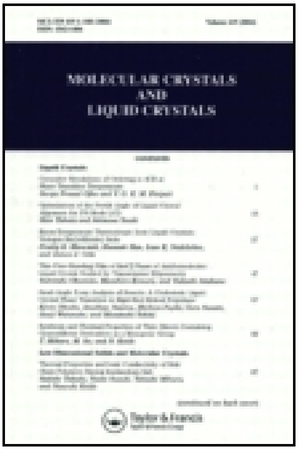

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Theoretical Analysis of the IR and Visible Absorption Spectral Change by the Phase Transition of the Crystals of 2,3-Diphenylthio- and 2,3-Di(p-chlorothiophenyl)-1,4-Naphthoquinones

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Theoretical Analysis of the IR and Visible Absorption Spectral Change by the Phase Transition of the Crystals of 2,3-Diphenylthio- and 2,3-Di(p-chlorothiophenyl)-1,4-Naphthoquinones

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Abstract The isomerization mechanism of 2,3-Diphenylthio- and 2,3-Di(p-chloro thiophenyl)-1,4-Naphthoquinones was determined by using *ab initio* calculations and compared IR and visible absorption spectra. The optimized geometries using RHF/3-21G* method were determined with C_2 symmetry for the *violet* form, and with C_s symmetry for the *red* one. Visible spectra were identified by the charge transfers from thiophenyl group to naphthoquinone ring of these two isomers. The lowest allowed excitated states of these isomers were characterized by the the charge transfer (CT) from next-HOMO to LUMO in the violet form, and from HOMO to LUMO in the red form. The IR active CO stretching mode in the naphthoquinone ring appear as the symmetric type on the violet form, and anti-symmetric type on the red one.

Introduction

The number of organic molecules change thier visible color by the conformational alternations [1]. These reactions were interpretated by the charge transfor mechanisms. The crystals of 2,3-dithiophenyl-1,4-naphthoquinone (DPNQ) have dimorphism, one is the *violet* form (monoclinic form) and the other is the *red* form (orthorhombic form) [2]. The isomerization of these crystals was studied by *ab initio* calculations for determining the electronic structures of the dimorphism of 2,3-dithiophenyl-1,4-naphthoquinone and comparing with the temperature variable IR and visible absorption spectra.

Method of Calculations

All *ab initio* molecular orbital calculations were performed with GAUSSIAN 94 program [3]. The numerical calcuations were carried out on IBM RS/6000 590 and SP2 parallel computers and NEC SX-3 supercomputer at the Instiute for Molecular Science (IMS) computer center. The geometries of these two isomers were fully optimized at the RHF/3-21G* level and one point calculations are performed with the second order-Møller-Plesset (MP2) calculations on the optimized geometries. Vibrational analysises were also performed to characterize the stationary points. These calculated values are not directly comparable with the experimental ones and we multiplied 0.89 to the computed frequencies to improved the agreemnt with the experimental spectra. Excitation energies for each isomer are determined by configuration interaction singles (CIS) method and to assign the observed visible spectra.

Results and Discussion

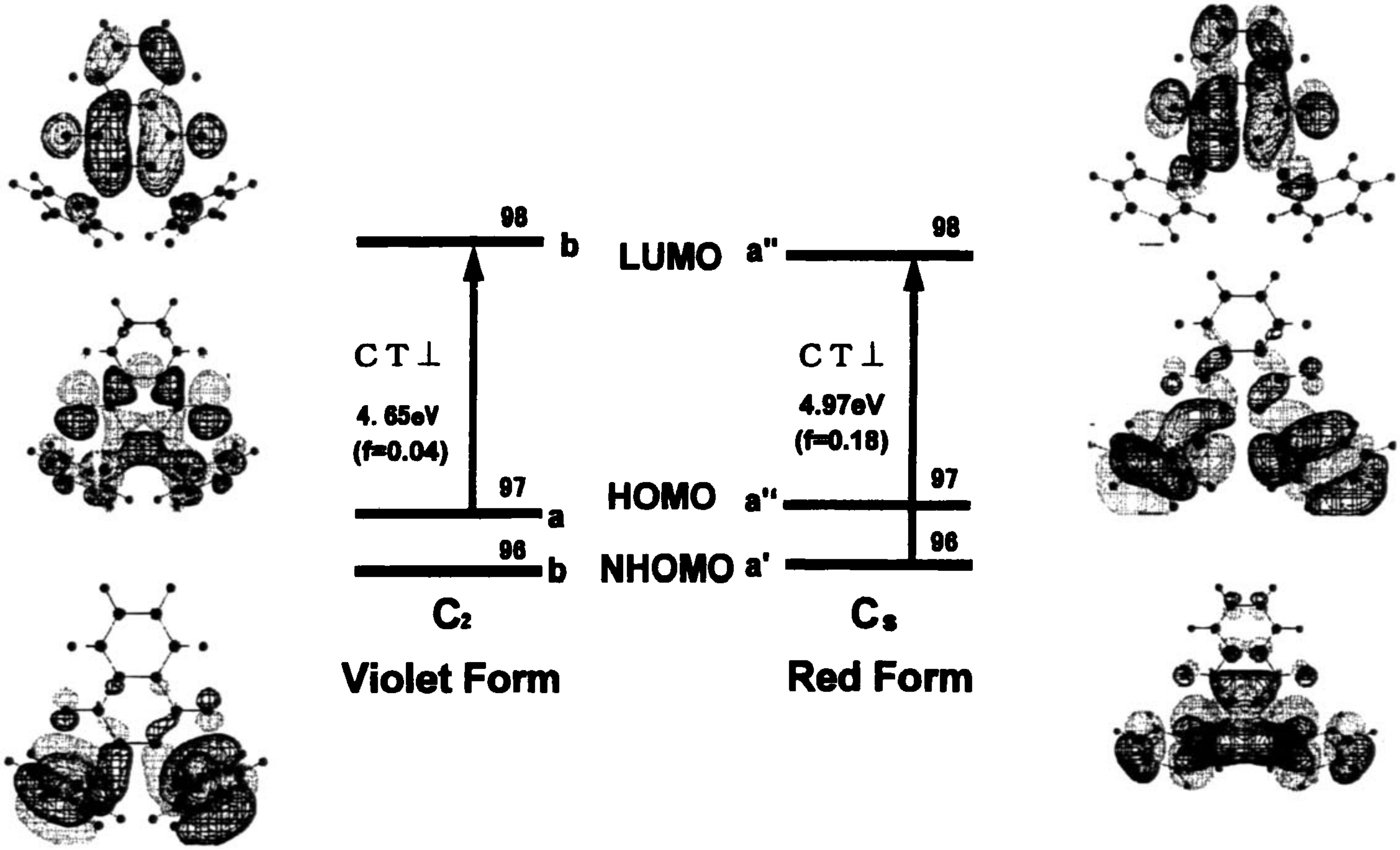
The geometry optimizations with RHF/3-21G* were performed with C_2 symmetry for the *violet* form, and with C_s symmetry for the *red* one. Two isomers have the almost same energy values. With the MP2/3-21G*//RHF/3-21G* calculations, the *violet* form was more stable than *red* one in which the energy difference was $\Delta E=0.4$ kcal/mol. In the *violet* form one thiophenyl group is located on the molecular plane of naphthoquinone and the other thiophenyl group is located under the naphthoquinone plane, while two thiophenyl groups are located on the same side of the naphthoquione in the *red* form. These results supported the observed structures from X-ray diffraction method.

Figure 1 depicts orbital energy level diagram and each next-HOMO, HOMO, and LUMO of DPNQ molecules in the red and violet forms of DPNQ. Table 1 shows the lowest allowed excitation energies and its wave functions with the oscillator strengths. The LUMO is located at NQ, but the next-HOMO and HOMO are located at two phenylthio rings. The theoretical analysis shows that the 600 nm band of the violet form is assigned to the transition (B) between the HOMO (b) of the phenylthio groups and the LUMO (a) of NQ group, and that the 500nm band of the red form is assigned to the transition(A") between the next-HOMO(a') of the phenylthio group and the LUMO(a") of NQ group. The main configuration of these lowest allowed excitation were characterized by the the charge transfer from thiophenyl group to naphthoquinone ring of these two isomers.

TABLE 1: Total energies and excitation energies of DPNQ for the red and the violet forms at the optimized structures using the RHF/3-21G* method.

		Violet	Red
Ground State			
RHF/3-21G*		-1776.786928	-1776.784879
MP2/3-21G*//RHF/3-21G*		-1779.181208	-1779.180511
Excited State			
CIS/3-21G*		-1776.616169	-1776.602237
	state symmetry	$({}^1B)$	$({}^1A")$
	excitation energy (nm)	266.8	249.5
	oscillator strengths	0.04	0.18
	CI coeffcient	0.60	0.53
	main configuration	LUMO ← (next HOMO)	LUMO ← HOMO

FIGURE 1. Molecular Orbitals and its Orbital Energy Diagram in the Violet and the Red Forms of DPNQ.

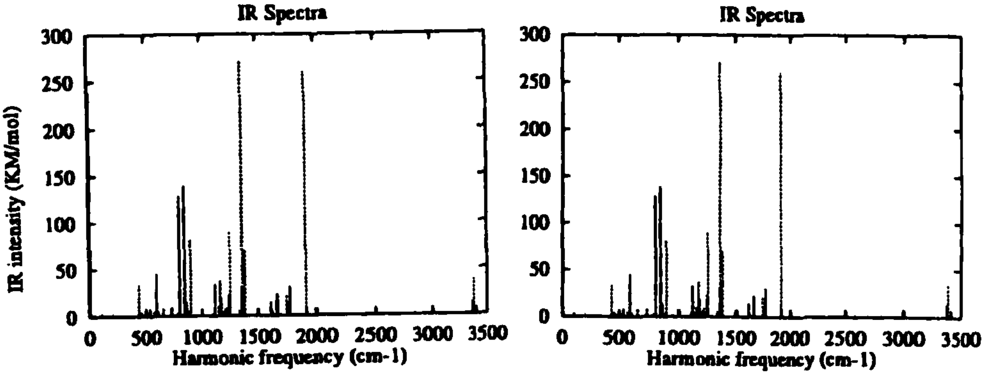


The DPNQ has 114 vibronic modes on these conformations. Figure 2 shows the IR vibronic frequencies calculated with RHF/3-21G* method. Table 2 shows the numerical frequencies belonging to the CO stretching mode on the naphthoquinone ring in order to compare with the experimental one. The calculated vibrational frequencies show that IR active CO stretching mode appear as anti-symmetric type in the *violet* form, and symmetric type in the *red* one. This assignment is due to the molecular symmetry in the optimized strcture of these conformations. These IR active CO stretching mode belong to B symmetry on the violet form, and A" symmetry on the red one. On the other hand, Raman active CO stretching mode appear as symmetric type in the *violet* form, and anti-symmetric type in the *red* one. These Raman active CO stretching mode belong to A symmetry on the violet form, and A' symmetry on the red one. These tendencies are in good agreement with the observed IR spectra. Observed IR spectra has two CO stretching modes near the transition area from violet to red form. These phenomena are suggested that the symmetric and the anti-symmetric modes appear as the IR spectra on these transition area.

TABLE 2: Theoretical and Experimental values for CO stretching mode of DPNQ(cm^{-1}).

	Violet	Red
RHF/3-21G*		
IR active	symmetric 1698 (B)	anti-symmetric 1702 (A")
Raman active	anti-symmetric 1700 (A)	symmetric 1703 (A')
experiment		
IR	1659 1647	1668

FIGURE.2: IR Vibronic Frequencies calculated with RHF/3-21G* method.



Violet

Red

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