

## N-메틸루티돈의 電子構造와 光化學反應性에 關한 研究

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### Electronic Structure and Photoreactivity of N-Methyllutidone

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**요 약.** 4-피리돈과 루티돈의 전자구조를 SCF MO-CI PPP 방법과 configuration analysis 법을 사용하여 연구하였다. 계산결과와 스펙트럼 분석치와는 잘 일치하였으며 첫번째 ( $\pi, \pi^*$ ) 단일상태는 두 화합물 모두 장축 방향으로 편극되어 있다. Configuration analysis 결과 가장 낮은 ( $\pi, \pi^*$ ) 단일 상태에서는 C=O 작용기의  $\pi$  결합체도로 부터 디비닐아민 부분의  $\pi^*$  반결합 체도로 전하가 이동되어 있으나 가장 낮은 ( $\pi, \pi^*$ ) 삼중상태에서는 반대로 디비닐아민 부분으로 부터 C=O 작용기 쪽으로 전하가 이동되어 있음을 알 수 있다.

**ABSTRACT.** The electronic structures of 4-pyridone and lutidone are studied by the SCF MO-CI PPP method and by the configuration analysis method. The spectral data are consistent with the values calculated by the method. The polarization of  $S_1(\pi, \pi^*)$  state is along the long molecular axis in both compounds. The lowest ( $\pi, \pi^*$ )<sup>1</sup> state shows significant charge transfer (16~18%) from  $\pi$  bonding orbital of C=O moiety to  $\pi^*$  antibonding orbital of divinyl amine moiety. The lowest triplet state shows much larger charge transfer (24~29%) but in opposite direction compared to that of  $S_1(\pi, \pi^*)$  state.

#### INTRODUCTION

N-Methyl-4-pyridone and N-methyllutidone, model compounds for pyrimidine bases, do not give C<sub>4</sub>-cyclodimers on irradiation with UV light in aqueous solution unlike uracil and thymine.<sup>1,2</sup> The triplet energy of N-methyllutidone was found to be 85.1 kcal/mole,<sup>3</sup> surprisingly high compared to that of  $\alpha, \beta$ -conjugated enones. The lowest triplet state is ( $\pi, \pi^*$ )<sup>3</sup> state and

unreactive to dimerization because of an efficient intersystem crossing from the triplet state to the ground state.

The electronic structure of the excited states of 4-pyridone and lutidone is examined by SCF MO-CI PPP method and configuration analysis (CA) method.<sup>4</sup> The spectral data and photoreactivity of the compounds are compared with the results obtained from the calculation.

## METHODS

Transition energies, oscillator strengths, polarization directions, electron density and bond orders were calculated by the SCF MO-CI PPP (Pariser-Parr-Pople) method.<sup>4</sup> The semiempirical integrals used in the computation are listed in Table 1.<sup>5</sup> The two-center electron repulsion integrals of the form  $\langle rr/ss \rangle$  are estimated according to the Mataga and Nishimoto formula.<sup>6</sup>

The SCF CI wavefunctions of the molecule can be expressed in terms of the corresponding wavefunctions of "reference" orbitals by using CA method.<sup>7</sup> Details of the CA procedure are reported elsewhere<sup>8</sup> and are not reported here.

## RESULTS AND DISCUSSION

The MO calculations were carried out for 4-pyridone and lutidone instead of N-methyl derivatives of the compounds and hence the steric effect of methyl groups is neglected. In lutidone, only the inductive effect of two methyl groups is considered in one case and then hyperconjugation of the methyl groups is also included in the other calculation.

The results of the calculation for singlet-singlet and singlet-triplet transition energies, oscillator strength, and the angle  $\theta$  between the emitting oscillator and a given exciting oscillator are summarized in Table 2. The experimental absorption maxima obtained for 4-pyridone derivatives are listed in Table 3. The transition ( $\pi \rightarrow \pi^*$ ) energies give a reasonably good agreement between experimental and calculated

values. The consideration of hyperconjugation gives better agreement but it is very interesting to note that 4-pyridone has longer wavelength maxima than lutidone in both cases contrary to experimental observations. The inductive and hyperconjugation effect of methyl groups are obviously operating in opposite direction to each other and the inductive effect is a little over-emphasized in the calculation since 4-pyridone and lutidone have about the same absorption maximum in the spectra. Fig. 1 shows the calculated polarizations in 4-pyridone and lutidone when the inductive effect alone is considered. The strong absorption accounted by  ${}^1L_a$  state is predicted to be long axis polarized in both compounds.

The electron densities and mobile bond orders in the ground, lowest singlet ( $\pi, \pi^*$ ), and triplet states are shown in Fig. 2. The  $\pi$ -electron polarization in carbonyl group is in opposite direction compared to ordinary aromatic carbonyls decreasing  $\pi$ -electron density on oxygen atom upon excitation, especially in the excited singlet state and the polarization is more evident when inductive rather than hyperconjugation effect of methyl group is considered. From the change of  $\pi$ -electron density at nitrogen atom upon excitation, the acidity of the N-H proton can be predicted to increase in the excited states as in the case of lumichrome<sup>12</sup> and hydroxypsoralens,<sup>13</sup> particularly in the excited singlet state than in the triplet state. The effect is negligible in lutidone when the hyperconjugation of methyl groups is considered. The mobile bond orders decrease drastically in C=C double bonds ( $\sim 40\%$ ) in the singlet ( $\pi, \pi^*$ ) state when inductive effect alone is considered while no significant change is observed in C=O bond in pyridone and lutidone. The change is much smaller in the triplet state (16~17%). When the hyperconjugation is considered in lutidone,

Table 1. Semiempirical integrals (in eV) for PPP calculations.

Atom	Ionization Potential ( $-W_{2p}$ )	$\langle rr/rr \rangle$	$\beta_{ex}$
C	11.16	11.13	-2.39
N	14.12	12.34	-2.39
O	32.90	21.53	-2.12

Table 2. The excited states of pyridone and lutidone calculated by the SCF MO-CI method (PPP).

Compound	Singlet states					Triplet states				
	State Fn.	$E^{ev}$	$\lambda_{max}$ (nm)	$f$	$\theta$	State Fn.	$E^{*ev}$	$\lambda_{max}$ (nm)	$f$	$\theta$
Pyridone (inductive)	$\Psi_0$	0.0				$\Psi_1$	2.625	472		
	$\Psi_1$	4.017	309	0.074	0°	$\Psi_2$	2.867	432	0.003	0°
	$\Psi_2$	4.652	267	0.412	-90°	$\Psi_3$	4.346	258	0.0	90°
	$\Psi_3$	5.950	208	0.125	0°	$\Psi_4$	5.096	243	0.173	0°
						$\Psi_5$	5.599	221	0.036	90°
Lutidone (inductive)	$\Psi_0$	0.0				$\Psi_1$	3.154	393		
	$\Psi_1$	4.530	274	0.033	0°	$\Psi_2$	3.407	364	0.0	0°
	$\Psi_2$	5.037	246	0.340	-90°	$\Psi_3$	4.219	294	0.0	90°
	$\Psi_3$	5.808	213	0.249	0°	$\Psi_4$	5.277	235	0.110	0°
						$\Psi_5$	6.152	202	0.002	90°
Lutidone (Hyperconjugation)	$\Psi_0$	0.0				$\Psi_1$	2.840	530		
	$\Psi_1$	4.151	299	0.076	-42°	$\Psi_2$	3.569	404	0.003	-44°
	$\Psi_2$	4.715	263	0.261	-67°	$\Psi_3$	4.362	321	0.117	27°
	$\Psi_3$	5.659	219	0.585	49°	$\Psi_4$	5.186	265	0.048	22°
	$\Psi_4$	6.054	205	0.296	-62°	$\Psi_5$	5.795	234	0.031	46°
						$\Psi_6$	5.859	231	0.001	-7°

\*After adding 0.5 to the original  $E^{ev}$ 

Table 3. Absorption maximum wavelengths for pyridone derivatives.

Compound	Solvent	$\lambda_{max}$ (nm)	$\epsilon$	$\log \epsilon$
4-Pyridone <sup>9</sup>	EtOH	256	14450	4.16
	EtOH-HCl	235		3.99
	NaOEt-EtOH	243		4.05
		260 <sup>14</sup>		3.85
N-Methyl-4-Pyridone <sup>9</sup>	MeOH	260	15800	4.2
	MeOH-HCl	237		4.0
Lutidone <sup>10</sup>	EtOH	257	14450	4.16
N-Methyl-lutidone <sup>1,11</sup>	MeOH	261	16800	4.23
	H <sub>2</sub> O	301	3.1	
		258	15000	
		211	14670	

the change of mobile bond orders is slightly bigger in the triplet state (22.6 %) than in the singlet state (21.8 %). The magnitude of the change is much smaller than that of coumarin in which the bond order for C=C in the pyrone moiety experiences a 50 % decrease in the

excited state<sup>14</sup> backing up the fact that the triplet state of coumarin yield head-to-head C<sub>4</sub>-cyclodimer with a high efficiency at this site.<sup>15</sup> The same kind of photochemical reactivity is observed in thymine triplet state and thence 4-pyridone and lutidone are also expected to give

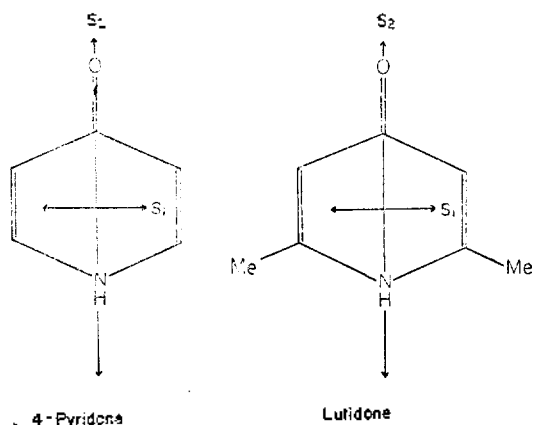


Fig. 1. Polarizations of transition moments.

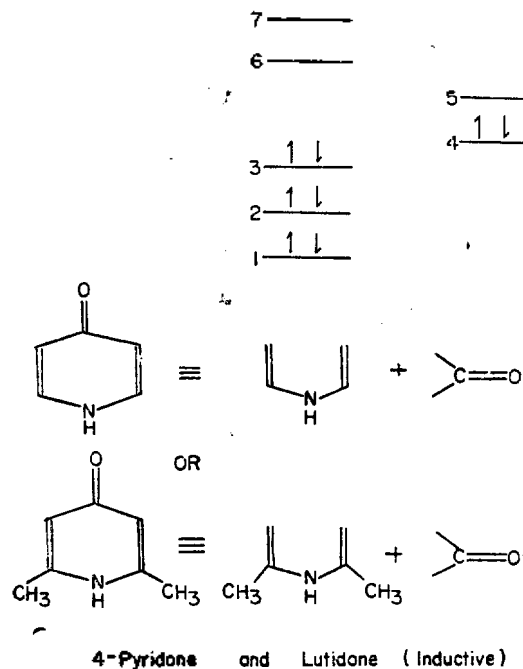


Fig. 3. Orbital diagram for two reference fragments of 4-pyridone and lutidone (inductive).

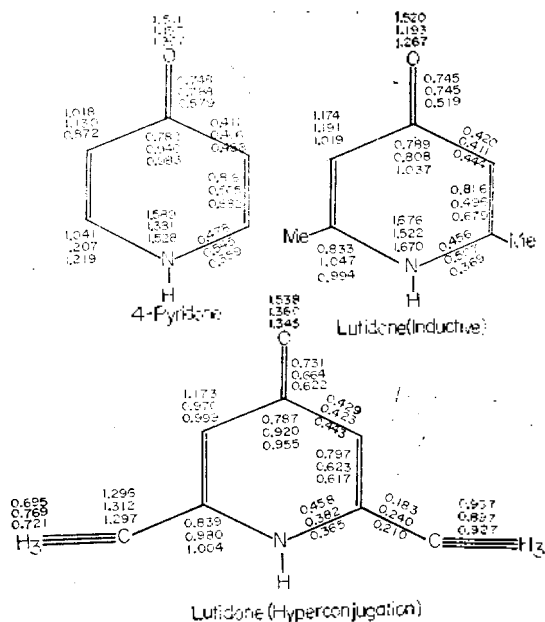


Fig. 2. The  $\pi$ -electron density distribution and mobile bond order. Top, middle and bottom numbers at each atom and between atoms refer to the ground ( $S_0$ ), singlet ( $S_1$ ) and triplet ( $T_1$ ) states, respectively.

the same type of  $C_4$ -cyclodimer from the triplet state even though the change of mobile bond orders is much smaller than that in the case of coumarin and consequently much weaker reactivity than coumarin triplet state is predicted.

However, no  $C_4$ -cyclodimer of *N*-methyl-4-pyridone or *N*-methyl-lutidone was observed on direct irradiation of the compounds in aqueous solution or in acetonitrile.<sup>1</sup> Either the small change of bond orders on excitation does not give enough reactivity to triplet states ( $T_1$ ) or the efficient intersystem crossing from this  $T_1$  to  $S_0$  inhibits  $C_4$ -cyclodimerization of 4-pyridone and lutidone.

Fig. 3 shows the configuration analysis diagram for 4-pyridone and lutidone (inductive) in terms of two reference molecules and the configuration analysis data for these compounds are summarized in Table 4. In both compounds, the  $S_1$  ( $\pi, \pi^*$ ) state is predominantly determined by the  $S_1$  (3~6) configuration of divinyl amine reference molecule even through some excitation localization on the carbonyl group (19%) can be seen in lutidone. Some charge transfer from carbonyl group to divinyl amine moiety in  $S_N$

Table 4. Configuration analysis for 4-pyridone (I) and lutidone (inductive) (II) in the ground ( $S_0$ ), singlet ( $S_1$ ) and triplet ( $T_1$ ) excited states (weight in percent corrected for the total weights).

Reference Wave Function	Singlet state				Triplet state	
	$S_0$		$S_1$		$T_1$	
	I	II	I	II	I	II
$\phi_s^0$ (0~0)	70.8	70.6	0.0	0.1		
$\phi_1^0$ (3~6)	0.0	0.0	76.5	60.0	0.0	0.0
$\phi_2^0$ (3~7)	0.7	0.6	0.0	0.1	42.0	38.2
$\phi_3^0$ (2~6)	0.0	0.0	0.0	0.4	3.8	3.1
$\phi_4^0$ (2~7)	0.0	0.0	0.4	1.0	0.0	0.0
$\phi_5^0$ (1~6)	0.0	0.0	0.6	0.3	0.0	0.0
$\phi_6^0$ (1~7)	0.0	0.0	0.0	0.0	0.1	0.1
$\phi_7^0$ (4~5)	0.2	0.2	0.0	18.9	17.9	23.7
$\phi_{CT}^0$ (4~6)	0.0	0.0	21.8	16.3	0.0	0.0
$\phi_{CT}^0$ (4~7)	1.6	1.1	0.0	0.0	6.9	6.4
$\phi_{CT}^0$ (3~5)	25.4	26.5	0.0	1.1	29.0	28.3
$\phi_{OCT}^0$ (2~5)	0.0	0.0	1.3	3.0	0.0	0.0
$\phi_{CT}^0$ (1~5)	1.3	1.0	0.0	0.0	0.1	0.2
Total weight	96.6	96.7	78.8	98.0	86.2	85.3

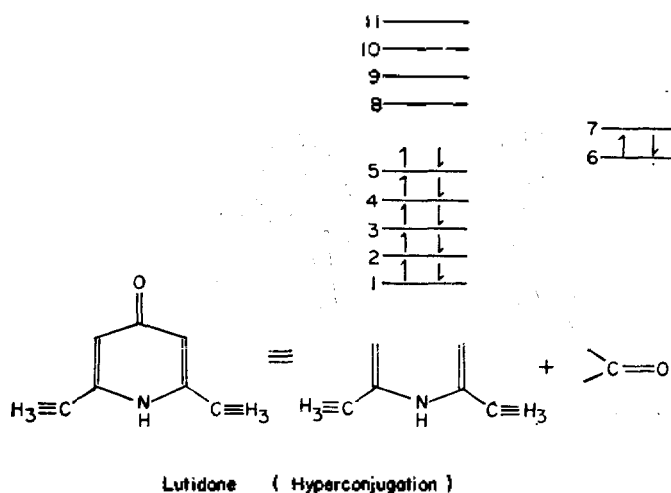


Fig. 4. Orbital diagram for two reference fragments of lutidone (hyperconjugation).

( $\pi, \pi^*$ ) state is also evident in pyridone (22 %) and lutidone (16 %). In  $T_1$  ( $\pi, \pi^*$ ) state, the charge is transferred from divinyl amine

moiety to carbonyl fragment in pyridone (29 %) and lutidone (28 %) which is exactly the opposite direction to that of  $S_1$  ( $\pi, \pi^*$ ) state. The low reactivity of lutidone triplet state may be attributed to this significant charge transfer. The orbital diagram for configuration analysis of lutidone including hyperconjugation of methyl groups is shown in Fig. 4 and numerical results are given in Table 5. The results are in agreement more closely with that of 4-pyridone than the case when the inductive effect alone is considered. The lowest<sup>1</sup> ( $\pi, \pi^*$ ) state is again predominantly determined by the  $S_1$  (5~8) configuration of divinyl amine reference (75.5 %) as in the case of 4-pyridone. No significant

Table 5. Configuration analysis for lutidone (hyperconjugation) in the ground ( $S_0$ ), singlet ( $S_1$ ) and triplet ( $T_1$ ) excited states (weight in percent corrected for the total weights).

Reference Wave Function	Singlet states		Triplet state
	$S_0$	$S_1$	$T_1$
$\phi_0^\circ$ (0~0)	69.5	0.5	
$\phi_1^\circ$ (5~8)	0.1	75.5	52.9
$\phi_2^\circ$ (5~9)	0.3	0.0	3.7
$\phi_3^\circ$ (5~10)	0.0	0.0	1.7
$\phi_4^\circ$ (4~8)	0.1	0.1	0.1
$\phi_5^\circ$ (4~9)	0.0	0.6	0.6
$\phi_6^\circ$ (4~10)	0.0	0.1	0.0
$\phi_7^\circ$ (3~8)	0.0	0.0	0.1
$\phi_8^\circ$ (3~9)	0.1	0.0	0.0
$\phi_9^\circ$ (3~10)	0.0	0.0	0.0
$\phi_{16}^\circ$ (6~7)	0.3	0.4	5.9
$\phi_{CT}^\circ$ (6~8)	0.2	18.0	5.0
$\phi_{CT}^\circ$ (6~9)	0.5	0.0	2.1
$\phi_{CT}^\circ$ (6~10)	0.0	2.2	0.7
$\phi_{CT}^\circ$ (5~7)	27.7	0.7	24.4
$\phi_{CT}^\circ$ (4~7)	0.0	1.4	2.6
$\phi_{CT}^\circ$ (3~7)	0.3	0.0	0.0
$\phi_{CT}^\circ$ (1~7)	0.9	0.0	0.0
Total weight	95.3	76.7	73.2

excitation localization in the C=O group is observed in contrast to the case where the inductive effect of the methyl groups is emphasized. The charge transfer from carbonyl to divinyl amine moiety in  $S_1$  ( $\pi, \pi^*$ ) state is about the same as that of 4-pyridone. The charge transfer in  $T_1$  ( $\pi, \pi^*$ ) state is in reverse direction to that of  $S_1$  ( $\pi, \pi^*$ ) state as in 4-pyridone, i.e., from divinyl amine moiety to carbonyl fragment (24 %).

Even though a large portion of the excitation is localized in divinyl amine region in the lowest ( $\pi, \pi^*$ ) triplet state of 4-pyridone derivatives (42~50 %), the overall electronic structure of the compounds can be more adequately described in terms of excitation over the entire region of

molecules and thus the low photoreactivity of C=C bonds in the lowest triplet state of the compounds is justified.

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