BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (3), 939—940 (1979)

Electronic Properties and π-π* Absorption Spectra of 1- and 2-Methyl-4-amino-5*H*-[1]benzopyrano[3,4-*c*]pyridin-5-one

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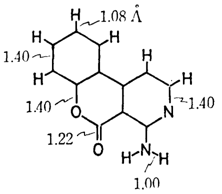
(Received August 7, 1978)

Synopsis. The tautomerization of 4-amino-5*H*-[1]-benzopyrano[3,4-*c*]pyridin-5-one (BPP) in the ground state has been briefly discussed by the CNDO/2 method. The π-π* absorption spectra of 1-methyl-4-amino-5*H*-[1]benzopyrano[3,4-*c*]pyridin-5-one (1-MBPP) and 2-methyl-4-amino-5*H*-[1]benzopyrano[3,4-*c*]pyridin-5-one (2-MBPP) in solution have been obtained. Based on the MO calculations of BPP, assignment of the observed π-π* absorption bands of 1-MBPP and 2-MBPP have been made.

Recently, the thermodynamic properties of the hydrogen bond of 1- and 2-alkyl-4-amino-5*H*-[1]benzopyrano[3,4-*c*]pyridin-5-one with alcohols have been studied both experimentally and theoretically.[1] Also, the fluorescence of the proton-transferred excited species (tautomer) between 2-MBPP and acetic acid has been investigated,[2] but as yet the absorption spectra of 1-MBPP and 2-MBPP have not been discussed. In this paper, the possibility of tautomerization of BPP in the ground state and the π-π* absorption spectra of 1-MBPP and 2-MBPP are reported.

Results and Discussion

Electronic Properties in the Ground State. Dipole moments, charge densities, and π-bond orders of BPP, 1-MBPP, and 2-MBPP in the ground state have already been discussed in a previous paper.[1] In this paper the calculation of the total energies of the following three kinds of the models **1**, **2**, and **3** were conducted to clarify the tautomerization from **1** to **2** and **3** in the ground state by the CNDO/2 method using the parameters of Pople, Santry, and Segal.[3] The calculated total energies (a. u.) and dipole moments are as follows: **1**: −151.47204 (3.735 D); **2**: −151.42766 (9.483 D); **3**: −151.42170 (8.043 D).



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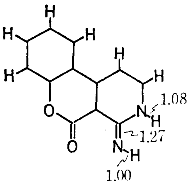

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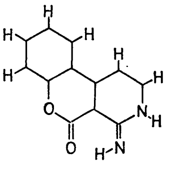

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The energy differences between **1** and **2**, and **1** and **3** are 27.84 and 31.58 kcal/mol suggesting that the tautomerization from model **1** to **2** and **3** may be difficult in the ground state. Therefore, the most stable structure corresponds to model **1** with an intramolecular hydrogen bond between the carbonyl and amino groups as discussed in a previous paper.[1]

π-π Absorption Spectra of 1-MBPP and 2-MBPP.* 1-MBPP, 2-MBPP, isooctane (2,2,4-trimethylpentane), and ethanol were the same as reported previously.[1]

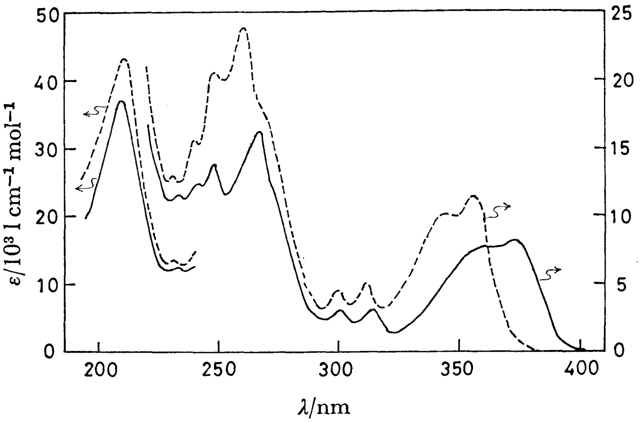

Fig. 1. Absorption spectra of 1-MBPP (——) and 2-MBPP (----) in isooctane solution.

Table 1. Calculated transition energies (E) and oscillator strengths (f) of the singlet π,π^* excited states of BPP and the corresponding observed π,π^* bands of 1-MBPP and 2-MBPP

No.	BPP			1-MBPP		2-MBPP	
	E/eV	λ/nm	f	λ/nm	f	λ/nm	f
1	3.631	342	0.213	374	0.122	356	0.135
2	3.892	319	0.082	315	0.015	311	0.026
3	4.137	300	0.186	303	0.017	299	0.020
4	4.633	268	0.522	266	0.267	263	0.391
5	4.915	252	0.446	248	0.143	243	0.184
6	5.162	240	0.431	242		240	
7	5.284	234	0.411	232		231	
8	5.596	222	0.002	209		210	
9	5.699	218	0.095				
10	5.793	214	0.244				
11	5.944	209	0.085				
12	6.046	205	0.032				
13	6.135	202	0.175				
14	6.198	200	0.141				

The absorption spectra of 1-MBPP and 2-MBPP in isooctane at room temperature are shown in Fig. 1, and the band maxima and corresponding oscillator strengths are listed in Table 1. The first absorption band of 1-MBPP appears at a wavelength longer than that of 2-MBPP. A trend is found in other alkyl compounds (alkyl group: *n*-pentyl-, *n*-nonyl-).[1]

It was necessary to establish whether (1) the first excited state was of π,π* character or not, and (2) the first absorption band of 1-alkyl compounds appeared at a wavelength longer than that of the 2-alkyl compounds or not. To this end the energies of the

Table 2. The energies of the next highest occupied molecular orbital (NHOMO), the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) of 1-MBPP, 2-MBPP, and BPP (in a. u.)

MO	1-MBPP	2-MBPP	BPP
NHOMO	−0.4091 (n)	−0.4178 (n)	−0.4238 (n)
HOMO	−0.3930 (π)	−0.4026 (π)	−0.4040 (π)
LUMO	0.0496 (π^*)	0.0522 (π^*)	0.0498 (π^*)

highest occupied and lowest unoccupied π-molecular orbitals and the n-orbitals of BPP, 1-MBPP, and 2-MBPP[1b)] were calculated using the CNDO/2 method,[3)] results of which are shown in Table 2. It may be seen that the highest occupied MO is of π-character and the next occupied MO is of n-character for the three molecules. These results suggest that the lowest excited state is of π,π^* character and that the n,π^* state may be higher than the first excited π,π^* state.

The absorption spectra of 1- and 2-alkyl benzopyranopyridines are displaced to a wavelength longer by the addition of ethanol[1)] and this suggests that the absorption bands may be assigned to the π-π^* transition.

The energy gap between the highest occupied and the lowest unoccupied orbitals of 2-MBPP is larger than that of 1-MBPP and BPP and indicates qualitatively that the lowest π,π^* state of 2-MBPP is higher than that of 1-MBPP, as shown in the absorption spectra in Fig. 1.

The P-P-P SCF-MO-CI method[4–6)] was applied to calculate the π-π^* transition energies and corresponding oscillator strengths of BPP. The following empirical parameters were used for the present calculation:

Atom, μ	I_μ/eV	A_μ/eV
C	11.42	0.578
-N=	14.12	1.78
NH_2	27.525	13.435
=O	17.32	2.649
-O-	33.50	11.97

The value −2.10 eV was used for all the resonance integrals, and the Mataga-Nishimoto approximation[6)] was adopted for the two-center Coulomb integral. The 36 singly excited configurations were built into the configuration interaction matrix elements. In the present calculation the effect of the intramolecular hydrogen bond was not taken into account.

The calculated transition energies and corresponding oscillator strengths of BPP are listed in Table 1. The calculated directions of the transition moment are shown in Fig. 2 in which the length of the transition moment is proportional to the magnitude of the oscillator strength. Referring to the calculated results in Table 1 and Fig. 2 the assignment of the absorption bands for 1-MBPP and 2-MBPP were made. The band assignments are given in Table 1.

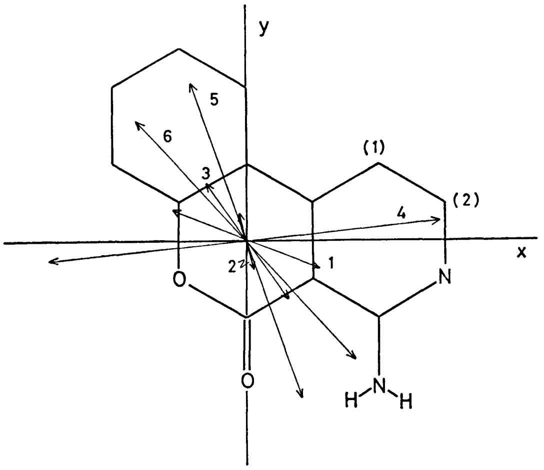

Fig. 2. Polarization directions of six π-π^* transitions in BPP predicted by the P-P-P SCF-MO-CI method.

The first band of BPP calculated at 342 nm is mainly polarized along the x axis. The second and third bands are weak and their transition moments are mainly polarized along the y axis as shown in Fig. 2. The bands near 266 nm for 1-MBPP and 263 nm for 2-MBPP correspond to the fourth band of BPP calculated at 268 nm which is polarized along the x axis, and with a relatively strong oscillator strength. The fourth band has a shoulder on the longer-wavelength side, which disappears in alcoholic solution. 2-MBPP has two bands at 240 and 231 nm in isooctane solution. These bands are observable at 241 and 233 nm in ethanol solution. The behavior of the two bands in polar solvents suggests that they belong to the different electronic states. These bands were assigned to the bands calculated at 240 and 234 nm. For 1-MBPP, the corresponding bands at 240 and 231 nm were observed at 242 and 232 nm. The strongest bands of 1-MBPP and 2-MBPP at 209 and 210 nm were tentatively assigned to the remaining transition bands from the eighth to the fourteenth transition band. The total oscillator strengths thus become equal to 0.774.

The authors acknowledge the assistance of the staff of Tokyo Denki University Computing Center in the present work.

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