

# The Structure-Photosensitivity Relationships of the Hydrazone-based Hole-transport Materials

Zhongping Huang, Qingsen Yu, Jinhong Pan, Ruisen Lin, and Hanxing Zong  
Department of chemistry, Zhejiang University, Hangzhou, P.R. China, 310027

## Abstract

The photosensitivities of a series of hydrazone-based hole-transport materials were correlated with their molecular structures. According to the electron density of the frontier orbital in the neutral molecule and cation radical of the charge transport material, the concept of the active hole-transport N atom was proposed. The relationships among photosensitivities, numbers of the active hole-transport N atom and the HOMO energy level of CTMs was investigated. The results showed that photosensitivity was strongly correlated to the numbers of the active hole-transport N atom and the HOMO energy level of CTMs. Therefore, it indicated that the hole injection process from CGL to CTL and hole transport process in CTL play significant role in photosensitivity.

## Introduction

For the double-layered organic photoreceptors, comprised of the charge generation layer (CGL) and the charge transport layer (CTL), the hole injection efficiency from CGL to CTL and the hole transport ability are considered to be two important factors to determine the photosensitivity of the photoreceptors, in addition to the carrier generation efficiency.<sup>1-4</sup> Many investigations into the hole injection process and hole transport process of the low-molecular-weight charge transport materials (CTMs) in some molecularly dispersed polymer binders<sup>5-8</sup> have been reported.

The hole injection process is considered to correlate to the HOMO energy level of CGM and CTM.<sup>9-10</sup> The hole transport is characterized by an electric field driven chain of redox process between the neutral molecules (N) and their cationic radicals (N<sup>+</sup>), and the rate of hole transport depends on the type of compounds, the concentration of the active species, electric field and temperature.<sup>11</sup> From the viewpoint of molecular design of the CTMs with high mobility, Kitamura and Yokoyama<sup>12</sup> proposed a new concept, called the hole unit, which takes charge of the hole transport, and studied the relationship between photosensitivity of a series of hydrazone derivatives and their chemical structures.

In this study, we further deepened the hole unit and proposed another new concept, called the active hole-transport N atom, which is designated by the electron density variation of the frontier orbital in the neutral molecules and its cation radical. Based on this definition,

the relationships among photosensitivities, numbers of the active hole-transport N atom, and the HOMO energy levels of CTMs were investigated.

## Initial Molecular Structures and Computational Method

CT1-CT7 are composed of two separated portions, one substituted aniline and one substituted hydrazone. The crystal structure of CT2 shows that these two portions neatly share one common  $\pi$ -system. The  $\pi$ -system is extended from the amine N atom on the diethylaniline portion to the amine N atom on the diphenylhydrazone portion. One of the phenyl groups on the diphenylhydrazone portion lies coplanar to the extended  $\pi$ -system.<sup>13</sup> At last, the coplanar structure was selected as the initial basic skeleton structure of CT1-CT7. The similar initial structures were selected for CT8 and CT9. CT10 is triphenylamine. It has two kinds of stable conformations, planar form and spiral form. The total energies of these two conformations were calculated and compared. All initial structures were further optimized by AM1 method in HYPERCHEM 4.5 program.

## Results and Discussion

### A. Molecular Structure

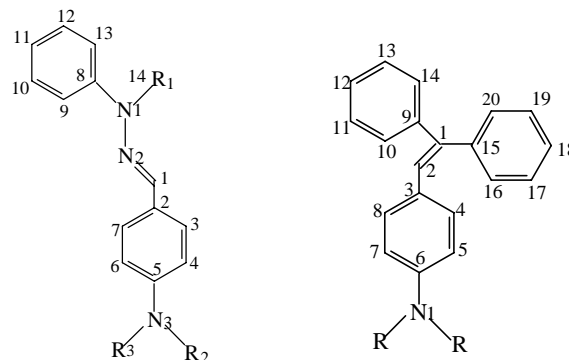


Figure 1. Molecular basic skeletons of CT1-CT9 (CT1: R1=-Ph; R2=R3=-C<sub>4</sub>H<sub>9</sub>; CT2: R1=-Ph; R2=R3=-C<sub>2</sub>H<sub>5</sub>; CT3: R1=-Ph; R2=R3=-CH<sub>3</sub>; CT4: R1=-CH<sub>3</sub>; R2=-Ph; R3=-CH<sub>3</sub>; CT5: R1=-Ph; R2=-Ph; R3=-CH<sub>3</sub>; CT6: R1=-Ph; R2=R3=-(p-CH<sub>3</sub>Ph); CT7: R1=R2=R3=-Ph; CT8: R=-(p-CH<sub>3</sub>Ph); CT9: R=-Ph)

The calculational results show that two separate portions of CT1-3, 5-7 share one common  $\pi$ -system. This large  $\pi$ -system is extended from the amine N atom on the aniline portion to another amine N atom on the hydrazone portion. The phenyl groups on the hydrazone portion lies coplanar to the extended  $\pi$ -system. For CT4, one phenyl group linked to the N atom of the hydrazone portion (compound CT4) is replaced by methyl group, which leads to the formation of an angel between the phenyl groups on the hydrazone portion and  $\pi$ -system (28.8°). The reason is due to the difference in that the methyl group is the electron-donating group, while the phenyl group is the electron-withdrawing group. The molecular structures of CT8 and CT9 are similar to that of CT4. Their phenyl groups on the ethylene portion can't lie coplanar to the extended  $\pi$ -system. Their dihedral angles (46.4° and 46.1°) are larger than that of CT4 (28.8°). For CT10, the total energy (-99.80981 a.u.) of its spiral form is far lower than that (-99.66627 a.u.) of its planar form. In other words, its spiral form is far more stable than its planar form. Thus more stable spiral form is used in the following study. Their part dihedral angles were listed in Table I.

### B. Determining the Active Hole-Transport N Atom

In the chemical terms, the hole transport is considered to be a chain of redox reactions due to one-electron transfer between the neutral molecule and the cation radical. The hole transport begins from transfer of an electron of CTM to the cation radical of CGM molecule; Then the closest CTM molecule transfers an electron to the cation radical of CTM molecule; The process is repeated until the hole reaches to the negative surface of the photoreceptor. The whole process of the hole transport is expressed by the following three reactions.



**Table I. Typical of the dihedral angles (°) of CT1-CT9**

	N2C1C2C7	N1N2C1C2	C8N1N2C1	C9C8N1N2	N3C5C4C3	C14N1N2C1
CT1	7.8	174.6	164.3	0.7	-176.5	18.1
CT2	14.0	175.2	164.9	1.4	-177.7	16.3
CT3	13.3	174.9	164.6	-0.1	-176.4	19.2
CT4	-21.4	-174.4	-162.6	28.8	-174.8	-16.1
CT5	9.3	174.3	164.8	0.6	-175.5	18.1
CT6	12.0	176.1	166.6	-3.1	179.2	17.1
CT7	9.4	175.1	165.2	0.7	179.2	18.3
	C1C2C3C4	C9C1C2C3	C10C9C1C2	C15C1C2C3	N1C6C5C4	C16C15C1C2
CT8	-10.5	-178.8	46.4	0.4	-178.6	-92.6
CT9	-13.7	-178.3	46.1	0.7	-178.7	-93.1

**Table II. Electron density variations of all N atoms and a part of C atoms with more positive electron density variations**

	N1	N2	N3	F*	S*
CT1	+0.21	+0.09	+0.16	+0.15(C2)	+0.15(C5)
CT2	+0.23	+0.07	+0.14	+0.14(C5)	+0.11(C2)
CT3	+0.26	+0.06	+0.09	+0.15(C5)	+0.09(C2)
CT4	+0.10	+0.08	+0.21	+0.19(C2)	+0.15(C5)
CT5	+0.24	+0.06	+0.14	+0.14(C5)	+0.09(C2)
CT6	-0.05	+0.04	+0.42	+0.15(C2)	+0.06(C5)
CT7	+0.06	+0.09	+0.30	+0.11(C2)	+0.08(C5)
CT8	+0.48	--	--	+0.13(C3)	+0.06(C6)
CT9	+0.49	--	--	+0.14(C3)	+0.08(C6)
CT10	+0.46	--	--	+0.03(linking to N atom)	--

\* F and S represent C atom of the largest positive electron density variation and C atom of second largest positive electron density variation. Symbol in the () represents position of C atom in Figure I.

The reaction (3) among them is the fastest. Therefore, the theoretical studies were focused on the slow reaction 1-2. Kitamura and Yokoyama<sup>12</sup> defined the N-phenyl group as a hole unit that takes charge of electron transfer. In fact, the easily oxidized portion on N-phenyl group is only the N atom. For Kitamura and Yokoyama's definition, there exists a question, about if all N-phenyl groups in this molecule take charge of hole transport or only part of atoms among them do. If the atom that takes charge of hole transport in this molecule can be clearly pointed out, this will be more scientific and reasonable, compared to the hole unit. Based on such consideration, we used the atomic electron density variation of the frontier orbital in the neutral molecule and cation radical to settle the question. According to the frontier orbital theory,<sup>14</sup> the electron density in the neutral and cation radical states can influence hole transport. Therefore, the atomic electron density of the highest occupied molecular orbital (HOMO) in each neutral molecule and semi-occupied molecular orbital (SOMO) in the cation radical was compared. Table II listed the positive electron density variations of all N atoms and a part of C atoms with more positive electron density variations.

The results show that only one N atom among three N ones has the largest positive electron density variation in all atoms of CT1-CT7. The position of this N atom in each molecule is different. For CT1-CT3 and CT5, they are N1 whereas they are N3 for CT4 and CT6-CT7. However, this N atom belongs to N atom in the hole unit defined by Kitamura and Yokoyama.<sup>10</sup> N2 atom that doesn't belong to N atom in the hole unit shows smaller positive electron density variation. But not all N-atoms in the hole unit show more positive electron density variation. For example, N1 in CT6 show negative electron density variation (-0.05). N1 in CT7 show smaller positive electron density variation (+0.06), which is smaller than that of N2 (+0.09). CT8-CT10 has only one N atom and its electron density has the largest positive variation in all atoms of the molecules. Finally, we proposed a new concept called the active hole-

transport N atom. Its idea is that the active hole-transport takes charge of hole transport. When a neutral CTM molecule loses an electron, the active hole-transport N atom should lose more charge. In other words, the active hole-transport N atom shows larger positive electron density variation. As is known to all, N2 atom in a series of hydrazone derivatives doesn't belong to the hole unit, and doesn't take charge of the hole transport. Thus the positive electron density variation of N2 atom is proposed to be a standard quantity. If the molecule doesn't contain this N atom, the positive electron density of C atom that shows the largest positive electron density is considered to be a standard quantity. If the positive electron density variation of the N atom is larger than the standard quantity, this N atom in N-phenyl group is defined as the active hole-transport N atom. If smaller, this N atom in N-phenyl group isn't the active hole-transport atom. Based on the definition, CT1-CT5 has two active hole-transport N atoms whereas CT6-CT10 has one.

### C. Relationship Between Photosensitivity and Molecular Structure

For the double-layered photoreceptors composed of the same CGM and different CTMs, the photosensitivity variations may be dependent on the hole injection process from CGL to CTL and hole transport process in CTL. The hole injection process is considered to correlate to the HOMO energy level of CGM and CTM.<sup>9-10</sup> Since the common CGM was used, the hole injection should only correlate to the HOMO energy level of CTM. Since the hole transport is mobile by the hopping way from one N site to another N site, two active hole-transport N atoms in the molecule increase the concentrations of the N site. In other words, it shortens the hopping distance. This point has been verified by the experiments of the CTM concentration dependence on the hole drift mobility.<sup>11</sup> Therefore, the influence of the numbers of active hole-transport N atom and HOMO energy level of CTM on photosensitivity were considered. Their equations are:

$$\begin{aligned} \log E_{50} &= -0.16179N + 1.19137, \\ S &= 0.0880, \quad F = 8.467, \quad r = 0.717, \quad n = 10 \end{aligned} \quad (4)$$

$$\begin{aligned} \log E_{50} &= -0.20000N - 0.94833E_H - 6.19042, \\ S &= 0.0473, \quad F = 24.983, \quad r = 0.937, \quad n = 10 \end{aligned} \quad (5)$$

Equation 4 shows that logE50 correlates to the numbers of active hole-transport N atom in some degree. The more the active hole-transport N atoms in the molecule, the better the photosensitivity is. When HOMO energy levels of CTMs were further considered, the correlation coefficient is improved obviously, varying from 0.717 to 0.937. It indicates that the hole injection process from CGL to CTL and hole transport process in CTL play significant role on photosensitivity variations.

**Table III. Data of the HOMO energy level ( $E_H$ ), the numbers of active hole-transport N atom (N) and photosensitivity ( $E_{50}$ )**

Type	$E_H$ /eV	N	$E_{50}$ /Lux $\cdot$ S <sup>15</sup>
CT-1	-7.8753	2	6.85
CT-2	-7.8543	2	6.6
CT-3	-7.8807	2	8.0
CT-4	-7.9149	2	7.1
CT-5	-7.9009	2	8.5
CT-6	-7.7328	1	8.0
CT-7	-7.8192	1	10.0
CT-8	-7.7500	1	9.1
CT-9	-7.8496	1	12.3
CT-10	-7.9564	1	15.7

### Conclusion

Based on the atomic electron density variations of the frontier orbital in the neutral molecule and its cation radical of the hole transport molecule, the concept of the active hole-transport N atom was proposed. As is known to all, N2 atom in a series of hydrazone derivatives doesn't belong to the hole unit, and doesn't take charge of the hole transport. Thus the positive electron density variation of N2 atom is proposed to be a standard quantity. If the molecule doesn't contain this N atom, the positive electron density of C atom that shows the largest positive electron density is considered to be a standard quantity. If the positive electron density variation of the N atom in N-phenyl group is larger than the standard quantity, this N atom is defined as the active hole-transport N atom. Vice versa if smaller, the N atom in N-phenyl group isn't the active hole-transport atom. The relationship among photosensitivity, the numbers of the active hole-transport N atom and the HOMO energy level of CTMs was investigated. The results showed that photosensitivity were correlated strongly to numbers of the active hole-transport N atom and the HOMO energy level of CTMs. Therefore, it is concluded that the hole injection process from CGL to CTL and hole transport process in CTL play significant role on photosensitivity variations.

### References

1. K. Y. Law, I. W. Tarnawskj and Z. D. Popovic, *J. Imaging Sci. and Technol.*, **38**, 118 (1994)
2. M. Umeda, T. Niimi and M. Hasshimoto, *Japance J. Appl. Phys.* **29**, 2746 (1990)
3. Z. D. Popovic, *Chem. Phys.* **86**, 311 (1984)
4. E.R. Menzel and Z. D. Popovic, *Chem. Phys. Lett.* **55**, 177 (1978)
5. A. Kakuta, Y. Mori and H. Morishita, *IEEE IA-17* 382 (1981)
6. T. Kitamura and M. Yokoyama, *J. Imaging Sci.* **34**, 197 (1990)
7. R. Takahashi, S. Kusabayasi and M. Yokoyama, *Electrophotography* **25**, 17 (1986)

8. L. B. Schein and J. X. Mack, *Chem. Phys. Lett.* **149**, 109 (1988)
9. K. Y. Law, *Chem. Rev.* **93**, 449 (1993)
10. Z. P. Huang, J.H. Pan, G. Q. Cai, Q. S. Yu, R. S. Lin, *Acta Physico Chimica Sinica* **14**, 557 (1998)
11. M. Stelka, J. F. Yanus, and D. M. Pai, *J. Phys. Chem.* **88**, 4707 (1984)
12. T. Kitamura and M. Yokoyama, *J. Appl. Phys.* **89**, 821 (1991)
13. J. Pacansky, A. D. Mclean and M. D. Miller, *J. Phys. Chem.* **94**, 90 (1990)
14. J. Fleming, *Frontier Orbitals and Organic Chemical Reactions* (wiley, London, 1976), Chapter 5.
15. T. Kitamura and M. Yokoyama, *Electrophotography*, **27**, 31 (1988).
16. Yokoyama, M.; Akiyama, K.; Yamamori, N.; Mikawa, M.; Kusabayashi, S., *Polym. J.*, **17**, 545 (1985).

## Biography

Mr. Zhongping Huang received a B.S. in Analytical Chemistry from Chinese Geology University and a M.S. in Quantum Chemistry from Sichuan University in 1993 and 1996, respectively. He earned Ph. D. in Physical Chemistry in Zhejiang University in 1999. His current research interests focus on computer-aided in molecular design of materials, synthesis of the carrier generation and transport materials, electrophotographic performance and mechanistic studies of organic photoconductive materials. He is a member of the IS&T.