

THEORETICAL STUDIES ON THE PHOTOCHEMISTRY OF PYRAZINYLQUINOXALINYLETHYLENE

JA HONG KIM¹, SUNG HO SOHN¹ and SUNG WAN HONG*²

¹Department of Chemistry Education, Chonbuk National University, Chonju 561-756, Korea

²Department of Chemistry, Woosuk University, Wanju 565-701, Korea

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Abstract – Electronic structures and excited states for pyrazinylquinoxalinyethylene are investigated using PM3-UHF-CI and Molecular Mechanics force field. The results indicate that pyrazinylquinoxalinyethylene has extensively mixed (π , π^*) and (n , π^*) states while the (n , π^*) transition band does not appear in the absorption spectrum clearly and seems to be submerged under the more intense (π , π^*) bands.

INTRODUCTION

The introduction of nitrogen atoms into phenyl rings noticeably affects the photophysical behavior of diazastilbene because of the involvement of (n , π^*) state in the reaction. It is expected that the relative positions of the (π , π^*) singlet states influence the photochemical behavior of aromatic compounds. In *trans*-styrylpyridines, in particular, the ¹(n , π^*) state was thought to be lower in energy than the ¹(π , π^*) state in order to explain the differences in the fluorescence and *trans-cis* photoisomerization behavior with respect to stilbene, on the basis of more effective radiationless transitions in the aza-analogues.^{1,2}

The complex photophysical behavior of 1-phenyl-2-(2-naphthyl)ethene(2-NPE) has been attributed to the presence of an equilibrium mixture of aryl-rotational conformers.^{3,4}

Trans-2-pyrazinylquinoxaliny ethylene (2-PyQxE), which is an aza-analogue of *trans*-2-StN, has both photophysical and steric abnormalities with respect to 2-StN. The replacement of naphthyl group by quinoxaline and styryl group by pyrazinylethylene, which has the lowest non-fluorescent (n , π^*) state, should make the (n , π^*) states and the (π , π^*) states in *trans*-2-PyQxE very close like *trans*-2-StQx.^{5,6}

In this investigation, we have studied the photophysical behavior of the excited states of *trans*-PyQxE using PM3-UHF-CI calculation to elucidate the role of nitrogen heteroatoms in the conformational equilibrium.

MATERIALS AND METHODS

The electronic optimized structures of each excited states for PyQxE were calculated by the PM3-UHF-CI

* To whom correspondence should be addressed.

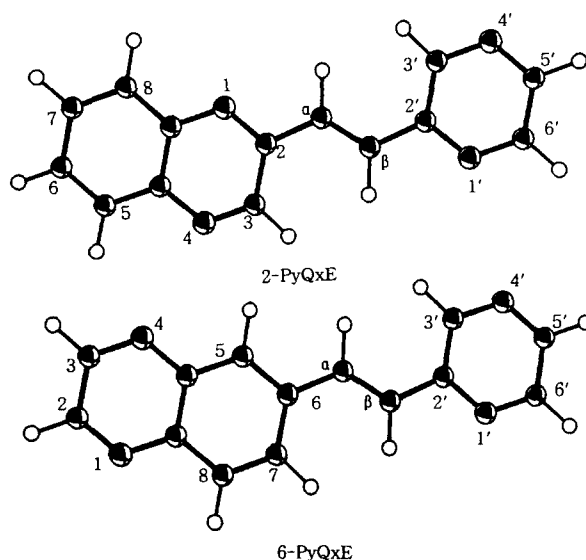


Figure 1. The numbering schemes for 2-PyQxE and 6-PyQxE.

calculation.⁷ In molecular mechanics, a molecule is considered to be a collection of atoms held together by elastic and harmonic forces. These forces can be described by potential energy functions of structural features like bond lengths, bond angles, nonbonded interaction, and so on. Molecular mechanics calculations were performed by using MM2 force field and BDNM method as a minimum algorithm.^{8,9}

The numbering schemes for 2-PyQxE and 6-PyQxE are shown in Fig. 1.

RESULTS AND DISCUSSION

The results of the calculation for optimized geometries of the excited *trans*-6-PyQxE are summarized in Table 1.

Table 1. Optimized geometries for the singlet and triplet states of *trans*-2-PyQxE and 6-PyQxE by PM3-MECI calculation.

Compound	Geometry	Singlet	Triplet	Compound	Geometry	Singlet	Triplet
<i>trans</i> -2-PyQxE	C _α - C _β	1.36	1.46	<i>trans</i> -6-PyQxE	C _α - C _β	1.35	1.33
	C ₂ - C _α	1.46	1.37		C ₂ - C _α	1.47	1.47
	C ₂ ' - C _β	1.46	1.39		C ₂ ' - C _β	1.47	1.47
	C ₂ - C _α - C _β	125.94	121.41		C ₆ - C _α - C _β	124.36	123.23
	C _α - C _β - C ₂ '	125.13	121.08		C _α - C _β - C ₂ '	122.63	122.06
	C ₃ -C ₂ - C _α - C _β	3.68	3.68		C ₇ - C ₆ - C _α - C _β	29.16	29.16
C _α -C _β - C ₂ ' - C ₃	-8.73	-8.73	C _α - C _β - C ₂ ' - C ₃	-36.24	-36.24		

* Bond lengths are in Å and bond angles in degree.

Table 1 shows optimized geometries for the singlet and triplet states of pyrazinylquinoxaliny ethylene. It shows the carbon-carbon double bond of *trans*-2-PyQxE bond lengthening appears to be responsible for the presence of the carbon-carbon double bond conformation. And also, bond distance for the C_α-C_β double bond and C₂-C_α single bonds between *trans*-2-PyQxE and *trans*-6-PyQxE, as calculated from mobile bond orders increase and decrease upon excitation, respectively. The dihedral angle C_α-C_β - C₂' - C₃' of *trans*-2-PyQxE was obtained as -8.73° but *trans*-6-PyQxE dihedral angle was calculated to be -36.24°

The calculated energies and photochemical quantum yields of PyQxE are shown in Table 2. It is in good correlation with MM2 calculation and experiment in that all the energy levels of ¹(n, π*) and ¹(π, π*) states are lowered with nitrogen substitution and lowering of ¹(n, π*) states are greater than that of ¹(π, π*) states, thus indicating that all the aromatics have lowest ¹(n, π*) state. The quantum yield of internal conversion of PyQxE has a low value, and aromatic moiety of high intersystem crossing efficiency.

In the molecular mechanics calculation, the isomerization energy barrier of *trans* → *phantom* is 11.94 Kcal/mol for 2-PyQxE and 13.62 Kcal/mol for 6-PyQxE and *cis* → *phantom* isomerization is 14.90 Kcal/mol for 2-PyQxE and 15.71 Kcal/mol for 6-PyQxE. It suggests that the

steric hindrance was decreased by nitrogen substitution, in near ethylene moiety replacement.^{10,11}

The CINDO/S calculation (Fig. 2, 3) about the effect of nitrogen substitution on transition energy level is also in agreement with spectral data.¹² The result of calculation is most prominent in PyQxE and it is expected that PyQxE has extensively mixed (π, π*) and (n, π*) states while the (n, π*) transition band does not appear in the absorption spectrum clearly and seems to be submerged under the more intense (π, π*) bands.

The lowest excited states of 2-PyQxE and 6-PyQxE shown in Figs. 2 and 3 are very close as observed in styrylnaphthalene. This can be attributed to the proximity effect between (π, π*) and (n, π*) states of PyQxE. Because of the extensive vibronic mixing between lowest (π, π*) states and (n, π*) states, the efficient internal conversion or intersystem crossing seem to be the favorable radiationless decay processes observed for other aza-aromatics.¹³ The difference between the two conformers of PyQxE appears to be dependent on the electronic structure of the lowest excited state involved in the photophysical processes and therefore a molecular orbital description of these states is expected to provide useful information about the properties of PyQxE. It was suitable for describing the non-bonded interactions between hydrogen atoms of the ethylenic and naphthalenic subunit in PyQxE.

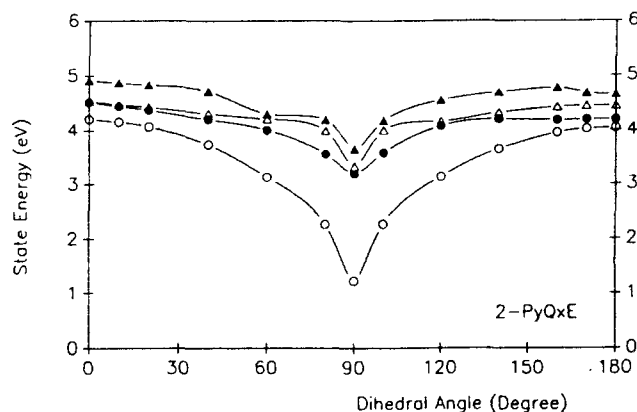


Figure 2. UV-transition energy from with changing dihedral angle for 2-PyQxE by CINDO/S.

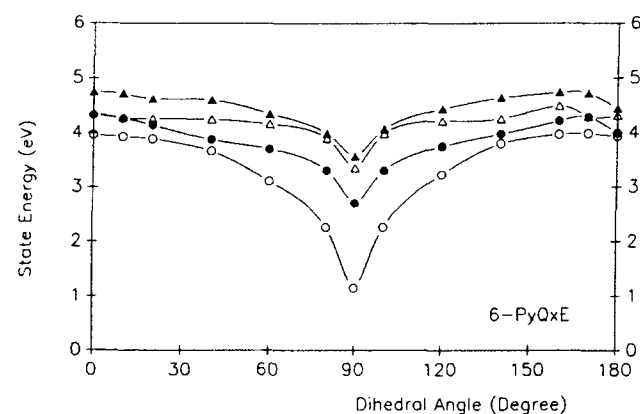


Figure 3. UV-transition energy from with changing dihedral angle for 6-PyQxE by CINDO/S.

Table 2. The photophysical properties and quantum yields of photoisomerization of *trans*-2-PyQxE and *trans*-6-PyQxE.

Compound	Etotal(in Kcal/mol)	Φ_f^a	Φ_{ic}^a	Φ_{isc}^a	Φ_{1-c}^a
<i>trans</i> -2-PyQxE	49.132	0.0014	0.66	0.33	0.17
<i>trans</i> -6-PyQxE	48.916	0.001	0.74	0.26	0.12

^aShim, S.C., The proceeding of the 99th Academic Research and Industry work interchanging meeting, KOSEF, 1-10 pp. 1993.

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