

## Electronic Spectra and Quenching of Dimethylanilines

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### Dimethylaniline 의 Electronic Spectra 와 消光

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#### 要約

10 種의 N,N-dimethylaniline 에 대하여 electronic spectra 와 消光常數를 결정하였다. DMA 의  $250m\mu$  (C) band 가 소광의 주원인이 되고 있음을 밝혔고 이 band 가  $n \rightarrow \pi^*$  band 임을 치환기 효과와 용매 효과를 통하여 밝힐 수 있었다.

이 band 에 의하여 흡수된 energy 는 삼중항 상태로 전이되고 결국은 가장 적은 energy 의 삼중항 상태,  $^3L_a$ , 로 떨어져 여기서 無복사 충돌에 의하여 energy 를 상실케된다.

#### Abstract

Electronic spectra and quenching constants for ten N,N-dimethylanilines (DMA) have been determined. The  $250m\mu$  absorption band (C band) of DMA was shown to be mainly responsible for the quenching. This band was confirmed as an  $n \rightarrow \pi^*$  band through substituent and medium effects on the spectra shifts.

The energy absorbed by this band then transfers to triplet and down to the lowest triplet state,  $^3L_a$ , where the energy is lost by non-radiative collisions.

#### Introduction

Electronic spectra of N, N-dimethylanilines (DMA) have been investigated by many authors with the views to elucidating the nature of absorption bands and to demonstrate the steric inhibition of resonance. Klevens and Platt<sup>1</sup> have reported electronic spectra of seven DMA and shown that they had four absorption bands near 180, 210, 250 and  $300m\mu$  which were designated A, B, C and D respectively. They have demonstrated

the steric inhibition of resonance in ortho-substituted DMA by the decrease in total oscillator strength, which were almost linearly correlated with the van der Waals radii of the groups substituted in the ortho position.

There has been, however, some differences of opinion concerning the assignment of the C band in DMA. Klevens and Platt<sup>1</sup> argued that the benzene band near  $250m\mu$  retained its identity in DMA while other workers<sup>2</sup> regarded the closeness of the low wave-length

locations to be entirely coincidental and it was the D band which was related to the 250m $\mu$  band of benzene.

On the other hand, theoretical analysis by molecular orbital calculations lead Murrell<sup>3</sup> to conclude that C band corresponded to an electron-transfer band, involving the excitation of a non-bonding electron on the amine nitrogen to an antibonding  $\pi$ -orbital. Some experimental evidence in support of this view has been reported<sup>4</sup>.

Obviously these are in contrary to the conclusion of Klevens and Platt.

In the previous report,<sup>5</sup> we have shown that the quenching constant,  $q$ , associated with dimethylanilines in liquid scintillation counting decreased (i.e. less quenching) as substituents were introduced in the ortho position, and this was interpreted as a result of  $n \rightarrow \pi$  interaction of the non-bonding electrons.

In an attempt to find the correlation between the electronic spectra and the mechanism of quenching, we have now measured quenching constants and electronic spectra (C and D bands) of ten DMA and considered the mechanism of quenching in detail.

### Experimental

**Materials:** — DMA used in this work were purified by refluxing with acetic anhydride and distilling under reduced pressure. Physical constants of these compounds have already been reported<sup>6</sup>.

Scintillator solvent was ACS toluene, and solutes, *p*-terphenyl and POPOP, were scintillator grade obtained from Nuclear Enterprises Ltd., Britain.

Solvents for spectra measurement, *n*-hexane and absolute ethanol, were ACS spectrograde and Merck GR grade.

*n*-Hexadecane-*t* was a reference material purchased from the Radiochemical Centre, Amersham, England.

**Determination of Quenching Constants:** — Procedure adopted was similar to that described previously<sup>5</sup>. Scintillator solution consisted of 3.0g/l of *p*-terphenyl and 0.1g/l of 1,4-di-(2,5-phenyloxazolyl)-benzene (POPOP) in toluene. The weighed amount of DMA was dissolved in active scintillator solution containing radioactive *n*-hexadecane-*t*.

A series of 20ml. counting solutions were then prepared for each compound by mixing aliquots of this solution with the inactive ordinary scintillator solution.

These solutions were counted in a Tracer-Lab liquid scintillation counter, LSC-10B semi-automatic type. Counting conditions were kept constant throughout these studies. Quenching constants were then determined applying least square method on the equation,

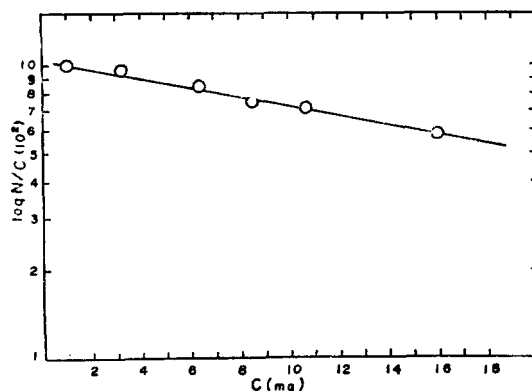
$$\log (N/C) = \log S - q \cdot C/2.303$$

where  $N(\text{cpm})$  is the observed counting rate for the DMA concentration of  $C(\text{mg})$  in 20ml. counting solution.

$S$  is the specific activity of the DMA, (constant), and  $q$  is the quenching constant. The plot of  $\log(N/C)$  versus  $C$  gives the constant  $q$  as the slope of the straight line. A typical result is shown in Table I and Fig. 1.

**Table I.** Quenching of *p*-methyl-N,N-dimethylaniline

| C (mg.) | N (cpm) | N/C  |
|---------|---------|------|
| 1.064   | 1064    | 1000 |
| 3.19    | 3070    | 962  |
| 6.38    | 5344    | 837  |
| 8.51    | 6320    | 742  |
| 10.64   | 7563    | 711  |
| 15.96   | 9317    | 584  |



**Fig.1.** Determination of quenching constant.

The quenching constants determined are summarised in Table I.

**Determination of Electronic Spectra:** — Accurately weighed amount of DMA was dissolved in solvent, *n*-hexane, in a volumetric flask keeping the temperature constant,  $(20 \pm 0.02^\circ\text{C})$  and diluted to give  $\sim 10^{-5}$  mole/l, which was then sealed in ampoules. Breaking

the ampoules immediately before use, maximum absorption wave lengths,  $\lambda_{max}$ , and molar extinction coefficients,  $\epsilon$ , at these wave lengths were determined with Beckman DU and DK-A type Spectrophotometers. The results are summarised in Table I.

**Table I.** Extinction coefficient and quenching constant

| Substituent         | q-value<br>( $\times 10^2$ ) | C band                                   |                               | D band                                   |                               |
|---------------------|------------------------------|--|-------------------------------|--|-------------------------------|
|                     |                              | $\epsilon_{max}$<br>( $\times 10^{-3}$ ) | $\lambda_{max}$<br>(m $\mu$ ) | $\epsilon_{max}$<br>( $\times 10^{-3}$ ) | $\lambda_{max}$<br>(m $\mu$ ) |
| H                   | 3.51                         | 15.5                                     | 250                           | 2.33                                     | 296                           |
| o-Me                | 2.61                         | 6.19                                     | 247                           | —  | —                             |
| o-OMe               | 2.79                         | 8.52                                     | 254                           | 2.99                                     | 284                           |
| o-Cl                | 2.66                         | 7.32                                     | 254.6                         | —  | —                             |
| 2,4-Me <sub>2</sub> | 2.78                         | 6.25                                     | 247.5                         | 1.07                                     | 282.5                         |
| m-Me                | 4.26                         | 16.17                                    | 254                           | 2.92                                     | 295                           |
| m-Cl                | 4.28                         | 17.33                                    | 255                           | 2.87                                     | 303                           |
| p-Me                | 3.57                         | 12.11                                    | 253.2                         | 1.70                                     | 303                           |
| p-Br                | 4.38                         | 19.43                                    | 259                           | 2.67                                     | 311                           |
| p-I                 | 4.46                         | 22.66                                    | 261                           | 1.02                                     | 302                           |

In Table II, transition energies ( $E_T$ ) calculated from the maximum absorption wave length are listed with the Hammett substituent constant,<sup>7</sup>  $\sigma$ .

**Table II.** Substituent constant and transition energy

| Substituent         | $\sigma^*$ | Transition energy (C band)<br>kcal./mole |
|---------------------|------------|--|
| H                   | 0.00       | 114.0                                    |
| o-Me                | -0.170     | 115.8                                    |
| o-OMe               | -0.39      | 112.6                                    |
| o-Cl                | +0.20      | 112.4                                    |
| 2,4-Me <sub>2</sub> | -0.481     | 115.5                                    |
| m-Me                | -0.069     | 112.6                                    |
| m-Cl                | +0.373     | 112.1                                    |
| p-Me                | -0.170     | 112.9                                    |
| p-Br                | +0.232     | 110.4                                    |
| p-I                 | +0.276     | 109.5                                    |

\* Taken from Ref. (7).

**Table III.** Transition energy of N,N-dimethylaniline and Z-values of ethanol solution.

| Ethanol %<br>in water | Z-value* | Transition energy (C band)<br>kcal./mole |
|-----------------------|----------|--|
| 100%                  | 78.99    | 113.5                                    |
| 70%                   | 86.43    | 114.4                                    |
| 50%                   | 89.42    | 115.2                                    |
| 30%                   | 92.44    | 116.4                                    |
| 10%                   | 94.11    | 117.2                                    |

\* Z-values were taken from Ref. (8).

UV spectra in various ethanol-water mixtures were obtained similarly. The results of transition energies are given in Table IV with the Kosower's Z-values.<sup>8</sup>

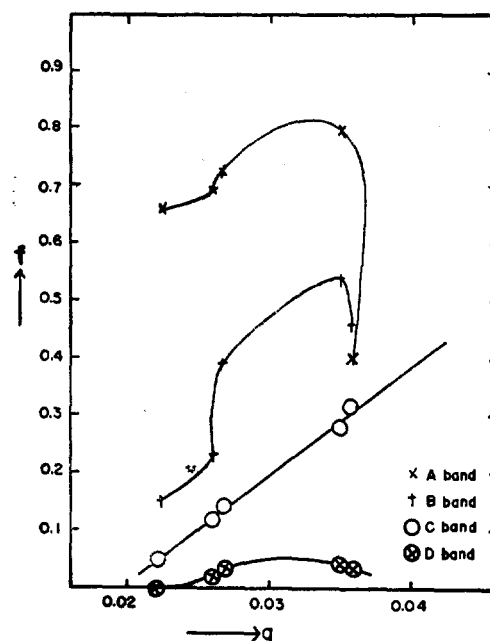
## Results and Discussion

In a previous report,<sup>5</sup> we have shown that the most probable process leading to quenching by dimethylanilines(DMA) is the energy migration, i.e., the energy jump from solvent molecule to solvent molecule until it arrives in the vicinity of DMA, which subsequently consumes the absorbed excitation energy by a radiationless degradation. This process of energy transfer is quite similar to that of solvent-solute energy transfer in liquid scintillation counting.<sup>9</sup>

We will now consider in some detail the mechanism of quenching by DMA once the energy arrived in the neighborhood of the molecule.

It is known that the efficiency of energy transfer to a solute or quencher molecule increases with the degree of overlap between the emission band of solvent and the absorption band of solute.<sup>9</sup> Thus it can be said that the C and D bands of DMA are most likely to be responsible for the energy absorption.<sup>5</sup>

This aspect is nicely shown in Fig. 2, where we have plotted the oscillator strengths ( $f=4.319 \times 10^{-9} \int \epsilon d\nu$ ) of each bands against quenching constants obtained



**Fig. 2.** Oscillator strength vs. quenching constant.

in this work. It is obvious from this figure that the C band alone gives satisfactory linearity with the quenching constants. In Fig. 3, we have further shown with more DMA's that molar extinction coefficient of C band is linearly related with the quenching constants. Since the oscillator strength and molar extinction coefficients can be taken as an extent of the total energy transferred,<sup>10</sup> we can conclude that the quenching of DMA is due to the absorption of 250m $\mu$  band.

Although there has been some differences of opinion about the nature of the C band, it is now generally accepted that the C band is an intra-molecular charge transfer<sup>4</sup> or electron-transfer band<sup>3</sup> arising from the transfer of a lone-pair(non-bonding) electron of the amine nitrogen to the anti-bonding  $\pi$ -orbital.

This is known as  $n \rightarrow \pi^*$  type transfer.<sup>11</sup> Thus we are lead to establish that the C band is truly an  $n \rightarrow \pi^*$  band by investigating the effects of substituent and medium.

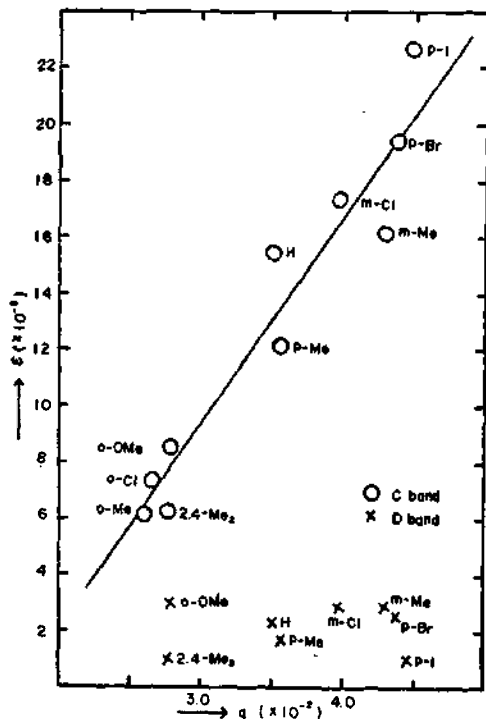


Fig. 3. Maximum molar extinction coefficient vs.  $q$ -value.

Orgel and others<sup>12</sup> argued that substituents which can act as electron donors should produce a blue shift of the  $n \rightarrow \pi^*$  spectra since they stabilize the ground state

more than the upper state, while electron withdrawing substituents should cause a red shift due to the larger stabilizations in the excited state than in the ground state. Neglecting solvent interaction effects (i. e., entropy effects), a linear relationship is thus to be expected between Hammett  $\sigma$ -values and the transition energies of the C band with negative slope as suggested by Eq. (1)<sup>13</sup>,

$$\delta_R \Delta H = a\sigma \quad (1)^*$$

or

$$E_T = a\sigma + \text{constant}$$

where we again assumed  $\Delta H = \Delta E$ , and  $a$  is a constant, determined by a slope of the plot of transition energy versus  $\sigma$ . For  $n \rightarrow \pi^*$  band we expect  $a$  to be negative, while by the similar argument for  $\pi \rightarrow \pi^*$  we expect  $a$  to be positive.<sup>14</sup>

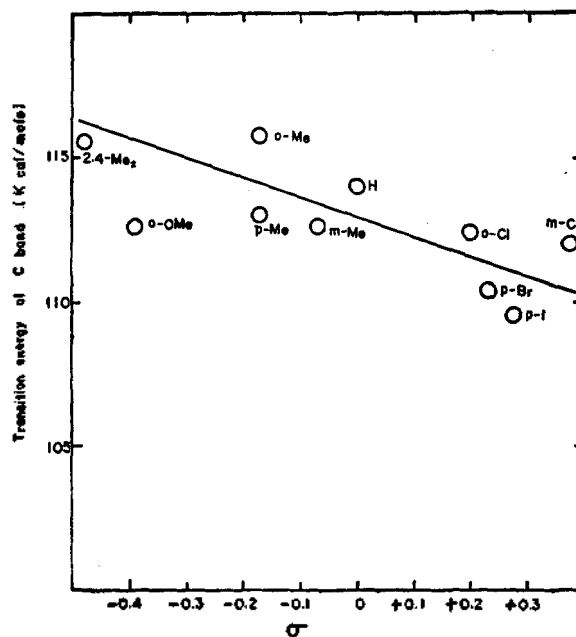


Fig. 4. Transition energy vs. substituent constant.

The plot of transition energies versus  $\sigma$  is shown in Fig. 4, where we can see the predicted negative slope for the  $n \rightarrow \pi^*$  band. The assumption of negligible entropy effect may be the cause of some scatter in the plot.<sup>13</sup>

\* This is a special form of the general equation derived previously by us.<sup>15</sup>  $\delta_R$  represents the effect of substituents. Note that negative  $a$  corresponds to positive  $\rho$  of the Hammett equation.

Thus the effect of substituents on the spectra shifts of C band is in accord with our assignment of the band.

Further support may be obtained by the medium effect. In the hydrogen bonding media,  $n \rightarrow \pi^*$  bands are known to give blue shifts.<sup>16</sup> For the C band of DMA, this blue shift was actually observed by Ungnade.<sup>17</sup> We have confirmed this property of C band by measuring  $\lambda_{max}$ , ( $E_T$ ), for various ethanol-water mixtures and applying Kosower's Z-test.<sup>8</sup> As has been discussed in a previous work,<sup>18</sup> Kosower's relationship may be transformed in the form,

$$\delta_M \Delta H = a''Z \quad (2)$$

or

$$E_T = a''Z + \text{constant}$$

where we again put  $\Delta H = E_T$ , and  $\delta_M$  denotes the medium effect.

Kosower<sup>8</sup> has shown that for  $n \rightarrow \pi^*$  band the slope of the plot,  $E_T$  versus  $Z$  is positive, i.e.,  $a'' > 0$ , while it is negative for  $\pi \rightarrow \pi^*$  band, i.e.,  $a'' < 0$ .

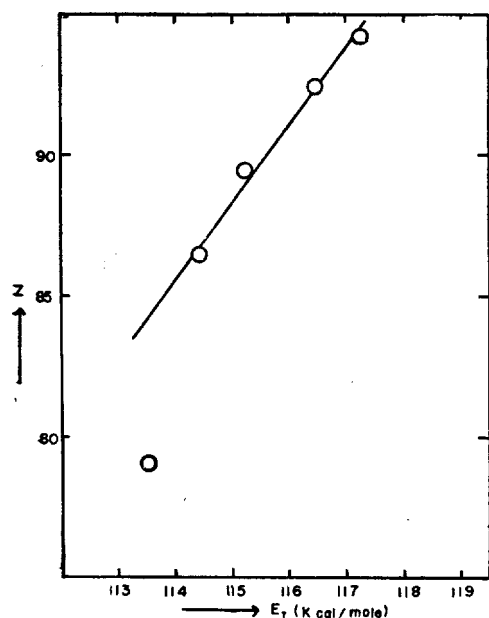


Fig. 5. Transition energy vs.  $Z$  for dimethylaniline.

The result of our investigation is quite consistent with our assignment of the band as shown in Fig. 5.

Since the singlet to triplet transition of C. T. state ( $^1P_{n-\pi^*} \rightarrow ^3P_{n-\pi^*}$  transition) is known to occur fairly easily due to spin orbit interaction,<sup>19</sup> the DMA mole-

cule would then be in its lowest triplet state after successive  $T' \rightarrow T$  type transitions.<sup>20</sup> From the lowest triplet state, which has been identified as  $^3La$  state,<sup>4</sup> the transition to the ground state (G) is forbidden and thus  $^3La$  state would have comparatively long life before the energy is consumed in non-radiative collisions.<sup>20</sup>

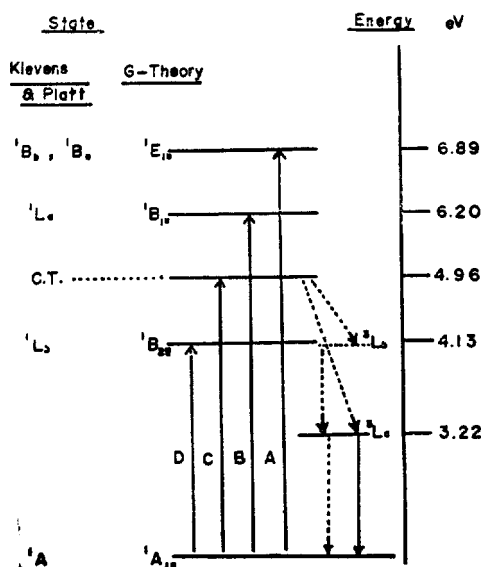


Fig. 6. Term-level diagram of dimethylaniline.

Thus the energy level diagram of DMA may look as shown in Fig. 6.

A, B and D bands are the benzene analogs (BA) and C is the charge-transfer ( $n \rightarrow \pi^*$ ) band. The energy migrated in the neighborhood of DMA molecule is absorbed by DMA, mainly through the excitation of non-bonding electron into anti-bonding  $\pi$ -orbital. This  $n \rightarrow \pi^*$  singlet then transfers to triplet and then down to the lowest triplet state,  $^3La$ .

Since in solution, the chance of losing the energy by collision is much greater than the forbidden  $T \rightarrow G$  transition (phosphorescence emission), non-radiative degradation down to the ground state transforming the excitation energy into thermal energy is then followed. Probable path of energy loss can then be shown as indicated by broken arrows in Fig. 6.

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