133. Color Chemistry as Reflected in *Helvetica Chimica Acta*

by **Heinrich Zollinger**

Technisch-Chemisches Laboratorium der Eidgenössischen Technischen Hochschule,
ETH-Zentrum, CH-8092 Zürich

The aim of this contribution to the 75th anniversary of *Helvetica Chimica Acta* (HCA) is the same as that of the other essays published for that occasion, namely to assess the impact of papers on color chemistry in this journal on the world-wide development of color chemistry in particular, and of chemistry in general. To keep this review reasonably short, we will concentrate predominantly on research achievements that influenced work carried out at a significantly later date. Admittedly, this policy has some subjective character, but it seems to the author more interesting than an unpersonal ('colorless') compilation of as many papers per page as possible.

Furthermore, it is, in our opinion, appropriate for this specific aspect of chemistry in Switzerland, to illustrate first very briefly the development of the chemical sciences and technology in our country *before* the *Swiss Chemical Society* had decided to publish a national journal in 1917.

Surveying the situation in Switzerland between the birth of modern chemistry in the late 18th century and 1917, we recognize clearly two periods: before the late 1850's, there was only one chemist with a really international reputation in Switzerland, *Christian Friedrich Schönbein* (1799–1868). He was born in Metzingen (Württemberg), he studied in Tübingen, London, and Paris, and became professor of chemistry and physics at the University of Basle in 1828 (chemistry only after 1852). His major achievements were the discovery of ozone (1834) and the nitration of cellulose (trinitrocellulose = gun-cotton, dinitrocellulose solutions = collodium). His international charisma is reflected also in his correspondences with *Jöns Jakob Berzelius*, *Michael Faraday*, and *Justus von Liebig* (all published, in part reprinted as late as 1970!, see also his biography in *Bugge*'s book [1]).

Who knows, if there had been other leading personalities like *Schönbein* later in Switzerland, whether a development that started in 1859 might not have happened? This development influenced the course of chemistry in Switzerland in an extremely favorable way which can be even marked with numbers!¹)

What was that event in 1859? In that year, *Alexander Clavel*, owner of a silk dyeing mill in Basle, started to produce 'fuchsine'. Professor *Emanuel Verguin* discovered that red dye in Lyon and gave the patent rights to the dye mill *Renard Frères et Franc* in Lyon. This company obtained a French patent in April 1859. The company owner, *Joseph Renard*, was married to a stepdaughter of *Alexander Clavel* and, therefore, *Clavel* heard about 'fuchsine'. As there was no patent law in Switzerland at that time, it was legal to produce 'fuchsine' in Basle, as long as it was not exported to France.

---

¹) Per capita, Switzerland belongs to the leading countries in chemical science (number of *Nobel Prizes* to chemists working in Switzerland) and in industrial chemistry (export of chemical products).

Three years later, *Jean* and *Armand Gerber*, two chemists in Mulhouse, discovered another synthesis for 'fuchsine', and the dye was produced in the silk dyeing mill of *Monnet et Dury* in Lyon, until *Renard Frères et Franc* filed an appeal against *Monnet et Dury*. That mill had to stop production. The two *Gerber*s, however, emigrated in 1864 to Basle and started to produce 'fuchsine' at the Klybeckstrasse. Their plant, that of *Clavel* and the firm *Bindschedler* and *Busch* subsequently became the nucleus of the *Gesellschaft für Chemische Industrie in Basel* (*Ciba*). No less than three other Alsacian chemists, *Jean Caspar Dollfus*, *Louis Durand*, and *Edouard Durand*, came at about the same time (1860) to Basle and founded the dye-manufacturing company *Durand-Huguenin* (later part of *Sandoz*). Last, but not least, the firm of *Johann Rudolf Geigy*, founded in 1758 as importer of exotic extracts and spices, also started to produce dyes in 1862, and in 1991, *Ciba-Geigy* was the manufacturer with the highest production of colorants (on a value basis) in the world! Dyestuff production was also the starting point for the other areas of the Swiss chemical industry, areas which are today larger and more profitable than dyes²).

In conclusion, the very successful development of the Swiss chemical industry was due to the nonexistence of Swiss patent law! Even in 1881, the *Bindschedler* and *Busch* company petitioned the Federal government on behalf of the chemical industry not to introduce a patent law. The latter was implemented only in 1907 under pressure from Germany, who refused in 1904 to sign a commercial treaty with Switzerland as long as this country had no extensive patent legislation. Today, the situation has changed completely, as the Swiss chemical industry fights for longer and tougher protection by patents. *Tempora mutantur, nos et mutamur in illis!*

It is, however, not only the development of the chemical industry which owes its prosperity to those early dye pioneers, but also academic chemistry. The existence of a flourishing chemical industry convinced many gifted young people to study chemistry. In the 19th century and up to the 1930's, it was first of all the *Swiss Federal Institute of Technology* in Zurich (*ETH*) which profited from that development, but later also the Swiss universities and the Swiss Federal Institute of Technology in Lausanne (until 1969 part of the University of Lausanne). For chemistry, open and mutual relations between industry and academia are, in our opinion, a definite advantage for both sides. We will return to this question in the context of specific items related to the papers published in *HCA*.

A last point to the time *before* 1917: which famous investigations made in Switzerland would (or could) have been published in *HCA*, if that journal had existed earlier? That question can be asked, of course, for all branches of chemistry, but we will mention here only one specific paper and a debate of two authors. Both are highly relevant for color chemistry.

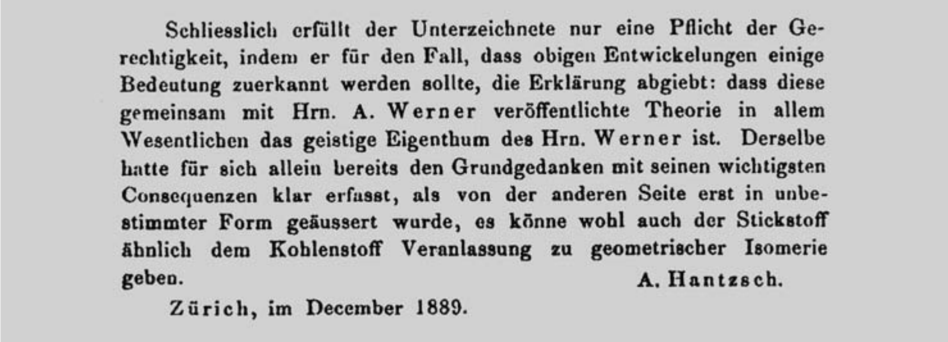
The specific paper is *Traugott Sandmeyer*'s communication to the *Berichte der Deutschen Chemischen Gesellschaft* in 1884, in which he describes the reaction of arenediazonium salts with halogenide and related ions in the presence of cuprous salts, forming the respective halogenoarenes, *i.e.* the *Sandmeyer* reaction [3]. His discovery was not only remarkable because of its utility in the synthesis of many halogenated benzene derivatives and substituted benzonitriles, but also because *Sandmeyer* was an autodidact. He received

---

²) For a comprehensive and unbiased history of the origins of the synthetic dyestuffs industry in Western Europe, see the new book of *Travis* [2].

his knowledge in chemistry by virtue of being a laboratory assistant to Professor *Victor Meyer* and later to Professor *Arthur Hantzsch* at ETH-Zurich (1882–1888). There, he developed 'his' reaction. In 1888, he obtained a job as research chemist for the *J. R. Geigy* company in Basle, where he finally became a member of the board. Therefore, the reader of this paper will agree with the opinion that it is a pity that *HCA* did not exist in 1884!

The debate that will now be discussed briefly, is something, however, which gave a considerable amount of work and some headache to the Editor of *HCA* at the turn of the century! At a time when typewriters were hardly commodities, when mail was slow (probably as B-mail in Switzerland today), and when telefax was an unknown word, two authors were able to write and publish in one year (1894), in the same journal, 17 papers between them in a ping-pong like back and forth exchange of arguments – without co-authors! That was the first year of *Hantzsch*'s and *Bamberger*'s debate on the structure of the two isomeric arenediazoates[3]), called *syn*- and *anti*-diazotates by *Hantzsch*, *normal* and *iso* by *Bamberger*. The subject is closely related to Switzerland, to Zurich in particular. *Hantzsch* was Professor at ETH-Zurich from 1885 to 1893, and during that time he, an organic chemist, had a fruitful cooperation with his colleague in inorganic chemistry at the University of Zurich, *Alfred Werner*[4]). Their joint paper published in 1890 [5] demonstrates that the genius of *Werner* went beyond the stereochemistry of metal complexes and also included stereochemical problems in organic chemistry. *Hantzsch* and *Werner* recognized the two known forms of aromatic oximes (Ar–CH=NOH) as stereoisomers. That paper is, apart from that result, extraordinary for several reasons: the foresight of the authors demonstrated great presentiment of discoveries based on their postulate that double-bonded nitrogen compounds (R–N=X, X = N, C, *etc.*) should exist in (*Z*)/(*E*)-pairs, discoveries which were made experimentally in part only decades later (*e.g.* (*Z*)- and (*E*)-azobenzene in 1937). That paper is also a fine example of the successful cooperation between an inorganic chemist, who was the pioneer in the stereochemistry of coordination compounds, and an organic chemist, who used physicochemical methods at a time, when this was not at all done in organic chemistry. Finally, that communication of *Hantzsch* and *Werner* is remarkable because of the short postscriptum



Schliesslich erfüllt der Unterzeichnete nur eine Pflicht der Gerechtigkeit, indem er für den Fall, dass obigen Entwickelungen einige Bedeutung zuerkannt werden sollte, die Erklärung abgiebt: dass diese gemeinsam mit Hrn. A. Werner veröffentlichte Theorie in allem Wesentlichen das geistige Eigenthum des Hrn. Werner ist. Derselbe hatte für sich allein bereits den Grundgedanken mit seinen wichtigsten Consequenzen klar erfasst, als von der anderen Seite erst in unbestimmter Form geäussert wurde, es könne wohl auch der Stickstoff ähnlich dem Kohlenstoff Veranlassung zu geometrischer Isomerie geben.

A. Hantzsch.

Zürich, im December 1889.

Fig. 1

---

[3]) Compounds of the type $Ar-N_2O^-$ were originally called diazotates, in IUPAC nomenclature they became diazoates in 1979.

[4]) See *Venanzi*'s contribution [4] to this series of papers.

of *Hantzsch* (*Fig. 1*). These sentences show a characteristic of *Hantzsch* that is clearly different from his aggressive (but still objective) style in scientific disputes.

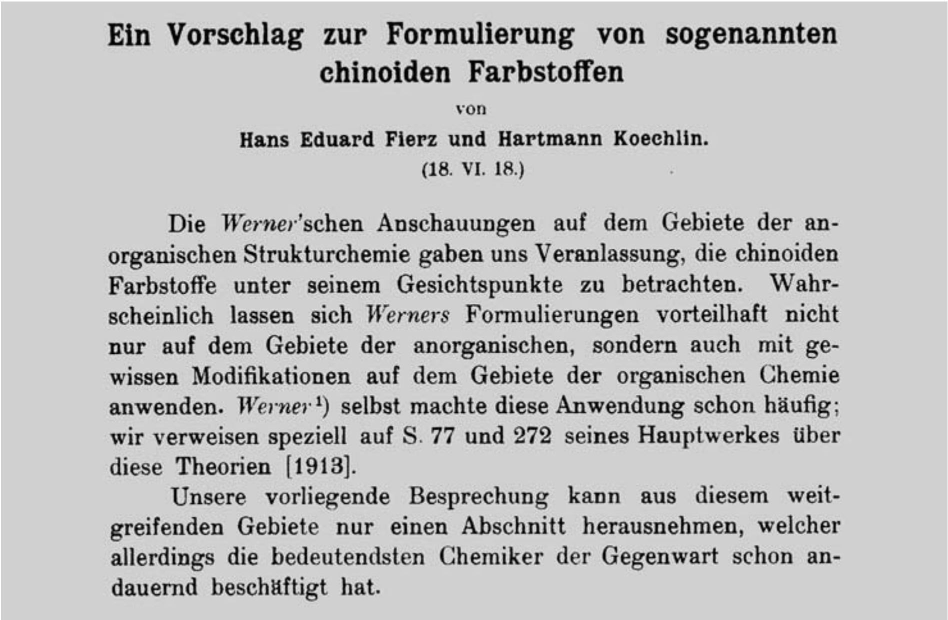
For that postscriptum only, it is a pity that *HCA* did not exist in 1890!

Since the diazoates can be considered to be derived from the oximes by substitution of nitrogen for the methine group, *Hantzsch* [6] put forward the hypothesis that stereoisomerism was also occurring here, just as in the oximes, hydrazones, and 1,2-substituted ethenes. *Bamberger* considered the two forms of diazoates as structural isomers, being present at the level of the addition product of a diazonium ion with the hydroxyl ion, for which *Bamberger* postulated the two isomers to be, in present nomenclature, the (*E*)-arenediazo-hydroxide $(\mathrm{Ar{-}N{=}N{-}OH})$ and the *N*-nitrosamine  $\left(\mathrm{Ar{-}N}\begin{smallmatrix}\mathrm{N{=}O}\\ \mathrm{H}\end{smallmatrix}\right)$ [7].

We will not follow the debate between *Hantzsch* and *Bamberger* further, because it is not the proper purpose of this paper, except for the fact that at least *Bamberger*'s following 26 papers on this subject could have been published in a Swiss chemical journal, because he received *Hantzsch*'s professorship at ETH-Zurich in 1893, when *Hantzsch* moved to the University of Würzburg. It is a strange coincidence that *Hantzsch* also published another 26 papers on this subject! The debate came to an end in 1912, when *Bamberger* [8] abandoned his negative attitude towards the stereoisomerism of diazoates.

We conclude the present discussion on the 'prehistoric' time of *HCA* with the remark that the *Hantzsch-Bamberger* debate ended with *Hantzsch*'s victory, because be used the methods of physical chemistry mentioned before at a time, when that was most unusual in the organic field; in other words, he was a 'prehistoric' physical organic chemist. We will refer to other pioneering work of *Hantzsch* later in this paper.

Fig. 2



Ein Vorschlag zur Formulierung von sogenannten chinoiden Farbstoffen

von

Hans Eduard Fierz und Hartmann Koechlin.

(18. VI. 18.)

Die *Werner*'schen Anschauungen auf dem Gebiete der anorganischen Strukturchemie gaben uns Veranlassung, die chinoiden Farbstoffe unter seinem Gesichtspunkte zu betrachten. Wahrscheinlich lassen sich *Werners* Formulierungen vorteilhaft nicht nur auf dem Gebiete der anorganischen, sondern auch mit gewissen Modifikationen auf dem Gebiete der organischen Chemie anwenden. *Werner* 1) selbst machte diese Anwendung schon häufig; wir verweisen speziell auf S. 77 und 272 seines Hauptwerkes über diese Theorien [1913].

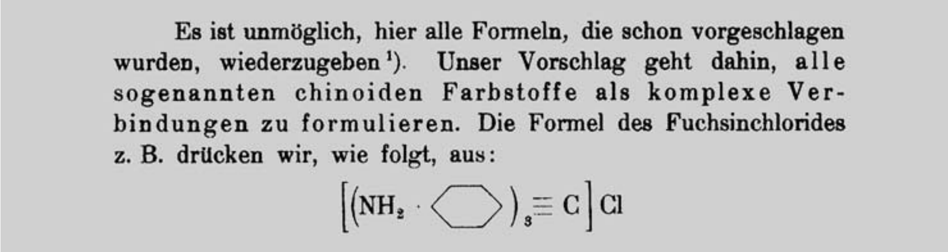
Unsere vorliegende Besprechung kann aus diesem weitgreifenden Gebiete nur einen Abschnitt herausnehmen, welcher allerdings die bedeutendsten Chemiker der Gegenwart schon andauernd beschäftigt hat.

We will start the discussion of papers related to color chemistry published in *HCA* with contributions to the most essential scientific problem of colored organic compounds: what are the underlying causes that dyes absorb visible light in contrast to the great majority of organic compounds? This question has been the subject of many papers since 1917. We will concentrate on general contributions to this problem.

Two papers published in the *Volume 1* are worth discussing here, namely those of *Fierz* and *Koechlin* [9] (*Fig. 2*) and *Kehrmann* and *Sandoz* [10].

Hans Eduard Fierz (1882–1953) was elected professor of organic technology at ETH-Zurich in 1917 after many years of industrial work in England and in Basle (*J. R. Geigy AG*). He became very well known for his books on dyes (see later in this review). ***Hartmann Koechlin*** was the first of his many graduate students at ETH. After graduation *Koechlin* worked for *J. R. Geigy AG* and finally became head of all technical operations at *Geigy*.

The first paragraph has already indicated that *Fierz* and *Koechlin*'s paper is based on *Werner*'s coordination chemistry. This becomes evident from the formula proposed for Fuchsine (*Fig. 3*).



Es ist unmöglich, hier alle Formeln, die schon vorgeschlagen wurden, wiederzugeben[1]. Unser Vorschlag geht dahin, alle sogenannten chinoiden Farbstoffe als komplexe Verbindungen zu formulieren. Die Formel des Fuchsinchlorides z. B. drücken wir, wie folgt, aus:

$$\left[\left(NH_2 \cdot ⬡\right)_3 \equiv C\right] Cl$$

Fig. 3

With reference to *Werner*'s evaluation of ammonium chloride, the authors write: '*Das Fuchsinchlorid ist ein Carboniumsalz und kein Salz des Ammoniaks*'. This statement seems to be a truism today, but it was not generally accepted in 1918, and even *Fierz* and *Koechlin* write later in the same paper that the occurrence of color in triphenylmethane dyes is *not* a consequence of ionization.

Before we follow that problem further, the first contribution of *Kehrmann*'s school at the University of Lausanne should be mentioned. ***Friedrich Kehrmann*** (1864–1929) studied chemistry in Germany. Later, he was an assistant of *Graebe* in Geneva and worked for some years in the German dyestuff industry before he obtained (1910) the chair in organic chemistry in Lausanne. His work was, at least in Switzerland, a pioneering advance in a new approach to color chemistry, namely measurements of visible absorption spectra of colorant solutions as a basis for structural investigations. The authors used a *Paaschen* spectrograph that contained, in addition to the light source, dye solution and collimating lens, a quartz prism in a black box with a photographic glass plate, calibrated with the help of the sodium line. An example of such a spectrum is given in *Fig. 4*.

Kehrmann and *Sandoz* also occasionally reported in this and in the following parts of the series on ultraviolet absorption spectra, but they did not clearly realize that for their

Fig. 4

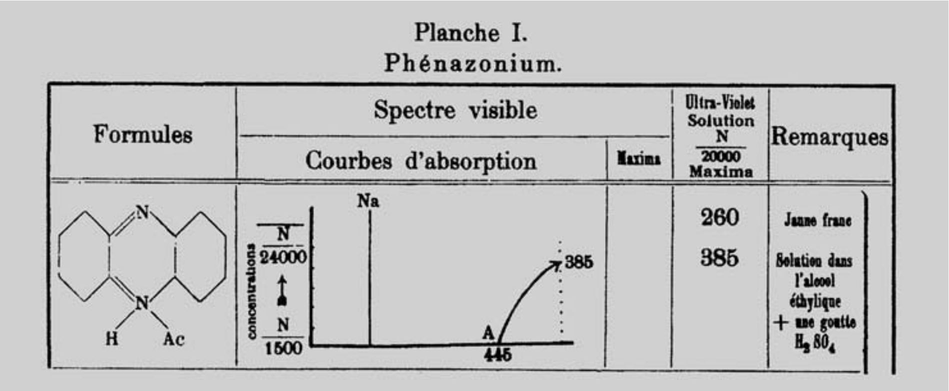


Planche I.
Phénazonium.

Formules	Spectre visible		Ultra-Violet Solution N/20000 Maxima	Remarques
	Courbes d'absorption	Maxima		
			260 385	Jaune franc Solution dans l'alcool éthylique + une goutte H_2SO_4

goal – the interpretation of chemical structures with the help of spectra – visible *and* ultraviolet spectra might both be useful. In this context, ***Jean Piccard***[5]) should be mentioned because of his work on 'second-order colors' [11]. As indicated in *Piccard*'s introductory paragraph, he found that, when the chain lengths of polymethine dyes was increased, one does not get only a bathochromic shift of colors from yellow to orange, red, blue, and green, but finally becomes yellow, because a second band moves from the ultraviolet into the visible spectrum[6]).

The formula in *Fig. 4* brings us back to the problem discussed by *Fierz* and *Koechlin*: *Kehrmann* and *Sandoz* write here the phenazonium salt as a covalent molecule with pentavalent N-atom (Ac does not stand for acetate, but the anion of *any* acid, here hydrogen sulfate). *Kehrmann* subsequently published four additional papers in *HCA* on his 'onium theories' of dyes. In the first [12], there is a non-specific critical remark on *Fierz* and *Koechlin*'s paper (*'les formules ... proposées par* H. Fierz *et* H. Koechlin, *en s'inspirant des idées de* Werner, *sont singulièrement impuissantes à décrire ... les phénomènes dont nous allons nous occuper'*). In the following communications, an ambiguous position on the application of *Werner*'s coordination chemistry can be recognized, *e.g.* in the second paper published in 1921 [13] (*Fig. 5*).

The word '*Haftstelle*' (sticking position) indicates in our opinion that *Kehrmann* dit not realize clearly *Werner*'s conclusion that in an ammonium salt the anion is not bound specifically to the N-atom. How emotional *Kehrmann* was, when he wrote that paper, is evident from two quotations: '*... die Formulierung der Onium-Körper der* Werner'*schen Theorie anzupassen,* [hat] *vielfach dazu geführt, das Kind mit dem Bade auszuschütten*' (p. 527); '*die* Werner'*schen Anschauungen ... zwing*[en] *uns aber keineswegs, ... eine Art Vogel-Strauss-Politik zu treiben ...*' (p. 536). In the following paper [14], no further reference is made to *Werner* and nitrogen compounds, and groups are again presented

---

[5]) *Jean Piccard* was the first student who received a Ph. D. in chemistry at ETH-Zurich (1909). Previously, theses written at ETH had to be submitted to the University of Zurich. *Piccard* was the twin brother of the physicist *Auguste Piccard*, who became well known for his balloon ascents to the stratosphere.

[6]) Actually, that second band is also present in dyes that are green: the perception of green in transmission and reflexion results from *two* absorption bands in the 400–450- and 600–700-nm ranges.

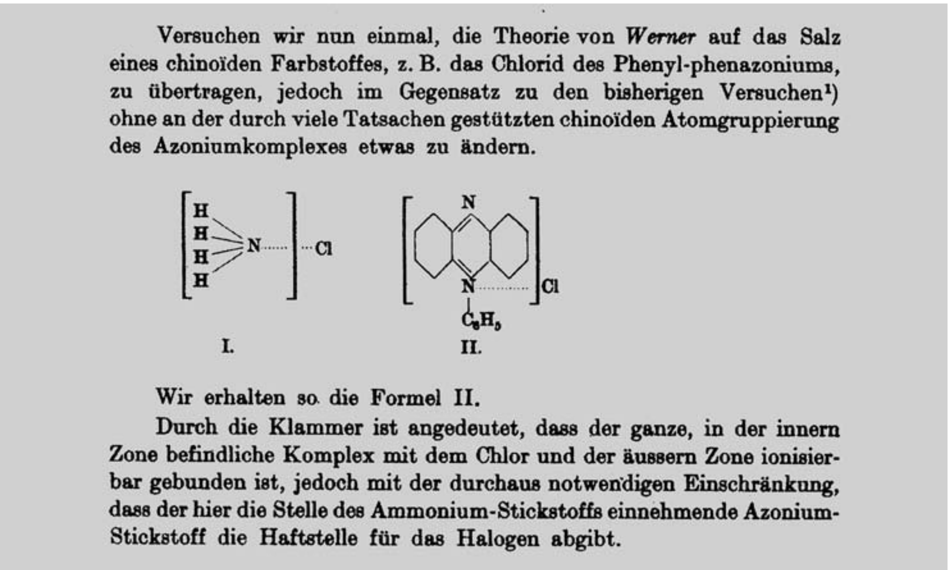


Fig. 5

Versuchen wir nun einmal, die Theorie von *Werner* auf das Salz eines chinoïden Farbstoffes, z. B. das Chlorid des Phenyl-phenazoniums, zu übertragen, jedoch im Gegensatz zu den bisherigen Versuchen[1]) ohne an der durch viele Tatsachen gestützten chinoïden Atomgruppierung des Azoniumkomplexes etwas zu ändern.

Wir erhalten so die Formel II.

Durch die Klammer ist angedeutet, dass der ganze, in der innern Zone befindliche Komplex mit dem Chlor und der äussern Zone ionisierbar gebunden ist, jedoch mit der durchaus notwendigen Einschränkung, dass der hier die Stelle des Ammonium-Stickstoffs einnehmende Azonium-Stickstoff die Haftstelle für das Halogen abgibt.

with pentavalent nitrogen, *e.g.* organic ammonium hydroxide groups $(-\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{N}}\equiv \mathrm{R}_3)$ and diazohydroxide groups $(-\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{N}}\equiv \mathrm{N})$.

Kehrmann's last paper on this subject was published under the title '*Nochmals zur Frage nach der Konstitution der chinoïden organischen Onium-Salze*' [15]. This paper contains the statement that his earlier formulation of triphenylmethyl salts (**I**) may be replaced by **II** (*Fig. 6*). He emphasizes, that the '*Säurerest*' (Ac, *i.e.* anion) is located in the 'outer sphere', but still in the '*Aktionsradius*' (range of action) of the C-atom labelled with X.

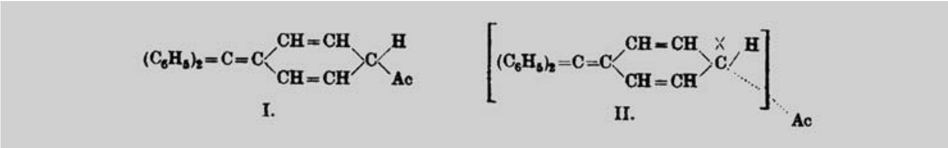


Fig. 6

This paper is very short (2½ pages), but it is obviously an answer to four papers of *Hantzsch* in *Berichte* [16] with a total of 57 pages! These papers are remarkable from two points of view. *Hantzsch* concentrated the major arguments on triphenylmethyl halogenides and triphenylcarbocation (his nomenclature: triphenylcarbonium) salts with halogenide anions. He discussed the corresponding compounds with substituents in the 4-position of the benzene rings (NH_2 *etc.*) only on the basis of the experimental results with the first mentioned compounds. Second, his arguments are based on experimental techniques of physical chemistry that were, in the early 1920's, still very rarely used in organic chemistry, namely spectral determinations of the equilibria, conductivity measurements, and spectra of acid-base equilibrium forms. These methods were supplemented by chemical comparisons of isomers. His major conclusions (p. 2611) can be summarized in two sentences: Compounds of the type $(C_6H_5)_3CHlg$ exist in two sharply separated (*'scharf gesonderte'*) groups, which changed mutually, but discontinuously, into one another. These are the colorless and non-conductive triphenylmethyl compounds $(C_6H_5)_3C{-}Hlg$ and the yellow and conductive triphenylcarbonium salts $(C_6H_5)_3C^+Hlg^-$ [7]).

Before we end the review on color-chemistry papers in the 1920's, we should mention that *Kehrmann*'s school also investigated syntheses of new colorants. In one of his early papers (on dyes based on 3,4-dihydroacridine), ***Henri Goldstein*** (1897–1987) was a co-author for the first time [17]. *Goldstein* became *Kehrmann*'s successor to the chair for organic chemistry in Lausanne in 1929 and was a frequent author of communications on the synthesis of di- and higher substituted benzene derivatives in *HCA* until 1958.

Gerold Schwarzenbach at the University of Zurich and ***Hans Kuhn*** at the University of Basle started significant and really pioneering work on correlations between color and chemical structure of colorants in the 1930's and 1940's, respectively.

Luigi Venanzi and the present author arranged beforehand those parts of the broad spectrum of *Schwarzenbach*'s research activities that should be reviewed in the paper on coordination chemistry [4] or in this contribution. Here, some of *Schwarzenbach*'s work which had an impact on color chemistry and on general organic chemistry will be discussed. As already mentioned by *Venanzi* [4], *Schwarzenbach* liked to call his contributions to analytical chemistry of transition-metal ions *'messende Komplexchemie'*. This anchoring of his scientific conclusions in (quantitative) measurements is the red thread in *all* his work[8]).

In the first of a series of papers with the general title *'Molekulare Resonanzsysteme'* [18], he states in 1937 that in his previous work he realized that the dissociation constants of organic (*Brønsted*) acids often cannot be understood by an additive combination of electrostatic and electronic effects, but that groups like COOH have to be interpreted *'als Ganzes ..., als ein einheitliches Resonanzsystem'*. He makes reference to the scientists who developed the resonance concept (*Pauling*, *Arndt* and *Eistert*, *Robinson*; later he refers also to *Ingold* and *G. N. Lewis*), but he mentions thoughts, the importance of which were not yet realized clearly in 1937 (*e.g. Hückel*'s 1930 paper). After discussing simple inorganic anions (COO^-, NO_2^-, NO_3^-, *etc.*), he applies that basis to triphenylmethine dyes (then called triphenylmethane dyes). The paragraphs reproduced in *Fig. 7* refer to aurin and benzaurin.

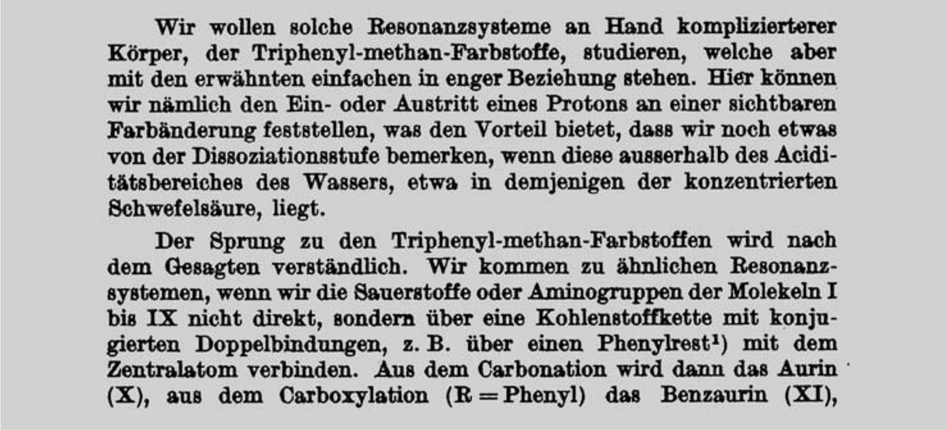
The pioneering character of these investigations also becomes evident from the reference to *Hammett*'s concept of acidity functions, when, in the second paper of the series [19], a pK_a value of -2 is reported for a diphenylamino-sulfophthalein. Today, more than half a century later, this figure does not affect chemists anymore, but in 1937 practically all Swiss chemists grew up with the idea that the pH scale is limited to the

---

[7]) For the sake of correctness, it should be mentioned that *Hantzsch* did not then write charges, but placed brackets around the cation *e.g.* $[C(Ar)_3]X$.

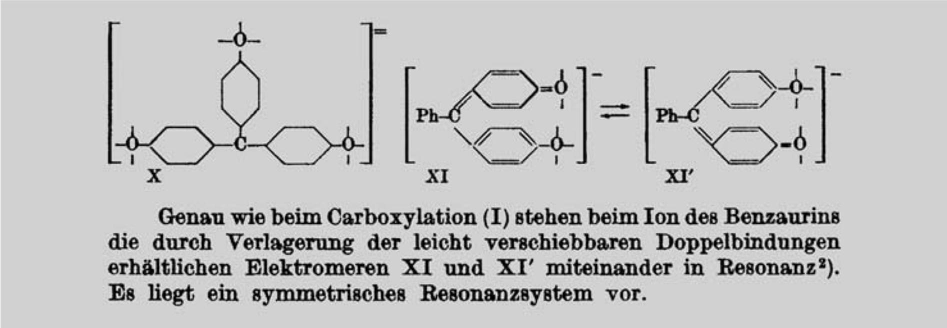
[8]) So far as the present author is aware, having checked *Schwarzenbach*'s work, this statement is not an exaggeration.

Fig. 7



Wir wollen solche Resonanzsysteme an Hand komplizierterer Körper, der Triphenyl-methan-Farbstoffe, studieren, welche aber mit den erwähnten einfachen in enger Beziehung stehen. Hier können wir nämlich den Ein- oder Austritt eines Protons an einer sichtbaren Farbänderung feststellen, was den Vorteil bietet, dass wir noch etwas von der Dissoziationsstufe bemerken, wenn diese ausserhalb des Aciditätsbereiches des Wassers, etwa in demjenigen der konzentrierten Schwefelsäure, liegt.

Der Sprung zu den Triphenyl-methan-Farbstoffen wird nach dem Gesagten verständlich. Wir kommen zu ähnlichen Resonanzsystemen, wenn wir die Sauerstoffe oder Aminogruppen der Molekeln I bis IX nicht direkt, sondern über eine Kohlenstoffkette mit konjugierten Doppelbindungen, z. B. über einen Phenylrest[1]) mit dem Zentralatom verbinden. Aus dem Carbonation wird dann das Aurin (X), aus dem Carboxylation (R = Phenyl) das Benzaurin (XI),



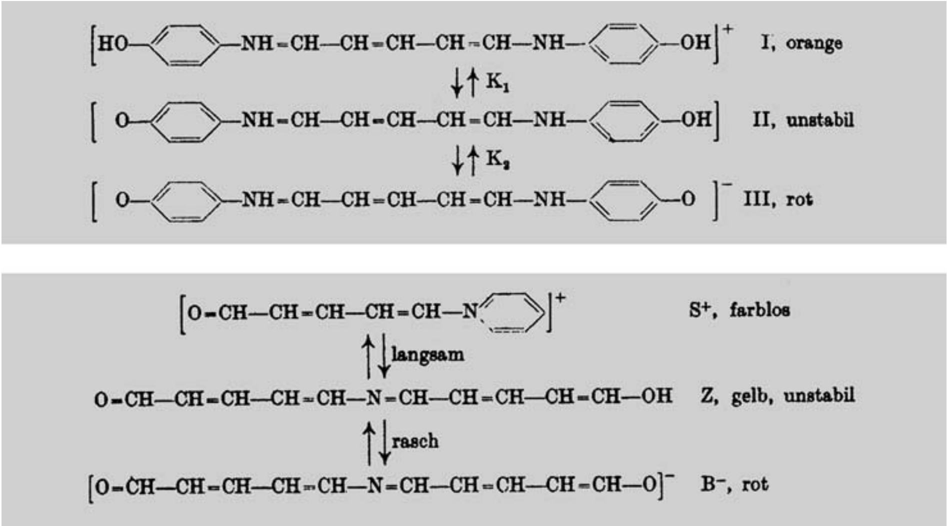
Genau wie beim Carboxylation (I) stehen beim Ion des Benzaurins die durch Verlagerung der leicht verschiebbaren Doppelbindungen erhältlichen Elektromeren XI und XI' miteinander in Resonanz[2]). Es liegt ein symmetrisches Resonanzsystem vor.

range of 0 to 14! *Schwarzenbach* not only used *Hammett*'s acidity scale for the superacidic range, but he also extended it to the superalkaline side (pH 14–19, corresponding to 1–20M NaOH in H_2O). Data on concentrated aqueous solutions of NaOH from this paper [20] are still widely used and cited. Although highly alkaline NaOH/H_2O and KOH/H_2O solutions and melts are often used in the technology of dye intermediates (*e.g.* hydroxy-dehalogenations) and of anthraquinone vat dyes, nobody (so far we are aware) investigated correlations of rates or product ratios of such reactions as a function of *Schwarzenbach*'s extended pH scale.

Another basically interesting and novel result of *Schwarzenbach*'s investigations on the influence of acidity on acid-base equilibria of indicators are the two papers in which the dibasic acids 5-pyridinium-glutacondialdehyde perchlorate [21] (first scheme in *Fig. 8*) and 4,4'-dihydroxy-dianil-glutacondialdehyde [22] (second scheme, in *Fig. 8*) were studied.

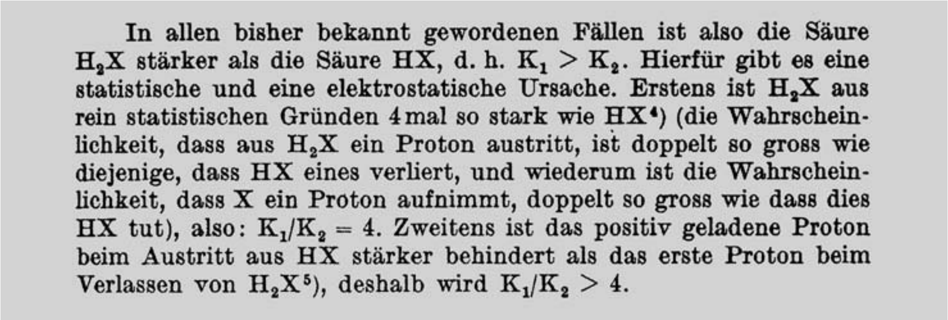
By addition of NaOH to the pyridinium ion S^+, the OH^- ions is added at one of the two CH groups in α,α'-positions, and the pyridine ring is opened in a relatively slow reaction. The OH group formed in that reactions (*Z*) is subject to rapid dissociation by a second equiv. of NaOH. This two-step reaction is the very first case of dibasic acids in which the acidity constant of the first step (K_1) is *smaller* than that of the second (K_2). In

Fig. 8



all the classical dibasic acids, the reverse inequality ($K_1 > K_2$) was found, *e.g.* in H_2SO_4, in oxalic acid, in resorcinol *etc.* The explanation for these cases was already known at the time of the publication of these two papers (1943). *Schwarzenbach* summarizes them as given in *Fig. 9*.

Fig. 9



In allen bisher bekannt gewordenen Fällen ist also die Säure H_2X stärker als die Säure HX, d. h. $K_1 > K_2$. Hierfür gibt es eine statistische und eine elektrostatische Ursache. Erstens ist H_2X aus rein statistischen Gründen 4mal so stark wie HX[4]) (die Wahrscheinlichkeit, dass aus H_2X ein Proton austritt, ist doppelt so gross wie diejenige, dass HX eines verliert, und wiederum ist die Wahrscheinlichkeit, dass X ein Proton aufnimmt, doppelt so gross wie dass dies HX tut), also: $K_1/K_2 = 4$. Zweitens ist das positiv geladene Proton beim Austritt aus HX stärker behindert als das erste Proton beim Verlassen von H_2X[5]), deshalb wird $K_1/K_2 > 4$.

Experimentally, the case of the pyridinium-ion indicator S^+ is characterized by a steeper curve, when the molar extinction coefficient ε is plotted against the logarithm of the OH^--ion activity. In *Fig. 10*, this is shown by curve *I*. Curve *II* corresponds to the change of spectrum observable for a monobasic acid[9]).

---

[9]) Unfortunately, *Schwarzenbach* did not include the curve for a 'normal' dibasic acid ($K_1 > K_2$), *e.g.* with $pK_1 = 12$ and $pK_2 = 14$. It has two steps. Such a curve was later published in *HCA* by *Wittwer* and *Zollinger* [23], p. 1956.

Fig. 10

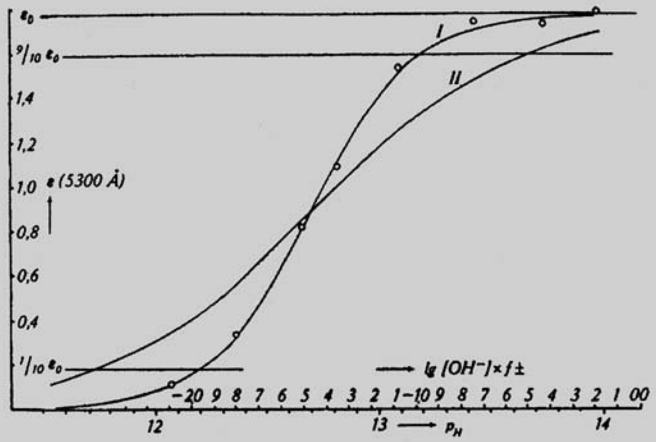


Fig. 1.

Messpunkte: Extinktionskoeff. des Pyridinium-glutacondialdehyd-perchlorates.

$$\left.\begin{array}{ll}\text{Kurve I:} & \dfrac{\varepsilon}{\varepsilon_0-\varepsilon}=\left(\dfrac{\mathrm{K}}{\mathrm{H}}\right)^2 \\ \text{Kurve II:} & \dfrac{\varepsilon}{\varepsilon_0-\varepsilon}=\dfrac{\mathrm{K}}{\mathrm{H}}\end{array}\right\}\begin{array}{l}\varepsilon_0 = 1{,}76 \\ \lg \mathrm{K} = -12{,}7\end{array}$$

The reason for the abnormal inequality $K_1 < K_2$ for the indicator S^+ is clear: the ring opening of a pyridinium ring by OH^- is definitely a slower reaction than the subsequent dissociation of the OH group formed in the first step. As soon as the OH group is formed, it will be dissociated with a second OH^- ion. *Schwarzenbach* writes, therefore, with spaced letters: 'Zwei Hydroxylionen in einem Schritt'. At that time (1943), this statement was acceptable, but since the work of *Eigen* in the late 1950's, we know that it is very unlikely that such reactions are really one-step processes. It is – surprisingly – not mentioned in that paper that the unusual two-step equilibrium of S^+ can be easily understood by considering the fact that in this two-step acid-base reaction step two different types of acids are involved: S^+ is a *Lewis* acid, Z is a *Brønsted* acid.

In the second paper [22], however, a dibasic acid with two *Brønsted* steps (*i.e.* two deprotonations) was found, contradicting the classical arguments for $K_1 > K_2$ mentioned above. *Schwarzenbach* explains this with the gain in resonance energy: the second deprotonation leads to a larger gain in resonance energy than the first.

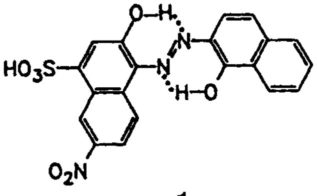
How important are dibasic acids characterized by the unusual inequality $K_1 < K_2$ and how often does this inequality occur? The fact that no data-base information was able to answer this question in 1992 indicates that such cases are relatively rare. We shall discuss later in this paper, however, one case which *is* important.

Before we come to some concluding remarks about *Schwarzenbach*'s impact on color chemistry in Switzerland, we briefly draw attention to his determinations of the equilibrium concentration of enols in simple ketones like acetone. One might ask if that question is relevant for color chemistry. It is, because a larger number of enolizable carbonyl compounds are important azo-coupling components for industrial dyes and pigments, *e.g.* aceto-acetanilides and 3-methyl-1-phenyl-5-pyrazolone derivatives. For many decades, it was discussed repeatedly whether it is the ketone or the enol that enters the coupling reaction with arenediazonium ion – until it finally became clear (in the 1950's) that it is the (*common*) conjugate base that reacts! *Schwarzenbach* worked analogously to *Hantzsch* who decided to investigate first *un*substituted triphenylmethyl halogenide to obtain basic information on the structure of more complex dyes of that type (see above). *Schwarzenbach* worked on the keto/enol equilibrium and the acidity constant of acetone. The knowledge gained from that simple ketone is relevant information for the understanding of the more complex enolizable ketones mentioned before for azo-dye chemistry in general. Finally, it was even found that azo coupling of acetone does take place – but this reaction was discovered only in 1960 [24].

Schwarzenbach and *Wittwer* [25] developed a self-made apparatus which may be called a precursor of the stop-flow equipment used today. This equipment was used for the determination of very small equilibrium concentrations of enols by bromination of the enol and kinetic determination of the free bromine with a Pt electrode[10]). The application of this apparatus for the determination of the enol content of aqueous acetone gave a figure of $2.5 \times 10^{-4}\%$, corresponding to an equilibrium value $pK_{enol} = \log [enol]/[keto] = 5.6$ [27]. This was the first determination of this equilibrium constant. It is, therefore, historically important, although it was later shown to be subject to systematic errors. Only in 1979 was a kinetic and a thermochemical method developed by *Guthrie* and *Cullimore* [28] that both gave practically the same result ($pK_{enol} = 7.0$ and 7.2, respectively) and which are, therefore, likely to be reliable.

What was the impact of *Schwarzenbach*'s work on industrial color chemistry and on general chemistry (general chemistry in the sense of the classic book of *Linus Pauling*) in Switzerland?

It took a very long time, until the Swiss chemical industry realized that *Schwarzenbach*'s work has importance for problems in industrial chemistry and its coloring matters' branch in particular, namely until the late 1940's, when some cooperation started with *J.R. Geigy AG*. The most important indicator for *Schwarzenbach*'s complexometric titrations of metal ions was *Eriochrome Black T* (see formula **1**). This dye was discovered in 1904 by *H. Hagenbach* in the *Geigy* laboratories and is today still one of the chromium mordant dyes for wool with the highest production volume in the world. Former graduate students worked at *Geigy*'s dyestuff research laboratories successfully since that time.



1

---

[10]) The idea of determining enol contents by halogenations goes back to an early paper of *Bartlett* [26].

Schetty (who was already mentioned in *Venanzi*'s review [4], p. 46, and who became well known by several papers on the stereochemistry of metal complexes of azo dyes published in *HCA* between 1952 and 1976) was, however, a graduate student of *Fichter* at the University of Basle. Nevertheless, even in academic circles, it was not realized for a considerable time that *Schwarzenbach* was indeed at the forefront of scientific findings and ideas in many fields of general chemistry – perhaps, often so far ahead that others were unable to follow him! It is, therefore, not surprising that this situation influenced his psychic reactions, *e.g.* when he mentioned that he had to become a full professor at the University of Zurich (1947), before he received a key to the main door of the chemistry building! As soon as he gained confidence in somebody, he became friendly and very relaxed. Therefore, he deserves to have some pages describing his historical achievements.

About a decade after *Schwarzenbach* started his series '*Resonanzsysteme*', ***Hans Kuhn***, a young 'Privatdozent' in the Department of Physical Chemistry at the University of Basle, began to investigate spectra of colorants with the help of what was later called the free-electron model. In the introduction to his first communication [29], he mentions classical molecular orbital investigators (*Hückel*, *Mulliken*, *Coulson*, *etc.*) who calculated the absorption of polyenes, but their results were not in satisfactory agreement with experimental data. '*Es fehlte daher bisher ein befriedigender Weg zur quantitativen Deutung der Absorption organischer Farbstoffe.*' For his approach, *Kuhn* used a model that corresponds basically to that developed by *Sommerfeld* for the electrons in solid metals, the '*Elektronengasmodell*' (in English called the free-electron model).

Within this model, the wave functions of the molecular π electrons are treated as waves in a 'box', whose size corresponds to the shape of the dye particle (molecule or ion). In the simplest case, one examines the energies of an electron in a one-dimensional box, corresponding in its length roughly, for example, to an (all-*trans*)-polymethine chain. Stationary states are then characterized by standing waves, the length of the box (L) in which the electron moves being equivalent to an integral multiple ($n = 1, 2, 3 \ldots$) of the half wavelength λ ($L = \lambda/2$). The energy levels ε_n corresponding to these waves are occupied from $n = 1$ onwards with 2π electrons each and correspond to molecular orbitals. The energy difference ΔE between the highest occupied orbital E_{HOMO} (HOMO = highest occupied MO) and the next highest, *i.e.* the lowest unoccupied orbital E_{LUMO}[11]), yields the $\pi \rightarrow \pi^*$ transition energy in terms of the physical constants h and m (mass of the electron) and the length (L) of the system of conjugated double bonds of the polymethine dye (*Eqn. 1*). Use of the *Einstein-Bohr* frequency condition yields the frequency of the absorption band or its wavelength.

$$\Delta E = E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}} = \frac{h^2}{8\,mL^2}\,(n^2_{\mathrm{HOMO}} - n^2_{\mathrm{LUMO}}) \qquad (1)$$

Fig. 11, showing a symmetric cyanine dye, is a typical example of *Kuhn*'s gift of representation. Shortly after that figure, he mentions also the essence of all work on electronic spectra in a spaced sentence (in most color/constitution investigations, this basic principle was neglected) (*Fig. 12*).

---

[11]) The acronyms HOMO and LUMO were proposed by *Fukui* in his frontier orbital method (for a review, see [30]).

Fig. 11

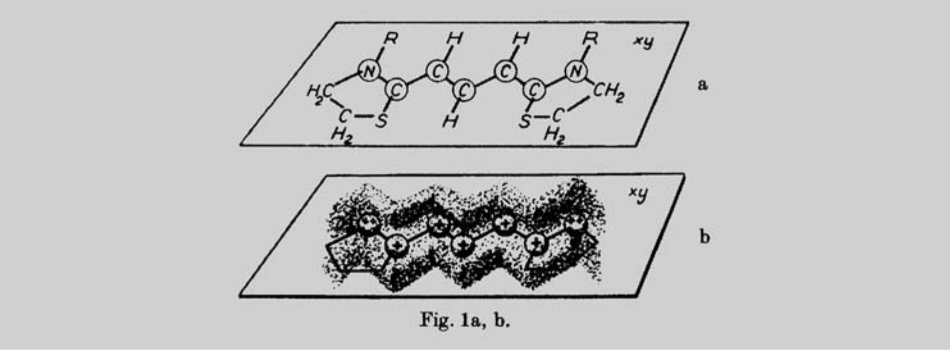
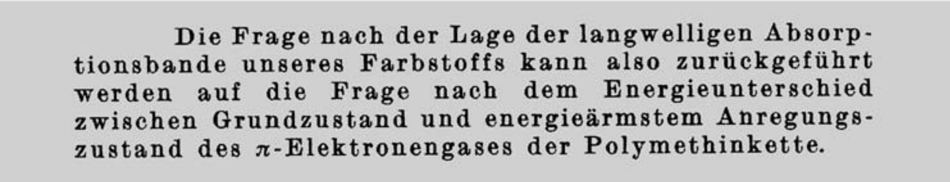


Fig. 1a, b.

Fig. 12

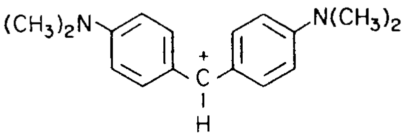


Die Frage nach der Lage der langwelligen Absorptionsbande unseres Farbstoffs kann also zurückgeführt werden auf die Frage nach dem Energieunterschied zwischen Grundzustand und energieärmstem Anregungszustand des π-Elektronengases der Polymethinkette.

The results of *Kuhn*'s method were indeed quite remarkable. For example, for the cyanine dye shown in *Fig. 11*, the absorption maximum was calculated to be at 453 nm, a result that compares well with the experimental value (445 nm). This is also the case for the whole series of cyanine dyes with 1, 3, 5, 7, 9, and 11 methine groups. Soon afterwards, *Kuhn* expanded his model by including branched electron systems (*verzweigtes Elektronengas*), calculation of extinction coefficients (a subject that was previously, but also later, badly neglected), and the replacement of methine groups by heteroatoms [31]. Later investigations of *Kuhn* were published in other journals, because he accepted the offer of a chair at the University of Marburg in 1953, where he developed a large analog computer for calculations of more complex systems.

As discussed later in this review, the free-electron model was superceded in the 1960's by various other methods which became more applicable, when more sophisticated computing opportunities were available. The vividness of the free-electron model is still unsurpassed, however, in teaching colour/structure correlations for non-specialists (see *Försterling* and *Kuhn*'s textbook of physical chemistry for undergraduate students [32]). It is noteworthy also that the two physical chemists who discovered in 1966 the first dye lasers, *P.P. Sorokin* (*IBM Research Laboratory*, Yorktown Heights, USA) and *F.P. Schäfer* (University of Marburg), both said that the idea of constructing a tunable laser with the help of organic dyes was based on their knowledge of the free-electron model of *Hans Kuhn* (see, *e.g. Schäfer* [33]). *Sorokin*'s and *Schäfer*'s invention initiated intensive research work on dyes which are suitable for these lasers, but unfortunately this and most other fields of the so-called functional dyes (= dyes for other purposes than dyeing) are still neglected in Switzerland's dye industry. A noteable exception will be discussed later.

Coming back to *Kuhn*'s original work at the time he was still in Basle, a by-product (in an almost literal sense) of his work arose there, because he had to measure many spectra of very old and outdated industrial dyes for which no reliable spectral information was available from the scientific or technical literature. The director of dyestuff research at *Ciba*, *Richard Tobler*, offered to have these dyes synthesized and purified. This task was given to the present author, then working in *Tobler*'s department. At that time, my main responsibility was to investigate whether pretreatments of the then new polyacrylonitrile fiber *Orlon* could increase its insufficient dyeability. Among the dyes to be synthesized for *Kuhn* was *Michler*'s hydrol (**2**), a blue salt, that was known since the 1880's, but not used as a dye for more than half a century.



2

It so happened that a chemist was treating *Orlon* fibers with metal salts and manufacturing pure *Michler*'s hydrol for a physical chemist at the same bench and at the same time. In other words, by coincidence he was working on two entirely different projects.

Why then should he not perform an experiment which the old Alchemists called a *mixtura mirabilis* (a wonderful mixture) in two entirely different fields of work? Why not put a few *Orlon* fibers into a test tube with a dilute solution of *Michler*'s hydrol? After holding it for five minutes over the gas burner, the *Orlon* turned blue, and the solution became colorless. All of the dye in the solution was adsorbed by the supposedly undyeable acrylic fiber.

Within no time, *Ciba* was able to introduce its first commercial dye for polyacrylonitrile fibers. It soon became clear that the affinity of *all* cationic dyes (which were not longer used in the 1950's for textile dyeings) was due to the presence of (anionic) sulfato groups in polyacrylontrile.

This discovery was, of course, a clear case of serendipity, but, even so, it may be said that quantum chemical work led also to a commercially interesting development – as the development of dye lasers mentioned before.

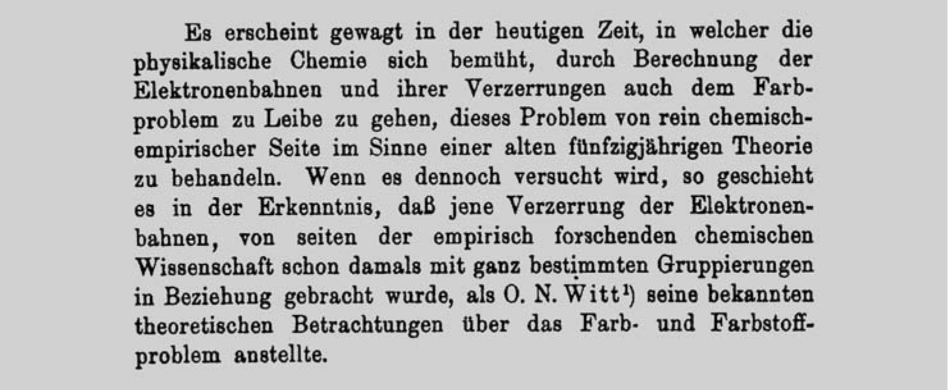
With the development of the hardware for digital computers, application of methods closer to *ab initio* for calculating the electronic spectra of organic compounds became realistic. An example is the paper of *Grinter* and *Heilbronner* [34], in which they showed that, by applying the molecules-in-molecules (MIM-MO) technique, one can correctly explain a classical problem.

The spectra of the three *o*-, *m*-, and *p*-isomers of nitrophenol, cyanophenol, and nitro-*N*,*N*-dimethylaniline, *i.e.* benzene derivatives with a donor and an acceptor substituent, cannot be understood on the basis of simple consideration of their mesomeric structures: the *o*- and *m*-compounds absorb very similarly over the whole range above 220 nm, whereas the absorption bands of the *p*-isomers are not only hypsochromically displaced but also quite different in type. *Grinter* and *Heilbronner* showed that the cause of these shifts to longer wavelengths lies in the fact that the energy of the excited state does not correspond to that which would be expected from a consideration of the usual mesomeric structures. *Grinter* and *Heilbronner*'s work also made it possible to understand the absorption of light by benzene derivatives substituted with an acceptor and two donor substituents, the so-called 'rule of the distribution of auxochromes', a phenomenon that is important for anthraquinone colorants and quinacridone pigments.

The MIM-MO method is, however, not the last word. The cases mentioned were later also evaluated by the *Pariser-Parr-Pople* (PPP-MO) method [35]. It is, at present, the most frequently used MO approximation for calculating electronic spectra of organic compounds. This development indicates that PPP-MO is not likely to be the last word either! It is definite, however, that qualitative hypotheses are now outdated.

One of their last proponents in Switzerland was ***Robert Wizinger*** (1896–1973), a graduate student of and later (1927–1938) a colleague of the coordination chemist *Pfeiffer*12) at the University of Bonn. There he developed, in part in cooperation with *Dilthey*, his '*Farbentheorie*'. In 1938, he came as a refugee to the University of Zurich, and he was elected as the first head of the Institut für Farbenchemie at the University in Basle in 1947 (see below). In his theory, *Wizinger* remained true to principles that *Dilthey* and he had already expressed in 1928 [36] (*Fig. 13*).

Fig. 13

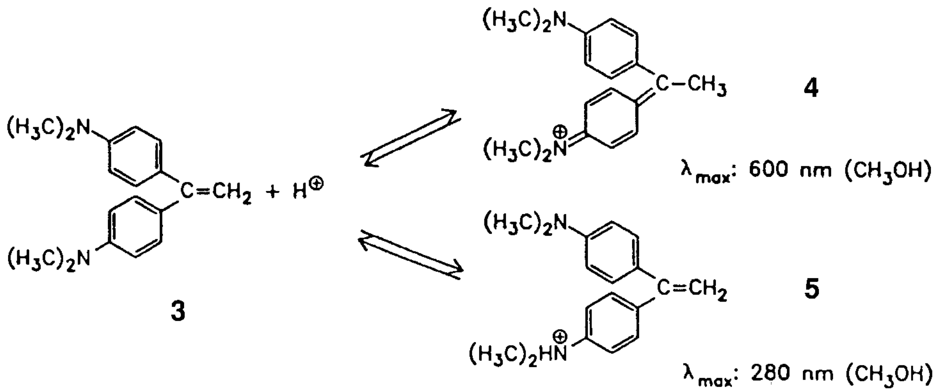

Es erscheint gewagt in der heutigen Zeit, in welcher die physikalische Chemie sich bemüht, durch Berechnung der Elektronenbahnen und ihrer Verzerrungen auch dem Farbproblem zu Leibe zu gehen, dieses Problem von rein chemisch-empirischer Seite im Sinne einer alten fünfzigjährigen Theorie zu behandeln. Wenn es dennoch versucht wird, so geschieht es in der Erkenntnis, daß jene Verzerrung der Elektronenbahnen, von seiten der empirisch forschenden chemischen Wissenschaft schon damals mit ganz bestimmten Gruppierungen in Beziehung gebracht wurde, als O. N. Witt1) seine bekannten theoretischen Betrachtungen über das Farb- und Farbstoffproblem anstellte.

Wizinger's lasting merit is the discovery of stable addition products of electrophilic reagents to 1,1-diphenylethene derivatives in which he (correctly) saw an analogy to what we now call σ-complexes or *Wheland* intermediates in electrophilic aromatic substitution. In 1928, *Pfeiffer* and *Wizinger* [37] reported that 1,1-bis(4-dimethylaminophenyl)ethene (**3**) becomes reddish-blue on acidification (*Scheme*). Although *Wizinger*'s conclusion that addition of H^+ (or E^+) takes place at C(2) is correct with regard to the colored product **4**, compound **3** adds protons dominantly or exclusively (in DMSO) at one of the N-atoms (**5**), as *Bernasconi et al.* [38] showed in 1973. *Wizinger* observed analogous color changes in bromination and in azo coupling of **3** [39].

---

12) *Paul Pfeiffer* (1875–1951) stayed at the University of Zurich from 1901 to 1916 as 'Privatdozent' and 'ausserordentlicher' Professor.

Scheme

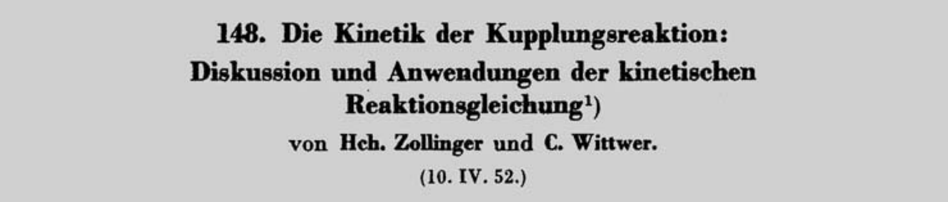


The work of *Wizinger* and *Cyriax* [39] brings us to the industrially most important class of colorants, the azo dyes and pigments. The chemist who worked most intensively in that field, seen with respect to publishing in the 75 years of *HCA*, was ***Paul Ruggli*** (1884–1945). *Ruggli* joined the Chemische Anstalt of the University of Basle in 1917 for instruction in the newly established laboratory for dyeing and printing (a gift of the *Sandoz* company). In 1922, he became 'ausserordentlicher' and in 1937 'ordentlicher' professor. Between 1929 and 1947, he was senior author of 61 papers in the series '*Mitteilungen über Azofarbstoffe und ihre Zwischenprodukte*' (in part published *posthum*). The papers deal with the synthesis and properties of aromatic azo dyes that cannot be obtained by straightforward azo-coupling reactions and with the constitution of intermediates. An important example is the elucidation of the NO_2-group position in the nitration of 1-diazo-2-naphthol-4-sulfonic acid, the diazo component for the dye *Eriochrom Black T* (**1**, see above). Following classical degradation techniques, it was found that nitration takes place at C(6), just 25 years after production of this dye started in the *Geigy* company [40]!

The present author hesitated to review his own work and thought originally that it might be included in *Heimgartner* and *Hansen*'s contribution on organic reaction mechanisms [41] in this series of papers. These authors suggested, however, to include the work on diazo compounds and on the azo-coupling mechanism in the present contribution. Indeed, it links the technology of azo dyes with the physical organic aspects of their formation.

Soon after starting work on azo dyes as an industrial chemist at the *Ciba Aktiengesellschaft* in Basle (1945), I realized the wealth of experience in azo chemistry, a wealth the basis of which had, however, been subjected to very little systematic investigation with respect to its scientific relevance. At the beginning, investigations were conducted on optimizing yields of azo-coupling reactions as a function of the acidity of the reaction medium. Kinetic measurements were, therefore, made as a function of pH. (Fortunately since *ca.* 1948, the first pH-meter was available in the laboratory of Dr. *R. Rometsch*, the physical chemist in the research department of the Pharma Division of *Ciba*!). The observed linear increase of the logarithm of the so-called stoichiometric rate constant (log k_s) *vs.* pH was easy to understand on the acidic side. The index s indicates that the rate constant refers to stoichiometric concentrations of the reagents. If equilibrium concentrations of the reactive components were used, however, the intrinsic rate constant k was found to be independent of pH [42] (*Fig. 14*).

Fig. 14



148. Die Kinetik der Kupplungsreaktion: Diskussion und Anwendungen der kinetischen Reaktionsgleichung[1])

von **Hch. Zollinger** und **C. Wittwer.**

(10. IV. 52.)

This result corroborated the conclusion that the arenediazonium ion reacted with phenoxide ions and with the base of amine-coupling components only, even at low pH values where only extremely small fractions of these equilibrium forms were present. Yet, when extending those measurements into the alkaline range (pH 12.0–13.2), a puzzling observation was made: the rate constant k_s did not decrease tenfold per pH unit, as expected on the basis of the equilibrium diazonium ion ⇄ diazohydroxide, but a hundredfold. Fortunately, these investigations were conducted with *C. Wittwer* of the analytical laboratory of *Ciba*. He was a former student of *Schwarzenbach* and, therefore, acquainted with *Schwarzenbach*'s work '*Zwei Protonen (Hydroxylionen) in einem Schritt*'. In analogy to that work, he concluded, therefore, that the equilibrium $ArN_2^+ \rightleftarrows (Z)\text{-}ArN_2OH \rightleftarrows (Z)\text{-}ArN_2O^-$ is another case showing the unusual inequality $K_1 < K_2$. As a consequence, we postulated [23] that the (Z)-diazo-hydroxide is not present in measurably large concentrations at any pH value – a conclusion that violated a number of *Hantzsch*'s arguments in the *Hantzsch-Bamberger* debate on the structure of diazoate (but *not* violating his main argument!). These investigations still fitted the basic hypothesis that azo-coupling rate constants k, but not k_s are pH-independent [23] (*Fig. 15*).

Fig. 15

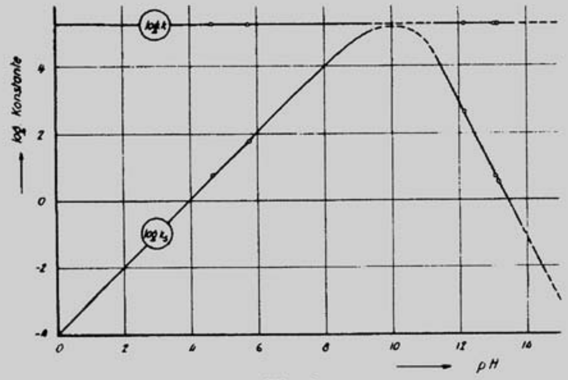


Fig. 3.
Geschwindigkeit der Kupplung von diazotierter Metanilsäure mit 2-Naphtol-6-sulfosäure (0°, $\mu = 0{,}73$).

Nevertheless, just a year later, that hypothesis seemed to lose its validity [43] (*Fig. 16*).

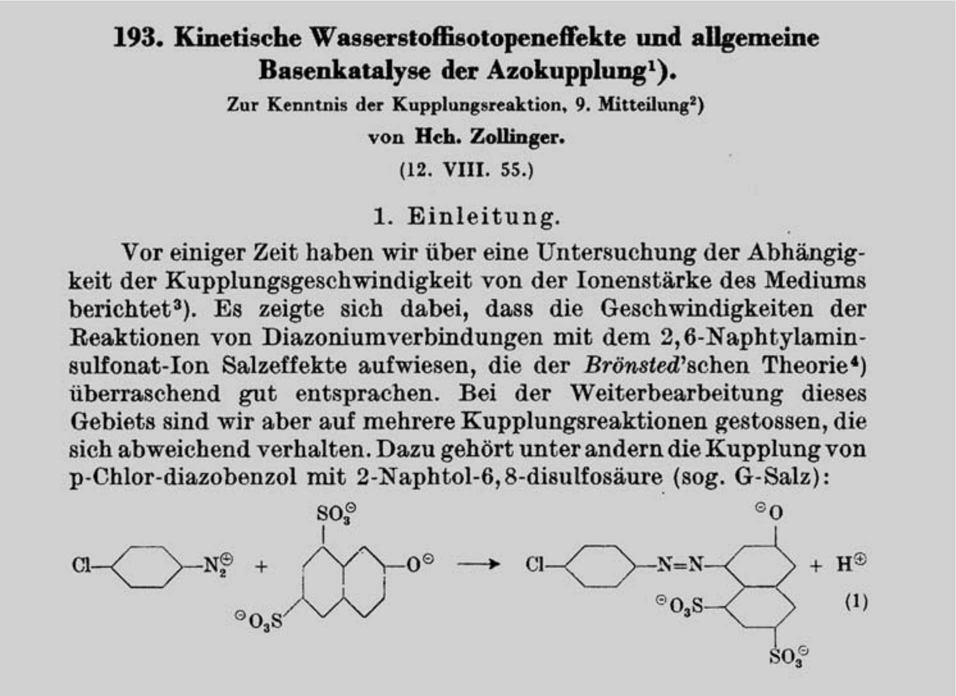


Fig. 16

193. Kinetische Wasserstoffisotopeneffekte und allgemeine Basenkatalyse der Azokupplung[1]).

Zur Kenntnis der Kupplungsreaktion, 9. Mitteilung[2])

von **Hch. Zollinger.**

(12. VIII. 55.)

1. Einleitung.

Vor einiger Zeit haben wir über eine Untersuchung der Abhängigkeit der Kupplungsgeschwindigkeit von der Ionenstärke des Mediums berichtet[3]). Es zeigte sich dabei, dass die Geschwindigkeiten der Reaktionen von Diazoniumverbindungen mit dem 2,6-Naphtylaminsulfonat-Ion Salzeffekte aufwiesen, die der *Brönsted*'schen Theorie[4]) überraschend gut entsprachen. Bei der Weiterbearbeitung dieses Gebiets sind wir aber auf mehrere Kupplungsreaktionen gestossen, die sich abweichend verhalten. Dazu gehört unter andern die Kupplung von p-Chlor-diazobenzol mit 2-Naphtol-6,8-disulfosäure (sog. G-Salz):

(1)

The evaluation showed, however, that the apparent violation of the hypothesis is not related to the pre-equilibria but to the substitution properties, because the release of the proton after the addition of the diazonium ion becomes part of the rate-determining process in some (by far not all!) coupling reactions (*Fig. 17*).

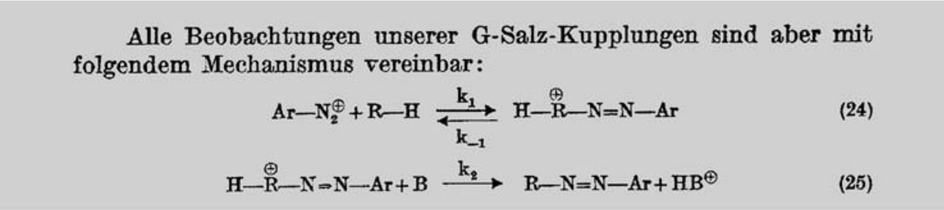
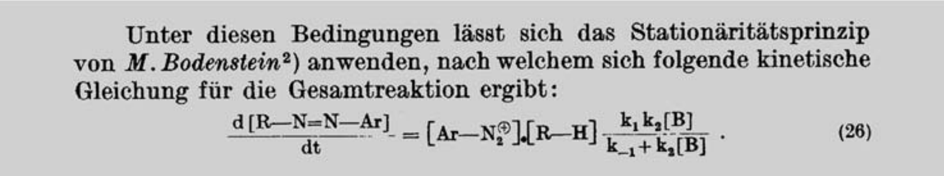


Fig. 17

Alle Beobachtungen unserer G-Salz-Kupplungen sind aber mit folgendem Mechanismus vereinbar:

$$\text{Ar—N}_2^{\oplus} + \text{R—H} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{H—}\overset{\oplus}{\text{R}}\text{—N=N—Ar} \qquad (24)$$

$$\text{H—}\overset{\oplus}{\text{R}}\text{—N=N—Ar} + \text{B} \xrightarrow{k_2} \text{R—N=N—Ar} + \text{HB}^{\oplus} \qquad (25)$$



Unter diesen Bedingungen lässt sich das Stationaritätsprinzip von *M. Bodenstein*[2]) anwenden, nach welchem sich folgende kinetische Gleichung für die Gesamtreaktion ergibt:

$$\frac{d[\text{R—N=N—Ar}]}{dt} = [\text{Ar—N}_2^{\oplus}]\cdot[\text{R—H}]\cdot\frac{k_1 k_2 [\text{B}]}{k_{-1} + k_2[\text{B}]}\,. \qquad (26)$$

The nonlinear rate dependence on the concentration of the proton acceptor [B] in Eqn. 26 was indeed verified and evaluated for a series of pyridine derivatives. The anticipated *Brønsted* relationship for general base catalysis is nicely followed.

In addition, a kinetic isotope effect was observed, if the coupling component was substituted by deuterium in the reacting position of the coupling component in those azo-coupling reactions that were characterized by general base catalysis, but not the others. The magnitude of the kinetic isotope effect k_H/k_D is dependent on the ratio $k_2[B]/k_{-1}$ (equation 26 slightly rearranged). The ratio k_2/k_{-1} is a function of steric crowding at the reacting position, as shown by the distance to the HSO_3 groups in the coupling component, as seen by the four hydroxynaphthalene-sulfonic acids in reactions with 4-chlorobenzenediazonium ions [43] [44] (*Fig. 18*).

Fig. 18

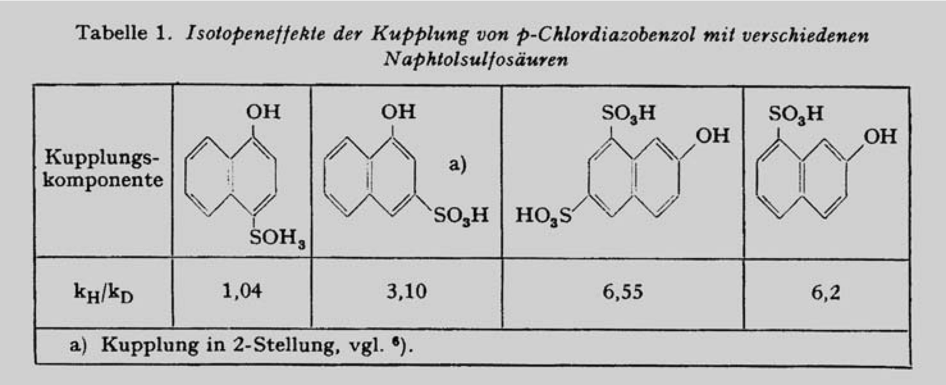


Tabelle 1. *Isotopeneffekte der Kupplung von p-Chlordiazobenzol mit verschiedenen Naphtolsulfosäuren*

Kupplungs-komponente	OH SOH$_3$	OH a) SO$_3$H	SO$_3$H OH HO$_3$S	SO$_3$H OH
k_H/k_D	1,04	3,10	6,55	6,2

a) Kupplung in 2-Stellung, vgl. [6]).

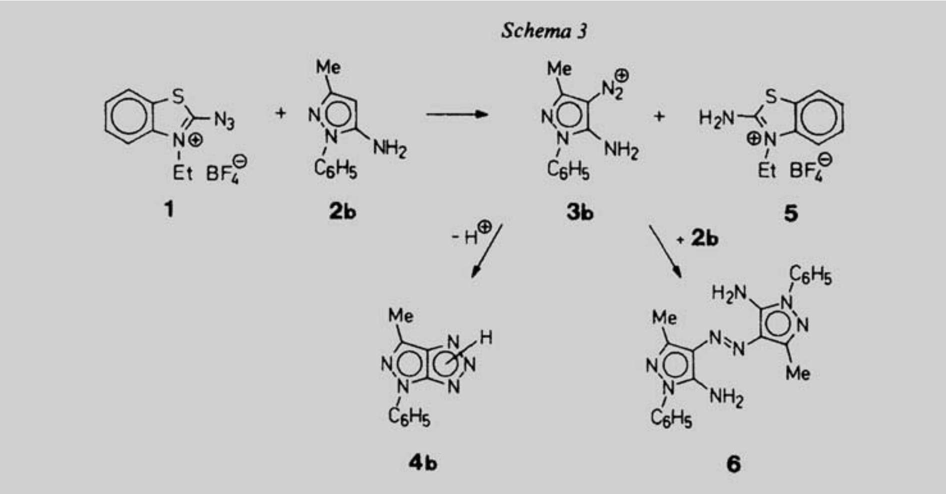
The result with 2-hydroxynaphthalene-8-sulfonic acid was reported only three years later based on a suggestion made at one of the (American) *Reaction Mechanisms Conferences* (Chicago, 1958). *P. D. Bartlett* said that the series of the three other reactions has only one minor blemish, namely that the number of HSO_3 groups is not the same. That remark resulted in the measurement of k_H/k_D for 2-hydroxynaphthalene-8-sulfonic acid. It would not be mentioned here, if this review had not been written for the 75th Anniversary of *HCA*: the corresponding paper [44] is publication No. 1 of a chemist who at that time was an ETH student. He spent a summer in Basle, during which time he made this measurement. Thirty three years later he became a *Nobel* Laureate – ***Richard Ernst***!

These investigations were accepted very well by the international guild of chemists. It is interesting, however, that frequently only the isotope effects were mentioned, but not the general base catalysis that is their cause. Notable exceptions are, at an early time, *Ingold*'s book, and recently, *Taylor*'s book on electrophilic aromatic substitution [4] [5]. *Ingold* and *Taylor* realized that the nonlinear rate dependence on base concentration [B] is the unambiguous evidence for the $A_E + D_E$ mechanism (old nomenclature: S_E2).

Work on the mechanism of azo-coupling reactions was also published by other authors in *HCA*. The groups of *Bourne* [46] and *Rys* investigated the seemingly inexplicable observation that, if solutions of arenediazonium ions and of 1-naphthol or of some of its sulfonic-acid derivatives are mixed in the stoichiometric ratio 1:1, one observes, in addition to the expected monoazo products coupled in 2- and 4-position, relatively large amounts of 2,4-diarylazo-1-naphthol. This effect was found to be caused by the very fast chemical reaction at the phase boundary which exists for fractions of a second (< 1 ms), when the two solutions are mixed.

The discussion of the azo-coupling reaction brings us to the diazo-transfer reaction with azidinium salts, a subject that ***Heinz Balli*** started to investigate, while he was still at the University of Marburg [47], and which he continued intensively after being elected as *Wizinger*'s successor as head of the Institut für Farbenchemie of the University of Basle in 1966. The well-known and often used synthesis of diazoalkanes by diazo transfer with tosyl azide has the disadvantage that, in the case of hydroxyarenes and heteroarenes, the cyclic quinone diazide reacts with the educt forming an azo compound. *Balli et al.* [48] showed that the more reactive azidinium salt 2-azido-3-ethylbenzothiazolium tetrafluoroborate (**1**, *Fig. 19*) gives higher yields, if an optimal acidity of the medium is selected. With aromatic and heteroaromatic amines the primary reaction products can be cyclized to a *v*-triazole, if the initial acid solution is buffered after 90 min with NaOH. If the ratio of reagents is 1:2, and the solution is not buffered, azo coupling takes place. In this way, the azidinium salt **1** yields, depending on conditions, 4-phenyl-6-methylpyrazolo[3,4-*d*]-[1,2,3]triazole (**4b**, 80% yield) or 5,5′-diamino-3,3′-dimethyl-1,1′-diphenyl-4,4′-azopyrazole (**6**).

Fig. 19

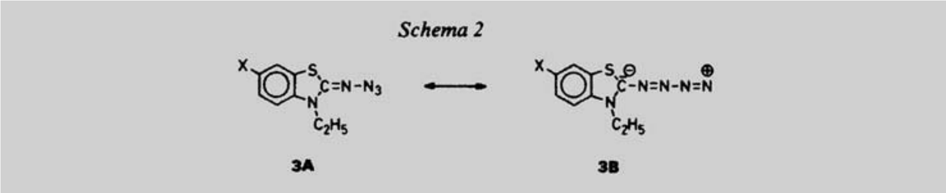


Azidinium salts can also be used for the synthesis of tetrazo compounds, which were previously unknown[13]). They are obtained by addition of azide ions to azidinium salts [49] under dediazoniation of 1 equiv. of N_2 (**5A**–**5B**, *Fig. 20*).

---

[13]) As suggested by *Balli*, compounds with two diazonio groups (${}^{+}N_2{-}X{-}N_2^{+}$) should be called bisdiazonium compounds; tetrazo compounds are characterized by the group $-N_2{-}N_2^{+}$.

Fig. 20

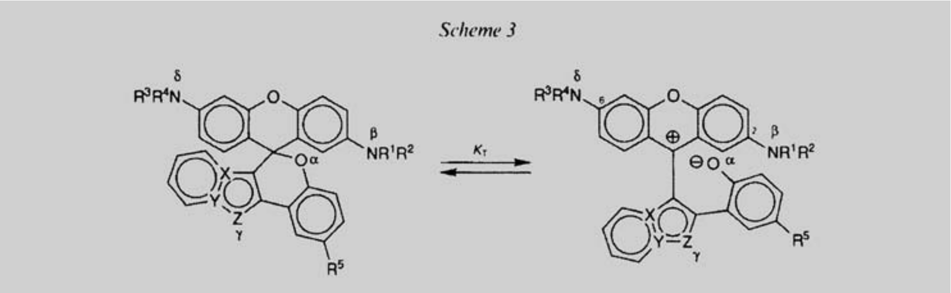

Schema 2

Tetrazo compounds are very interesting, as their thermolysis at 0° in DMFA or THF, by further dediazoniation of 2 equiv. of N_2, generates nucleophilic carbenes, whose trapping by electrophilic compounds, *e.g.* with the starting material (**3A**–**3B**) or with arenediazonium ions, provides evidence of their nucleophilicity [50].

In our opinion, such investigations are appropriate for an academic institution devoted to color chemistry, although 'classical' color chemists might say that they are not related to dyes in the industrial sense.

Balli's investigations, however, also include such work. This is demonstrated, for example, by his investigations on halochromic molecules, *i.e.* compounds that become colored on acidification. We refer to a series of 9 parts on such compounds published since 1979 and, in particular, to the investigation on the new chromogens of the type presented in a recent publication [51] (*Fig. 21*; X = N or C, Y = C or N, Z = CMe or N). These 6,11-dihydrospiro[benzopyrano[4,3-*b*]indole-6,9′-9′*H*-xanthene]-2′,6′-diamines and their aza analogues are new chromogens that are interesting for carbonless, pressure-sensitive copying systems, because the halochromic forms absorb light over the whole of the visible spectrum, *i.e.* they are black. The spectrum was interpreted successfully with the PPP-MO method.

Fig. 21


Scheme 3

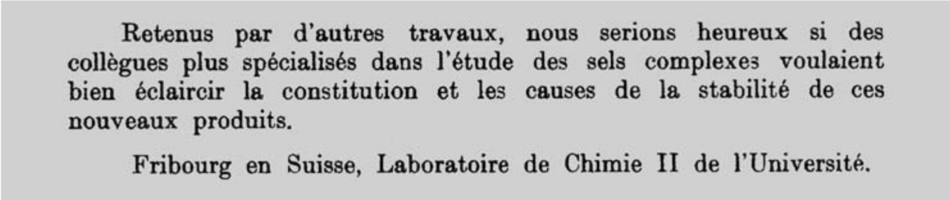
This paper of *Balli* has to be mentioned here for another reason, too: it is, in the present definition, an investigation on functional dyes. It is, therefore, one of the very few exceptions for the statement about the neglect of work on functional dyes in Switzerland. Therefore, we have to consider also to the industrial activity of *Ciba-Geigy* on dyes for carbonless copying systems.

Balli's new chromogen is unlikely to become important for large-scale colorant production because of its complex and expensive synthesis. Novel chromogens are, however, still sought after, industrially, but also for scientific reasons. Three very important classes of such compounds were either structurally identified or developed in Switzerland during the 75 years of *HCA* – each of them of world-wide importance in its field. This fact is remarkable, because in the same period less than three such types of structure were found in all the other parts of the world together!

The first class is that of azulene and its derivatives, the structure of which was elucidated by *Pfau* and *Plattner* in 1936 [52]. We classify azulene as the *scientifically* most interesting colored organic compound of this century (... extrapolating to 1999!) Azulene has already been discussed in the contribution of *Heimgartner* and *Hansen* [41].

The two other new classes of chromogens are the copper phthalocyanines and the pyrolo-pyrrole-diones. Both are industrially very important and scientifically interesting.

Copper phthalocyanine is the parent compound of the second class of novel chromogens. To say that it is the most important industrially *and* scientifically would not be an exaggeration. In 1927, ***Henri de Diesbach*** (1880–1970), professor of organic chemistry at the University of Fribourg (1920–1955), published a paper [53] with his coworker *von der Weid* in which they described an insoluble blue reaction product obtained in the thermolysis of 1,2-benzodinitrile in the presence of Cu^{II} salts. Elemental analysis of the product gave the correct result for the constitution of copper phthalocyanine, but they did not investigate its structure. At the end of their paper, they wrote the following sentence (*Fig. 22*).



Retenus par d'autres travaux, nous serions heureux si des collègues plus spécialisés dans l'étude des sels complexes voulaient bien éclaircir la constitution et les causes de la stabilité de ces nouveaux produits.

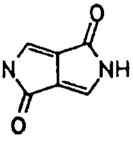
Fribourg en Suisse, Laboratoire de Chimie II de l'Université.

Fig. 22

Unfortunately, nobody had a presentiment for the treasure that could be found behind *de Diesbach* and *von der Weid*'s invitation to dig for it!

Independently and casually, *Dandridge*, *Dunworth*, *Drescher*, and *Thomas* of *Scottish Dyes Ltd.* (now part of *ICI*) in the 1930's constantly found blue residues in the iron vessel in which they prepared phthalimide from phthalic anhydride and ammonia. This powder was given to *Linstead* at the Imperial College of Science and Technology in London, who in 1933 determined its structure as iron(II) phthalocyanine [54]. He found that other transition metals including copper gave analogous complexes. *Robertson* confirmed the structure by means of X-rays at a time (1935), when this method was in its infancy [55]. For obvious reasons, *ICI* became the first manufacturer of copper-phthalocyanine pigments and, a short time later, derivatives of it were introduced as dyes.

The third new chromogen of industrial *and* scientific interest found in Switzerland is represented in the 3,3′-diaryl derivatives of pyrrolo[3,4-*c*]pyrrole-1,4-dione (**6**) which became very successful as the so-called DPP pigments. They are the result of an open-minded literature study made by the two *Ciba-Geigy* chemists *A. Iqbal* and *L. Cassar* in the early 1980's. From the point of view of the present review, their work has only one



6

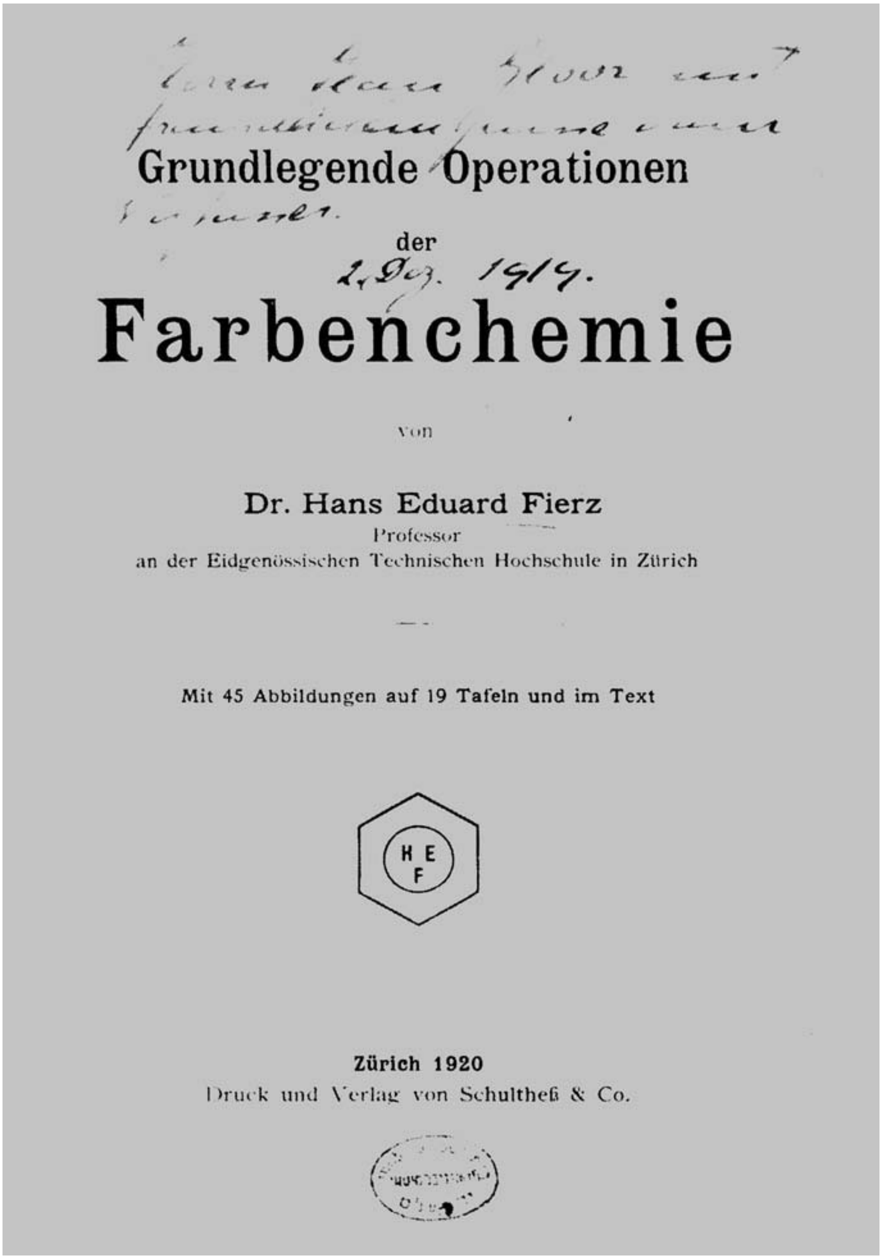
disadvantage: the results were published (in spite of the well-known reserve of the dyestuff industry), but *not* in HCA. Therefore, we should not report on the quite fascinating story of their work, but only provide the reference [56]!

These remarks bring us back to the interface of industrial and academic work on colorants. It was mentioned already that a major activity of *Fierz* were his books. After he moved from the *Geigy* company in Basle to ETH-Zurich (1917), he wrote his '*Grundlegende Operationen der Farbenchemie*' [57] published in eight German editions (1920–1952) and an English edition (1949). The book contains detailed and reliable descriptions of specific reactions used frequently for the synthesis of dyes and their intermediates. The book also contains remarks on plant equipment *etc*. The style of the book is comparable to the well-known series '*Organic Syntheses*' (published two decades later). The first edition is also historically interesting: *Fierz* wrote that book based on procedures used before 1917 by the *Geigy* company. This was, of course, illegal, but *Geigy* decided not to sue him, because he was at the ETH-Zurich in an important position to educate and interest students in dyestuff chemistry. *Fig. 23* shows the title page of the first edition of that book with the hand-written dedication of *Fierz* to *Jean Gloor*, who was the caretaker of the Department of Industrial Chemistry of ETH at that time.

Finally, two industrial color chemists will be mentioned, because they accomplished pioneering work in developing new dyes and in cultivating mutual interactions between the Swiss chemical industry and Swiss universities, including ETH. ***Gadient Engi*** (1881–1945) grew up in the Grisons, studied chemistry at ETH, and joined *Ciba* (then *Gesellschaft für Chemische Industrie* in Basel) in 1904. The turn of the century was the hey-day of vat dyes, when ***Karl Heumann*** (1850–1894, adjunct professor at ETH since 1874) developed the first industrially feasible synthesis of indigo, and when ***René Bohn*** (1862–1922), a former graduate student of *Heumann* at ETH discovered indanthrone, the first anthraquinone vat dye. In 1907, *Engi*'s bromination product of indigo, 5,5′,7,7′-tetrabromoindigo (*Ciba Blue 2B*) was manufactured for the first time. It was a success from the beginning, because this dye possesses clear advantages in application properties relative to indigo. *Ciba Blue 2B* is the only indigoid dye of a large group of indigo derivatives that is still produced today by what is now *Ciba-Geigy*. Indigo itself was almost given up worldwide thirty years ago, but it had its unexpected renaissance because its *low* abrasion fastness, a property that was, and still is, important for fashion reasons for dyeing denim cotton ('blue jeans')!

Engi finally became vice-president of the board of *Ciba* and was in charge of all technical matters, including research, for that enterprise. To start *HCA* in 1918, his capacity as Treasurer ('Schatzmeister') of the Swiss Chemical Society was important, as expressed in the following address ('... *your election as treasurer was the most fortunate and beneficial step ..., when the journal was started*') (*Fig. 24*).

Fig. 23



Herrn Jean Gloor zur
freundlichen Erinnerung [illegible]
[illegible].
2. Dez. 1919.

Grundlegende Operationen
der
Farbenchemie

von

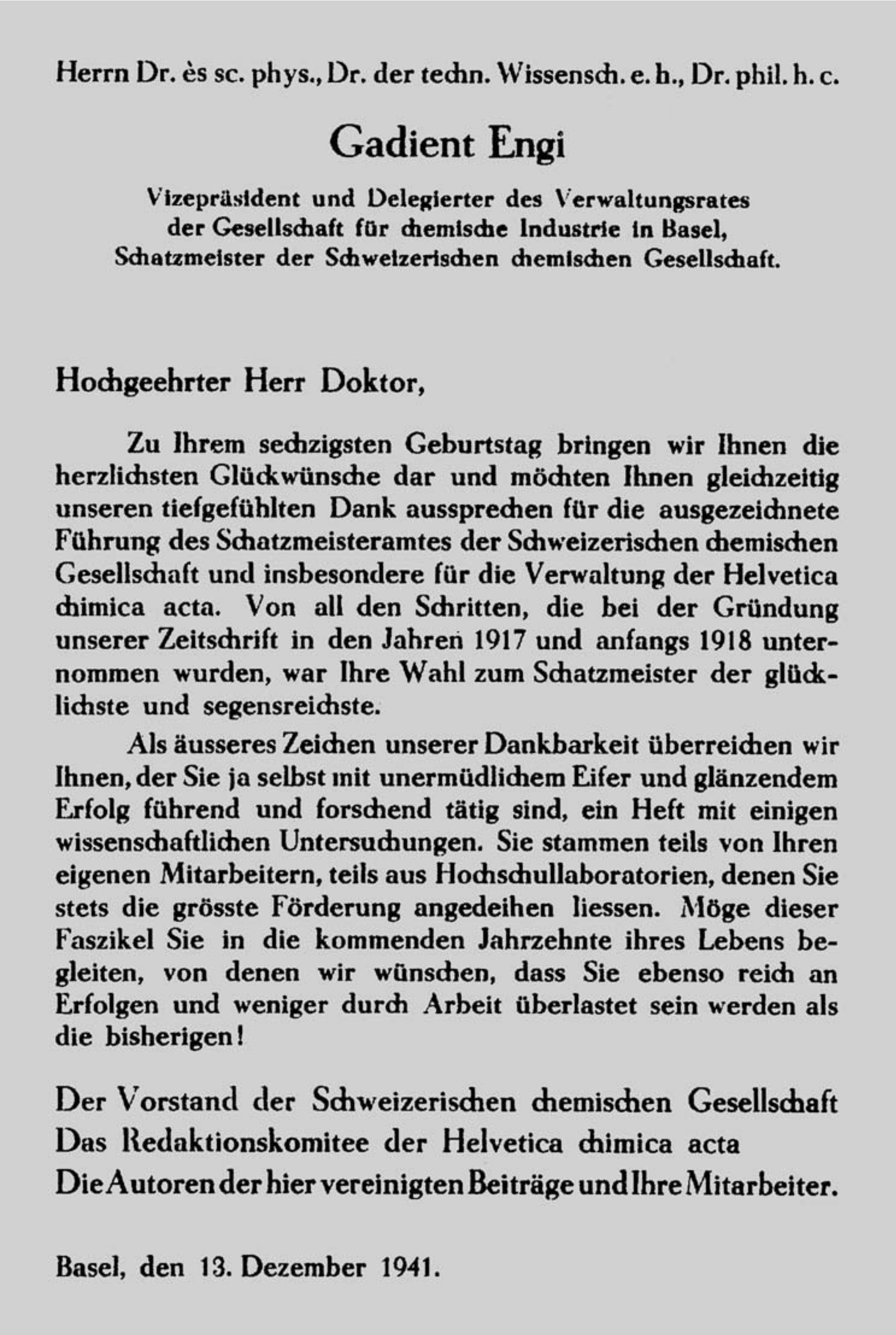
Dr. Hans Eduard Fierz
Professor
an der Eidgenössischen Technischen Hochschule in Zürich

Mit 45 Abbildungen auf 19 Tafeln und im Text

Zürich 1920
Druck und Verlag von Schultheß & Co.

Title page of the book H. E. Fierz, *'Grundlegende Operationen der Farbenchemie', first edition, 1920, with dedication of the author to* Jean Gloor *(ETH).* Original in the *Library of the Sidney M. Edelstein Center for the History of Science and Technology*, Hebrew University Jerusalem.

Fig. 24



Herrn Dr. ès sc. phys., Dr. der techn. Wissensch. e. h., Dr. phil. h. c.

Gadient Engi

Vizepräsident und Delegierter des Verwaltungsrates
der Gesellschaft für chemische Industrie in Basel,
Schatzmeister der Schweizerischen chemischen Gesellschaft.

Hochgeehrter Herr Doktor,

Zu Ihrem sechzigsten Geburtstag bringen wir Ihnen die herzlichsten Glückwünsche dar und möchten Ihnen gleichzeitig unseren tiefgefühlten Dank aussprechen für die ausgezeichnete Führung des Schatzmeisteramtes der Schweizerischen chemischen Gesellschaft und insbesondere für die Verwaltung der Helvetica chimica acta. Von all den Schritten, die bei der Gründung unserer Zeitschrift in den Jahren 1917 und anfangs 1918 unternommen wurden, war Ihre Wahl zum Schatzmeister der glücklichste und segensreichste.

Als äusseres Zeichen unserer Dankbarkeit überreichen wir Ihnen, der Sie ja selbst mit unermüdlichem Eifer und glänzendem Erfolg führend und forschend tätig sind, ein Heft mit einigen wissenschaftlichen Untersuchungen. Sie stammen teils von Ihren eigenen Mitarbeitern, teils aus Hochschullaboratorien, denen Sie stets die grösste Förderung angedeihen liessen. Möge dieser Faszikel Sie in die kommenden Jahrzehnte ihres Lebens begleiten, von denen wir wünschen, dass Sie ebenso reich an Erfolgen und weniger durch Arbeit überlastet sein werden als die bisherigen!

Der Vorstand der Schweizerischen chemischen Gesellschaft
Das Redaktionskomitee der Helvetica chimica acta
Die Autoren der hier vereinigten Beiträge und Ihre Mitarbeiter.

Basel, den 13. Dezember 1941.

This address and *Engi*'s portrait introduce a '*Fasciculus extraordinarius*' of *HCA*, a volume of some 400 pages with 36 scientific contributions from many industrial and academic laboratories between Geneva, Basle, and Zurich. It is the only 'Festschrift', published by *HCA* and separately paginated (as an appendix to *Vol. 24*). *Engi*'s very positive influence on chemistry in Switzerland became evident from the comparatively large percentage of young men (no women at that time!) from the Canton of Grisons, *Engi*'s home state, who studied chemistry at ETH early in this century and subsequently worked for *Ciba* in Basle.

The other chemist to be mentioned here is ***Richard Tobler*** (1892–1961). He was the second graduate student of *Fierz* after *Hartmann Koechlin* (see beginning of this review). The subject of his thesis, the synthesis of 2,2′,3,3′-naphthindigo, was published in *HCA* [58]. It is remarkable, because various naphthindigo isomers and derivatives were introduced into production after *Tobler* joined *Ciba* in 1920. Here, we mention him for another reason: he was the major promoter for the Institut für Farbenchemie at the University of Basle after the Second World War, when he was responsible for research of the *Dye Division* of *Ciba*. The foundation of that Department in 1947 was possible thanks to a very generous donation of *Ciba* and *Sandoz*.

It is realistic to conclude this review with the statement that color chemistry in 1992 no longer has the same relative importance in Switzerland as it had in 1917, when *HCA* was founded. The internationally high reputation of Swiss chemistry today originated in the early development of color chemistry. In the opinion of the present author, it can still contribute to the future development of chemistry in Switzerland, if Swiss color chemists integrate themselves in scientific problems of general chemistry and realize that there are new, challenging tasks for them in the application of colored organic and inorganic compounds in areas of industrial activities that supplement traditional applications.

I thank Dr. *M. D. Revenscroft*, postdoctoral fellow at ETH-Zürich (1982–85), for his help in improving the manuscript, and Prof. *A. Gossauer* and Prof. *H. Wyler* for information concerning the Universities of Fribourg and Lausanne, respectively, and Mr. *M. Ron*, librarian of the *Sidney M. Edelstein Center for the History of Science and Technology*, Hebrew University, Jerusalem, for providing a copy of the title page of the book of *Fierz*.

REFERENCES

[1] G. Bugge, 'Das Buch der grossen Chemiker', Weinheim 1929, p. 458–468.

[2] A. S. Travis, 'The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe', Lehigh University Press, Bethlehem PA, and Associated University Presses, London, 1992.

[3] T. Sandmeyer, *Ber. Dtsch. Chem. Ges.* **1884,** *17,* 2650–2653.

[4] L. M. Venanzi, *Helv. Chim. Acta* **1992,** *75,* 21–61.

[5] A. Hantzsch, A. Werner, *Ber. Dtsch. Chem. Ges.* **1890,** *23,* 11–30.

[6] A. Hantzsch, *Ber. Dtsch. Chem. Ges.* **1894,** *27,* 1702–1725.

[7] E. Bamberger, *Ber. Dtsch. Chem. Ges.* **1894,** *27,* 359–379.

[8] E. Bamberger, O. Baudisch, *Ber. Dtsch. Chem. Ges.* **1912,** *45,* 2054–2059.

[9] H. E. Fierz, H. Koechlin, *Helv. Chim. Acta* **1918,** *1,* 210–218.

[10] F. Kehrmann, M. Sandoz, *Helv. Chim. Acta* **1918,** *1,* 270–277.

[11] J. Piccard, *Helv. Chim. Acta* **1918,** *1,* 134–135; J. Piccard, F. de Montmollin, *ibid.* **1923,** *6,* 1101–1019.

[12] F. Kehrmann, M. Sandoz, *Helv. Chim. Acta* **1921,** *4,* 31–44.

[13] F. Kehrmann, *Helv. Chim. Acta* **1921,** *4,* 527–537.

[14] F. Kehrmann, *Helv. Chim. Acta* **1922,** *5,* 158–163.

[15] F. Kehrmann, *Helv. Chim. Acta* **1922,** *5,* 69–71.

[16] A. Hantzsch, *Ber. Dtsch. Chem. Ges.* **1921,** *54,* 2569–2627.
[17] F. Kehrmann, H. Goldstein, P. Tschudi, *Helv. Chim. Acta* **1919,** *2,* 379–397.
[18] G. Schwarzenbach, M. Brandenberger, G.H. Ott, O. Hagger, *Helv. Chim. Acta* **1937,** *20,* 490–498.
[19] G. Schwarzenbach, G.H. Ott, O. Hagger, *Helv. Chim. Acta* **1937,** *20,* 498–513.
[20] G. Schwarzenbach, R. Sulzberger, *Helv. Chim. Acta* **1944,** *27,* 348–362.
[21] G. Schwarzenbach, *Helv. Chim. Acta* **1943,** *26,* 418–424.
[22] G. Schwarzenbach, R. Sulzberger, *Helv. Chim. Acta* **1943,** *26,* 453–459.
[23] G. Wittwer, H. Zollinger, *Helv. Chim. Acta* **1954,** *37,* 1954–1968.
[24] Z.J. Allan, J. Podstata, *Collect. Czech. Chem. Commun.* **1960,** *25,* 1324–1336.
[25] G. Schwarzenbach, C. Wittwer, *Helv. Chim. Acta* **1947,** *30,* 656–658.
[26] P.D. Bartlett, *J. Am. Chem. Soc.* **1954,** *56,* 967-969.
[27] G. Schwarzenbach, C. Wittwer, *Helv. Chim. Acta* **1947,** *30,* 669–674.
[28] J.P. Guthrie, P.A. Cullimore, *Can. J. Chem.* **1979,** *57,* 240–248; J.P. Guthrie, *ibid.* **1979,** *57,* 797–802.
[29] H. Kuhn, *Helv. Chim. Acta* **1948,** *31,* 1441–1455.
[30] K. Fukui, *Angew. Chem.* **1982,** *94,* 852–861; *ibid. Int. Ed.* **1982,** *21,* 801–810.
[31] H. Kuhn, *Helv. Chim. Acta* **1949,** *32,* 2247–2272; *ibid.* **1951,** *34,* 1308–1324, 2371–2402; Wernhard Huber, H. Kuhn, Walter Huber, *ibid.* **1953,** *36,* 1597–1611; and papers published in other journals.
[32] H.-D. Försterling, H. Kuhn, 'Moleküle und Molekülanhäufungen, eine Einführung in die physikalische Chemie', Springer Verlag, Berlin, 1983, p. 75–102.
[33] F.P. Schäfer, in 'Wie die Zukunft Wurzeln schlug', Ed. R. Gerwin, Springer Verlag, Berlin, 1989, p. 206–211.
[34] R. Grinter, E. Heilbronner, *Helv. Chim. Acta* **1962,** *45,* 2496–2516.
[35] K.P. Krishnan Namboodiri, S. Viswanathan, R. Ganesan, V.C. Jyothi Bhasu, *J. Comput. Chem.* **1981,** *2,* 392–401.
[36] W. Dilthey, R. Wizinger, *J. Prakt. Chem.* **1928,** *118,* 321–348.
[37] P. Pfeiffer, R. Wizinger, *Liebig's Ann. Chem.* **1928,** *461,* 132–154.
[38] C.F. Bernasconi, T. Iijima, W. Koch, M. Wakae, H. Zollinger, *Helv. Chim. Acta* **1973,** *56,* 2667–2680.
[39] R. Wizinger, B. Cyriax, *Helv. Chim. Acta* **1945,** *28,* 1018–1037.
[40] P. Ruggli, F. Knapp, E. Merz, A. Zimmermann, *Helv. Chim. Acta* **1929,** *12,* 1034–1051; P. Ruggli, A. Zimmermann, F. Knapp, *ibid.* **1930,** *13,* 748–756.
[41] H. Heimgartner, H.J. Hansen, *Helv. Chim. Acta* **1952,** *35,* 1209–1223.
[42] H. Zollinger, C. Wittwer, *Helv. Chim. Acta* **1952,** *35,* 1209–1223.
[43] H. Zollinger, *Helv. Chim. Acta* **1955,** *38,* 1597–1616, 1617–1622, 1623–1631.
[44] R. Ernst, O.A. Stamm, H. Zollinger, *Helv. Chim. Acta* **1958,** *41,* 2274–2278.
[45] C.K. Ingold, 'Structure and Mechanism in Organic Chemistry', 2nd edn., Cornell University Press, Ithaca, 1969, p. 374; R. Taylor, 'Electrophilic Aromatic Substitution', John Wiley, Chichester, 1990, p. 258.
[46] J.R. Bourne, E. Crivelli, P. Rys, *Helv. Chim. Acta* **1977,** *60,* 2944–2947, and later papers.
[47] H. Balli, *Liebigs Ann. Chem.* **1961,** *647,* 11, and following papers.
[48] H. Balli, U. Müller, A. Sezen-Gezgin, *Helv. Chim. Acta* **1978,** *61,* 104–107.
[49] H. Balli, F. Kersting, *Liebigs Ann. Chem.* **1963,** *663,* 103–107; H. Balli, *Helv. Chim. Acta* **1974,** *57,* 1912–1919.
[50] H. Balli, H. Grüner, R. Maul, H. Schoepp, *Helv. Chim. Acta* **1981,** *64,* 648–656.
[51] S. Gunzenhauser, H. Balli, *Helv. Chim. Acta* **1990,** *73,* 359–379.
[52] A.S. Pfau, P.A. Plattner, *Helv. Chim. Acta* **1936,** *19,* 858–879.
[53] H. de Diesbach, E. von der Weid, *Helv. Chim. Acta* **1927,** *10,* 886–888.
[54] R.P. Linstead, *Br. Assoc. Adv. Sci. Rep.* **1933,** 465–468.
[55] J.M. Robertson, *J. Chem. Soc.* **1935,** 615–621.
[56] A. Iqbal, M. Jost, R. Kirchmayr, J. Pfenninger, A.C. Rochat, O. Wallquist, *Bull. Soc. Chim. Belg.* **1986,** *97,* 615–628.
[57] H.E. Fierz, 'Grundlegende Operationen der Farbenchemie', 1st edn., Schulthess, Zürich, 1920; H.E. Fierz-David, L. Blangey, 'Grundlegende Operationen der Farbenchemie', 8th edn., Springer, Wien, 1952; English edn. Fundamental Processes of Dye Chemistry, Interscience, New York, 1949.
[58] H.E. Fierz-David, R. Tobler, *Helv. Chim. Acta* **1922,** *5,* 557–560.