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ELECTRICAL AND MAGNETIC PROPERTIES OF ORGANIC SOLIDS

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Contract No. AF 19(604)-8475
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Abstract

Some of the optical, electrical, and magnetic properties of molecular complexes (in solution and in the solid state) of riboflavin and its derivatives (both alloxazine and isoalloxazine ring systems) with aromatic phenols have been investigated. In addition, through the use of electron spin resonance spectroscopy, we have been able to determine the distribution of unpaired spin density in the free radical semiquinones of riboflavin derivatives.

Introduction

This project is concerned with the study of complexes of riboflavin, and its derivatives, with aromatic phenols. The experimental approach has included studies of optical absorption spectra of solutions and of crystals, electron paramagnetic resonance studies of solutions and of crystals, and electrical conductivity investigations of single crystals.

Summary of Research

Acid solutions (in H_2O, ethanol or acetone) of riboflavin and its derivatives (including both other isoalloxazines and alloxazine derivatives) have been found to form molecular complexes with aromatic phenols. In many cases, highly colored crystalline substances can be isolated. Analysis has indicated that the solid complexes consist of one mole of flavin to two moles of phenol. One to two moles of HCl are also included, the first mole being tightly bound and the second considerably more loosely bound and, in fact, capable of being removed from the solid complex by either evacuation or heating.

Optical spectra of solutions of the complexes show an absorption similar to that of the alloxazine or isoalloxazine in concentrated acid. The main difference, in the visible region of the spectrum, is a broadening of the absorption into the green.

The complex solutions exhibit an ESR absorption identical to that of the flavin semiquinone prepared by direct reduction with zinc or dithionite. The radical concentration represents approximately 0.3% of the flavin present. Illumination of these solutions with white light reversibly increases the radical concentration.

Studies of the pH-dependence of complex formation have indicated that it is the monoprotonated flavin species which is acting as the electron acceptor in these systems.

Studies of the concentration-dependence of complex formation in 7NHCl have indicated that a 1:1 complex is formed and that the paramagnetism exhibits a first-order dependence upon the concentration of both donor and acceptor. The significance of this result, as compared with the formation of a 1:2 complex in the solid state (see above), is not clear at present.

An approximate value of 0.8 liter/mole has been obtained for the stability constant of the FMN-pyrogallol complex. Thus, this is a quite stable complex.

A number of crystalline complexes have been isolated thus far. Of these, the riboflavin-hydroquinone, the riboflavin-resorcinol and the lumiflavin-hydroquinone have been most intensively studied. Only small crystals of the lumiflavin complex have been obtained thus far. These are diamagnetic upon isolation and become highly paramagnetic upon heating. Both of the riboflavin complexes are paramagnetic upon isolation and their paramagnetism increases upon heating. All of the complexes exhibit only a single-line ESR spectrum as polycrystalline powders. However, single crystals of the riboflavin-hydroquinone complex exhibit a hyperfine structure which is anistropic with respect to the direction of the applied magnetic field. The most unique pattern is found when the field is perpendicular to the large plane face of the crystal (the crystals are rectangular in cross-section). Eight lines are observed with a separation between components of approximately 10 gauss. Along the other two orthogonal directions one finds a doublet and a broad singlet.

The highest radical concentration which could be obtained by heating in this system before decomposition occurred, corresponded to 1.5% of the complex having an upaired spin. This is comparable to what has been observed in other molecular complexes.

The paramagnetism follows the Curie Law indicating a doublet, rather than a triplet species.

Some of our results on conductivity measurements in these systems are summarized below:

Compound	Specific Resistivity (Room T)(Ω-cm)
riboflavin (pressed pellet)	$> 5 \times 10^{12}$
riboflavin-hydroquinone	
single crystal (initial value)	1×10^{6}
after 30 hrs. electrolysis	1×10^{8}
riboflavin-resorcinol	
single crystal (initial value)	1.5×10^{8}
after 30 hrs. electrolysis	1.5×10^{8}
lumiflavin-hydroquinone	
single crystal	2×10^{10}

Both of the riboflavin complexes have been found to increase their electrical conductivity upon illumination with white light. Time constants for rise and decay are of the order of one minute for the hydroquinone complex and several seconds for the resorcinol complex.

In order to more clearly understand the fundamental nature of these complexes, an understanding of the structure of the isoalloxazine and alloxazine semiquinones was felt to be desirable. For this reason, we have undertaken an investigation of the ESR spectra of these substances The results of these

studies are summarized below.

A. Phenazine and the N-alkyl phenazines

These substances were studied as models for the more complicated flavin derivatives. The ESR spectra of the phenazine semiquinone has been recorded in other laboratories and the splitting constants worked out in detail. The broad seven line spectrum observed in dilute HCl is explained by attributing equal coupling constants to the two nitrogens and amino hydrogens. Each constant has a magnitude of six gauss. The α and β protons on benzene rings have small splittings of one and one half gauss respectively.

When phenazine methosulfate is dissolved in HCl and reduced with Zn, the semiquinone of N-methyl phenazine is formed. The ESR spectrum of this species has clearly ten broad lines upon which the α and β proton interactions are superimposed. If one assumes the splitting constants of the methyl hydrogens are identical to the two nitrogens and the amino hydrogen, the ten line spectrum is predicted. Upon preparation of the radical in DCl a nine line spectrum is observed. This is consistent with the above interpretation, if one considers the replacement of the amino hydrogen with a deuteron.

From these data we conclude that for systems similar to the phenazines, the N and CH_3 interactions are equal.

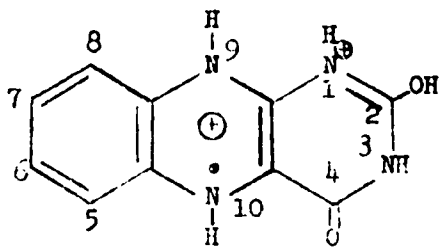
The semiquinone of N-ethyl phenazine was prepared in HCl-saturated dimethylformamide solution. Only in this solvent could any hyperfine structure be resolved, and this in no way resembled that of the previous semiquinones. Although the spectrum is not well enough resolved for a complete interpretation to be made, we must conclude that interactions from N-methylene groups are not simple extensions of those from N-methyl groups.

B. Alloxazines

The EPR signal of alloxazine in concentrated HCl consists of eleven lines each separated by two of smaller intensity. From the spectrum recording using DCl as a solvent, we observe twenty-five lines superimposed on a broad four line background. Apparently the alloxazines do not form semiquinones in dilute acid as do the other systems.

Upon replacing the protons at positions 6 and 7 with magnetically inactive chlorines, the original eleven line spectra is seen to be reduced to ten lines with only one smaller peak between major lines.

Utilizing all the above data, the following semiquinone structure and splitting constants are proposed. Reconstructed spectra using these values agree with the experimentally observed spectra with regard to line positions and intensities.



$A_{N_{10}} = 7.8$ gauss

$A_{N_9} = 3.9$ gauss

$A_{H(ring)} = 2.3$ gauss

$A_{H_{10}(amino)} = 7.8$ gauss

$A_{H_9(amino)} = 3.9$ gauss

$A_{H(ring)} = 1.5$ gauss

C. Flavins

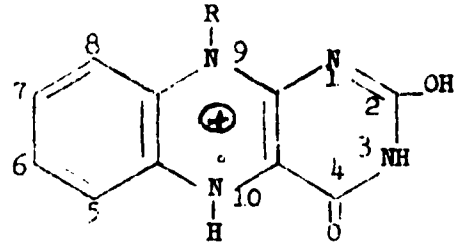
Upon preparation of the semiquinone of 6,7 dichloro 9-ethyl isoalloxazine in dilute HCl, we observe a seventeen line ESR spectra with separation

between components of 2.3 gauss. In dilute DCl we observe only fifteen lines, again separated by 2.3 gauss. (The observation of a decrease of two lines or 4.6 gauss upon replacing hydrogen by deuterium is common to all the flavins.)

The ESR spectra of the semiquinone of 9-ethyl isoalloxazine in dilute DCl consists of sixteen lines separated by 2.3 gauss. It is clear that the replacement of the protons in positions 6 and 7 with chlorine results in a spectral change of one line. This reduction by one line can be accounted for by the loss of only one proton interaction. This observation seems to indicate that spin density in the benzene ring exists on alternate carbons.

In dilute DCl the spectrum of the semiquinone of 9-methyl isoalloxazine consists of twenty lines or a four line increase over the analogous ethyl derivative.

Using all the observations above, the following semiquinone structure and coupling constants are proposed. In each case the values allow a complete reconstruction of the observed spectra with regard to line positions and intensities.



A_{N_1} = 6.6 gauss

$A_{N_{10}}$ = 4.4 gauss

A_{N_9} = 2.3 gauss

A_{H_7} = 1.4 gauss

$A_{H_{10}}$ = 4.4 gauss

$A_{H(CH_2}$ 9-ethyl der.) = 2.3 gauss

$A_{H(CH_3}$ 9-methyl der.) = 4.4 gauss

$A_{CH_3(7)}$ = 1.5 gauss
(lumiflavin and riboflavin)

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