

Ab Initio MO and ¹H NMR NOE Studies of Photochromic Spiroanthoxazine

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Spiroanthoxazine has received considerable attention owing to its high fatigue resistance and high photoresponse rate. This photochromic molecule is expected to have various applications, and many interesting experimental studies have already been reported.¹ In order to develop future applications, an understanding of the compound on a molecular level is of crucial importance. Recently, detailed information on the initial event of the relevant photochemical process has been reported on the basis of femto- and picosecond laser spectroscopy.² The X-ray structure of the closed form has been obtained,³ but the structure of the open form, which is the key structure responsible for the deep blue color of this molecule, still remains to be established, most probably because of the unstable character of the open form. X-ray data have been reported for the related molecule dinitrospiropyran^{4a} and for spiroindolinobenzothiopyran,^{4b} and detailed NMR data have been presented for spirobenzoselenazolinobenzopyran.^{4c}

Molecular orbital calculations can be useful aids because they can provide optimized structures and thermodynamic relative stabilities as well as molecular information, such as dipole moments, bond characters, and electronic transitions. The semiempirical MO method is useful for the qualitative understanding of photochromic systems, and studies based on the semiempirical method have been previously reported for spirooxazines⁵ as well as for diarylethenes.⁶

In this paper, we report the results of an ab initio calculation of spiroanthoxazine, focusing on the determination of the most stable structure of the colored form. The results of the calculations are supported by NMR evidence. For a long time, the structure of the most stable isomer has been unknown. First, the optimized structure of the closed form is compared with the established X-ray data, and then the open form structures are obtained. The

Table I. Comparison of the Calculated Structure and the X-ray Structure of the Closed Form (in Å and deg)

	calcd	X-ray ^a
C _{spiro} -O	1.458	1.465
C _{spiro} -C	1.512	1.509
C _{spiro} -C(CH ₃) ₂	1.578	1.557
C _{spiro} -N	1.441	1.425
C=N	1.260	1.257
C-C _{spiro} -O	109.8	109.6
C(CH ₃) ₂ -C _{spiro} -N	103.6	104.1

^a Taken from ref 3.

relative stabilities, geometrical features, and bond characters are reported.

The optimum geometries for the closed form and four important open form isomers were obtained by means of the energy gradient method at the Hartree-Fock level⁷ with the split valence 3-21G basis set.^{8a} With the geometries obtained by this method, the energetics were estimated at the RHF level with the 6-31G** basis set^{8b} and at the MP2 level⁹ with the 3-21G basis set. In the process of optimization, all degrees of freedom were optimized without any symmetry constraints (such as planar), except that C-H bonds and angles were kept at the standard values. The central CH_α bond, however, was optimized.

The geometries of the optimized closed form were compared to those obtained from the X-ray data of a similar molecule,³ in which the only difference was a pendant NC₂H₄OCH₃ in the indoline part. Important bond angles and distances are listed in Table I. The results are in very good agreement with the X-ray data. Therefore, the reliability of our calculation method is confirmed.

The stabilities of four open form isomers relative to the closed form are shown in Figure 1. The numbers given are those obtained with the 6-31G** basis set on the 3-21G-optimized geometries (in kcal/mol), and the numbers in parentheses are those obtained at the MP2 level with the 3-21G basis set. All of the isomers converged to the planar structure through the optimization, although the initial guesses were deliberately slightly deformed from the planar form. The most stable isomer turns out to be the TTC (trans-trans-cis) form, which is about 7 kcal/mol endothermic relative to the closed form. The next most stable is the CTC (cis-trans-cis) form, about 2.0 kcal/mol more unstable than the TTC form. The stability of the TTC and CTC forms can be attributed to the electrostatic interaction between the central hydrogen and the carbonyl oxygen (2.085 Å in TTC and 2.071 Å in CTC).¹⁰ However, H-H repulsion between the central hydrogen and the closest hydrogen of the naphthalene ring destabilizes the TTT (1.818 Å) and CTT (1.793 Å) isomers. The results of these calculations indicate that the TTC isomer is the most stable isomer, but the calculated result may corre-

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(1) Chu, N. Y. C. In *Photochromism: Molecules and Systems*; Durr, H., Bouas-Laurent, R. H., Eds.; Elsevier: Amsterdam, 1990; Chapters 10 and 24 and references cited therein. Guglielmetti, R. *Ibid.* Chapter 23.

(2) (a) Tamai, N.; Masuhara, H. *Chem. Phys. Lett.* 1992, 191, 189. (b) Aramaki, S.; Atkinson, G. H. *Chem. Phys. Lett.* 1990, 170, 181. (c) Aramaki, S.; Atkinson, G. H. *J. Am. Chem. Soc.* 1992, 114, 438.

(3) Osano, Y. T.; Mitsuhashi, K.; Maeda, S.; Matsuzaki, T. *Acta Crystallogr.* 1991, C47, 2137.

(4) (a) Nakatsu, K.; Fukushima, Y.; Yoshioka, H.; Arakawa, S. To be published. (b) Hirano, M.; Miyashita, A.; Nohira, H. *Chem. Lett.* 1991, 209. (c) Hirano, M.; Miyashita, A.; Shitara, H.; Nohira, H. *Chem. Lett.* 1991, 1873.

(5) (a) Aoto, M.; Nakamura, S.; Maeda, S.; Tomotake, Y.; Matsuzaki, T.; Murayama, T. *MRS Int. Meeting on Adv. Mat.* 1989, Material Research Society, Vol. 12, p 219. (b) Malatesta, V.; Ranghino, G.; Romano, U.; Allegrini, P. *Int. J. Quantum Chem.* 1992, 42, 879.

(6) (a) Nakamura, S.; Irie, M. *J. Org. Chem.* 1988, 53, 6136. (b) Uchida, K.; Nakamura, S.; Irie, M. *Bull. Chem. Soc. Jpn.* 1992, 65, 430.

(7) Gaussian 88: Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkly, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1988.

(8) (a) Binkly, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* 1980, 102, 939. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* 1972, 56, 2257.

(9) Möller, C.; Plesset, M. S. *Phys. Rev.* 1934, 46, 618.

(10) The Mulliken charges on the H_α and O atoms for the TTC isomer are 0.208 and -0.612, respectively, and 0.208 and -0.613 for the CTC isomer (cf. 0.118 and -0.594 for the TTT isomer and 0.115 and -0.598 for the CTT isomer).

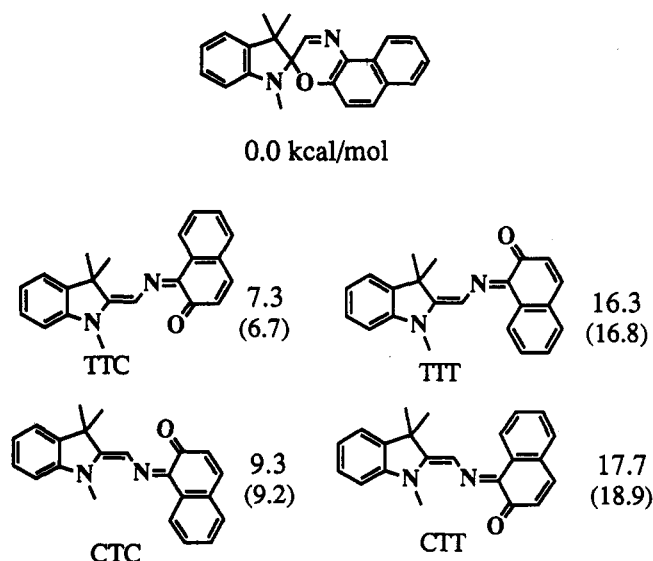


Figure 1. Thermodynamic relative stabilities calculated at the RHF level with the 6-31G** basis set and at the MP2 level with the 3-21G basis set (in parentheses) on the geometries optimized at the RHF level with the 3-21G basis set.

Table II. Calculated Dipole Moments and Charges on the C=O Bonds

	closed form	TTC	CTC	TTT	CTT
dipole moment ^{a,b}	0.59	1.80	2.97	4.84	3.63
charge ^{a,c} on C	+0.439	+0.541	+0.539	+0.549	+0.548
O	-0.761	-0.612	-0.613	-0.594	-0.578

^a The 6-31G** basis set was used on 3-21G optimized structures.

^b In debye. ^c Mulliken population.

spend to the gas-phase result. Considering the polarity of these isomers as indicated by their dipole moments (see Table II) and the small difference in energy between the TTC and CTC isomers (about 20 kcal/mol), there is the possibility that the CTC isomer may be more stable than the TTC isomer, depending on the polarity of the solvent or polymer.

In order to obtain experimental evidence for the most stable conformation of the open form, we carried out ¹H NMR nuclear overhauser effect (NOE) measurements.¹¹ All of the signals of the ¹H NMR spectrum of the colored open-form spironaphthoxazine had been assigned by means of ¹H¹H-COSY.¹² Irradiation of the protons in the NCH₃ moiety (3.79 ppm) produced positive NOEs of 10% at the H7 aromatic proton (7.49 ppm) and 19% at the H_α olefinic proton (10.22 ppm) (Figure 2). Irradiation of the H_α olefinic proton produced a 12% enhancement of the NCH₃ protons (Figure 3). These observations indicate that the geometrical structure of the colored open form of spironaphthoxazine is the TTC form.¹³

(11) ¹H NMR spectra were taken on a JEOL-GX270 (270 MHz) spectrometer with TMS as an internal standard. Photoirradiation was carried out with a 500-W mercury lamp. Light around 366 nm was selected by a visible absorbing filter (UVD-33S) and a UV cut filter (UV-35). Spironaphthoxazine (Nippon Kanko Shikiso) was recrystallized from methanol solution. Methyl alcohol-*d*₄ (100 atom % D, Janssen Chimica) was used as the solvent for the NMR studies. Spironaphthoxazine (1 mg) was dissolved in CD₃OD (1 mL), and the solution was irradiated with 366-nm light at -78 °C. Then NMR spectrum of the deep blue colored sample was measured while the temperature of the tube was kept below -45 °C.

(12) Kakishita, T.; Matsumura, K.; Hosoda, M.; Matsumoto, K.; Kiyotsukuri, T. *Nippon Kagaku Kaishi*. 1992, 1131.

(13) The same TTC structure has been reported for related molecules (ref 4).

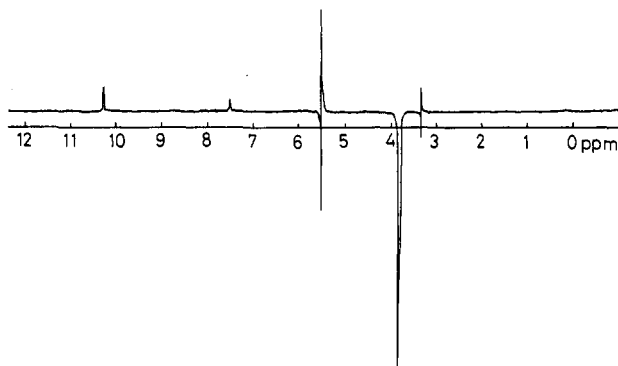
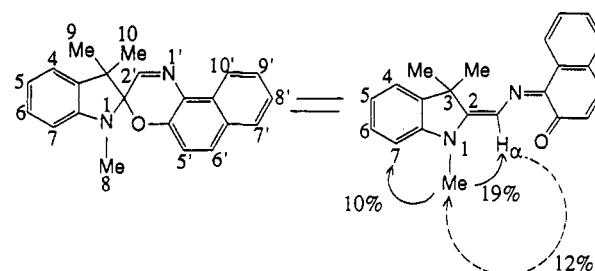


Figure 2. ¹H NMR NOE difference spectrum of the colored open form obtained upon irradiation of the N-CH₃ protons (see ref 11).



Figure 3. ¹H NMR NOE difference spectrum of the colored open form obtained upon irradiation of the olefinic proton H_α (see ref 11).



For these isomers, the important bond angles and distances obtained from the calculation are listed in Table III. All C=N bonds show double bond character, for example, the C=N bond distance is 1.281 Å in TTC. Although the bond characters in Figure 1 are displayed as either formal double or single bonds, other bonds in the azomethine bridge appear to have intermediate character. Namely, in the TTC and CTC isomers, the bond lengths of the C_{spiro}-N and C(H)-N bonds are only slightly longer than that of the adjacent C_{spiro}=C bond, and in the TTT and CTT isomers, the bond lengths of the C_{spiro}-N, C(H)-N, and C_{spiro}=C bonds are very close. The similarities in these bond lengths indicate the extended conjugation. The H-H repulsion and resulting large bond angle of C(H)-N-C (see Table III) are clearly shown to be responsible for the destabilization of the TTT and CTT forms.

Is the electronic structure best represented as ketone-like or zwitterionic? This is an important question not only from a theoretical point of view but also from the standpoint of applications. Calculations with multireferences plus the inclusion of extended electronic correlation, together with spectroscopic evidence, should pro-

Table III. Optimized Structures of the Four Isomers (in Å and deg)

	TTC	CTC	TTT	CTT
C _{spiro} -C(CH ₃) ₂	1.534	1.540	1.536	1.539
C _{spiro} =C	1.350	1.351	1.356	1.358
C _{spiro} -N	1.371	1.366	1.365	1.358
C(H)-N	1.376	1.374	1.359	1.357
C=N	1.281	1.283	1.271	1.274
C(N)-C(O)	1.491	1.490	1.507	1.506
C=O	1.227	1.227	1.221	1.221
C _{spiro} -C-N	119.6	122.6	117.3	120.4
C(H)-N-C	128.6	128.1	139.9	139.2

vide a complete answer. Moreover, the electronic structure should be strongly dependent on the polarity of the environment. The current results support ketone-like rather than zwitterionic character. The C=O distance is

in the region of the normal carbonyl bond length of 1.22 Å. The charges on the C and O atoms shown in Table II for the open form are comparable to the charges of acetone (+0.502 on C and -0.528 on O, calculated with the same basis set), and the polarization in the open forms is only slightly more pronounced than that in acetone.

In summary, the results of ab initio MO calculations and NOE experiments lead to the conclusion that the most stable colored open form of spironaphthoxazine is the TTC structure. These studies also define bond orders and indicate a ketone-like electronic ground state.

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