Triplet-Triplet Absorption Spectrum of *N,N*-Dimethylaniline (DMA) measured by the Flash Photolysis Technique

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(Received February 19, 1968)

Land and Porter[1] have studied the photolysis of DMA in liquid paraffin at room temperature by the flash-photolysis technique, and assigned a transient absorption spectrum whose maxima are at 3140 and 4000 Å tentatively to the anilino radical ($C_6H_5\dot{N}CH_3$). In our previous work,[2] the flash photolysis of TMPD[3] in solution has been studied in detail and it has been shown that a transient spectrum obtained in liquid paraffin, which is similar to the absorption of $TMPD^+$, is due to the triplet-triplet (T-T) absorption. Except TMPD, so far, no T-T absorption spectra have been reported for benzene derivatives having electron donating groups such as the amino group.

A liquid-paraffin solution of DMA (about 10^{-4} mol/*l*) was deoxygenated by purging with dry nitrogen. The electronic absorption spectra of transient species formed by the flash illumination at room temperature were measured for various delay times by using the flash-photolysis apparatus in our laboratory.[2] The transient spectrum obtained with a delay time of 5 μsec, as shown in Fig. 1, consists of a fairly sharp band whose maximum is at 3400 Å and a broad band whose maximum is at 4800 Å. It was also found that the absorption at 4800 Å decays with a half-decay time of about 100 μsec. The spectrum shown in Fig. 1 may be assigned to the T-T transitions of DMA from the following reasons:

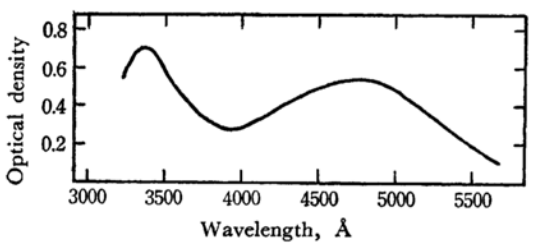

Fig. 1. A transient absorption spectrum obtained with a delay time of 5 μsec by the flash photolysis of DMA in liquid paraffin at room temperature.

1) The life time of the absorption measured at 4800 Å is comparable to that reported for the T-T spectrum of TMPD.[2]

2) In the present work, in order to confirm that the spectrum shown in Fig. 1 is attributable to T-T transitions, we also employed the steady-cross-illumination method with an EPA rigid glass of DMA at 77°K, and it was found that almost the same absorption spectrum is obtained as that by the flash illumination and its decay time is almost identical to that of the phosphorescence.[4]

3) The energy levels of triplet states of DMA have recently been calculated theoretically, by taking into account the configurational interactions between the locally-excited triplet configurations of benzene and the intramolecular charge-transfer (CT) configurations.[5] One of the present authors recalculated the triplet energy levels of DMA by selecting energy values of the CT configurations so as to reproduce the energy of the lowest triplet level estimated from the phosphorescence spectrum.[6] From this calculation, it has been confirmed that the band at about 4800 Å (2.58 eV) is due to a transition to the intramolecular CT state, its calculated energy being 3.10 eV ($f_{calc.}=0.05$), and the band at 3400 Å is concluded to correspond to a transition to one of the split states of $^3E_{2g}{}^+$ states of benzene ($f_{calc.}=0.03$), and furthermore a weak absorption ($f_{calc.}=0.01$) should exist at around 5500 Å due to a transition characteristic of one of the split states of the $^3E_{2g}{}^-$ states of benzene. It may be considered that the observed broad band probably includes this weak absorption in the longer wavelength side.

4) From our recent studies of the low temperature photolysis of DMA,[7] it has been found that the spectrum shown in Fig. 1 does not coincide with that of DMA^+ nor the anilino radical.

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1) E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2027 (1963).

2) N. Yamamoto, Y. Nakato and H. Tsubomura, This Bulletin, **39**, 2603 (1966).

3) *N,N,N',N'*-Tetramethyl *p*-phenylenediamine.

4) Very recently, one of the present authors (H. T.) learned from Dr. K. D. Cadogan that he and A. C. Albrecht have measured the T-T absorption spectrum of DMA by cross-illumination technique.

5) K. Kimura and H. Tsubomura, *Mol. Phys.*, **11**, 349 (1966).

6) K. Kimura, Preprints for The 20th Annual Meeting of Chemical Society of Japan (Tokyo, April, 1967).

7) S. Arimitsu, K. Kimura and H. Tsubomura, Preprints for The 20th Annual Meeting of Chemical Society of Japan (Tokyo, April, 1967).