Theoretical Studies on the Photochemical Behavior of Styrylquinoxaline

Ja Hong Kim*, Mi Joo Kim, Ki Taek Lee†, Yoon Sup Lee†, and Sang Chul Shim†

Department of Chemistry Education, Chonbuk National University, Chonju 560-756
†Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 136-791
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The lowest excited state of styrylquinoxaline (StQx) has been studied by the SCF-MO-CI P-P-P and MM2 method. Results suggest that the lowest excited state is of a $\pi, \pi^*(S_1)$ nature with the $n, \pi^*(S_2)$ state lying slightly above it. On the basis of these calculations the observed electronic spectra are discussed. The calculated absorption spectra are qualitatively similar to experimental ones with their characteristic visible bands. MM2 force field calculation suggested that the postulated conformers are different from each other in energy and planarity and are seperated by a barrier of about 4 Kcal/mole.

Introduction

The photochemical behavior of stilbene has been studied extensively and trans-cis photoisomerization mechanism is fairly well understood in terms of a singlet mechanism.[1-3] The excitation to S_1 state is followed by internal rotation about the central double bond leading to a temperature-dependent $S_1 \rightsquigarrow S_1$ internal conversion. Once the molecule is in the S_2 state after vibrational relaxation, it undergoes internal conversion $S_2 \rightsquigarrow S_0$ in the twisted geometry producing both isomers and thereby isomerization.[4-6] The introduction of nitrogen atoms into the phenyl rings noticeably affects the photophysical and photochemical behavior of stilbene because of the involvement of (n, π^*) state in the reaction. A systematic study was carried out for styrylpyridines (StP) in order to determine the effect of the introduction of (n, π^*) states by comparing them with stilbene. A similar singlet mechanism is operative with a concurrent internal conversion for the 2- and 4-Stp. Interestingly, however, the direct photoisomerization of bispyrazinylethylene (BPyE) proceeds through a triplet manifold in contrast to stilbene because the intersystem crossing in BPyE proceeds much more rapidly than any other processes.

The phenomenon "proximity effect" is believed to be a consequence of vibronic interaction between the (π, π^*) and (n, π^*) states, which leads to the potential energy distortion and displacement along the vibronically active out-of-plane bending modes. Theoretical investigations of the proximity effect indicate that for a sufficiently small energy separation between the interacting states, the vibronically active mode could become the dominant accepting mode for the radiationless transition.

In this paper, we are trying to establish the ordering of the low lying electronic excited states of trans-2-styrylquinoxaline (StQx) at a couple of important points on the potential energy surface. Of particular interest is the role of the (n, π^*) states which have been often proposed to be the main factors causing many unusual photochemical and photophysical properties in these compounds.

Calculations

The electronic transition energies were calculated by the SCF-MO-CI P-P-P method. Being based on the P-P-P framework, this method retains the one center exchange integrals, in order to provide a better description of the energies of the (n, π^*) states having different multiplicities. Coulomb repulsion integrals are described by the Mataga-Nishimoto formula[7] because other semi-empirical parameters are less satisfactory in obtaining triplet energies.[8,9] The molecules were considered in terms of geometry and the structural parameters were based on those used in previous calculations.[10]

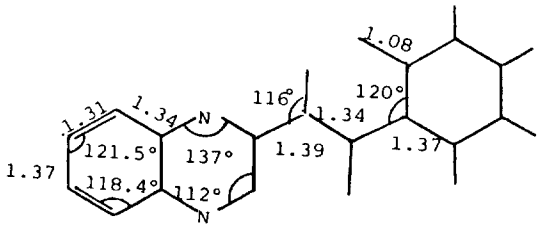


Figure 1. Geometry used in the calculation for styrylquinoxaline.

In order to provide some insight into the comparative analysis of the two conformers, molecular mechanics calculation were performed by using "Macro Model" with MM2 force field and BDNR method as a minimum algorithm.[11] In searching for energy minima, a series of geometries corresponding to small, systematic internal rotation around both the two essential single bonds connecting the quinoxalinyl group and phenyl group were input and allowed to relax fully by using BNDR minimization scheme. If a particular conformation was found initially to occupy a local energy minimum, conformations with dihedral angles slightly different from those in that first-discovered minimum energy geometry were input, and minimization was allowed to occur again to ensure the accurate identification of an equilibrium geometry.

Results and Discussion

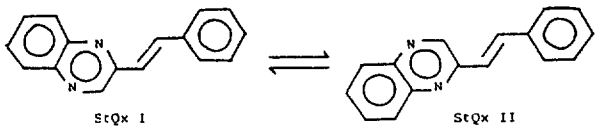
The results of the calculation for transition energies and oscillator strengths are summarized in Table 1,2. Trans-2-styrylquinoxaline (trans-2-StQx), which is an aza analogue of trans-2-styrylnaphthalene (trans-2-StN), has both photophysical and steric abnormalities with respect to 2-StN. The replacement of the naphthyl group by quinoxaline, which has

Table 1. Transition Energies and Oscillator Strengths(F) of Trans-2-tyrylquinoxaline (StQx-I)

Transition state		E(eV)	λ(nm)	O.S.(F)
S_π-S_0	S_1	3.52	352	1.21
	S_2	4.30	288	0.55
	S_3	4.48	277	0.01
	S_4	5.67	219	0.22
	S_5	6.02	206	0.08
	S_6	6.36	195	0.25
T_π-S_0	T_1	1.84	674	0.51
	T_2	3.01	443	0.35
	T_3	3.75	331	0.42
	T_4	4.26	291	0.44
	T_5	4.90	253	0.05
	T_6	5.92	209	0.04

Table 2. Transition Energies and Oscillator Strengths(F) of trans-2-Styrylquinoxaline (StQx-II)

Transition state		E(eV)	λ(nm)	O.S.(F)
S_π-S_0	S_1	3.47	357	1.01
	S_2	4.37	284	0.78
	S_3	4.48	277	0.01
	S_4	5.68	218	0.25
	S_5	6.01	206	0.15
	S_6	6.23	199	0.34
T_π-S_0	T_1	1.86	666	0.34
	T_2	3.01	412	0.43
	T_3	3.75	331	0.46
	T_4	4.03	308	0.19
	T_5	5.53	224	0.06
	T_6	4.25	292	0.35



Scheme 1

the lowest non-fluorescent[1] (n, π^*) state ($\Phi \approx 0.00$, $\Phi_{ph} \approx 0.42$)[12] should make the n, π^* states and the π, π^* states in trans-2-StQx very close. Moreover, an increase in planarity as a result of lower steric crowding originating from nitrogen heteroatoms in the ortho position of the quinoxalyl group should result in changes in the conformational equilibrium and photophysical parameters of trans-2-StQx conformers with respect to those of trans-2-StN conformers (Scheme 1). The calculated and experimental absorption spectra of trans-2-StQx shown in Figure. 2. are somewhat different from those of the corresponding hydrocarbons and other aza analogues. The absorption band at 287 nm and 347-362 nm in *n*-hexane are probably quinoxalinic and ethylenic absorption bands respectively. However, it is noteworthy that the long wavelength ethylenic band is very much red shifted with respect to the bands of the corresponding hydrocarbons and other aza analogues (315 nm for both trans-2-StN[13] and trans-3-StQ[14]). The calculated transition energies are in reasonably good agreement with the experimental measurements. As reported earlier for trans-2,2-NPE[15] and trans-2-styryl-pyridine (trans-2-StP) which have nitrogen heteroatoms in the ortho position, the red shift of the ethylenic absorption band is probably due to the strong electronegativity of nitrogen atoms.[16]

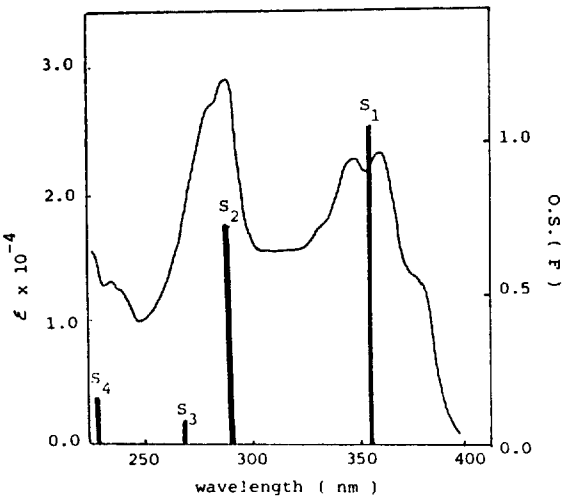


Figure 2. Calculated absorption spectrum of trans-2-StQx I by PPP-SCF-CI(— experimental, — calculated).

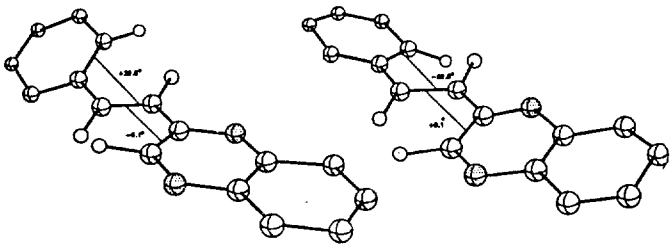


Figure 3. Geometries of StQx conformers by MM2 calculation (conformer I).

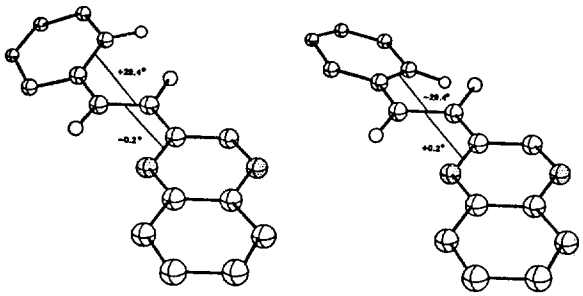


Figure 4. Geometries of StQx conformers by MM2 calculation (conformer II).

The MM2 calculation predicted four equilibrium geometries (two sets of two enantiomeric geometries) for StQx (Figure 3,4). One set of enantiomeric geometries (conformer II) which have lower energies (about 0.8 Kcal/mole) lower than others are planar in quinoxalinyl groups and ethylenic double bonds but have twisted phenyl rings (+29.4° of −29.4°). Other set of enantiomeric geometries (conformer I) have twisted geometries both in quinoxalinyl ring (−9.2° or +9.2°) and phenyl ring (+29.8° or −29.8°). It seems that

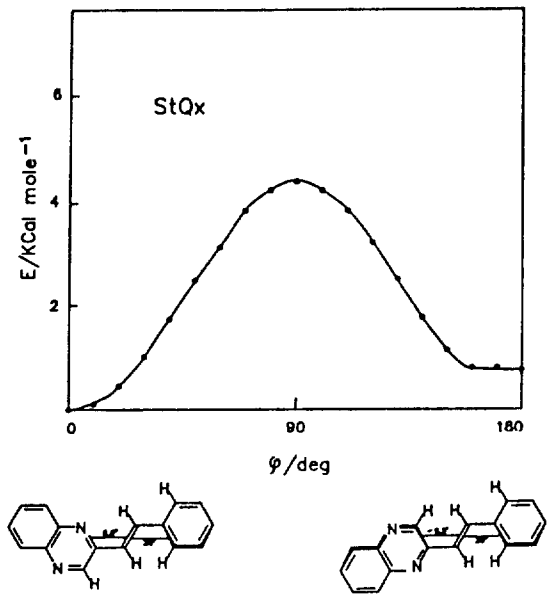


Figure 5. Rotational energy barrier of StQx conformers.

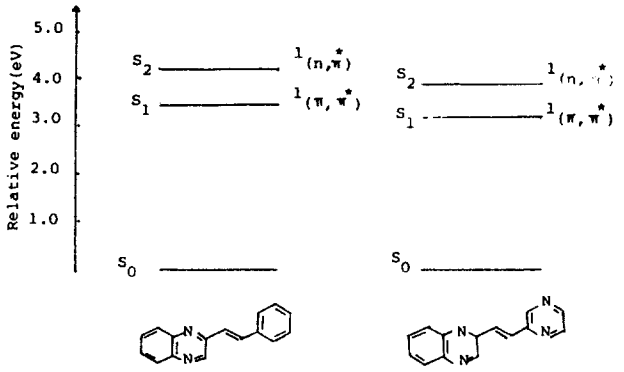
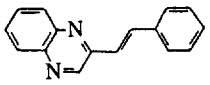
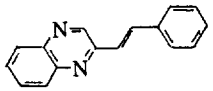


Figure 6. Expected energy level of StN derivatives of excited states.

the main cause of lower energy in one set of conformers is increasing of conjugative interaction due to good planarity by absence of hydrogen repulsion between ethylenic hydrogen and ortho hydrogen of quinoxalinyl group which are present in other set of conformers. The calculated energy difference between two conformers at the equilibrium at room temperature are predicted to be about 0.8 and 0.2, respectively. However, this values may not be the true values in solution because the true population in solution is controlled also by solvation. The rotational energy barrier of quinoxalinyl ring was also derived from an dihedral angle driver calculation and the energy profile of rotation is presented in Figure 5. The energy barrier of rotation is 4.0 Kcal/mole indicating that the rotation can be neither entirely free nor entirely hindered.

The lowest states, S_1 in the two isomers, have the same nature and oscillator strength and appear at the same energy as the corresponding BPyE state. The $S_3(n, \pi^*)$ states lie at a higher energy than S_2 by $\simeq$0.1-0.2 eV in two isomers. As far as triplet states are concerned, the relevant results are as follows; the lowest state, $T_1(\pi, \pi^*)$, lies at the same energy and is of the same nature as in BPyE[17]. It is expected that the relative positions of the (π, π^*) and (n, π^*) singlet states influence the photochemical and photophysical behaviour of aromatic compounds. In trans-StPs, in particular, the $^1(n, \pi^*)$ state was thought to be at lower energy than the $^1(\pi, \pi^*)$ state in order to explain the differences in the fluorescence and trans-cis photoisomerization behaviour with respect to stilbene, on the basis of more effective radiationless transitions in the aza analogues. It one considers both the effect of nitrogen substitution and extension of aromatics on the singlet excited states, energy states diagram (Figure 6) of aza-StNs can be expected as follows; 1). (π, π^*) state of StN is lowered than that of stilbene 2). (π, π^*) state of NPyE is lowered slightly and (n, π^*) state lie above that. 3). In the case of StQx and DiQxE (n, π^*) states and (π, π^*) states are mixed extensively.

Table 3. Calculated Dipolemoment of *trans*-2-Styrylquinoxaline

Compound	Structure	Dipole moment (Debye)
trans-2-Styrylquinoxaline(StQx-I)		1.10
trans-2-Styrylquinoxaline(StQx-II)		1.16

From these results we can obtain some information about the photophysical properties of the trans-2-StQx. As shown in Table 3, the calculation of dipole-moments suggest that StQx II will be somewhat more stable than StQx I in excited states. Given the nature of T_1, we expect for its energy surface to have the same flat shape as in BPyE and thus a similarly fast intersystem crossing process to the ground state. The lowest singlet S_1, in principle, has another efficient decay channel available with respect to stilbene, namely S_1 - $T(n, \pi^*)$, due to the large spin-orbit coupling interaction usually encountered between (π, π^*) and (n, π^*) states.

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Crystallographic Evidence for the Reduction of CO in Partially Dehydrated Silver Zeolite A

Yang Kim*, Seong Hwan Song, and Karl Seff†

Department of Chemistry, Pusan National University, Pusan 609-735
†Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822-2275. *Received November 11, 1988*

The crystal structure of Ag^+-exchanged zeolite A vacuum-dehydrated at 370 °C and then treated with carbon monoxide at 23 °C has been determined by single crystal x-ray diffraction methods in the cubic space group $Pm3m$ at 23(1) °C; a = 12.116 (2) Å. The structure was refined to the final error indices R_1 = 0.061 and R_2 (weighted) = 0.068 using 349 independent reflections for which $I>3\sigma(I)$. 3.6 Ag^+-CO complexes, where -CO may represent -CHO or $-CH_2OH$, were found in each large cavity. By coordination to silver atoms followed by reaction with Ag° and H^+ within the zeolite, carbon monoxide has been partially reduced. In about 28% of the sodalite units, a $Ag_6(Ag^+)_2$ cluster may be present. In about 37% of the sodalite units, three Ag^+ ions are found on threefold axes where they may be bridged by three water molecules. The remaining 35% of the sodalite units are empty of silver species. Two Ag^+ ions per unit cell are associated with 8-ring oxygens. The remaining *ca* 3 Ag^+ ions per unit cell have been reduced during the synthesis and have migrated to form small silver crystallities on the surface of the zeolite single crystal.

Introduction

Hydrated Ag^+-exchanged zeolite A undergoes partial decomposition when heated under vacuum to form, within its sodalite unit, uncharged molecular Ag_6 clusters, each of which is stabilized by coordination within a cube of eight Ag^+ ions.[1,2] The number of silver clusters in seven separate crystallographic determinations has been found to depend upon the dehydration time and temperature.[2] Hermerschmidt and Haul also identified $(Ag_6)^{n+}$ ($n\leq 6$) clusters in the sodalite cavity of dehydrated Ag^+-exchanged zeolite A using esr spectroscopy[3] and their results were duplicated by Grobet and Schoonheydt.[4] This was reverified by the careful work of Morton and Preston who did esr measurements on isotopically pure samples of Ag-A.[5]

When ethylene is sorbed by dehydrated Ag_{12}-A,[6] the Ag_6 molecules are hardly effected: their number remains the same, and the Ag-Ag distances decrease from slightly greater to slightly less than that in silver metal.[6] Ethylene acts as a titrating agent which forms lateral π complexes with two of the eight 6-ring[7] Ag^+ ions; the remaining six Ag^+ ions remain firmly complexed to the ligand molecule Ag_6.

As a continuation of the study of the unusual chemistry of silver ions, silver clusters, and molecules within zeolite A, a carbon monoxide sorption complex of partially dehydrated Ag_{12}-A was prepared and its crystal structure determined. It was initially hoped that CO gas would reduce some of the Ag^+ ions in zeolite A to form Ag atoms and clusters which might be examined crystallographically. If Ag^+ were not reduced by CO, the structure of some Ag^+–C≡O complexes might be learned.

Experimental

Crystals of zeolite 4*A* were prepared by Charnell's method.[8] A single crystal about 0.08 mm on an edge was lodged in a fine capillary. $AgNO_3$ (0.05 M) was allowed to flow past the crystal at about 1.0 cm/sec for 3 days. Since the exchange of Ag^+ for Na^+ has been shown to be facile and complete after much milder treatment, complete exchange was assured in this case.[1,2,9] The clear, colorless hydrated Ag^+-exchanged crystal was dehydrated for 2 days at 370 °C and 2×10^{-6} Torr. Under these conditions, most water molecules should be removed, affording open channels and coordinately unsaturated Ag^+ ions for reaction with CO; simultaneously relatively few Ag atoms should have been generated,[1,2] so the zeolite should have suffered little or no damage. After the crystal was cooled to 21(1) °C, it was treated with *ca* 740 Torr of CO gas (Union Carbide, research grade). Microscopic examination showed that it had become dark grey. After 1 hr, the crystal, still in its CO atmosphere, was sealed in its capillary by torch.

X-Ray Data Collection. The cubic group $Pm3m$ (no systematic absences) was used throughout this work for reasons