[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

Spectroscopic Study of Wurster's Blue and Tetramethyl-*p*-phenylenediamine with Assignments of Electronic Transitions[1]

BY ANDREAS C. ALBRECHT[2] AND WILLIAM T. SIMPSON

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The visible and near ultraviolet bands of Wurster's Blue, and the ultraviolet bands of N,N,N',N'-tetramethyl-*p*-phenylenediamine are studied experimentally and given qualitative theoretical interpretation. Relative symmetry classification of the electronic wave functions is achieved by the method of polarized photoöxidation. This information together with one absolute symmetry classification based on the pleochroism of crystals of Wurster's Blue perchlorate leads to assignment of the 2600 Å. band of benzene as $A_{1g} \rightarrow B_{2u}$, and the 2000 Å. band of benzene as $A_{1g} \rightarrow B_{1u}$. Orientation effects in polarized photoöxidation experiments are given quantitative consideration.

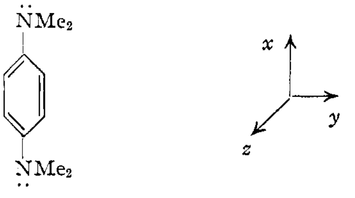
Introduction

When the present research was begun the main object was to use the system N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD) and Wurster's Blue (WB) to furnish information about the electronic states of benzene itself. The object has been realized as will be described in this paper. However, while the research was in progress, a second method for investigating the benzene states was adopted, namely, the spectroscopic study of thin single crystals of *p*-dimethoxybenzene. This research is described elsewhere,[3] and the description includes the reasoning which one uses to infer the species of excited electronic states of benzene from experimental findings for para disubstituted benzene derivatives. Accordingly the emphasis in the present paper will be not so much on the application to the benzene problem, as on the characteristics of the electronic states of TMPD and WB themselves. The work consists mainly of polarized photoöxidation experiments, much like those which were first performed by Lewis, Lipkin and Bigeleisen,[4] also on TMPD and WB. It is hoped that the present research serves to round out and extend the pioneering early work.

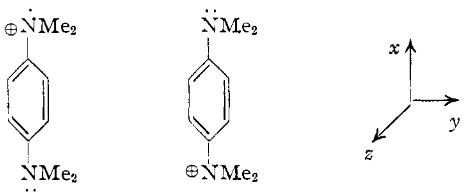
We take as the principal experimental problem the determination of the energies and polarizations of the excited electronic states in the two compounds under consideration. Briefly, the solution to the problem is based on the production of an oriented sample of WB in a rigid medium according to the scheme

$$\text{TMPD(random)} + h\nu\text{(polarized)} = \text{WB(oriented)} + e^-\text{(solvated)}$$

In order to clarify the method it will be useful to anticipate several of the final results. It is found that at 3180 Å., TMPD absorbs light in the *y*-direction, referred to the following diagram



Hence, if 3180 Å. light is incident normal to the plane of the paper and polarized horizontally, parallel to the lines of type, the typical molecule out of a random set absorbing radiation will be essentially lined up as above except tilted (about the *y*-axis) out of the plane of the paper. Therefore the purple color of WB will show orientation effects. In fact the purple will appear most intense when viewing with light polarized vertically, or perpendicular to the lines of type, so that the direction of charge oscillation for WB is in this instance deduced as either *x* or *z*, with *x* suggested by the structures[5]



It will be appreciated that in general only the relationship *parallel* or *perpendicular* can be established between the absorbing electronic oscillation direction in the parent molecule (TMPD) and any given electronic oscillation in the daughter molecule (WB). Because of this limitation a determination of the crystal structure of Wurster's Blue perchlorate was carried out[6] and it was found from an examination of the pleochroism of single crystals[6] that the visible band (purple color) indeed arises from an *x*-charge oscillation. This single determination on an absolute basis is the key to the determination here of the polarizations of two other bands for WB and two bands for TMPD.

In what follows we present first the experimental details of the work. Next comes a section which systematically marshalls the facts to answer the main questions, and in the final section the results are interpreted. Theoretical aspects of the experimental work are to be found in the Appendix.

Experimental

a. Materials.—TMPD was obtained from the Eastman Kodak preparation of its dihydrochloride salt. When at first only crude TMPD-diHCl was available purification was effected by two recrystallizations from *n*-butyl alcohol

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(2) Shell Pre-Doctoral Research Fellow 1952–1953. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. This paper is taken from the writer's Ph.D. thesis.

(3) A. C. Albrecht and W. T. Simpson, *J. Chem. Phys.*, **21**, 940 (1953); and another paper in press, *ibid.*

(4) G. N. Lewis and D. Lipkin, THIS JOURNAL, **64**, 2801 (1942); G. N. Lewis and J. Bigeleisen, *ibid.*, **65**, 520 (1943); **65**, 2419, 2424 (1943).

(5) W. T. Simpson, *ibid.*, **75**, 597 (1953).

(6) J. D. Turner and A. C. Albrecht, *Acta Cryst.*, submitted for publication.

solutions saturated with HCl. Fine white needles were obtained which showed excellent stability. The more recent commercial preparations used required no further purification. Ethanolamine (not always pure, see below) or a dilute solution of it in propyl alcohol was used to convert the TMPD-diHCl to its free base in solution. When pure material was desired, the Eastman Kodak product was freshly distilled before use.

The perchlorate salt of WB was synthesized after the method of Michaelis and Granick,[7] using exactly one-half the scale reported by them. The crystals obtained were purified by two recrystallizations from methyl alcohol. Analysis for the elements checked within experimental error.

The solvents used in making rigid media were: isopentane, Phillips petroleum, Pure Grade (minimum purity 99%); methylcyclohexane, Eastman Kodak, white label (b.p. 100-101°); isopropyl alcohol, Eastman Kodak, white label (98-99%); *n*-propyl alcohol, Eastman Kodak, white label (b.p. 96-98°); and *n*-butyl alcohol, Eastman Kodak, white label (b.p. 116-118°). In most of the work it was necessary to redistil only the *n*-butyl alcohol. When especially pure hydrocarbons were required several washings with concd. H_2SO_4 followed by thorough water washings and drying sufficed.

b. **Absorption Spectra at Room Temperature.**—All absorption spectra observed were taken using the Beckman Model DU spectrophotometer. TMPD was studied in propyl alcohol solutions while Wurster's Blue perchlorate was studied in aqueous solutions. Since solutions of both compounds are sensitive to air oxidation a special procedure was applied to obtain satisfactory accuracy in the extinction coefficient measurements. First, extinction coefficients were obtained accurately at only two or three wave lengths by preparing solutions of known concentration and taking density readings as a function of time at the chosen wave lengths. Extrapolations were then made to zero time. The remainder of the absorption curves were fitted to these known extinction coefficients by preparing fresh solutions of the sample (concentration unknown) and recording densities in narrow portions of the spectrum including, however, a reading at one of the critical wave lengths for each solution. The extinction coefficients for the entire spectrum obtained in this way are believed to be accurate to ±3% for TMPD and ±1% for WB. The TMPD samples were prepared by adding a many-fold excess of ethanolamine to solutions of TMPD-diHCl.

The absorption studies in the near infrared of WB perchlorate were made using a Perkin-Elmer Model 21 spectrophotometer as well as a modified Perkin-Elmer Model 12-C spectrophotometer in the 1-2 μ region, and the Beckman Model DU spectrophotometer in the 0.7-1 μ region. Because of solvent absorption, cells as thin as 0.15 mm. were used. They were made of microscope slides with Teflon spacers cemented with silicone grease. Solutions in water, acetone and methyl alcohol were studied. Density measurements also were made in the visible in order to determine the approximate concentrations.

c. **Absorption Spectra at −195°.**—Quantitative absorption spectra at −195° were obtained using an apparatus which permitted low temperature measurements to be made on the Beckman Model DU spectrophotometer. A technique first developed at the University of California for molding a rigid glass and then releasing it from the mold was adapted to the problem at hand. A brass mold was designed to produce a rigid glass (called an optical block, or, by the discoverers, a "popsicle") having the dimensions of a rectangular solid with a square cross-section (1 cm. × 1 cm. × 10 cm.). A holder was then built to fix the position of the optical block with constant geometry within a quartz dewar containing liquid nitrogen. The dewar, which was cylindrical, ten inches high, and having an inside diameter of one inch, was unsilvered in the lower portion to permit light transmission. An important feature of the optical block holder was a bakelite disc which fitted inside the dewar below the optical block and served to direct the nitrogen bubbles through appropriately cut holes away from the optical path. A wooden attachment was built to replace the usual Beckman cell compartment and to carry the dewar containing the optical block. The entrance slit to the wooden attachment was 2.5 mm. high and 2 mm. wide and acted as both the aperture and field stop (the measuring beam being essentially parallel).

The optical block itself was made so that the upper portion contained the sample to be studied while the lower portion served as the blank. Measurements were carried out by raising and lowering the optical block in the beam of measuring light to give density readings of the sample directly just as is usually done on the Beckman. The vertical motion of the optical block was achieved manually by a geared screw attachment which was fastened to the optical block holder. The optical block with its holder moved while the dewar containing the coolant remained stationary. In this fashion errors due to inhomogeneity of the quartz or due to the round surfaces of the dewar were avoided.

To prevent ice formation in the coolant extreme drying precautions were taken and only fresh liquid nitrogen was used. In order to detect unwanted differences in absorption between the blank and the sample sections of the optical block, measurements were taken in spectral regions where no absorption by the sample occurred. Differences were found and were tolerated and corrected for when they did not exceed 0.005 density unit at $D \sim 0.400$. While density readings were usually reproducible to within ±0.001 density unit, the over-all accuracy is believed to be ±0.003 density unit, the main source of error arising from the absence of optically flat surfaces on the block.

The lower wave length limit for absorption measurements appeared to be fixed by the transparency of the liquid nitrogen. Samples of liquid nitrogen alone in the Dewar were found to become opaque below 2500 Å. While appearing perfectly transparent in the visible, the liquid nitrogen possibly contained a sufficient number of tiny ice particles to become turbid at 2500 Å.

The rigid media used in this work were glasses made of critical mixtures of isopentane and *n*- or isopropyl alcohol or *n*-butyl alcohol. These glasses are sufficiently polar to dissolve many substances in more than spectroscopic amounts and are not sensitive to moisture as are the EPA glasses conventionally used. Mixtures of isopentane (7 parts by volume) and *n*-butyl alcohol (3 parts) or isopentane (8 parts) and *n*- or isopropyl alcohol (2 parts) formed excellent glasses even when used directly without drying.

While the TMPD samples were prepared as already described, it was not possible to use solutions of WB perchlorate as samples for low temperature measurements because their color changes at low temperatures.[8] Instead, an optical block containing TMPD was prepared and then photooxidized with unpolarized and unfiltered light (to avoid orientation of the sample) to provide a sample of WB at low temperatures.

Because of the difficulty in obtaining the concentration of the sample and the thickness of the cell in photoöxidation experiments, the determination of extinction coefficients is complicated. However by assuming that, while the detailed shape of an absorption curve may change considerably on cooling the sample to low temperatures, the integrated intensity for any one absorption band should change very little, an approximation to the extinction coefficients may be obtained. By matching the room temperature spectrum (where extinction coefficients are known) to the low temperature spectrum, band for band, a parameter was determined which implicitly contained the product of the concentration of the sample and the thickness of the optical block. This parameter, once determined, was applied to the density readings wave length by wave length to give the extinction coefficients in detail.

d. **The Photoöxidation.**—The apparatus, coolant and the rigid media used during the photoöxidation experiments were precisely those used in the low temperature spectrophotometry work already described. In those photooxidation experiments which required absorption measurements to be made in the visible only (reported in Table I) optical blocks were made of TMPD solution throughout, while the lower unphotoöxidized portion, being transparent in the visible, served as the blank. For experiments which included measurements in the ultraviolet (see Figs. 4, 5 and 6), however, a blank section consisting of solvent alone had to be used. The source of the photoöxidizing radiation was a water-cooled, high pressure General Electric mercury

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[7] L. Michaelis and S. Granick, THIS JOURNAL, **65**, 1747 (1943).

[8] In all probability the color change is the result of formation of an ionic bond with perchlorate.

lamp, model A-H6. The light, focussed onto the sample by a spherical quartz lens, was polarized by reflection from a stack of quartz plates set at the Brewsterian angle for blue light.[9] The beam struck the sample about 1 cm. from the bottom of the optical block illuminating an area 1 cm. wide by 0.5 cm. high. To minimize loss of intensity by reflection, light was made to enter the dewar polarized horizontally. The photoöxidizing light was filtered to provide light of the desired wave length for the photoöxidation. Sets of photoöxidation experiments were carried out for excitation in each of the two main absorption bands of TMPD. For excitation in the 2620 Å. region a 1-cm. path of an aqueous cyclic cyanine dye[10] solution (22.5 mg./100 cc.) was employed in combination with a Corning #9863 filter. Radiation for excitation in the 3180 A. region was isolated by using a piece of $^1/_4''$ lucite in combination with the Corning filter, #9863. This filter combination effectively isolated the long wave-length side of the 3180 Å. band. The Corning filter served to prevent unnecessary heating of the sample.

Photoöxidation in either of the spectral regions was carried out until a visible density (at *ca.* 5600 Å.) of about 0.2 had been obtained. The time required for this varied from as short a period as 10 minutes to as long as 1.5 hours, and depended largely on two factors: (1) the age of the A-H6 lamp, and (2) the amount of impurity present in the TMPD sample. Optical blocks were generally photoöxidized on both the front and the rear surfaces in order to obtain a more diffuse sample. While no organized study was made of the effect of impurities on the rate of photoöxidation, impurities were intentionally introduced in order to speed the photoöxidation. The crude preparation of TMPD-diHCl was often used and at times impure ethanolamine was used when converting the di-HCl to the free base. In both cases the rate of photoöxidation was enhanced. Care was always taken never to introduce impurities in spectroscopic amounts.

Measurements made on the oriented molecules of WB were carried out as described in the section on low temperature spectrophotometry except that polarized measuring light was used. For the preliminary experiments polarized light was obtained by setting two polaroids vertically and horizontally in the filter slide of the Beckman spectrophotometer. Readings were taken in such a manner that errors arising from partially polarized light emerging from the Beckman, or from any differences in the absorption characteristics of the two Polaroids, were eliminated. Measurements on what will be called the *ab* face of the optical block were obtained by rotating it 90° in its holder. In the later experiments (as in Figs. 5 and 6), a spectrum with unpolarized light was taken of the TMPD sample before photoöxidation in every case, so that proper background corrections could be applied to the WB spectrum.[11] In these experiments the spectra of the oriented WB molecules were taken using a Glan-Thomson polarizing prism mounted in a holder which fits onto the Beckman ahead of the sample and which permitted a rotation of the prism through an angle of about 95°. The prism transmitted to 2900 Å.

e. The Emission Spectrum of WB.—A Bausch and Lomb 250 mm. focal length grating monochromator was converted into a grating spectrograph. The slide at the entrance slit was replaced by a Hartmann diaphragm while the slide at the exit slit was entirely removed to accommodate the photographic plate. A slight adjustment was made in the position of the concave collimating and condensing mirror in order to focus the entrance slit onto the plate emulsion. After careful focusing, the sodium yellow doublet (5895.9–5890.0 Å.) was clearly resolved. The entire monochromator was enclosed in a light tight box which contained a shutter and was designed to permit control of the Hartmann diaphragm from the outside. The sample whose emission was to be photographed was placed in a holder built so that it could slide in the shutter slot of the light tight box. The sample could thus be moved in and out of a fixed position, permitting constant and reproducible geometry. Since the emitting sample acts as a source, it was situated directly in line with the condensing system of the monochromator.

The source used to excite the emission was a General Electric lamp model A-H6. Light was focussed onto the sample by means of a quartz spherical lens in a manner such that the direction along which the emission was observed was perpendicular to the direction of illumination. Appropriate filters were used for both the exciting and emitting beams to minimize effects of scattered light.

The sample of Wurster's Blue was prepared by prolonged photoöxidation of a concentrated solution of TMPD contained in a rigid glass. In these studies the sample was not contained in an optical block, but in a quartz (1 cm.) Beckman cell whose adjacent walls were polished. This cell was held in a holder designed to fit into the quartz dewar already described. A transparent glass made from mixtures of isopentane and methylcyclohexane occupied the space between the inside walls of the dewar and the outside walls of the Beckman cell. The liquid nitrogen coolant was allowed to circulate below and above this solid block of glass through brass tubing which was part of the holder. This solid section of glass permitted an optical path entirely free of liquid nitrogen so that adverse effects of scattering by bubbles and ice particles were eliminated. Consequently no drying precautions were necessary. The feature of having an ice-free and bubble-free optical path proved especially valuable when long exposures had to be taken in order to look for long-lived emission with a phosphoroscope.

A concentration of Wurster's Blue was produced sufficient to yield a strong red emission when illuminated with a sharply focussed beam of exciting light.

By controlling the Hartmann diaphragm three exposures could be taken on one plate. For any one setting of the grating a spectral region of more than 3000 Å.[12] could be photographed with a dispersion of 62 Å./mm. Several photographs were taken and in Fig. 3 is shown a tracing of one of the best plates obtained. Eastman Kodak I–N plates were used and for the spectrum reported an exposure of two minutes was required. No corrections were made for any systematic errors in the apparatus nor for the emulsion properties. However, spectral sensitivity curves available indicate that the I–N plates have fairly flat response in the region of interest (6300 to 9000 Å.), so that the spectrum obtained is representative in its gross features.

Exposures also were made using a phosphoroscope but no evidence of long-lived emission was found within the range of the spectral sensitivity of the I–N plates.

Results

In this section first the absorptions are presented, giving the transition energies; and then the determination of the polarizations is described. Having the polarizations is equivalent to knowing the species of the excited electronic states.

The absorption of TMPD in isopropyl alcohol is shown in Fig. 1. There are peaks at 3180 and 2620 Å., which are taken to correspond to the benzene 2600 and 2000 bands, respectively.[13] The absorption of WB perchlorate in water is given in Fig. 2. The molar extinction coefficient at 5650 Å. is 12,470 ± 60, to be compared with the values of

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(9) The Brewsterian angle is not a strong function of the wave length of light nor is the per cent. polarization a strong function of the angle of reflection. The angle was set, therefore, using blue light for convenience.

(10) M. Kasha, *J. Opt. Soc. Amer.*, **38**, 929 (1948).

(11) The daughter molecule WB and parent TMPD both absorb in the 2500–3500 Å. region. If photoöxidation is not complete the true density for WB can be obtained only after correction for the TMPD remaining. This is complicated if the WB produced is oriented, because then the TMPD remaining is also oriented. Briefly the correction procedure involves the determination of the amount of TMPD photoöxidized, the orientation of the TMPD holes, and the subtraction of these hole densities from the density for random TMPD before photoöxidation. This gives the effective background density to be used in conjunction with the apparent WB densities to give the corrected final D_a, D_b and D_c for the daughter molecule. The correction for orientation of the holes turned out to be not important in Figs. 5 and 6 owing to the fact that the amount of TMPD remaining after photoöxidation was comparatively large.

(12) The 3000 Å. spectral width is limited in part by a falling off of intensity on either side of the center.

(13) L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947); **71**, 2414 (1949).

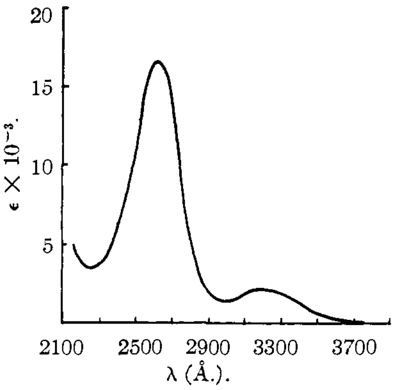

Fig. 1.—Absorption spectrum of tetramethyl-*p*-phenylenediamine in isopropyl alcohol.

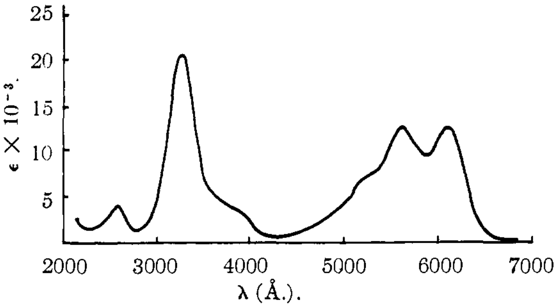

Fig. 2.—Absorption spectrum of Wurster's Blue perchlorate in water.

10,000 ± 500[14] and 12,080[15] obtained previously. The spectrum is interpreted as consisting of four regions corresponding to separate electronic transitions, called the 5650, 3950, 3250 and 2580 Å. bands. That the several peaks in the 5650 Å. region are to be attributed to vibrational structure is indicated by the fact that the emission spectrum is the mirror image of the entire absorption region (Fig. 3) and supported by the fact that the polarization of absorption is constant throughout the band. The 3950 Å. band is found to be a distinct electronic transition from the polarized photoöxidation experiments. The low temperature spectrum of WB produced by photoöxidation (as well as the spectrum of TMPD) is given in Fig. 4. A comparison with Fig. 2 reveals the identity of the photoöxidation product with the chemically prepared perchlorate salt.

The infrared region was examined for absorption bands, not only because such a search should be a routine "precaution" in electronic state spectroscopy but also because there are theoretical reasons for expecting to find a low lying electronic transition.[16] Although concentrated solutions were employed no new bands were found.[17] A quantitative statement of the result of the search is that no absorption having $\epsilon_{max} > 200$ could be found out to 20,000 Å.

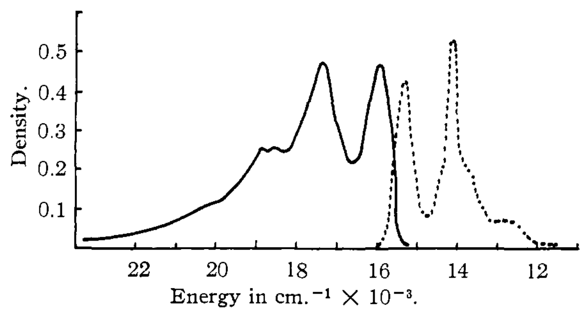

Fig. 3.—Absorption (solid line) and emission (dotted line) spectra of Wurster's Blue contrasted (−195°). Solvent is a glass of methylcyclohexane and isopentane.

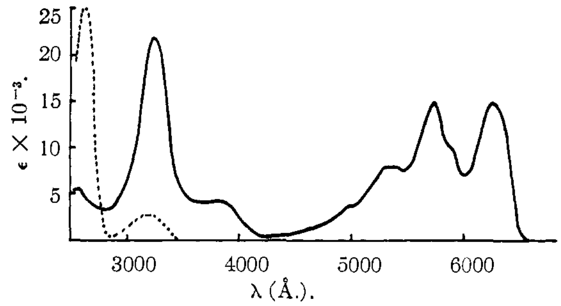

Fig. 4.—Low temperature absorption spectra of Wurster's Blue (solid line) and tetramethyl-*p*-phenylenediamine (dotted line) at −195°. Wurster's Blue produced by photooxidation.

The polarizations of the WB and TMPD bands are obtained from absorption spectrophotometry of the partially oriented product of the photoöxidations, as explained in the Introduction. The curves giving the qualitative results are shown in Figs. 5 and 6, and the geometry of the experiments is defined in Fig. 7. The photoöxidations were carried out with light polarized horizontally (*c* direction) incident on the *ac* face of the optical block. Viewing was on the *ac* and *ab* faces, but the curves in Figs. 5 and 6 were both obtained with viewing on the *ac* face.

In the experiment of Fig. 5, where photoöxidation was restricted to the 2620 Å. band of the parent, it is seen that the oriented WB shows greatest absorption in the *c* direction when viewed in the 5650 and 3250 Å. regions. This means that the charge oscillations giving rise to the 2620 Å. band of the parent and the 3250 and 5650 Å. bands of the daughter are all parallel. Since the direction for the 5650 Å. band has been absolutely determined as x, as discussed in the Introduction, there is qualitatively an assignment of x for all three bands. In the experiment of Fig. 6 the photoöxidation took place in the 0,0-vibrational region of the 3180 Å. band of TMPD. The D_c and D_a curves are reversed, indicating first that the 3180 Å. band of TMPD is perpendicular to x, hence y or z (in agreement with the earlier experiments of Lewis and coworkers[4]) and second that the 3950 Å. band of the radical is parallel to the 3180 Å. TMPD band. The latter two parallel bands must in fact be polarized

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[14] R. K. McDonald, Thesis, University of Washington, 1951.

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

[16] M. Goeppert-Mayer and K. J. McCallum, *Rev. Mod. Phys.*, **14**, 248 (1942).

[17] A band at 7100 Å. was detected but it was found not to obey Beer's Law, and more particularly from the deviation from Beer's Law it was found to be caused by a dimer of WB. The absorption is derived from the same electronic transition as the 5650 Å. band, modified by resonance forces.

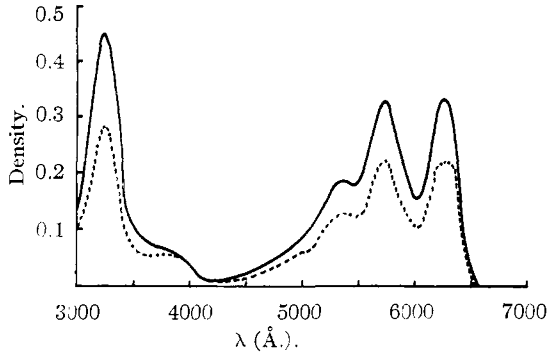


Fig. 5.—Absorption spectra of oriented Wurster's Blue produced by photoöxidation with polarized light at 2600 Å. Solid line is D_c, dotted line is D_a. Photoöxidizing light polarized along *c*-direction.

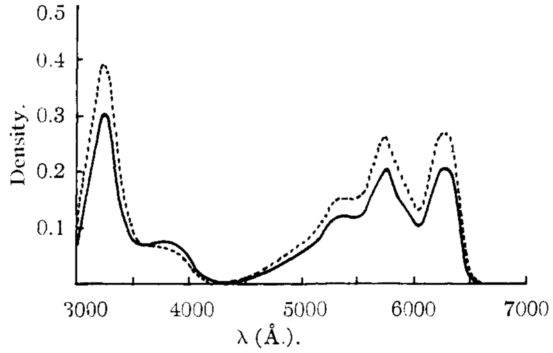


Fig. 6.—Absorption spectra of oriented Wurster's Blue produced by photoöxidation with polarized light at 3200 Å. Solid line is D_c, dotted line is D_a. Photoöxidizing light polarized along *c*-direction.

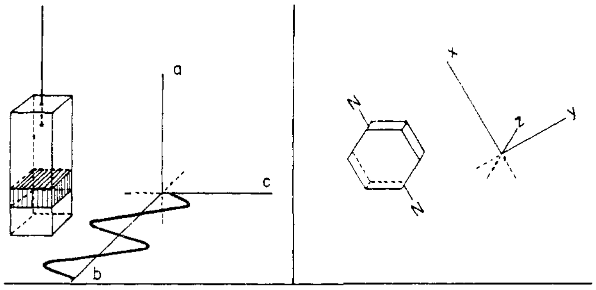


Fig. 7.—Geometry of photoöxidation experiments, showing laboratory fixed axes (*a*,*b*,*c*) and molecule fixed axes (*x*,*y*,*z*). Light incident along *b*, polarized along *c*.

predominantly *y* and not *z*, since the 3180 Å. band comes from the 2600 Å. band of benzene which is known to be of N,V origin (see also ref. 3).

The argument by which the polarizations are deduced can be made quantitative. When this is done it is found that according to the most straightforward model for the experiment (assuming, *e.g.*, perfect rigidity, no energy transfer, and no migration of electrons) there should be D_c/D_a ratios of three and of one half. The former ratio is for the so-called normal case in which the charge oscillations in the parent and daughter molecules, for photoöxidation and viewing, are parallel; the latter ratio is for the abnormal case of perpendicular charge oscillations.

Table I presents the results obtained in ten separate photoöxidation experiments divided equally between the 2620 Å. type and the 3180 Å. type. Here the oriented daughter molecule is viewed at only one wave length, but observations are made on two faces of the sample. The D_c/D_a ratios lead to the same conclusions about the polarizations of the 2620, 3180 Å. bands of TMPD and the 5650 Å. band of WB as were drawn from an examination of Figs. 5 and 6. The ratios D_c/D_a in Figs. 5 and 6 and Table I are not equal to the theoretical and in the Appendix an attempt is made to explain the discrepancy. The explanation is based on a more elaborate model for the polarized photoöxidation experiment.

TABLE I

DICHROISM OF WURSTER'S BLUE PRODUCED BY POLARIZED PHOTOÖXIDATION

Popsicle no.	Region of photo-oxidation, A.	Density ratios at 5800 Å. D_c/D_a	D_a/D_b	Apparent anisotropy of absorption for TMPD r_x	$(r_y + r_z)$
1		0.65	1.07	0.11	0.89
2	3180	.71	1.02	.16	.84
3		.69	1.02	.14	.86
4		.75	1.02	.18	.82
5		.78	..	.20	.80
6		1.57	1.00	0.60	0.40
7	2620	1.65	0.98	.63	.37
8		1.76	0.97	.67	.33
9		1.67	1.00	.64	.36
10		1.44	..	.55	.45

The main result of the quantitative treatment is to show that the TMPD *y*-band in the region to the red of 3180 Å. is 92 ± 8% *y* and 8 ± 8% *x* while the *x*-band in the region near 2620 Å. is 83 ± 17% *x* and 17 ± 17% *y*. The range indicated conveys some idea of the experimental precision, but not according to any standard formulation of error. The photoöxidation of the *y*-band was carried out, roughly speaking, over the low energy or long wave length part (the zero-zero region) where vibrational perturbation of the selection rules is smallest. It has been found qualitatively that the percentage of *x* in the *y*-band increases markedly in the high energy portion, and this behavior was also observed in the experiments on dimethoxybenzene.[3]

It was considered that there might be some long-lived emission from the radical corresponding to a quadruplet derived from a state with two excited electrons in separate orbitals. A search was made using N type plates and also visual examination and no long-lived emission was detected. There was phosphorescence for the parent amine observed by McDonald,[14] however, and we have estimated that corresponding to this emission there is a first singlet-triplet absorption for TMPD with a peak at about 4300 Å.

To summarize the Results section, the absorptions of tetramethyl-*p*-phenylenediamine, are 2620 Å. (*x*) and 3180 Å. (*y*); while those of the positively charged free radical, Wurster's Blue, are 2580 Å. (?), 3250 Å. (*x*), 3950 Å. (*y*), and 5650 Å. (*x*).

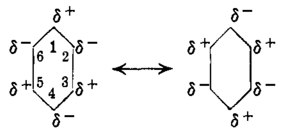
Discussion

The correlation of the *x* and *y* bands of TMPD with the benzene bands[13] leads to the conclusion that the benzene bands at 2000 and 2600 Å. represent transitions to states of species B_{1u} and B_{2u}, respectively.[3] This finding provides a confirmation of the theoretical approach to benzene which used molecular orbitals, a fact which can be shown most compactly using group theory.[3] Nevertheless it is possible to give a pictorial account of the observed spectroscopic behavior, based on structures. This requires a few preliminary notions.

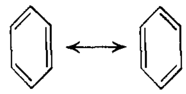
It can be shown by a somewhat involved quantum mechanical argument that when a large number of benzene molecules come under the influence of an electro-magnetic field (of proper frequency) there is on the average a certain small fraction of them (those undergoing transition) whose electronic distribution is actively oscillating back and forth. This oscillation is with the frequency $\Delta E/h$ where ΔE is the transition energy for the molecule (for the B_{1u} upper state for benzene it corresponds to 2000 Å.) and this frequency is also the frequency of the light. During the oscillation the positions of the atomic nuclei stay fixed but the electronic distribution changes.

For transitions from a totally symmetric ground state to upper states of species B_{1u} and B_{2u} there is only weak interaction with the radiation, going to zero in the limit of perfect hexagonal symmetry (no distortion of the molecules by vibrations). While the transitions are taking place, the electronic distribution fluctuates as represented by the following diagrams (the two-headed arrow is here meant in the lateral sense).

(A_{1g}, B_{1u})

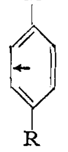


(A_{1g}, B_{2u})



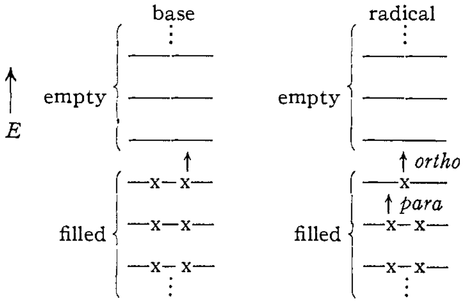
In neither case are the molecules in a stationary state, but in a time dependent state, a state which is particularly well suited for giving us an intuitive understanding of the light absorption.

Let us now consider the nature of the oscillation for the 2000 Å. transition for benzene (A_{1g}, B_{1u}). There is a fluctuating dipole in the 1,4-direction and two exactly compensating shorter dipoles at 2,3- and 5,6. If 1,4-disubstitution is introduced the balance between the 1,4-dipole moment and the sum of the 2,3- and 5,6-moments is upset, with a net charge oscillation resulting, along a line parallel to the substituents. This leads to enhanced absorption in the direction that we have called x. The effect of the same substitution on the zero (in the limit) dipole moment of one of the Kekulé structures would be to introduce a dipole which by symmetry must be along the y-axis



(consider the R groups to be, say, electron repelling). Further, the dipole must be directed oppositely for the other Kekulé structure. In the time dependent or oscillating state there is, therefore, a charge oscillation in the y-direction for the transition related to the 2600 Å. band of benzene.

We turn now to the spectrum of Wurster's Blue, and attempt to understand the experimental findings. First we shall examine the relationship between a compound with an even number of electrons (base) and the radical derived from it by ejection of an electron. Orbital energy diagrams for two such compounds are as follows:



The main point is that according to the simple orbital picture there are transitions possible in which there is a close correspondence between base and radical; and also for the radical new transitions into the half-filled orbital, with no corresponding transitions at all for the base. We shall refer to the former type as *ortho* and the latter as *para*. The classification is only applicable to the extent that excited states having different dispositions of the electrons among the orbitals remain separate (absence of configurational interaction). This condition is known to be fulfilled fairly well for even-electron compounds, though for the allyl radical it is not fulfilled.[18] It is believed that the WB 5650 Å. band is so far away from the nearest band having the same polarization (3250 Å.), that little mixing has occurred here. We shall now analyze the WB spectrum into *ortho* and *para* bands, only with due respect for configurational interaction.

The most important step in the assignment of the bands is the establishment of a correspondence between the y bands of TMPD and WB at 3180 and 3950 Å., respectively. It is to be expected that the y-band for WB ought to lie at longer wave lengths, as is observed, for the following reason. The lowest energy one-electron transition for the base splits into two bands, separated in energy by twice the value of the exchange integral. The singlet comes at 3180 Å., and the triplet at 4300 Å. according to the estimate given in the Results section. For the radical the principal exchange interaction is missing, hence there should be a band in between the singlet and triplet bands of the base. It is believed this is the 3950 Å. band of the radical.[19] The

(18) W. M. Moffitt, *Proc. Roy. Soc.* (*London*), **A218**, 486 (1953); H. D. Hunt, D. L. Peterson and W. T. Simpson, to be published.

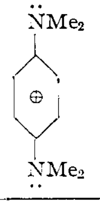
(19) Factors which make this simple discussion not entirely adequate include the fact that the nuclear positions are not the same for the radical and the base. While the radical is planar (ref. 6) the base has a permanent dipole moment (K. B. Everard, L. Kumar and L. E. Sutton, *J. Chem. Soc.*, 2807 (1951)). We attribute the dipole moment to a twisting of the dimethylamino groups in the ground state of the base, a twisting that is related to the repulsion of the non-bonding pairs in hydrazine and hydrogen peroxide, though in TMPD communicated across the benzene ring by π-electron interactions.

3950 Å. band is thus *ortho*. It is natural, then, to assign the 3250 Å. band also as *ortho*, because together the bands constitute a representation of the benzene bands at 2600 and 2000 Å. just as for the 3180 and 2620 Å. bands of the parent compound, TMPD. Moreover, an examination of intensities nicely bears out this interpretation (Fig. 4). The transition moments calculated from the areas of the curves (which required some guess work for the 3950 Å. band of WB) are, for TMPD, for the x- and y-bands, respectively, 0.95 and 0.35 Å.; while for WB, for the x- and y-bands, respectively, 0.97 and 0.43 Å.

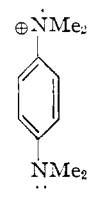
With these assignments we exhaust the possibilities for correspondence between base and radical bands and so are required to assume that the 5650 Å. band is *para*. Additional evidence of a purely empirical nature for assuming the band is *para* is its unnatural appearance. Usually (though not invariably), when a band has a marked vibrational structure it is orbital symmetry forbidden, being made allowed by some vibration. The 5650 Å. band is certainly not forbidden (transition moment 1.00 Å.). The exceptional structure no doubt means here that the equilibrium nuclear configuration for the upper state is displaced abnormally from that for the ground state.

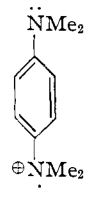
No attempt is made to assign the WB 2580 Å. band.

Finally we consider the question of the specific orbitals involved in the long wave length transition. According to the suggestion of Goeppert-Mayer and McCallum[16] the prominent vibrational interval is a carbon–carbon stretching frequency. It will be observed (Fig. 3) that the vibration frequency for the ground state (emission spectrum) is smaller, indicating tighter binding in the benzene ring in the excited state. This is consistent with the idea that the ground state partakes mainly of the structure

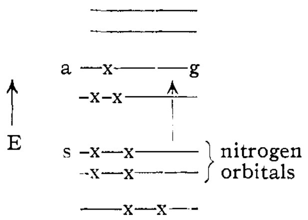


with contributions from





(Kekulé resonance understood) while the excited state is composed of the last two structures, the first being ruled out by symmetry. This same situation may be depicted by means of an orbital energy diagram, based on the simple L.C.A.O. approach, and on the usual practice of assuming nitrogen orbitals to be rather low-lying



The labels s and a mean symmetric and antisymmetric with respect to reflection in a plane perpendicular to and bisecting the line joining the nitrogens. The transition indicated by the arrow is *para*, allowed; and is assumed to be the 5650 Å. band. There is predicted another *para* transition involving essentially a transfer of an electron from one benzene orbital to another having very nearly the same energy. This is the forbidden transition classified as $B_{3g} \rightarrow B_{1g}$ by Goeppert-Mayer and McCallum[16] (g to g in the diagram). It may be asked why the search carried out in the infrared failed to turn up an extra electronic transition. The transition could come unexpectedly in the visible, and so be hidden, though we think this is unlikely (compare ref. 13). However Platt[20] has called attention to the fact that transitions in which there is no parity change (as g to g) should be more highly forbidden than transitions for which there is a parity change. The forbidden $A_{1g} \rightarrow B_{2u}$ transition for benzene at 2600 Å. (g to u) has an $\epsilon_{\max}$ of ≈ 200 and in the present research it was established only that there were no electronic transitions out to 20,000 Å. with $\epsilon_{\max} > 200$.[21]

Appendix

Polarized Photoöxidation. a. Theory.—Lewis and Bigeleisen[4] have given a mathematical theory of photoöxidation experiments which, however, is not quite satisfactory for our purposes, because it is too idealized. We outline here a general treatment.

In Fig. 7 two sets of coördinates are given, the space set (a, b, c) and the molecule-fixed set (x, y, z). Assigning these a common origin we then specify the orientation of a molecule in space using Eulerian angles θ, φ and ψ. The cosines of the angles[22] between the axes of the two sets of coördinates are

	x	y	z
a	$\cos\theta$	$\sin\theta\sin\psi$	$\sin\theta\cos\psi$
b	$\sin\theta\sin\varphi$	$(\cos\psi\cos\varphi - \cos\theta\sin\varphi\sin\psi)$	$(-\sin\psi\cos\varphi - \cos\theta\sin\varphi\cos\psi)$
c	$-\sin\theta\cos\varphi$	$(\cos\psi\sin\varphi + \cos\theta\cos\varphi\sin\psi)$	$(-\sin\psi\sin\varphi + \cos\theta\cos\varphi\cos\psi)$

These nine direction cosines are abbreviated as for example t_{ax}.

The probability that a single molecule will be

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(20) J. R. Platt, *J. Chem. Phys.*, **19**, 1418 (1951).

(21) There is a line of reasoning which would lead to the conclusion that there is no low-lying level. According to this line of reasoning if there were a low-lying singlet excited level there would have been no fluorescence observed because empirically it has been found (Kasha) that there is fluorescence only from the lowest excited singlet state in a large variety of compounds. This reasoning probably does not apply here because the low-lying level would have a different parity from the level responsible for the observed fluorescence, and also might be quite far away, energywise.

(22) Here we shall use the angles as defined by Goldstein ("Classical Mechanics," Addison-Wesley Press, Inc., Cambridge, Mass., 1950, p. 107). His coördinates x,y,z, and x',y',z', are our b,c,a, and y,z,x, respectively.

photoöxidized is proportional to the square of the projection of the absorbing axis of the molecule onto the axis of the space coördinate system along which the incident photoöxidizing beam is polarized. The probability of molecules absorbing is similarly determined, and the probability of first photoöxidizing and then viewing the same molecule is proportional to the product of these probabilities. Thus for a molecule at $\bar{\theta}$, $\bar{\varphi}$ and $\bar{\psi}$ the probability of photoöxidation through y absorption with light incident on the ac face polarized along c is $\bar{t}_{\mathrm{cy}}{}^{2}$; while for viewing the x axis of the daughter molecule with light polarized along a we have $\bar{t}_{\mathrm{ax}}.^{2}$ The combined relative probability is $\bar{t}_{\mathrm{cy}}{}^{2}\bar{t}_{\mathrm{ax}}{}^{2}$.

To generalize let us assume that at a given wave length contributions to absorption arise from all three axes of the parent molecule. Of the total density the fractions effective along the x-, y- and z-axes of the molecule are r_{x}, r_{y} and r_{z}. Similarly we assume that for viewing the daughter molecule at a particular wave length the absorption is split up among the axes according to q_{x}, q_{y} and q_{z}. Finally we consider the photoöxidizing beam is incident along b, polarized by an amount p along a and $(1 - p)$ along c. The expression for the probability of photoöxidation is then

$$p[r_{\mathrm{x}}t_{\mathrm{ax}}{}^{2} + r_{\mathrm{y}}t_{\mathrm{ay}}{}^{2} + r_{\mathrm{z}}t_{\mathrm{az}}{}^{2}] + (1 - p)[r_{\mathrm{x}}t_{\mathrm{cx}}{}^{2} + r_{\mathrm{y}}t_{\mathrm{cy}}{}^{2} + r_{\mathrm{z}}t_{\mathrm{cz}}{}^{2}]$$

and for viewing with light polarized, say, along a is

$$q_{\mathrm{x}}t_{\mathrm{ax}}{}^{2} + q_{\mathrm{y}}t_{\mathrm{ay}}{}^{2} + q_{\mathrm{z}}t_{\mathrm{az}}{}^{2}$$

with analogous expressions for viewing along the b- and c-axes. The combined probability is again proportional to the product of two independent probabilities. To use these expressions we integrate them over the Eulerian angles

$$\int_0^{2\pi} \mathrm{d}\psi \int_0^{2\pi} \mathrm{d}\varphi \int_0^{\pi} \sin\theta \mathrm{d}\theta$$

For the optical density for viewing with light polarized along the b-axis we have after integration

$$D_{\mathrm{b}} \propto d_{\mathrm{b}} = r_{\mathrm{x}}q_{\mathrm{x}} + r_{\mathrm{y}}q_{\mathrm{y}} + r_{\mathrm{z}}q_{\mathrm{z}} + 2[q_{\mathrm{x}}(r_{\mathrm{y}} + r_{\mathrm{z}}) + q_{\mathrm{y}}(r_{\mathrm{x}} + r_{\mathrm{z}}) + q_{\mathrm{z}}(r_{\mathrm{x}} + r_{\mathrm{y}})] \quad (1)$$

and along the a- and c-directions, using d_{b} as an abbreviation

$$D_{\mathrm{a}} \propto d_{\mathrm{a}} = (1 - p)d_{\mathrm{b}} + p[3(r_{\mathrm{x}}q_{\mathrm{x}} + r_{\mathrm{y}}q_{\mathrm{y}} + r_{\mathrm{z}}q_{\mathrm{z}}) + q_{\mathrm{x}}(r_{\mathrm{y}} + r_{\mathrm{z}}) + q_{\mathrm{y}}(r_{\mathrm{x}} + r_{\mathrm{z}}) + q_{\mathrm{z}}(r_{\mathrm{x}} + r_{\mathrm{y}})] \quad (2)$$

$$D_{\mathrm{c}} \propto d_{\mathrm{c}} = (1 - p)[3(r_{\mathrm{x}}q_{\mathrm{x}} + r_{\mathrm{y}}q_{\mathrm{y}} + r_{\mathrm{z}}q_{\mathrm{z}}) + q_{\mathrm{x}}(r_{\mathrm{y}} + r_{\mathrm{z}}) + q_{\mathrm{y}}(r_{\mathrm{x}} + r_{\mathrm{z}}) + q_{\mathrm{z}}(r_{\mathrm{x}} + r_{\mathrm{y}})] + pd_{\mathrm{b}} \quad (3)$$

To illustrate the use of these equations we consider two hypothetical experiments in which the photooxidizing light is polarized along the c-axis ($p = 0$), the daughter molecule is viewed in a pure x-band ($q_{\mathrm{x}} = 1$ and $q_{\mathrm{y}} = q_{\mathrm{z}} = 0$) and the parent molecule absorbs parallel ($r_{\mathrm{x}} = 1$) and then perpendicular ($r_{\mathrm{y}} = 1$, say). Viewing is on the ac face. This is an idealization of the experiments of Figs. 5 and 6, using the set-up in Fig. 7. For the first case, $r_{\mathrm{x}} = 1$, we have $d_{\mathrm{a}} = 1$ and $d_{\mathrm{c}} = 3$ so the $D_{\mathrm{c}}/D_{\mathrm{a}}$ ratio is 3. For the second case, $r_{\mathrm{y}} = 1$ and we have $d_{\mathrm{a}} = 2$, $d_{\mathrm{c}} = 1$ so that the $D_{\mathrm{c}}/D_{\mathrm{a}}$ ratio is 0.5. These ideal ratios were not found in our experiments.

b. **Analysis of Experiments.**—First we see from eq. 1 and 2 that if the light is completely plane polarized, with $p = 0$ (direction of polarization along b as in Fig. 7) then $D_{\mathrm{a}}/D_{\mathrm{b}} = 1$. The experiments recorded in Table I have $D_{\mathrm{a}}/D_{\mathrm{b}}$ ratios so close to unity that we shall take $p = 0$ as experimentally determined. The examination of the crystals of Wurster's Blue perchlorate[6] shows that there can be very little absorption in the visible band other than x, as otherwise the degree of transparency obtained in a favorable direction would not be as high. We thus take $q_{\mathrm{x}} = 1$, $q_{\mathrm{y}} = q_{\mathrm{z}} = 0$ at 5800 Å.

These assumptions permit the determination of r_{x} and $(r_{\mathrm{y}} + r_{\mathrm{z}})$, using eq. 2 and 3 together with the observed $D_{\mathrm{c}}/D_{\mathrm{a}}$ ratios. The r values are listed in Table I.

To go farther we need to distinguish between apparent r-values, as found above, and molecular or intrinsic r-values which are a measure of the directional properties of the oscillating probability distributions responsible for light absorption. To see the difference, note that if the parent molecule absorbed with a pure x oscillation, but then could rotate in the rigid glass, the daughter molecule would on the average be randomly oriented just as if the parent molecule absorbed equally in all three directions. The differences in r-values in Table I from one popsicle to another are far outside of the experimental error associated with the photometry and thus show that some randomization is taking place. (Intrinsic properties of the molecule would be reproducible.) Possible causes are local heating from light absorption, or migration either of electrons or protons.

If we exclude popsicle #1 because of the faulty $D_{\mathrm{a}}/D_{\mathrm{b}}$ ratio then in the first group of experiments we see that the least randomization occurred for #3 (nearest to the theoretical value of $D_{\mathrm{a}}/D_{\mathrm{b}} = 0.5$). Similarly out of the second group we select #8.

If we now assume that for these popsicles with least randomization there has actually been no randomization the r-values may be considered intrinsic. On the other hand, all departures from the theoretical $D_{\mathrm{c}}/D_{\mathrm{a}}$ ratios of 3 and 0.5 may be considered caused by randomization, so that intrinsic r-values must be either zero or one. These two viewpoints allow the establishment of limits on the r values. To summarize, then, from the 3180 Å. photoöxidation we have as a description of the 3180 band that intrinsically $r_{\mathrm{x}} = 0$ to 0.14, $(r_{\mathrm{y}} + r_{\mathrm{z}}) = 1$ to 0.86; and from the 2620 Å. photoöxidation, we find that the 2620 band is $r_{\mathrm{x}} = 1.00$ to 0.67, $(r_{\mathrm{y}} + r_{\mathrm{z}}) = 0$ to 0.33. Finally if we assume $r_{\mathrm{z}} = 0$ intrinsically (N,V nature of the bands[3]), we have the values reported in the Results section of the text.

We have used eq. 1, 2 and 3 to analyze the experimental results more elaborately than described above, particularly to obtain quantitative values for the q's of the Wurster's Blue ultraviolet bands. The results are consistent with the qualitative picture given in the text based on Figs. 5 and 6.

It should be pointed out that the regions within the bands for which the r-values are experimentally determined depend on choice of filters, quantum yield for photoöxidation as a function of frequency, etc. We have tried to confine our experimentation to approximately the long wave length one third of both bands of the parent amine (zero-zero region). This very low resolution is required by the need for sufficient intensity.

SEATTLE 5, WASH.