# Liebig–Wöhler Controversy and the Concept of Isomerism

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The chemical revolution in the late 18th and early 19th centuries was marked by a number of significant breakthroughs, including the downfall of the phlogiston theory and Dalton's theory of atoms and molecules. At the same time, ways of communicating research results grew as scientific journals, academies, and meetings were founded. The exchange of ideas also gave rise to disagreements that often led to scientific battles. However, sometimes, these controversies were the origins of friendships and scientific collaborations. Such was the case with Justus Liebig and Friedrich Wöhler (Figure 1).

These two great scientists had many things in common: both were German, lived in the same period, were disciples of brilliant chemists in their youth, and worked successfully in different fields of chemistry. Nevertheless, the most important point of connection in their lives was perhaps their scientific disagreement that contributed to the emergence of the concept of isomerism.

This article retells the story of the Liebig–Wöhler controversy and their later friendship and shows how the seemingly contradictory findings of the two scientists led to the development of the theory of isomerism. These bits of history can serve as anecdotes to add life to university lectures and to increase interest in science at the high school level.

## Early Years of Liebig and Wöhler

Liebig and Wöhler emerged in the 1820s as part of the second generation of important chemists who were disciples of the great masters of the time, such as Berzelius and Gay-Lussac. Justus Liebig (1803–1873) was born in Darmstadt, Germany, into a lower-middle class family, and his interest in chemistry might have been due, in part, to his father's business in drugs, dyes, and chemicals. The increasing poverty of his parents, caused by the economic depression after the Napoleonic wars, led to Liebig's withdrawal from the gymnasium and his apprenticeship to a pharmacist. The latter experience lasted only for six months, probably due to lack of finances or to the detonation of an explosive he had prepared at home (1). Later, Liebig attended Bonn and Erlangen University to study chemistry, as well as French, Latin, mathematics, and botany. His impressive accomplishments led the Grand Duke of Hessen–Darmstadt to give Liebig a travel grant to study in Paris, the center of European science at that time.

Liebig attended lectures by prestigious scientists, such as Thénard and Gay-Lussac, and he was able to learn organic analyses in Gay-Lussac's lab. As a result, he was able to continue his studies on derivatives of fulminic acid, the explosive of his childhood (2). By applying the newest techniques of analysis, Liebig determined the composition of silver fulminate. He finished the analyses and published them together with Gay-Lussac in 1824 (3).

Friedrich Wöhler (1800–1882) was born in a town near Frankfurt, Germany, the son of a veterinary surgeon. He began
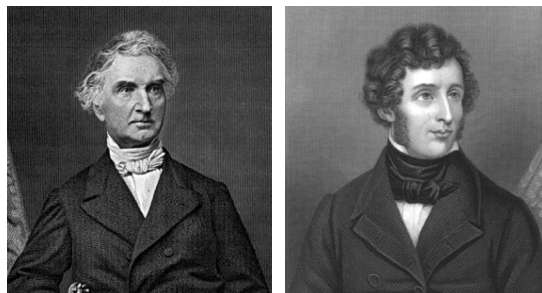


Figure 1. Justus Liebig (left) and Friedrich Wöhler (right).

to study medicine, but he always felt a great attraction for experimenting in chemistry. After completing his medical degree in 1823, Wöhler studied chemistry under Gmelin and Berzelius, and beginning in 1825, Wöhler taught chemistry, initially at the Technical School of Berlin, later at Cassel, and finally at the University of Göttingen. Brilliant as professor, he was also a great researcher. Among other achievements, his investigations of quinone and hydroquinone were noteworthy in the development of organic chemistry. But after 1839, he mainly focused on inorganic chemistry and made important contributions to the study of boron, silicon, and phosphorus, as well as the preparation of aluminum. Nevertheless, Wöhler's name is generally associated with his synthesis of urea (1828) because of the decisive contribution to the overthrow of vitalism (4).

Like Liebig, Wöhler was also learning analytical techniques during the 1820s but in another city, Stockholm. While working in the laboratory of Berzelius, Wöhler analyzed a silver compound, silver cyanate, and concluded that it was a silver salt of an unknown acid (cyanic acid). The results of this quantitative analysis were the same as those of Liebig (5). The obvious conclusion was that one of the analyses must be wrong, and one of the chemists must be a poor analyst! Liebig, pushed by his aggressive character, rapidly accused Wöhler of erroneous results. But Liebig analyzed a sample of the silver cyanate supplied by Wöhler and verified that they were correct (6). At this point, Liebig openly admitted that he had made a mistake in his initial accusation. And curiously this was the starting point of a friendship and even a scientific collaboration between the two scientists (7).

The contradictory findings of Wöhler and Liebig created a dilemma: two compounds with many different properties had the same composition. At the same time, this conclusion could not be possible since it was assumed that the properties of a substance were correlated with its composition according to the law of definite proportions. Gay-Lussac argued that the difference in properties could be due to different arrangements of the elements, and other chemists, such as Gmelin or Davy, were of the same opinion (8). But no real explanation could be found for this phenomenon.

The answer was given by one of the greatest chemists of that century, Jöns Jacob Berzelius (1779–1849), the Swedish master of Wöhler. Initially, he posed some doubts about Leibig's and Wöhler's results, but later Berzelius admitted that the composition of cyanates and fulminates was identical, although the compounds had different properties. Moreover, other facts of this type were observed:

- In 1825, Faraday studied the oily material obtained as by-product in the preparation of illuminating gas by heating whale oil. From that material, Faraday isolated two products: one of them was a liquid, benzene ($C_6H_6$), and the other, the more volatile portion, was a gas. The percentage composition of the new gas proved to be identical to that of the well-known olefiant gas, although the densities were different (double in the first case). Nowadays, we know that these gases are, respectively, isobutylene ($C_4H_8$) and ethylene ($C_2H_4$).

- In 1822 Berzelius observed two different tin oxides with the same composition, and in 1825, he noted two forms of phosphoric acid with identical compositions.

- In 1828 Wöhler obtained urea, which had the same composition as ammonium cyanate ($CH_4N_2O$), but different properties.

- Mitscherlich, in 1823, observed that sulfur crystals had different forms (monoclinic or rhombic), according to the method of preparation *(9)*.

- Aragonite and calcite were both crystalline forms of calcium carbonate. Iron pyrite and marcasite were both $FeS_2$.

- It was known that diamond and graphite were both carbon.

- In about 1826, it was discovered that tartaric and racemic acids had identical compositions but some different properties *(10)*.

With the above data in mind, Berzelius devised a system that could cover all these cases.

## The Same, but Not the Same

In 1831–1832 Berzelius proposed the concept of *isomer* (from Greek for *equal parts*). According to Berzelius, isomers have the same composition, being identical in their relative and absolute numbers of atoms but different properties. So it happened with silver fulminate and silver cyanate, but not with olefiant gas and isobutylenee, which have equal relative numbers of atoms but different absolute numbers. Some years later (1841) Berzelius proposed the term *allotrope* for the different varieties of an element (e.g., diamond and graphite or the different forms of sulfur), whereas *polymorphism* was used for the case of compounds that occurred in more than one crystalline form *(11)*. The central issue in all these cases was why two apparently identical materials could be, however, not the same.

## The Concept of Isomerism

Berzelius justified the phenomenon of isomerism by proposing that atoms can unite within their molecules in different ways. His idea, which was understandable in terms of Dalton's atomic theory, had general acceptance. At the time, the concept of molar mass was still hazy, but the term *isomer* gradually acquired its present-day meaning: compounds with equal composition and molar mass, but different properties.

The first explanation of isomerism involved differences in connectivity (*constitution*), so that the corresponding molecules would have different structural formulas, depending on the order of attachment of the atoms (e.g., cyanic acid, H–OCN, and fulminate acid, H–CNO, or urea and ammonium cyanate). Butane and methylpropane, 1-propanol and 2-propanol, and ethanol and dimethylether also represent pairs of constitutional isomers. Acceptance of the existence of isomers led to the important concept of the constitution of molecules as the ultimate cause of the properties of compounds.

Isomerism became a fundamental tenet of organic chemistry, which in turn provided many examples of isomers of different types. These findings reinforced the concept of isomers, and they also led to an entire theory of isomerism. As time went by, the initial concept of isomerism became more complicated. Compounds with the same connectivity also showed different properties. These molecules had to be understood from the perspective of stereochemistry, that is, how atoms in a molecule are arranged in space relative to one another. This led to the concept of permanent shape (*configuration*), which explained differences in some molecules, such as the two forms of tartaric acid (separated by Pasteur in 1841) or maleic and fumaric acids.

A more subtle kind of isomerism appeared when differences were observed despite identity in constitution and configuration. The temporary shape or *conformation* is due to the different geometry of molecules because of rotation around single bonds. Generally, the amount of energy required for this rotation is low, so it can occur easily. However, the small differences in energy between conformers sometimes play a decisive role in the chemical behavior of compounds such as enzymes.

The discovery of isomerism represented the beginning of structural chemistry, opening the way to the establishment of structural formulas and contributing to the explanation of the great abundance of organic compounds *(12)*. As a result, it was possible to classify organic compounds and understand their structures, making organic chemistry clearer and, in the words of Wöhler, not a "dark forest with few or no pathways".

## Liebig–Wöhler Friendship

During his stay in Paris, Liebig met the famous geographer and scientist Alexander von Humboldt, who recommended him for an academic position at the University of Giessen (1824). There he taught chemistry for 28 years and established a teaching and research school of chemistry. His international reputation inspired students from throughout the world to study practical chemistry in his laboratory, mainly qualitative and quantitative analysis *(13)*. In 1852, Liebig moved to the University of Munich where he remained until his death in 1873. He made major contributions to organic analysis, but he also worked in other fields of chemistry. He is considered the founder of agricultural chemistry because of his experimental studies on artificial manures *(14, 15)*. In physiological chemistry, he devised an effective method to produce an extract from meat that was commercialized in 1865. He was also a prolific writer and starting in 1832 he became the editor of *Annalen*

*der Chemie und Pharmacie (16).* For all his merits, he became baron (Freiherr) in 1845, and since then his name was Justus "von" Liebig.

Liebig, although sincere and good-natured, had an aggressive temperament, which caused him to enter often into bitter controversies with other scientists, such as Pasteur *(17),* Mitsherlich *(18),* or Berzelius *(19).* Wöhler, on the contrary, was quiet and avoided all types of disputes. In spite of the differences in their temperaments, after their short controversy, the two scientists maintained a lifelong friendship, as indicated by the ca. 1000 letters exchanged between them *(20).* Liebig expressed their relationship in an 1829 letter to Wöhler, "I am convinced that our friendly relationship will never suffer an upset from the skirmishes which we have afforded and still will afford one another" *(21).*

Besides being close friends, Liebig and Wöhler agreed in many scientific issues *(22)* and collaborated in research. In particular, their studies of uric acid and the oil of bitter almonds were especially noteworthy. The result of the latter investigation was the discovery in 1832 of the first radical with three different elements, the benzoyl radical, which represented "the beginning of a new day in vegetable chemistry", in the words of Berzelius *(23).*

## Conclusions

The unifying talent of Berzelius was necessary to give a satisfactory explanation of the observations described above. Nevertheless, the research of Liebig and Wöhler on silver fulminate and silver cyanate was certainly the key point for Berzelius' idea of isomerism. Their apparently contradictory results contributed to build a new doctrine in chemistry and, of equal importance, their initial conflict led to a long research collaboration.

## Significance for Chemistry Education

Because of the general decline in the number of students in the sciences, enhancing the interest for science at the high school level is essential. Science fairs and workshops are created to satisfy this need. But incorporation of science history into the curriculum can also be helpful *(24),* because, among other aspects, it is a source of examples to create student interest.

The material presented in this article provides several opportunities to generate classroom interest. Aside from gaining an understanding of the concept of isomerism, students can appreciate the role of teamwork in scientific research, the need for exacting laboratory technique, the importance of seemingly incongruous results, the remarkable advances that can arise from scientific controversies, and the careers and accomplishments of famous scientists. Students can also be motivated to undertake additional activities (e.g., molecular model-building, lab experiments, classroom debates, and Internet searches) to improve their understanding of isomerism and to increase their interest in science.

## Literature Cited

1. Brock, W. H. *The Fontana History of Chemistry;* Fontana Press: London, 1992; pp 199–200.
2. Kurzer. F. *J. Chem. Educ.* **2000,** *77,* 851–857.
3. Gay-Lussac, J. L.; Liebig, J. *Ann. Chim. Phys.* **1824***, 25,* 285–311.
4. Lipman, T. O. *J. Chem. Educ.* **1965***, 42,* 396–397.
5. Wöhler, F. *Poggendorffs Ann. Phys. Chem.* **1824***, 1,* 117–124.
6. Liebig, J. *Schweiggers Jahrbuch der Chemie und Physik.* **1826***, 18,* 380.
7. Hierbert, E. N. *Isis.* **1960***, 51 (2),* 244–246.
8. Rocke, A. J. *Chemical Atomism in the Nineteenth Century. From Dalton to Cannizzaro;* Ohio State University Press: Columbus, OH, 1984; pp 168–169.
9. Levere, T. H. *Affinity and Matter;* Clarendon Press: Oxford, 1971, pp 153–154.
10. Bensaude, B.; Stengers, I. *Histoire de la Chimie;* La Découverte: Paris, 1992; pp 189–190.
11. Ihde, J. I. *The Development of Modern Chemistry;* Dover Publications Inc.: New York, 1984; pp 170–173.
12. Metzger, H. *Chemistry;* Locust Hill Press: West Cornwall, CT, 1991; pp 115–119.
13. Van Closter, H. S. *J. Chem. Educ.* **1956***, 33,* 493–497.
14. Scharrer, K. *J. Chem. Educ.* **1949***, 26,* 515–518.
15. Black, G. W., Jr. *J. Chem. Educ.* **1978***, 55,* 33.
16. Van Closter, H. *J. Chem. Educ.* **1957***, 43,* 27–29.
17. Hein, G. E. *J. Chem. Educ.* **1961***, 38,* 614–618.
18. Liebig, J. *Ann.* **1840***, 34,* 97.
19. Rea, R. *J. Chem. Educ.* **1976***, 53,* 715.
20. Partington, J. R. *A History of Chemistry,* Macmillan and Co., Ltd.: London, 1961–1970; Vol. 4, pp 327–332.
21. *Aus Justus Liebigs und Friedrich Wöhlers Briefwechsel in den Jahren 1829–1873;* Schwarz, R., Ed.; Verlag Chemie GmbH: Weinheim, Germany, 1958; p 12.
22. De Mayo, P.; Stoessi, A.; Usselman, M. R. *J. Chem. Educ.* **1990,** *67,* 552–553.
23. Liebig, J.; Wöhler, F. *Ann.* **1832***, 3,* 249–282.
24. Stock, J. T. *J. Chem. Educ.* **2004***, 81,* 793–794.

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# Fulminic Acid in the History of Organic Chemistry

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Fulminic acid has a long and fascinating history. There can hardly be another simple compound whose story more consistently reflects the development of organic chemistry over the past two hundred years and has on occasion contributed more significantly to its progress. The unraveling of fulminic acid's seemingly simple structure posed subtle difficulties that tested the powers of some of the foremost chemists of successive generations (among them Berthollet, Liebig, Kekulé, Nef, and Pauling), and only in most recent times has it given up its last secrets to the concerted efforts of spectroscopists and theoretical chemists.

The present article traces the stages of this long and interesting quest, illustrating many of the highlights in the evolution of structural organic chemistry from the early endeavors of 18th century experimentalists to today's wave-mechanical interpretations. In the interaction between pure research and technological exploitation, fulminic acid has played an equally significant role: its mercury salt was for nearly a hundred years the only available practical detonator suitable for firing conventional explosives for both peaceful and warlike purposes.

## The Discovery of Fulminates

It seems appropriate that the story of the highly unstable fulminates should begin with an explosion. This occurred in the laboratory of the 17th century chemist Johannes Kunckel (1630–1703), where mercury fulminate first made a fleeting, though unrecognized appearance. Kunckel was a reputable chemical operator, the inventor of gold ruby glass, and an independent discoverer, along with Brand and Robert Boyle, of phosphorus. Like many of his contemporaries, he subscribed to the alchemistic notion that mercury was a constituent of all metals. In one of his numerous experiments using this metal, he unwittingly encountered mercury fulminate, but did not isolate it, since it was immediately destroyed in the ensuing explosion. The following (translated) graphic description of this experiment is found in his well-known *Laboratorium Chymicum*, which appeared posthumously in 1716 (*1*) (Figs. 1, 2).

> I once dissolved silver and mercury together in aqua fortis, and, having added spiritus vini, set the vessel aside in the stable. When by the next day, its temperature had [spontaneously] risen, there occurred such a thunder clap, that the groom thought someone had shot at him through the window, or that the very devil had appeared in the stable. But I realized that it was my experiment that had exploded.

It has been speculated (*2*) that an even earlier production of mercury and silver fulminates may possibly be attributed to the Dutch scientist Cornelis Drebbel (1572–1634), who was well versed in the manufacture of explosives for military purposes. Although the preparation of fulminates was not explicitly claimed by him (*3*), his writings suggest (*4*) that his experimental work was likely to lead to the production of fulminates; details of these activities may well have been suppressed for political reasons.

Brief reference may be made to a group of explosive substances, which, though known as "fulminating mercury (*5*), silver (*6*), and gold" (*7*) are not related to fulminic acid. They are precipitated from solutions of the corresponding metal nitrates by ammonia and have been identified as nitrides or imides (e.g. $Ag_3N$, $Ag_2NH$); they are noticed here to emphasize their structural distinctness from true fulminic acid derivatives and to preclude any confusion that has often arisen.

### Discovery of Mercury Fulminate

Fulminic acid was discovered by the English chemist Edward Howard (*8*), who first prepared and investigated the compound in the form of its mercury and silver salt in 1800 (*9*). The discovery was the outcome of experiments that were in fact targeted at the synthesis of "muriatic" (hydrochloric) acid, which, according to prevailing ideas, was regarded as a combination of the hypothetical element "murium" with hydrogen and oxygen (*10*). This led Howard to attempt to combine both hydrogen and oxygen simultaneously with a suitable metal substrate, with the object of obtaining the corresponding metal "muriate". His use of mercury oxide as the "base" and of nitric acid and alcohol as the sources of oxygen and hydrogen, respectively, could not, of course, produce the intended result, but resulted in the fortuitous discovery of the first fulminate.

Thus mercury or its oxide, dissolved in nitric acid and treated with alcohol, reacted vigorously on warming and deposited a copious white crystalline precipitate. When this was tested for chloride with concentrated sulfuric acid in the usual manner, there ensued a violent detonation. Howard



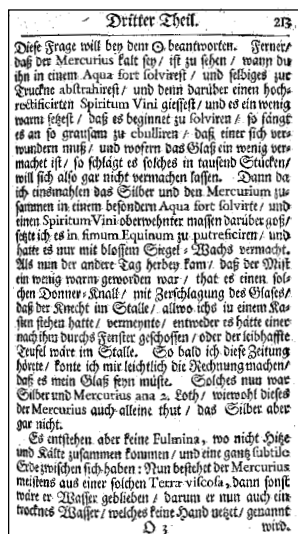Figure 1. The title page of Johannes Kunckel's *Laboratorium Chymicum.*

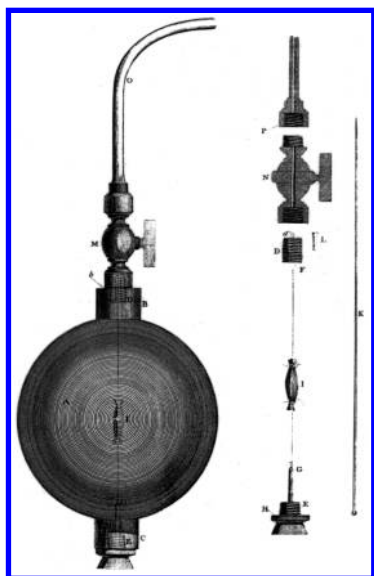Figure 2. Description of Kunckel's experiment producing mercury fulminate.

Figure 3. Howard's apparatus for performing controlled explosions of mercury fulminate.

thereupon did not neglect to perfect the method of producing this new "fulminate" and to study its properties. He had indeed been fortunate in his choice of the metal: apart from mercury and silver, no other metal undergoes this remarkably complex reaction (see section on the structure of fulminic acid).

The most conspicuous property of the fulminate was its explosiveness; it greatly exceeded gun powder in the speed and violence of its decomposition. Its preparation had to be restricted to a small scale, never exceeding the use of 500 grains (32.5 g) of mercury. The compound was detonated sharply by the blow of a hammer, by heating to ca. 185°, or by an electric spark. Howard examined the products of controlled small-scale explosions performed in a thick-walled closed glass globe, in which known amounts of fulminate, suspended in paper sachets, were fired by an electrically heated wire (Fig. 3).

The action of mineral acids on the fulminate gave various solid and gaseous products that were identified with difficulty and sometimes incorrectly, as for example the supposed



Figure 4. The Royal Military Academy in Woolwich, ca. 1800.

mercury oxalate. The lack of methods of quantitative organic analysis and the primitive state of chemical theory precluded an even remotely rational interpretation of the obscure genesis and nature of the new fulminate. Howard's gallant attempt to describe the substance as "a combination of mercury oxalate and 'nitrous etherized gas' [ethyl nitrite] with excess of oxygen" was wisely tempered with his own caution (*9*):

> I will not venture to state with accuracy, in what proportion its constituent principles are combined. The affinities I have brought into play are complicated, and the constitution of the substances I have to deal with, not fully known.

Silver fulminate proved even more dangerously explosive than its mercury counterpart. A safe method of producing it from silver in very small quantities was worked out in collaboration with William Cruickshank (*11*) at the Royal Military Academy, Woolwich (Fig. 4).

Not surprisingly, the remarkable new compounds attracted a great deal of attention in the scientific world. Howard's extensive paper in the prestigious *Transactions of the Royal Society* was reprinted simultaneously in the more widely disseminated British periodicals (*12*), and full translations appeared in the leading French (*13*) and German (*14*) journals. At home, the achievement of the young investigator was recognized by the award to him of the coveted Copley Medal, the highest distinction in the gift of the Royal Society. In France, the illustrious Berthollet, examining the new reactions for himself (*15*), found no evidence for the presence of oxalic acid in the fulminate, but was also unable to offer any rational suggestions concerning its chemical nature. Howard realized that he had penetrated the secrets of his reaction as far as current knowledge allowed; moreover, he had been badly injured at least twice in the course of his experiments, and was obviously not sorry to forsake this dangerous field for other projects, as the following passage of his paper shows (*9*):

> I once poured 6 drams of concentrated sulfuric acid upon 50 grains of mercury fulminate. An explosion nearly at the instant of contact was effected; I was wounded severely, and most of my apparatus destroyed. ... I must confess that I shall feel more disposed to prosecute other chemical subjects.

### Fulminic Acid and Isomerism

In 1823–25, fulminic acid was directly involved in Liebig and Wöhler's classical researches that led to the establishment of the fundamental new concept of isomerism of organic compounds. Liebig's youthful zeal for chemical experimentation and his special fascination with silver fulminate has been vividly narrated by Volhard (*16*). His interest in this labile substance persisted (*17*), and his first significant research, performed in Gay-Lussac's laboratory in Paris, was its quantitative analysis (*18*). To his surprise, its percentage composition proved to be identical with that of silver cyanate, an entirely different compound that had only recently been prepared and analyzed by Wöhler (*19*). Never inhibited by excessive humility, Liebig cast doubts on the accuracy of Wöhler's analyses, but had presently to admit their correctness. As is well known, this inauspicious first encounter of the two men marked the beginning of a close and lasting friendship and a brilliant and fruitful collaboration over many years.

Once firmly established, the results led to the realization that two or more distinct compounds may indeed have the same composition, their individuality being due to a different arrangement of the same atoms within their molecules (*20*). The phenomenon was repeatedly discussed by Berzelius in his influential *Annual Reports* (*21*): it was he who coined the term *isomerism*, which, in all its ramifications was destined to pervade the very fabric of structural chemistry. It may be noted in passing that Gay-Lussac, Liebig's preceptor at that time, had pointed out as early as 1814 that the percentage compositions of acetic acid and cellulose were identical and that "the arrangement of the [atoms] within a compound has the greatest influence on its neutral, acid or alkaline character", thus foreshadowing the possibility of isomerism (*22*).

## The Structure of Fulminic Acid

The discovery of the isomerism of fulminic and cyanic acid had required no knowledge of their actual structural pattern, but with the growth of organic chemistry in the second half of the 19th century, the problem of precise molecular architecture became of paramount interest.

Although the fulminic acid molecule is at first sight one of the simplest chemical entities, consisting of one atom each of hydrogen, carbon, nitrogen, and oxygen, so opaque and subtle are the chemical changes involved in its formation and reactions that the task of elucidating its structure proved unusually difficult, and its solution extended over the better part of two centuries. Not the least of the difficulties was the question of its molecular size. Believed to originate from ethanol, fulminic acid was long regarded as a two-carbon compound, $C_2H_2N_2O_2$, an assumption that gave rise to many false starts. The checkered history of a succession of proposed and discarded formulations has been chronicled by Scholl (*23*) and Wieland (*24*); here, only the chief milestones on the road to ultimate success are noticed.

The first rational approach to the problem was made by Kekulé in 1857, in the wake of Gerhardt's type theory, when he introduced methane as the fundamental origin of all organic molecular structures. He included fulminic acid among the first examples to illustrate his ideas. Although still considered a two-carbon compound and, in agreement with its explosive nature, formulated erroneously as nitroacetonitrile, Kekulé assigned it with great insight to its logical position between acetonitrile and chloropicrin in his system (*25*).
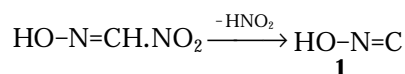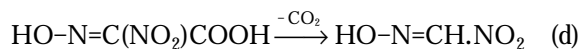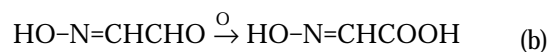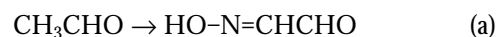
| | | | | | |
|---|---|---|---|---|---|
| C | H | H | H | H | Methane |
| C | H | H | H | Cl | Methyl chloride |
| C | NO$_2$ | Cl | Cl | Cl | Chloropicrin |
| C | NO$_2$ | H | H | CN | Fulminic acid |
| C | H | H | H | CN | Acetonitrile |

Shortly thereafter, P. Griess (*26*) expressed the lability of fulminic acid in terms of the diazoacetic acid structure, $N_2CH–COOH$, in analogy with the explosive diazonium salts that he had recently discovered. Several alternatives, still based on the two-carbon formula, continued to be proposed (*27*) despite the significant observation in 1882 by Ehrenberg (*28*) and independently by Steiner (*29*) that fulminates are cleaved by acid hydrolysis quantitatively to hydroxylamine and the one-carbon formic acid:

$$HCNO + 2H_2O \xrightarrow{H^+} HCOOH + NH_2OH$$
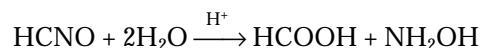
The most significant contribution was made in 1892 by the American chemist J. U. Nef (*30*), whose original and penetrating views on structure and reactivity did not exclude the existence of divalent carbon where this seemed appropriate. His proposed carbon monoxide oxide structure for fulminic acid, $C=N.OH$, came closest to accounting for its known properties and remained its accepted formulation until well into the present century.
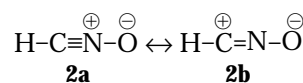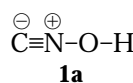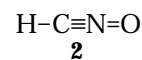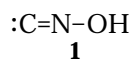
On the strength of it and on the basis of his own experimental work, H. Wieland (*31*) at last offered a reasonable interpretation of Howard's remarkable original preparation of mercury fulminate. The proposed multistage process is initiated by the oxidation of the alcohol to acetaldehyde (which affords better yields of fulminate) and then proceeds by oxidation, nitration, and decarboxylation stages (a–d) via methylnitrolic acid (d) to the final product. The high yield (of **1**) afforded by this complex sequence is indeed remarkable:

$$CH_3CHO \rightarrow HO–N=CHCHO \qquad (a)$$

$$HO–N=CHCHO \xrightarrow{O} HO–N=CHCOOH \qquad (b)$$

$$HO–N=CHCOOH \rightarrow HO–N=C(NO_2)COOH \quad (c)$$

$$HO–N=C(NO_2)COOH \xrightarrow{-CO_2} HO–N=CH.NO_2 \quad (d)$$

$$HO–N=CH.NO_2 \xrightarrow{-HNO_2} HO–N=C$$
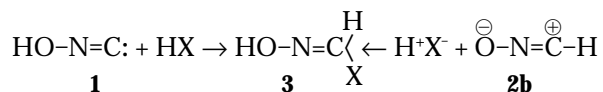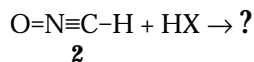$$\mathbf{1}$$

Meanwhile, the classical work in physical chemistry of Raoult, Ostwald, and Beckmann had supplied the theoretical background and practical techniques for determining molecular weights of dissolved substances by their colligative properties. Applying cryoscopic and conductometric methods to solutions of sodium fulminate, Lothar Woehler confirmed the monomeric formula of fulminic acid experimentally in 1905 (*32*).

Although Nef's structure **1** continued to serve as an acceptable basis for the discussion of the chemistry of fulminic acid, the alternative formyl nitrile oxide structure **2** had been canvassed as early as 1899 (*33*) and the possible occurrence of tautomerism between **1** and **2** had been considered (*34*). However, uncertainties continued to prevail, and the persistent hold of Nef's oxime structure **1** is reflected by its retention in the most respected and widely used textbooks well into the 1950s (*35*).

A powerful argument against **1** had in fact been advanced on purely theoretical grounds in 1926 by Linus Pauling (*36*). He showed that according to the calculated free energy content, the formyl nitrile oxide molecule **2** was more stable than the alternative **1**, and should therefore be regarded as the true representation of fulminic acid. This important paper passed relatively unnoticed, presumably because independent experimental support was as yet lacking.

$$:C=N–OH \qquad\qquad H–C≡N=O$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

$$\overset{\ominus}{C}≡\overset{\oplus}{N}–O–H \qquad H–C≡\overset{\oplus}{N}–\overset{\ominus}{O} \leftrightarrow H–\overset{\oplus}{C}=\overset{\ominus}{N}–O$$
$$\mathbf{1a} \qquad\qquad \mathbf{2a} \qquad\qquad \mathbf{2b}$$

Growing insight into the nature of the chemical bond (*37*) during the 1930s provided the concepts for refining the formulation of **1** and **2** in accord with the emerging electronic theory of valency and resonance. Thus the oxime formula was reinterpreted in terms of **1a**, and the nitrile oxide, in its ground state, as the mesomer **2a 2b**, thus removing the need for invoking divalent carbon and pentacovalent nitrogen in the respective structures.

$$O=N\equiv C-H + HX \rightarrow \textbf{?}$$
$$\textbf{2}$$

$$HO-N=C: + HX \rightarrow HO-N=C\Big\langle \begin{smallmatrix} H \\ \\ X \end{smallmatrix} \leftarrow H^+X^- + \overset{\ominus}{O}-N=\overset{\oplus}{C}-H$$
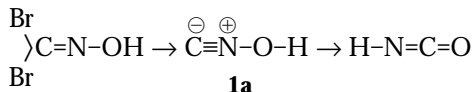$$\textbf{1} \qquad\qquad\qquad \textbf{3} \qquad\qquad\qquad\qquad \textbf{2b}$$

A serious objection to the formyl nitrile oxide structure **2** had been the remarkable readiness of fulminic acid to add hydrogen halides, yielding the halogenated formylhydroxamic acids **3**, of established structure. This was readily explicable by a 1,1-diaddition to **1** at its divalent carbon, but was difficult to account for in terms of the nitrile oxide structure **2**. Eventually, in the context of his extensive studies of 1,3-dipolar addition reactions of unsaturated systems, including nitrile oxides, Huisgen reinterpreted the observations more convincingly as 1,3-additions to the mesomeric species **2b**, thus providing strong support for the nitrile oxide structure (**2a**, **2b**) (*38*).

Not until the advent of the techniques of molecular spectroscopy was final proof of structure **2** obtained. Between 1965 ard 1971, Beck and his co-workers studied the IR spectrum of free fulminic acid, which they had isolated for the first time in the pure state (*39*). The anhydrous gaseous compound and its deuterated analogue produced peaks in the infrared region that were clearly attributable to **2** rather than **1**. A detailed analysis of microwave spectra of fulminic acid and five of its isotopomers confirmed this assignment (*40*), as did the study of the far-infrared spectra (between 100 and 1000 cm$^{-1}$) (*41*). With this conclusive structural confirmation, fulminic acid assumed its due place as the parent compound of the extensive class of nitrile N-oxides

$$R-\overset{\oplus}{C}\equiv\overset{\ominus}{N}-O \leftrightarrow R-\overset{\oplus}{C}=\overset{\ominus}{N}-O$$
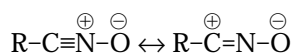
that had long played a prominent role in synthetic organic chemistry (*42*) .

The discarded oxime formula **1** came once again into its own when the last of the four possible CHNO isomers, the so far elusive isofulminic acid, was first obtained by a matrix isolation technique upon irradiation of dibromoformoxime in argon at 12 K, and was detected transiently by IR spectroscopy (*43*):

$$\begin{smallmatrix} Br \\ \\ Br \end{smallmatrix}\Big\rangle C=N-OH \rightarrow \overset{\ominus}{C}\equiv\overset{\oplus}{N}-O-H \rightarrow H-N=C=O$$
$$\textbf{1a}$$

Its observed spectral characteristics agreed adequately with the values for the carbon monoxide oxime structure **1a**. It is noteworthy that speculations based on sophisticated spectral data have been voiced concerning the possible occurrence of isofulminic acid in interstellar space (*44*), in analogy with that of cyanic acid, H−O−C≡N (*45*).

With the final establishment of the structure of fulminic acid some 175 years after its discovery (*46*), interest in this molecule is by no means exhausted. The characteristics of its

**Table 1. Bond Lengths and Bond Angles in Fulminic Acid**
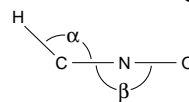


| Derived from | Ref | Bond Length/Å | | | Bond Angle/deg | |
|---|---|---|---|---|---|---|
| | | H–C | C–N | N–O | α | β |
| Microwave spectra | *49* | 1.027 | 1.161 | 1.207 | — | — |
| Ab initio calculations | *51, 52* | 1.0615 | 1.1648 | 1.2025 | 165.13 | 176.5 |

simple four-atom H−C−N−O sequence have attracted the continued attention of spectroscopists and theoreticians alike, resulting in spectroscopic data and ab initio calculations of ever increasing rigor. They have provided information concerning the molecular dimensions, geometry, energy content, and fine spectroscopic details for both fulminic acid and several of its isotopomers (*47, 48*) (Table1).

The sum of the evidence suggests that fulminic acid is a classical example of a "quasi linear" four-atom molecule (*49*), occupying a position between rigid linear and rigid bent configurations. This view is based on the anomalous shortening of its C−H bond, inconsistent with linearity at this end of the molecule (Table 1), and on the position of its IR H−C−N bending vibration at 224 cm$^{-1}$ (*47*), contrasting with the bending fundamentals of (linear) HCN at 711 cm$^{-1}$ or of H−C−C in linear H−C−C−F at 594 cm$^{-1}$ (Table 2) (*50*). Certain characteristics of the microwave spectra of fulminic acid and its H$^{13}$CNO isotopomer also support the slightly bent structure (*51*).

The experimentally observed spectral and other parameters (see, for example, Table 2) have been approached with varying precision in numerous ab initio calculations (*47, 48*). In spite of its apparent simplicity, the fulminic acid molecule presents a formidable problem in the theoretical treatment of its structure; accurate predictions concerning its equilibrium structure are only obtainable by the use of extensively correlated wave functions and large one-particle basis sets and by a careful optimization of all the structural parameters (*52*). Satisfactory results recently achieved by the coupled cluster method, CCSD(T), are shown in Table 1 (*52*).

The extensive ongoing work on fulminic acid has been complemented by the parallel exploration of its isomers, so that comparable spectroscopic (*53*) and theoretical (*45*) data relating to all four CHNO structures—isocyanic (HNCO), cyanic (HOCN), fulminic (HCNO) and isofulminic (HONC) acids—are now available. Indeed, the work has been extended to the sulfur analogues, with the result, for example, that isothiocyanic acid (HNCS) is recognized as the most quasi-linear of all known nominally bent molecules (*54*).

**Table 2. The IR Spectrum of Fulminic Acid**

| Band | Frequency/cm$^{-1}$ [a] |
|---|---|
| $\nu_1$ CH stretching | 3336 |
| $\nu_2$ CN stretching | 2196 |
| $\nu_3$ NO stretching | 1254 |
| $\nu_4$ CHO bending | 537 |
| $\nu_5$ HCN bending | 224 |

[a]Data from refs *47, 50*.

## Mercury Fulminate in Explosives Technology

In the field of chemical technology, fulminic acid has played a part no less significant than in the history of pure organic chemistry. The discovery of mercury fulminate in 1800 occurred at the height of the Industrial Revolution in England, when the application of science to useful industrial and commercial ends was uppermost in the minds of men. The obvious potential of mercury fulminate as a new explosive raised hopes for its possible use for both warlike and peaceful purposes.

Howard's initial attempts to employ the fulminate as a more powerful form of gun powder were frustrated by the extraordinary speed and violence (the *brisance*) of its detonation. Sporting guns had their barrel split and the breach torn open by small charges of fulminate, and pistols were similarly destroyed. In field trials at the Royal Military Academy in Woolwich (Fig. 4) the same unfavorable experiences were produced with artillery pieces, shells, and grenades. It had to be accepted that the inherent properties of mercury fulminate precluded its use both in ballistics and for blasting in mines and quarries, putting an end to any hopes of its usefulness. It is one of the ironies of history that it was presently brought into prominence precisely *because* of the violence of its explosion, as the ideal detonator for firing conventional explosives.

Ever since the introduction of gun powder in the 13th century, the actual firing of guns had remained a clumsy and uncertain operation. In cannon, it was effected by matches, fuses, or even glowing coals, and in small firearms by sparks generated by flint locks. The cumbersome procedure was superseded in the 18th century by "percussion" firing, in which the sharp detonation of a small "initiator" induced the reliable explosion of the main gun powder charge (*55*). At first, these primers were mixtures based on potassium chlorate (*56*), but their sensitivity to atmospheric moisture impaired their reliability; moreover, they liberated chlorine on detonation, which tended to hasten the corrosion of the gun (*57*). The introduction of mercury fulminate as a greatly superior primer is credited to E. G. Wright, a country gentleman who combined his fondness of field sports with a lively interest in chemistry (*58*). In 1822, he attended chemical lectures in which mercury fulminate was one of the popular demonstration experiments. He thereupon prepared the compound himself (wisely, it may be noted, in an outbuilding on his estate) and found it a greatly improved primer for the gun powder used in his sporting activities. The use of fulminate percussion in sporting guns was soon universally adopted. In contrast, equipping the European armies with the new system of firing was persistently opposed by military authorities and governments alike. In Britain, for example, it was adapted to the infantry musket (the "Brown Bess") only in 1842, after exhaustive tests carried out at Woolwich. In the 1840s and 1850s its introduction throughout Europe became irresistible and created an ever-increasing demand for mercury fulminate, which remained, for the next 80 years, the only practical detonator for firing projectiles of every kind. In the early years of the 20th century, the annual production was estimated at 100,000 kg in Germany alone (*59*).

Howard's original reaction of 1800 remained the only method of producing mercury fulminate in quantity. Since
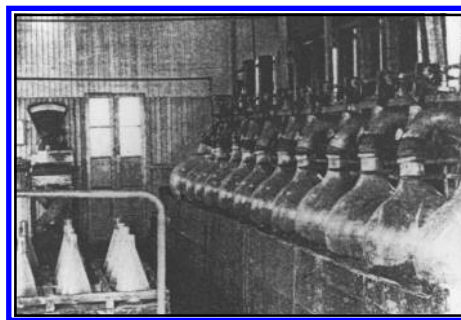


Figure 5. Batch production of mercury fulminate. On the left, conical flasks in which mercury is dissolved in nitric acid. On the right, large round-bottomed flasks in which the reaction with alcohol is carried out (courtesy Kluwer Academic Publishers, Dordrecht).
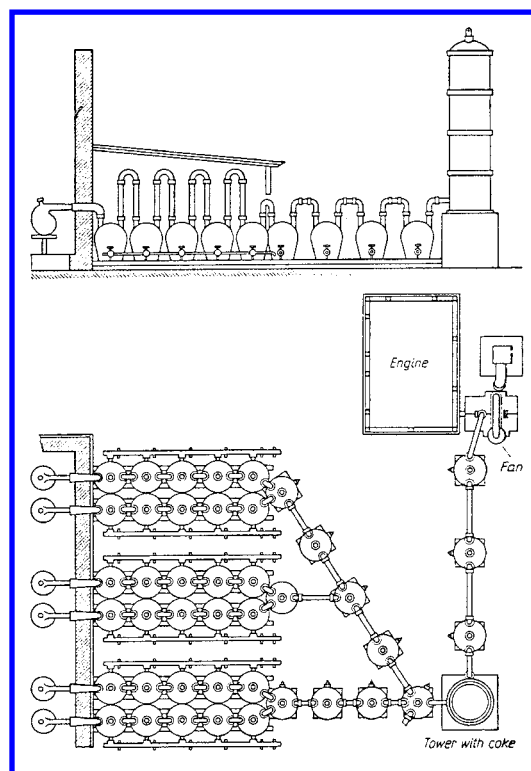


Figure 6. Batch production of mercury fulminate. Plan and elevation of the plant, with absorption trains for the disposal of the noxious fumes.

it was far too hazardous a process to be translated to the large scale, the industrial production remained essentially a laboratory operation, carried out in batteries of many individual batches of limited size (*60*) (Figs. 5, 6). The manufacture of mercury fulminate, including the subsequent granulation process, was in fact acknowledged to be one of the most dangerous branches of the explosives industry (*61*) and was run at a rate at which the fulminate was consumed *on site* in the manufacture of the percussion devices. Its undisputed reign began to be challenged only in the 1920s, as more convenient alternatives, especially lead azide, became accessible.

*Peaceful Applications*

Mercury fulminate played an equally crucial role in the development of explosives for peaceful purposes, especially in the context of Alfred Nobel's invention of dynamite (*62*). By absorbing nitroglycerine, itself a highly explosive and dangerously unpredictable liquid, in a porous material such as kieselguhr, Nobel had obtained the much less shock-sensitive "dynamite", which combined excellent blasting powers with a good safety record. However, a remaining serious obstacle to its wider adoption was its difficult detonation by fuse or spark. This problem was overcome at one stroke by Nobel's successful introduction of reliable percussion firing by mercury fulminate cartridges. This innovation, embodied in Nobel's seminal patents of 1864, 1867, and 1875 (*63*), signaled a new era in the safe use of this "explosive of peace" in mining, quarrying, tunneling, and civil engineering, stimulating the construction of roads, railways, and harbors on a scale unknown before. Nobel himself (*64*) emphasized the indispensable part played by mercury fulminate in these developments.

Might it, therefore, not be speculated with some justification that over and above its intrinsic significance, fulminic acid is entitled to a share, however modest, in the establishment of the Nobel Prize? Without the intervention of mercury fulminate, the success of dynamite might have been less decisive and Nobel's fortune and freedom of action correspondingly circumscribed. However this may be, there is no doubt that the story of fulminic acid provides an excellent illustration of the advancement of science and of the interaction of pure research and technology to the mutual benefit of both.

## Literature Cited

1. Kunckel, J., Baron von Löwenstern. *Collegium Physico-Chymicum oder Laboratorium Chymicum…* Engelleder, J. C., Ed.; Samuel Heyls: Hamburg & Leipzig, 1716; p 213. Davis, T. L. *J. Chem Educ.* **1927,** *4,* 105–113.

2. Tierie, G. *Cornelis Drebbel (1572–1633)*; H. S. Paris: Amsterdam, 1932.

3. Drebbel, C. *De Quinta Essentia Tractatus editus cura J. Morsi*, Henricus Carstens: Hamburg, 1621. Drebbel, C. *Abhandlung von der Quintessenz*, in *Neue Alchymistische Bibliothek*, Vol. I, Part ii; Schröder, F. J. W., Ed.; Heinrich L. Bronner: Frankfurt & Leipzig, 1772; pp 291–314. See also Ferguson, J. *Bibliotheca Chimica*, James Maclehose: Glasgow, 1906; Vol. I, pp 223–224; Vol. II, pp 342–344.

4. Romocki, S. J. von. *Geschichte der Explosivstoffe*, Vol. 1; Robert Oppenheim: Berlin, 1895–96; p 367.

5. Fourcroy, A. F. *Ann. Chim.* **1789,** *2,* 219–225.

6. Berthollet, C. L. *Ann. Chim.* [1] **1789,** *1,* 52. See also Jenkins, I. D. *J. Chem. Educ.* **1987,** *64,* 1640.

7. Beguin, J. *Tyrocinium Chymicum e Naturae Fonte et Manuali Experentia Depromptum*, 2nd ed.; Apud Antonium Boetzerum: Cologne, 1612.

8. Edward Charles Howard (1774–1816) was a member of one of the first aristocratic families of England, being the younger brother of the 12th Duke of Norfolk. He chose to pursue a scientific career, in which he achieved notable success. See Kurzer, F. *Ann. Sci.* **1999,** *56,* 113–141.

9. Howard, E. *Philos. Tran. R. Soc.* **1800,** *90 I,* 204–238. For a preliminary communication, see Nicholson, W., Ed. Note in *J. Nat. Philos. Chem. Arts* **1799,** *3*(Aug)*,* 263.

10. For contemporary ideas on the composition of muriatic acid, see LeGrand, H. E. *Ann. Sci.* **1974,** *31,* 213–226.

11. For accounts of Cruickshank's important scientific contributions made in his post as lecturer in chemistry at the Royal Military Academy, Woolwich, see Sanderson, P. M.; Kurzer, F. *Chem. Ind.* **1957,** 456–460. Coutts, A. *Ann. Sci.* **1959,** *15,* 121–133.

12. Howard, E. *Tilloch's Philosophical Magazine* **1800,** *8,* 17–35, 122–131; *Nicholson's Journal* **1801,** *4,* 173–178, 200–209, 249–254.

13. Howard, E. *Biblioteque Britannique* **1800,** *15,* 46–57, 139–156, 321–340; **1801,** *16,* 59–73. *Ann. Chim.* **AN VIII,** *32,* 205; **AN IX,** *38,* 323–324.

14. Howard, E. *Scherer's Allgemeines J. Chem.* **1801,** *5,* 606–647; *Gilbert's Ann. Phys.* **1811,** *37,* 75–97.

15. Berthollet, C. L. *Bibliotheque Britannique* **1801,** *18,* 259–261; reported in *Tilloch's Philosophical Magazine* **1802,** *12,* 91–92.

16. Volhardt, J. *Ann. Chem.* **1903,** *328,* 1–40 (p 1).

17. Liebig, J. *Rep. Pharm.* **1822,** *12,* 412–422; **1823,** *15,* 361–391.

18. Liebig, J. *Ann. Chim.* **1823,** *24,* 294–318. Gay-Lussac, J. L.; Liebig, J. *Ann. Chim.* **1824,** *25,* 285–311; Liebig, J. *Ann. Chim.* **1826,** *33,* 207–214.

19. Wöhler, F. *Ann. Phys. Chem.* **1824,** *1,* 117–124; **1825,** *5,* 385–389. See also Berl, E. *J. Chem. Educ.* **1938,** *15,* 553–562.

20. Freund, I. *The Study of Chemical Composition*, University Press: Cambridge, 1904; Chapter XVIII. Brock, W. H. *Justus von Liebig*, University Press: Cambridge, 1997; especially Chapter 3.

21. Berzelius, J. J. *Jahresberichte über die Fortschritte der Physischen Wissenschaften* **1825,** *4,* 110–117; **1826,** *5,* 85–94; **1831,** *10,* 82; **1832,** *11,* 44. See also Winderlich, R. W. *J. Chem. Educ.* **1948,** *25,* 501–505.

22. Gay-Lussac, J. L. *Ann. Chim.* **1814,** *41,* 149.

23. Scholl, R. *Entwicklungsgeschichte … der sogenannten Knallsäure und ihrer Derivate*, J. F. Lehmann: München & Leipzig, 1893.

24. Wieland, H. In *Sammlung Chemischer und Chemisch-Technischer Vorträge*, Vol 14; Ahrens, F. B.; Herz, W., Eds.; Ferdinand Enke: Stuttgart, 1909; pp 385–461.

25. Kekulé, A. *Ann. Chem.* **1857,** *101,* 200–213; **1858,** *105,* 279–286; **1858,** *106,* 129–159. See also Russell, C. A. *The History of Valency*, Leicester University Press: Leicester, 1971; pp 62–63.

26. Griess, P. *Ann. Chem. Pharm.* **1861,** Suppl. 1, 100–104.

27. Scholl, R. *Ber. Deutsch. Chem. Ges.* **1890,** *23,* 3505–3519. Divers, E.; Kawakita, M. *J. Chem. Soc.* **1884,** *45,* 13–19. Divers, E. *J. Chem. Soc.* **1884,** *45,* 19–24. Armstrong, H. E. *J. Chem. Soc.* **1884,** 25–27. Bergfeld, L. *Z. ges. Schiess-und Sprengstoffwesens* **1942,** *37,* 84–86 (*Chem. Abstr.* **1943,** *37,* 5592).

28. Carstanjen, E.; Ehrenberg, A. *J. Prakt. Chem. [2]* **1882,** *25,* 232–248. Ehrenberg, A. *J. Prakt. Chem. [2]* **1884,** *30,* 38–60 (p 41).

29. Steiner, A. *Ber. Deutsch. Chem. Ges.* **1883,** *16,* 1484–1486, 2419–2420.

30. Nef, J. U. *Ann. Chem.* **1894,** *280,* 291–343 (p 305).

31. Wieland, H. *Ber. Deutsch. Chem. Ges.* **1907,** *40,* 418–422.

32. Woehler, L. *Ber. Deutsch. Chem. Ges.* **1905,** *38,* 1351–1359; **1910,** *43,* 754–756.

33. Ley, H.; Kissel, H. *Ber. Deutsch. Chem. Ges.* **1899,** *32,* 1357–1368.

34. Palazzo, F. C. *Atti Acad. Lincei [5]* **1912,** *21V,* 713.

35. Sidgwick, N. V. *The Organic Chemistry of Nitrogen*, 2nd ed.;

Clarendon: Oxford, 1937; pp 338–342; C=N.OH or C≡N.OH. Karrer, P. *Organic Chemistry*, 1st ed.; Elsevier: Amsterdam-New York, 1938; pp 212–213; C=N.OH. Wheland, G. W. *Advanced Organic Chemistry*, 2nd ed.; Wiley: New York, 1949; p 649; HO–N̈=C:, HO–N̈≡C̈. Campbell, N. *J. Schmidt's Organic Chemistry*, 7th ed.; Oliver and Boyd: London, 1955; p 352; C=N–OH. Finar, I. L. *Organic Chemistry*, 3rd ed.; Longmans: London, 1959; C≡N.OH.

36. Pauling, L.; Hendricks, S. B. *J. Am. Chem. Soc.* **1926,** *48*, 641–651.

37. Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1938 (1st ed.), 1945 (2nd ed.); esp. Chapter VI.

38. Huisgen, R. *Proc. Chem. Soc.* **1961,** 357–369.

39. Beck, W. ; Feldl, K. *Angew. Chem.* **1966,** *78*, 746; *Angew. Chem., Int. Ed. Engl.* **1966,** *5*, 722–723. Beck, W.; Swoboda, P.; Feldl, K.; Tobias, R. S. *Chem.Ber.* **1971,** *104*, 533–543.

40. Winnewisser, M.; Bodenseh, H. K. *Z. Naturforsch.* **1967,** *22A*, 1724–1737; **1969,** *24A*, 1966–1972, 1973–1979.

41. Winnewisser, B. P.; Winnewisser, M.; Winther, F. *J. Mol. Spectrosc.* **1974,** *51*, 65–96.

42. Grundmann, C.; Grünanger, P. *The Nitrile Oxides. Versatile Tools of Theoretical and Preparative Chemistry*; Springer: Berlin–New York, 1971.

43. Maier, G.; Teles, J. H.; Hess, B. A.; Schaad, L. J. *Angew. Chem.* **1988,** *100*, 1014–1016; *Angew. Chem., Int. Ed. Engl.* **1988,** *27*, 938–939.

44. Winnewisser, G.; Herbst, E. *Top. Curr. Chem.* **1987,** *139*, 119. Winnewisser, M. *Chem. Unserer Zeit* **1984,** *18*, 1, 55.

45. McLean, A. D.; Loew, G. H.; Berkowitz, D. S. *J. Mol. Spectrosc.* **1977,** *64*, 184–198.

46. Winnewisser, M.; Winnewisser, B. P. *Chem. Listy* **1976,** *70*, 785–807 (*Chem. Abstr.* **1976,** *85*, 158.751k).

47. Albert, S.; Winnewisser, M.; Winnewisser, B. P. *Microchem. Acta* **1997,** *14*, 79–88.

48. Handy, N. C.; Murray, C. W.; Amos, R. *Philos. Mag.* **1994,** *69*, 755–762.

49. Yamada, K.; Winnewisser, B. P.; Winnewisser, M. *J. Mol. Spectrosc.* **1975,** *56*, 449–470. See also ref *45*.

50. Iachello, F.; Manini, N.; Oss, S. *J. Mol. Spectrosc.* **1992,** *156*, 190–200. See also Keedy, C. R. *J. Chem. Educ.* **1992,** *69*, A296–A298.

51. Preusser, J.; Winnewisser, M. *Z. Naturforsch.* **1996,** *51A*, 207–214.

52. Koput, J.; Winnewisser, B. P.; Winnewisser, M. *Chem. Phys. Lett.* **1996,** *255*, 357–362.

53. Teles, J. H.; Maier, G.; Hess, B. A.; Schaad, L. J.; Winnewisser, M.; Winnewisser, B. P. *Chem. Ber.* **1989,** *122*, 753–766.

54. Yamada, K.; Winnewisser, M.; Winnewisser, G.; Szalanski, L. B.; Gerry, M. C. L. *J. Mol. Spectrosc.* **1977,** *64*, 401–414.

55. Wyndham Hulme, E. In *The Rise and Progress of the British Explosives Industry*; VII International Congress of Applied Chemistry, London, 1909; pp 94–111.

56. Forsyth, A. J. Apparatus for Discharging Artillery etc. by Means of Detonating Compounds; Br. Patent 3032, 1807.

57. Romocki, S. J. von. *Geschichte der Explosivstoffe*, Vol. 2; Robert Oppenheim: Berlin, 1895–96; pp 51–52.

58. Goode Wright, E. *Tilloch's Philosophical Magazine* **1823,** *62*, 203–204.

59. Meyer, V.; Jacobson, P. *Lehrbuch der Organischen Chemie*, Vol. 1, 2nd ed.; Walter de Gruyter: Berlin & Leipzig, 1903–1920; Part 2, p 1302. Rinkenbach, H.; Audrieth, L. F. *J. Chem. Educ.* **1945,** *22*, 522–524. Harris, B. W. *J. Chem. Educ.* **1987,** *64*, 541–544.

60. Urbanski, T. *Chemistry and Technology of Explosives*, Vol. 3; Pergamon: Oxford, 1967; pp 149–156.

61. Knoll, R. *Das Knallquecksilber und Ähnliche Sprengstoffe*; A. Hartleben: Wien & Leipzig, 1908.

62. de Mosenthal, H. *J. Soc. Chem. Ind. (London)* **1899,** *8*, 443–451. Thompson, A. F. *J. Chem Educ.* **1943,** *20*, 151–154.

63. Nobel, A. Manufacturing and Applying Explosive Compounds; Br. Patent 1813, Jul 20, 1864; Improvements in Explosive Compounds and in the Means of Igniting the Same; Br. Patent 1345, May 7, 1867; Improvements in Explosive Compounds; Br. Patent 4179, Jun 2, 1875.

64. Nobel, A. *J. Soc. Arts* **1875,** *23*, 611–626.