(curve I_A, Fig. 3) agrees much better with the observed curve.

Discussion

The deduction of structures from visually estimated electron diffraction data can rightfully be subjected to a certain amount of criticism since such interpretations are based on subjective impressions. The identification of what the eye sees with the peaks and valleys found in the computed curve requires both care and practice. In this Laboratory, we have been able to compare patterns, traced by a microphotometer, of electron diffraction photographs taken with a sector, with visually estimated patterns taken in the usual manner. We found, as has been observed previously, that the eye accentuates various features, making shoulders sometime appear as prominent as peaks and introducing minima where inflections in the shoulders appear. However, the eye *does not* introduce new features in the pattern. Hence for an experienced investigator it is possible to state with a considerable amount of assurance when an assumed model has been eliminated. The use of a radial distribution curve, based upon visual data, can serve only to help find the best combination of distances and angles for a given model. Since the relative weights of the radial distribution peaks cannot be considered quantitatively, it is not legitimate, as yet, to base the entire analysis upon this argument. In the selection of the model and the distances finally reported above, both the intensity curves and radial distribution curves were considered.

The B–Be distance deduced is quite short when compared with the sum of the covalent radii for beryllium and boron ([5]1.06 + 0.85 − 0.05 = 1.86 Å.). This, however, can be explained as follows. If we consider diborane, aluminum, beryllium and lithium borohydride, the ionic character of the compounds increases[1c] in the order listed. The B–Be bond, therefore, probably is highly polar. Usually, increasing the ionic character of a bond has little influence on its length, since the radius of the electropositive atom decreases by about the same amount as the radius of the electronegative atom increases. In this case, however, the BH_4 group is electron deficient, so that the effective radius of boron toward beryllium will not be altered, although the beryllium radius will be shortened with increasing amounts of ionic character. This results in a B–H distance which is shorter than expected for one with considerable one-electron bond character, and a B–Be distance which is shorter than the sum of the covalent radii. Because of the increase in ionic properties, and the corresponding change in bond distances from aluminum to beryllium to lithium borohydride, we predict that the Li–B bond distance will be found to be considerably less than the sum of the covalent radii, and the B–H distance to be smaller than that observed in the beryllium compound.

Summary

From an electron diffraction study of beryllium borohydride vapor a configuration for the molecule was deduced which is analogous to that previously reported for aluminum borohydride. In beryllium borohydride, H″–B–Be–B–H″ are linearly arranged, with three hydrogen atoms (H′) uniformly spaced in the girdle of each boron atom. B–Be = 1.66 ± 0.04 Å.; B–H″ = 1.15 ± 0.05 Å.; B–H′ = 1.19 ± 0.05 Å.; ∠BeBH′ = 85 ± 5°. Proton bridge structures were considered for both the beryllium and aluminum borohydrides; these were definitely eliminated.

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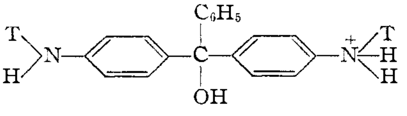
(5) V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

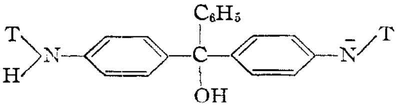
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Absorption Spectra of the Negative Ions of Two Diaminotriphenylmethane Dyes

BY BERT M. TOLBERT AND GERALD E. K. BRANCH

If a carbinol of a diaminotriphenylmethane dye having hydrogen atom on each nitrogen atom is treated with dilute acid a positive ion may be formed (I), or if treated with a strong alkali a negative ion (II) may be formed

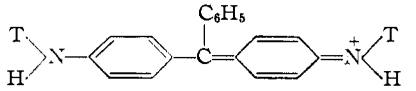

(I)

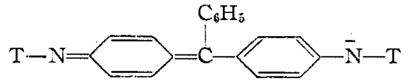

(II)

where T represents a terminal group. The equilibrium constants for such reactions are approximately equal to those for the formation of the positive ion or the negative ion, respectively, from the base of which the dye is a derivative. The positive ion is therefore formed in dilute acid solution, but the negative ion is obtainable only in very strongly basic solutions.

Each of these ions is in equilibrium with a quinoidal ion, (III) or (IV), obtained by the loss of one molecule of water.

An estimate of the relative stability of the quinoidal ion with respect to the benzenoidal ion may be obtained by a comparison of the reso-


(III)


(IV)

nance energies of these ions. The main resonances in the benzenoidal positive ion are three benzene resonances and an aniline type resonance ($THNC_6H_5$, $THN^+{=}C_6H_5^-$). In the quinoidal ion there are two benzene resonances, an aniline type resonance and an amidinium ion resonance (the shift of charge from one nitrogen atom through the connecting conjugate system to the other nitrogen atom ($HTN^+{=}R{-}NHT$, $HTN{-}R^+{-}NHT$, $HTN{-}R{=}N^+HT$), where R represents a conjugate system). These are the resonance interactions as they appear in the classical formulas, each of which has two benzenoidal rings, one of which has an amino group. The change of the benzenoidal positive ion to the quinoidal one is therefore assisted by an amidinium ion resonance and opposed by a benzene resonance. Actually the quinoidal positive ion is stable with respect to the benzenoidal ion, which shows that the amidinium ion resonance has a large energy, comparable with that of benzene.

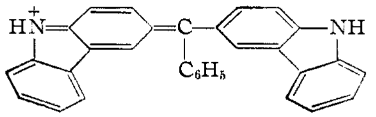
The main resonances of the benzenoidal negative ion are three benzene resonances, an aniline resonance and the resonance of an anilide ion ($C_6H_5NT^-$, $TN{=}C_6H_5^-$). Those of the quinoidal ion are a resonance of a quinoidal amidide ion ($TN^-{-}R{=}NT$, $TN^-{-}R^{+-}NT^-$, $TN{=}R{-}NT^-$), two benzene resonances, and an anilide ion resonance. Therefore, the change of the benzenoidal negative ion to the corresponding quinoidal ion is assisted by the amidide ion resonance and opposed by a benzene resonance and an aniline resonance. Except for this last resonance, the entropy and bond energy effects should be similar for the change from the benzenoidal to quinoidal structure for both kinds of ions. But the additional resonance in the benzenoidal negative ion should make the quinoidal negative ion much less stable with respect to its benzenoidal counterpart than the quinoidal positive ion is with respect to the benzenoidal positive ion. Thus the quinoidation occurs less in the negative ion than in the positive ion to about the extent that an aromatic amine would be less neutralized than an aliphatic amine in a very weak acid.

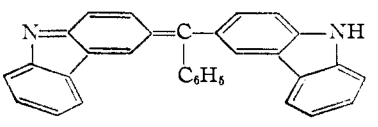
Thus, even though the quinoidal positive ion is favored over the benzenoidal positive ion, the benzenoidal negative ion probably is favored over the quinoidal negative ion. Hence, there are two reasons for the greater difficulty of getting the negative ion than the positive ion: the weakness of the acid and the unfavorable equilibrium. The weakness of the acid can be overcome by making the dye from very acidic amines, *e. g.*, carbazole, and by using strongly basic solutions. Since neutralization is faster than benzenoidation, the other difficulty can be overcome by adding alkali to the positive ion or the anhydro base and studying the quinoidal negative ion before it has a chance to go completely to the benzenoidal form.

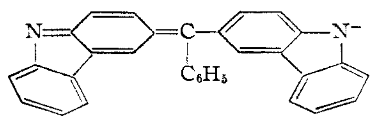
When a methanol solution of 3,3′-dicarbazylphenylmethyl chloride, V, (which we shall call the dicarbazyl dye) is treated with concentrated sodium hydroxide a transient green color is obtained,[1] while with a weaker base only the red to red-violet color of the anhydro base appears. When acetone is used as the solvent instead of methanol the same colors are obtained, but they last for much longer periods; and the spectra of the solutions can be measured with a spectrophotometer with the aid of extrapolation.

In acetone the dye can have three colors: a blue-green in acid or neutral solution, a red in weakly basic solution, and a green in strongly basic solution. The change from one color to another is rapid and reversible as the basicity is altered. Intermediate colors can be obtained, but they are such as could be obtained from mixtures of the three colors mentioned above.

The colors can be attributed to three main absorption bands at 601, 496 and 727 mμ. When the solution is acid $\lambda_{\max.}$ is at 601 mμ. As the solution is progressively made more basic this band disappears and its place is taken by the band at 496 mμ; and then this band, in its turn, is replaced by the band at 727 mμ. There are, therefore, two colored forms in addition to the singly charged positive ion, from which they are derived by successive removals of a proton. These additional colored forms of the dye are the quinoidal anhydro base, VI, and the quinoidal negative ion, VII.


(V)


(VI)


(VII)

The color of a slightly acid solution of the dye in acetone is permanent, even if water or an alcohol is added; but both the red and the green alkaline solutions fade. The rate of fading is greatly enhanced by adding water or an alcohol. When the faded solution is acidified the blue-

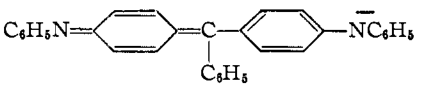
[1] Branch, Tolbert and Lowe, THIS JOURNAL, **67**, 1693 (1945).

green color of the positive ion returns, and the red color of the anhydro base or the green color of the negative ion can be obtained by adding the requisite alkali. Similarly the colorless solution of the methyl ether of the dye develops neither red nor green tints at any degree of basicity; but turns blue-green when acidified. The quinoidal positive ion is therefore stable with respect to its benzenoidal counterpart, but the quinoidal anhydro base and the quinoidal negative ion are unstable with respect to benzenoidal compounds.

However, spectroscopic examination of a strongly basic solution of the methyl ether of the dye in acetone showed that traces of the quinoidal ion were formed, since there was some absorption in the region 700–750 mμ. Assuming equal molecular extinctions of the positive and negative quinoidal ions, the absorption corresponded to less than one-tenth of a per cent. conversion.

The equilibrium between the anhydro base and its negative ion is markedly affected by the solvent. Acetone and related ketones are very effective solvents for the formation of the negative ion. When either hexane or water are added to a green solution in acetone the color changes to red.

Attempts to prepare a green negative ion (VIII) from viridine green, and its anhydro base in methyl alcohol were unsuccessful.



(VIII)

However, when solutions of viridine green or its anhydro base in acetone or diethyl ketone were shaken with solid potassium hydroxide or solid tetraethylammonium hydroxide green colors were obtained. Qualitatively these solutions behave in the same way as the similar green solutions obtained from the dicarbazyl dye. The chief difference between the two dyes is that the anhydro base of the dicarbazyl dye appears to be a much stronger acid than the corresponding derivative of viridine green. Even under the most basic conditions the solution obtained from viridine green had a strong absorption band at the wave length of $\lambda_{\text{max.}}$ of the anhydro base. If one assumes that the ratios of $\epsilon_{\text{max.}}$ of the anhydro base and the negative ion are the same for both dyes, the anhydro base of the dicarbazyl is more than a hundred times as strong an acid as the anhydro base of viridine green.

Alternation of colors with successive removals of a proton is a common phenomenon in dyes with two auxochromic amphoteric groups. It can be attributed to the accompanying alternations between linear symmetrical and less symmetrical derivatives. In the former the two most important of the resonating structures are equivalent, and in consequence the symmetrical derivatives absorb light of longer wave length than the unsymmetrical ones. The alternation between red and green colors can be extended by another step with the two dyes under consideration by dissolving them in mixtures of acetic acid and sulfuric acid. Doubly charged positive ions with red colors are formed. A very large proportion of sulfuric acid is needed for this in the case of the dicarbazyl dye.

The spectra of the negative ions of both dyes were measured in the spectral ranges permitted by the unavoidable presence of anhydro bases and benzenoidal derivatives. In the case of the dicarbazyl dye this range includes the visible, but the spectrum of the quinoidal negative ion of viridine green was obtained only from 600 to 800 mμ, because the solutions contained large amounts of the anhydro base, which has an absorption band at 459. The proportions of anhydro base, quinoidal negative ion and benzenoidal compounds in the solutions were not determined, so the spectra obtained were plots of the extinctions, not of the molecular extinction coefficients, against the wave lengths.

Experimental Procedure

The spectra of the negative ions of the dicarbazyl dye and of viridine green were measured with a Beckman quartz spectrophotometer. Owing to the fading of the solutions during the measurements the extinction at each wave length was repeatedly measured at noted times, and extrapolated to zero time. To control the temperature the absorption cells were immersed in a small bath through which water from a thermostated bath was circulated. This small bath was part of the optical system, being substituted for the usual cell compartment. The cells were 1 cm. square glass tubing ground optically flat on two sides and equipped with tapered joints and stopcocks, permitting evacuation of the cells and rapid introduction of the solution by suction. This apparatus was designed by Dr. W. K. Wilmarth.

The procedure used in making the measurements was as follows: two absorption cells were filled, respectively, with an alkaline acetone solution of the dye and a solution containing no dye but otherwise as nearly identical as possible, even with respect to the age. These precautions were necessary because the extinction in the violet and ultraviolet of an alkaline solution of acetone increases with time. The cells were placed in the thermostated bath and measurements were made at 20 mμ intervals between 900 and 350 mμ. The times of these measurements were noted. The measurements at the same wave lengths were repeated as often as necessary. The solutions were allowed to stand until the reaction of fading was complete and the extinctions were again measured at the chosen wave lengths. In the case of the dicarbazyl dye the final extinctions, which were generally very small, were subtracted from the measured extinctions and the logarithms of the results plotted against the times of measurements. The resultant plots were linear, and the slopes of the lines were the same at all wave lengths. The spectrum could then be obtained by interpolating the lines obtained at all wave lengths to a common time, for the relative extinctions at different wave lengths were independent of the time. Actually, the spectrum was obtained by extrapolating back to a time that roughly corresponded to the time of mixing.

In the case of viridine green extremely alkaline solutions were necessary, and when the solutions were allowed to stand long enough to reach equilibrium between the quinoidal and benzenoidal ions, the blanks were so strongly colored that extinctions at zero time could not be accurately attributed to the dye. Therefore the extinctions at each wave length were obtained by extrapolating the logarithms of the measured values to the time of mixing. These curves were linear over large changes of extinction at long wave lengths and for small changes at shorter wave lengths. The shape of the spectral curve was not affected by small changes in the choice of a zero time.

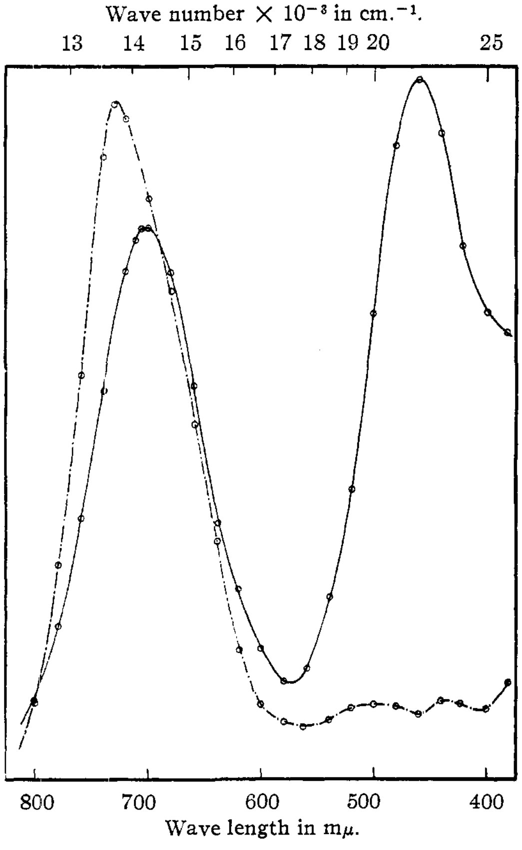


Fig. 1.—Absorption spectra: —, mixture of $C_6H_5NC_6H_4C(C_6H_5)C_6H_4NHC_6H_5$ and $C_6H_5NC_6H_4C(C_6H_5)C_6H_4NC_6H_5^-$;

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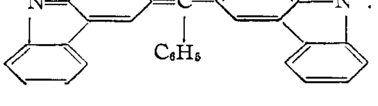

The dicarbazyl dye was obtained from its methyl ether by precipitation from benzene solution with ethereal hydrochloric acid. The preparation of the methyl ether has been described by Branch, Tolbert and Lowe.[1] The viridine green was made by the method described by Hill, Branch and Patapoff.[2]

The Spectra

In Fig. 1 the absorption spectra of the negative ions of the two dyes studies are shown. Experimental points are indicated. The spectrum of the negative ion of viridine green shown in Fig. 1 was measured at 1° in an acetone solution dried with solid potassium hydroxide and in which the active base was tetramethylammonium hydroxide. Measurements were made in closed cells. The spectrum for the negative ion of the dicarbazyl dye shown in Fig. 1 was measured in acetone containing 10% water by volume and 3.4×10^{-2} *M* with respect to tetraethylammonium hydroxide.

The spectra of both compounds show a strong band in the neighborhood of 700 mμ and another band at the wave length of the x-band of the corresponding anhydro base, 460 mμ for viridine green and 500 mμ for the dicarbazyl dye. The bands at 460 and 500 mμ were never completely removed, even with more base, but since they both increase while the longer wave length bands decrease when the solution is made less alkaline, they must be attributed to the anhydro base rather than to the negative ions. In the case of viridine green the band at 460 mμ was never reduced sufficiently to allow the observation of any band in its neighborhood. But in the dicarbazyl dye a small band appears with a maximum at 430 mμ when the alkali is strong enough to reduce absorption of the anhydro base to moderate proportions. This band does not appear in the spectra of any other derivative of the dicarbazyl dye investigated. It must be attributed to the negative ion. It is probably the *y*-band of the negative ion.

The small extinction coefficient of the *y*-band of the negative ion of the dicarbazyl dye, and its large separation from the *x*-band ($\bar{\nu}_y - \bar{\nu}_x$ = 9,500 cm.$^{-1}$ as compared to 5880 cm.$^{-1}$ for the positive ion) are particularly interesting. The extinction maximum of the *y*-band of the positive ion is a quarter of that of its *x*-band. The extinction maximum of the *y*-band of the negative ion is one-ninth of that of its *x*-band, and probably an appreciable proportion of this ninth is due to absorption by its higher frequency bands, and to absorption by benzenoidal derivatives.

Lewis and Calvin[3] attribute the *y*-band of a diaminotriphenylmethane dye to vibration of a

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[2] Hill, Branch and Patapoff, THIS JOURNAL, **67**, 454 (1945).

[3] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

charge in an axis perpendicular to the x-band vibration between the nitrogen atoms. On this basis the frequency difference and relative extinction of the x- and y-bands of a dye would depend on the relative contribution of resonating structures in which the central carbon atom is doubly bonded to the non-aminated phenyl group. In a structure of this type this phenyl group or one of its side groups is positively charged. When the contribution of these structures is great, the y-band would not differ greatly from the x-band in frequency and extinction. The contribution of these structures must be less in the negative than in the positive ion; it is therefore not surprising to find that the y-band is very small and much displaced from the x-band in the negative ion.

It was not possible to measure the spectra of the negative ions over wide variations of solvent. But some changes in the solvent were made by using diethyl ketone instead of acetone, and in the case of the dicarbazyl ion by using drier acetone. The value of $\lambda_{\text{max.}}$ of the negative ions was found to change with the solvent much more than $\lambda_{\text{max.}}$ of the positive ion. The wave lengths for both negative ions are longer in diethyl ketone than in acetone, and $\lambda_{\text{max.}}$ for the negative ion of the dicarbazyl dye was found to increase when the acetone is dried. On the other hand the spectra of the positive ions of these dyes are very little affected by the solvent. The values obtained for $\lambda_{\text{max.}}$ in different solvents are shown in Table I.

TABLE I

ABSORPTION MAXIMA OF THE NEGATIVE IONS

Compound	Solvent	Base	λ, mμ
Viridine green	Acetone	Metallic Na	704
Viridine green	Acetone[a]	$(CH_3)_4NOH$	703
Viridine green	Diethyl ketone	Metallic Na	710
Dicarbazyl dye	Acetone	40% NaOH (aqueous)	735
Dicarbazyl dye	(10% water) (90% acetone)	$(C_2H_5)_4NOH$	727
Dicarbazyl dye	Diethyl ketone	40% NaOH (aqueous)	745

[a] The temperature in this experiment was 1°, in the others it was 25°.

Solutions of the negative ions were made with sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide and tetraethylammonium hydroxide. The base used did not affect the positions of the absorption bands. However, the quaternary ammonium hydroxides appeared to be more effective than the alkali metal hydroxides in neutralizing the anhydro bases.

In the case of the positive ions viridine green absorbs at a longer wave length (approximately 30 mμ) than the dicarbazyl dye. This is only true for the singly charged positive ion. For the negative ions, the anhydro bases and the doubly charged positive ion $\lambda_{\text{max.}}$ of the dicarbazyl derivative is greater than $\lambda_{\text{max.}}$ of the viridine green derivatives.

In a discussion of the carbazyl derivatives of malachite green,[1] of which the dicarbazyl dye is an example, Branch, Tolbert and Lowe suggested that there are two opposing effects on the wave length of $\lambda_{\text{max.}}$ produced by the substitution of resonating groups on the N-positions, an increase of $\lambda_{\text{max.}}$ due to the increase in the number of resonating structures, and a decrease in $\lambda_{\text{max.}}$ due to the decrease of basicity of the auxochromes. The latter effect is predominant only when the basicities of the amino groups are very small, and so only in the singly charged positive ion is it the predominant factor in determining the relative values of $\lambda_{\text{max.}}$ of the diphenylamine and carbazyl derivatives. In a comparison of $\lambda_{\text{max.}}$ of the quinoidal positive and negative ions, both factors tend to make $\lambda_{\text{max.}}$ for the negative ion greater than $\lambda_{\text{max.}}$ for the positive ion. This was found to be the case for both dyes. The value of $\lambda_{\text{max.}}$ of the negative ion of viridine green is 66 mμ greater than that of its positive ion, assuming that in changing from methanol to acetone solutions there would be no effect on $\lambda_{\text{max.}}$ of the positive ion. The value of $\lambda_{\text{max.}}$ of the negative ion of the dicarbazyl dye is 126 mμ greater than that of its positive ion.

Summary

The absorption spectra of the quinoidal negative ions of viridine green and 3,3′-dicarbazylphenylmethyl chloride have been measured in acetone solution. The spectra of the quinoidal negative ion of the carbazyl derivative show a strong band at 727 mμ and a weak band at 430 mμ. The negative ion of viridine green show a strong band at 704 mμ, but the existence of another band could not be shown owing to absorption by unneutralized anhydro base.

The greater instability of the quinoidal negative ions as compared to the quinoidal positive ions has been discussed.

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