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# Conformations of nitro-substituted spiropyran and merocyanine studied by low-temperature matrix-isolation infrared spectroscopy and density-functional-theory calculation

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## Abstract

Infrared spectrum of a spiropyran, 1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-[2H]indole], in a low-temperature argon matrix was measured with a Fourier transformed infrared spectrophotometer. The conformation of this spiropyran was determined by comparison of the observed spectrum with a spectral pattern obtained by the density-functional-theory calculation. This conformation differs from the optimized geometry derived from an HF/6-31G\* calculation. The conformations of a merocyanine produced from the spiropyran upon UV irradiation were also determined by the same method.

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## 1. Introduction

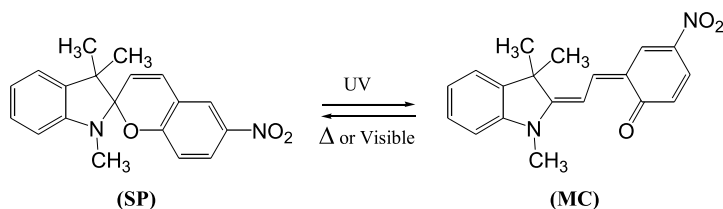
A spiropyran, 1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-[2H]indole] (we call it SP hereafter), is known as a photochromic compound; SP changes upon UV irradiation to a colored species, a merocyanine dye, (we call it MC hereafter), which returns to the original colorless

form, SP, thermally or upon visible-light irradiation (see Scheme 1).

The photochromism and the subsequent thermal relaxation processes of SP have been widely investigated [1–8], from the standpoint of possible applications of the reversible photochemical process to photonic devices such as erasable optical memories and optical switches [9–11]. The geometrical structure of its photoisomer, MC, plays an important role in this photo-switching process, but only few vibrational spectra have yet been reported, because MC is thermally unstable [12–14]. Takahashi et al. [12] used time-resolved

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Scheme 1.

resonance Raman spectroscopy to measure spectra of the colored transient species produced from SP in various solvents. They assigned the observed Raman bands to all four possible isomers, TTC, CTC, TTT and CTT of MC shown in Fig. 1b, and another short-lived TCC isomer, where T and C denote *trans* and *cis*, respectively, around the N–C=C–C, C=C–C=C, and C–C=C–CO bonds. On the other hand, Raman spectra of the aggregates formed under prolonged UV irradiation of SP in non-polar solvents were reported, where some of the observed bands due to transient spe-

cies were attributed to the four possible isomers of MC [15–17]. In spite of these studies, the geometrical structure of photoinduced MC does not seem to be elucidated clearly because MC exhibits complicated behavior in solutions due to photoinduced or thermal reverse reaction, photoisomerization, solvent effects and other various photoprocesses.

Recently, Cottone et al. [18] performed ab initio calculations at the HF/6-31G\* level to obtain the optimized geometries and vibrational wavenumbers for SP and MC. However, it is difficult to

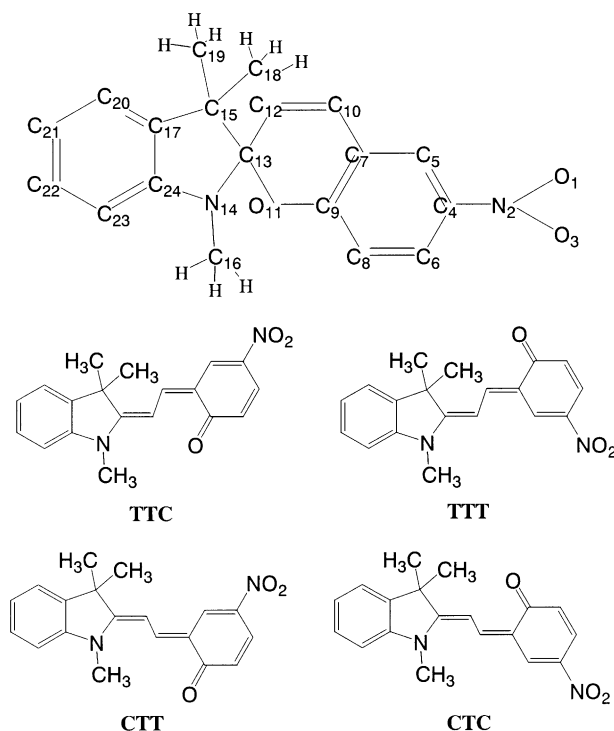


Fig. 1. Molecular structures of (a) spiropyran and (b) four possible isomers of merocyanine. Numbering of heavy atoms is given in spiropyran.

assess the reliability of their results, because no comparison has yet been made with the corresponding observed vibrational spectrum. In the present study, we have isolated SP in a low-temperature argon matrix to measure its infrared spectrum. The matrix-isolation technique can provide much better-resolved infrared bands than the previous ones measured in solution, solid or film [13,14]. After the measurement, the matrix sample has been exposed to UV light to induce production of MC from SP. MC in a low-temperature argon matrix is stable enough chemically and physically to enable easy measurement of its vibrational spectrum with a Fourier transformed infrared spectrophotometer. By a comparison of the observed spectra with the calculated spectral patterns obtained by the density-functional-theory (DFT) calculation, we have determined the geometrical structures of molecules as large as SP and MC including their conformations.

## 2. Experimental and calculations

The sample in an argon matrix was prepared by gradually heating a solid sample of SP (about 1 mg), stored inside a 1/4 inch sample reservoir, to about 360 K. The evaporated species of the sample were mixed with argon gas (Nippon Sanso, purity 99.9999%), which was introduced through a stainless-steel pipe. The amount of argon gas was controlled by a needle valve to achieve sufficient isolation. The mixed gas of argon and SP was expanded through a stainless-steel pipe and deposited directly on a CsI plate. This plate was cooled to 8 K by a closed-cycle helium cryostat (IWATANI GAS, CW303).

The matrix sample was later exposed to UV/Visible light from a superhigh-pressure mercury lamp (Ushio) to induce photoisomerization through a water filter that avoided thermal reactions of the sample. Suitable wavelengths were selected using B390 and O54 filters separately when needed.

Infrared spectra of the matrix samples were measured with an FTIR spectrophotometer (JEOL, JIR-WINSPEC50). The data were collected at a resolution of  $0.5\text{ cm}^{-1}$ , and 64 scans

were accumulated to ensure an acceptable signal-to-noise ratio. Other experimental details were reported elsewhere [19,20].

The DFT calculations were performed by using the GAUSSIAN 98 program [21] with the 6-31G\* basis set. Becke's three-parameter hybrid density functional [22], in combination with Lee–Yang–Parr correlation functional (B3LYP) [23], was used for optimization of the geometrical structures and energies of SP and MC and for calculation of their vibrations.

## 3. Results and discussion

### 3.1. Infrared spectrum of spiropyran

Fig. 2a shows an argon matrix-isolation infrared spectrum of SP, with band widths much sharper than those observed in solution, solid or film [13,14]. It is compared with a spectral pattern obtained by the DFT/B3LYP/6-31G\* calculation in Fig. 2b, where a scaling factor of 0.96 and a band width of  $2\text{ cm}^{-1}$  are assumed. The calculated pattern reproduces the observed spectrum satis-

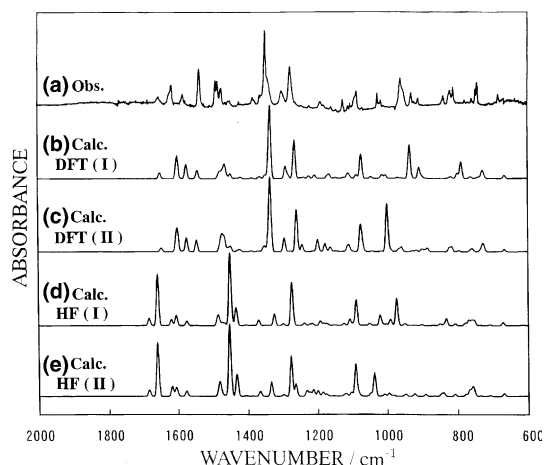


Fig. 2. Observed and calculated infrared spectra of spiropyran. (a) Observed in an Ar matrix at 8 K; (b) DFT/B3LYP/6-31G\* calculation based on structure (I); (c) DFT/B3LYP/6-31G\* calculation based on structure (II); (d) HF/6-31G\* calculation based on structure (I); (e) HF/6-31G\* calculation based on structure (II), reported in [18]. The structures are shown in Fig. 3. Scaling factors are 0.96 and 0.8929 for DFT and HF, respectively.

factorily, although the relative intensities are slightly inconsistent. The observed and calculated wavenumbers and relative intensities are summarized in Table 1. In contrast, the spectral pattern calculated by Cottone et al. [18] based on the HF/6-31G\* level does not agree with the observed spectrum, as shown in Fig. 2e. This discrepancy probably arises from that their calculation was optimized at a *metastable* point and that the HF method is less suitable than DFT for calculation of vibrational wavenumbers and intensities [24,25]. The geometrical parameters of our optimized

structure are compared in Table 2 with Cottone's [18]. The dihedral angle between the indole and benzopyran rings,  $D(C_{12}-C_{13}-C_{15}-C_{17})$ , in our structure is  $-150.7^\circ$ ; SP is bent at the bridging carbon atom,  $C_{13}$ , as shown in Fig. 3a. On the other hand, this angle in Cottone's optimized structure is  $-88.6^\circ$ , where the indole and benzopyran rings are linked straightly along the molecular axis, as shown in Fig. 3b. The positions of the three methyl groups bonded to the indole ring are inconsistent with our structure. In addition, their  $O_{11}-C_{13}$  length in the benzopyran ring, 1.417 Å, is

Table 1  
Observed and calculated vibrational wavenumbers (in  $\text{cm}^{-1}$ ) and relative intensities of spiropyran

Obs. <sup>a</sup>		Calc. <sup>b</sup>		Obs. <sup>a</sup>		Calc. <sup>b</sup>	
$\bar{\nu}$	Int.	$\bar{\nu}$	Int.	$\bar{\nu}$	Int.	$\bar{\nu}$	Int.
1654	11	1649	8			1143	0
1622	22	1600	20	1144	3	1123	1
1615	26	1598	13	1125	17	1112	4
		1589	0	1109	8	1108	4
1583	13	1573	19			1103	1
1535	54	1541	12	1101	13	1086	5
		1480	4	1084	28	1072	33
1487	36	1479	2	1068	1	1044	2
		1475	6	1025	17	1013	5
1482	36	1469	9	1015	8	1003	5
1472	30	1463	16			969	1
		1460	2			960	1
1459	11	1459	1			938	1
		1456	2	959	40	934	47
1449	10	1447	7			928	0
		1432	1			925	1
1421	5	1419	2	929	18	907	15
		1386	1	908	9	900	3
1381	10	1366	1			896	1
		1363	2			889	0
1363	12	1348	5			830	0
		1339	8			825	0
1348	100	1334	100	838	11	818	3
1300	20	1290	17	819	18	799	7
		1282	5	810	20	788	23
1275	57	1264	54	777	2	762	3
		1248	1			748	0
		1238	2	757	5	740	2
1221	2	1223	4			730	8
1187	11	1206	5	743	27	728	2
		1170	3			725	4
1179	7	1164	5	708	1	695	0
		1146	1	685	13	666	4

<sup>a</sup> Observed in an argon matrix at 8 K.

<sup>b</sup> Calculated by DFT/B3LYP/6-31G\*. A scaling factor of 0.96 is used.

Table 2

Optimized geometrical parameters (in Å and degrees) for spiropyran and merocyanine

Parameters <sup>a</sup>	Spiropyran		Merocyanine	
	DFT <sup>b</sup>	HF <sup>c</sup>	DFT <sup>b</sup>	HF <sup>c</sup>
<i>R</i> (O <sub>1</sub> –N <sub>2</sub> )	1.234	1.195	1.237	1.197
<i>R</i> (N <sub>2</sub> –O <sub>3</sub> )	1.233	1.195	1.236	1.199
<i>R</i> (N <sub>2</sub> –C <sub>4</sub> )	1.461	1.450	1.451	1.438
<i>R</i> (C <sub>4</sub> –C <sub>5</sub> )	1.393	1.383	1.370	1.348
<i>R</i> (C <sub>4</sub> –C <sub>6</sub> )	1.399	1.386	1.432	1.441
<i>R</i> (C <sub>5</sub> –C <sub>7</sub> )	1.395	– <sup>d</sup>	1.423	– <sup>d</sup>
<i>R</i> (C <sub>6</sub> –C <sub>8</sub> )	1.387	1.378	1.359	1.337
<i>R</i> (C <sub>7</sub> –C <sub>9</sub> )	1.413	1.395	1.490	1.479
<i>R</i> (C <sub>7</sub> –C <sub>10</sub> )	1.453	1.462	1.403	1.382
<i>R</i> (C <sub>8</sub> –C <sub>9</sub> )	1.403	1.389	1.462	1.468
<i>R</i> (C <sub>9</sub> –O <sub>11</sub> )	1.347	1.336	1.244	1.212
<i>R</i> (C <sub>10</sub> –C <sub>12</sub> )	1.341	1.320	1.401	1.405
<i>R</i> (O <sub>11</sub> –C <sub>13</sub> )	1.483	1.417		
<i>R</i> (C <sub>12</sub> –C <sub>13</sub> )	1.502	1.511	1.388	1.373
<i>R</i> (C <sub>13</sub> –N <sub>14</sub> )	1.449	1.456	1.365	1.351
<i>R</i> (C <sub>13</sub> –C <sub>15</sub> )	1.587	1.571	1.538	1.540
<i>R</i> (N <sub>14</sub> –C <sub>16</sub> )	1.453	1.443	1.456	1.450
<i>R</i> (C <sub>15</sub> –C <sub>18</sub> )	1.534	– <sup>d</sup>	1.548	– <sup>d</sup>
<i>R</i> (C <sub>15</sub> –C <sub>19</sub> )	1.547	– <sup>d</sup>	1.548	– <sup>d</sup>
<i>R</i> (N <sub>14</sub> –C <sub>24</sub> )	1.405	– <sup>d</sup>	1.410	– <sup>d</sup>
<i>R</i> (C <sub>15</sub> –C <sub>17</sub> )	1.521	1.519	1.521	1.518
<i>R</i> (C <sub>17</sub> –C <sub>20</sub> )	1.386	1.373	1.387	1.376
<i>R</i> (C <sub>17</sub> –C <sub>24</sub> )	1.403	1.395	1.399	1.385
<i>R</i> (C <sub>20</sub> –C <sub>21</sub> )	1.404	– <sup>d</sup>	1.402	– <sup>d</sup>
<i>R</i> (C <sub>21</sub> –C <sub>22</sub> )	1.395	1.381	1.397	1.383
<i>R</i> (C <sub>22</sub> –C <sub>23</sub> )	1.402	1.394	1.399	1.391
<i>R</i> (C <sub>23</sub> –C <sub>24</sub> )	1.393	1.381	1.392	1.380
<i>A</i> (O <sub>1</sub> –N <sub>2</sub> –C <sub>4</sub> )	117.8	117.8	118.4	117.7
<i>A</i> (O <sub>3</sub> –N <sub>2</sub> –C <sub>4</sub> )	117.8	117.8	117.7	118.4
<i>A</i> (N <sub>2</sub> –C <sub>4</sub> –C <sub>6</sub> )	119.3	119.3	119.3	119.4
<i>A</i> (C <sub>5</sub> –C <sub>4</sub> –C <sub>6</sub> )	121.5	121.5	121.3	121.0
<i>A</i> (C <sub>4</sub> –C <sub>5</sub> –C <sub>7</sub> )	119.7	– <sup>d</sup>	121.2	– <sup>d</sup>
<i>A</i> (C <sub>4</sub> –C <sub>6</sub> –C <sub>8</sub> )	119.3	119.2	119.9	120.2
<i>A</i> (C <sub>5</sub> –C <sub>7</sub> –C <sub>9</sub> )	119.0	– <sup>d</sup>	119.2	– <sup>d</sup>
<i>A</i> (C <sub>9</sub> –C <sub>7</sub> –C <sub>10</sub> )	117.3	117.1	123.2	123.6
<i>A</i> (C <sub>6</sub> –C <sub>8</sub> –C <sub>9</sub> )	119.9	119.7	112.7	122.6
<i>A</i> (C <sub>7</sub> –C <sub>9</sub> –C <sub>8</sub> )	120.6	120.9	115.7	115.6
<i>A</i> (C <sub>7</sub> –C <sub>9</sub> –O <sub>11</sub> )	122.2	122.0	123.3	123.5
<i>A</i> (C <sub>7</sub> –C <sub>10</sub> –C <sub>12</sub> )	121.3	120.3	126.6	128.2
<i>A</i> (C <sub>10</sub> –C <sub>12</sub> –C <sub>13</sub> )	123.7	123.5	125.9	124.8
<i>A</i> (C <sub>12</sub> –C <sub>13</sub> –C <sub>15</sub> )	115.6	113.1	130.4	121.1
<i>A</i> (N <sub>14</sub> –C <sub>13</sub> –C <sub>15</sub> )	103.2	102.7	108.6	108.6
<i>A</i> (C <sub>13</sub> –C <sub>15</sub> –C <sub>17</sub> )	100.5	99.8	101.4	100.9
<i>A</i> (C <sub>15</sub> –C <sub>17</sub> –C <sub>24</sub> )	108.8	108.6	109.4	109.5
<i>A</i> (C <sub>20</sub> –C <sub>17</sub> –C <sub>24</sub> )	120.2	120.3	119.9	120.1
<i>D</i> (C <sub>9</sub> –C <sub>7</sub> –C <sub>10</sub> –C <sub>12</sub> )	0.0	–1.2	0.0	0.0
<i>D</i> (C <sub>7</sub> –C <sub>10</sub> –C <sub>12</sub> –C <sub>13</sub> )	–0.8	1.3	180.0	179.9
<i>D</i> (C <sub>10</sub> –C <sub>12</sub> –C <sub>13</sub> –N <sub>14</sub> )	120.3	120.1	180.0	180.0
<i>D</i> (C <sub>10</sub> –C <sub>12</sub> –C <sub>13</sub> –C <sub>15</sub> )	–121.7	–125.3	0.0	0.0
<i>D</i> (C <sub>12</sub> –C <sub>13</sub> –C <sub>15</sub> –C <sub>17</sub> )	–150.7	–88.6	180.0	179.9

<sup>a</sup> Numbering of atoms is given in Fig. 1a. *R*, *A*, and *D* denote bond length, bond angle, and dihedral angle, respectively.<sup>b</sup> Present result calculated by DFT/B3LYP/6-31G\*.<sup>c</sup> Reported by Cottone et al. [18]. The calculation level was HF/6-31G\*.<sup>d</sup> Not reported in [18].

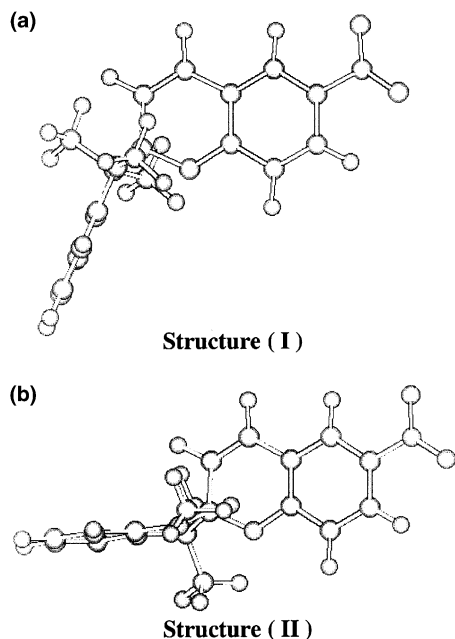


Fig. 3. Comparison of optimized geometry of spiropyran. (a) Present result obtained by DFT/B3LYP/6-31G\*. (b) Cottone's result obtained by HF/6-31G\* [18].

about 0.07 Å shorter than that in our structure. Their N–O length in the nitro group, 1.195 Å, is also about 0.04 Å shorter. We have performed the geometrical optimization of SP at the same DFT calculation level by using Cottone's structure [18] as an initial model and obtained almost the same optimized geometry as theirs. This structure, however, is found to be *metastable*, where the relative energy is 11.3 kJ mol<sup>-1</sup> higher than that of the most stable SP structure. This finding suggests that the population of Cottone's optimized structure has only negligible Boltzmann distribution even at the sublimation temperature of the solid sample, 360 K.

The spectral patterns of the optimized geometries obtained by the DFT and HF methods, based on structures (I) and (II) shown in Fig. 3, are compared in Fig. 2. The patterns obtained by the HF method, Figs. 2d,e, are both inconsistent with the observed spectrum. This reconfirms the much higher utility of DFT than HF for calculation of infrared spectral patterns [24,25]. Note also that the pattern of optimized geometry obtained by the DFT method based on structure (II), Fig. 2c, is inconsistent with the

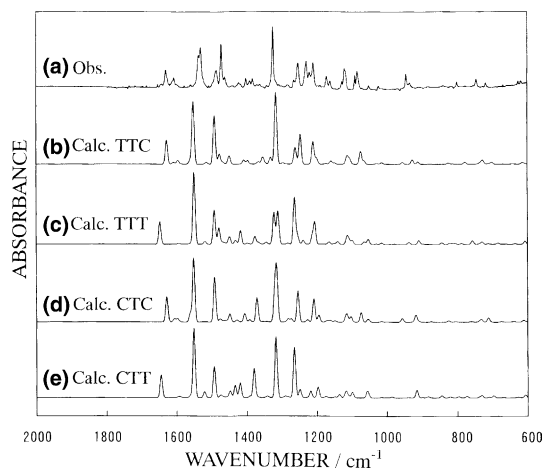


Fig. 4. Observed and calculated infrared spectra of merocyanine. (a) Observed in an Ar matrix at 8 K after UV irradiation through a band pass filter B390, where bands of spiropyran are subtracted computationally; (b)–(e) Calculated spectral patterns of TTC, TTT, CTC, and CTT, respectively, obtained by DFT/B3LYP/6-31G\*, where a scaling factor of 0.96 is used.

observed spectrum in the region lower than 1100 cm<sup>-1</sup>, especially the modes related to the benzopyran ring. Thus we conclude that only the

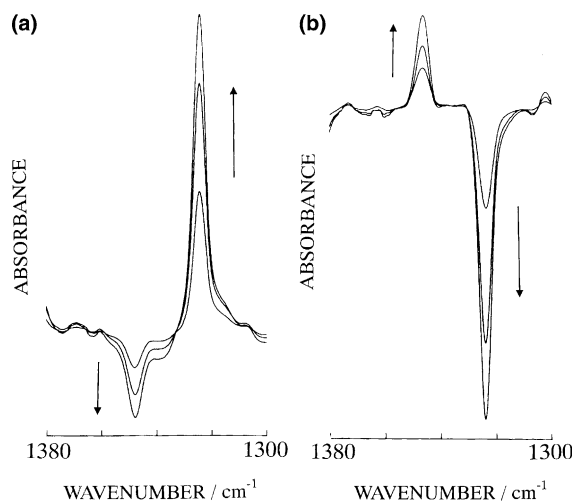


Fig. 5. Infrared spectral changes in photochromism of spiropyran and merocyanine. (a) UV irradiation through a bandpass filter of B390. Intensity of the SP band at 1348 cm<sup>-1</sup> decreases and that of the MC band at 1324 cm<sup>-1</sup> increases as the irradiation time increases 10, 30, and 60 min; (b) Visible-light irradiation through a short-cut filter of O54. The SP and MC bands increases and decreases, respectively, as the irradiation time increases 25, 40, and 55 min.

spectral pattern of structure (I) obtained by DFT can reproduce the observed spectrum.

### 3.2. Infrared spectrum of merocyanine

After measurement of the spectrum of Fig. 2a, the matrix sample was exposed to UV light from a superhigh-pressure mercury lamp through a water filter and a bandpass filter B390 ( $340 < \lambda < 490$  nm). Fig. 4a shows the infrared spectrum of the photoproduct, where the bands of SP are sub-

tracted computationally. Fig. 5a shows the spectral changes in the range from 1300 to 1380  $\text{cm}^{-1}$  measured at various irradiation times, where the decreasing and increasing bands are due to SP and the colored photoproduct, respectively. When the matrix sample was irradiated by Visible light through a water filter and a short-cut filter O54 ( $\lambda > 540$  nm) after the UV irradiation for 1 h, the photoproduct band decreases, while the SP band increases, as shown in Fig. 5b. The photoreaction between SP and the photoproduct is completely

Table 3

Observed and calculated vibrational wavenumbers (in  $\text{cm}^{-1}$ ) and relative intensities of merocyanine

Obs. <sup>a</sup>		Calc. <sup>b</sup>		Obs. <sup>a</sup>		Calc. <sup>b</sup>	
$\tilde{\nu}$	Int.	$\tilde{\nu}$	Int.	$\tilde{\nu}$	Int.	$\tilde{\nu}$	Int.
1628	33	1627	33			1118	0
		1607	2	1126	21	1113	11
1604	19	1595	5	1119	36	1107	6
		1590	1			1106	0
1557	6	1560	5	1090	27	1103	4
529	73	1551	88	1086	38	1073	18
1482	31	1513	3	1048	8	1063	5
1469	75	1490	68			1027	1
		1477	6	1022	6	1013	2
1459	17			1475	9	1005	0
		1466	3			965	0
		1461	0	943	26	954	2
		1453	0			939	0
		1452	0	933	10	926	6
		1452	0			922	0
1420	6	1448	11			913	0
		1430	0	907	9	910	3
1399	12	1407	6			898	0
1388	8	1396	5			878	0
		1371	0			831	0
		1365	3	801	8	825	2
1380	11	1353	10			814	0
		1346	1			807	0
		1331	9	777	2	778	3
1324	100	1316	100			738	1
1281	4	1296	2			737	0
1264	13	1263	12	745	11	731	3
1252	44	1260	14			727	4
1229	48	1247	42			710	1
1219	28	1210	31	719	7	702	3
1209	46	1200	9			669	0
1188	6	1173	1	625	6	641	1
1170	24	1159	4	617	3	614	2
1161	15	1149	2			607	1

<sup>a</sup> Observed in an argon matrix at 8 K.

<sup>b</sup> Calculated by DFT/B3LYP/6-31G\*. A scaling factor of 0.96 is used.



reversible. This finding suggests that the colored species produced from SP can be assigned to MC [12–17]. In order to confirm our identification, we have performed DFT calculations for four possible isomers of MC shown in Fig. 1b. The calculated spectral patterns are compared with the observed spectrum in Fig. 4. The calculated pattern of TTC reproduces the observed spectrum, especially in the region between 1200 and 1400  $\text{cm}^{-1}$ , more satisfactorily than the other isomers. On the other hand, the calculated band for TTT corresponding to the strongest band observed at 1324  $\text{cm}^{-1}$  splits with a peak interval of 10  $\text{cm}^{-1}$ , and the calculated strong bands at 1371 and 1380  $\text{cm}^{-1}$  for CTC and CTT, respectively, do not appear in the observed spectrum. Thus, we conclude that TTC is mainly photoproducted from SP. This isomer is the most stable one among the MC isomers; the calculated relative energies scaled from SP for TTC, TTT, CTC, and CTT are 23.8, 30.6, 32.9, and 35.9  $\text{kJ mol}^{-1}$ , respectively. The hydrogen atom bonded to  $\text{C}_{10}$  is hindered by the methyl group bonded to  $\text{N}_{14}$  in CTT and CTC, resulting in the twist of the indole ring around the  $\text{C}_{12}=\text{C}_{13}$  bond by  $10^\circ$  and  $12^\circ$  for CTT and CTC, respectively. On the other hand, TTC and TTT are planar because the hydrogen atom is settled in the middle space of the two methyl groups bonded to  $\text{C}_{15}$ . An intermolecular hydrogen bonding,  $\text{C}=\text{C}-\text{H} \cdots \text{O}=\text{C}$ , may play a significant role in stabilizing TTC more than TTT, where the  $\text{C}=\text{O}$  bond in TTC, 1.244 Å, is longer than that in TTT, 1.238 Å. As a result, TTC is the most stable isomer. All the other isomers whose central conformation is *cis*, i.e., TCT, TCC, CCT, and CCC, are found to be unstable because of steric hindrance. The observed wavenumbers and relative intensities are compared in Table 3 with the corresponding calculated values for TTC of MC.

Cottone et al. [18] also performed *ab initio* calculation for MC at the HF/6-31G\* level and correctly predicted that the most stable isomer was TTC. As for the geometrical parameters of their optimized structure, however, Table 2 shows that their N–O and C=O lengths are shorter than ours by 0.04 and 0.03 Å, respectively, while the  $\text{C}_{12}-\text{C}_{13}-\text{C}_{15}$  angle is about  $10^\circ$  smaller. They also calculated the wavenumbers and intensities of the

infrared bands for TTC, but their calculated spectral pattern is very distant from our observed spectrum shown in Fig. 4a. As in the case of SP discussed in Section 3.1, HF/6-31G\* does not work well for the vibrational calculations.

Our conclusion on the stability of isomers differs from that of Pachter et al. [26] based on semi-empirical calculations at the AM1 level. They claimed that CTT was the most stable whereas TTC was the least stable. A detailed discussion on this problem must have needed a higher level of calculation.

In summary, we have provided further evidence that a combination of the DFT calculation and low-temperature matrix-isolation technique is a useful source of information on molecular structure and conformation.

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