

Quantum Chemistry Study on Properties of Several Aromatic Amine Organic EL Materials*

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Abstract: Several aromatic amine compounds E-12, E-13, E-14, and E-15 are all organic electroluminescent (EL) and photoluminescent (PL) materials with good characteristics. Quantum chemistry calculations have been made. Their geometric configurations have been optimized by RHF/AM1. Their electronic spectra have been calculated by RHF/CIS. The calculated results are essentially consistent with experimental values.

Key words: EL materials, RHF/CIS method, Electronic spectrum

1 Introduction

Study on organic molecule and polymer film electroluminescent (EL) materials, devices have become one of fascinating areas of researches in the world^[1-3]. Compared with inorganic materials, organic materials have much higher luminescence efficiency and much wider ranges of colour selection.

Chihaya Adachi *et al.* examined more than ten blue light-emitting organic EL materials^[4], and obtained their electroluminescent spectra and photoluminescent spectra. By means of quantum chemistry semi-empirical method RHF/AM1, we carried out theoretical calculations for several materials, E-12, E-13, E-14 and E-15, including geometric optimization, vibrational analysis and electronic spectrum calculation.

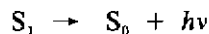
2 Theory and research method

Luminescence colours of EL devices depend on the fluorescence spectra of luminescent materials. A molecule in the first excited state S_1 can drop to the ground state S_0 by giving off the energy in the form of light. This process, which generally happens within 10^{-9} sec, is called

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fluorescence. This fluorescence procession can be presented as follows:



We adopted RHF/AM1 method to optimize the four compounds' geometrics with all parameters. Vibrational analyses were exerted for the optimized configurations. On this basis, their electronic spectra were calculated by RHF/CIS (single excited state configuration interaction).

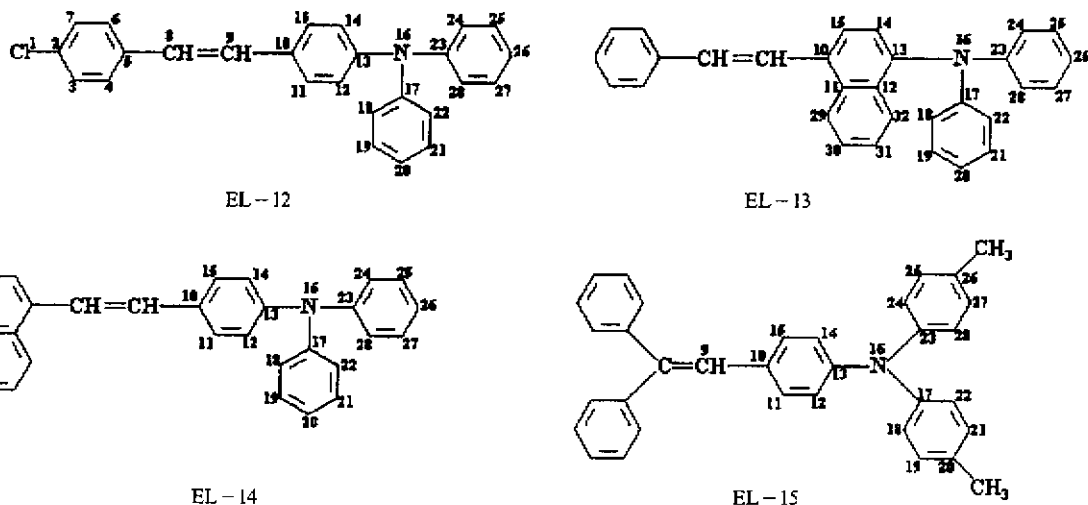


Fig. 1 Structural formulas of the four compounds

Because of our calculating condition, we only selected 24 higher occupied orbitals and 24 lower unoccupied orbitals, plus reference state (ground state as reference state) to obtain 1153 configurations (abbreviated by 24×24). By CIS calculation, vertical transition energy and corresponding vibrational strength were worked out. These are the theoretical calculation values of the electronic spectrum.

3 Calculated results and discussions

3.1 Geometries

Generally speaking, the structural characteristic of strong fluorescent organic materials is that the molecule has a rigid planar structure and a big delocalized bond. And it has the lowest single electron excited state, with being π_i , π_i^* type. Geometric optimization results of E-12 ~ E-15 indicates that they partly have above-mentioned structural features. Table 1 and table 2 list total energy, heat of formation and structural parameters for these four compounds respectively. From table 2, we know that the nitrogen atoms in E-12, E-14 and E-15 have a sp^2 hybridization, while the nitrogen atom in E-13 has a hybridization type between sp^2 and sp^3 . On the other hand, the three aromatic rings connected with the nitrogen in above-mentioned compounds undergo certain torsions, so they don't have an exactly rigid

Table 1 Total energy and heat of formation for the four compounds

Compounds	Total energy/kJ mol ⁻¹	Heat of formation/kJ mol ⁻¹	Convergent gradient/kJ mol ⁻¹ Ang ⁻¹
E-12	-403139.201	-495.460	0.00418
E-13	-420404.984	-522.793	0.000418
E-14	-420416.930	-535.303	0.000418
E-15	-477775.931	-188.982	0.00418

Table 2 Some structural parameters of the four compounds

Compounds	Bond angles/(°)	Torsion angles/(°)	Compounds	Bond angles/(°)	Torsion angles/(°)
E-12	∠13-16-23=120.1	∠12-13-16-17=32.2	E-14	∠13-16-23=120.1	∠12-13-16-17=32.7
	∠13-16-17=120.1	∠22-17-16-23=35.2		∠13-16-17=120.1	∠22-17-16-23=35.0
	∠17-16-23=119.7	∠24-23-16-13=35.5		∠17-16-23=119.8	∠24-23-16-13=35.2
E-13	∠13-16-23=117.8	∠12-13-16-17=42.9	E-15	∠13-16-23=120.2	∠12-13-16-17=32.5
	∠13-16-17=117.0	∠22-17-16-23=44.4		∠13-16-17=120.1	∠22-17-16-23=35.6
	∠17-16-23=119.1	∠24-23-16-13=44.9		∠17-16-23=119.7	∠24-23-16-13=35.3

planar structure. But they are still able to form a delocalization system to a certain extent^[5].

3.2 Vibrational analysis

Whether a molecule is in a stable configuration is dependent on whether there are imaginary frequencies in its vibrational spectrum^[6]. We performed vibrational analyses for the four compounds, optimized configurations, and found that there were no imaginary frequencies in their IR spectra. The three smallest vibrations, frequencies and strength of each compound are shown in table 3.

Table 3 Vibrational analyses for the four compounds

Compounds	The three smallest vibrational frequencies/cm ⁻¹			Strength/kmmol ⁻¹		
E-12	7.55	11.83	23.24	0.00407	0.20368	0.21753
E-13	11.82	15.94	18.73	0.01658	0.09206	0.26095
E-14	9.03	14.45	22.35	0.01136	0.34008	0.23495
E-15	9.31	11.67	19.98	0.01015	0.34866	0.11118

3.3 Frontier molecular orbitals' energy

Electronic absorption spectra of organic molecules are closely related to the energy level distribution of frontier molecular orbitals. Frontier molecular orbital energy of four compounds are listed in table 4. We take FOMO, TOMO, SOMO, HOMO as the fourth, the third, the second and the highest occupied orbitals, respectively, and LUMO, SUMO, TUMO, FUMO as the lowest, the second, the third and the fourth unoccupied orbitals.

Table 4 indicates that because of conjugate π bonds in the four compounds, the energy level difference ΔE between HOMO and LUMO is much smaller. So that, the delocalized π electrons are readily excited. If electrons' exchange integral and coulomb integral are wholly omitted, the vertical transition energy between HOMO and LUMO may be calculated by ΔE

values^[7]. According to their configurations, we can see that the delocalization effects of π electrons in the four compounds are close to each other, therefore their ΔE values are close to each other. This is shown in table 4.

Table 4 Frontier molecular orbitals' energy of the four compounds (eV)

Compounds	FOMO	TOMO	SOMO	HOMO	LUMO	SUMO	TUMO	FUMO	ΔE
E-12	-9.7805	-9.7607	-8.8366	-7.9113	-0.6448	0.1009	0.1809	0.2871	7.2665
E-13	-9.4477	-9.2400	-8.6481	-8.0086	-0.6928	0.0475	0.1076	0.2179	7.3158
E-14	-9.3629	-9.3515	-8.5130	-7.8620	-0.6128	-0.0296	0.1362	0.1793	7.2492
E-15	-9.5031	-9.3819	-8.7788	-7.7502	-0.3065	0.1594	0.3844	0.4179	7.4437

Besides, it could be seen that the LUMO energies of the four compounds are negative respectively. It is to be expected that the four compounds will be capable of forming negative ions in chemical reactions.

3.4 Electronic spectra

By means of single excited state configuration interaction (CIS) method, we calculated the electronic absorption spectra of the four compounds respectively. Electronic spectrum parameters of frontier orbital energy levels are presented in table 5.

Table 5 Electronic spectra of the four compounds

Compounds	HOMO	LUMO	Transition components	Transition coefficients	λ /nm (cal.)	λ /nm (exp.) ^[4]
E-12	(68)	(69)	(68) \rightarrow (69)	0.5234	413	470
E-13	(74)	(75)	(74) \rightarrow (75)	0.5624	406	450
E-14	(74)	(75)	(74) \rightarrow (75) (74) \rightarrow (76)	0.4567 0.3478	411	469
E-15	(85)	(86)	(85) \rightarrow (86)	0.5315	401	459

Restricted by calculating conditions, we selected at most 1153 configurations ($24 \times 24 \times 2 + 1$). The calculated results are essentially consistent with experimental values (table 5). If more occupied and unoccupied orbitals can be chosen in configuration interaction, the results will be closer to experimental values. From the data in table 6, it is suggested that the wave length λ of the electronic spectrum increases with increase of configuration numbers of CIS, namely there is red shift in electronic spectrum, but there is no linear relationship. When the wavelength increases to a certain degree, the increase amplitude gradually decreases. If enough configurations can be chosen, it is expected that the calculated values of E-12 and E-13 will be close to

Table 6 The relation between CIS configuration numbers and maximum wave length λ in electronic spectra of compounds E-12 and E-13

	CIS($n \times n$)	2 \times 2	4 \times 4	8 \times 8	12 \times 12	16 \times 16	20 \times 20	24 \times 24
E-12	λ_{max}/nm	321	358	385	401	407	409	413
E-13	λ_{max}/nm	332	362	373	394	401	404	406

420 ~ 430 nm, and more consistent with experimental values 470 nm and 460 nm^[4].

4 Conclusion

The calculated results of quantum chemistry semi-empirical method indicate that compounds E-12, E-13, E-14 and E-15 are all better organic electroluminescent materials. The electronic spectrum wavelengths produced by the transition between HOMO and LUMO are in the range of blue light of visible light. Theoretical calculation is based on pure gaseous materials, the deviations of 10% ~ 13% can be permitted.

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几种芳香胺类有机 EL 材料性质的量子化学研究*

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摘要: 几种芳香胺类化合物 E-12、E-13、E-14 和 E-15 均为性能良好的有机电致发光 (EL) 和光致发光 (PL) 材料。采用量子化学计算方法, 用 RHF/AM1 方法优化其构型, 用 RHF/CIS 方法计算其电子光谱, 计算结果与实验值基本吻合。

关键词: EL 材料; RHF/CIS 方法; 电子光谱

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