

## A ZINDO/1-CI Study of Substituted Triphenylamines for Use as Charge Transfer Materials

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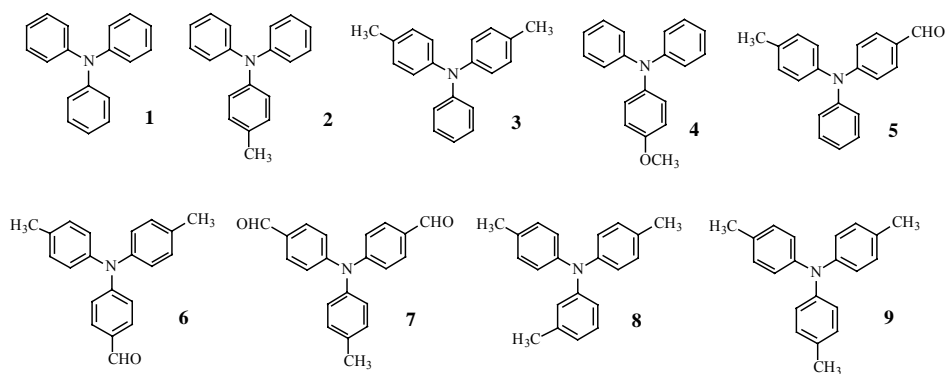
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**Abstract:** Electronic spectra of substituted triphenylamines are investigated in this paper by time dependent perturbation theory and ZINDO/1-CI calculation.

**Keywords:** Electroluminescence, triphenylamine, ZINDO, organic LED.

Electroluminescence (EL) devices based on organic thin layers have attracted much interest because of possible application in large-area light-emitting devices. The electroluminescence is generated by recombination of holes and electrons. Various  $\pi$ -conjugated electroluminescent materials have been synthesized to be used in organic light-emitting diodes (OLEDs)<sup>1</sup>.

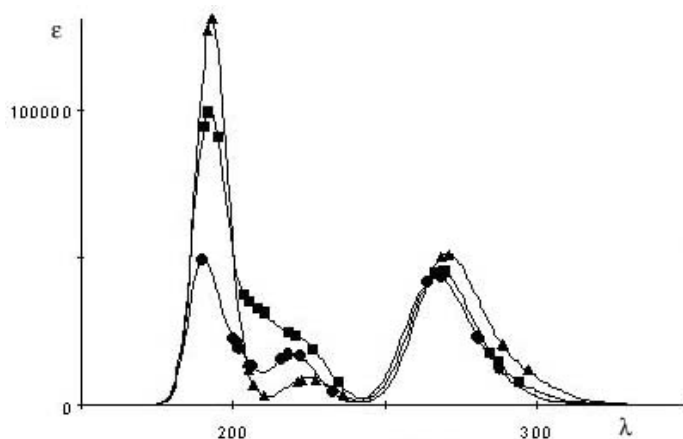
**Figure 1** Substituted triphenylamines



1 TPA; 2 MTPA; 3 DMTPA; 4 MOTPA; 5 MFTPA; 6 DMFTPA; 7 MDTPA; 8 DpMmMTPA; 9 TpMTPA

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**Figure 2** UV-Vis spectra calculated for **1**(●), **8**(+) and **9**(△).  $\epsilon$ : molar absorptivity in L/(mol·cm<sup>-1</sup>);  $\lambda$ , wavelength in nm.



The substituted triphenylamines investigated are shown in **Figure 1**. Their structures were obtained by geometric optimization using semiempirical method PM3, perturbation theory<sup>2</sup> and ZINDO/1-configuration interaction (CI)<sup>3</sup>. 8 occupied and 8 virtual molecular orbitals were used in constructing single excited CIs to calculate the singlet ground and excited states in vacuum.

Oscillator strength  $f_{0 \rightarrow k}$  from initial state  $|0\rangle$  of the molecule to the final state  $|k\rangle$  is determined by corresponding energies  $E_0$  and  $E_k$  and transition moment  $R = \langle 0|\mu|k\rangle$  as

$$f_{0 \rightarrow k} = \frac{2}{3}(E_k - E_0) |\langle 0|\mu|k\rangle|^2 \quad (\text{in a.u.}), \quad (1)$$

where  $\mu$  is the electric dipole moment operator<sup>2</sup>. Suppose the molar absorptivity  $\epsilon$  is of Gaussian lineshape,  $\epsilon = \epsilon_0 e^{-4 \ln 2 (\tilde{\nu} - \tilde{\nu}_0)^2 / \Delta \tilde{\nu}^2}$  (L/mol·cm<sup>-1</sup>), and then  $\epsilon_0 = 2.1746 \cdot 10^8 \cdot f_{0 \rightarrow k} / (\Delta \tilde{\nu})$ , where half-width  $\Delta \tilde{\nu}$  is assumed as 3200cm<sup>-1</sup> in calculation. Sum of  $\epsilon$  for all transitions gives the curve of total molar absorptivity as shown in **Figure 2**. Each dot in it represents electronic transition from ground state  $|0\rangle$  to corresponding excited states  $|k\rangle$ . The wavelength and transition moment are listed in **Table 1**.

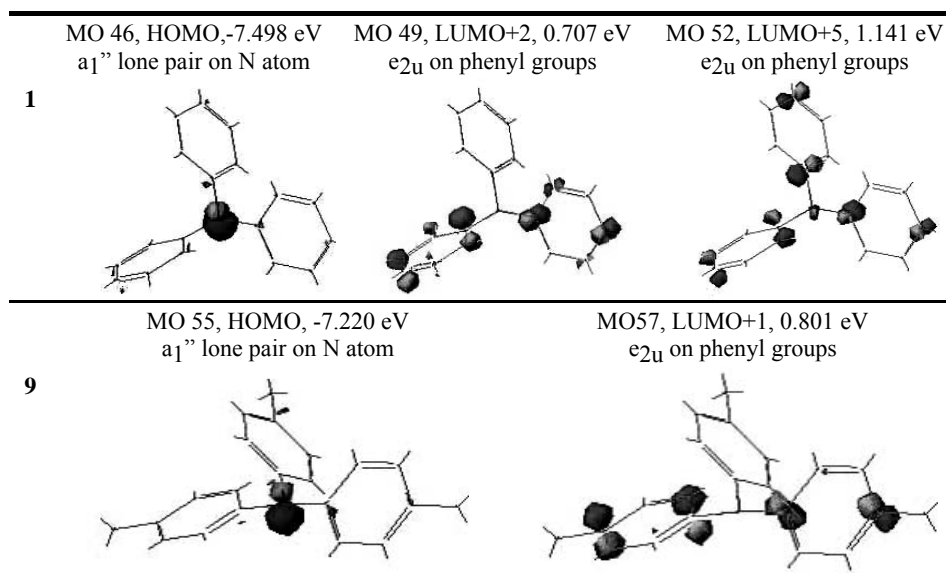
**Figure 2** reveals the effect of the methyl substitution and its position from **1**, **8**, to **9**. The position and the intensity of the band at 267 nm for **8** and **9** remains the same as that for **1**, however the intensity of the band at 193 nm goes up dramatically. The reason can be understood after examining the predominant component of the molecular orbital involved in the pertinent transition. The probability of singly excited configurations (SEC) in excited states responsible for the band at 190 nm for **1** and **9** was listed in **Table 2**. The predominant contribution on it for **9** comes from SEC 59, which is due to the transition from HOMO(MO 55) to LUMO+1(MO 57). It is equivalent to the electronic transfer from lone pair at central nitrogen atom to two phenyl groups (**Figure 3**). However, contribution on it for **1** is quite diverse. The second high contribution, 0.160, from SEC 63, which is due to the transition from HOMO (MO 46) to LUMO+5 (MO 52), gives no contribution to electric dipole moment and to transition moment  $R$  (**Figure 3**).

**Table 1** Main electronic transitions from ground state  $|0\rangle$  to the excited states  $|k\rangle$  for molecule **9**.

Transition	$\langle 0 \mu k\rangle/\text{Debye}$			wavelength $\lambda / \text{nm}$	$f_{0\rightarrow k}$
	X	Y	Z		
$ 0\rangle \rightarrow  1\rangle$	1.2314	1.4049	-0.0566	296.7	0.0554
$ 0\rangle \rightarrow  2\rangle$	-0.4373	0.4014	1.6787	288.8	0.0517
$ 0\rangle \rightarrow  4\rangle$	2.9963	-3.1438	-1.5547	271.0	0.3698
$ 0\rangle \rightarrow  5\rangle$	-1.1678	1.2888	-4.2463	268.5	0.3693
$ 0\rangle \rightarrow  7\rangle$	1.3871	1.2050	0.0697	227.0	0.0701
$ 0\rangle \rightarrow  14\rangle$	0.4566	-1.1539	-5.8608	193.2	0.8747
$ 0\rangle \rightarrow  16\rangle$	1.9286	2.5857	-2.3299	191.5	0.3893

**Table 2** Probability of SECs in excited states responsible for the band at 190 nm for **1** and **9**

Compound <b>1</b> , $ 0\rangle \rightarrow  14\rangle$ 190.0 nm			Compound <b>9</b> , $ 0\rangle \rightarrow  14\rangle$ 193.2 nm		
SEC	MO	Probability in $ 14\rangle$	SEC	MO	Probability in $ 14\rangle$
12	(40 $\rightarrow$ 49)	0.113	59	(55 $\rightarrow$ 57)	0.543
60	(46 $\rightarrow$ 49)	0.228	60	(55 $\rightarrow$ 58)	0.207
63	(46 $\rightarrow$ 52)	0.160	61	(55 $\rightarrow$ 59)	0.091

**Figure 3** Schematic diagram of molecular orbitals important in **Table 2**

**Table 3** Main bands of electronic spectra for compounds listed in **Figure 1**

Cmpd.	$\lambda_{\max}(\text{expl.})/\text{nm}^5$ (in ethanol)	$\lambda_{\max}(\text{calc.})/\text{nm}$ (in vacuum)	$\lambda_{\max}(\text{calc.})/\text{nm}$ (in ethanol)
1	238.0, 291.8	190.4*, 267.6**	190.3*, 264.7**
2	214.0, 298.0	211.2**, 261.4*	192.7*, 284.8**
3	214.5, 298.0	192.8*, 245.0**	192.9*, 265.0**
4	214.5, 299.5	192.3*, 266.7**	192.4*, 263.3**
5	NA†	193.1*, 291.5**	192.9*, 265.6**
6	216.5, 365.5	193.5*, 293.5**	193.1*, 291.1**
7	213.5, 318.0	191.6*, 301.5**	192.2*, 302.6**
8	NA	194.4*, 264.0**	192.6*, 261.6**
9	NA	193.5*, 269.4**	192.6*, 257.5**

\*: Transition with the highest  $f_{0 \rightarrow k}$ ; \*\*: with the second highest  $f_{0 \rightarrow k}$ ; †: Not available

The corresponding spectra in ethanol were calculated by self-consistent reaction field solvent model with dielectric constant  $\epsilon = 24.5$ , refractive index at 20°C  $n = 1.36$ , and cavity radius  $5\text{\AA}^4$ . Results were listed in **Table 3**, and they are quite reasonably consistent with corresponding experimental data.

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