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Photochemistry of 2-(methylamino)pyridine in a low-temperature argon matrix: Amino–imino tautomerism and rotational isomerism

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Abstract

Photoreaction of 2-(methylamino)pyridine in a low-temperature argon matrix was investigated by infrared spectroscopy and density functional theory calculation. The two amino tautomers with nearly isoenergetic conformation (TA and CA) around the C–N(HCH_3) bond for 2-(methylamino)pyridine change into *N*-2(1*H*)-pyridinylidenemethanamine as the methyl-imino tautomers (TMI and CMI) by intramolecular hydrogen-atom (or proton) transfer upon UV irradiation ($320 > \lambda \geq 300$ nm). The reverse tautomerism occurs by longer-wavelength light irradiation ($370 > \lambda \geq 340$ nm), where only the amino tautomer TA is reproduced from the methyl-imino tautomer TMI.

Keywords: Amino–imino tautomerism; Rotational isomerism; 2-(Methylamino)pyridine; Matrix-isolation infrared spectroscopy; DFT calculation

1. Introduction

Molecular isomerism and tautomerism are fundamental chemical reactions and frequently appear in biological systems; rotational isomerization around single bond happens in almost all polypeptides [1] and photoinduced *cis–trans* isomerization takes place in carotenoids such as retinal [2,3], while photoinduced tautomerism occurs in DNA bases. It is well known that UV light damages DNA bases to yield serious DNA mutation, in which UV-induced tautomerism may be involved [4,5]. The DNA tautomerism is possible to occur through a hydrogen-atom (or proton) migration in a DNA base [6] and through double proton transfer in intermolecular hydrogen-bonded complexes such as DNA base pair [7,8] and DNA–water [9]. There are two kinds of intramolecular tautomerism in DNA bases; one is enol–keto and the other is amino–imino. For example, cytosine is possible to have both kinds of tautomerism and to form five tautomers (Scheme 1).

One of the simplest model for the enol–keto tautomerism is the 2-hydroxypyridine/2(1*H*)-pyridinone system (Scheme 2), which has been investigated by many researchers [10–16], while the 2-aminopyridine/2(1*H*)-pyridinimine system that is one of the simplest model for the amino–imino tautomerism has been reported by only a few researchers [17–19]. Especially, photochemistry for the system had not been reported so far. We have recently investigated photoinduced amino–imino tautomerism of 2-aminopyridine [20] and 2-amino-5-methylpyridine [21], where photoinduced reversible amino–imino tautomerisms have been found by matrix-isolation infrared spectroscopy and density functional theory (DFT) calculation. In the present study, photoreaction of 2-(methylamino)pyridine having two conformations (Fig. 1) is investigated with a view to simultaneous occurring photoinduced amino–imino tautomerism and rotational isomerism by a similar method reported previously [20,21]. In addition, an infrared spectrum of *N*-2(1*H*)-pyridinylidenemethanamine as the methyl-imino tautomer for 2-(methylamino)pyridine is measured for the first time to our knowledge.

2. Experimental and calculation methods

2-(Methylamino)pyridine (Alfa Aesar) was diluted with pure argon gas (Nippon Sanso, 99.9999%) to about 1000

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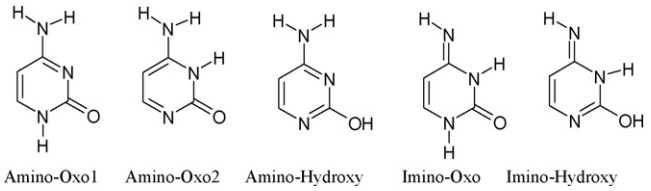
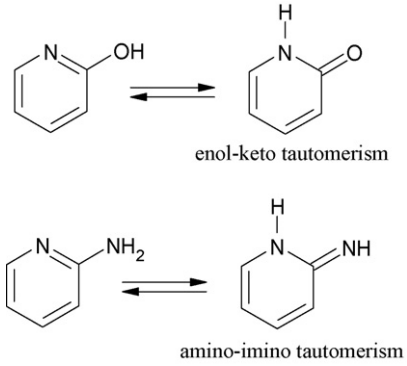


Scheme 1.



Scheme 2.

times. The premixed gas was deposited onto a CsI plate at 12 K. Absorption spectra were measured with an FTIR spectrophotometer (JASCO, FT/IR-615), where accumulation was 100 times and spectral resolution was 1 cm^{-1}. UV radiation from a superhigh-pressure mercury lamp (USHIO, SX-UI 501HQ) was used to induce photoreaction with short-wavelength cutoff filters, Sigma UTF-30U ($\lambda \geq 300$ nm), UTF-34U ($\lambda \geq 340$ nm) and SCF-37L ($\lambda \geq 370$ nm), and band-pass filters, VPF-313 ($\lambda_{max} = 314$ nm, FWHM = 309–319 nm) and VPF-326 ($\lambda_{max} = 328$ nm, FWHM = 322–333 nm). Other experimental details were reported elsewhere [22].

DFT calculations were performed using the Gaussian 03 program [23]. The density functional, B3LYP [24,25], with a basis set of 6-31++G** was used to estimate conformational energies, optimized geometries and vibrational wavenumbers. The validity of transition geometries was confirmed by an imaginary vibration wavenumber and its vibrational mode.

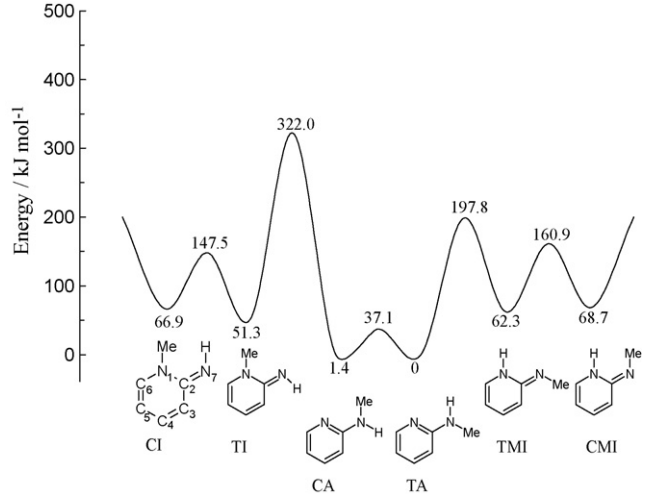


Fig. 1. Illustration of the potential curve of six tautomers for 2-(methylamino)pyridine (TA and CA), *N*-2(1*H*)-pyridinylidenemethanamine (TMI and CMI) and 1-methyl-2(1*H*)-pyridinimine (TI and CI).

3. Results and discussion

3.1. Relative energies and optimized geometries of tautomers

The DFT calculation at the B3LYP/6-31++G** level estimates optimized geometries and relative energies for 2-(methylamino)pyridine (the *trans* amino (TA) and *cis* amino (CA) tautomers), *N*-2(1*H*)-pyridinylidenemethanamine (the *trans* methyl-imino (TMI) and *cis* methyl-imino (CMI) tautomers) and 1-methyl-2(1*H*)-pyridinimine (the *trans* imino (TI) and *cis* imino (CI) tautomers) and transition potential barriers between them. The geometry of each tautomer and its relative energy are shown in Fig. 1, where the horizontal axis represents a virtual reaction coordinate between the two tautomers. The amino tautomers TA and CA are more stable by about 65 kJ mol^{-1} than the methyl-imino tautomers TMI and CMI like 2-aminopyridines [20,21]. The amino tautomer TA is more stable by 1.4 kJ mol^{-1} than the amino tautomer CA and the rotational barrier from TA to CA is 37.1 kJ mol^{-1}. On the other hand, the methyl-imino tautomer TMI is more stable by 6.4 kJ mol^{-1} than the methyl-imino tautomer CMI and the rotational barrier from TMI to CMI is 98.6 kJ mol^{-1}. The imino tautomer TI is more stable than TMI and the methyl-imino tautomer CI by 11.0 and 15.6 kJ mol^{-1}, respectively, and the rotational barrier from TI to CI is 96.2 kJ mol^{-1}. The tautomerism barrier from TA to TMI is 197.8 kJ mol^{-1} and that from CA to TI is 320.6 kJ mol^{-1}. The calculated results indicate that the amino tautomers TA and CA account for a large share of population for 2-(methylamino)pyridine at room temperature and the other tautomers exist little.

The optimized geometrical parameters are summarized in Table 1. Most of the bond lengths between the two rotational conformations, i.e., TA and CA or TMI and CMI, are the same with each other within 0.01 Å (1 Å = 10^{-10} m). Almost all the geometrical parameters are very close to those for non-substituted 2-aminopyridine and 2(1*H*)-pyridinimine [20]. For the amino tautomer TA, the $N_1 \cdots HN_7$ distance (2.387 Å) is shorter than the sum of the van der Waals radii of N and H atoms (2.75 = 1.55 + 1.20 Å), indicating the existence of the intramolecular hydrogen bond. The tautomer TMI also has hydrogen bond in $N_1H \cdots N_7$ (2.408 Å), which is supported by that the N_1–H bond length is longer by 0.004 Å than that of the tautomer CMI. It is noted that the $N_1 \cdots HN_7$ hydrogen bond length in TA (2.387 Å) is clearly shorter than that in 2-aminopyridine (2.433 Å), which might mean that amino–imino tautomerism in 2-(methylamino)pyridine proceeds easer than 2-aminopyridine.

3.2. Infrared spectrum of 2-(methylamino)pyridine

A matrix spectrum immediately after deposition without light irradiation is shown in Fig. 2a, which is compared with

Table 1
Optimized geometrical parameters of the six tautomers for 2-(methylamino)pyridine obtained at the B3LYP/6-31++G** level

Parameter[a]	TA	CA	TMI	CMI	TI	CI
Bond length (Å)						
N_1–C_2	1.349	1.343	1.410	1.412	1.414	1.421
C_2–C_3	1.414	1.417	1.457	1.453	1.454	1.454
C_3–C_4	1.390	1.385	1.367	1.361	1.363	1.360
C_4–C_5	1.399	1.404	1.431	1.438	1.428	1.433
C_5–C_6	1.396	1.391	1.367	1.359	1.365	1.361
C_6–N_1	1.336	1.342	1.360	1.375	1.366	1.376
C_2–N_7	1.373	1.377	1.290	1.293	1.297	1.295
N_7–H	1.009	1.008	2.408	–	1.019	1.018
N_7–Me	1.447	1.454	1.452	1.449	2.669	–
N_1–H	2.387	–	1.013	1.009	–	–
N_1–Me	–	2.775	–	–	1.462	1.458
Bond angle (°)						
N_1–C_2–C_3	122.2	122.3	113.3	113.6	114.5	114.4
C_2–C_3–C_4	118.3	118.5	121.4	122.0	122.2	122.5
C_3–C_4–C_5	119.9	119.5	121.6	121.0	120.4	120.3
C_4–C_5–C_6	117.4	117.5	117.6	118.1	117.9	118.1
C_5–C_6–N_1	124.2	124.3	120.9	120.9	122.5	122.4
C_6–N_1–C_2	118.1	117.9	125.2	124.4	122.5	122.3
N_1–C_2–N_7	115.4	117.3	116.4	124.5	117.2	125.2
C_2–N_7–H	114.1	116.1	–	–	109.9	113.5
C_2–N_7–Me	124.2	122.1	118.2	118.2	–	–
H–N_1–C_2	–	–	114.1	117.3	–	–
Me–N_1–C_2	–	–	–	–	116.8	118.0
N_1–C_2–N_7–H	8.8	−14.9	–	–	180.0	0.0
N_1–C_2–N_7–Me	−9.8	10.3	180.0	0.0	–	–
H–N_1–C_2–N_7	–	–	0.0	0.0	–	–
Me–N_1–C_2–N_7	–	–	–	–	0.0	0.0

[a] The values of other parameters are available upon request.

calculated spectra for the TA (Fig. 2b) and CA (Fig. 2c). The DFT calculations show a little energy difference between TA and CA, 1.4 kJ mol^{-1}, which suggest that both the amino tautomers coexist with similar population ratio in the matrix [26]. In fact, two distinguishable bands appearing at 1524 and 1510 cm^{-1} seem to be assigned to TA calculated at 1528 cm^{-1} and CA calculated at 1516 cm^{-1}, respectively. However, definite band assignments to each tautomer are impossible by only the comparison of the deposition spectrum with the calculated spectra, because of no experimental distinction of the infrared bands. The band assignments are performed in Section 3.4.

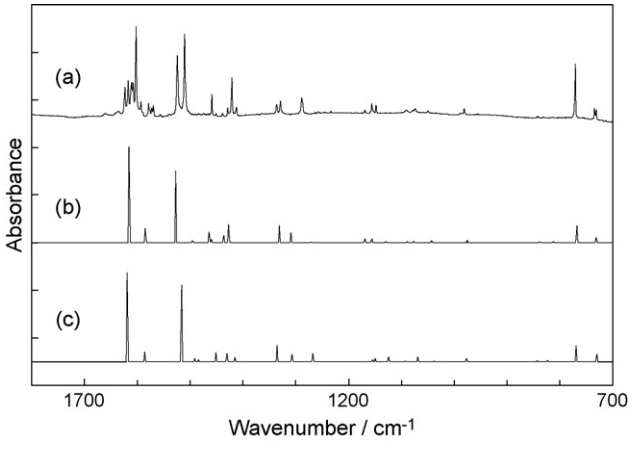


Fig. 2. Matrix-isolation infrared spectra of 2-(methylamino)pyridine: (a) observed spectrum; (b) and (c) calculated spectra of the tautomers TA and CA, respectively.

3.3. Photoinduced tautomerism from amino to imino

Photoinduced reaction for the amino tautomers of 2-(methylamino)pyridine occurs by UV irradiation through not a VPF-326 band-pass filter, but a VPF-313. Fig. 3a shows an observed difference spectrum (spectrum measured after UV irradiation minus before), where upward and downward bands are due to photoproducts and the reactant, respectively. The comparison of Fig. 3a with Fig. 2a shows that the intensity of the 1510 cm^{-1} band decreases faster than that of the 1524 cm^{-1} band upon UV irradiation, indicating that the two observed bands should be assigned to the different tautomers.

By analogy with photoreaction of 2-aminopyridine [20], candidates of the photoproducts are imino tautomers of 2-(methylamino)pyridine. Two tautomerism pathways are possible in this system; the amino tautomer TA produces the methyl-imino tautomer TMI by intramolecular hydrogen-atom (or proton) migration, and the amino tautomer CA produces the imino tautomer TI by methyl-group migration. Then, each calculated spectrum of the imino tautomers is shown in Fig. 3 to compare the observed spectrum. The calculated spectrum of the tautomer TMI reproduces the observed one satisfac-

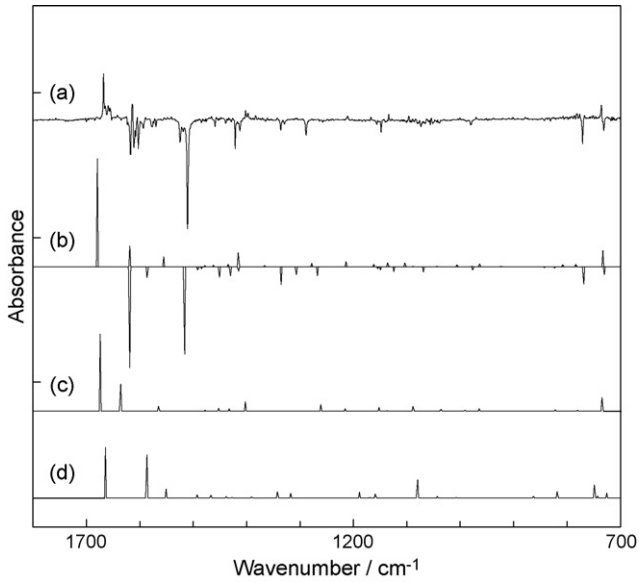


Fig. 3. Infrared spectra of photoproducts of 2-(methylamino)pyridine: (a) the spectrum measured after UV irradiation through VPF-313 band-pass filter for 30 min minus that before irradiation; (b) calculated spectrum of the tautomer TMI (upward) and CA (downward); (c) and (d) calculated spectra of the tautomer CMI and TI, respectively.

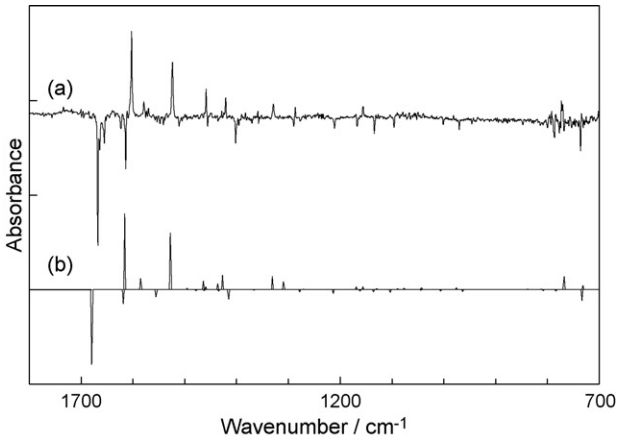


Fig. 4. Difference spectrum: (a) the spectrum measured after the second irradiation through UTF-34U short-wavelength cutoff filter for 5 min minus that after the first UV irradiation through VPF-313 band-pass filter for 30 min; (b) calculated spectrum of the amino tautomer TA (upward) and the imino tautomer TMI (downward).

torily, while that of TI does not. In addition, the observed spectrum is dissimilar to the experimental infrared spectrum of 1-methyl-2(1*H*)-pyridinimine [27], which is corresponding with the calculated spectrum (Fig. 3d). It is because that the high tautomerism barrier might inhibit methyl-group migrated tautomerism from CA to TI in vibrational relaxation process like hydrogen-atom migration in 2-aminopyridines [20,21]. Then, the photoproduct is identified as the tautomer TMI. The infrared spectrum of the methyl-imino tautomer has measured for the first time, to our knowledge. Most of the upwards bands in Fig. 3a are associated with the tautomer TMI, but the observed bands at 1656 and 1383 cm^{-1} seem to be due to the tautomer CMI. Although there is no clear proof that the tautomer CMI is produced, it is expected that the tautomer CMI coexist with the tautomer TMI in photoinduced equilibrium like 2(1*H*)-pyridinimine [20] and 5-methyl-2(1*H*)-pyridinimine [21].

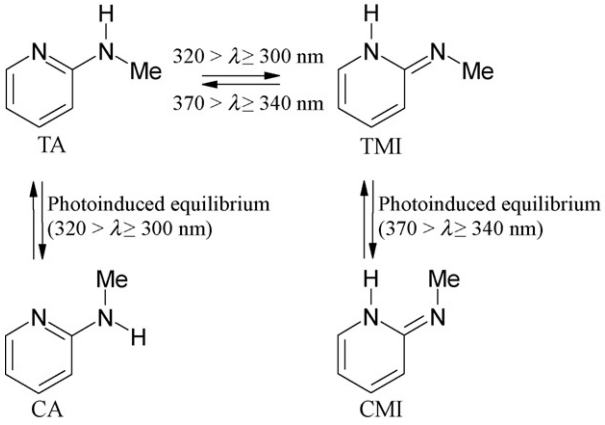
3.4. Reverse tautomerism from imino to amino

The methyl-imino tautomers change into the amino tautomer TA upon longer-wavelength irradiation with not an SCF-37L short-wavelength cutoff filter, but an UTF-34U. Fig. 4a shows a difference spectrum, where the spectrum measured immediately after the first UV irradiation through the VPF-313 band-pass filter is subtracted from that after the second light irradiation through the UTF-34U filter. The calculated spectrum of the tautomers TA and TMI is shown in Fig. 4b in upward and downward, respectively. The bands decreasing in intensity are associated with the methyl-imino tautomer TMI (and CMI), while the increasing bands are due to only the amino tautomer TA, not CA; i.e., the 1524 cm^{-1} band increases but the 1510 cm^{-1} band does not in Fig. 4a. Then, the band assignments for the amino tautomers TA and CA are completely accomplished by the comparison of Fig. 2 with Figs. 3 and 4, and are summarized in Table 2. The observed and calculated wavenumbers for the imino tautomer TMI together with CMI are also shown in Table 3.

3.5. Photoreaction mechanism of 2-(methylamino)pyridine

According to the present study, we have elucidated the photoreaction mechanism of 2-(methylamino)pyridine in the Ar matrix (Scheme 3).

Both the amino tautomers TA and CA change into the methyl-imino tautomer TMI upon UV irradiation ($320 > \lambda \geq 300$ nm; ca. 375–400 kJ mol^{-1}), indicating that the rotational isomerism and amino–imino tautomerism would take place in 2-(methylamino)pyridine simultaneously during UV irradiation. The UV irradiation excites both the amino tautomers TA and CA [17], which isomerize with each other through the electronically excited states. On the same UV irradiation, only



Scheme 3.

Table 2
Observed and calculated wavenumbers of 2-(methylamino)pyridine with their relative intensities

TA				CA			
Observed		Calculated		Observed		Calculated	
ν	Int.	ν[a]	Int.	ν	Int.	ν[a]	Int.
3480	35.3	3573	15.6	3504	31.6	3582	11.4
		3155	1.8			3151	4.8
		3150	7.1	3025	<3	3129	7.7
		3121	3.6			3112	2.3
3005	<5	3099	8.6	2999	<3	3100	9.5
2939	<5	3073	6.4			3078	5.9
2898	<5	2994	13.7	2918	<3	3039	11.8
2823	<5	2937	27.7	2821	<3	2960	27.3
1603	100.0	1616	100.0	1617[b]	28.0	1619	100.0
1579	15.4	1585	14.6	1610[b]	21.8		
1570[c]	10.7			1583	3.5	1586	11.1
1524	63.8	1528	74.9	1510	100.0	1516	86.6
		1496	2.3			1491	3.7
1459	30.9	1464	11.4			1484	2.1
		1460	3.6	1439	<3	1451	10.5
1430	7.1	1437	8.2	1421[d]	18.8	1430	9.1
1421	20.1	1427	18.8	1413	6.5	1415	4.6
1329	12.5	1331	17.8	1336	6.6	1336	18.3
1287	7.1	1309	11.0	1289	11.6	1307	8.2
1243	6.9	1271	0.8			1268	9.4
		1169	4.2			1154	1.9
1156	13.1	1156	4.0	1148	9.7	1149	3.4
		1130	1.4			1125	4.9
		1089	1.1			1092	0.2
		1077	1.9	1073	5.0	1069	5.3
		1043	2.4			1038	0.2
982	5.6	975	2.8	981	<3	977	3.5
		975	0.0			974	0.0
		957	0.1			957	0.1
		838	0.5			843	1.1
		812	1.0			823	1.5
771	12.9	768	17.1	771[d]	15.2	769	17.7
735	13.1	731	5.6	731	5.8	730	8.0
		628	0.3			624	0.9
		573	2.8			610	1.6
		520	1.1			522	3.3
		470	4.2			450	5.3
		420	9.1			412	1.5
		384	23.8			347	38.7
		228	0.4			219	3.6
		221	0.9			213	0.2
		155	0.3			128	0.5
		71	4.1			106	4.1

[a] Values calculated at the B3LYP/6-31++G** level are scaled by 0.98.
[b] The bands at 1617 and 1610 cm^{-1} exhibit band splitting.
[c] The band is assigned to a combination tone.
[d] The bands are overlapped with those of the tautomer TA.

the tautomer TA is possible to change into the methyl-imino tautomer TMI. The above explanation is supported by the experimental result that the intensity of the 1510 cm^{-1} band assigned to CA decreases faster than that of the 1524 cm^{-1} band assigned to TA in relatively early irradiation time. The amino–imino tautomerism probably proceeds in the vibrational relaxation process, which occur after internal conversion from electronically excited states to higher vibrational levels in the ground state like 2-aminopyridine derivatives [20,21].

The reverse tautomerism occurs upon longer-wavelength light irradiation ($370 > \lambda \geq 340$ nm; ca. 323–352 kJ mol^{-1}), which is not enough to excite the amino tautomer TA and CA, but enough to excite the methyl-imino tautomer TMI and CMI. The methyl-imino tautomers TMI and CMI coexist in photoinduced equilibrium, and the tautomer TMI changes into only the amino tautomer TA. The amino tautomer TA is produced from the methyl-imino tautomer TMI directly, while the tautomer CA is not. Since the tautomer TA is not excited by the

Table 3
Observed and calculated wavenumbers of *N*-2(1*H*)-pyridinylidenemethanamine with relative intensities

Observed		Calculated			
ν	Int.	TMI		CMI	
		ν[a]	Int.	ν[a]	Int.
3430	28.6	3534	9.9	3574	9.3
		3177	0.8	3172	1.6
		3167	0.5	3164	0.8
		3151	0.5	3148	0.9
		3119	2.5	3127	2.6
		3040	7.2	3044	8.7
		2944	11.3	2902	18.1
2979	7.4	2902	21.0	2866	27.8
1668[b]	100.0	1679	100.0		
1656[b]	22.3			1674	100.0
1614	28.9	1619	19.1	1636	35.1
1590	<3				
1558	4.3	1555	9.1	1565	6.3
1554	<3	1478	0.8	1478	1.2
1548	<3	1478	0.8	1477	0.0
1541	<3	1462	1.3	1453	3.9
1467	<3	1434	1.9	1433	3.2
1402[b]	18.2	1415	12.4		
1383	7.2			1403	12.2
1371	<3	1367	0.7	1377	0.1
		1278	3.0	1261	8.9
1211	8.2	1214	4.6	1216	3.0
1167	5.5	1162	1.8	1152	5.0
1134	11.6	1136	3.2	1137	0.9
1096	7.8	1103	3.5	1088	6.1
		1089	0.1	1079	0.1
		1044	0.3	1036	2.4
1001	3.4	1006	1.5	991	1.4
		978	0.0	977	0.0
971	6.6	964	2.6	964	3.4
		924	0.0	913	0.0
		808	1.3	822	2.2
786/782/777	7.7	784	1.8	781	1.2
736	30.6	733	14.7	735	17.8
		698	0.1	691	0.6
646	23.8	670	6.1	608	0.4
		611	0.1	583	3.8
		552	2.4	572	1.7
		461	0.1	455	11.4
		457	6.6	443	0.2
		382	0.3	387	3.7
		233	2.0	237	1.1
		228	0.6	232	0.5
		143	0.1	173	0.2
		114	0.0	118	0.0

[a] Values calculated at the B3LYP/6-31++G** level are scaled by 0.98.
[b] The bands exhibit splitting.

light irradiation, the tautomer CA does not increase, which suggests that the tautomerism and rotational isomerism are stepwise reactions through electronically excited states upon light irradiation.

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