these derivatives have been studied. One of the degradation products of IV, namely, 3,6-dimethoxy-4-bromo-2,5-dimethylphenylacetic acid XIV, and one of the degradation products of XVIII, namely, the bis-acetic acid XXII, have been synthesized by independent methods starting with *p*-xylohydroquinone.

4. When *p*-xyloquinone reacts with sodiomalonic ester, the chief product is the cyclic isocoumaranone VIIA; this is accompanied by a small amount of the double isocoumaranone XX. These products are derived from *hydroquinones*, which are the primary products of the reaction; when the bromoquinone reacts with the enolate, the primary products are *quinones*.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

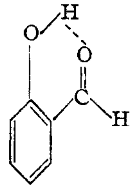
The Polymerization of the Free Radicals of the Wurster Dye Type: the Dimeric Resonance Bond

BY L. MICHAELIS AND S. GRANICK

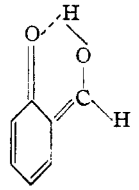
1. Introduction: the α- and β-Forms of Wurster Dyes

The univalent oxidation products of aromatic paradiamines, or Wurster dyes, exist in dilute solution as free radicals and have been, as such, exhaustively discussed in a preceding paper.[1] In solutions of higher concentration, or at low temperature, and also in the crystalline state, most of them form polymers which differ in color from the free radical. The free radicals represent what Piccard[2] had designated as the α-forms, the polymerized compounds are Piccard's β-forms. Whereas the radicals all show two distinct absorption bands in the visible spectrum, separated by about 300 Å., in various regions of the spectrum according to the degree of methylation of the amino groups, the β-forms are all deep green-blue in the crystalline state, macroscopically almost black; microscopically, observed through a polarizer, dichroitic, usually blue and yellow. Whether or not a radical polymerizes under proper conditions of concentration, temperature, or in the solid state, is easy to recognize by the difference in color whenever the radical is yellow or red, but this is practically impossible when the radical is blue, as in the tetramethyl compound. Piccard came to the conclusion that the unmethylated, the monomethyl, and the dimethyl compounds in the crystalline state are entirely in the β-form, the trimethyl and the tetramethyl compounds in the crystalline state are α-forms (which we can confirm only for the tetramethyl compound). Magnetic measurements for the crystalline state by Katz,[3] and Katz and Kuhn,[4] and furthermore by Rumpf and Trombe,[5] revealed that the crystalline form of the dimethyl compound (Wurster's red) is diamagnetic and consequently a polymer, whereas the crystalline form of the tetramethyl compound (Wurster's blue) is paramagnetic, and so a free radical.

No structural formula has been proposed as yet for the polymers. A closer investigation into the matter has shown that this process of polymerization of free radicals discloses a type of chemical bond which depends on a special type of resonance, combined with a kind of hydrogen bond. In general, a hydrogen bond is established by a shared proton. In addition, it has been recognized that a hydrogen bond may cause a resonance in a conjugated bond structure so that, in addition to the shared proton, a pair of electrons is shared. For instance, in salicylic aldehyde, a resonance will be established with the limiting structures I and I-a.



I



I-a

This scheme does not take into consideration that structure I is also in resonance with another structure in which the Kekulé structure of the ring is reversed, whereas in I-a no such reversal is possible. Very likely, the resonance of the two

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[1] L. Michaelis, M. P. Schubert and S. Granick, THIS JOURNAL, **61**, 1981 (1939).

[2] (a) J. Piccard, *Ann.*, **381**, 351 (1916); (b) J. Piccard, *Ber.*, **59**, 1438 (1926).

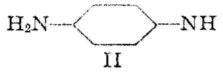
[3] H. Katz, *Z. Physik*, **87**, 238 (1933).

[4] R. Kuhn and H. Katz, *Z. angew. Chem.*, **46**, 478 (1933).

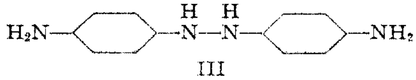
[5] P. Rumpf and F. Trombe, *J. Chim. Phys.*, **35**, 110 (1938).

Kekulé structures of I is more important than the resonance I ⟷ I-a and the structure I-a contributes but a small share to the real structure. This kind of hydrogen bond may essentially be considered as a shared proton, yet the proton is closer to the one oxygen than to the other. In quinhydrone, and in the compounds to be discussed in this paper, the situation is different. Here, the resonance plays an essential part. However, one may imagine the detailed structure of the quinhydrone crystal, one has to assume shared protons, and in addition a resonance between benzenoid and quinoid structures, and that the two limiting structures of the resonance system are perfectly equivalent. Although no experimental evidence is as yet available, it is safe to assume that in the average the proton is equidistant from the two oxygen atoms. The resonance is of the same type as in an organic dyestuff with equivalent resonance, say the anion of phenolindophenol, except for the fact that the two resonating moieties are held together here by a rigid atomic structure and cannot separate, whereas in quinhydrone they are held together only by the shared proton. Although all cases from a plain hydrogen bond, without resonance, up to those with equivalent resonance, may occur, the latter deserves especial attention and may be designated as a hydrogen bond involving equivalent resonance, or a quinhydrone bond, or a dimeric resonance bond. For the case of quinhydrone, this type of bond may still be considered as a special case of a hydrogen bond. In the compounds to be discussed in this paper it would no longer be adequate to speak of hydrogen bonds, the bonding essentially being due to an establishment of equivalent resonance.

In any case, in Wurster dyes the dimer is not merely the union of two semiquinone radicals established by simply pairing two odd electrons. If formula II is the free radical derived from *p*-phenylenediamine, one might imagine that the dimer is III, which is *p*,*p*'diaminodiphenylhydrazine. Such a compound apparently has never been described in the literature. Its structure would not account for the intense color of the polymerization product of the free radical.



II

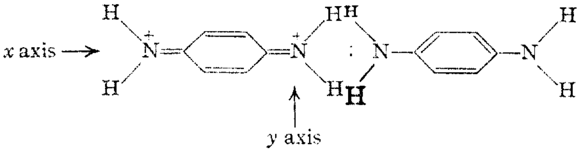


III

Now, both II and III are observed only as salts, and instead of II one has to write the cation IV.

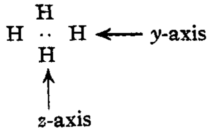
IV

The crystalline compound considered as a dimer, contains two halogen atoms according to analysis and so one has to add two protons to III. At first sight, one might add one proton to each NH_2 group of III. Hereby the color is not accounted for either. In building up polymers, the rings may be imagined either to lie flat upon each other, or all in one plane. The writers have tentatively suggested the first possibility for quinhydrone in order to account for the fact that duroquinone does not form any quinhydrone. However this may be, for the polymers of Wurster dyes it can be safely ruled out that the rings should lie flat upon each other, because here the substitution of all hydrogen atoms at the ring does not at all inhibit polymerization. On the other hand, the substitution of all four hydrogen atoms in the middle of formula *V* entirely prevents any polymerization of the radical (in Wurster's blue). A highly resonating, meriquinone-like structure can be established by attaching the two protons to the inner two NH groups of III, and rearranging the electronic configuration. Such a suggestion, of course, has to be confirmed by X-ray studies. If one tries to pursue this suggestion, the two rings lie in the same plane, as shown in formula V.



V

This structure consists of one doubly charged cation of quinone diimine and one uncharged phenylenediamine. In the diiminium cation, the double bond of the N toward the ring forces the two H nuclei to lie in the plane of the ring. In the diamine there is no such restriction, and the two H's of the NH_2 group will adapt themselves so as to produce the least strain. One H (in heavy type) will lie in front of the plane of the paper, the other (in small type) behind the plane of the paper. These four inner H nuclei lie at the corners of a square, perpendicular to the plane of the rings. On making a cross section, showing the *y*-*z* plane in the center of V, one arrives at the picture VI. The double dot in the middle represents a pair of electrons lying in the space between the two N nuclei and around it there are four H nuclei, of which two, lying on the *y*-axis, may be said to belong to the diiminium cation, and two, lying on the *z*-axis, belong to the diamine. Structure V is in resonance with another, with right and left sides exchanged. Then, without shifting the H nuclei of VI, one may say that now the two H's on the *y*-axis belong to the diamine, those on the *z*-axis to the diiminium cation. The electron pair shown as two dots in the center of VI and in V, may be said to belong alternately to the one and to the other N. The four hydrogen atoms are somewhat closely packed in this structure, but the resonance energy of the whole structure may overcome this strain. Furthermore one has to consider that the square of the four H nuclei represents just an average position, but not necessarily the most probable position at any given instant of time.



VI

As has been stated already, substitution of all the four inner H atoms in formula V prevents entirely any polymerization. One has now to consider the intermediate case when only two of the four H's in VI are substituted by methyl groups. Such a case arises when a Wurster salt is made of symmetrical diamino-*p*-phenylenediamine, or of trimethyl-*p*-phenylenediamine. It is certain that in such a case the space between the four atoms or atom groups is more restricted than in the unsubstituted compound, and the building up of a dimer would require more strain than in the original case. Whether this strain will be sufficient to prevent entirely any dimerization, or whether a bond, although a weaker one, is still formed, is difficult to foresee. Experiment shows that the bond is formed indeed, but that it is a much weaker one. The weakness of the bond can be inferred from the instability of these compounds in the crystalline state. They are well-crystallized compounds when freshly prepared but rapidly undergo irreversible changes, becoming discolored and deliquescent.

2. The All-or-none Law for the Magnetic Behavior in the Crystalline State

At this point a very interesting problem arises. Whenever a dimeric bond in a β-form of a Wurster dye is weak, one may expect that an equilibrium between the monomer and the dimer is established. This is true in fact for the dissolved state. The degree of association increases considerably on lowering the temperature, and that in a reversible way. However, magnetic studies have revealed that, in the crystalline state, there is never a mixture of the paramagnetic radical and the diamagnetic polymer. Wurster's blue is, in the crystalline state, to 100% a free radical, and forms as such a perfectly stable compound as a perchlorate, even when kept over a period of months. All the other compounds are entirely polymerized and diamagnetic, even if the dimeric bond is so weak that rapid irreversible decomposition of the crystals occurs. This striking fact can be accounted for by assuming that no molecular collisions resulting in chemical interaction can occur in the solid state, and except for atomic vibrations only electrons are free to move. In the crystalline state only resonance, but no chemical reaction, occurs. Since resonance between limiting structures having a different number of unpaired electrons is forbidden, the compound in the crystalline state has to stay entirely either fully paramagnetic or fully diamagnetic, whichever represents the state of lower energy content in the particular case. This behavior resembles the behavior of heavy metal complex compounds in which usually the magnetic state is either one of the two possible extremes, or the other, but no intermediate state occurs because a resonance among those two does not occur.[6] If the strength of the dimeric bond is extremely weak or absent (in Wurster's blue), the crystalline compound is all free radical. As the dimeric bond becomes stronger, the compound will be entirely diamagnetic, even if a very perishable molecule should result. The difference in the behavior of these compounds and heavy metal complexes is that the "all-or-none" law for the metal complexes usually holds also in the dissolved state, whereas for the Wurster dyes it holds only for the crystalline state for easily understandable reasons.

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(6) Linus Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 108.

3. Formation of High Polymers

So far only dimerization has been considered. It is, however, quite possible and probable that the resonance may stretch across the whole length of the crystal and result in the formation of a high polymer whenever the two outer amino groups of formula V are not completely methylated. Since each benzenoid ring may be imagined to resonate among two Kekulé structures at least, the number of limiting states is largely increased for a high-polymer as compared with a dimer. In Wurster's red, such a polymer would not be possible, and only dimers are imaginable. For the other compounds, one monomer may dimerize, in rapid succession, now with its right-hand neighbor, now with the left-hand one. This would considerably increase the resonance energy by the increase of the number of limiting states in equivalent resonance with each other.

The following phenomenon can be considered as an evidence for this hypothesis. The compound $Me_2NC_6H_4NHCH_3$ can form only a dimer, because no bond can be established with Me_2N. However, $MeHNC_6H_4NHMe$ is not prevented from forming higher polymers. In both cases the crystalline, diamagnetic Wurster salt is much more unstable than the one derived from H_2N-$C_6H_4NH_2$, but whereas the one able to form a high polymer is stable enough to allow magnetic measurements before decomposition occurs, the other, which can form only a dimer, is so utterly unstable that disintegration is very far progressed before any magnetic measurement can be carried out.

In solution a chemical equilibrium between the radical and the quinonoid monomer, the benzenoid monomer, and the polymer is established. All of the equilibrium constants involved in such a complicated equilibrium have been previously measured for the case of phenanthrene quinonesulfonate.[7] The degree of dimerization for one particular compound depends on concentration, temperature and solvent. A radical has the chance of combining either with the solvent or with another radical. Since aromatic molecules combine more readily with alcohol than with water, it is understandable why dimerization is always stronger in water than in alcohol. It is also understandable why dimerization in water is stronger in the diamino-durene compound than in the diamino-benzene compound. This competitive phenomenon reveals the weakness of the dimeric bond which may be considered as varying in strength within the same range, according to conditions, as the strength of a regular hydrogen bond may vary.

All of these polymers are on the same oxidation level as a semiquinone radical. For a particular case, that of arabinoflavin, Kuhn and Ströbele[8] have claimed the existence of various crystalline polymers on the oxidation level either of a semiquinone or on a level between a quinone and a semiquinone, or between a hydroquinone and a semiquinone. There is no cogent evidence for an analogous behavior of Wurster dyes as yet. A reinvestigation of the matter for the flavin dyes might be worth while.

To conclude this discussion it may be pointed out that a mechanism of polymerization has been accounted for very different from that encountered in the formation of rubber or plastics. The bonds considered here are considerably weaker and can be classified among those usually attributed to "residual valences." This type of polymerization differs also essentially from that described by Rabinowitch and Epstein[9] for cationic dyestuffs such as methylene blue. A property common to the latter type and the one presented in this paper is the fact that polymerization is stronger in water than in alcohol.

Experimental Part

1. Color Test in Solution.—A rather concentrated solution of the hydrochloride of the diamine in almost saturated sodium chloride solution, which allows the temperature to be lowered sufficiently below 0°, is partially oxidized by addition of aqueous bromine solution. Table I shows the reversible change of color on varying the temperature from -12 to $+25°$. The color depends somewhat on the concentration of the semiquinone according to the amount of bromine added. The table indicates the state for a sufficiently dilute solution. At higher concentration, at room temperature, a color intermediate between that indicated for the two temperatures may appear. The polymerization partially occurring even at 25° differs in degree for the various compounds. It is particularly high for *p*-diaminodurene, showing that the methyl groups at the benzene ring do not at all interfere with polymerization. It can be concluded from the table that all radicals of yellow or red color polymerize at low temperature and that for those radicals of blue color no change of color can be recognized, making it impossible to decide whether or not polymerization occurs. Even in

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[7] L. Michaelis and M. P. Schubert, This Journal, **59**, 133 (1937).

[8] R. Kuhn and R. Ströbele, *Ber.*, **70**, 1113 (1937).

[9] E. Rabinowitch and L. F. Epstein, This Journal, **63**, 69 (1941).

TABLE I

POLYMERIZATION, EVIDENCED BY CHANGE OF COLOR WITH CHANGE OF TEMPERATURE

In $R_1(C_6H_3Me)R_2$, the methyl group of C_6H_3Me is in *ortho* position to R_2. Solvent: acetate buffer, *p*H 4.6, almost saturated with NaCl.

Parent substance	Color after addition of bromine, at room temperature	Color, at −12°
$H_2NC_6H_4NH_2$	Yellow	Green
$H_2NC_6H_3MeNH_2$	Yellow	Green
$H_2N(Me_2C_6Me_2)NH_2$	Yellow	Green
$H_2N(C_6H_3SO_3H)NH_2$	Yellow, very unstable	Green, rapidly changing irreversibly
$H_2N(C_6H_3Cl)NH_2$	Yellow, unstable	Green, rapidly fading
$H_2NC_6H_4NHMe$	Pink	Green
$MeHNC_6H_4NHMe$	Orange-red	Greenish-brown
$MeHN(Me_2C_6Me_2)NHMe$[a]	No color	No color
$H_2NC_6H_4NMe_2$	Red	Dark brownish-violet
$Me_2NC_6H_4NHMe$	Deep purple red	More brownish red[b]
$Me_2NC_6H_4NMe_2$	Deep blue	Deep blue (no change)
$(HOOCCH_2)_2NC_6H_4N(CH_2COOH)_2$	Deep blue	Deep blue (no change)

[a] Here the solvent is without NaCl, to avoid precipitation. [b] The change of color is slight but under proper conditions of concentration, distinct and reversible.

such radicals which are unstable compounds themselves due to their own, "direct" instability, in consequence of steric hindrance of the resonance,[1] one can usually judge the occurrence of dimerization fairly readily.

The degree of polymerization depends also upon the solvent, as has been discussed before.

2. **Preparation of Crystalline Compounds.**—The preparation of the bromides has been described by Willstätter and Piccard.[2,10] These authors did not succeed in obtaining a reproducible bromide of Wurster's blue. They prepared an analogous compound by oxidizing tetramethyl-*p*-phenylenediamine with nitrous oxide. Obviously such preparations are of variable composition and color and are not pure substances. Later, Katz[3] prepared a more stable perchlorate. We prepared bromides and perchlorates according to the particular case. No satisfactory stable iodides could be obtained. For one particular case the peculiar behavior of the iodide will be presently described. In a few cases both bromides and perchlorates of the same cation could be prepared with equal ease, and in these cases it was obvious that neither the color nor the magnetic behavior depends on the nature of the anion. All preparations were analyzed for the anionic constituent and most of them for their level of oxidation by measuring the amount of hydrogen taken up with colloidal palladium as catalyst using the Warburg method. The stability of the crystals varies greatly, the perchlorates being more stable than the bromides. Some are stable for months (Wurster's blue perchlorate), others become deliquescent or resinous in time, some of them finally form crystalline compounds usually of pale color, which are obviously the result of irreversible reactions. Sometimes this change was so slow that all investigations could be carried out, in other cases (trimethyl-*p*-phenylenediamine iodide) the well-formed intensely colored crystals obtained originally changed so fast that no accurate magnetic measurements with the original compound were possible. The degree of stability according to their structure is accounted for in the preceding discussion.

The following nomenclature of the crystalline compounds will be used. It is in agreement with, and an extension of, that used previously by the authors.[11] The substances will all be designated by the name of the diamine from which they are derived. If the compound is on the oxidation level of a semiquinone but no commitment is made as to whether it is a free radical or a polymer, the prefix σ is used. If the crystalline state is recognized as a free radical, the prefix *s* is added; if it is decidedly a polymer the prefix π is used. No distinction is made as to whether the compound is a true dimer or a higher polymer, because there is only indirect experimental evidence as yet for this distinction.

The oxidation of the diamine was always carried out with bromine (except for one case with iodine). No more than seven-tenths of the equivalent amount of bromine was added in order to avoid over-oxidation. It is necessary to bear in mind that the two steps of oxidation overlap and any attempt to obtain what may seem a theoretical yield results in impurity of the preparation.

1. **π-1,4-Diaminobenzene Bromide** $(H_2NC_6H_4NH_2Br)_n$.—Preparation according to Piccard[2a]: 2.2 g. of *p*-phenylenediamine in 20 cc. of acetic acid + 40 cc. of absolute ethanol, cooled in ice–salt mixture, 0.54 cc. of bromine dissolved in 12 cc. of acetic acid + 40 cc. of ethanol added slowly, filtered, washed with alcohol and anhydrous ether. A perchlorate was prepared also on a small scale. The crystals of both the bromide and the perchlorate are too intensely colored to permit observation of their optical properties.

2. **π-1,4-Bis-(methylamino)-benzene Perchlorate** $(MeHNC_6H_4NMeH{\cdot}ClO_4)_n$.—*p*-Phenylenediamine was tosylated, and then methylated with dimethyl sulfate, and the tosyl groups removed as described previously.[1] The methylation of the tosylated compound also proceeds readily with diazomethane.

3.64 g. of 1,4-bis-(methylamino)-benzene dihydrochloride was dissolved in 80 cc. of saturated aqueous solution of sodium perchlorate and cooled to −10°. Then 67 cc. of 0.185 *N* aqueous bromine solution was added dropwise with stirring. It was filtered, washed with ice cold water, pressed dry, washed three times with anhydrous ether and

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[10] R. Willstätter and J. Piccard, *Ber.*, **41**, 19458 (1908).

[11] S. Granick, L. Michaelis and M. P. Schubert, THIS JOURNAL, **62**, 1802 (1940).

rapidly dried *in vacuo*. Washing with methanol was avoided because of the great solubility of this preparation in it; yield 1.3 g.; density 1.450 at 20°. Calculated for Cl, 15.07; found, 15.12. After five days in the vacuum desiccator the intensely colored crystals had turned to a red-brown resin. The fresh crystals are dichroitic, blue and yellow.

3. (a) **π-1-Amino-4-dimethylaminobenzene Bromide ($(H_2NC_6H_4NMe_2Br)_n$) (Wurster's Red).**—6.9 g. of the dihydrochloride of the parent diamine was converted into the free base with sodium hydroxide and extracted with ether. The ether was dried with anhydrous sodium sulfate and distilled off. The base was taken up in 80 cc. of methanol + 40 cc. of acetic acid, the solution cooled to −10° and 0.60 cc. of bromine dissolved in 12 cc. of acetic acid + 40 cc. of methanol added dropwise. The crystals were filtered off, washed with cold methanol–acetic acid, methanol and dry ether, and dried *in vacuo;* bromine calculated, 37.0; found, 37.1.

(b) **Perchlorate of the Same Base.**—Ten grams of *p*-dimethylamino-aniline hydrochloride was dissolved in 100 cc. of H_2O + 100 cc. of saturated aqueous sodium perchlorate solution. There was added without cooling, but with stirring, 250 cc. of aqueous bromine solution, 0.147 *N* (about 0.64 equivalents). The preparation was filtered, washed with ice cold water, twice with very little methanol, and abundantly with dry ether; chlorine, calculated, 15.06; found, 14.74.

When the long axis of the rod-shaped crystal is parallel to the electric vector of the polarized beam, its absorption is very intense, very thin crystals appearing sky-blue. The absorption remains the same even though the crystal is rotated about its long axis, still remaining parallel to the electric vector. When the long axis is perpendicular to the electric vector, the color is light emerald green. This suggests that the molecules lie with the plane of the benzene rings perpendicular to the long axis of the rods, and alternately strings of the benzene rings probably as dimeric units are parallel and perpendicular to the end face of the rod.

4. (a) **π-1-Dimethylamino-4-methylaminophenylene Bromide** ($(Me_2NC_6H_4NHMeBr)_n$).—1-Dimethylamino-4-aminobenzene was tosylated and then methylated. Methylation with dimethyl sulfate, as previously,[1] was ineffective when used on a preparation of somewhat larger scale, but diazomethane reacted smoothly. The reaction mixture was permitted to stand overnight to ensure complete methylation. After hydrolyzing off the tosyl group,[1] the free base was prepared; 4 g. of it was dissolved in 30 cc. of acetone + 40 cc. of glacial acetic acid + 350 cc. of ether, and 2.1 g. of bromine dissolved in 100 cc. of ether was added slowly in the cold. The crystals were filtered, washed with ether and dried *in vacuo*. Quite fresh, they are purple needles; the finished product is brown, not very intensely colored, very hygroscopic. The solution of the freshly prepared crystals shows only faintly the characteristic spectrum of the trimethyl radical. Somewhat older preparations show no trace of it. Attempts to prepare a more stable perchlorate were not more successful.

(b) **Iodide of the Same Base.**—The solid free base, prepared from 4.93 g. of the dihydrochloride of $Me_2HC_6H_4NHMe$ by means of sodium hydroxide and extraction with ether was dissolved in 50 cc. of methanol, cooled to −10°, then 2 g. of iodine dissolved in 60 cc. of methanol slowly added. The crystalline precipitate was washed with dry ether; yield 2.2 grams of blue-black crystals, turning light-emerald green after one hour. They suffer no loss of weight hereby when kept in the desiccator; however, the secondary green crystals are very hygroscopic in the air. Analysis, the green form, on the third day: iodine, 45.4, 46.0 (calculated, 46.3).

An aqueous solution of the secondary, green crystals shows distinctly a certain amount of the trimethyl free-radical with its characteristically located two absorption bands in addition to a more diffuse absorption.

5. **s-1,4-Bis-(dimethylamino)-benzene Perchlorate (Wurster's Blue)** $Me_2NC_6H_4NMe_2ClO_4$ decidedly monomeric, hence the prefix *s*).—Four grams of tetramethyl-*p*-phenylenediamine hydrochloride was dissolved in a solution of 70 cc. of water + 115 cc. of methanol containing 50 g. of sodium perchlorate. It was cooled to −10°; 127 cc. of 0.126 *N* aqueous bromine solution was added dropwise. The crystals were filtered, washed several times with small portions of ice-cold methanol, then abundantly with dry ether; yield 3.4 g.; density, 1.398. The crystals have a brown metallic luster. Very thin needles, observed under the polarizing microscope when the long axis is parallel to the electric vector, absorb very intensely and are steel-gray-blue; when perpendicular to the vector they are indigo blue. The solutions show the characteristic bands of the Wurster's blue free radical. The crystals are not hygroscopic and did not change in any of their observed properties over months.

6. **π-1,4-Diamino-2,3,5,6-tetramethylbenzene Perchlorate** ($(H_2N(Me_2C_6Me_2)NH_2ClO_4)_n$).—One gram of *p*-diaminodurene bihydrochloride was dissolved in 20 cc. of water; to this was added 7 cc. of water containing 4 g. of sodium perchlorate, and then dropwise within three minutes 20 cc. of 0.158 *N* aqueous bromine solution was added. Then there was added 3 cc. of water containing 1.5 g. of anhydrous sodium acetate (to increase *p*H for optimum conditions), and the mixture cooled and filtered. It was twice washed with very little ice-cold methanol and abundantly with dry ether and dried *in vacuo;* Cl, calculated, 13.45; found, 13.33. The crystals are dark green; very thin crystals microscopically observed in polarized light have symmetrical extinction and are deep blue-green along one optic axis and yellow along the other.

Magnetic Measurements

The details are presented here for one example, Wurster's blue perchlorate (Compound 5 of the preceding list). The micro or deflection method, a modification of the Gouy method, was used as described previously.[12] The length of each compartment of the double vessel was 11 cm., the inner diameter about 0.5 cm.; the upper compartment had a capacity from the septum up to a mark quite close to the upper brim of 1.918 cc. The pole gap was usually in the neighborhood of

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(12) L. Michaelis, This Journal, 63, 2446 (1941).

1.3 cm. For the particular case described here in detail the deflection, Δ, with water in the upper compartment, measured at 7 amperes and recalculated for 10 amperes, was −159 lines; with air in the upper compartment, measured at 2.5 amperes and recalculated for 10 amperes, Δ was +2008 lines. The difference, 2147 lines, corresponds to a change in volume susceptibility amounting to 0.749×10^{-6} (-0.720×10^{-6} for water, $+ 0.029 \times 10^{-6}$ for air). Consequently one line of deflection at 10 amperes corresponds to an increment of volume susceptibility amounting to 3.47×10^{-10} c. g. s.

Finely powdered crystals of Wurster's blue perchlorate are filled into the upper compartment; 0.5912 g. is contained in 1.918 cc., hence, 1 cc. of the packing contains 0.308 g. of substance. Its density is 1.398. The 0.308 g. occupies a volume of 0.22 cc., and there is 0.78 cc. of air in 1 cc. of the packing. Δ, measured at 1.582 amperes and recalculated for 10 amperes, is +5780 lines (average of 8 readings deviating from the average at the most ±2%). Δ for air alone is +2008 lines, so the difference of the susceptibility of 1 cc. of the packing and of 1 cc. of air is $+(5780 - 2008) \times 3.47 \times 10^{-10} = 1.31 \times 10^{-6}$. The susceptibility is due to 0.308 g. (or 0.22 cc.) of the crystals and 0.78 cc. of air. The contribution of this 0.78 cc. of air is $+0.024 \times 10^{-6}$; hence, the susceptibility due to 0.308 g. of the crystals is $+1.286 \times 10^{-6}$, consequently χ (per gram) $= +4.18 \times 10^{-6}$ and, taking the molecular weight = 263, the result is $10^6 \chi_{\text{mol.}} = +1100$. This is the resultant of both the diamagnetic contribution of the molecule, which, according to the Pascal method, is calculated $= -138 \pm 16$ per mole, and of the paramagnetic contribution due to the electron spin (the ± in the Pascal correction will be explained later). So, the paramagnetic molar susceptibility of the substance, due to the electron spin, is $(1238 \pm 16) \cdot 10^{-6}$. The measurement was made at 24°; calcd. using the simple, unmodified Curie law, for 24°, 1260×10^{-6} which corresponds to a moment of $\sqrt{3}$ Bohr magnetons. The agreement is excellent, giving evidence at the same time of the validity of the unmodified Curie law.

The results obtained with various crystalline compounds are given in Tables II and III. The molar susceptibility is that of the solid substance. Correction for the air space between the solid particles of the filling has been applied as shown in the preceding example. Susceptibility is referred to one equivalent of the substance, that is to say, to one mole if it be a free radical, or to half a mole if it be a dimer.

As regards the susceptibilities of the diamagnetic compounds (Table II) it can be seen directly that there is no gradual change from the fully diamagnetic state (χ about -100×10^{-6}) to the fully paramagnetic state of the tetramethyl compound (Table III, $\chi = +1260 \times 10^{-6}$). The limits of error indicated for the observed values are estimated according to experience with this method on solid diamagnetic compounds of known susceptibility under equal experimental conditions and in consideration of individual conditions. The limits of error indicated for the calculated values have the following significance. The value is calculated for the corresponding diamine, using Pascal's atomic increments and the structural correction for a benzene ring. Now, on comparing the molar susceptibilities of hydroquinone and of quinone determined with the same method, the observed value, −66, for hydroquinone, turns out to agree reasonably well with the calculated one, −64, but the observed value for quinone, −34.5, is distinctly smaller than the calculated one, even with correction for two doubly bonded oxygen atoms, −58. The difference of hydroquinone and quinone was 32. It is not known how a molecule on the oxidation level of a semiquinone might behave. It may have an intermediary state. So, the limits of error have been taken such that they compass the value for the diamine, and that for the diimine, which is supposed to differ from the former as much as quinhydrone differs from quinone.[13]

As regards the exceptional case of Wurster's blue perchlorate there is every evidence for a high purity of this substance, and the perfect stability observed now over a period of three months makes this substance perhaps the best representative of a free radical in the solid state. Its molar susceptibility (average of observations stretching over a period of twenty-five days with the same preparation) corrected for the diamagnetic contribution and referred to electron spin alone, equals within the limits of error, 1260×10^{-5} at

(13) In an actual experiment, the susceptibility for one equivalent weight of quinhydrone was found -63.5×10^{-6}, very close to that of hydroquinone, and distinctly more diamagnetic than quinone. One cannot be sure that this behavior is the same in the compounds of this paper. The limit of error was estimated in consideration of this uncertainty.

TABLE II

THE DIAMAGNETIC COMPOUNDS

Parent substance	Salt	Halogen content, % Calcd.	Halogen content, % Found	H_2 adsorbed catalytically, % o that expected for a semiquinone[a]	Susceptibility (per monomeric mole) Obsd. per equiv., $\chi \cdot 10^6$	Susceptibility (per monomeric mole) Calcd.
(1) $NH_2C_6H_4NH_2$	Bromide	41.5	41.4	89.2	-109 ± 10	-98 ± 16
(2) $NH_2(C_6Me_4)NH_2$	Perchlorate	13.45	13.33	79	-129 ± 10	-138 ± 16
(3) $MeNHC_6H_4NHMe$	Perchlorate	15.07	15.12	70	-96 ± 25[b]	-114 ± 16
(4) $H_2NC_6H_4NMe_2$	Perchlorate	15.06	14.74	102	-143 ± 10	-114 ± 16
(5) $H_2NC_6H_4NMe_2$	Bromide	37.0	37.1		-102 ± 10	-106 ± 16
(6) $MeHC_6H_4NMe_2$	Bromide	Too unstable			-100 ± 30[c]	
(7) $MeHC_6H_4NMe_2$	Iodide	46.3	45.4		-120 ± 30[d]	-133 ± 16

[a] These analyses with the Warburg apparatus, with colloidal palladium as catalyst, were made on somewhat aged preparations. In all cases where there is less than 100% of the expected amount there was distinctly a small insoluble residue indicating a slight decomposition. [b] The preparation, green needles, dichroitic blue and yellow when quite fresh remain so for a certain time, but become, in the closed vessel, deliquescent and resinous, brown, after a day, the volume of the content has then shrunk considerably. This property causes a larger error in calculation of volume susceptibility. [c] The freshly prepared substance, crystalline, dichroitic, when filled into the vessel became deliquescent and shrunk during the measurement, causing a larger error in value of volume susceptibility. [d] The freshly prepared substance, blue-black, well-crystallized, rapidly changed into light emerald-green crystals and remained so for days when kept *in vacuo*, but was very hygroscopic in the air. Its aqueous solution still contains some of the free trimethyl radical according to its absorption spectrum, in addition to other material with diffuse absorption. There is some irreversible rearrangement without essential change of the iodine content.

TABLE III

THE PARAMAGNETIC COMPOUND (WURSTER'S BLUE ONLY)

			Same preparation	
Parent substance		(8) $Me_2NC_6H_4NMe_2$	After 18 days	After 25 days
Salt		Perchlorate	....	....
Halogen content, %	Calcd.	13.45	....	....
	Found	13.5	....	....
Level of oxidation, %		97	....	....
Suscep. per mole obsd. at 22° × 10^6		+1114	+1120	+1100
Diamag. cor. acc. to Pascal × 10^6		-138 ± 16	....	....
Due to electron spin	Paramag. suscep. × 10^6	+1252	$+1258 \pm 16$	+1238
	Moment, μ, (Bohr magnetons)	1.73 ± 0.01	....	....

22°, corresponding to a magnetic dipole moment of 1.73 Bohr magnetons, the spin moment of one unpaired electron on the assumption that the Curie law $= 2.84 \sqrt{\chi T}$ is strictly valid.

Summary

Wurster dyes, which are free semiquinone radicals when in dilute solution, polymerize at low temperature, or at higher concentration, and especially in the crystalline state in which they can be obtained as bromides or perchlorates. Only the radical derived from tetramethyl-*p*-phenylenediamine (Wurster blue) does not polymerize and remains a very stable free radical even in the solid state. In solution there is equilibrium established for the monomeric and polymeric form. In the solid state however there is an all-or-none law: the crystals are completely polymerized and diamagnetic with the susceptibility expected for a regular organic molecule, or they are entirely in the free radical state and paramagnetic with the susceptibility as expected for an organic molecule with one odd electron. The latter case is true only for Wurster blue. The polymerization may consist either in forming dimers or higher polymers. Polymerization can occur when the diamine from which the compound is derived has at least one unsubstituted hydrogen atom at each of its two amino groups.

The dimerized (or polymerized) molecule is a structure resonating between a compound of one molecule of the diamine and one molecule of the (doubly positively charged) diiminium ion. The resonance consists in an alternately occurring exchange of the quinonoid and benzenoid structures of the two rings, which lie in the same plane. The quinone–benzene resonance is synchronized with an exchange of an electron pair between the two adjacent N atoms. The four atoms attached to these two N atoms lie in a plane perpendicular to that of the benzene rings. If these four atoms are not all H atoms but in part CH_3 groups, steric hindrance weakens this bond and makes the compound unstable. If all four H's are substituted by CH_3, no bond can be established and the compound remains a monomeric free radical even in the solid state.

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A Differential Moving Boundary Method for Transference Numbers

BY L. G. LONGSWORTH

Introduction.—A boundary between two different concentrations, c' and c'', of the same electrolyte, such as 0.2 N LiCl:0.5 N LiCl, for example, will move, on passage of an electric current, if the corresponding cation transference numbers, T' and T'', are different. The relation[1] connecting these variables with the displacement, Δv, of the boundary and the number, f, of coulombs passed is

$$T'' - T' = \Delta v(c'' - c')f/F \qquad (1)$$

or simply $\Delta T = \Delta V \Delta c$ if ΔV is the displacement per faraday, F. In this expression c is in equivalents per milliliter if ΔV is in milliliters.

These "concentration" boundaries have been studied theoretically by Kohlrausch,[2] Planck,[3] Miller[4] and von Laue[5] and experimentally by Smith.[6] The latter investigation followed the boundary movement with the aid of the simple optical arrangements then in use in this field. As long as a boundary remains uniformly sharp, as do those characteristic of the direct moving boundary method, its movement may be followed accurately without difficulty. At a concentration boundary, on the other hand, the forces counteracting diffusion are relatively weak and, in general, an initially sharp boundary soon becomes indistinct due to the spreading effect of diffusion. By passing sufficiently heavy currents, Smith was able to keep his boundaries visibly sharp during the period of observation and the displacements he observed were, in most instances, in the proper direction and of the right order of magnitude. Under the conditions of his experiments, however, errors due to convection may have been introduced. In the present investigation this difficulty has been overcome by recording photographically, with the aid of the schlieren scanning method,[7] both the magnitude and the position of the refractive index gradients in the boundaries. Owing to the close proportionality[8] of the refractive index to the salt concentration the electrolyte distribution may be computed readily from the refractive index gradient curve. As will be shown below, the position of a concentration boundary whose gradients may be spread over several centimeters can be defined with almost the same precision as one in which the change occurs within a small fraction of a millimeter. It is the purpose of this paper to show that this method may be used to determine, with accuracy, the change of the transference number with the concentration and that it is of utility in cases in which the direct moving boundary method is difficult to apply.

Experimental

The solutions were prepared from reagent grade chemicals and their concentrations were checked conductometrically. The quantity of electricity was computed from observations of the time and current. Readings of the latter, determined as the potential drop across a known resistance, were made at intervals during the experiment with a precision of 0.1%. In contrast with the cell containing a regular moving boundary, the resistance of the cell with concentration boundaries changes but slightly during an experiment. These changes, due to polarization of the cell and the B batteries that supply the current, are quite regular and amount to only 1 or 2%. Consequently the averaged value for the current has essentially the same precision as the individual observations and the use of a constant current device is unnecessary. With the differential method described here the concentrations and electrical quantities do not need to be known as precisely as in the case of the direct moving boundary method and the procedure just outlined is adequate for the determination of transference number differences with a precision of $\pm 1 \times 10^{-4}$.

The cell in which the boundaries are formed and observed

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[1] For a derivation of this relation, together with a discussion of the various types of moving boundaries, see MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, N. Y., 1939, p. 87.

[2] Kohlrausch, *Ann. Physik*, **62**, 209 (1897).

[3] Planck, *ibid.*, **40**, 561 (1890).

[4] Miller, *Z. physik. Chem.*, **69**, 436 (1909).

[5] von Laue, *Z. anorg. Chem.*, **93**, 329 (1915).

[6] Smith, *Bur. Standards J. Research*, **6**, 917 (1931).

[7] Longsworth, THIS JOURNAL, **61**, 529 (1939).

[8] Lamm, *Nova Acta Regiae Soc. Sci. Upsaliensis*, Ser. IV, **10**, No. 6 (see p. 64) (1937).