4-Chloro-AMS.—A solution of 154.5 g. of *p*-chloroacetophenone in 700 ml. of ether was added slowly with cooling and stirring to 1.2 moles of methylmagnesium iodide in 1200 ml. of ether. The crude tertiary alcohol obtained as a product was dehydrated at 15 mm. pressure by heating with 2 g. of sodium acid sulfate. Rectification gave 110 g. (71% yield) of the desired AMS, b. p. (10 mm.) 86°, d^{25}_{25} 1.073, n^{25}D 1.5540.

Anal. Calcd. for C_9H_9Cl: Cl, 23.23. Found: Cl, 23.09. 22.90.

2,3-Dimethoxy-AMS.—A solution of 77 g. (0.4 mole) of methyl 2,3-dimethoxybenzoate in 300 ml. of ether was reacted with 0.8 mole of methylmagnesium iodide in 700 ml. of ether to obtain the tertiary alcohol which was dehydrated by slow distillation at normal pressure from 5 g. of phosphorus pentoxide. The resulting AMS was obtained in 28.5 g. (42% yield); b. p. (3 mm.) 78°, d^{25}_{25} 1.026, n^{30}D 1.5237.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.89, 73,80; H, 7.89, 7.76.

3,5-Dibromo-AMS.—A solution of 200 g. of anthranilic acid in 2 l. of methanol was saturated with hydrogen chloride and refluxed for twenty hours. The ester solution was treated with 160 ml. of bromine in 400 ml. of concentrated aqueous potassium bromide maintaining the temperature at 25–30°. After three hours the dibromo ester (376 g., 83% yield) was precipitated in 25 liters of water. A solution of 154.5 g. of the ester in a mixture of 50 ml. of water, 50 ml. of acetic acid and 300 ml. of 95% ethanol was heated to boiling and treated with 85 g. of isopropyl nitrite added slowly over a period of three hours. The deaminated acid (88 g., 62% yield) was precipitated by pouring into 2 liters of water. It was esterified by saturating the solution in 1 l. of methanol with hydrogen chloride and refluxing for eight hours. The ester (86.5 g., 94% yield) separated on cooling as long white needles, m. p. 62–63°.

A solution of 99 g. (0.34 mole) of methyl 3,5-dibromobenzoate in 300 ml. of benzene was reacted with 0.7 mole of methylmagnesium bromide in 650 ml. of ether. Distillation of the resulting tertiary alcohol from 4 g. of phosphorus pentoxide at 20 mm. pressure and rectification of the product gave 65 g. (70.3%) yield of the desired AMS; b. p. (3 mm.) 98°, d^{25}_{25} 1.750, n^{30}D 1.6097.

Anal. Calcd. for $C_9H_8Br_2$: C, 39.16; H, 2.92. Found: C, 39.33, 39.40; H, 2.78, 2.85.

Polymerization Experiments.—Each monomer was copolymerized with butadiene on a small scale (2.5 g. of AMS) to approximate the rate, then on a larger scale (50 g. or more of AMS) to compound, cure and test the rubber. The polymerization recipe was: butadiene 75 parts, AMS 25 parts, soap 5 parts, OEI (a mercaptan mixture from the Naugatuck Chemical Company) 0.6 part, a peroxide salt 0.3 part, water 175 parts by weight. The polymerizations were done in small sealed Pyrex tubes or quart size soda water bottles immersed and rotated in a thermostat bath. The conditions and results are summarized in Tables I and II.

Summary

The copolymerizations of eleven different nuclearly substituted α-methylstyrenes with butadiene have been studied. The effects of the natures and positions of the substituents on the rates of copolymerization have been discussed and the hindrance of *ortho* substituents has been indicated. Six new α-methylstyrenes have been prepared and characterized.

LAFAYETTE, INDIANA RECEIVED JULY 23, 1947

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

Some Properties of Phenanthrene Semiquinone

BY L. MICHAELIS AND S. GRANICK

It has been shown in previous papers[1,2,3,4] that phenanthrenequinone or its sulfonate on partial reduction establishes a compound intermediate between the quinone and the hydroquinone. This intermediate compound, when in the dissolved state, is in equilibrium with the two "parent substances" and furthermore exists in two modifications which also are in equilibrium with each other, namely, the free paramagnetic semiquinone radical and its diamagnetic, quinhydrone-like dimerization product. All of the equilibrium constants for an aqueous solution at 30° and at different acidities have been determined. The equilibrium between the free radical, the quinone and the hydroquinone is displaced in favor of the radical by increase of *p*H up to about 11, and remains constant at its maximum value on further increase of *p*H. The percentage of dimerization of the free radical is increased with increasing total concentration, as expected for a bimolecular reaction. Two more properties of that intermediate compound will be described in this paper.

(1) The dimerization of the free radical is counteracted by water-miscible organic solvents such as ethanol or pyridine. Even at a very high concentration of potassium phenanthrenequinone-3-sulfonate, 0.05 *M*, no noticeable dimerization of the free radical takes place if the solvent is 50% pyridine instead of pure water. Evidence for this statement is produced by the measurement of the change of magnetic susceptibility of the quinone in alkaline solution during the slow reduction by glucose using the method described previously.[5] In the three experiments plotted in Fig. 1 the alkalinity is always great enough to make the semiquinone formation constant maximal and independent of minor variations of *p*H. In a purely aqueous solution, at the very high concentration of the substance used in this experiment, the change of susceptibility in time is such as to indicate *in maximo* not more than about 16% (3) of the substance in the state of a free radical. Such

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(1) L. Michaelis and M. P. Schubert, *J. Biol. Chem.*, **119**, 133 (1927).

(2) L. Michaelis and E. S. Fetcher, THIS JOURNAL, **59**, 2460 (1937).

(3) L. Michaelis, G. B. Boeker and R. K. Reber, *ibid.*, **60**, 202 (1938).

(4) L. Michaelis, R. K. Reber and J. A. Kuck, *ibid.*, **60**, 214 (1938).

(5) L. Michaelis, *ibid.*, **63**, 2446 (1941). (1) Calculated as shown in (5).

a value is compatible with results obtained previously with different initial concentrations of the substance. When the same experiment is carried out with 50% pyridine as a solvent, the change of susceptibility in time is much larger and indicates, at the maximum point, the presence of 64% of the substance as a free radical. There is no evidence, either spectrophotometrically or otherwise, for any appreciable, measurable amount of the dimer.

(2) The free radical disappears both for solutions in water and in 50% pyridine (or alcohol) on addition of a small amount of a salt of calcium (or strontium or barium, but not magnesium or zinc or nickel). Instead of the brown radical an intensely emerald-green calcium compound of it is formed which is diamagnetic. During the reduction of the quinone by glucose in the presence of calcium no change of susceptibility is observed but the color changes observed during the reduction go from light yellow through green to light yellow (Fig. 1).

It is desirable to confirm the existence of the three modifications of the intermediate reduction product spectrophotometrically. In fact, they can be distinguished. Figure 2 shows first of all that the absorption of the quinone and the hydroquinone above 400 mμ is almost negligible. It is worth while mentioning that in such an alkaline solution the yellow color of the hydroquinone is more intense than that of the quinone, as can also be inferred from the graph. Figure 2 shows the molar absorption curve of the free radical. The relative values are quite reliable although the absolute values may be in error by 10 or perhaps even 20% because of the uncertainties involved in the calculation of the concentration of the free radical, as described in the legend of Fig. 2. Anyhow, it is obvious that the molar absorption coefficient of the free radical is much smaller than that of a "good" dyestuff such as methylene blue. This seems to be true for most of the free semiquinone radicals.

Curve O—O shows, as well as possible, the molar absorption curve for the dimer as it arises in purely aqueous alkaline solution of high concentration of the quinone on partial reduction. The calculations may be much more in error than for curve •—•, especially for the absolute values, but the fact that this spectrum represents a compound which is different from the free radical is established without doubt.

The absorption curve for the green calcium complex, curve X—X, is quite reliable for the relative values although the absolute values may be somewhat in error.

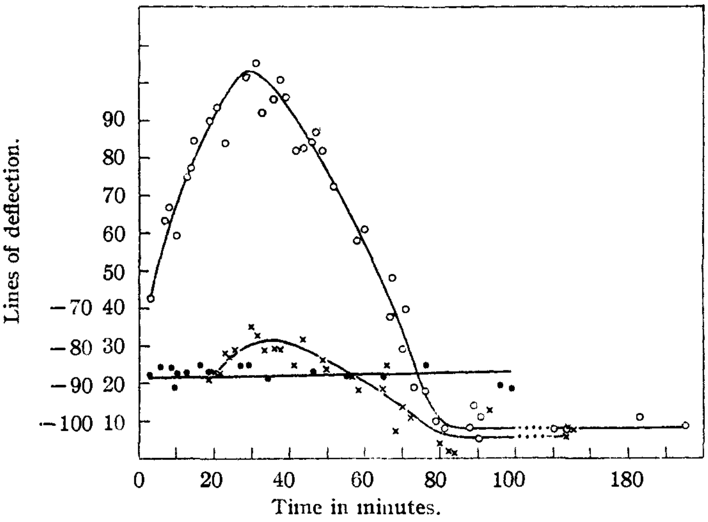
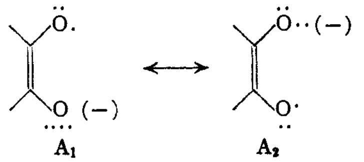


Fig. 1.—Change of magnetic susceptibility of potassium phenanthrenequinone-3-sulfonate during the reduction by glucose in an alkaline solution. The solution of the substance is contained in the upper compartment of the "double vessel" (or "compensation vessel"); the lower compartment is permanently filled with an agar gel. The ordinate is magnetic pull in terms of lines of deflection, measured always at an amperage close to 8.5 and recalculated for 10 amperes. One line of deflection corresponds to an increment of susceptibility 4.20 × 10^{-10} c. g. s. u. The solution is made up of 0.0407 g. of potassium phenanthrenequinone-3-sulfonate, 0.150 g. of glucose, and brought to a volume of 2.5 cc.: 1, for O—O by a solution made from 25 cc. of pyridine, 25 cc. of water and 1 cc. of 7.3 *N* NaOH; 2, for X—X by a solution made from 50 cc. of water + 1 cc. of 7.3 *N* NaOH; 3, for ●—● by an aqueous solution of $Ca(OH)_2$, 0.047 *N*. At time "O" the reduction has started already. The intermediate color is: red-brown for O—O; brown for X—X; green for ●—●.

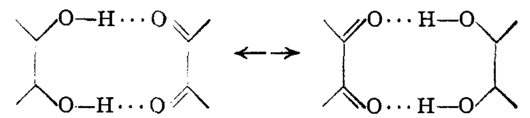
Discussion

The structure of the three molecular species, intermediate in oxidation between quinone and hydroquinone, may now be considered. It is easy to account for the structure of the free radical. It may be in analogy to the structure previously proposed for the semiquinone of duroquinone, symbolized by a structure resonating essentially between two equivalent "limiting structures," A_1 and A_2.



A_1 A_2

In order to understand the structure of the dimer one has to keep in mind the fact that the dimerization constant d/s^2, where d is the concentration of the dimer and s that of the free radical, was found (2) to be = 2 × 10^6 at *p*H 4.6, but as low as 70 at *p*H 12. Such a high dependence on *p*H is compatible only with the assumption that the dimer does not consist of two negatively charged semiquinone ions as represented by the structure A_1, A_2, but that it consists of two uncharged molecules of the free radical with protons attached. So the dimer may be symbolized as B_1 in resonance with B_2. This formula is analogous



B_1 B_2

to the one suggested for the diamagnetic benzoquinhydrone as it exists in the solid state, and to a minute extent also in solution[6] probably with the difference that for this ortho-quinoid compound both moieties lie in one plane, *i. e.*, the dimer is coplanar, whereas there was reason to assume that for the para-quinonoid compounds such as benzoquinhydrone in the dissolved state, the two rings lie stacked upon each other. The bond that holds together the two moieties may be classified among the "dimeric resonance bonds."[8] This resonance differs from most other cases of resonance in so far as it represents the only force holding together the two moieties, whereas usually resonance only increases the stability of a molecule which may be imagined to form a molecular unit even without that resonance.

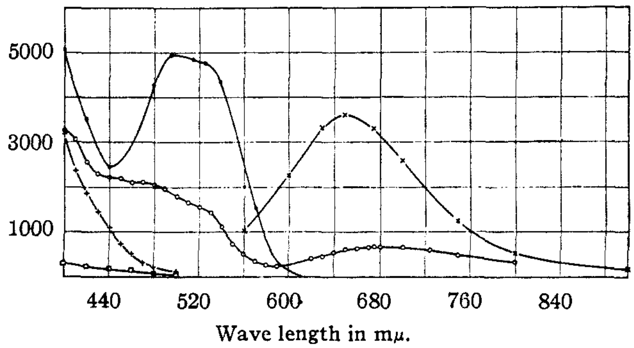
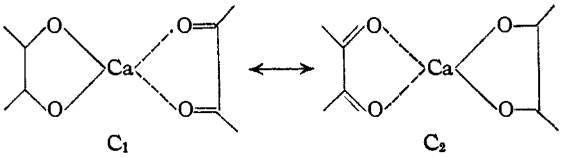


Fig. 2.—The ordinate is molar absorption coefficient, $1/(cd) \log (I_0/I)$, where I_0 is light transmitted through blank, I that transmitted by the solution; c is concentration in gram moles per liter; d is light path through the absorption cell in centimeters. All solutions are 0.073 N in sodium hydroxide and 1.048×10^{-4} molar in potassium phenanthrene-quinone-3-sulfonate, unless otherwise stated. O—O Solution of the quinone itself in 50% pyridine in a 1-cm. absorption cell; x—x, same, after complete reduction by glucose to the hydroquinone; +, the free semiquinone radical. (The two maxima at 490 and at 525 mμ are distinctly visible also in the hand spectroscope.) This curve has been obtained as follows. The alkaline solution of the dye in 50% pyridine was completely reduced by $Na_2S_2O_4$, slightly reoxidized by air, transferred to the absorption cell and sealed with mineral oil to keep the level of oxidation constant for a sufficiently long time. Readings of optical density at various wave lengths were taken. These values were translated into molar absorption coefficients as follows. The alkaline solution of the quinone plus some glucose was transferred to the absorption cell and the optical density for one particular wave length was watched while the reduction proceeded. After a certain time the optical density passes through a maximum. It is known from previous potentiometric measurements that *in maximo* 64% of the dye exists in the form of the free radical. This is true for any solution of $pH > 11$. These data are sufficient to convert the optical densities observed into molar absorption coefficients. There may be an error of 10% or even 20% with respect to the absolute values, but there is no appreciable error in the relative values. Since the hydroquinone, at least at the left hand of this curve, also absorbs somewhat, the curve has been slightly corrected by subtracting the absorption due to the hydroquinone which at 50% reduction of the quinone was supposed to be present to the extent of 18% of the total dye. × is the diamagnetic dimer of the radical, or the "quinhydrone." The solvent contains no pyridine. A 0.0193 M solution of the dye in 0.05 M sodium hydroxide is prepared. This concentration of the dye in the alkaline, aqueous solution is high enough to have the intermediate form to a very large extent in the dimeric form. The absorption cell had a diameter of 0.00578 cm. as described previously.[7] In principle the curve was obtained in the same way as for +. so no corrections for the presence of some free radical and of the quinone and the hydroquinone were applied. The absolute values may be considered as reliable only as to the order of magnitude, the relative values somewhat better, but no accuracy is claimed. Nevertheless, it is obvious that the absorption is much more diffuse than that of the free radical. The essential result is that the difference between two forms, the free radical and its dimeric "quinhydrone," is substantiated also spectrophotometrically. × is the green calcium complex of the radical, measured in a 1-cm. cell: 1 cc. of 2.47×10^{-3} M stock solution of the dye in 0.05 N NaOH + 9 cc. of 0.05 N NaOH + 0.4 cc. of saturated solution of $Ca(OH)_2$. The curve is obtained in the same way as in +. (Since a slight cloud of colorless precipitate appears, a corresponding solution in the completely oxidized, practically colorless state, was chosen as a blank for the readings. The dye was completely reduced with $Na_2S_2O_4$, and during the reoxidation by air the maximum point of absorption at any one wave length was watched.) It is assumed that *in maximo* practically all of the dye exists as the calcium quinhydrone. This may involve an error perhaps up to 20% or even more in the absolute values, but no essential error as to the relative values of the extinction coefficients.

For the calcium complex we may imagine the two H atoms replaced by Ca:



C_1 C_2

The fact that a structure can hardly be imagined otherwise than in coplanar configuration is in favor of the coplanarity, also of the calcium-free

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(6) L. Michaelis and S. Granick, THIS JOURNAL, **66**, 1023 (1944).

(7) L. Michaelis and S. Granick, *ibid.*, **67**, 1212 (1945).

(8) L. Michaelis and S. Granick, *ibid.*, **65**, 1747 (1943).

dimer. It may be mentioned that a comparable effect of calcium was not observed with quinone, duroquinone, or 1,4-or 1,2-naphthoquinone.

The fact that organic solvents prevent the dimerization, at least in the absence of calcium, is not easy to explain. This effect is quite analogous to the effect of organic solvents on the dimerization of regular (quinonoid, not semiquinone) dyestuffs, such as methylene blue, recognizable by spectrophotometric methods. Here also alcohol prevents dimerization. In alcohol such dyestuffs obey Beer's law: in water they do not because there is an equilibrium established between the monomer and the dimer, depending on concentration and temperature. Furthermore, it may be added that according to preliminary experiments the dimerization of the free radicals of the "Wurster's dye" type, obtained by partial oxidation of aromatic *para*-diamines, is counteracted also by alcohol to a certain extent.

Summary

The semiquinone radical of phenanthrene-quinone-3-sulfonate is paramagnetic. In aqueous solution it is in equilibrium with its quinhydrone-like, diamagnetic dimer. The dimerization is prevented by pyridine or alcohol. In presence of calcium ion the radical forms a diamagnetic calcium complex of green color.

NEW YORK, N. Y. RECEIVED MAY 15, 1947

[CONTRIBUTION FROM THE AMERICAN CYANAMID COMPANY, STAMFORD RESEARCH LABORATORIES]

The Dipole Moments of Diazines

BY WILLIAM C. SCHNEIDER

During the course of an investigation of the dipole moments of some thiouracil derivatives,[1] it was deemed desirable to determine the dipole moments of some simpler pyrimidine derivatives and other similar heterocyclic nitrogen compounds in order to obtain a value for the carbon–nitrogen bond moment in this type of molecule which could be used in calculating the electric moments of the more complex thiouracils. Although these thiouracil derivatives later proved to be too complicated for a detailed analysis, the simpler heterocyclic compounds were found to be of sufficient interest in themselves to warrant discussion.

Experimental

The apparatus and measuring technique will be described in another article.[1] Dioxane used as solvent was purified as follows: Commercial dioxane was partially frozen, and the liquid portion discarded. The remaining solid after remelting was refluxed over sodium to remove water and finally distilled through an efficient fractionating column to remove any remaining impurities. The best dioxane obtained in this manner had the following properties: b. p. (uncor.), 100.5°, d^{35}_4 1.01690, ϵ_{35} 2.1874, n^{35} 1.4150.

TABLE I

Compound	M. p., °C.
Pyridazine[a]	......
Pyrimidine[a]	18–20
Pyrazine[b]	52–53
4-Oxypyrimidine[b]	163–164
2,5-Dichloropyrimidine[c]	57–57.5
2-Mercapto-5-chloropyrimidine[c]	221–222
2-Methoxy-5-chloropyrimidine[c]	53–54

[a] Furnished by Dr. R. C. Lord, The Johns Hopkins University. [b] Furnished by Dr. I. F. Halverstadt, these Laboratories. [c] Furnished by Dr. J. P. English, these Laboratories.

The compounds investigated are listed in Table I. Table II gives the experimental values of ϵ, dielectric constant, d density and w, weight fraction for dioxane solutions at 35°. Dipole moments were calculated by a modified Hedestrand method similar to that introduced by Halverstadt and Kumler,[2] differing in that densities were used rather than specific volumes. The empirical equation used may be written as

$$_\infty p_T = \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \times \frac{1}{d_0}\left[1 - \beta/d_0\right] + \frac{3\alpha}{(\epsilon_0 + 2)^2 d_0} \qquad (3)$$

where ϵ_0 = extrapolated dielectric constant of solvent
d_0 = extrapolated density of solvent
$_\infty p_T$ = specific polarization at infinite dilution
α = slope of dielectric constant *vs.* weight fraction curve
β = slope of density *vs.* weight fraction curve.

The total molar polarization at infinite dilution, $_\infty P_T$, is obtained from the specific polarization by multiplying by the molecular weight. Atomic polarization was neglected, and molecular refractions were calculated from the atomic refractions listed in the "Landolt–Börnstein Tabellen." The values obtained from these calculations are listed in Table III, where P_D and P_0 refer to the distortion and orientation polarizations, respectively.

Discussion

To determine whether or not the carbon–nitrogen linkage can be adequately represented by a single constant in heterocyclic ring systems, its moment was calculated from the observed moment of pyridine, 2.3*D*,[3] assuming a value of 0.4*D* for the carbon–hydrogen link and a plane hexagonal structure for the pyridine ring. A value of 1.9*D*

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(1) Paper to be published shortly.

(2) Halverstadt and Kumler, THIS JOURNAL, **64**, 2988 (1942).

(3) Goethals, *Rec. trav. chim.*, **54**, 299 (1935).