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Molecular Orbital Calculations for Acid Induced Ring Opening Reaction of Spiropyran

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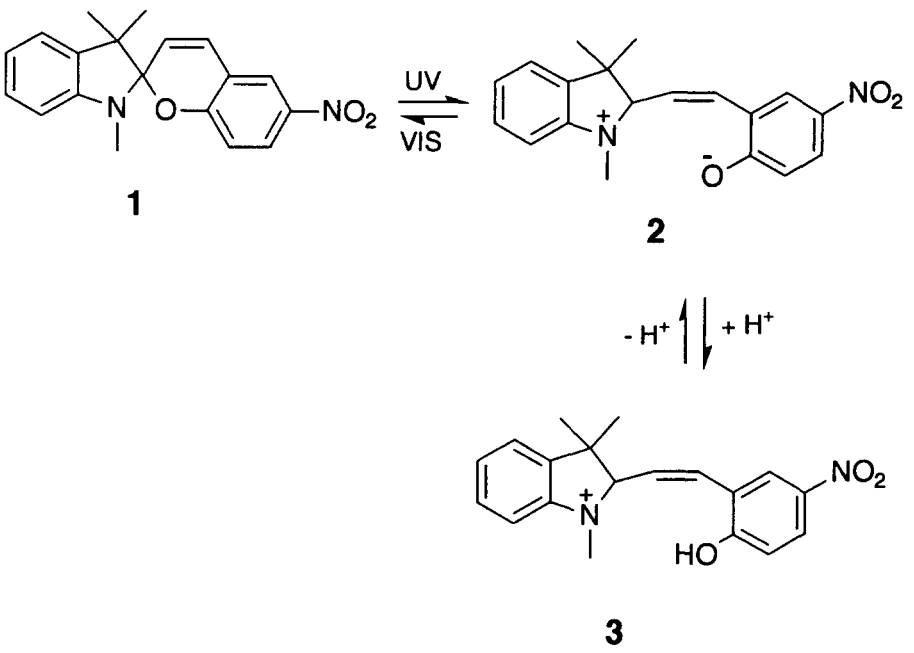
ABSTRACT

It was found that the acid induced ring opening reaction of spiropyran proceeded in the dark to give the cis *form which was further isomerized to the* trans *form by UV irradiation. The mechanisms of these reactions were well explained by molecular orbital calculations. The structure of the transition state of the acid induced ring opening reaction was optimized by MOPAC with PM3. The structure revealed the direction of the ring opening of spiropyran. Subsequent geometry optimizations gave a protonated open* cis *form as a transient of this dark reaction. © 1997 Elsevier Science Ltd. All rights reserved*

Keywords: Spiropyran, molecular orbital calculation, tautomerism, geometry optimization, transition state.

INTRODUCTION

Spiropyrans are well known as functional dyes which undergo chromisms, such as photo-, thermo- and piezo-chromisms, associated with a bond cleavage of the spiropyran ring.[1] Photo-responsive membranes, incorporating 6-substituted spiropyrans, have been studied as a photochromic application of spiropyrans.[2,3] The membrane-bound spiropyran exhibited photochromisms to produce a colorless form under visible light irradiation and a colored form under UV light irradiation. Under acidic condition the open-ring form **2** may be protonated to a positively charged form **3** (Scheme 1).[2] Therefore, membrane-bound spiropyran is thought to possess a positive charge under acidic conditions and UV light irradiation. A photo-induced



Scheme 1

potential change of the membrane containing the 1′,3′,3′-trimethyl-6-nitrospiro[2*H*-benzopyran-2,2′-indoline], **1**, was observed only in the pH range below 7.[2] It is generally assumed that a thermo-sensitive equilibrium exists between the spiropyran and a colored opened form, and that an acid shifts this equilibrium toward the opened form. This implies that some spiropyrans undergo ring-opening and protonation in the very low pH range without UV irradiation and then attain the positive charge. Therefore, the photo-induced potential change induced by UV irradiation seems to be prevented under such conditions, because the spiropyran already has a positive charge prior to the UV irradiation. Thus, there is a pH range within which the membrane potential can be effectively changed by UV irradiation. This pH range can be expected to be altered by substituents.

Recently, Keum *et al.* reported the interconversion of the photo-insensitive spiropyrans to the corresponding merocyanines, consisting of an acid induced ring opening of the spiropyrans.[4] The mechanism of this reaction should be simpler than that of the 6-nitro spiropyrans, since it does not involve photochromic reactions. They suggested the presence of a protonated open *cis* form as a transient of the acid induced ring opening reaction. However, the reaction mechanism has not yet been reported in detail. I have observed that 1′,3′,3′-trimethylspiro[2*H*-benzopyran-2,2′-indoline], **4**, underwent a reversible acid-induced ring opening reaction without UV

irradiation in the dark, and that the absorption band of the resulting colored form was shifted to longer wavelength by UV irradiation (300 nm). It is relevant to use the compound **4** for studying the reaction mechanism of the acid induced ring opening reaction of spiropyrans, because **4** is also photo-insensitive. In this report, I explain the mechanism of this reaction using molecular orbital calculations, and propose some guidelines for molecular design in order to modify the photo-responsive pH range of the membranes.

EXPERIMENTAL

Spiropyran **4** was supplied by Dr Hao of the Swiss Federal Institute of Technology, Zurich. Absorption spectra of **4** in the concentration of 6.1×10^{-5} mol dm^{-3} in ethanol solution, with or without a trace amount of sulfuric acid, were measured at room temperature using a Shimadzu UV-260 spectrophotometer. An Hitachi 650-10M fluorescence spectrophotometer was used as a light source for light irradiation at around 300 or 430 nm.

METHOD OF CALCULATIONS

Geometry optimizations of spiropyran and opened colored forms were performed using the MOPAC 6.01 program[5] with the AM1 and PM3 Hamiltonians. Spectral calculations were performed using the AMPAC 4.5 program[6] with PM3. The *ab initio* molecular orbital calculations were performed with restricted Hartree–Fock theory using the Gaussian 94 program.[7] The STO-3G basis set was employed for the geometry optimization of **4**, and the single point calculation was performed using the 6-31G* basis set. In this paper, the solvent effect was not considered due to the difficulty of evaluating its precise effect, although the solvent may affect the structure of the compounds in acidic solutions.

RESULTS AND DISCUSSION

Absorption spectra of **4** under various conditions are shown in Fig. 1. The closed form absorbs in the UV region, but absorbs in the visible region by adding acid in the dark. The absorption spectrum of the closed form was reproduced by neutralizing the acidified solution. Irradiation with UV light at around 300 nm to the acidified solution (curve b, Fig. 1) produced a bathochromic shift to 440 nm (curve c), accompanied by an increase of the optical density. Heiligman-Rim *et al.*[8] observed the following transfor-

mations: (1) UV irradiation of an indolinonaphthalo-spiropyran produced the colored merocyanine form, absorbing at λmax 570 nm, which was assigned to the *trans* form; (2) the merocyanine form was converted into the protonated species, absorbing at λmax 480 nm, when acid was added to the solution after UV irradiation. The protonated species is also presumed to be the *trans* form. The absorption spectrum of the protonated species was very similar to the absorption curve c in Fig. 1. From these results, together with the spectral changes shown in Fig. 1, the absorption curves b and c were assigned to the *cis* and *trans* forms, respectively. The photochromic reactions between 'b' and 'c' were reversible, and the absorption curve b was reproduced by visible-light irradiation at around 430 nm to a solution of 'c'.

Molecular orbital calculations were performed to confirm the above assignment. There are several options for molecular orbital calculations, but it is very important to select suitable software. The MOPAC program was used for the major part of this study, because the target reaction system is

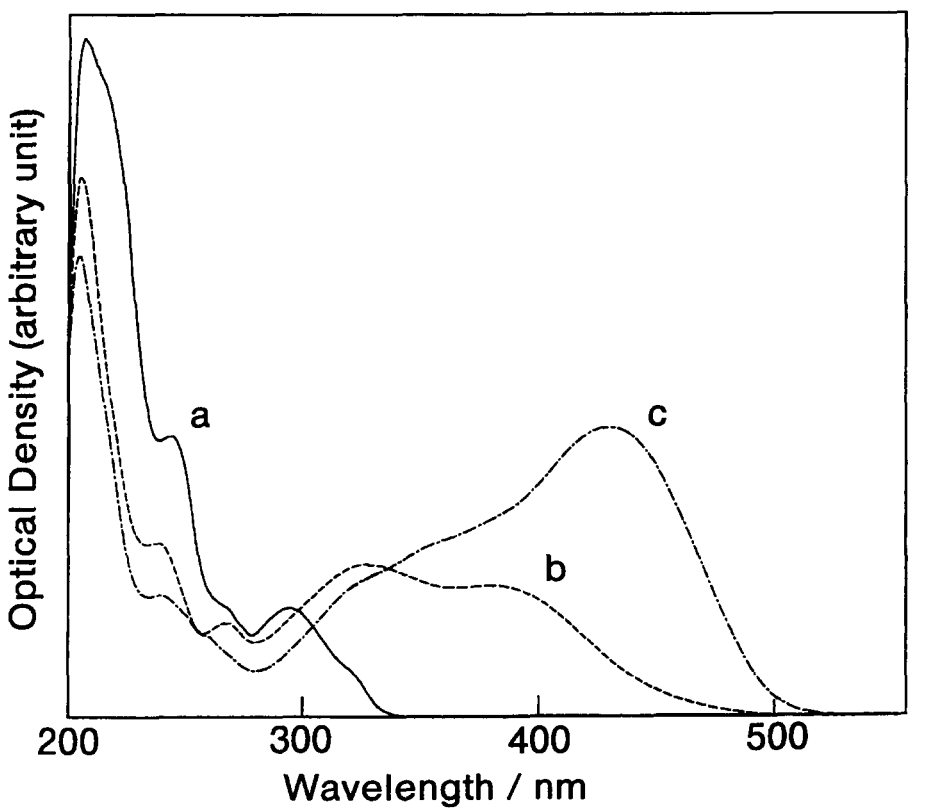


Fig. 1. Absorption spectra of **4** under various conditions: a, 6.1×10^{-5} mol dm^{-1} in EtOH; b, 0.42 mol dm^{-1} of H_2SO_4 added to 'a'; c, 'b' irradiated by UV-light at around 300 nm.

too large for *ab initio* calculation. The crystallographic data[9] and the *ab initio* calculations for the closed form **4** were used to check the reliability of the results obtained by MOPAC.

The crystallographic and calculated results are shown in Table 1. Although large differences were not observed in the bond lengths calculated, AM1 gave an opposite twist angle at the pyran ring. This twist angle is very important, because the angle affects the direction of the ring opening of spiropyran. The results of the PM3 and the *ab initio* calculations, and the crystallographic data, suggested that the ring opening direction is toward 'A' of Fig. 2, whereas AM1 suggested the opposite direction of 'B'. In addition, AM1 showed that the nitrogen atom at the 1′-position is more nucleophilic than the oxygen atom at the 1-position. It was concluded that PM3 gave better results for spiropyran than AM1.

The structure at the transition state for this acid induced ring opening reaction was optimized with PM3. The reaction pathway between **4** and the imaginary acid H_3O^+ is shown in Fig. 3. In the transition state, the bond between the proton of H_3O^+ and O(1) was formed with the length of 1.215 Å, and the C(2)–O(1) bond lengthened up to 1.517 Å. The geometry of the transition state showed that the pyran ring will be opened toward the direction 'A' in Fig. 2. When the distance between the proton of H_3O^+ and O(1) was slightly shortened by manual operation in the course of the PM3 calculation, the reaction proceeded automatically to form H_2O and compound **5**. The heat of formation of 171.68 kcal mol^{-1} of compound **5** was then calculated without the H_2O. The forms **6** and **7** were obtained by forced rotation of the

TABLE 1
Geometrical Parameters and Net Atomic Charges of **4**

	Experimental[a]	*AM1*[b]	*PM3*[c]	Ab initio[d]
Bond length (Å)				
C(2)–O(1)	1.474	1.454	1.436	1.449
C(2)–C(3)	1.498	1.504	1.504	1.532
C(2)–N(1′)	1.434	1.494	1.519	1.498
C(2)–C(3′)	1.566	1.606	1.601	1.594
O(1)–C(8a)	1.369	1.376	1.372	1.393
Angle (deg)				
C(7a′)–N(1′)–C(3′)–C(2)	150.2	162.4	160.8	147.6
C(8a)–O(1)–C(3)–C(2)	−162.4	160.3	−164.1	−159.3
Charge				
O(1)		−0.220	−0.191	−0.746
N(1′)		−0.233	0.000	−0.682

[a]Taken from[9].
[b]Calculated by AM1.
[c]Calculated by PM3.
[d]Calculated by Gaussian 94 program with the STO-3G basis set for geometry optimization and the 6-31G* basis set for single point calculation.

C(4)–C(4a) bond of **5**. The heats of formation were 174.19 kcal mol^{-1} and 173.86 kcal mol^{-1}, respectively. The form **5** showed the lowest heat of formation. However, the differences in the heats of formation among them were small, and **6** and **7** might be present in the reaction mixture.

From the calculated results shown in Table 2, bond orders of C(2)–N(1′) and C(3)–C(4) are of double bond character and **5** can be drawn with the limiting structure shown in Scheme 2.

The geometries of the *trans* forms **8**, **9**, **10** and **11** were also optimized by MOPAC with PM3. All the isomers converted to the planar structure through the optimizations. The calculated heats of formation of the forms **8**,

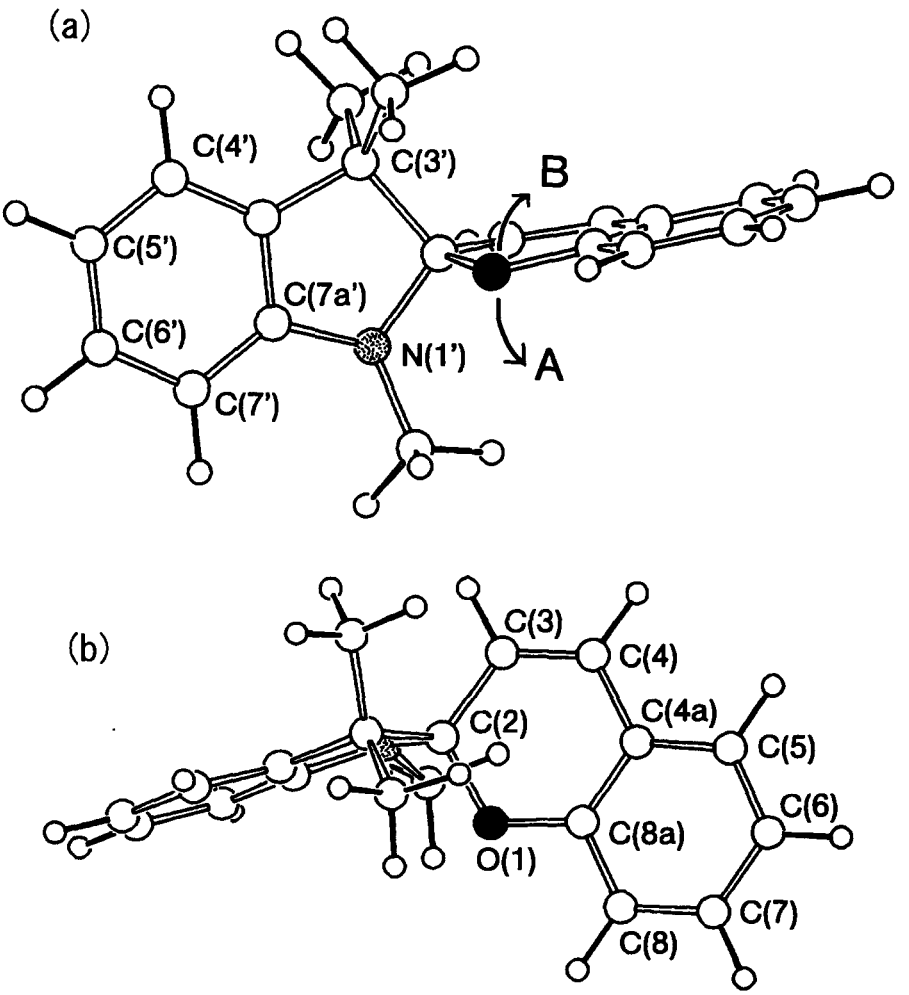


Fig. 2. Structures of **4** optimized by MOPAC with PM3: (a) view from indoline ring; (b) view from pyran ring.

9, **10** and **11** were 167.21 kcal mol^{-1}, 169.02 kcal mol^{-1}, 167.87 kcal mol^{-1} and 166.42 kcal mol^{-1}, respectively, suggesting that form **11** is the most stable isomer of the *trans* forms. However, as in the case of the *cis* form, other isomers may be present in the solution, because the differences in the heats of formation were very small. Recently, Nakatsu and coworkers[10] reported the crystallographic data for form **11**, prepared from spiropyran **4** and HBr. This result supports the reliability of the calculated results.

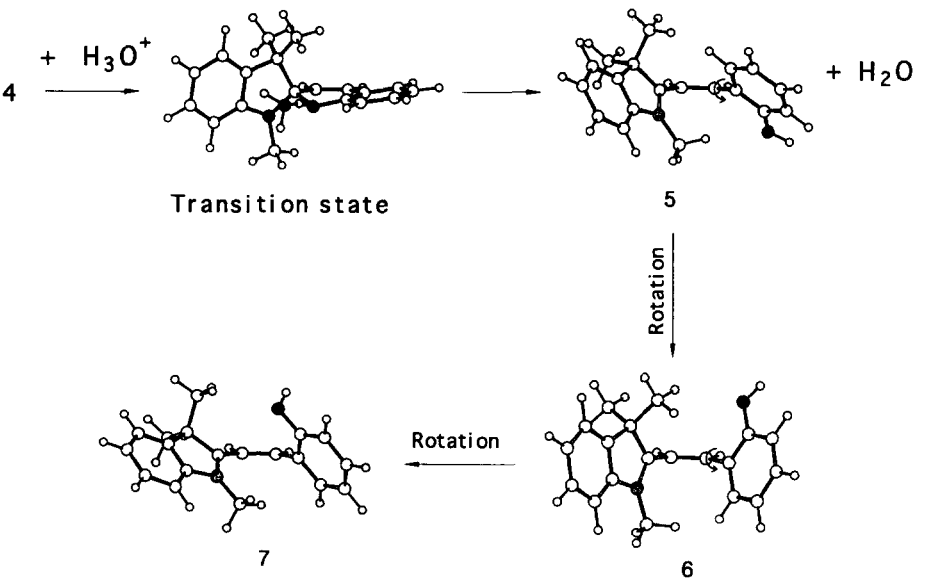


Fig. 3. The optimized structures in acid induced isomerization to produce the forms **5**, **6** and **7** via the transition state.

TABLE 2
Geometrical Parameters, Bond Orders and Net Atomic Charges of **5** by PM3

	Bond length (Å)	*Bond order*
C(2)–C(3)	1.444	1.046
C(3)–C(4)	1.343	1.820
C(4)–C(4a)	1.457	1.033
C(4a)–C(8a)	1.410	1.333
C(8a)–O(1)	1.363	1.080
C(2)–N(1′)	1.339	1.696
Charge		
C(2)	−0.009	
C(3)	−0.240	
C(4)	0.101	
O(1)	−0.227	
N(1′)	0.510	

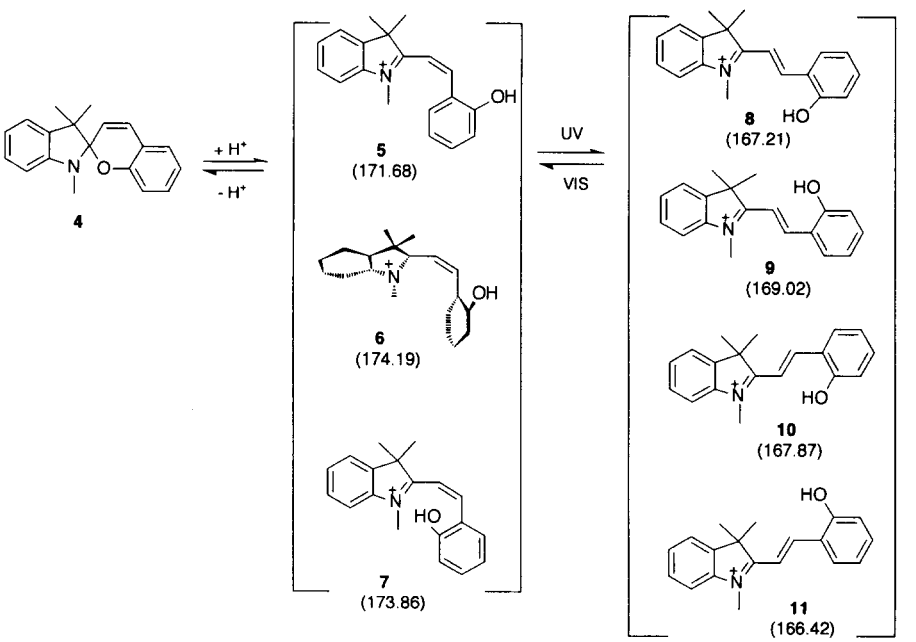
The absorption spectra of the forms **4**, **5** and **11** were calculated by AMPAC (Table 3). The calculated absorption bands agreed well with the experimental results shown in Fig. 1. All the calculation results supported the above assignment for the spectral changes of **4**, and the proposed reaction mechanism shown in Scheme 2 for the acid-induced ring opening reaction of spiropyran is thus confirmed.

Molecular orbitals, especially frontier orbitals, indicate useful information for molecular design. A large coefficient of the highest molecular orbital (HOMO) of the closed form **4** was calculated at the 5′-carbon atom of the indoline ring, suggesting that an electron-withdrawing substituent at the 5′-position stabilizes the energy level of the HOMO and increases the ionization

TABLE 3
Absorption Spectra Calculated by AMPAC[A]

Compound	*nm (Oscillator strength)*
4	288.5 (0.117), 271.2 (0.163)
5	412.3 (0.256), 332.2 (0.100), 308.9 (0.090)
11	468.7 (0.976), 361.7 (0.091)

[a]The geometries optimized by MOPAC with PM3 were used.



Scheme 2

potential of **4**. Therefore, such a substituent is expected to shift the equilibrium toward the closed form and to extend the photo-responsive range to a lower pH range.

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