



Heinz A. Staab

Heinz A. Staab (1926–2012)

Heinz A. Staab, who was for many years Director at the Max Planck Institute (MPI) for Medical Research in Heidelberg, and previously President of the Max Planck Society (MPG) and the Gesellschaft Deutscher Chemiker (GDCh, German Chemical Society), passed away on July 29, 2012 at the age of 86 in Berlin after a long illness.

Heinz Staab was born on March 26, 1926 in Darmstadt. His diploma and dissertation research on polyenyl phenyl ketones were completed under the supervision of the Nobel Laureate Richard Kuhn at the MPI for Medical Research in Heidelberg. After his diploma in chemistry in 1951 at the University of Tübingen and his doctorate in 1953 at the University of Frankfurt, he worked at the MPI for Medical Research with Richard Kuhn and, from 1959, with Georg Wittig at the nearby Institute for Organic Chemistry of the University of Heidelberg. Within the second half of the 1950s he completed his habilitation there in 1957 on the development of azolide chemistry, published his textbook "Introduction to Theoretical Organic Chemistry" in 1959, and simultaneously also accomplished a doctorate in medicine in 1960. In 1962, he was made Associate Professor and one year later Professor of Organic Chemistry at the University of Heidelberg. From 1964, Heinz Staab was Director of the Institute for Organic Chemistry. In 1974, he became a scientific member of the MPG and Director of the Organic Chemistry department at the MPI for Medical Research, which he headed until he reached emeritus status in 1996.

The textbook "Introduction to Theoretical Organic Chemistry", with 760 pages and 1300 references, was a scientific bestseller for a young chemist who had completed his doctorate only a few years previously. It was the first German and first European book on physical organic chemistry, and it became a standard work because of its clarity. It was published in four editions and was reprinted several times from 1959–1975, and was also translated into Russian and Polish. The German version also found use in the USA.^[1]

At the beginning of his independent academic career, Heinz Staab observed that *N*-acetylimidazole is highly reactive in transacetylations, similar to acetyl chloride. The "azolide chemistry"^[2] that he thus developed peaked with the discovery of *N,N'*-carbonyldiimidazole (CDI) **1**. This reagent has thousands of applications as phosgene substitute and reagent for imidazole transfer, acylations, phosphorylation, dehydration, condensation, and activation. Until the mid-1960s, Heinz Staab and his group had published the most important basic reactions of the azolides in more than 50 publications, and in 1998 he published, together with two

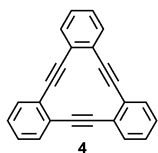
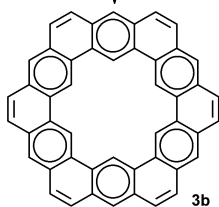
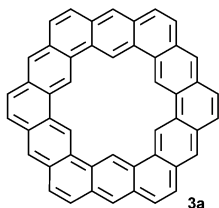
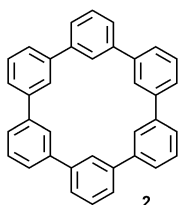
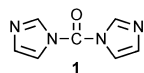
of his longstanding colleagues, a book on the rapid development of azolide chemistry over the 40 years since its beginnings during his habilitation.^[3]

In the 1960s, the emerging technique of ¹H NMR spectroscopy was used to elucidate chemical structures. The temperature dependence of ¹H NMR spectroscopy was used very early on to investigate rotational isomerism as a consequence of hindered rotation around single bonds of amides, aryl and diaryl ketones, and diarylboranes and to determine the height of rotational barriers. With these methods, it could also be shown that *syn-anti* isomerization of substituted imines involves inversion at nitrogen and not rotation about the C=N bond. Staab was one of the first to study reaction mechanisms with ¹³C-labeled compounds by using ¹³C NMR spectroscopy. In 1966, he began a X-ray crystallography laboratory in cooperation with Gerhard M. J. Schmidt of the Weizmann Institute in Israel.

The publication of the synthesis of hexa-*m*-phenylene **2** in 1964 was the beginnings of a series of almost 40 publications by Heinz Staab on conjugation in macrocyclic systems, his second major field of research. As the *meta* linkage of the benzene rings prevents a continuous cyclic conjugation, no interaction of the π electrons is observed for **2** exceeding the diphenyl system, as expected. In contrast, for the cycloarene **3**, annulene-like resonance structures such as **3a** can be formulated with an [18]annulene inside and a [30]annulene outside. At the centennial celebrations for Kekulé's benzene structure in Bonn in 1965, Heinz Staab reported the first attempts to synthesize "superbenzene" **3**, which he named "kekulene" in honor of the occasion. However, the synthesis of **3** was not successfully achieved until 1978. The ¹H NMR spectrum and X-ray crystal structure showed that kekulene has a much higher benzenoid aromaticity than the annulenoid, so that the formulation **3b** with the largest possible number benzenoid π -electron sextets, displayed as circles, best describes the bonding situation. Furthermore, numerous benzannulated [12], [14], and [18]annulenes were synthesized and investigated to study the boundary between benzenoid and annulenoid aromaticity.

Heinz Staab was also a pioneer in the synthesis and investigation of rigid phenylacetylene-based macrocycles. The cyclic trimer (1966; **4**) and hexamer (1974; **5**) of phenylacetylene are nowadays used as the basis of advanced materials.^[4]

In 1970, Heinz Staab published the first work on cyclophanes, which then became his main research area. Cyclophanes allow arenes to be fixed face-to-face, so that intermolecular interactions and electron-transfer processes in defined geometries can be studied. The series of pyrenophanes **6** was synthesized to investigate the electron interaction that causes the formation of excimers upon photon radiation of pyrene solutions. The sensational discovery of the strong orientational dependence



of charge-transfer interactions in the quinhydrone–cyclophanes **7** and **8** led to research into many other donor–acceptor cyclophanes. In the mid-1980s, extension of this work into bioorganic chemistry followed, with the synthesis of flavin–flavin and nicotiamide–flavin cyclophanes as biomimetic models for the active sites in flavoenzymes, and a number of porphyrin–quinone cyclophanes, such as **9** and **10**, with which the charge separation in the photosynthetic reaction centers can be imitated. Compound **10** was designed such that substituents X vary the acceptor strength and the distance between the acceptor and donor can be decreased stepwise, in that the bridging anthracene is substituted by biphenylene, naphthalene, or benzene. The light-induced electron transfer from porphyrin to quinone of these model compounds for the photosynthetic center was investigated in cooperation with Maria-Elisabeth Michel-Beyerle (TU München) by using time-resolved laser-pulse spectroscopy.

A further body of research from the 1980s was aromatic diamines with proton-sponge properties and their structure–functional relationship. While searching for compounds more active than the original naphthalene proton sponges, the strong fluorene sponge **11** (X = CH₂) for example, with linear N⋯H⁺⋯N hydrogen bonds, was synthesized.

Heinz Staab's scientific work, which involved about 150 doctoral students and several other co-workers and was documented in more than 340 publications, impressed with a mixture of synthetic skill and new physical methods, which he repeatedly recognized and pioneered for their utility in organic chemistry. The molecules that he conceptualized as models for investigating basic scientific questions were also aesthetically intriguing.

He was a great believer in the freedom of science and was prepared to accept responsibilities so that this could be maintained. Indeed, he took over the role of Dean in 1968 and Vice President in 1969 at the University of Heidelberg during that period of particular unrest. He was active on the Committee of the German Research Council (DFG) for almost 20 years, and on the Federal Scientific Advisory Board from 1976 to 1979, three years of which he was Chairman of the Research Committee. In contrast to his predecessor and successors, he was also a passionate scientist during his term of office as President of the MPG (1984–1990) and remained director of the MPI for Medical Research, during which time 36 doctorates were completed. He also took over the office of President of the GDCh from 1984–1985. As scientific organizer, he showed much skill in dealing with politics, and for example achieved budget increases of the MPG and DFG for many years in 1986. After the Presidency of the MPG, he took up many other offices, such as the Presidency of the Heidelberg Academy of Sciences (1994–1996). He was also the editor of several chemistry journals.

One of his utmost concerns was normalizing the relationship between Israel and Germany and to encourage exchanges with Israeli scientists. He was thus one of the first German scientists to begin a cooperation with the Weizmann Institute in the mid-1960s, and he was on the committee of the Minerva Foundation, which supervised most of the scientific cooperation between Germany and Israel, from 1965 to 1984. He was the first MPG President to publicly discuss the involvement of scientists of the Kaiser Wilhelm Society (the predecessor society of the MPG) in the atrocities of the Nazi regime.

Heinz Staab received many honors for his involvement and efforts in chemistry and in science policy, such as the Adolf von Baeyer Memorial Medal of the GDCh in 1979, an honorary doctorate from the Weizmann Institute in Rehovot in 1984, the Weizmann Award in the Sciences and Humanities in 1990, the Grand Medal Cross with Star of the Federal Republic of Deutschland in 1990, the Adolf von Harnack Medal of the MPG in 1994, and honorary membership of the GDCh in 1999.

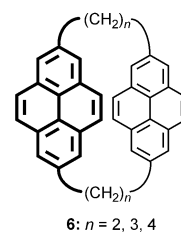
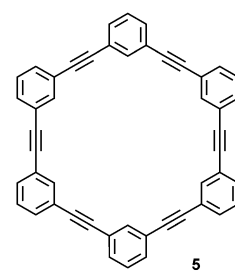
Heinz Staab found encouragement in particular from his wife Ruth, who supported him throughout his life, and his two children. Long Sunday walks on the Königstuhl above Heidelberg revitalized him. His friend Karl H. Hausser, who was for many years Director of the Molecular Physics Department of the MPI for Medical Research, often accompanied him, and they then discussed the projects they were both involved in together. We students, the University of Heidelberg, the MPG, GDCh, and sciences in general have much to thank Heinz Staab for.

Matthias W. Haenel

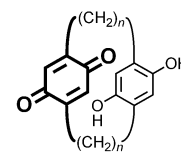
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Mülheim an der Ruhr

- [1] E. Berliner, *J. Am. Chem. Soc.* **1959**, *81*, 6344–6345.
- [2] Azolides are heterocyclic amides, the amide N-atom part of which is a derivative of an azole ring, such as imidazole, pyrazole, triazoles, tetrazole, benzimidazole, benzotriazole, and the substituted derivatives. H. A. Staab, *Chem. Ber.* **1956**, *89*, 1927–1940; Review: H. A. Staab, *Angew. Chem.* **1962**, *74*, 407–423; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 351–367.
- [3] H. A. Staab, H. Bauer, K. M. Schneider, *Azolides in Organic Synthesis and Biochemistry*, Wiley-VCH, Weinheim, **1998**, p. 502.
- [4] Reviews: a) C. S. Jones, M. J. O'Connor, M. M. Haley, *Acetylene Chemistry* (Eds.: F. Diederich, P. J. Stang, R. R. Tykwinski), Wiley-VCH, Weinheim, **2005**, pp. 303–385; b) Y. Tobe, R. Umeda, *Science in Synthesis*, Vol. 43 (Ed.: H. Hopf), Thieme, Stuttgart, **2008**, pp. 393–433.

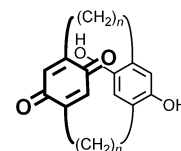
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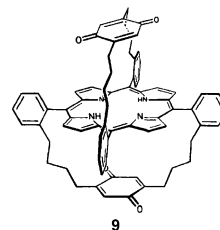
6: n = 2, 3, 4



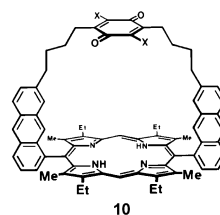
7: n = 2, 3



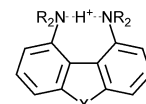
8: n = 2, 3



9



10



11: X = CH₂, O, S, Se,
-CH=CH-, -CH₂-CH₂-