

N-메틸루티돈의 루미네센스에 관한 연구

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Luminescence Studies of N-Methylrutidone, an Unusually High Triplet Energy Sensitizer

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요 약. 77°K 에탄올 매트릭스에서 N-메틸루티돈의 발광에 대한 연구를 하였다. 형광은 관찰되지 않았으나 양자 수득률이 0.1과 수명 0.2초의 강한 인광이 관찰되었다. 인광의 0-0띠로부터 이 화합물의 삼중상태 에너지가 85.1 kcal/mole 임을 알았으며 2-헥센, 트랜스-1,4-디클로로부텐-2와 같은 높은 삼중상태 에너지를 가진 올레핀들이 N-메틸루티돈에 의해 효과적으로 시스 \rightleftharpoons 트랜스광이성질화 반응을 일으키는 것으로 보아 이 높은 삼중상태 에너지가 정당함을 알 수 있다. 0-0띠의 polarization 이 음의 값을 갖는 것으로부터 발광상태가 $(\pi, \pi)^3$ 상태임을 알 수 있다. LiCl 과 같은 알카리염의 양이온과 N-메틸루티돈이 배위결합을 함으로써 $(\pi, \pi)^3$ 와 $(n, \pi)^3$ 상태 사이의 에너지 차이가 크게 되기 때문에 알카리 금속염은 인광의 세기를 증가시킨다.

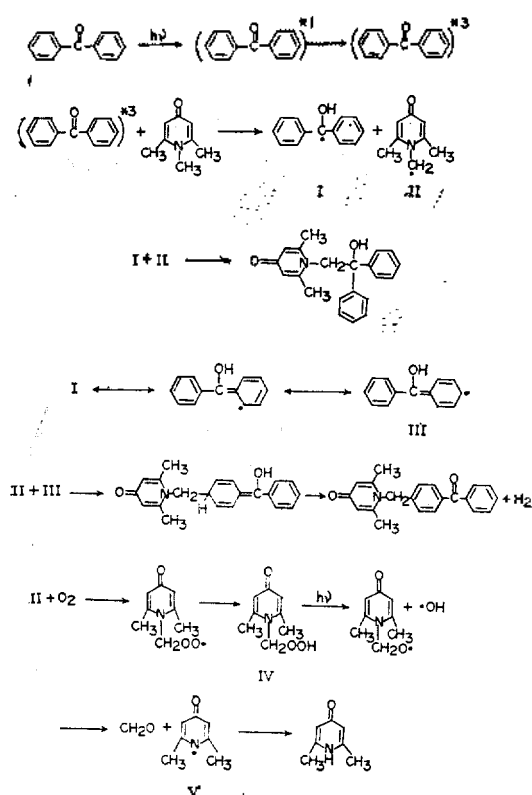
ABSTRACT. The luminescence of N-methylrutidone is studied in ethanol matrix at 77°K. No fluorescence is observed but a strong phosphorescence with the quantum yield of 0.1 and the lifetime of 0.2 sec is recorded. An unusually high triplet energy of 85.1 kcal/mole is determined for the compound from the 0-0 band of phosphorescence. The *cis* \rightleftharpoons *trans* photoisomerization of high triplet energy olefins such as 2-hexene and *trans*-1,4-dichlorobutene-2 is efficiently sensitized by N-methylrutidone substantiating the high triplet energy of the compound. The negative polarization of 0-0 band reveals the emitting triplet state to be $(\pi, \pi^*)^3$ state. Alkaline metal salts such as lithium chloride enhances the phosphorescence intensity through cation-N-methylrutidone coordination widening the gap between $(\pi, \pi^*)^3$ and $(n, \pi^*)^3$ states.

INTRODUCTION

Pyrimidine bases such as thymine and uracil are known to form C_4 -cyclodimers when they are irradiated with UV light in the presence of

triplet sensitizers.^{1,2} A model compound for pyrimidine bases, N-methylrutidone, is therefore expected to undergo the same type of C_4 -photocyclodimerization when irradiated with triplet sensitizers as pyrimidine bases and α, β -unsatu-

rated ketones.³ However, N-methyllutidone did not give any C₄-cyclodimers when irradiated with 313 nm UV light in the presence of benzophenone as a triplet sensitizer in acetonitrile solution but gave instead N-(benzhydrylmethyl)lutidone, lutidone, and N-(4-benzoylbenzyl)lutidone with the quantum yields of 5.07×10^{-3} , 1.84×10^{-3} , and 1.43×10^{-3} respectively.⁴ These products are very likely to be derived from benzophenone triplet state itself rather than from N-methyllutidone triplet formed via energy transfer from benzophenone triplet state. The following reaction mechanism was proposed for the reaction⁴.



It is very interesting to observe no C₄-cyclodimer of N-methyllutidone in the reaction. Either no triplet energy is transferred from benzophenone to N-methyllutidone because the triplet energy of N-methyllutidone is higher than that

of benzophenone or the triplet state of N-methyllutidone is not reactive enough to form C₄-cyclodimers unlike other enones such as coumarins⁵ and pyrimidines. The luminescence studies of N-methyllutidone is therefore undertaken to determine the triplet energy of the compound and to study the nature of the excited states of the compound.

EXPERIMENTAL SECTION

Materials

N-Methyllutidone was synthesized as reported in the literature,⁶ lithium chloride is used as received. Indole was purissimum grade of Aldrich Chemical Co. and purified further by recrystallization from an ethanol-water mixture immediately prior to use. Ethanol was spectrograde of U. S. Industrial Co. and used without further purification. 2-Hexene was obtained from Poly Science Corporation made for Gas chromatographic analysis standards and used as received. 1,4-Dichloro-2-butene (Eastman Kodak Co.) was used after redistillation.

Methods.

Phosphorescence Spectra⁷. The corrected luminescence spectra, electronically compensated for instrumental bias as a function of wavelength, were obtained on a Perkin-Elmer spectrophotofluorometer (Model MPF-3).

Phosphorescence Polarization Spectra.^{8,9} The polarization of phosphorescence was measured on Aminco-Bowman Spectrophotofluorometer with a Glan-Prism accessory. Light from a Xenon lamp passes through a grating monochromator, and a Glan-Prism polarizer before passing through the sample which is immersed in liquid nitrogen. The emitted light is observed in the direction perpendicular to that of the exciting light. The emitted light is then passed through another Glan-Prism polarizer, a monochromator, and is incident on the photomultiplier tube. The

signal is amplified and recorded on a X-Y recorder.

The polarization was measured at 2.5~5 nm intervals and calculated by the formula of Azumi and McGlynn:⁹

$$P = \frac{I_{EE} - I_{EB}(I_{BE}/I_{BB})}{I_{EE} + I_{EB}(I_{BE}/I_{BB})}$$

where I_{EE} , I_{EB} , I_{BE} and I_{BB} represent the intensity for four different orientations of the prism polarizers. The subscripts E and B refer to the electric vector in the vertical and horizontal plane respectively.

Phosphorescence Lifetime.¹⁰ Phosphorescence lifetime was determined as follows. The Aminco-Keirs phosphoroscope was replaced with a similar cylindrical shutter with a wide window.

This shutter is spring loaded and will rotate 90° when released from a cocked position. When the shutter is in the cocked position, the sample is exposed to the exciting light and the steady emission intensity is detected by a PM tube. When the spring is released, the shutter rotates 90° so that the exciting light is cut off and the sample phosphorescence emitted into the emission monochromator and PM tube begins to decay. The signal from the PM tube is fed into an Analab Oscilloscope with a type 700 dual channel plug-in. A micro-switch on the shutter assembly triggers the sweep as the shutter is released. The decay curve is then photographed with a type 3,000 single frame oscilloscope camera. With this attachment, lifetimes longer than 10⁻³ sec can be accurately measured.

Phosphorescence Quantum Yield. Phosphorescence quantum yield (Φ_p^s) of N-methylrutidone was calculated by the following equation.

$$\Phi_p^s = \Phi_p^r \cdot \frac{\int I_p^s(\nu) d\nu}{\int I_p^r(\nu) d\nu} \cdot \frac{OD_\lambda^r}{OD_\lambda^s} \cdot \frac{n_r^2}{n_s^2} \quad (1)$$

where Φ_p^r is the phosphorescence quantum yield

of a reference compound. But Φ_p^r is used only to measure the intensity of exciting light. Therefore, the fluorescence quantum yield, Φ_F^r , can be used instead of Φ_p^r .

Then equation (1) can be written as follows.

$$\Phi_p^s = \Phi_F^r \cdot \frac{\int I_p^s(\nu) d\nu}{\int I_F^r(\nu) d\nu} \cdot \frac{OD_\lambda^r}{OD_\lambda^s} \cdot \frac{n_r^2}{n_s^2} \quad (2)$$

where I_p and I_F are corrected phosphorescence and fluorescence intensity respectively, n is refractive index of solvent. Optical density (OD) of reference and sample compounds were kept identical to minimize errors due to Maclaurin's approximation and band pass differences between absorption and emission measurements. The refractive index correction in different solvents and temperature is not necessary in the above equation since reference and sample fluorescence and phosphorescence were measured under identical conditions. In this experiment, the reference compound was indole (Φ_F^r : 0.74). In equation (2), the second integral term is identical to the area ratio of the sample phosphorescence spectrum and reference fluorescence spectrum.

Photostationary States.

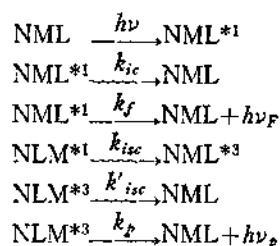
Sample solutions of olefins with photosensitizers were irradiated with 450 W Hanovia medium pressure mercury lamp (Type 679 A 36) through appropriate filters. The irradiated samples were analyzed by gas chromatography (Varian Aerograph 2800 Series) using flame ionization detector and 20 % Dinonylphthalate column (6 m) for 2-hexene and 10 % Apiezon L column (2.5 m) for 1,4-dichloro-2-butene.

RESULTS AND DISCUSSION

One of the best and simplest methods to study the nature of the lowest excited states is emission spectroscopy. The total emission spectra were

taken in ethanol matrix at 77 °K. No fluorescence was observed but a strong phosphorescence was recorded as shown in Fig. 1.

When N-methylglutidone (NLM) is excited to the S_1 state by light absorption and no photo-reactions occur from this state, the following kinetic scheme should adequately describe the deactivation of the excited states of NML.



The specific rate constants for the internal conversion to S_0 , fluorescence, intersystem crossing from S_1 to T_1 , intersystem crossing from T_1 to S_0 , and phosphorescence are represented by k_{ic} , k_f , k_{isc} , k'_{isc} , and k_p respectively. The fluorescence quantum yield, Φ_f , can be calculated by the following equation.

$$\Phi_f = k_f / (k_{ic} + k_f + k_{isc})$$

In ethanol matrix at 77 °K, k_{ic} is negligibly small and therefore it is evident that k_{isc} is much larger than k_f in NML from no fluorescence. In other words, the intersystem crossing from S_1 to T_1 state is the major deactivation path for NML S_1 state and the intersystem crossing yield from S_1 to T_1 should be large in NML.

In general, fluorescence is not observed in the compounds which have the $(n, \pi^*)^1$ state as the lowest excited singlet state because of the efficient intersystem crossing to triplet state through the extensive spin-orbit coupling¹¹. This phenomenon is especially outstanding in aromatic N-heterocyclic compounds such as quinoline, pyrimidines and pyrazines with the lowest $(n, \pi^*)^1$ state as no or very weak fluorescence is observ-

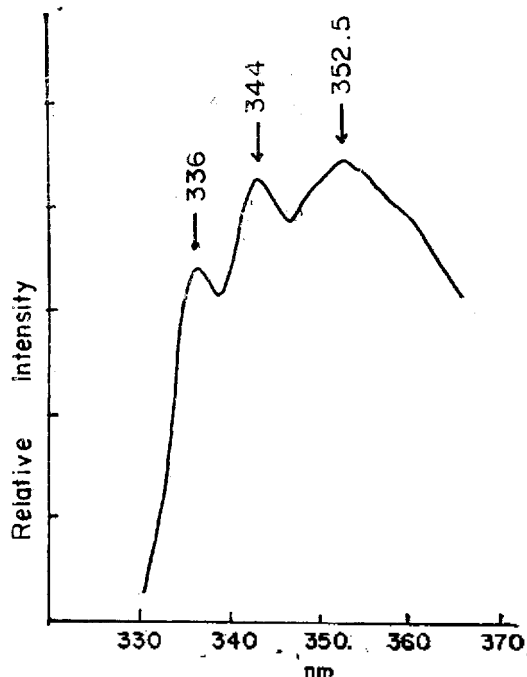


Fig. 1. The phosphorescence spectrum of N-methylglutidone in ethanol at 77 °K. The excitation wavelength is 262 nm.

ed in these compounds. The absorption spectrum⁴ of NML shows the first absorption maximum at 308 nm with molar absorption coefficient of 3.1. Therefore the lowest excited singlet state can be assigned as $(n, \pi^*)^1$ state from the low molar absorption coefficient and the large Φ_{isc} and no fluorescence can be justified.

The 0-0 band of phosphorescence is located at 336 nm indicating the surprisingly high triplet energy of 85.1 kcal/mole. It is therefore clear now that no triplet energy is transferred from benzophenone (E_T 68.5 kcal/mole) to NML and photochemistry between benzophenone and NML can be easily explained as proposed⁴. The absence of NML C_4 -cyclodimer in direct irradiation of NML also indicates that the triplet state of NML is not reactive enough to dimerize since an efficient intersystem crossing from S_1 to T_1 should have produced triplet state of NML in

good yields.

The vibrational fine structure of phosphorescence spectrum shows vibrational bands at 336, 344 and 352.5 nm and the separations of 690 cm^{-1} correspond to a C—H out-of-plane vibration (690 cm^{-1}) of the ethylenic double bond in the lutidone ring of NML.^{7,10} Since the ethylenic double bonds are part of π system of NML, the phosphorescent state can therefore be assigned to $(\pi, \pi^*)^3$ rather than to $(n, \pi^*)^3$ state.

The intensity of phosphorescence is enhanced by alkaline metal salts such as lithium chloride (LiCl) as shown in Fig. 2. This is very unusual since salts generally quench both fluorescence and phosphorescence of organic compounds through the enhancement of intersystem crossing from S_1 to T_1 and T_1 to S_0 . In NML, the energy levels of $(\pi, \pi^*)^3$ and $(n, \pi^*)^3$ states probably are very close in the absence of salts and hence these states are mixed extensively causing the efficient intersystem crossing from T_1 to S_0 . The absence of C₄-cyclodimer of NML in direct irradiation can be an indirect evidence for this efficient intersystem crossing. When alkaline metal salt is added to the system, $(n, \pi^*)^3$ state is lifted to the higher energy state through the $(n, \pi^*)-M^+$ complex formation¹²⁻¹⁵ and the population of the lowest, phosphorescent $(\pi, \pi^*)^3$ state increases because of a less efficient $(n, \pi^*)^3$ - $(\pi, \pi^*)^3$ mixing and consequently a less efficient intersystem crossing from T_1 to S_0 . This result reinforces the proposition that the phosphorescent state is $(\pi, \pi^*)^3$ state based on the vibrational fine structure of the phosphorescent spectra.

The polarized phosphorescence spectrum of NML in ethanol at 77°K is shown in Fig. 3. The polarization at 336(0-0), 344(0-1), and 352.5 nm (0-2) bands is weakly negative with respect to excitation wavelength of 262 nm which is $\pi^* \leftarrow \pi$ transition. This implies that the phosphorescence intensity is attributed to the out

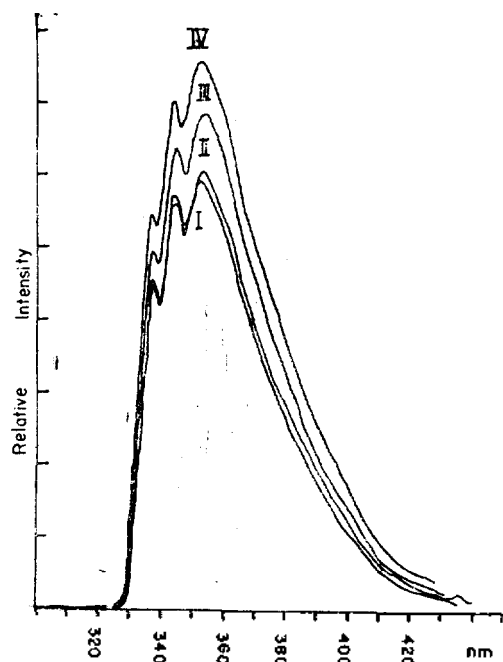


Fig. 2. The phosphorescence spectrum of N-methyl-lutidone (0.06 O.D.) in ethanol at 77°K as a function of LiCl concentration. λ_{ex} : 262 nm, slit: 2 nm and 14 nm I. 0 M, II. 0.25 M, III. 0.5 M, IV. 1 M.

of-plane component and that the lowest state is $(\pi, \pi^*)^3$ state rather than $(n, \pi^*)^3$ state.^{7,10}

The lifetime of phosphorescence is measured from the first order decay curve of the emission as shown in Fig. 4. The lifetime, τ , is calculated by the equations:¹⁶

$$I = I_0 e^{-t/\tau}$$

$$\log I = \log I_0 - t/2.303\tau$$

where I_0 and I are the phosphorescence intensity at time $t=0$ and $t=t$.

The phosphorescence lifetime of 0.205 sec was obtained which is relatively long and $(\pi, \pi^*)^3$ state can be assigned to the emitting state.¹⁷ The lifetime of 0.205 is relatively short compared to that of ordinary, pure $(\pi, \pi^*)^3$ state and a little too long for $(n, \pi^*)^3$ state. Therefore relatively short triplet lifetime indicates some

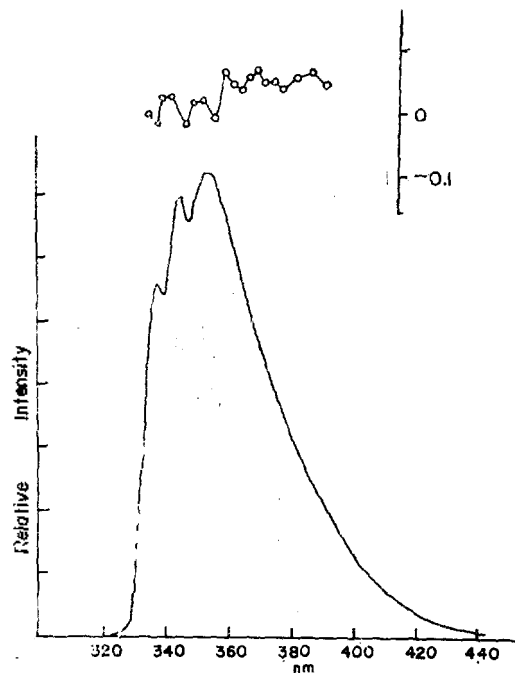


Fig. 3. The phosphorescence polarization spectrum of N-methylglutidone in ethanol at 77°K. λ_{ex} : 262 nm, Excitation band pass: 3.2 nm, Emission band pass: 2.0 nm.

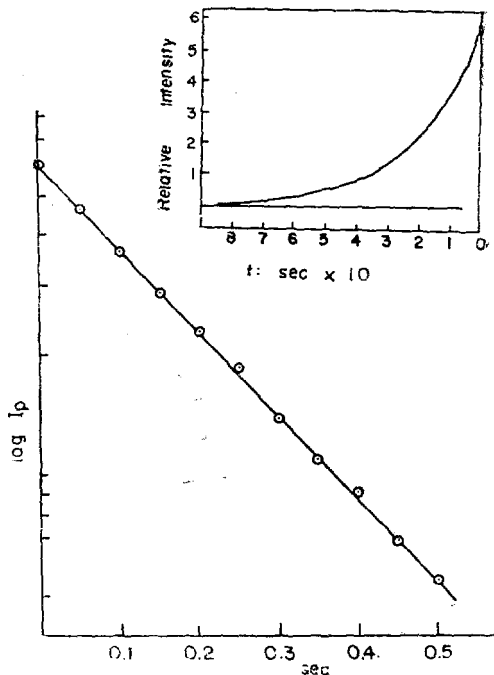


Fig. 4. A typical exponential decay curve of phosphorescence of N-methylglutidone in ethanol at 77°K. Above: Photograph taken by oscilloscope camera. Below: Graph represented by semi logarithmic graphical method of above curve.

Table 1. Photosensitized *cis-trans* isomerization of 1,4-dichloro-2-butene (0.2 M).

Sensitizer	E_T (kcal/mole)	Sensitizer concentration	Filter	Photostationary <i>cis/trans</i> ratio
Acetone	80	Neat	Pyrex	0.33
NML	85.1	0.05M in CH_3CN	Quartz	0.39

Table 2. Photosensitized *cis-trans* isomerization of 2-hexene (0.2 M).

Sensitizer	E_T (kcal/mole)	Sensitizer Concentration	Filter	Photostationary <i>cis/trans</i> ratio
Acetone ¹⁸	80	Neat	Pyrex	0.59
NML	85.1	0.1 M in <i>t</i> -BuOH	Quartz	0.61

mixing of $(n, \pi^*)^3$ and $(\pi, \pi^*)^3$ state because of small difference in their energy contents.

A relatively small phosphorescence quantum yield of 0.1 compared to large Φ_{isc} supports this

speculation. The efficient mixing of $(n, \pi^*)^3$ and $(\pi, \pi^*)^3$ should enhance intersystem crossing from T_1 to S_0 and consequently the phosphorescence lifetime is shortened.

An unusually high triplet energy of NML obtained from phosphorescence spectra was tested by NML sensitized isomerization of high triplet energy olefins as shown in *Table 1* and *2*. The photostationary *cis/trans* ratio of olefins in NML sensitized reaction is same as that of acetone sensitized reaction and indicates an efficient triplet energy transfer from NML to 2-hexene and 1,4-dichloro-2-butene substantiating the high triplet energy of 85.1kcal/mole for NML.¹⁸ Thus NML is a very promising photosensitizer for the reactions requiring high triplet energy.

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