dye industry and BASF made huge profits.

In 1901, Johannes Pflieger, Chemist and Head of experimental department of Degusa Company, modified Heumann's 1890 synthesis of indigo, which greatly improved the yield. Pflieger used, in addition to sodium hydroxide in *Scheme 21*, potassium

Scheme 21 (top). Heumann indigo synthesis, 1890.

Scheme 22 (bottom). Heumann indigo synthesis, 1893.

The economic production of anthranilic acid was made possible through an accidental discovery of oxidation of anthracene phthalic anhydride by Eugene Sapper of BASF,



Scheme 23 (top). Pflieger indigo synthesis, 1901.

Scheme 24 (bottom). BASF process for phenylglycine, 1925.

hydroxide and sodium amide, a more powerful base, which made the difference for the cyclisation of phenylglycine to indoxyl (*Scheme 23*).

This method became even more cost effective, when, in 1925, an alternative process for the manufacture of phenylglycine was developed by BASF (*Scheme 24*).

From 1897, the industrial production of indigo steadily increased. In that year, the world production of natural indigo from both indigo plants and woad was about 19,000 tons, which dropped to less than 4,000 tons in 1907 and by 1917 it was less than 1,000 tons. In terms of both cost and quality, the natural indigo had lost out to the artificial dye. For the Indian indigo-cultivating farmers it was a terrible setback, because the main source of their livelihood was taken away.

Although many artificial blue dyes that are as good as or even better than indigo have since been produced, the fascination for indigo has remained intact, and its present annual production is about 18,000 tons, which is more than the quantity of any other single dye. Surprisingly some small amounts of natural indigo are still made from plants grown in India, particularly in northern Karnataka, some parts of Africa and Central America.

When the cultivation of indigo had to be terminated, its cultivators in India, no doubt, suffered immensely. But others, particularly the people in Europe, thought otherwise. Describing Baeyer's

For the Indian indigo-cultivating farmers it was a terrible setback, because the main source of their livelihood was taken away.

work at the Nobel Prize award ceremony in 1905, Anders Lindstedt, the president of the Royal Swedish Academy of Sciences, said, "... Indigo, the most gorgeous pigment of the indigo plant, has been considered the most important of all pigments..., and the annual tribute which the West used to pay India for it amounted to a very considerable sum... The result is striking. Already the price of indigo has fallen to a third of its former price and Germany's export of synthetic indigo in 1904 could be valued at over 25 million marks... The effect of this discovery... can already be traced as far as the banks of Ganges ... the immense fields, which up to now have been used for cultivation of indigo plant will instead become available to produce cereals and other food stuffs for starving Indian millions..." Today, after more than a century, very few would remember or know what had happened to the indigo cultivators of Bihar and Bengal. The artificial indigo has definitely released a large tract of land for cultivation of the more important food crops, though, at that time, it was a big loss in export earnings for British India.

Hydroaromatic Compounds

Another significant and the largest contribution of Baeyer was in the area of hydroaromatic compounds. Here, his efforts were aimed mainly at providing proof to the essential correctness of Kekule's benzene structure and he largely succeeded in this by carrying out many well-designed experiments. In the process he got deeply involved in the reactions of aromatic hydrocarbons, their derivatives and their hydrogenated products. The common methods of hydrogenation⁹ or reduction then were metal-acid reaction, mostly zinc or tin and hydrochloric acid, sodium and alcohol, and sodium amalgam and water. Baeyer used the last combination mainly. (Scientists of that day called such reduction as hydrogenation by nascent hydrogen).

Kekule had suggested a ring structure for benzene with alternating single and double bonds, first in 1865, which he then modified in 1866, but he proposed the final one (**3**) in 1872. It was not accepted readily, because, as many pointed out, benzene

"The effect of this discovery... can already be traced as far as the banks of Ganges ... the immense fields, which up to now have been used for cultivation of indigo plant will instead become available to produce cereals and other food stuffs."

– Anders Lindstedt.

⁹ Catalytic hydrogenation was not known at that time. It was discovered in 1897 by the French chemist Paul Sabatier who won the Nobel Prize for it in 1912 along with Victor Grignard.

The largest contribution of Baeyer was in the area of hydroaromatic compounds. Here, his efforts were aimed mainly at providing proof to the essential correctness of Kekule's benzene structure.



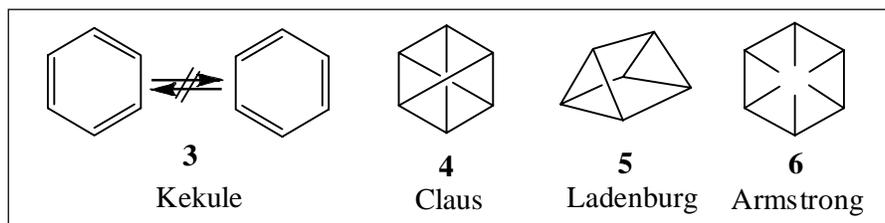


Figure 3.

did not show the properties characteristic of compounds containing double bond/s. In order to correct this flaw several other structures were proposed (*Figure 3*), such as the “diagonal formula” (**4**) by Adolf Claus (1867), the “prismatic formula” (**5**) by Albert Ladenburg (1869), the “centric formula” (**6**) by Henry Armstrong (1890). Baeyer, starting from 1866 till 1894, published about 40 research papers covering nearly 500 pages relating to this area.

The work involves condensation reactions, to obtain substituted benzenes, of ketones like acetone, esters like diethyl malonate (trimerisation to 6-membered ring compounds), diethyl succinate (dimerisation to 6-membered ring compounds), partial or complete reduction of substituted benzene derivatives to the corresponding 6-membered unsaturated and saturated derivatives and then proving their structures systematically. From such studies Baeyer was able to adduce sufficient evidence to show that the formulae **4** and **5** cannot explain the observed results. But he was not able to decisively choose between the Kekule formula (**3**) and the Armstrong formula (**6**). He could not decide on the Kekule structure, because it was too early in the theory of chemical bonding for even a mastermind like Baeyer to envision an explanation as to why the six-membered ring with one or two double bonds behaves similar to its open-chain analogue, while the third double bond confers far more stability. Considerable variations in the reactivity of benzene and a variety of its derivatives observed by Baeyer led him to conclude that “the two formulae are the two limiting states of benzene and the nature of benzene ring in any derivative may be intermediate between the extremes.”

Baeyer discovered
cis-, *trans*-
isomerism in ring
compounds and the
ring strain

During the period of this research, Baeyer discovered *cis*-, *trans*-

isomerism in ring compounds and the ring strain in them as a consequence of the degree of difficulty or ease of formation of anhydride of a dicarboxylic acid with the two carboxylic groups substituted at different positions relative to each other in the ring.

Baeyer's work on hydroaromatic compounds is quite vast and it is impossible to give even a summary of it here. However, a few examples are presented in *Schemes 25–27*. Note here the limited number of reagents used, reduction and re-oxidation to establish the size and nature of the ring, step-wise reduction to finally give cyclohexane derivative.

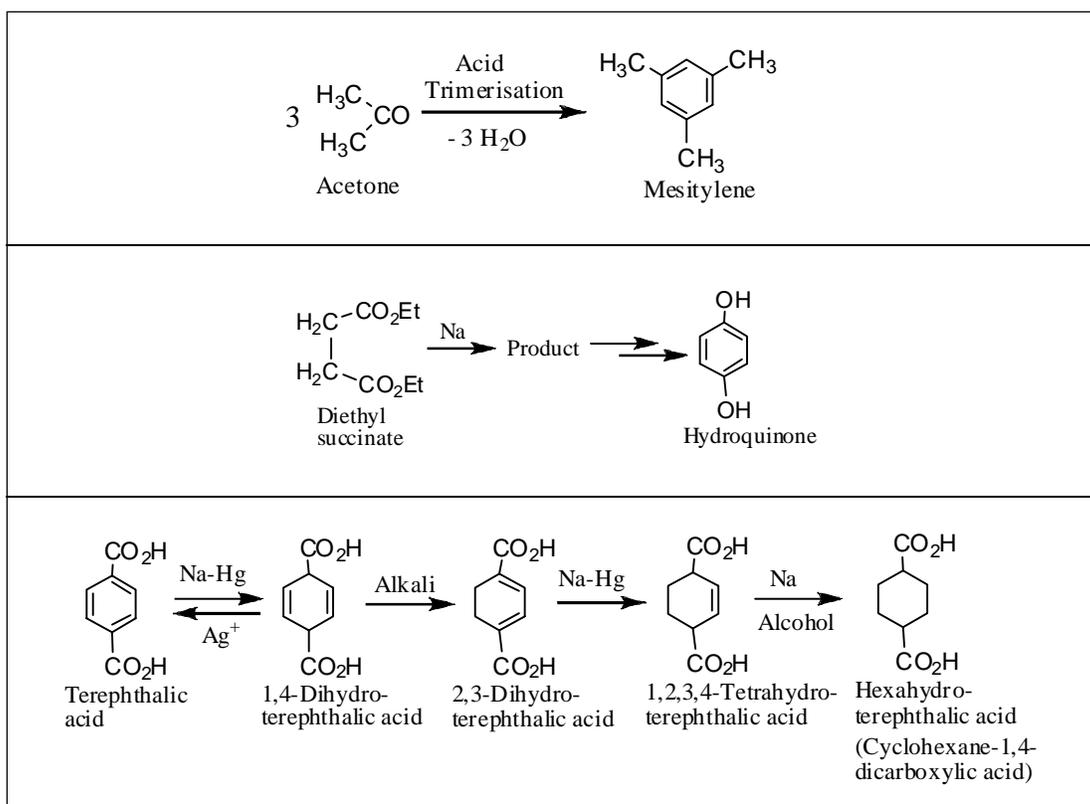
Using similar procedures Baeyer reduced phthalic acid and isophthalic acid and studied their properties. He established the *cis*-, *trans*-geometry of the dicarboxylic acids obtained in these reactions.

Scheme 25 (top). Acetone trimerisation to mesitylene (1,3,5-trimethylbenzene).

Scheme 26 (center).

Dimerisation of diethyl succinate to hydroquinone.

Scheme 27 (bottom). Reduction of terephthalic acid to 1,4-cyclohexanedicarboxylic acid.



An interesting aspect of this work is that, among his 305 publications, this does not constitute even one full paper, but forms only an additional note of about two pages at the end of a paper dealing with acetylenes published in the year 1885.

Having a correct perspective of the structure and properties of benzene and other aromatic compounds was of great importance for the advancement of the chemistry of aromatic compounds. A correct understanding of the structure and properties of these compounds greatly helped the fledgling dyes industry, which had enormous potential to bestow tremendous economic prosperity.

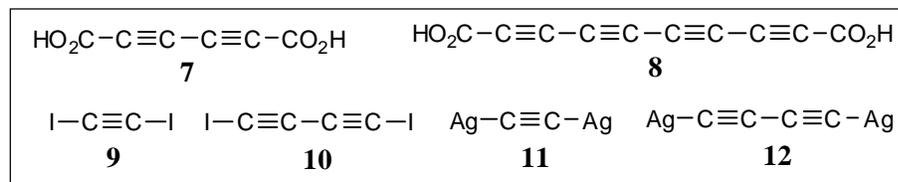
The Strain Theory

Baeyer's work was prolific and spread over many areas of organic chemistry. However, for the students of chemistry, particularly at the undergraduate level, his name is most familiar in association with the Strain Theory of ring compounds. An interesting aspect of this work is that, among his 305 publications, this does not constitute even one full paper, but forms only an additional note of about two pages at the end of a paper dealing with acetylenes published in the year 1885. Yet this concept of ring strain has made Baeyer's name a commonly occurring one in undergraduate chemistry textbooks that describe alicyclic compounds and the stereochemistry of ring compounds.

The strain theory was based on Baeyer's observation of very high reactivity of acetylenes he had synthesised, namely, diacetylene dicarboxylic acid (**7**), tetraacetylene dicarboxylic acid (**8**), diiodoacetylene (**9**), diiododiacetylene (**10**) and the silver salts of acetylene (**11**) and diacetylene (**12**), etc (*Figure 4*). He found them to be so reactive that they would explode even by just rubbing a small amount between fingertips.

The concept of ring strain was prompted also by the work of his doctoral student W H Perkin, Jr. (1860–1920), on the synthesis and reactions of small ring compounds, which Baeyer believed

Figure 4.



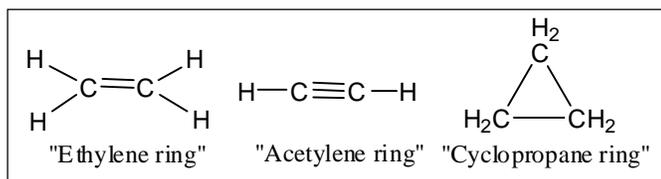


Figure 5. Baeyer's idea of rings.

to be unlikely to exist due to their unstable nature. However, against the advice of Baeyer and two of his former illustrious students, Emil Fischer and Victor Meyer, Perkin, Jr., successfully prepared “the small closed carbon chains” and studied their reactions and found them to be very reactive compounds.

Baeyer identified the similarity in the chemical behaviour of acetylenes, olefins and small ring compounds and attributed their high reactivity to deviation from the normal carbon valence angle of $109^{\circ} 28'$. For Baeyer, ethylene and acetylene were members of ring compounds, and considered them as two-membered rings (*Figure 5*). He also assumed that all ring compounds were planar, despite the fact that he was using some primitive molecular models with 3-dimensional features. He was so faithful to his idea of planar ring that he did not change it, even when Hermann Sachse (1862–1893) very clearly showed in 1890 that six-membered and larger rings need not be planar and that cyclohexane can exist in chair and boat forms.

However, chemists of that time failed to see the significance of Sachse's great imaginative understanding of shapes of molecules. The reasons for the failure of Sachse's idea are: (1) Sachse was very little known, and therefore hardly anyone noticed or cared about his suggestion, (2) his theory was mostly mathematical, because he used geometry and trigonometry extensively, which was not appealing or interesting to chemists then, (3) Sachse did not live long enough to defend or take forward his theory, and most importantly, (4) Baeyer was so well known an authority on organic chemistry matters that no one would question his opinion without a strong experimental evidence, and Sachse had no experimental proof. Sachse even had the vision to assign axial and equatorial positions to the substituents on cyclohexane ring and to suggest two chair conformations

For Baeyer, ethylene and acetylene were members of ring compounds, and considered them as two-membered rings.

Baeyer also assumed that all ring compounds were planar, despite the fact that he was using some primitive molecular models with 3-dimensional features.

While Sachse was 60 years ahead of his time, Bayer delayed the arrival of conformational theory by as much time.

and their possible interconversion. Baeyer conceded that Sachse might be right from a mathematical point of view, but he insisted that his own theory of planar rings was correct, though he was not clear why. Even though the cyclohexane chair conformation was observed by Earl Mohr in 1918 in the X-ray structure of diamond, it was only in 1950 that the idea of such conformation put forth by Derek Barton was accepted. Thus, while Sachse was 60 years ahead of his time, Bayer delayed the arrival of conformational theory by as much time.

Despite Baeyer's rejection of flexible non-planar rings (Baeyer had remarked that Sachse might be right), his view about ring strain due to deviation in the tetrahedral angle of carbon bonds is very much true. We now call this 'angle strain' or 'Baeyer's strain' which is one of the three important factors in deciding the stability of a cyclic molecule, the other two factors being Pitzer strain and van der Waals strain that are due respectively to conformational restrictions and transannular effect.

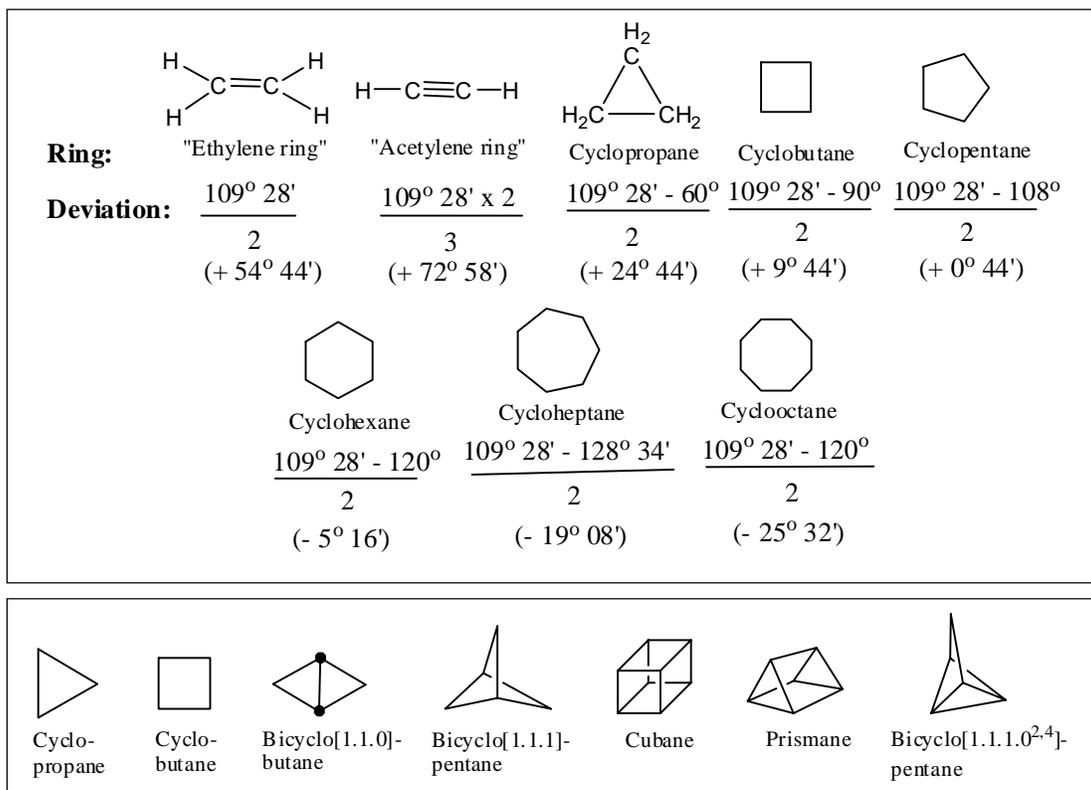
Baeyer's angle strain calculation was quite simple. He calculated the difference between the normal tetrahedral angle ($109^{\circ} 28'$) and the angle calculated on the basis of the geometric shape of the ring, and correlated strain to the degree of its deviation. Some examples are shown in *Figure 6*.

We can see, according to Baeyer, the cyclopentane ring to be the most stable, because it has the least angle strain. The stability of molecules with angle strain depends on the degree of deviation of their angles from $109^{\circ} 28'$ and their synthesis is correspondingly difficult. Even then organic chemists have taken that as a challenge and have succeeded in synthesising several highly strained molecules, such as those in *Figure 7*.

'Angle strain' or 'Baeyer's strain' is one of the three important factors in deciding the stability of a cyclic molecule.

Non-planar six-membered and larger rings are quite stable, as they are free of Baeyer strain, because they have normal tetrahedral angles. Leopold Ruzicka discovered some naturally occurring large ring compounds and accomplished their synthesis as well, for which he received the Nobel Prize. Since then, many





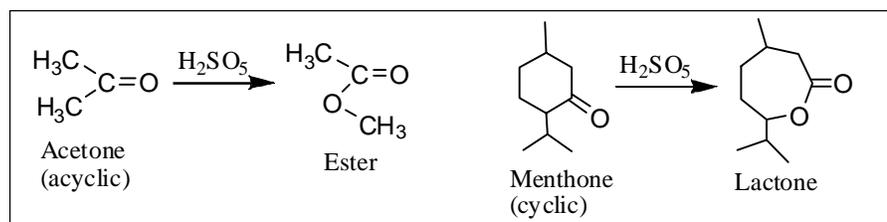
more large and very large ring compounds have been synthesised and shown to be stable.

Another common textbook topic with which Baeyer's name is associated is Baeyer–Villiger oxidation discovered by Baeyer and his doctoral student Victor Villiger in 1899. It is about the oxidation of ketones to esters or lactones using Caro's acid (persulphuric acid H_2SO_5), which his friend Heinrich Caro of BASF had discovered in the previous year (*Scheme 28*). It is one of the very useful reactions in organic synthesis and many procedural modifications have been brought about over a period

Figure 6 (top). Baeyer's angle strain calculation.

Figure 7 (bottom). A few highly strained molecules that have been synthesised.

Scheme 28. Baeyer–Villiger oxidation.



Yet another reaction that bears Baeyer's name is the 'Baeyer's Test for Unsaturation'.

of time, the most significant being the use of organic peracids, in particular *m*-chloroperbenzoic acid.

Yet another reaction that bears Baeyer's name is the 'Baeyer's Test for Unsaturation'. It is a test commonly used in undergraduate laboratory experiments and consists of treating a compound suspected to contain C=C double bond with dilute potassium permanganate solution. If the compound is unsaturated the pink colour of the solution disappears. This was one of the important distinguishing tests Baeyer used to differentiate cyclopropane from the isomeric propene which decolourises the pink colour easily, while the former does not.

Another important discovery made by Baeyer in 1872 was the condensation of phenol with formaldehyde. Though he obtained some oligomers of diphenylmethylenes as products, he failed to isolate any polymeric material. It was left to Leo Baekeland to use this reaction to make the first plastic in 1907 called Bakelite, which is one of the most important thermosetting plastics today.

Hands-on Experimenter and a Remarkable Guide

Baeyer reputedly conducted most of his experiments only in test tubes. His laboratory had hardly any mechanical gadgets, and manipulation like stirring was done manually.

Baeyer was a man of good build and looks with amiable disposition. These attributes along with his intellectual eminence would cast a spell on his associates and on his audience at scientific gatherings. He was a hard-working person and would not be satisfied with making only his students work, but he would spend a lot of time doing experiments in the laboratory. He was endowed with extraordinary experimental skill, which remained intact even at the age of 70. He reputedly conducted most of his experiments only in test tubes. His laboratory had hardly any mechanical gadgets, and manipulation like stirring was done manually. He was essentially an experimental chemist unlike his mentor Kekule or contemporary van't Hoff who were mainly theoretical chemists. However, he always tried to explain his experimental results. He asserted, "I considered it my mission to reapproach nature and to look at the substances themselves, quite the way they are".



Having served three institutions in their formative phase, Baeyer had the opportunity to build and develop his laboratories and the departments. In Berlin and Strasbourg, he could not, however, enjoy the fruits of his efforts long enough, particularly in the latter where his stay was the shortest. In Munich he set up a new laboratory for training students, which the department lacked, though his predecessor Justus von Liebig had built a big laboratory that served mainly the research activity.

Baeyer was a distinguished teacher and a master at the art of training students to develop experimental skills and free thinking. In attracting and inspiring students he was a worthy successor of Liebig. Students from all over the world congregated in his laboratory to do doctoral work, or to get postdoctoral training or simply to get additional knowledge and skill. Many who worked with him became great scientists and academicians. Among them, we can count the following: Carl Gräbe, Carl Liebermann, Victor Meyer, Emil Fischer, Marcell Nencki, Rainer Ludwig Claisen, Hans von Pechmann, Eugen Bamberger, Johannes Thiele, Richard Willstätter, Heinrich Wieland, Johann Ulrich Nef, Victor Villiger, William Henry Perkin, Jr., Edward Buchner, Walter Dieckmann, Carl Duisberg, Paul Friedländer, William Albert Noyes, Theodor Curtius, Otto Dimroth, Moses Gomberg, and several others who form indeed a formidable galaxy of great chemists.

William Henry Perkin, Jr., one of Baeyer's distinguished doctoral students, has very aptly described this outstanding chemist in his obituary thus, "... It is questionable whether any teacher or investigator ever exerted a greater influence on the development of chemical science, and especially of organic chemistry, than Baeyer has done, for not only was he a great teacher whose pupils are to be found in every civilized country, but his researches have also had many of the foundations on which the amazing structure of modern organic chemistry has been raised ... it is possible that his main influence on chemical thought was due to his magnetic personality and power of imparting to others some of his enthusiasm for discovery".

Baeyer was a distinguished teacher and a master at the art of training students to develop experimental skills and free thinking.

"... It is questionable whether any teacher or investigator ever exerted a greater influence on the development of chemical science..."

– Perkin, Jr.



Although Baeyer was immersed in his scientific activity, it was not all work for him and he knew how to enjoy life. He loved to have a good time in the company of scientists and literary personalities.

Despite his great achievements, Baeyer never made any pretence to that. During his 70th birthday celebrations, he reflected, “The fact that I had such sizable number of students and received recognition during my professional career is – so I believe – mainly due to very timely appearance on the scientific stage”.

Although he was immersed in his scientific activity, it was not all work for him and he knew how to enjoy life. He loved to have a good time in the company of scientists and literary personalities. (Baeyer’s mother’s family had made a good name in German literature). He entertained his friends and colleagues not only in Munich, but also in Starnberg, a village 30 km from Munich and close to the lake Starnberg, where he had a country house.

Baeyer spent his last two years of his post-retirement life in his Starnberg country house. He passed away there on August 20, 1917, and was buried at Waldfriedhof in Munich¹⁰.

¹⁰ Several different dates of death are to be found in the literature, the year being the same. For example, it is August 20th according to Huisgen and de Meijre [1, 2], August 23rd according to [15], September 5th according to Henrich [12]. For this article August 20th is chosen, which is reported by Huisgen, a distinguished Professor of Organic Chemistry at the University of Munich).

Suggested Reading

- [1] R Huisgen, *Adolf von Baeyer’s Scientific Achievements – a Legacy*, *Angew Chem Int Ed Engl*, Vol.25, pp.297–311, 1986.
- [2] A de Meijre, *Adolf von Baeyer: Winner of the Nobel Prize for Chemistry 1905*, *Angew Chem Int Ed Engl*, Vol.44, pp.7836–7840, 2005.
- [3] R Nietzki, *Chemie der organischen Farbstoffe*, 5th Ed, Julius Springer, Berlin, pp.325–351, 1906.
- [4] J C Cain and JF Thorpe, *The Synthetic Dyestuffs*, Griffin and Company, pp.155–165, 1905.
- [5] W C Sumpter, *Chemistry of Isatin*, *Chem Rev*, Vol.34, pp.393–434, 1944.
- [6] M V Orna, *The Chemical History of Color*, Springer, pp.111–125, 2013.
- [7] H Watts, M Moncrieff, P Muir and HF Morley, *Watts’ Dictionary of Chemistry*, Longmans Green and Co, pp.753–760, 1909.
- [8] R E Oesper, *J Chem Educ*, Vol.31, p.91, 1951.
- [9] W H Perkin Jr., *Nature*, Vol.100, pp.188–190, 1917.
- [10] J S Chamberlain, *A Textbook of Organic Chemistry*, P Blackston’s Son & Co, pp.706–711; 800–806; 866–883, 1921.
- [11] C Schorlemmer, *The Rise and Development of Organic Chemistry*, Revised Ed, Macmilland and Co., pp.252–263, 1894.
- [12] F Henrich, *J Chem Educ*, Vol.7, pp.1231–1248, 1930.
- [13] Several New Aspects of Indigo Chemistry, www.chemexplore.net/indigo.htm and other websites.
- [14] L Ruzicka, *Nobel Lecture*, 1945 (1935 Nobel Prize in Chemistry).
- [15] Editorial, *The Chemical Engineer*, Vol.25, (September), pp.242–243, 1917.
- [16] F H McCrudden, *Uric Acid*, The Fort Will Press, Boston, 1905.

Address for Correspondence
G Nagendrappa
Email:
gnagendrappa@gmail.com