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The Photo-ionization of Molecules in Solutions. III. Photo-ionization and Recombination Processes of *N, N, N′, N′*-Tetramethyl-*p*-phenylenediamine in Various Organic Solvent

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Flash photolysis studies of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) were made in various solvents at room temperature. The transient absorption spectrum of the cation, TMPD$^+$, was observed in polar solvents. The transient was also observed in a viscous, non-polar solvent. It has a spectrum different from that of TMPD$^+$. Its absorbance is proportional to the flash-light intensity, and it decays exponentially, with $\tau_e = 82\ \mu$sec. This absorption is attributed to the triplet-triplet transition of TMPD. With aerated solutions, no transient spectrum was observed. The fluorescence and the phosphorescence of TMPD caused by direct excitation were investigated, together with those induced by the recombination of electrons and TMPD$^+$ in non-polar matrices stimulated either thermally or by infrared light. The absorption spectra of TMPD in a non-polar matrix at a low temperature were investigated by means of the cross-illumination method, and the time dependence of the absorption was followed. The ionization and the recombination processes were then discussed by the use of these results.

It was found by Lewis and Lipkin¹⁾ that *N, N, N′, N′*-tetramethyl-*p*-phenylenediamine (TMPD) in a rigid matrix at the temperature of liquid air forms the TMPD$^+$ cation by ultraviolet irradiation. The electronic and vibronic properties of the excited states of TMPD and TMPD$^+$ were investigated using the technique of photoselection in a rigid medium at a low temperature.²⁾ Recently, the existence of an electron ejected into a medium by photo-ionization has been argued by an ESR study.³⁾ Albrecht and his collaborators have studied the photoionization process of TMPD⁴⁻⁶⁾ and the recombination process of the ionized species⁵⁻⁸⁾ in a nonpolar matrix at a low temperature. From these results, they concluded that a two-step mechanism involving the triplet state is responsible for the photo-ionization of benzene derivatives in rigid glasses.⁴⁾ Porter et al. sugested the same mechanism for the photo-ionization of aromatic hydrocarbons.⁹⁾ Claridge and Willard have found that photoejected electrons from TMPD in matrices containing alkyl halides cause the decomposition of alkyl halides, leading to the appearance of ESR signals of alkyl radicals.¹⁰⁾ Van Voorst and Hoijtink have recently found that solvated electrons are formed by the photo-ejection of electrons from aromatic negative ions in 2-methyl-tetrahydrofuran matrices.¹¹⁾ Hamill and his co-workers have also been studying similar electron-ejection and capture processes by using radiolysis techniques.¹²⁾

We ourselves have previously studied the photoexcitation and photo-ionization of TMPD and the recombination of the ionized species in a variety of media at various temperatures.¹³,¹⁴⁾ The work on the room-temperature photolysis has been mainly done by the flash-photolysis technique.

Experimental

Commercially-available TMPD dihydrochloride was neutralized in an aqueous solution with ammonia.

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1) G. N. Lewis and D. Lipkin, *J. Am. Chem. Soc.*, **64**, 2801 (1942).

2) A. C. Albrecht, ibid., **77**, 4454 (1955); **82**, 3813 (1960).

3) E. Dolan, *J. Chem. Phys.*, **37**, 2508 (1962).

4) K. D. Cadogan and A. C. Albrecht, ibid., **43**, 2550 (1965).

5) G. E. Johnson, W. M. McClain and A. C. Albrecht ibid., **43**, 2911 (1965).

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7) E. Dolan and A. C. Albrecht, *J. Chem. Phys.*, **37**, 1149 (1962); **38**, 567 (1963).

8) W. M. McClain and A. C. Albrecht, ibid., **43**, 465 (1965).

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11) J. D. W. van Voorst and G. J. Hoijtink, *J. Chem. Phys.*, **42**, 3995 (1965).

12) M. Kondo, M. R. Ronayne, J. P. Guarino and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 1297 (1964).

13) H. Tsubomura, N. Yamamoto, K. Kimura, T. Sato, H. Yamada, M. Kato, G. Yamaguchi and Y. Nakato, This Bulletin, **38**, 2021 (1965).

14) H. Tsubomura, N. Yamamoto and Y. Nakato, to be published.

The TMPD thus formed was extracted with ether, dried, and sublimed twice in a vacuum.

The solvent used in this experiment were MP (1 part methylcyclohexane, 1 part isopentane), EPA (5 parts ether, 5 parts isopentane, 2 parts ethanol), pyridine, *n*-heptane, ethanol, acetonitrile, liquid paraffin, and cyclohexanol. The ether was purified by distillation. The methylcyclohexane and isopentane were purified by passing them through activated silica gel. The ethanol was purified by drying it over magnesium ribbon and by distilling it in a 120 cm. column. The acetonitrile was refluxed over phosphorus pentoxide, distilled over anhydrous potassium carbonate to remove the phosphorus pentoxide, and finally fractionally distilled in the same column. The *n*-heptane was fractionally distilled. The EP-grade cyclohexanol, liquid paraffin and pyridine were used without further purification.

In the case of polar solvents, TMPD was dissolved in the solvent after it had been degassed by the freezed-pump-thaw technique. In the case of non-polar solvents, the solution was prepared by the conventional method, and then degassed by the same technique.

Flash-photolysis measurements at room temperature were made by the use of a glass cell with quartz windows (200 mm. long, 16 mm. in diameter). Two photolysis flash lamps, one placed at each side of the cell, were connected in series to a condenser a 5-μF capacity working up to 15 kV. Each lamp was made of a quartz glass tube, 20 cm. long and 1.0 cm. in diameter, with tungsten-electrodes at both ends. Those tubes were filled with argon up to a pressure of about 100 mmHg. A small quartz spectro-flash lamp, with a capillary middle portion, was connected to a 2.5 μF condenser working up to 7.5 kV. The lamps were fired by powerful trigger pulses. The time interval between the photolysis-flash and the spectro-flash can be controlled in the range from 1 μsec. to 1 sec. through a delay circuit. The electric power supply and the trigger pulse generator of this instrument were provided by the Nakano Electric Co. The duration times of both the photolysis-flash and the spectro-flash were found to be less than 3 μsec. The transient absorption spectra were obtained photographically with Fuji Neopan SSS film (ASA 200) by the use of a plane-grating spectrograph 1 m. in focal length (Shimadzu GE-100). The decay-curve measurements of the transient absorption were performed by recording the cathode currents of a photomultiplier (EMI 9552B) with a synchroscope or a recorder.

For the measurements of emission spectra at a low temperature, a degassed TMPD matrix contained in a cylindrical cell 10 mm. in diameter was put into a quartz Dewar. For the measurement of the usual fluorescence and phosphorescence spectra of TMPD, the sample was illuminated by focusing light from a 250-W. high-pressure mercury lamp (Ushio HMB-250D) through a filter (Toshiba UV-D2; transparent from 320 to 390 mμ). The emission of the sample was focused on the slit of a 50-cm. grating spectrograph (Nalumi RM 23), the emission spectra were then photographed. The emission spectrum induced by the infrared illumination of the ultraviolet-irradiated TMPD in the MP matrix was obtained by repeating the following procedures about eighty times: (1) ultraviolet irradiation for 30 sec., followed by (2) a 60-sec. dark period, then (3) infrared illumination and the photographing of the induced emission for 30 sec. The infrared light used was obtained from the mercury lamp through a filter (Toshiba VR-69) transparent from 690 mμ to 3 μ. For the measurement of the thermoluminescence spectrum, the sample was drawn out from the Dewar after irradiation by ultraviolet light at the temperature of liquid nitrogen; it was then held in front of the spectrograph until it melted. The decay of the emission spectra was measured in a MP matrix at 77°K by recording the cathode currents of a photomultiplier (RCA 1P28), placed near the sample, by means of a synchroscope through a cathode-follower circuit.

Results

The Flash Photolysis of TMPD.—The flash photolysis of about 5×10^{-4} mol./l. solutions of TMPD in some deoxygenated solvents at room temperature resulted in the appearance of transient absorption spectra, while in some other no new spectrum was obtained at all. These results are tabulated in Table I. The spectra obtained in ethanol, acetonitrile, and cyclohexanol agree with that of TMPD$^+$ formed by chemical oxidation. The spectrum obtained in liquid paraffin does not exactly agree with that of TMPD$^+$, though they have features similar to some extent, as Fig. 1 shows. Decay curves of the transient absorption spectra in a liquid paraffin solution and an ethanol solution are shown in Figs. 2 and 3 respectively. In the liquid paraffin solution, the decay is of the first order and the life-time is 82 μsec. In ethanol and in acetonitrile, the decay is, rather, of the second order and the life-time is very long. The characteristic violet color of TMPD$^+$ remains visible for more than a day. When these solutions were aerated, no transient absorption spectrum was observed by a flash illumination,

TABLE I. APPEARANCE OF TRANSIENT ABSORPTION BY FLASH ILLUMINATION AT ROOM TEMPERATURE

Solvent	Dielectric constant	Temp., °C	Viscosity (centipoise)	Temp., °C	Appearance
Ethanol	24.30	25	1.20	20	Yes (long life)
Acetonitrile	37.5	—	0.345	25	Yes (long life)
Cyclohexanol	15.0	25	68	20	Yes (weak)
Amyl alcohol	ca. 15	20	4.65	30	No
Pyridine	12.3	25	0.974	20	No
Heptane	ca. 1.8	20	0.409	20	No
Ether	4.2	27	0.24	20	No
Liq. paraffin	ca. 1.8	—	ca. 500	—	Yes (82 μsec.)

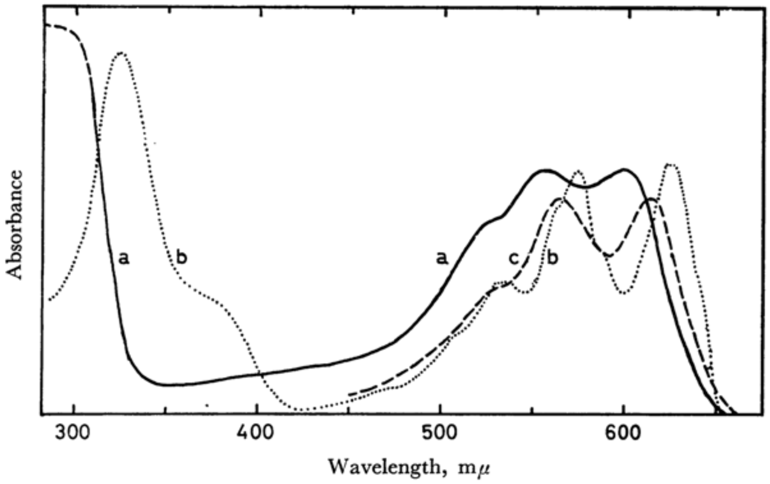

Fig. 1. a) Transient absorption spectrum formed by the flash photolysis of TMPD in liquid paraffin at room temperature.
b) Absorption spectrum formed by the ultraviolet illumination of TMPD in ethanol at 77°K.
c) Absorption spectrum of Wurster's blue perchlorate in ethanol at room temperature.

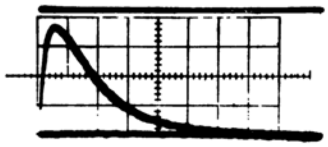

Fig. 2. A decay curve of a transient absorption at 560 mμ formed by flash photolysis of liquid paraffin of TMPD at room temperature. The upper and lower lines indicate 100% and 0% absorption, respectively. The time scale is 50 μsec. per main division.

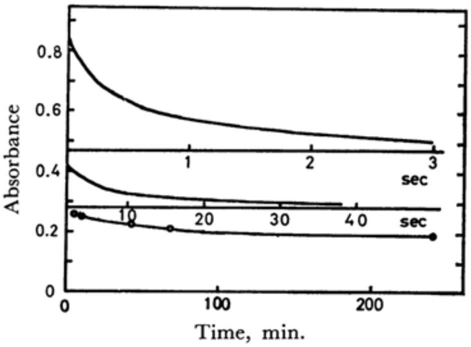

Fig. 3. Decay of the transient absorption ($\lambda=610$ mμ) in ethanol at room temperature produced by the flash photolysis of TMPD.

except in the acetonitrile solution.

The correlation between the transient absorption and the intensity of flash light was studied for 10^{-5} mol./l. liquid paraffin solutions of TMPD. Since the intensity curves of the flash light with respect to time do not change with the charging-up-voltages of the condenser, it may be assumed that the light intensity at any moment is proportional to the square of the voltage. The intensity of the transient absorption was found to be proportional to V^2, as Fig. 4 shows.

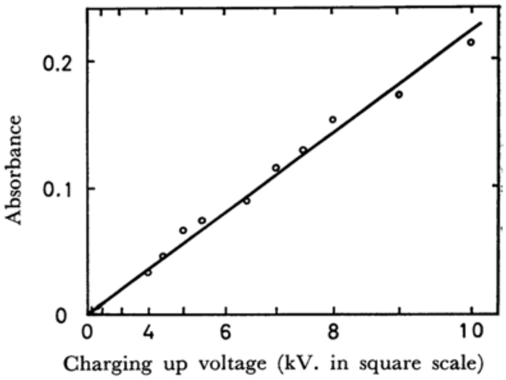

Fig. 4. Dependence of the transient absorption ($\lambda=560$ mμ) in liquid paraffin solution of TMPD on the flash light intensity. It is assumed that the flash light intensity is proportional to the square of charging-up-voltage of a 5 μF condenser.

Luminescence at a Low Temperature.—The UV-irradiated TMPD in non-polar (MP or liquid paraffin) matrices at 77°K shows an afterglow stimulated by infrared light or by warming up the matrix, as has been reported by Albrecht and his co-workers.[7,8] The spectra obtained photographically by the method described earlier in this paper are shown in Fig. 5 by curves b and c. The normal fluorescence (F, $\lambda=375$ mμ) and phosphorescence (P, $\lambda=470$ mμ) spectra of TMPD are

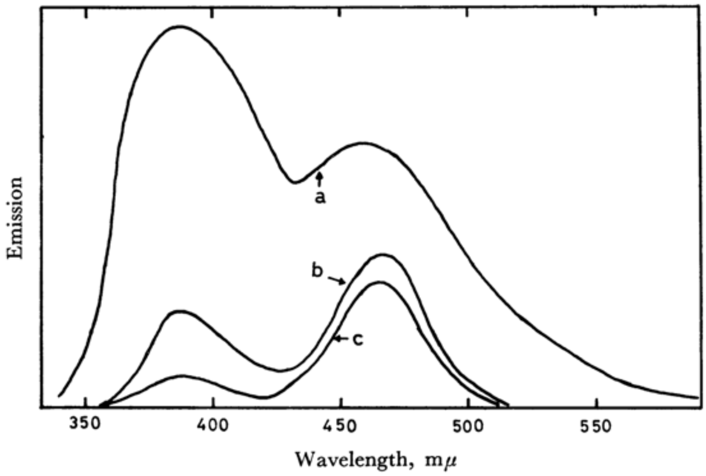

Fig. 5. Emission spectra in MP matrix at 77°K.

a) Emission spectrum of TMPD excited by ultraviolet (mainly 313 mμ). Two peakes at 376 mμ and 470 mμ are the fluorescence and the phosphorescence of TMPD, respectively.

b) Induced emission spectrum obtained by infrared illumination after ultraviolet irradiation.

c) Thermoluminescence spectrum obtained by elevating temperature.

also shown in Fig. 5a. The results of these emission spectra indicate that the induced emission consists of the fluorescence and the phosphorescence of TMPD respectively. The P/F ratios of the induced emission are larger than that of the normal emission of TMPD. In the case of the liquid paraffin matrix, the emission induced by infrared illumination was observed visually at temperatures ranging from 77°K to 120°K. Emission was found to continue until the temperature of the solution became about -30°C. However, no induced emission was observed in the case of polar matrices (ethanol or EPA) by any method. The time dependence of the IR-induced emission in the MP matrix at 77°K was also measured and found to agree with that reported by Albrecht et al.[8]

Absorption Spectra at Low Temperature.—In order to get more information on the nature of the transient absorption obtained by the flash photolysis of TMPD in a viscous solvent at room temperature, the abosprption spectra of about 10^{-5} mol./l. TMPD in a MP matrix at 77°K were measured photographically by means of the cross-illumination method. The 250-W. high-pressure mercury lamp, equipped with a Toshiba UV-D2 filter, was used as the exciting light source. As the spectral light source, a 500-W. Xenon lamp was used. The spectra were photographed by the use of a Nalumi RM 23 spectrograph. In Fig. 6, curve a shows the absorption spectrum taken by an exposure which began 5 sec. after the ultraviolet light came on and continued for 5 sec. Curve b shows the spectrum taken just before the ultraviolet light went off. Curve c shows the spectrum taken by the recording spectrophotometer many minutes after the ultraviolet light went off.

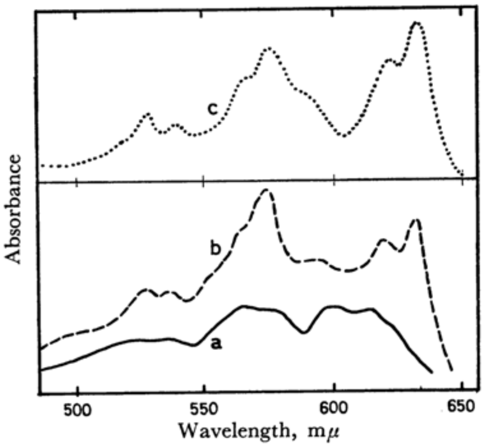

Fig. 6. Absorption spectra of MP matrix of TMPD obtained photographically by means of the cross illumination method at 77°K.

a) The absorption spectrum taken at 5 sec. after the UV light was on.

b) The sample was irradiated by UV light for 5 min. The absorption spectrum taken just before the UV light was off.

c) The absorption spectrum taken at many minutes after the UV light was off.

Discussion

We may conclude from the following reasons that the transient absorption spectrum obtained by the flash photolysis of TMPD in liquid paraffin (Fig. 1, curve a) is the T-T′ absorption of TMPD:

1) The spectral feature is different from that of TMPD$^+$ (Fig. 1).

2) Its absorption intensity is proportional to

the intensity of the photolysis flash light, while it would be proportional to its square if the two-step photo-ionization mechanism proposed by Albrecht et al. was correct.

3) Its absorbance is larger than that of $TMPD^+$ formed by a single-flash photolysis with the same flash apparatus of a degassed ethanol solution, while the quantum yield of $TMPD^+$ formation in a non-polar matrix at 77°K is much less than that in a polar matrix at 77°K.15) On the other hand, if it is the T-T′ absorption, the larger intensity in liquid paraffin can reasonably be attributed to its larger viscosity which stabilizes the triplet state.

4) The decay of the transient absorption in a liquid paraffin solution is exponential. This means a first-order decay process; therefore, it does not correspond to a recombination process between a cation and a free electron. The life-time (82 μsec.) is in the range of those of the triplet states of aromatic hydrocarbons.16)

The transient absorption spectra obtained in polar solvents at room temperature are identical to that of $TMPD^+$, and the decay curve is nearly a hyperbola. For polar solvents, therefore, photo-ionization is easily produced by flash illumination at room temperature and the ionized species has a remarkably long life-time (one or two days).

For solvents with low dielectric constants and low viscosities, no transient absorption is observed at room temperature. In this case, the first excited triplet state of TMPD is supposed to have a life-time so short that it is impossible to detect it. Also, TMPD is not photo-ionized in such solvents.

When these solutions are aerated, no transient absorption is observed, except for the acetonitrile solution. In a liquid paraffin solution at room temperature, the fluorescence of TMPD is not quenched by the existence of O_2.15) When ethanol or acetonitrile solution is aerated after the transient absorption is formed by the flash, no oxygen effect on the absorption is observed. It is also well known that an excited triplet state of aromatic hydrocarbon is quenched by O_2.16) Our results concerning the O_2 effect are consistent with the two-step mechanism of the photo-ionization which occurs via the triplet state of TMPD.

It was pointed out by Albrecht and McClain,8) on the basis of their photo-electric measurements, that the P/F ratio of the phosphorescence and fluorescence intensity in the induced emission is different from that in the normal TMPD emission. They, therefore, suggested that a direct transfer from the recombining electron to the triplet state occurs to some extent, for if the transfer occurs only to the singlet state, the P/F ratio should be the same as that for the normal emission of TMPD. Our results, shown in Fig. 5, curve b, is in agreement with their results, showing that the P/F ratio is much larger in the infrared-stimulated emission. The P/F ratio in the thermoluminescence, as shown by Fig. 5, curve c, is still larger, indicating that the probability of the transfer to the triplet state is larger in this case.

In polar media, no emission is observed either by infrared ($\lambda > 690$ mμ) or by elevating the temperature. This suggests that the potential trough for the electrons is so deep that the energy of infrared light is not sufficient to release it. At an elevated temperature, the electron recombination will lead to the ground state of TMPD. Ultraviolet-irradiated TMPD in an EPA matrix shows an ESR spectrum composed of ill-resolved quintets, which might correspond to a radical $CH_3\dot{C}HOH$,17) whereas in the MP matrix a strong sharp peak is obtained at the free-spin *g* value. The results in EPA seem to indicate that most of the ejected electrons react with the solvent, possibly causing $CH_3\text{-}\dot{C}HOH$ or $C_2H_5O^-$. However, to solve the question of whether the model of electrons-deeply-trapped-in-the-solvent does or does not apply in this case, we need more experimental knowledge on these matters.

The change in the absorption spectrum with time as measured by the cross-illumination method at a low temperature (Fig. 6) clearly indicates that two species are present. One corresponds to Curve a, which coincides well with the T-T′ absorption spectrum obtained by the flash illumination of the liquid paraffin solution at room temperature (Fig. 1a), although the vibrational structure is more evident in this case, probably because of the low temperature. Curves b and c are almost identical; they evidently represent the spectrum for $TMPD^+$. The change in these spectra with time is more clearly seen by Fig. 7. When the ultraviolet lamp is on, the T-T′ absorption rapidly increases within a few seconds, that is to say, it

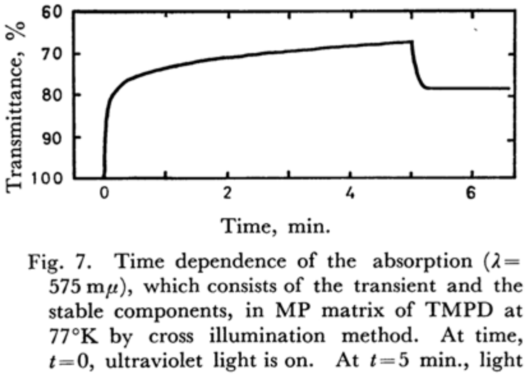

Fig. 7. Time dependence of the absorption (λ= 575 mμ), which consists of the transient and the stable components, in MP matrix of TMPD at 77°K by cross illumination method. At time, t=0, ultraviolet light is on. At t=5 min., light off.

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15) Unpublished results in our laboratry.

16) G. Porter and M. W. Windsor, *Discussions Faraday Soc.,* **17,** 178 (1954).

17) Unpublished results from our laboratry. The details will be reported in the near future.

is of the same order as the life-time, τ_e, of the triplet state. (The life-time, τ_e, of the triplet state of TMPD has been determined by us, from the decay of its phosphorescence, to be 2.12 sec.) Then the absorption increases almost linearly with time. During this period, it may be supposed that the T-T′ absorbance keeps a constant value and that the absorbance due to TMPD$^+$ steadily increases. When the ultraviolet lamp is off, the component of the absorbance arising from the T-T′ transition decays again within a few seconds, and the total absorbance drops to a constant value due to TMPD$^+$. These results, together with the flash-photolysis results with a liquid paraffin solution, clearly demonstrate that there are two bands due to different species in the same wavelength region. Their spectra have also been unambiguously determined.

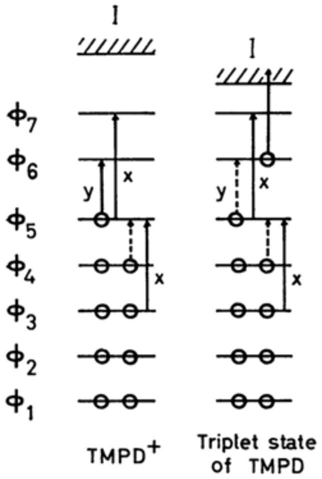

Fig. 8. Scheme of the molecular orbitals and the electron configurations of TMPD$^+$ and the triplet state of TMPD.

It is of theoretical interest to compare the two spectra and to interpret them on the basis of the molecular orbital theory. Figure 8 shows schematically the molecular orbitals (MO's) and the electron configurations of TMPD$^+$ and the triplet state of TMPD. It was determined by Albrecht that the visible spectrum of TMPD$^+$ is X-polarized, that the near ultraviolet hump (λ=370 mμ) is Y-polarized, and that the ultraviolet peak (λ=320 mμ) is X-polarized. According to calculations made by Kimura and Mataga,[18] these bands correspond mainly to the one-electron excitations, $\phi_3\rightarrow\phi_5$, $\phi_5\rightarrow\phi_6$, and $\phi_5\rightarrow\phi_7$. The $\phi_4\rightarrow\phi_5$ excitation should be in the infrared region, it may not appear because it is a forbidden transition.

If one assume that the MO's and the orbital energies of the triplet states are analogous to those for TMPD$^+$, the visible T-T′ band is clearly due to the $\phi_3\rightarrow\phi_5$ excitation. The $\phi_5\rightarrow\phi_6$ excitation in this case must inevitably lead to a singlet state, therefore, it is a forbidden transition. The absorption band corresponding to this transition must, therefore, be very weak. This explains very well the lack of a near ultraviolet hump for the spectra of the triplet state of TMPD. The ultraviolet absorption might then correspond to the $\phi_5\rightarrow\phi_7$ excitation. In this case, however, the ionization threshold will be considerably lower than that for TMPD. It is, therefore, doubtful whether the ultraviolet absorption is due to $\phi_5\rightarrow\phi_7$ excitation or to the transition leading to ionization ($\phi_6\rightarrow$I).

If we tentatively assume that the latter is the case, the wavelength at which the ultraviolet absorption starts (ca. 340 mμ) would correspond to the vertical ionization potential for the triplet-state TMPD in an MP matrix, leading to 3.6 eV., a bit larger than the value proposed by Cadogan and Albrecht (3.2 eV.). By the addition of the excitation energy from the ground to the triplet state of TMPD (3.0 eV.), the ionization potential is found to be 6.6 eV.

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[18] K. Kimura and N. Mataga, to be published in the near future.