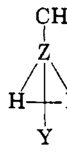
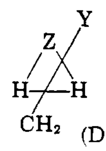

(C)


(D)

the more polar form with Y = halogen, this argument would imply that its proportion increased in solvents of high dielectric constant and that the long-range couplings become smaller as the methylene group is *trans* to the allylic substituent.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, NEW YORK]

Mixed Polarization in an Electronic Transition by the Method of Polarized Photoöxidation[1]

BY ANDREAS C. ALBRECHT

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The detailed polarization of the near ultraviolet band of N,N,N′,N′-tetramethyl-*p*-phenylenediamine is investigated by the method of polarized photoöxidation. The theory of this method, previously developed, is applied to translate the observed orientation of the photo-product, Wurster's Blue, into relative transition probabilities along the two in-plane axes of the parent molecule. The near ultraviolet band is thus analyzed at 5 mμ intervals and it is found that while in the low energy region short axis absorption is dominant, at the higher energies of the same band there is a reversal and long axis absorption predominates. Evidence indicates that this mixed polarization is not due to the overlap of two different electronic transitions but more likely represents the breakdown of selection rules based on nuclear coördinate independent electronic wave functions.

Introduction

Recently[2] the method of polarized photoöxidation has been employed to determine the gross polarization of certain electronic transitions in N,N,N′,N′ - tetramethyl - *p* - phenylenediamine (TMPD) and Wurster's Blue (WB). In that investigation work was directed toward answering the question: In which direction is a given electronic transition polarized? Such a question is prompted by theory based on equilibrium configuration electronic wave functions. Thus[3,4] to a first approximation the integrated intensity of a single electronic transition is related to the square of the transition moment

$$\mathfrak{M}^0_{g,k} = \int \Theta_g{}^0\, \mathbf{m}_e\, \Theta_k{}^0\, dx \qquad (1)$$

where $\mathbf{m}_e$ is the electronic part of the electric moment operator and both electronic wave functions $\Theta_g{}^0$ (ground state) and $\Theta_k{}^0$ (excited state k) are normally prescribed for the fixed equilibrium nuclear configuration of the ground electronic state. The integral is over the electron space only, x symbolizing electron coördinates. Group-theoretical analysis of the integrand leads to a prediction of the polarization of absorption (the direction of $\mathbf{m}_e$) given the symmetry properties of the combining wave functions. Conversely an observation of the polarization leads to predictions concerning the symmetry properties of the electronic functions. In the earlier investigation[2] (hereafter referred to as I) every transition studied revealed at least a predominant direction of polarization. On the basis of eq. 1 any deviation from perfect polarization must be regarded as anomalous (for molecules not too high in symmetry). Failure to obtain pure polarization was attributed either to inherent defects of the method or in one obvious case to the overlap of oppositely polarized bands. However, one set of observations never yielded to this sort of explanation. Polarized photoöxidation in the near ultraviolet band of TMPD gave good orientation only when illumination was confined to the low energy region of the band. Whenever the entire band was illuminated essentially no orientation was observed. These qualitative observations lead one to conclude that either this band consists of two strongly overlapped bands having opposite polarization or that the selection rules based on Eq. 1 have broken down.

In the present paper a detailed polarized absorption analysis of the near ultraviolet band of TMPD is presented. A reversal of polarization is found on going from the low to the high energy region. Evidence is marshalled indicating that the observed anomalous mixed polarization apparently implies the breakdown of the selection rules of Eq. 1. Such mixed polarization, however, is predictable on the basis of nuclear coördinate dependent electronic wave functions.[4]

Experimental

a. Materials.—TMPD was obtained from the Eastman Kodak preparation of its dihydrochloride salt. Purification of the salt was achieved by two recrystallizations from a 2-propanol solution saturated with HCl. A dilute solution of triethylamine (Eastman Kodak, white label) in 1-propanol was used as described below to obtain the free base. Isopentane (Phillips Petroleum, pure grade) was used with 1-propanol in making the rigid media. The 1-propanol (Eastman Kodak, white label) was rendered spectroscopically pure by one treatment with norite at elevated tempera-

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[1] (a) This work was supported in part by the National Science Foundation. (b) Presented in part before the Symposium on Molecular Structure and Spectroscopy, the Ohio State University, Columbus, Ohio, June, 1958.

[2] A. C. Albrecht and W. T. Simpson, THIS JOURNAL, **77**, 4454 (1955).

[3] R. S. Mulliken and C. A. Rieke, *Repts. Progr. in Phys.*, **8**, 231 (1941).

[4] For a detailed discussion of the problem treated here (and notation) see a paper entitled "Forbidden Character in Allowed Electronic Transitions," by A. C. Albrecht, *J. Chem. Phys.*, **33**, in press (1960).

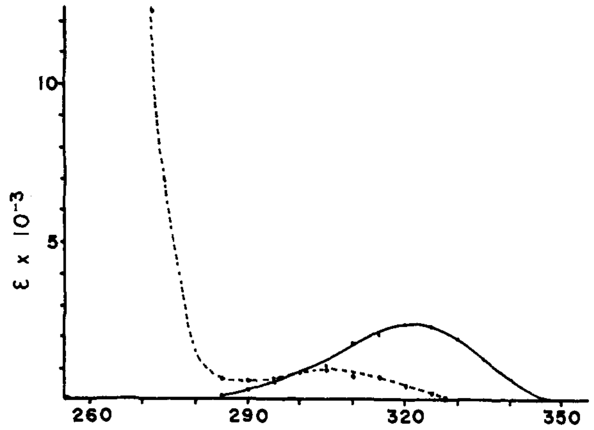

Fig. 1.—The decomposition of the near ultraviolet band of TMPD into two in-plane components: ———, short axis (y) absorption; ---------, long axis (z) absorption. The long axis absorption below 285 mμ belongs to the next electronic transition from which the anomalous absorption is "borrowed."

tures (50 to 60°), filtering and treating with 2,4-dinitrophenylhydrazine with a few drops of concentrated H_2SO_4. After allowing the mixture to stand for several hours, it was cooled to 0° and filtered. The filtrate was vacuum distilled to give 1-propanol spectroscopically clean down into the far ultraviolet. The Norite treatment served to increase transmission in the far ultraviolet region while the 2,4-dinitrophenylhydrazine served to completely remove the absorption in the 270 mμ region due apparently to a carbonyl impurity.

The absorption cells, obtained from Fisher and Porter and Co. (Hatboro, Penna.), were either of extruded Pyrex or quartz tubing of square cross section. They withstood the shock of low temperature exposure consistently well.

b. **The Polarized Photoöxidation.**—For monochromatic illumination a Bausch and Lomb 500 mm. focal length grating monochromator having a dispersion of 33 Å. per mm. was used in conjunction with a General Electric lamp model A-H6. The light was properly focused on the entrance slit using the condensing lens system provided with the instrument. The geometry was such that the exit slit of the monochromator was horizontal. Two quartz lenses at the exit side served to focus the image of the exit slit on the sample. The image was shaped as a horizontal band about $^1/_3$ cm. wide and 1 cm. long. Between the last lens and the sample was inserted a stack of nine thin quartz plates constituting a quartz-plates polarizer about 5 mm. thick. The quartz plates were set at Brewster's angle and the sample was tilted to an angle such that the horizontally polarized light was incident normal to the sample face. The sample was contained in a 1 cm. Pyrex Beckman type cell about 60 mm. high. (In experiment 3, below, a quartz cell of the same dimensions was used because of the shorter wave lengths employed.) The cell was mechanically centered by a special holder in the lower unsilvered portion of a cylindrical quartz Dewar having an inside diameter of 1″ and a length of 8″. It was mounted in a fixed, appropriately tilted position. The cell holder was independently mounted in such a way that its position in the beam of light could be sensitively controlled by a manual drive. The basic structural member of the cell holder consisted of a stainless steel tube which served also as a filling tube for the liquid nitrogen coolant. The Dewar assembly was capped with a Pyrex chimney which served excellently to keep out all moisture and thus to preserve a clear, transparent light path through the liquid nitrogen.

In all experiments the entrance and exit slits of the monochromator were set at 1 mm. to pass a band width of 3.3 mμ. This is a sufficiently narrow band width to warrant experiments at 5 mμ intervals and yet sufficiently broad to provide enough intensity for the photoöxidation.

In a typical experiment horizontal strips of purple (WB) were produced on the sample, each strip corresponding to a different illuminating wave length. The strips were well separated and in addition an un-photoöxidized area was preserved to serve later for blank measurements. Four to five strips could be produced conveniently on one sample. Typically about ten minutes of illumination was enough to produce a purple having an optical density of about 0.250 at 575mμ. However, when photoöxidizing in the wings of the near ultraviolet band both longer times and higher concentrations were necessary to obtain a suitable purple. The sample itself was prepared from a stock solution of TMPD about 7 × 10^{-3} M. This solution was made by adding purified TMPD-di HCl to purified 1-propanol containing 6% (by volume) of triethylamine; the concentration was determined spectroscopically. Sufficient triethylamine was present to ensure that all of the TMPD was present as the free base in the sample (determined spectroscopically). Approximately 0.6 ml. of the stock solution was made up to 2.5 ml. with 1-propanol and this solution was made up to 10 ml. with isopentane. The resulting solution was placed in the cell which was immersed in liquid nitrogen in the Dewar assembly to give a nice clear rigid glass at −195°. The concentration of TMPD in the glass is ~6 × 10^{-4} M; therefore the amount of WB produced (about 3 × $10^{-5}M$) represents only a small fraction of the TMPD originally present.

c. **The Measurement of Orientation.**—The quantity sought as a measure of the orientation of the WB molecules is the ratio of the optical densities taken with vertically polarized light and horizontally polarized light, respectively. After several strips of WB had been produced, the quartz plates polarizing stack was removed and the Dewar assembly was rotated into position directly in line with the exit slit with the sample at the focal point of the emerging beam. The exit and entrance slit were reduced to about 0.15 mm. each, and the wave length drum on the monochromator was set at 575 mμ to correspond to one of the peaks in the visible absorption band of WB. A Polaroid disc was mounted on an azimuthal scale and placed just after the sample. Beyond this was placed the search unit (with an 1P-21 photomultiplier tube) of the Photovolt photometer (series 520-M). With the narrower slit widths the measuring beam was smaller than the photoöxidizing beam. The sample then was raised gently (or lowered) to a position giving a minimum intensity reading corresponding to the center of one of the photoöxidized strips. At this point a series of intensity readings were taken with the Polaroid disc in each of two perpendicular positions. Usually a set of from eight to ten intensity readings were made for each strip and each position of the Polaroid. The average deviation for any one set was invariably better than 0.5%. There was no interference due to bubbling, although to achieve this great care was required to obtain dry liquid nitrogen. Each strip was located by seeking minima in the transmission. The blank readings were made in the un-photoöxidized strip. Upon returning to any one strip for further measurements, the reproducibility in the average observed intensity was about ±3%. The optical densities were taken as the logarithm of the quotient of the averaged blank intensity and the averaged sample intensity for a given position of the Polaroid. While there is some error in the optical densities, due to the lack of reproducibility of the intensities, their ratios for the two directions of polarizations are usually reproducible to better than ±5%. It appears that while it is difficult to relocate exactly a given strip for a second set of measurements the observed optical density ratio is not much harmed since it should not vary throughout a given strip.

The observed ratios for each of three separate experiments are listed in Table I where D_c and D_a refer to the optical densities with measuring light polarized vertically and horizontally, respectively. In addition a great number of experiments were carried out where only visual observation of the orientation was made.

Results

In order to relate the observed optical density ratios to intrinsic properties of the molecule, it is necessary to apply the equations previously derived in I for polarized photoöxidation experiments. Thus dividing Eq. 3 by Eq. 2 of I one obtains for parallel perfectly polarized photoöxidizing light (the measured polarization was more nearly 99%;

no correction was made for the fact that the photooxidizing beam was not perfectly parallel but error due to this is not believed serious)

$$\frac{D_c}{D_a} = \frac{3(r_x q_x + q_y r_y + r_z q_z) + q_x(r_y + r_z) + q_y(r_x + r_z) + q_z(r_x + r_y)}{r_x q_x + r_y q_y + r_z q_z + 2[q_x(r_y + r_z) + q_y(r_x + r_z) + q_z(r_x + r_y)]} \quad (2)$$

where the r's refer to the apparent fraction of absorption (at a given wave length) along each of three perpendicular axes of the parent molecule being photoöxidized. Similarly the q's refer to the fractional absorption (at a given wave length) along each of three perpendicular molecular axes in the daughter, product molecule. In contrast to previous usage and in keeping with recommended[5] usage, we shall label the long axis (axis connecting the substituents) the z axis, the in-plane short axis, the y axis, and the axis normal to the molecular plane, the x axis. It is known[2] that for WB at 575 mμ $q_z = 1$ and $q_x = q_y = 0$. We shall now define the r's in terms of intrinsic fractional absorption parameters R_x, R_y and R_z and a "degree of randomization" ϵ. The latter shall represent all deviation from ideality due to random effects which always appear to be present but whose origin is not yet fully understood. We shall assume[2] that intrinsically TMPD has no out of plane absorption in the spectral region considered; therefore $R_x = 0$ and $R_z = 1 - R_y$. Combining

$$\begin{aligned} r_x &= (1 - \epsilon)R_x + \epsilon/3 \\ r_y &= (1 - \epsilon)R_y + \epsilon/3 \\ r_z &= (1 - \epsilon)R_z + \epsilon/3 \end{aligned} \quad (3)$$

with Eq. 2, together with the assumptions listed, one obtains

$$\frac{D_c}{D_a} = \frac{2(1 - \epsilon)R_z + (1 + 2\epsilon/3)}{(2 - \epsilon/3) - (1 - \epsilon)R_z} \quad (4)$$

or, solving for $R_z(\epsilon > 1)$

$$R_z = \frac{(2 - \epsilon/3)Q - (1 + 2\epsilon/3)}{(1 - \epsilon)(2 + Q)} \quad (5)$$

where Q is D_c/D_a. It is now possible, given an ϵ for the experiment, to calculate the intrinsic fractional long axis (or anomalous) absorption for any photooxidizing wave length. In order to calculate ϵ and to obtain minimal estimates of R_z, it shall be assumed that in the low energy region (330 mμ and beyond) of the TMPD band the intrinsic R_z is zero. There is theoretical justification for this[4] and the constancy of Q in this region suggests it. Eq. 5 with $R_z = 0$ leads to a value for ϵ for each experiment and these are listed in Table I. If we further assume that this randomization is characteristic of the experiment and not any one illumination (this appears to be the case both here from the constancy of Q in the low energy region, and in I), then it is possible to obtain R_z for every wave length. These values are found in Table I. In Fig. 1 a decomposition based on these data is given for the near ultraviolet band of TMPD. The short axis (normal) absorption and long axis (anomalous) absorption are given separately.

As has been discussed there is some error in the reported Q's. However it is doubtful whether the variation in R_z at 295 and 330 mμ among the experiments is due simply to the errors discussed. There is much improvement needed in the method before subtle variation in R_z, say, can be resolved. However, qualitatively the information is correct. This is borne out by the great number of similar experiments which were performed where only visual observations of the polarization were made. In every case the direction of orientation of WB was ambiguous for photoöxidation in the region between 310–315 mμ. The orientation became more striking and oppositely directed the greater the distance one proceeded from either side of the region. No orientation means $Q = 1$. Eq. 5 shows that in this case $R_z = 0.33$ independent of the value of ϵ. This agrees qualitatively, at least, with what is found in Table I.

TABLE I

THE OBSERVED OPTICAL DENSITY RATIOS AND FRACTIONAL ANOMALOUS ABSORPTION AT DIFFERENT WAVE LENGTHS IN THE NEAR ULTRAVIOLET BAND OF TMPD

	Exp. 1		Exp. 2		Exp. 3	
λ, mμ	D_c/D_a	R_z	D_c/D_a	R_z	D_c/D_a	R_z
285					1.76	0.83
290					1.48	.67
295			1.39	0.58	1.19	.48
300	1.24	0.48				
305			1.18	.46		
310	0.94	.29				
315			0.90	.25		
320	.72	.13				
325			.68	.07		
330	.57	0[a]	.61	0[a]	0.65	0.01
335					.64	0[a]
340					.65	0.01
(Randomization factor) ϵ	0.16		0.25		0.32	

[a] Assumed zero.

Discussion

To interpret the observed mixed polarization one must first make certain whether or not it is a case of overlapping transitions. In Figs. 1 and 4 of I one finds the room temperature and liquid nitrogen temperature spectrum of TMPD, respectively. It is seen that while at room temperature the near ultraviolet band is overlapped considerably by the next higher absorption region, at the low temperature the blue shift of the low energy part of this region leaves the near ultraviolet band cleanly isolated. Furthermore it is sharper as a result of its own blue shift. On the other hand, there is absolutely no trace of any splitting of this band at the lower temperature. If the two components depicted here in Fig. 1 actually represent two distinct electronic transitions, then one would almost certainly expect some splitting at the low temperature as a result of the blue shift of the "long axis band." Finally, if two states of different symmetry are accidentally degenerate in one molecule, it is not likely that this accidental degeneracy will be precisely maintained on going to somewhat different molecules. Yet no conspicuous splitting of the near ultraviolet band of benzene derivatives of this type has been reported.

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(5) *J. Chem. Phys.*, **23**, 1997 (1955). The labelling used in I must be transformed as follows: $x \rightarrow z$, $y \rightarrow y$ and $z \rightarrow x$.

We now conclude that the band under discussion corresponds to a single electronic transition and that the presence of the long axis component (which represents 29% of the short axis intensity) is direct evidence for the break-down of selection rules based on Eq. 1.[6] A mathematical study[4] of this breakdown demonstrates that such anomalous absorption is not unexpected and in fact represents the "borrowing" of long axis intensity from the higher energy long axis absorption region through the perturbation of the pure electronic wave functions by suitably non-totally symmetric vibrations.

While these experiments have established the presence of mixed polarization, there is much that remains unexplained as far as the method of polarized photoöxidation is concerned. Although the parameter ϵ is useful for bringing different experiments into line, its origin is by no means understood nor therefore is it understood why it varies rather markedly from one experiment to the next (see also I in this connection). One of the mechanisms proposed in I for randomization involves the concept of local heating and momentary melting of the rigid environment about a molecule due to the degradation of electronic energy into heat. Unsuccessful attempts have been made to induce randomization of oriented WB molecules by illuminating with intense light for long periods of time. Apparently this mechanism is not important in this case. Other proposed mechanisms for randomization include energy transfer. It is hoped that some of these questions shall be answered through a more careful study of the problem now in progress.

(6) The short axis component is considered to be the normal component because it is found in the zero–zero region and to the red. Here there can be little question of vibrational perturbation in the excited electronic state.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

Reactions of Hydrogen and Hydrocarbons with Iodine Excited by 1849 Å. Radiation[1]

BY THOMAS A. GOVER AND JOHN E. WILLARD

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Previous work from this Laboratory has shown that iodine molecules excited by 1849 Å. radiation react with CH_4 to form CH_3I and HI. We have now found that similar reactions occur with C_2H_4, C_2H_6, C_4H_{10} and H_2. There is strong evidence that in the I_2–CH_4 system 1849 Å. radiation absorbed by the I_2 initiates steps which lead to carbon-carbon bond formation resulting in products such as C_2H_5I, C_3H_7I, C_4H_9I, C_2H_6 and C_3H_8. These products are formed with quantum yields in the range of 10^{-5} to 10^{-3} whereas the yields of the CH_3I and HI are about 5×10^{-2} (assuming a quantum yield of unity for the CH_3I–I_2 exchange activated by 1849 Å. light absorbed by CH_3I). The reactions of excited I_2 molecules with hydrocarbons to produce HI and the alkyl iodide appear to occur only on the first collision of an excited iodine molecule with the hydrocarbon. Evidence for this and information on the quenching cross sections has been obtained by studying the reaction yields as a function of total pressure. At low pressures the yields are low, increasing to a maximum at pressures where the average time between collisions is small compared to the fluorescence lifetime of the iodine molecule. Incidental to these investigations it has been found that the absorbancy index of I_2 at 1849 Å. is pressure sensitive, varying from about 10^4 at very low pressures to about 2×10^5 at atmospheric pressure.

Introduction

Iodine molecules activated by 1849 Å. radiation are able to react with CH_4[2] to form CH_3I and HI and with H_2[3] to form HI. These reactions are unique in that iodine atoms ($^2P_{1/2}$ and $^2P_{3/2}$) formed by the photodissociation of I_2 by radiation in the 5000 Å. region do not attack hydrogen or hydrocarbons at room temperature because of the endothermicity of the reactions. The observed reactions at 1849 Å. must result either from a step of the type $CH_4 + I \rightarrow CH_3 + HI$, made possible by electronic or kinetic excitation of the iodine atom, or from a step involving an excited I_2 molecule (*e.g.*, $CH_4 + I_2 \rightarrow CH_3I + HI$). The iodine atom has as its first two excited electronic levels $^2P_{1/2}$ at 7600 and $^4P_{5/2}$ at 54,600 cm.$^{-1}$ above the ground state.[4] 1849 Å. radiation (54,200 cm.$^{-1}$) is incapable of dissociating the iodine molecule (35 kcal./mole, 12,300 cm.$^{-1}$) and raising one of the atoms to the $^4P_{5/2}$ state. The $^2P_{1/2}$ state of I does not have enough energy to lead to reaction with CH_4. If an 1849 Å. photon absorbed by I_2 produced one atom in the ground state and one $^2P_{1/2}$ atom with the residual energy as kinetic energy each of the two atoms would have 49 kcal./mole as kinetic energy. This is somewhat greater than the endothermic heat of the reaction $I + CH_4 \rightarrow CH_3 + HI$ and is approximately equal to the heat of the reaction $I + CH_4 \rightarrow CH_3I + H$, but cannot be used for reaction because if momentum is to be conserved in the formation of the activated complex a maximum of 0.11 (*i.e.*, $M_{CH_4}/(M_I + M_{CH_4})$) of this energy can go into internal energy of the activated complex and so be available for causing bond rupture. These considerations plus spectroscopic evidence for an excited electronic state of iodine molecules in the 1850 Å. region[5] and the observation of fluorescence from iodine molecules following absorption of such radiation indicate that the observed chemical reactions require an electronically excited iodine molecule. Thus these systems offer the opportunity for further study of chemical processes initiated by a simple electron-

(1) Further details of this work are given in the Ph.D. thesis of Thomas A. Gover, filed with the University of Wisconsin library in November, 1959, and available from University Microfilms, Ann Arbor, Michigan.

(2) G. M. Harris and J. E. Willard, THIS JOURNAL, **76**, 4678 (1954).

(3) J. Gailey and J. E. Willard, unpublished.

(4) "Landolt–Börnstein Zahlenwerte und Funktionen," Springer-Verlag (1950), 6-I-I.

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