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The Absorption Spectra of Some N-Phenyl-*p*,*p*'-diaminotriphenylmethane Dyes

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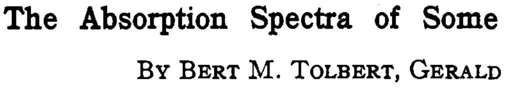
We have measured the absorption spectra of the following dyes: malachite green (I), N-dimethyl-N'-phenylmethyl-*p*,*p*'-diaminotriphenylmethyl chloride (II), N-dimethyl-N'-phenyl-*p*,*p*'-diaminotriphenylmethyl chloride (III), N-dimethyl-N'-diphenyl-*p*,*p*'-diaminotriphenylmethyl chloride (IV), *sym*-N,N'-dimethyldiphenyl-*p*,*p*'-diaminotriphenylmethyl chloride (V), N,N'-diphenyl-*p*,*p*'-diaminotriphenylmethyl chloride (VI) (viridine green), N,N'-tetraphenyl-*p*,*p*'-diaminotriphenylmethyl chloride (VII). Their formulas are


(I)


(II)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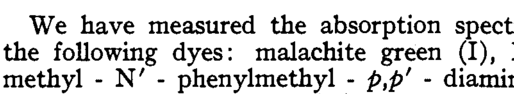
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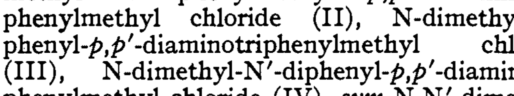
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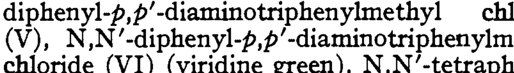
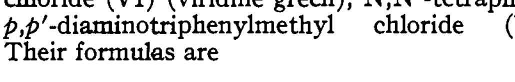

(VI)


(VII)

The dyes may be distinguished by designating the N-terminal groups only, and their formulas shortened by substituting R for $C_6H_4C(C_6H_5)C_6H_4$. In the remainder of this paper such abbreviations will be adopted.

The comparison of their spectra shows the effect on the wave lengths of the absorption bands of (1) substitutions of phenyl groups for methyl groups, (2) substitutions of hydrogen atoms for methyl groups when the substitution is on a nitrogen atom that has already been phenylated, (3) asymmetry of the two amino groups. The influence of the solvent on these effects and on the separate dyes has been studied by observing the spectra in three different types of solvents: (1) methyl alcohol, a hydroxylated solvent with a high dielectric constant; (2) acetic acid, a hydroxylated solvent with a low dielectric constant; (3) chloroform, a solvent with a low dielectric constant.

The Dyes.—The identities of the dyes were established by the methods of preparation, the analyses of their bases, either as carbinols or methyl ethers, the type of spectrum, and the formation of anhydro bases. The first of these criteria is fundamental, but cannot be taken as a proof of the structure. We are justified in assigning a formula only when the method of preparation is used in conjunction with the other criteria, which also serve as criteria of purity.

The symmetrical dyes were prepared by condensing the requisite amine and benzotrichloride with the aid of aluminum chloride, the unsymmetrical dyes by condensing the amine with N-dimethyl-*p*-aminobenzophenone, using aluminum chloride or phosphorus oxychloride as the condensing agent. The chlorides were recrystallized, and then converted to the methyl ether or carbinol, in which form they were further purified and analyzed. Melting points for these bases are given later. In many cases these melting points should not be considered as physical constants of definite substances, for the methyl ethers were

TABLE I

ABSORPTION MAXIMA AND THEIR MOLECULAR EXTINCTION COEFFICIENTS

R = $C_6H_4C(C_6H_5)C_6H_4$; * = broad peak; secondary maxima are given in parentheses.

Dye ion	Solvent	λ_x in mμ	$\epsilon_x \times 10^{-4}$	λ_y in mμ	$\epsilon_y \times 10^{-4}$	$\lambda_{x'}$ in mμ	$\epsilon_{x'} \times 10^{-4}$	$\bar{\nu}_y - \bar{\nu}_x \times 10^{-3}$
$[(CH_3)_2NRN(CH_3)_2]^+$	CH_3OH	618	9.2	426	1.85	318	1.75	7.29
	AcOH	620	9.6	428	1.85	320	1.76	7.24
	$CHCl_3$	622	10.3	430	1.92	320	1.87	7.18
$[(CH_3)_2NRNCH_3C_6H_5]^+$	CH_3OH	620	..	428	..	...	..	7.24
	AcOH	621	..	430	..	...	..	7.15
	$CHCl_3$	626	..	432	..	...	..	7.17
$[(CH_3)_2NRNHC_6H_5]^+$	CH_3OH	622	7.6	431	1.71	318	1.65	7.13
	AcOH	621	7.2	430	1.71	318	1.59	7.15
	$CHCl_3$	627	6.8	432	1.60	320	1.56	7.20
$[(CH_3)_2NRN(C_6H_5)_2]^+$	CH_3OH	625	5.9	437	1.53	300*	1.50	6.88
	AcOH	629	6.3	438	1.55	305*	1.67	6.93
	$CHCl_3$	638	6.5	443	1.61	320	1.67	6.90
$[CH_3C_6H_5NRNCH_3C_6H_5]^+$	CH_3OH	632	6.6	438	1.44	310*	1.74	7.01
	AcOH	633	6.3	440	1.76	310	1.95	6.94
	$CHCl_3$	636	6.1	445	1.66	320	1.83	6.75
$[HC_6H_5NRNHC_6H_5]^+$	CH_3OH	638	5.2	442	1.28	286(318)	1.92	6.70
	AcOH	637	4.7	447	1.31	285(320)	1.55	6.67
	$CHCl_3$	637	4.4	448	1.29	300*	1.56	6.62
$[(C_6H_5)_2NRN(C_6H_5)_2]^+$	CH_3OH	668	5.3	465	1.25	297(320)	1.99	6.54
	AcOH	670	5.1	470	1.54	290(330)	1.81	6.35
	$CHCl_3$	684	5.0	481	1.60	290(325)	1.95	6.17

prepared in ways that would leave them contaminated with their carbinols.

Early in the purification of a dye we obtained the chloride as a crystalline powder with red metallic luster, but generally only after repeated purification did we succeed in obtaining the base, either the carbinol or methyl ether, as a nearly white powder. We have taken a reasonably correct microanalysis of this base as a criterion of the identity of the compound.

Diaminotriphenylmethane dyes have a special type of spectrum between 900 and 240 mμ. This consists of three principal bands which we shall call the *x*-, the *y*- and the *x*'-bands.[1] The *x*- and *y*-bands are in the visible, and except for small deviations are nearly symmetrical in very dilute solution, especially in methyl alcohol. The *x*-band has the longer wave length and the greater extinction. Within the range of the structural variation we have covered, the ratio of λ_x to λ_y is nearly constant, varying between 1.43 and 1.45. The *x*'-band has a maximum not far from 300 mμ and an extinction of the order of magnitude of that of the *y*-band.

In general during a purification values of λ_x and λ_y change but little. During this period, however, the absorption in the ultraviolet decreases, becomes more regular, and a deeper minimum appears between the *y*- and *x*'-bands. When we have obtained this characteristic spectrum, we are justified in assuming that the product has the type of structure that would be obtained from the expected condensation and that the product is sufficiently pure to give λ_x and λ_y to within 2 mμ. We are not, however, justified in assuming any such accuracy for $\lambda_{x'}$.

When an aminotriphenylmethane dye having a hydrogen atom on the nitrogen atom is treated with an alkali, it forms a colored anhydro base before going over to the carbinol or ether. This reaction can be identified by the formation of a colored solution, which fades in the presence of an alcohol. When this test was applied to our products, strongly positive results were obtained with dyes III and VI, which have hydrogen to nitrogen bonds, but negative results were obtained with dyes I, IV, VII, in which such bonds are lacking. However, a slight red color was obtained with dyes II and V, in which hydrogen to nitrogen bonds are also lacking. When these dyes were treated with methyl sulfate, the color obtained in the test was greatly reduced, without altering the values of λ_x and λ_y. Our samples of dyes II and V were therefore contaminated to some extent by less methylated dyes, but not sufficiently to produce measurable errors in λ_x and λ_y. The source of these impurities was probably diphenylamine in the methyldiphenylamine used in the syntheses.

Dye II did not meet all of the above criteria of identity and purity. However, the values obtained for λ_x and λ_y agree so well with the values for the series of dyes that we have concluded the sample was the required dye contaminated with colorless impurities. On this basis we have shown the spectrum between 800 and 400 mμ. Owing to this impurity the molecular extinction coefficient had no significance.

In the preparation of some of these dyes, es-

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(1) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939); Lewis and Bigeleisen, THIS JOURNAL, **65**, 2107 (1943).

pecially II and III, we obtained varying quantities of a certain type of by-product, which was also a dye, when $POCl_3$ was used as the condensing agent. These by-products can be partially isolated by fractional precipitation of the chloride from a solution of a basic form in carbon tetrachloride with ethereal hydrochloric acid. They act as stronger bases and concentrate in the first fractions. They are blue dyes, whose spectra can be distinguished by the lack of a y-band. Their spectra can be obtained from a mixture of the dyes by partial neutralization. Under these conditions the solution changes from green to blue, the principal band shifts to a shorter wave length, and the y-band disappears.

The Spectra.—The spectra were measured with a Beckman quartz spectrophotometer. Measurements were made every 10 mμ in the visible, and every 5 mμ in the ultraviolet. Except in the case of dye II the solutions of the dyes were obtained by dissolving weighed amounts of the base, either the methyl ether or the carbinol, and acidifying. Any additional acid was present in equal amount in both the standard and sample cells. The molarities of the dye ranged from 8×10^{-6} to 1.2×10^{-5}. In methyl alcohol a hydrochloric acid molarity of 1.0×10^{-2} was used; in chloroform only sufficient acid was added to insure neutralization of the basic form of the dye. Beer's law was found to hold exactly for a twofold change in concentration of dyes V and VII in chloroform, and for VI in a mixture of methyl alcohol and benzene. The other dyes and solvents were not tested.

Table I shows the values λ_x, ϵ_x, λ_y, ϵ_y, $\lambda_{x'}$ and $\epsilon_{x'}$ for the dyes in the three solvents. From the points obtainable from this table, and the spectrum of the dye in one of the solvents as a model, one can draw a fairly correct spectrum of the dye in any solvent. For this reason we have shown the spectra of all the dyes only in methyl alcohol.

The Phenyl Group.—In Fig. 1 the spectra of malachite green and the two symmetrical dyes having two and four phenyl groups in place of the methyl groups are compared. Figure 2 and Table II show the effect on the frequencies of the x- and y-bands of substituting phenyl for methyl groups. This effect is shown under the headings $\Delta\bar{\nu}_x$ and $\Delta\bar{\nu}_y$; these are the wave numbers for the bands of the dye less the corresponding values for malachite green.

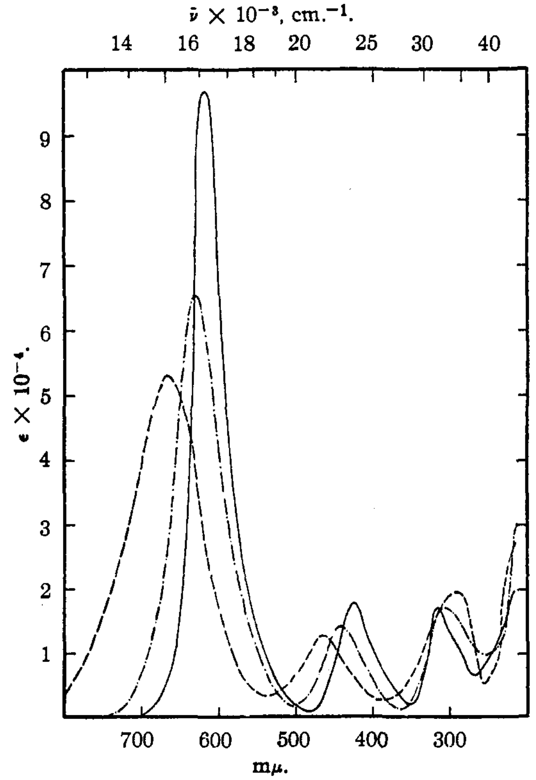


Fig. 1.—Effect on absorption spectrum of substituting phenyl groups for N-methyl groups ($R = C_6H_4C(C_6H_5)C_6H_4$): ————, malachite green in methyl alcohol; –·–·–·–, $(C_6H_5CH_2NRNC_6H_5CH_3)^+$ in methyl alcohol; – – – – –, $[(C_6H_5)_2NRN(C_6H_5)_2]^+$ in methyl alcohol.

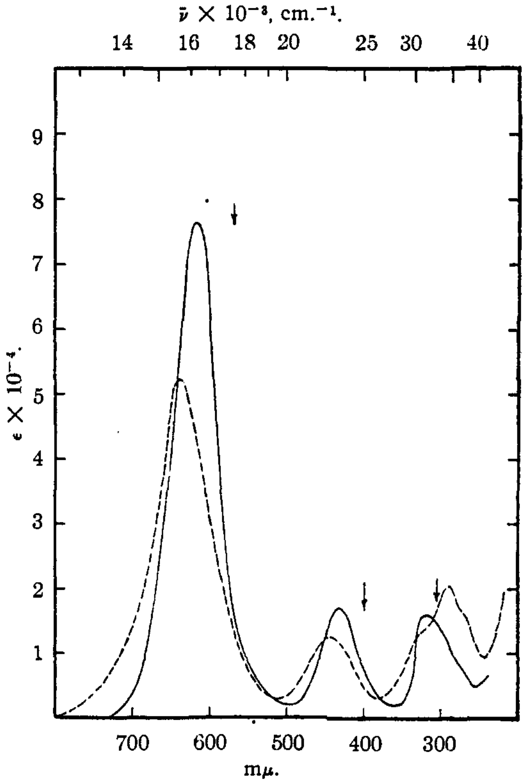


Fig. 2.—Absorption spectra of dyes with N-phenyl groups and N-hydrogen atoms in methyl alcohol ($R = C_6H_4C(C_6H_5)C_6H_4$): ————, $[(CH_3)_2NRNHC_6H_5]^+$; – – – – –, $(HC_6H_4NRNHC_6H_5)^+$. Arrows indicate the maxima in the spectrum of Döbner's violet in ethyl alcohol.

The effect of each phenyl group increases as the number of phenyl groups increases. This is only

TABLE II

EFFECT OF PHENYLATION

Dye, ion, R = $C_6H_4C(C_6H_5)C_6H_4$	No. of phenyl groups	Solvent	$\Delta\bar{\nu}_x$	$\Delta\bar{\nu}_y$
$(CH_3)_2NRNCH_3C_6H_5$	1	CH_3OH	− 52	− 110
	1	AcOH	− 26	− 109
	1	$CHCl_3$	− 103	− 108
$(CH_3)_2NRN(C_6H_5)_2$	2	CH_3OH	− 181	− 591
	2	AcOH	− 231	− 533
	2	$CHCl_3$	− 403	− 682
$CH_3C_6H_5NRNCH_3C_6H_5$	2	CH_3OH	− 358	− 643
	2	AcOH	− 331	− 637
	2	$CHCl_3$	− 354	− 784
$(C_6H_5)_2NRN(C_6H_5)_2$	4	CH_3OH	−1210	−1970
	4	AcOH	−1200	−2090
	4	$CHCl_3$	−1470	−2470

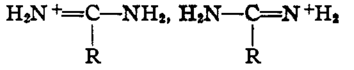
in part due to the fact that symmetrical and unsymmetrical dyes have been included in this table. For the unsymmetrical dyes one phenyl group decreases $\bar{\nu}_x$ by an average of 60 wave numbers, and two phenyl groups by an average of 272 wave numbers. For the symmetrical dyes two and four phenyl groups decrease $\bar{\nu}_x$ by an average of 348 and 1290 wave numbers, respectively. Similar relationships hold for the *y*-band. The increasing effect of the phenyl group is also noticeable in a comparison of wave lengths. This is shown quite clearly in Fig. 1.

It may be noticed that comparing only symmetrical with symmetrical, or unsymmetrical with unsymmetrical dyes, the effect of phenyl groups on the frequency is approximately proportional to the square of the number of phenyl groups. This relationship may be fortuitous, because the effect of phenyl groups on $\bar{\nu}$ is the result of the differences of its effects on the energies of the excited and ground states.

The effects of phenyl groups on the frequency is greater with *y*- than with *x*-bands. Hence $\bar{\nu}_y - \bar{\nu}_x$ decreases with phenylation (see Table I). The increase in the wave length produced by phenyl groups is just sufficient to compensate for the decrease in $\bar{\nu}_y - \bar{\nu}_x$ and λ_x/λ_y is nearly constant at 1.44.

The Hydrogen Atom.—The spectra of the two dyes having hydrogen atoms on nitrogen atoms are shown in Fig. 2. These dyes have longer wave lengths for the *x*- and *y*-bands than the corresponding dyes in which methyl groups replace the hydrogen atoms. The differences are small; for dye VI in methyl alcohol 6 and 4 mμ for λ_x and λ_y, respectively. But these small shifts toward the red are striking when compared with the shift in the opposite direction produced by subsitution of hydrogen atoms for methyl groups in malachite green. Meyer and Fischer[2] found absorption maxima at 568, 399 and 305 mμ for the *x*-, *y*- and *x'*-bands of Döbner's violet in ethyl alcohol. Thus substitution of all the methyl groups of malachite green with hydrogen atoms results in a decrease of λ_x of 50 mμ and a decrease of λ_y of 27 mμ. The position of the *x*-, *y*- and *x'*-bands of Döbner's violet are indicated by arrows in Fig. 2.

The diaminotriphenylmethane dyes belong to a large class of colored substances in which there is a resonance similar to that of an amidinium ion



$$H_2N^+{=}\underset{\displaystyle R}{\underset{|}{C}}{-}NH_2,\ H_2N{-}\underset{\displaystyle R}{\underset{|}{C}}{=}N^+H_2$$

The spectra of these compounds are often affected by a lack of symmetry in the substituents on the nitrogen atoms. The effects produced by the lack of symmetry due to different degrees of phenylation of the amino group are shown in Table III. In this table the effect is measured by $\Delta\lambda$, which is defined by the equation $\Delta\lambda = \lambda_{mean} - \lambda$, where λ_{mean} is the arithmetic mean of $\lambda_{max.}$ for the two symmetrical dyes and λ is $\lambda_{max.}$ for their hybrid. Lack of symmetry produced by a single phenylation had a negligible effect, but that produced by two phenylations noticeably decreased both λ_x and λ_y. But even with two phenyl groups the effect is small compared to deviations of over 100 mμ which have been observed when lack of symmetry has been produced by structural changes that do not appear to be any more drastic than a double phenylation.

TABLE III

BROOKER DEVIATION

Dye ion, R = $C_6H_4C(C_6H_5)C_6H_4$	Solvent	$\Delta\lambda_x$(mμ)	$\Delta\lambda_y$(mμ)
$(CH_3)_2NRNCH_3C_6H_5$	CH_3OH	5	4
	AcOH	6	4
	$CHCl_3$	3	6
$(CH_3)_2NRNHC_6H_5$	CH_3OH	6	6
	AcOH	8	7
	$CHCl_3$	3	7
$(CH_3)_2NRN(C_6H_5)_2$	CH_3OH	18	9
	AcOH	16	11
	$CHCl_3$	15	13

From a profound study of dyes having the amidinium ion type of resonance, Brooker and Sprague[3] have concluded that when the basic groups are of approximately equal base strengths, the wave length of the principal band of an unsymmetrical dye having the amidinium type of resonance is approximately equal to the arithmetic mean of the wave lengths of the bands of the symmetrical compounds of which the dye can be considered a structural hybrid; but when the basicities of the two groups differ widely the wave length of the principal band of the unsymmetrical dye is much shorter than this mean.

The authors of this generalization clearly stated that they were not using basicity in the sense of the power of an amine to add hydrogen ion, so that though phenylation does greatly reduce this

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(2) Meyer and Fischer, *Ber.*, **46**, 70 (1913).

(3) Brooker and Sprague, THIS JOURNAL, **63**, 3201 (1941); Brooker, *Rev. Mod. Physics*, **14**, 275 (1942).

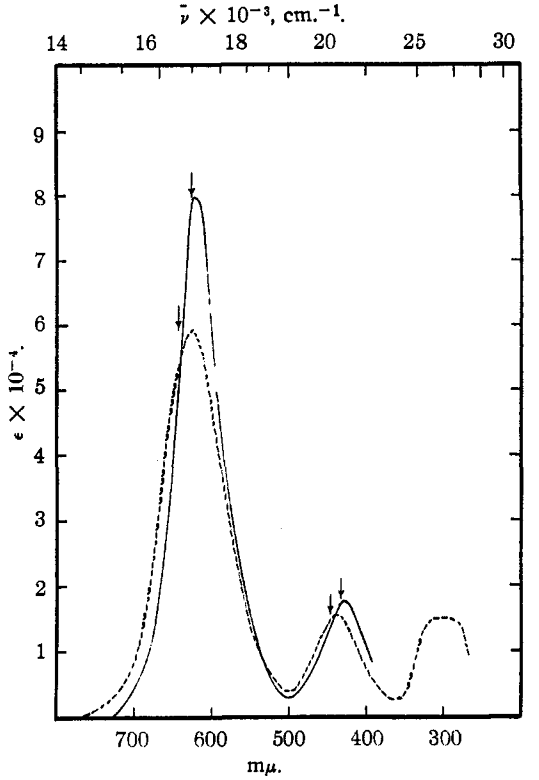
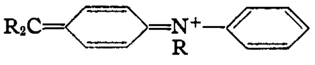


Fig. 3.—The Brooker deviation, absorption spectra in methyl alcohol (R = $C_6H_4C(C_6H_5)C_6H_4$) of: ————, $[(CH_3)_2NRNCH_2C_6H_5]^+$; - - - - -, $[(CH_3)_2NRN(C_6H_5)_2]^+$. Arrows indicate mean values of $\lambda_{max.}$ for the parent symmetrical dyes.

power, it need not have a comparable effect on $\Delta\lambda$. The basicity that determines the symmetry of the dye is the power of the terminal group to combine with a positively charged carbon atom to form a double bond, which is generally part of a conjugated system. This is related to the power of an amino group to assist the dissociation of hydroxide ion from an amino-carbinol by combining with the positively charged carbon atom to form a double bond.

The effect on the base strength of an amine produced by substituting a phenyl for an alkyl group or a hydrogen atom is due to the stabilization of the base by the resonance between the classical structure and quinoidal structures. This is not compensated by any resonance interaction between the phenyl group and the nitrogen atom in the ion form. If we start with a *p*-aminophenylcarbinol, the substitution of a phenyl group for an N-alkyl group or an N-hydrogen atom stabilizes the base by the resonance interaction between the amino group and the additional phenyl group. However, the resonance energy of the ion obtained by the dissociation of a hydroxide ion is also increased by the substitution of a phenyl group for an N-alkyl group or an N-hydrogen atom, since this ion has a quinoidal structure and a phenyl group extends the conjugate system in the way shown by formula VIII.



VIII

In consequence of this compensation the phenyl group decreases the basicity of the carbinol less than it does that of the amine. It can then be seen why the deviation found in the unsymmetrical dimethyldiphenyl dye is so much less than one would expect if only the relative base strengths of dimethylaniline and triphenylamine were considered. The spectra of this and another dye, the unsymmetrical dimethylphenylmethyl compound are shown in Fig. 3. The mean of the wave lengths of the dyes of which these dyes can be considered structural hybrids are shown by arrows.

Solvent Effects.—The values of λ_x and λ_y are little affected by the solvent. On the average the wave lengths are a little longer in chloroform than in the other two solvents. In changing from

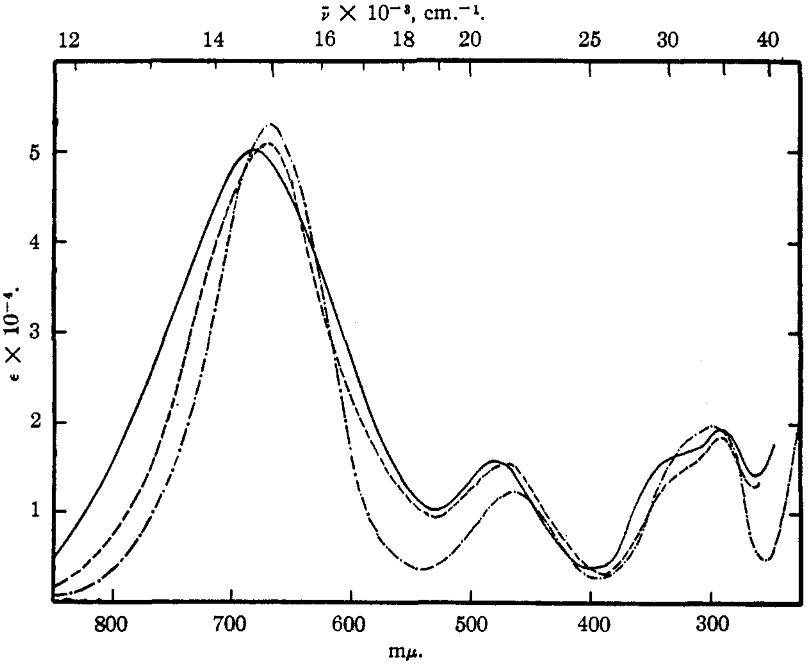


Fig. 4.—The solvent effect on the absorption spectrum of $[(C_6H_5)_2NC_6H_4C(C_6H_5)C_6H_4N(C_6H_5)_2]^+$: —·—·—·—, in methyl alcohol; - - - - -, in acetic acid; ————, in chloroform.

methyl alcohol to chloroform λ_x increases on the average by 7 mμ and λ_y by 5 mμ. In changing from methyl alcohol to acetic acid λ_x increases on the average by 1 mμ and λ_y by 2 mμ. The greatest effect of the solvent was found in the tetraphenyl compound. Its spectra is shown in the three solvents in Fig. 4. That the negative ion was acetate ion when the solvent was acetic acid, but chloride ion with the other solvents, appears to have had no effect. All the generalizations we have made are independent of the solvent.

The bulge, shoulder, or actual peak on the short wave length side of the *x*-band of triphenylmethane dyes has been previously observed.[4] This effect was noticed in chloroform solutions of all the dyes studied in this paper except in the N-dimethyl-N′-phenyl and N-dimethyl-N′-diphenyl compounds, where very limited ranges of acid concentrations were studied. It was also observed in the *sym*-dimethyldiphenyl dye in methyl alcohol at high acid concentrations—3 molar hydrochloric acid. Figure 5 shows the spectra of the *sym*-dimethyldiphenyl dye in chloroform in three different hydrochloric acid concentrations. The subsidiary band is observed to increase with increasing hydrochloric acid concentration. The effect decreased when triethylamine hydrochloride was added.

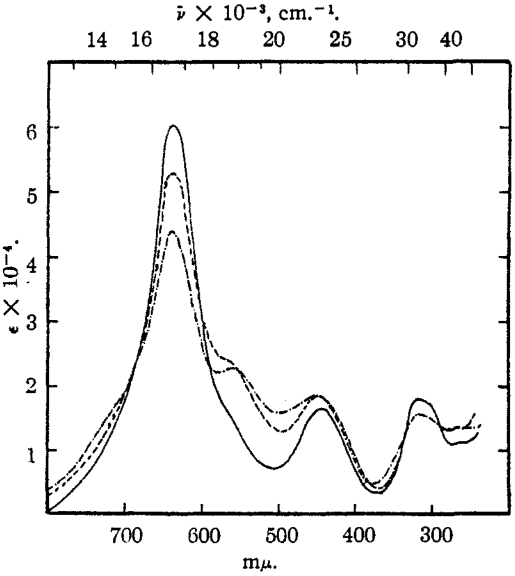


Fig. 5.—Effect of hydrochloric acid on the absorption spectrum of $[CH_3C_6H_5NC_6H_4C(C_6H_5)C_6H_4NCH_3C_6H_5]^+$ in chloroform: ————, no excess acid; - - - - -, 1.4 × 10^{-5} *M* HCl; - · - · -, 1 × 10^{-3} *M* HCl.

The phenomena can hardly be attributed to the *cis–trans* type of isomerism possible in the case of *sym*-dimethyldiphenyl dye, since it is shown by malachite green and dye VII. Lewis and coworkers[4] have proposed that a special type of stereoisomerism arising from the overlapping of the phenyl rings is the cause of this effect, and have shown that the subsidiary band increases with decrease in temperature. It seems probable that the phenomenon is due to the possibility of more than one stable arrangement of atoms in the solution, but whether they are different arrangements of the atoms in a single unit of the dye, or in more than one unit, is questionable.

The *x*′-Bands.—In the set of dyes studied the relationships between structure and the frequency of absorption bands are qualitatively the same for the *x*- and *y*-bands. Whether the same relationships hold for the *x*′-bands cannot be definitely stated. According to the values given in Table I the effects on the *x*′-band differ from those on the *x*- and *y*-bands. However, the *x*′-bands show structure, and it is not possible to know whether corresponding bands are being compared. Further, impurities affect these bands much more than they do the *x*- and *y*-bands. For instance, one would not know whether to use 320 or 297 mμ for $\lambda_{x'}$ of the symmetrical diphenyl dye. Either of these might correspond to the band at 318 mμ in the spectrum of malachite green and either of them may be due to impurities.

Experimental

Preparation of *sym*-N,N′-Dimethyldiphenyl-*p*,*p*′-diaminotriphenylmethylcarbinol.—One mole of methyldiphenylamine, one mole of aluminum chloride, a weight of paraffin wax equal to that of the amine, and one-half mole of benzotrichloride were heated three hours on the steam-bath. The hot paraffin was decanted, and the residue washed well with hot 1 *N* hydrochloric acid. The crude product was chilled, crushed. and washed several times with hexane and 1 *N* hydrochloric acid solution. The dye was dissolved in methyl alcohol, filtered, and added to a cold solution of sodium hydroxide in methyl alcohol containing sufficient base to neutralize all of the dye. The precipitated methyl ether was filtered and dried. It was dissolved in benzene and the chloride precipitated by adding hydrochloric acid dissolved in ether. This was repeated twice. The dye chloride was then mixed with benzene containing a few ml. of 40% sodium hydroxide solution, and shaken for one hour. The benzene solution of the carbinol was washed, dried, filtered, and the carbinol precipitated by adding hexane. The product was a slightly pink powder, insoluble in methyl alcohol, water or hexane, soluble in benzene, chloroform, carbon tetrachloride and ethyl ether; m. p. 141–142°.

Anal. Calcd. for $C_{33}H_{30}N_2O$: C, 84.2; H, 6.43; N, 5.95. Found: C, 84.2, 84.4; H, 6.30, 6.35; N, 5.83, 5.81.

Preparation of N-Dimethyl-N′-phenyl-*p*,*p*′-diaminotriphenylmethyl Methyl Ether.—One mole of diphenylamine, one mole of N-dimethyl-*p*-aminobenzophenone and two moles of aluminum chloride were heated at 145 to 150° for three hours. The reaction mixture was protected by a layer of nitrogen. The crude dye was washed twice with water, dissolved in concd. hydrochloric acid. filtered and diluted to 4 *N*. The precipitated dye was filtered, dissolved in a minimum amount of chloroform, and precipitated with ether. This last step was repeated four times. The dye was then dissolved in methyl alcohol, neutralized with sodium hydroxide and precipitated with water. The methyl ether was then dissolved in carbon tetrachloride, and partially precipitated with hydrochloric acid in ether. This solution was boiled and the carbon tetrachloride decanted; this boiling and decanting was repeated ten times.

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(4) Holmes, *Ind. Eng. Chem.*, **16**, 35 (1924); Lewis, Magel and Lipkin, THIS JOURNAL, **64**, 1774 (1942).

The final purification was achieved by fractional adsorption of the methyl ether with Nuchar 00. The chloride was converted to the methyl ether by neutralizing a solution of the dye chloride in methyl alcohol with sodium methylate. This solution was boiled with a small amount of Nuchar and filtered hot. The methyl ether was then adsorbed from the filtrate with a large amount of Nuchar, and extracted from the adsorbent with chloroform. After evaporation of the chloroform the residue was dissolved in methyl alcohol, and the final product precipitated with water and dried *in vacuo;* m. p. 58–60°.

Anal. Calcd. for $C_{26}H_{30}N_2O$: C, 82.4; H, 6.92. Found: C, 81.6, 81.8; H, 6.90, 6.99.

Preparation of N,N'-Tetraphenyl-*p,p'*-diaminotriphenylmethyl Methyl Ether.—The preparation of the chloride of this dye was similar to that of the chloride of IV, except that the reactants were heated on the steam-bath for twelve hours instead of three hours, and the washings were with 4 *N* hydrochloric acid solution instead of 1 *N* hydrochloric acid. The crude product was then washed with hexane and toluene several times. The dye was dissolved in methyl alcohol, neutralized with sodium hydroxide, and extracted with carbon tetrachloride and water. The carbon tetrachloride solution was washed, dried, filtered, and the dye precipitated by adding dry hydrogen chloride. The dye was converted into the methyl ether, which was extracted in benzene, dried, filtered, precipitated with hexane, and dried *in vacuo;* m. p. 138–140°.

Anal. Calcd. for $C_{44}H_{36}N_2O$: C, 87.0; H, 5.96. Found: C, 86.4, 86.1; H, 6.27, 6.29.

Preparation of N-Dimethyl-N'-diphenyl-*p,p'*-diaminotriphenylmethyl Methyl Ether.—One mole of dimethylaminobenzophenone, one mole of triphenylamine, and two moles of $POCl_3$ were heated for two hours at 130°. The reaction mixture was treated with water, and the product dissolved in methyl alcohol containing sodium hydroxide, and this solution extracted with water and carbon tetrachloride. After washing, drying, and filtering the solution, the dye was precipitated with dry hydrogen chloride. The dye was dissolved in methyl alcohol, neutralized with alcoholic sodium hydroxide solution, and treated with benzene and water. The benzene solution of the methyl ether was washed, dried, filtered, and the benzene evaporated. The amorphous dye was chilled in contact with methyl alcohol until firm, ground in a mortar while cold, and allowed to stand overnight with methyl alcohol. It was washed several times with methyl alcohol, filtered and dried *in vacuo;* m. p. indefinite.

Anal. Calcd. for $C_{34}H_{32}N_2O$: C, 84.3; H, 6.66; N, 5.78. Found: C, 84.8, 84.3; H, 6.56, 6.49; N, 5.93, 5.93.

Preparation of N-Dimethyl-N'-phenylmethyl-*p,p'*-diaminotriphenylmethyl Chloride.—The preparation and purification scheme for this dye is similar to that for III. The reaction mixture, however, was heated for forty-eight hours on a steam-bath. The yield was very poor.

Preparation of the Methyl Ether of Malachite Green.—A sample of malachite green from the National Aniline Co. was dissolved in methyl alcohol, neutralized with alcoholic sodium hydroxide, extracted with benzene, washed, dried, filtered, evaporated to dryness, dissolved in methyl alcohol, and precipitated with water; m. p. 138–140°.

Viridine Green.—Two samples were used, one a chloride, and the other a mixture of the carbinol and the anhydro base. Both were prepared by Dr. T. L. Hill.

Acknowledgment.—We wish to thank Mr. Charles W. Koch for the microanalyses reported in this article.

Summary

Six phenyl diaminotriphenylmethane dyes were prepared and their absorption spectra compared with the spectra of malachite green and Döbner's violet.

The phenyl group was found to increase the wave length of both *x*- and *y*-bands.

In the phenylated dyes the substitution of a hydrogen atom for a N-methyl group increased instead of decreased the wave lengths of both *x*- and *y*-bands.

The asymmetry produced by a double phenylation of one nitrogen atom decreased the wave length of both *x*- and *y*-bands.

These effects were shown to be independent of the solvent.

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Raman Spectrum of the Deuterohydroxylammonium Ion

BY O. REDLICH AND I. I. FRIEDMAN

The Raman spectra of deuterium compounds are known to be a useful aid in checking and completing the interpretation of vibration spectra.

Deuterohydroxylamine deuterochloride was prepared by exchange of 4.8 g. of recrystallized hydroxylamine hydrochloride with eleven portions of heavy water (99.5%). Finally the salt was dissolved in 5 g. of D_2O. The deuterium content was checked after the fourth exchange by a determination of the density of the water distilled off the substance. A mole fraction of 0.65 was found, while 0.60 was calculated from the amounts of heavy water. The mole fraction in the final solution was calculated to be 0.985. This corresponds to the mole fractions 0.94 for D_3NOD^+, 0.042 for D_2HNOD^+ in the solute, and 0.03 for HOD in the solvent.

The spectra of H_3NOH^+ and D_3NOD^+ contain several bands, very broad lines and only one sharp line 1005 and 987 cm.$^{-1}$, respectively. The centers are given in Table I. The last column shows the isotopic quotient *q*, *i.e.*, the ratio of the corresponding frequencies of the light and heavy compounds.

The results for the light compound agree well with the figures of Edsall[1] and the less complete spectra of Ananthakrishnan[2] and of Bernstein and Martin.[3]

The data for both compounds are in essential agreement with the discussions of Edsall and of

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(1) J. T. Edsall, *J. Chem. Phys.*, **5**, 225 (1937).

(2) R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, **A5**, 87 (1937).

(3) H. J. Bernstein and W. H. Martin, *Trans. Roy. Soc. Canada*, [III] **31**, 95 (1937).