On the Formation of Mauvein: Mechanistic Considerations and Preparative Results

Christoph Heichert and Horst Hartmann

Fakultät Mathematik und Naturwissenschaften, Technische Universität Dresden, Mommsenstr. 13, 01062 Dresden, Germany

Reprint requests to Prof. Dr. Horst Hartmann. E-mail: Hartmann@iapp.de

Z. Naturforsch. **2009**, *64b,* 747 – 755; received March 29, 2009

Dedicated to Professor Gerhard Maass on the occasion of his 60th birthday

The reaction of aniline ($\mathbf{AH_2}$) with an oxidizing agent in acidic solution gives rise to the formation of a mixture of products containing, besides a variety of oligoanilines named as Aniline Black or Polyaniline, Mauvein as a deeply purple phenazine derivative. Although this Mauvein synthesis was developed by W. H. Perkin more than 150 years ago and has opened the era of industrial dyestuff chemistry, the detailed mechanism of this reaction has remained rather unclear until today. The elucidation of the mechanism of the Mauvein formation as an oxidative coupling process of $\mathbf{AH_2}$ is hindered by the fact that several different types of coupling reactions occur simultaneously. Among them the *C,N*-coupling reaction is the most important one and responsible for the formation of Polyaniline and Mauvein. It gives rise to the formation of, *e. g*. 2 different aniline dimers, 7 trimers and more than 20 tetramers including Mauvein as one representative of these tetramers.

In the present study, the oxidative coupling of a mixture of $\mathbf{AH_2}$ and 4-amino-4′-(*N*-anilino)-diphenylamine ($\mathbf{T_aH_2}$) as one of the aniline trimers was studied in more detail. The reaction leads to the formation of Mauvein in satisfactory yields and, after some manipulations, widely free of by-products. By using simple aniline derivatives as co-reagents in the oxidative coupling with $\mathbf{T_aH_2}$, the reaction can be extended to the synthesis of different Mauvein derivatives most of which have been unknown to date.

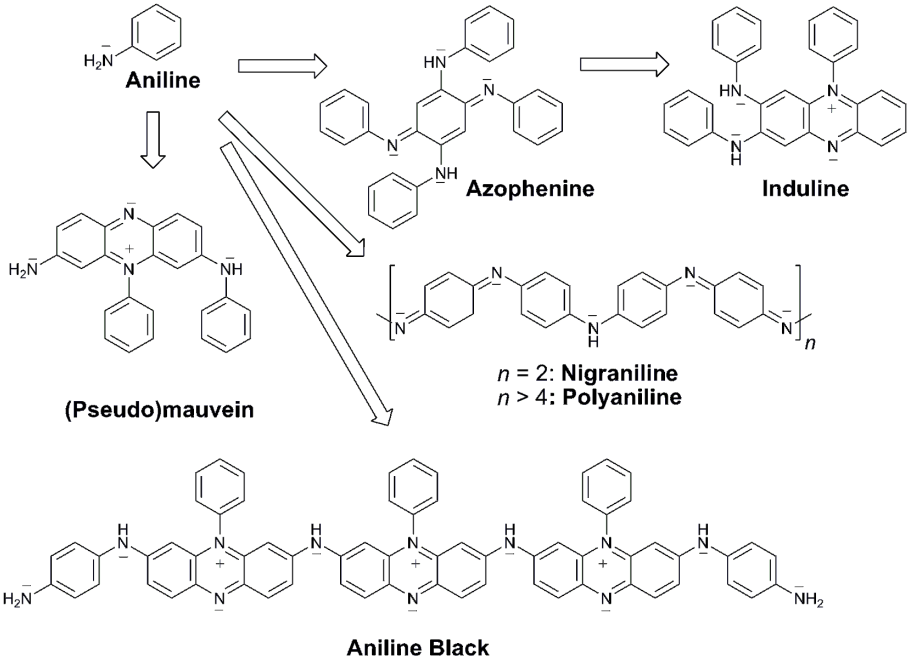
Key words: Mauvein, Phenazine Dyes, Synthesis, Mechanism

Introduction

Stimulated by an idea of August Wilhelm von Hofmann, *anno* 1856, his eighteen years old student William Henry Perkin tried to synthesize quinine by oxidation of crude aniline. Quinine, its chemical structure known only roughly as a nitrogen-containing compound and widely used at that time as an anti-malaria drug, was available only *via* an elaborated way from the Cinchona bark [1]. Other than expected, instead of the desired quinine, Perkin obtained in the course of his experiments with aniline and some of its derivatives a deeply colored reaction mixture which contained a purple compound able to dye wool and silk in brilliant shadows [2]. Therefore Perkin decided to finish his exploratory study and started to produce the novel dye on a technical scale. Under the name Aniline Purple, Mauvein or Mauve this product was sold immediately [3]. With this discovery the era of tar industry as the initiator of a large chemical industry in Europe and overseas was opened [4].

Remarkably, Perkin was not the first scientist who studied the oxidation of aniline and its derivatives, but he was the first one who produced a useful dyestuff in practicable amounts and brought it to the market. Before him the German chemist Friedlieb Ferdinand Runge, who isolated aniline for the time first from tar in 1838 and provided the basis for its inexpensive availability in larger amounts, had studied the oxidation of aniline also and thereby developed the synthesis of an intensively colored product named Aniline Black [5]. This product was able to dye textile fibres also, but it was not used practically later on due to its low dyeing quality. Therefore, Perkin entered the modern history as the pioneer of the dyestuff industry.

Although the procedure of Mauvein production was rather simple – a sulfuric acid solution of crude aniline is to treat with potassium bichromate [6] – it has sev-



Scheme 1.

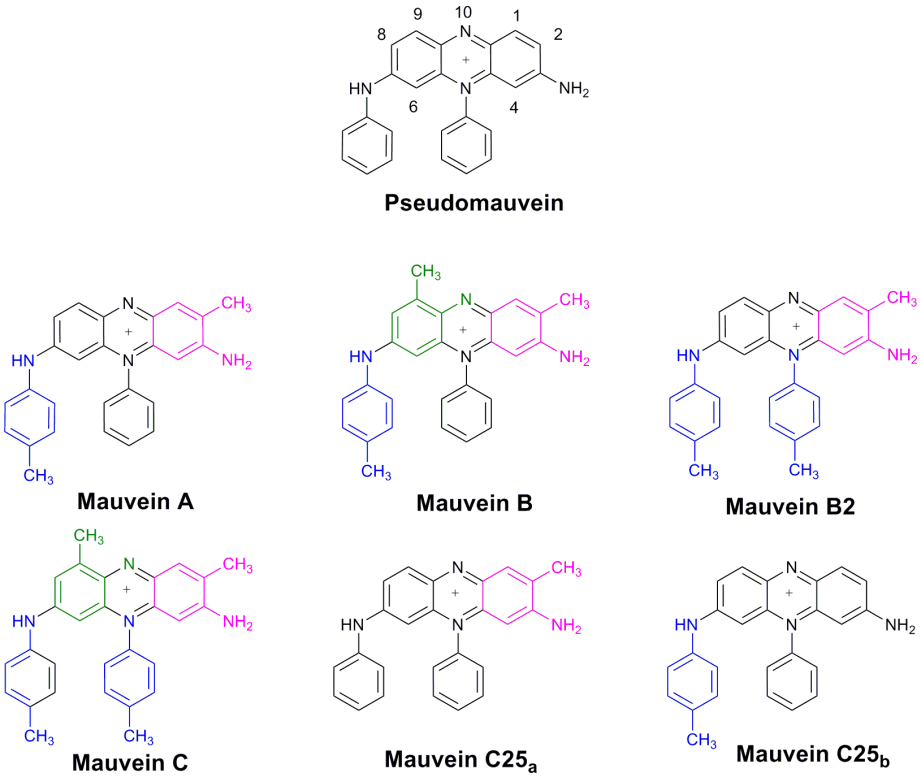
eral malices making it difficult to handle and demands of the producer a great deal of skillness and engagement. Especially the low yields of the pure dye were the most critical points indicating that the essential dye-forming process is rather complicated. It depends to a large extent on the quality of the starting aniline and gives better yields of product if some toluidines, especially *ortho*- and *para*-toluidine, are admixed to aniline.

Although Perkin soon recognized that his Mauvein is not an uniform product but consists of two different components at least, the structures of these compounds could not be elucidated by him correctly at this time. Sometimes later, however, Otto Fischer and Eduard Hepp as well as Rudolf Nietzki found that a phenazine moiety is the basic structure of Mauvein [7]. These chemists and few others found in the course of subsequent studies of the aniline oxidation process several further products derived from aniline, such as Azophenines, Indulines, and Nigranilines [8]. Moreover, different kinds of Aniline Blacks could be prepared in the meantime, and different suggestions for their structures have been made (Scheme 1) [9]. More recently Aniline Black received much attention as an organic electrically conducting material [10].

In respect to the Mauvein formation it is worth mentioning that the use of anilines with a free 4-position is a precondition for the formation of this oxidation product indicating that this position is essential for the reactions involved.

More detailed studies on the structure of Mauvein have demonstrated that an original technical sample of Perkins Violet consists of a mixture of seven different compounds containing methyl groups at different positions in the parent phenazine core [11]. The methyl groups originate from the starting material used, an aniline/toluidine mixture. The different Mauvein derivatives have been named, as depicted in Scheme 2, as Pseudomauvein, Mauvein A, Mauvein B, Mauvein B2, Mauvein C, Mauvein C25, and Mauvein C25b [12]. In accordance with the Chemical Abstract Service the enumeration of the ring positions is performed as depicted in Scheme 2.

Despite of a variety of different studies on the mechanism of the Mauvein formation, the process is not clear in all details as yet. As indicated by ESR and Raman spectroscopic measurements, the process starts with the formation of an aniline cation radical $\mathbf{AH_2}^{\bullet+}$ from aniline $\mathbf{AH_2}$ initiated by the oxidative agents applied [13]. This highly reactive cation radical $\mathbf{AH_2}^{\bullet+}$ attacks an unchanged aniline $\mathbf{AH_2}$, which under the experimental conditions is in an equilibrium with the corresponding anilinium ion $\mathbf{AH_3}^{+}$, giving rise to the formation of different types of products. As primary

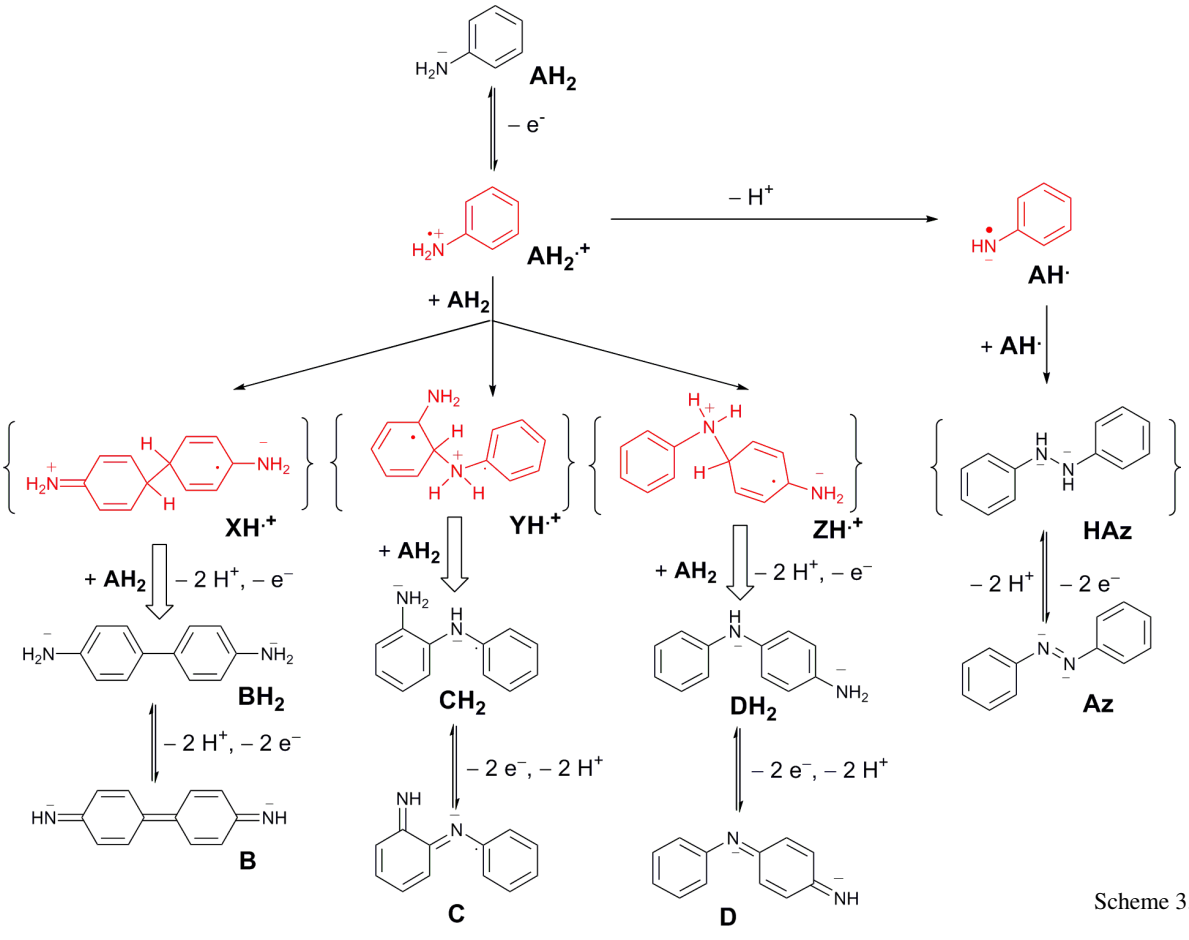


Scheme 2.

products of the reaction of the cation radical $\mathbf{AH_2}^{\bullet+}$ with the parent aniline $\mathbf{AH_2}$, benzidine $\mathbf{BH_2}$, *o*-amino-diphenylamine $\mathbf{CH_2}$ and *p*-amino-diphenylamine $\mathbf{DH_2}$ as well as hydrazobenzene **HAz** could be detected, which are transformed immediately into the corresponding oxidation products diphenquinone diimine **B**, *N*-phenyl-1,2-quinone diimine **C**, *N*-phenyl-1,4-quinone diimine **D**, and azobenzene **Az**, respectively (Scheme 3) [14].

Although no detailed information on the relative amounts of the formed products exists at yet, *N*-phenyl-1,4-quinone diimine **D** seems to be the main reaction product occurring in the course of this oxidative dimerization process and can be considered as the essential precursor in the Mauvein formation [15]. It is generated by the oxidation of *para*-amino-diphenylamine $\mathbf{DH_2}$ – probably by the attack of the aniline cation radical $\mathbf{AH_2}^{\bullet+}$ on $\mathbf{DH_2}$ – and can react either with the starting aniline $\mathbf{AH_2}$ or with its own 4-amino-diphenylamine precursor $\mathbf{DH_2}$ [16]. For these reactions three different pathways may be considered which give rise to the formation of either the trimers $\mathbf{T_aH_2}$, $\mathbf{T_bH_2}$, and $\mathbf{T_cH_2}$ or of the tetramers $\mathbf{Q_aH_4}$, $\mathbf{Q_bH_4}$, and $\mathbf{Q_cH_4}$, respectively (Scheme 4). Whereas the compounds $\mathbf{T_aH_2}$ and $\mathbf{Q_aH_4}$ can be generated in the course of an electrophilic attack of the imino group of quinone diimine **D** at the *para*-position of $\mathbf{AH_2}$ or $\mathbf{DH_2}$ (Route **a**), the other compounds can be formed in the course of a nucleophilic attack of the amino groups of $\mathbf{AH_2}$ or $\mathbf{DH_2}$ at the position *b* or *c* of the quinone diimine double bound of **D** (Route **b** or Route **c**, respectively) [16]. The electrophilic attack of the aniline cation radical $\mathbf{AH_2}^{\bullet+}$ at the 4′-position of 4-amino-diphenylamine $\mathbf{DH_2}$, analogous to its reaction with aniline $\mathbf{AH_2}$, has been discussed by several authors, but can be ruled out as an alternative route for generating $\mathbf{T_aH_2}$ because this reaction is overruled by the redox reaction mentioned before. It is worth mentioning that the radical cation $\mathbf{DH_2}^{\bullet+}$ formed in the course of the synproportionation of $\mathbf{DH_2}$ with **D** was made responsible for the formation of $\mathbf{Q_aH_4}$ by dimerization during the aniline oligomerization [17].

Unfortunately, no information on the relative amounts of the individual compounds formed in the reaction of **D** with $\mathbf{AH_2}$ or $\mathbf{DH_2}$ is available at yet. Nevertheless, in respect to their structure only the mentioned trimers $\mathbf{T_aH_3}$, $\mathbf{T_bH_3}$, and $\mathbf{T_cH_3}$ (R = H) are to be considered as Mauvein precursors. By contrast,



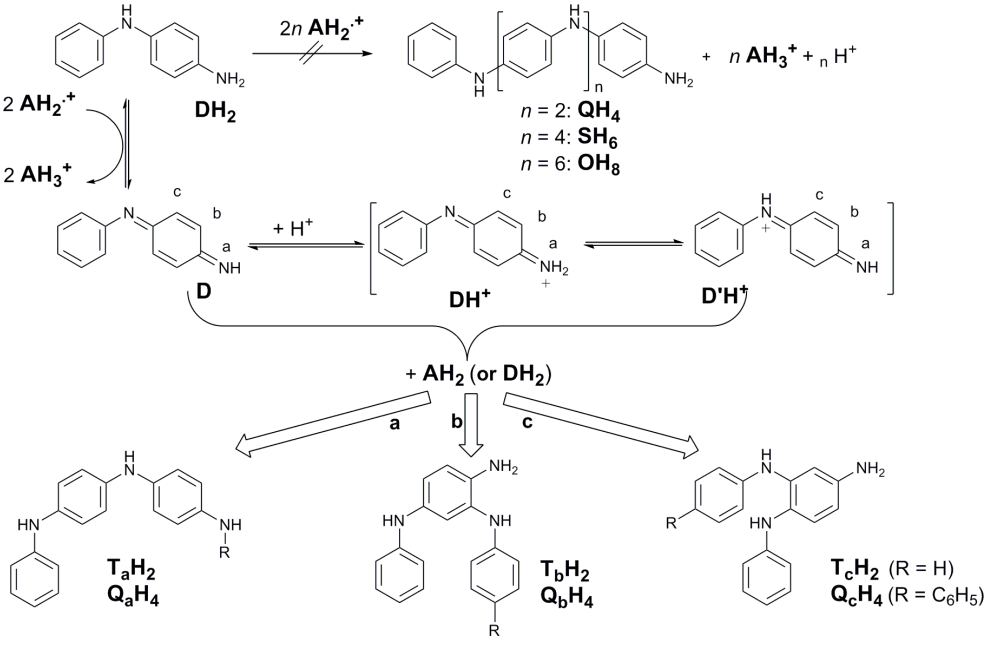
Scheme 3.

the corresponding tetramers $\mathbf{Q_aH_4}$, $\mathbf{Q_bH_4}$, and $\mathbf{Q_cH_4}$ (R = C_6H_5NH) can be considered solely as polyaniline precursors, of which $\mathbf{Q_aH_4}$ is the most favored product. In analogy to $\mathbf{DH_2}$, this aniline tetramer can react, after its oxidation, to the corresponding quinone diimine derivatives $\mathbf{Q_aH_2}$ or $\mathbf{Q_a}$, either with $\mathbf{DH_2}$ or with $\mathbf{Q_aH_4}$, forming oligomers with six ($\mathbf{SH_6}$) or eight ($\mathbf{OH_8}$) aniline moieties (Scheme 4).

Results and Discussion

Because the ability of the aniline trimer $\mathbf{T_aH_3}$ to function as an educt for Mauvein has not yet been studied, we have checked this possibility and found that this trimer is a versatile starting material for preparing the title compound in satisfactory yields. Simultaneously, we also checked the performance of the aniline dimer $\mathbf{DH_2}$ in the same reaction, and found that this compound can also serve as a Mauvein educt. However, the yields are rather low in this case, and the product is accompanied by a variety of by-products very difficult to separate from the target compound. This is in contrast to the oxidative coupling of $\mathbf{DH_2}$ with 3-amino-diphenylamine studied by Nietzki in 1896 which gives rise to the formation of Mauvein in satisfactory yield [7]. It has to be pointed out, however, that 3-amino-diphenylamine is no a direct aniline coupling product and therefore has to be synthesized by a special synthetic route.

The oxidative coupling of $\mathbf{T_aH_3}$ (or of $\mathbf{DH_2}$) with aniline and several of its derivatives $\mathbf{A_iH_2}$ was performed in analogy to a procedure used for the synthesis of Safranine [18] by adding an eqimolar mixture of the corresponding compounds dissolved in methanol into a solution of $K_3Fe(CN)_6$ in aqueous sodium acetate (0.5 M) and refluxing the mixture until no starting materials could be detected by TLC. In all cases this coupling gives rise to the formation of the corresponding



Scheme 4.

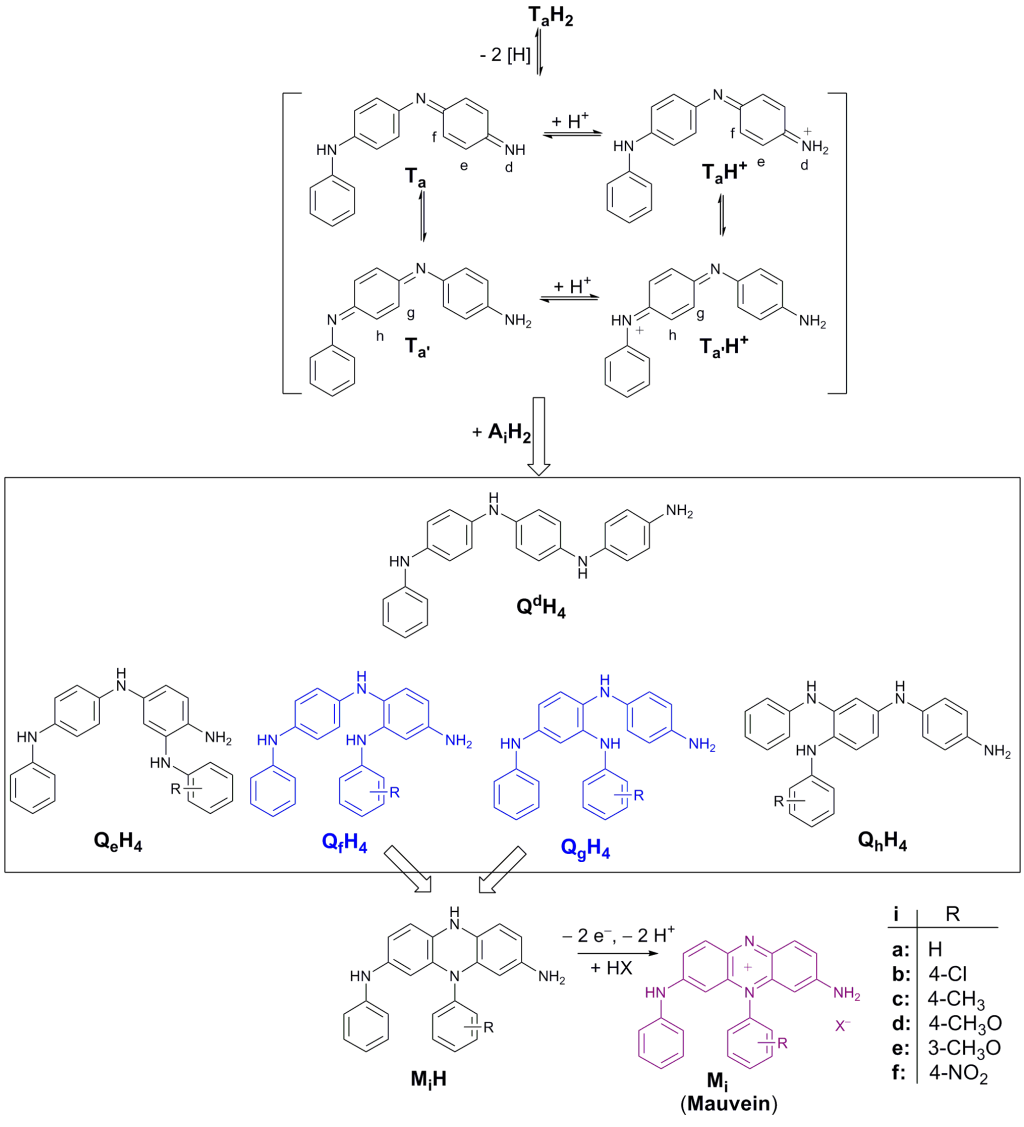
Mauvein derivatives $\mathbf{M_i}$. Whereas in the case of $\mathbf{T_aH_3}$ the corresponding Mauveins $\mathbf{M_i}$ were obtained in satisfactory yields, mostly and only accompanied with few other by-products, by starting with $\mathbf{DH_2}$ mainly a variety of other products, such as Polyaniline as well as different types of phenazines, were formed.

To separate these by-products from the target Mauveins the crude product was first extracted with boiling ethyl acetate and then with hot methanol. The methanolic solution was filtered after cooling to remove sparingly soluble Polyaniline and treated with an aqueous solution of Na_2ZnCl_4. This procedure removes the paramagnetic Polyaniline impurities and transforms the less soluble Mauvein acetates obtained as primary products into better soluble tetrachlorozincates which can finally be isolated as lustrous green, bronze-colored crystals.

It should be mentioned that the complete separation of paramagnetic Polyaniline is essential to obtain satisfactory ^{1}H NMR spectra of the Mauvein products.

From these preparative results it follows that the dye-forming process very probably starts, as depicted in Scheme 5, with the quinone diimine intermediates $\mathbf{T_aH}$ or $\mathbf{T_{a'}H}$ (or with their protonated species $\mathbf{T_aH_2}^+$ and $\mathbf{T_{a'}H_2}^+$) which are generated from the $\mathbf{T_aH_3}$ educt by oxidation. Immediately after their formation the appropriate aniline derivatives $\mathbf{A_iH_2}$ are added at their quinone diimine moieties. Thereby the aniline tetramers $\mathbf{Q_dH_4}$ – $\mathbf{Q_hH_4}$ are formed among which only the compounds $\mathbf{Q_fH_4}$ and $\mathbf{Q_gH_4}$ are the essential educts for the Mauvein formation. Whereas these aniline tetramers are subsequently transformed into the corresponding quinone diimine derivatives $\mathbf{Q_iH_2}$ (not depicted in Scheme 5), from which the Mauvein derivatives $\mathbf{M_i}$ can be generated *via* the intermediate formation of the dihydrophenazine derivatives $\mathbf{M_iH}$, the other aniline tetramers $\mathbf{Q_dH_4}$, $\mathbf{Q_eH_4}$ and $\mathbf{Q_hH_4}$ are transformed into higher aniline oligomers which contaminate the target Mauveins and make expensive purification procedures necessary for obtaining neat products.

The structure of the Mauvein derivatives $\mathbf{M_i}$ prepared as described above follows unambiguously from their analytical data. Thus, all Mauveins $\mathbf{M_i}$ exhibit in their mass spectra characteristic molecular ion peaks and give rise in their ^{1}H NMR spectra, in accordance with other studies [11, 12], to characteristic signals at 5.9, 6.3, 7.5, 8.0, 8.1, and 8.2 ppm, stemming from the protons attached to their phenazinium moieties. Whereas most of these signals are split into doublets, the signals at 7.5 ppm appear as double doublets. The doublets at 5.9 and 6.3 ppm stem from the protons attached to the 6- and 4-position of the phenazine moiety. These protons are significantly shielded by the ring current of the *N*-phenyl moieties at N(5), as can be seen, *e. g.* by comparing the ^{1}H NMR spectral data



Scheme 5.

of the Mauveins $\mathbf{M_i}$ with the corresponding data of 9-methyl-2,7-bis(methylamino)phenazinium perchlorate which exhibits a low-field singlet at 6.70 ppm for the protons at C(1) and C(9) [19]. According to X-ray diffraction [20] and gas phase electron diffraction studies [21] or DFT calculations [22] these phenyl rings are twisted from the phenazine plane with an angle of about 45°. Finally, the signals of the protons at the *N*-linked phenyl groups are found as multiplets between 7.1 and 8.1 ppm.

All Mauveins $\mathbf{M_i}$ exhibit, as can be seen in Fig. 1 for the parent Mauvein $\mathbf{M_a}$ as an example, deep colors originating from intense absorptions at about 550 nm. These absorptions are not much influenced by the substituents R at the *N*-phenyl moiety of the phenazine core and are responsible for the purple color of all Mauvein derivatives.

In summary, the previous considerations as well as the experimental data suggest that the aniline trimer *N*-(4-aminophenyl)-*N*′-phenyl-benzene-1,4-diamine ($\mathbf{T_aH_2}$) is an essential intermediate in the Mauvein formation process. This compound is able, after transformation into the corresponding quinone diimine derivative $\mathbf{T_a}$, to react with aniline at one of its C-C double bonds to yield four different aniline tetramers $\mathbf{Q_eH_4}$, $\mathbf{Q_fH_4}$, $\mathbf{Q_gH_4}$, and $\mathbf{Q_hH_4}$, of which

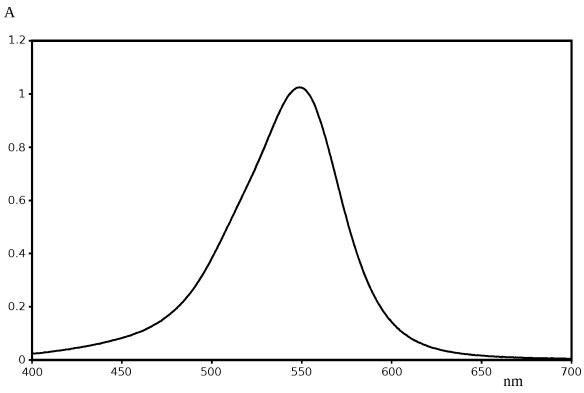


Fig. 1. Absorption spectrum of Pseudomauvein ($\mathbf{M_a}$), measured in methanol ($c = 10^{-5}$ mol L^{-1}).

only the second and third act as Mauvein educts, whereas the other ones and the trimeric precursors $\mathbf{T_bH_2}$ and $\mathbf{T_cH_2}$ are responsible for the other products formed. Alternatively, the quinone diimine derivative $\mathbf{T_a}$ can react with its precursor $\mathbf{T_aH_2}$ analogously to yield different types of aniline tetramers, such as $\mathbf{Q_aH_4}$, $\mathbf{Q_bH_4}$, $\mathbf{Q_cH_4}$ and $\mathbf{Q_dH_4}$, which are obviously unable to act as Mauvein precursors.

To get a more deeper insight in the Mauvein formation process and also, alternatively, into the process of the Aniline Black formation, it seems necessary to estimate implicitly the actual concentrations of all the intermediates formed as well as their reactivities and different reaction pathways under the experimental conditions applied. Although for such investigations the required physicochemical methods, especially spectro-electrochemical methods, are generally well-established, they unfortunately have not been employed at yet.

Experimental Section

General information

The following instruments and analytical techniques were used: Melting points: Kofler hot-stage microscope, corrected; NMR: Bruker 500 MHz spectrometer DRX 500P; [D_6]DMSO as solvent; δ in ppm (assignment); UV/Vis: Perkin Elmer spectrometer Lambda 900; methanol as solvent. MS: Bruker Esquire MS with Ion Trap detector and ESI-Source, measurement parameters: fragmentation voltage: 1 – 200 V, corona voltage 140 – 1800 V.

Preparation of N-(4-aminophenyl)-N′-phenyl-benzene-1,4-diamine

a) The preparation of the *N*-(4-nitrophenyl)-*N′*-phenyl-benzene-1,4-diamine precursor was performed according to the literature by reaction of *N*-phenyl-1,4-phenylene diamine with 4-fluoronitrobenzene in DMSO [23]. Yield 65 %; m. p. 139 – 140 °C (ref. [23a]: 132 – 134 °C; ref. [23b]: 139 °C).

b) Preparation of *N*-(4-aminophenyl)-*N′*-phenyl-benzene-1,4-diamine ($\mathbf{T_aH_2}$): Into a solution of *N*-(4-nitrophenyl)-*N′*-phenyl-benzene-1,4-diamine (1.53 g, 5,0 mmol) in acetic acid (15 mL) Zn dust (2.61 g, 40 mmol) was added in small portions with stirring at r. t. After the color of the reaction mixture had turned to yellow-brown (after about 3 min) methanol (40 mL) was added. Then the resulting slurry was filtered by suction through a pad of celite, the filter cake was washed with methanol (10 mL), and the combined filtrates were neutralized with methanolic KOH (0.25 M). The resulting filtrate was used directly for the Mauvein synthesis given below.

Preparation of Mauveins ($\boldsymbol{M_i}$). General procedure

a) Oxidative coupling: To a boiling solution of $K_3Fe(CN)_6$ (10.86 g, 33 mmol) in 0.5 M aqueous sodium acetate (200 mL) a solution of *N*-(4-aminophenyl)-*N′*-phenyl-benzene-1,4-diamine ($\mathbf{T_aH_2}$, 5 mmol) in methanol, followed by the appropriate aniline derivative $\mathbf{A_iH_2}$ (7.5 mmol) dissolved in methanol (5 mL), was added. The resulting mixture which turned immediately to deep purple was refluxed for 3 h. After addition of methanol (150 mL), refluxing was continued for further 30 min. The hot mixture was filtered by suction and the filter cake washed with methanol (50 mL) until the filtrate was pale purple. The filtrate was evaporated *in vacuo* and the residual aqueous phase left standing over night at 20 °C. The raw Mauvein precipitated was collected by filtration, washed with water (50 mL) and ethyl acetate (50 mL), and dried at 120 °C.

b) Purification of the raw material: The solid residue of step a) was first triturated and digested with boiling ethyl acetate (2×75 mL) to remove impurities and then refluxed with methanol (200 mL) for 2 h. After cooling to 20 °C, the mixture was filtered through a fine pore paper filter and the residual filter cake washed with methanol until the filtrate was pale purple. The combined filtrates were added to a refluxing solution of $Na_2[ZnCl_4]$ (12.63 g, 50 mmol) dissolved in 0.02 M HCl (100 mL). The mixture obtained was concentrated *in vacuo* at r. t. and the residual aqueous phase left standing over night at 20 °C. The solid product was filtered, washed with 0.02 M HCl (10 mL), water (25 mL) and ethyl acetate (50 mL), and dried at 120 °C.

Thus, the following Mauvein derivatives were obtained in black-green, bronze micro-crystals.

Bis-(3-amino-5-phenyl-7-phenylamino-5-phenazinium) tetrachlorozincate ($\boldsymbol{M_a}$)

Yield 40 %; m. p. 288 – 290 °C. – ^{1}H NMR: δ = 5.92 (d, J = 2.0 Hz, 1H), 6.25 (s, J = 2.0 Hz, 1H), 7.13 (m, 3H), 7.32

(m, 3H), 7.50 (dd, J = 2.0 Hz, J = 9.2 Hz, 1H), 7.64 (m, 2H), 7.75 (m, 1H), 7.81 (m, 2H), 8.00 (d, J = 9.2 Hz, 1H), 8.08 (m, 3H), 10.16 (s, 1H, NH). – UV/Vis: λ_{max} ($\log\varepsilon$) = 549 nm (5.01). – MS: m/z = 363.2 (calcd. 363.43 for $C_{24}H_{19}N_4$).

*Bis-[3-amino-5-(4-chlorophenyl)-7-phenylamino-5-phenazinium] tetrachlorozincate (**M$_b$**)*

Yield 16 %; m. p. 226 – 230 °C (dec.). – ^{1}H NMR: δ = 5.93 (d, J = 1.9 Hz, 1H), 6.23 (s, J = 1.9 Hz, 1H), 7.16 (m, 3H), 7.34 (m, 3H), 7.52 (dd, J = 1.9 Hz, J = 9.2 Hz, 1H), 7.72 (d, J = 8.6 Hz, 2H), 7.94 (d, J = 8.6 Hz, 2H), 7.99 (d, 5H), 8.00 (d, 1H, J = 9.3 Hz, 1H), 8.08 (d, J = 9.3 Hz, 1H) 8.12 (s, 2H, NH), 10.17 (s, 1H, NH). – UV/Vis: λ_{max} ($\log\varepsilon$) = 550 nm (5.06). – MS: m/z = 397.2 (calcd. 397.88 for $C_{24}H_{18}N_4$).

*Bis-[3-amino-5-(4-methylpheny)l-7-phenylamino-5-phenazinium] tetrachlorozincate (**M$_c$**)*

Yield 31 %; m. p. 273 – 275 °C (dec.). – ^{1}H NMR (in CD_3NO_2): δ = 2.56 (s, 3H, CH_3, 6.21 (s, 1H, NH), 6.23 (d, J = 2.2 Hz, 1H) 6.50 (d, J = 2.2 Hz, 1H), 7.21 (t, 1H), 7.26 (d, J = 7.5 Hz, 2H), 7.36 – 7.42 (m, 5H), 7.58 (dd, J = 2.2 Hz, J = 9.3 Hz, 1H), 7.65 (d, J = 8.2 Hz, 2H), 8.02 (d, J = 9.3 Hz, 1H), 8.07 (d, J = 9.3 Hz, 1H), 8.15 (2H, NH). – UV/Vis: λ_{max} ($\log\varepsilon$) = 548 nm (5.05). – MS: m/z = 377.2 (calcd. 377.46 for $C_{25}H_{21}N_4$).

*Bis-[3-amino-5-(4-methoxyphenyl)-7-phenylamino-5-phenazinium] tetrachlorozincate (**M$_d$**)*

Yield 19 %; m. p. 263 °C. – ^{1}H NMR: δ = 3.89 (s, 3H, CH_3O), 5.99 (d, J = 2.2 Hz, 1H), 6.34 (s, J = 2.2 Hz, 1H), 7.17 (m, 3H), 7.35 (m, 4H), 7.50 (dd, J = 2.2 Hz, J = 9.3 Hz, 1H), 7.56 (m, 2H), 8.04 (d, 1H), 8.08 (m, 2H), 10.12 (d, J = 3.8 Hz, 1H, NH). – UV/Vis: λ_{max} ($\log\varepsilon$) = 548 nm (5.01). – MS: m/z = 393.2 (calcd. 393.46 for $C_{25}H_{21}N_4O$).

*Bis-[3-amino-5-(3-methoxypheny)l-7-phenylamino-5-phenazinium] tetrachlorozincate (**M$_e$**)*

Yield 26 %; m. p. 248 – 250 °C (dec.). – ^{1}H NMR: δ = 3.83 (s, 3H, CH_3O), 5.99 (d, J = 2.2 Hz, 1H), 6.32 (d, J = 2.2 Hz, 1H), 7.17 (m, 4H), 7.31 – 7.36 (m, 5H), 7.48 (dd, J = 2.2 Hz, J = 9.3 Hz, 1H), 7.73 (m, 1H), 8.00 (d, J = 9.3 Hz, 1H), 8.09 (d, J = 9.3 Hz, 1H), 8.11 (s 1H, NH), 10.16 (s, 1H, NH). – UV/Vis: λ_{max} ($\log\varepsilon$) = 549 nm (5.04). – MS: m/z = 393.2 (calcd. 393.46 for $C_{25}H_{21}N_4O$).

*Bis-[2-amino-5-(2-methoxyphenyl)-7-phenylamino-5-phenazinium] tetrachlorozincate (**M$_e$**)*

Yield 41 %; m. p. 223 – 225 °C. – ^{1}H NMR: δ = 3.73 (s, 3H, CH_3O), 5.97 (d, J = 2.3 Hz, 1H) 6.28 (d, J = 2.3 Hz, 1H), 7.08 – 7.16 (m, 3H), 7.26 – 7.36 (m, 4H), 7.47 (dd, J = 2.2 Hz, J = 9.3 Hz, 1H), 7.50 (dd, J = 2.2 Hz, J = 9.3 Hz, 1H), 7.73 (t, 1H), 7.97 (d, J = 9.3 Hz, 1H), 8.9 (d, J = 9.3 Hz, 1H) 8.16 (s, 2H, NH), 10.19 (s, 1H, NH). – UV/Vis: λ_{max} ($\log\varepsilon$) = 550 nm (5.02). – MS: m/z = 393.2 (calcd. 393.46 for $C_{25}H_{21}N_4O$).

*Bis-[3-amino-5-(4-nitrophenyl)-7-phenylamino-5-phenazinium] tetrachlorozincate (**M$_f$**)*

Yield 2 %; m. p. 177 – 180 °C. – ^{1}H NMR: δ = 5.92 (s, 1H), 6.26 (s, 1H), 7.15 (m, 3H), 7.30 – 7.36 (m, 3H), 7.49 (d, 1H), 7.64 (d, 1H), 7.81 (m, 2H), 7.99 – 8.10 (m, 3H), 10.14 (s, 1H, NH). – UV/Vis: λ_{max} ($\log\varepsilon$) = 549 nm (5.03). – MS: m/z = 409.2 (calcd. 408.43 for $C_{24}H_{18}N_5O_2$).

[1] T. S. Kaufman, E. A. Rúveda, *Angew. Chem.* **2005**, *117*, 876 – 907; *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 854 – 885.

[2] a) A. S. Travis, *Bull. Hist. Chem.* **2007**, *32*, 35 – 44; b) O. Meth-Cohn, A. S. Travis, *Chem. Britain* **1995**, *31*, 547 – 549.

[3] a) W. H. Perkin, *J. Chem. Soc. Trans.* **1879**, *35*, 717 – 732; b) W. H. Perkin, *J. Chem. Soc.* **1896**, *69*, 596 – 694; c) W. H. Perkin, *J. Soc. Arts* **1869**, *17*, 99.

[4] a) H. Caro, *Ber. dt. chem. Ges.* **1892**, *III*, *25*, 955 – 1105; b) S. Garfield, *Mauve*, Faber and Faber, London, **2000**; c) S. Garfield, *Lila*, Siedler, Berlin, **2001**; d) J. W. Stadelhofer, *Erdöl and Kohle, Erdgas, Petrochemie* **1988**, *41*, 353 – 358.

[5] a) A. W. Hofmann, *Liebigs Ann. Chem.* **1843**, *47*, 37 – 87, b) G. Kränzlein, *Angew. Chem.* **1935**, *48*, 1 – 3; c) E. Nölting, A. Lehne, *Anilinschwarz und seine Anwendungen in Färberei und Zeugdruck*, Julius Springer, **1904**; d) H. T. Bucherer, *Ber. dt. chem. Ges.* **1907**, *40*, 3412 – 3419; e) H. Bucherer, *Ber. dt. chem. Ges.* **1909**, *42*, 2931 – 2933.

[6] A. Cobenzl, *Österr. Chemiker-Ztg.* **1925**, *28*, 25 – 28.

[7] a) O. Fischer, E. Hepp, *Ber. dt. chem. Ges.* **1888**, *21*, 2617 – 2624; b) O. Fischer, E. Hepp *Ber. dt. chem. Ges.* **1893**, *26*, 1194 – 1196; c) O. Fischer, E. Hepp *Liebigs Ann. Chem.* **1892**, *272*, 306 – 354; d) R. Nietzki, *Ber. dt. chem. Ges.* **1896**, *29*, 1442 – 1446.

[8] a) A. G. Green, A. E. Woodhead, *J. Chem. Soc. Trans.* **1910**, *97*, 2388 – 2403; b) A. G. Green, A. E. Woodhead, *J. Chem. Soc. Trans.* **1912**, *101*, 1117 – 1123; c) A. G. Green, A. E. Woodhead, *Proceedings of the Chemical Society*, **1911**, *26*, 223; d) A. G. Green, S. Wolff, *Ber. dt. chem. Ges.* **1911**, *44*, 2570 – 2587; e) A. G. Green, S. Wolff, *Ber. dt. chem. Ges.* **1912**, *45*, 1955 – 1958; f) A. G. Green, S. Wolff, *Ber. dt. chem. Ges.* **1913**, *46*, 33 – 49.

[9] I. S. Ioffé, V. Ya. Soloveichik, *Zh. Ob. Khim*. **1938**, *9*, 129 – 143.
[10] J. S. Jaworski, M. K. Kalinowski, in *The Chemistry of Functional Groups*, Vol. 16, Part 2 (Ed.: Z. Rappoport), John Wiley, **2007**, pp. 871.
[11] O. Meth-Cohn, M. Smith, *J. Chem. Soc., Perkin Trans. 1* **1994**, 5 – 7.
[12] a) J. Seixas de Melo, S. Takato, M. Sousa, M. J. Melo, A. J. Parola, *Chem. Commun*. **2007**, 2624 – 2626; b) M. M. Sousa, M. J. Melo, A. J. Parola, P. J. T. Morris, H. S. Rzepa, J. S. Seixas de Molo, *Chem. Eur. J*. **2008**, *14*, 8507 – 8513.
[13] a) F. A. Neugebauer, S. Bamberger, W. R. Groh, *Tetrahedron Lett*. **1973**, *14*, 2247 – 2248; b) F. A. Neugebauer, S. Bamberger, W. R. Groh, *Chem. Ber*. **1975**, *108*, 2406 – 2415; c) G. N. R. Tripathi, R. H. Schuler, *Chem. Phys. Lett*. **1984**, *110*, 542 – 545; d) G. N. R. Tripathi, R. H. Schuler, *J. Chem. Phys*. **1987**, *86*, 3795 – 3800.
[14] a) Y. Ding, A. B. Padias, H. K. Hall, Jr., *J. Polymer Sci. A* **1999**, *37*, 2569 – 2579; b) H. Yang, A. J. Bard, *J. Electroanal. Chem*. **1992**, *339*, 423 – 449; c) V. Kertesz, G. J. Van Berkel, *J. Am. Soc. Mass Spectrom*. **2002**, *13*, 109 – 117; d) A. Petr, L. Dunsch, *J. Electroanal. Chem*. **1996**, *419*, 55 – 59; e) L. Dunsch, *Electroanal. Chem. Interfac. Electrochem*. **1975**, *61*, 61 – 80.
[15] a) G. Ciric-Marjanovic, M. Trchová, J. Stejskal, *Collect. Czech. Chem. Commun*. **2006**, *71*, 1407 – 1426; b) V. Kertesz, H. Deng, K. G. Asano, R. J. Hettich, G. J. Van Berkel, *Electroanalysis* **2002**, *14*, 1027 – 1030; c) R. A. Genetti, EP 272238, **1987**; d) A. J. Solodar, EP 261096, **1987**.
[16] a) K. Sasaki, M. Kaya, J. Yano, A. Kitani, A. Kunai, *J. Electroanal. Chem*. **1986**, *215*, 401 – 407; b) A. Kitani, J. Yano, A. Kunai, K. Sasaki, *J. Electroanal. Chem*. **1987**, *221*, 69 – 75; c) M. A. Cotarelo, F. Huerta, C. Quijada, F. Cases, J. L. Vázquez, *Synth. Met*. **2005**, *148*, 81 – 85.
[17] A. Zimmermann, U. Künzelmann, L. Dunsch, *Synth. Met*. **1998**, *93*, 17 – 25.
[18] a) J. F. Corbett, E. P. Gamson, *J. Chem. Soc., Perkin II* **1972**, 1531 – 1537; b) J. F. Corbett, *J. Soc. Dyers Colorists* **1972**, *88*, 438 – 443.
[19] I. Yu. Garipova, V. N. Silnikov, *Molecules* **2003**, *8*, 505 – 519.
[20] M. A. Rodriguez, S. D. Bunge, *Acta Crystallogr*. **2003**, *E59*, o1123–o1125.
[21] V. A. Naumov, M. A. Tafipol'skii, A. V. Naumov, S. Samdal, *Russ. J. Gen. Chem*. **2005**, *75*, 923 – 932.
[22] V. Galasso, *Chem. Phys. Lett*. **2008**, *457*, 250 – 253.
[23] a) I. Kulszewicz-Bajer, I. Rózalska, M. Kurylek, *New. J. Chem*. **2004**, *28*, 669 – 675; b) R. Lantz, P. Obellianne, FP 1094452, **1953**.