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Utilization of a PPP method to study the structure and colour of aromatics having symmetrically substituted phenylethynyl groups

Bin Li, Weirong Miao, Qingwei Meng*, Lubai Cheng

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, People's Republic of China

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Abstract

The electronic absorption and fluorescence spectral data of a series of chemiluminescence fluorophores comprising of poly-aromatic-hydrocarbons symmetrically substituted by phenylethynyl groups were calculated using the PPP molecular orbital method. Optimal agreement between experimental and calculated results was achieved by adopting a generalized, empirically derived set of parameters.

Keywords: PPP molecular orbital method; Chemiluminescence; Phenylethynyl groups

1. Introduction

Aromatics with symmetrically substituted phenylethynyl groups are widely used in peroxyoxalate chemiluminescence, which is far superior to other known chemiluminescence processes both in quantum yield and light efficiency. Since the chemiluminescence properties of these compounds are largely determined by their fluorescence, the latter are of great interest in peroxyoxalate chemiluminescence studies. The aim of this work is to find a reasonably accurate quantitative method to predict the fluorescent performance of the structures that are to be designed and synthesized in peroxyoxalate chemiluminescence studies.

So far the design and development of this series of compounds have been largely dependent on experience, with few quantitative studies having been reported. Considering that the PPP method has been successfully applied to various planar compounds similar to the compounds studied in this paper, an attempt was made to apply this method to the absorption and fluorescence spectra of these compounds.

2. Experimental

The PPP molecular orbital method reported by Lubai Cheng was used [1]. Two-center electron repulsion integrals were determined by the Nishimoto–Mataga relationship and electronic excitation energies were refined by a limited

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* Corresponding author.
E-mail address: miaowr@chem.dlut.edu.cn (Q. Meng).

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configuration interaction (CI) treatment involving the first nine singly excited singlet configurations obtained by promoting an electron from the three highest occupied orbitals to the three lowest unoccupied orbitals.

The parameters used in the calculations are shown in Table 1. Standard bond lengths and angles were used in the computations wherever possible and literature values for β, the VSIP and the one-center electron repulsion integral (γnm = VSIPn-An) were employed unless otherwise stated.

The preparation of the compounds cited in this paper is well reported before [2,4–6].

3. Results and discussion

To optimize the agreement between experimental and calculated values for the compounds used, the parameters employed were modified as follows (shown in Table 1).

The bond resonance integral for the carbon–carbon triple bond was set as −2.90, and the excited bond length used in the calculation of fluorescence was set as 1.34.

Through calculation it was found that for the compounds with two substitutes on the anthracene rings, such as compounds **2**, **10**, **17**, and **18** (Table 2), the calculated results proved to be poor. It can be reasonably assumed that two substitutes within the same ring affect the molecule's electron energy state in a different way from that of a single one, and therefore, the parameters used for these compounds were modified as shown in Table 1. Using these modified parameters, better prediction of absorption and fluorescence data was achieved.

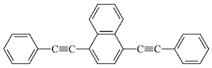
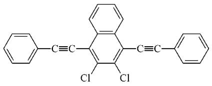
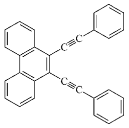
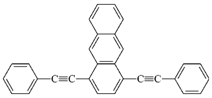
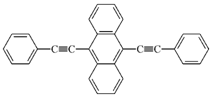
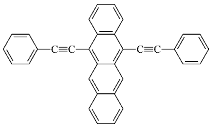
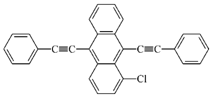
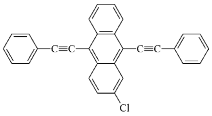
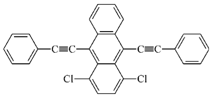
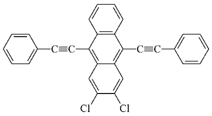
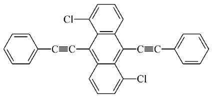
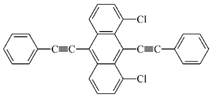
The experimental and calculated electronic absorption spectral data for the 24 compounds are compared in Table 2 and are also plotted in Figs. 1 and 2. The results show that the calculated results obtained using the PPP method generally were in reasonable agreement with the experimental values, although there were some

Table 1
PPP MO parameters for the calculation of absorption and fluorescence spectra

Bond X–Y	$r_{\mathrm{X-Y}}$[a] (A)	$\beta_{\mathrm{X-Y}}$[b] (eV)	$\mathrm{VSIP_Y}$[c] (eV)	A_Y[d] (eV)	Z_Y[e]	$\alpha_{\mathrm{X-Y}}$[f] (A)
C=C(aromatic)	1.40	−2.39	11.16	0.03	1	1.52
=C–C	1.45	−2.33	11.16	0.03	1	1.52
C≡C	1.20	−2.90	11.16	0.03	1	1.34
C≡N(cyano)	1.15	−2.67	14.18	3.50	1	1.31
C–CN(cyano)	1.40	−2.30	11.19	0.10	1	1.52
C–Cl	1.70	−2.46	23.30	12.50	2	1.75
C–CCl	1.40	−2.39	8.90	0.03	1	1.52
C–CCl[g]	1.40	−2.39	10.90	0.03	1	1.52
C–Br	1.85	−2.46	21.30	11.60	2	1.96
C–C–Br	1.40	−2.39	9.60	0.03	1	1.52
C–OMe	1.36	−2.60	32.90	11.43	2	1.41
C–COMe	1.40	−2.39	9.20	0.03	1	1.52
C–COMe[h]	1.40	−2.39	10.80	0.03	1	1.52
C–O–Ph	1.36	−2.60	32.90	10.40	2	1.41
C–COPh	1.40	−2.39	9.20	0.03	1	1.52

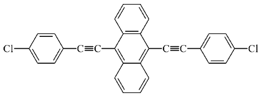
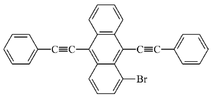
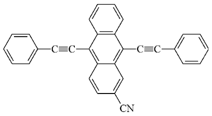
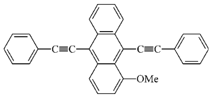
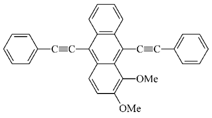
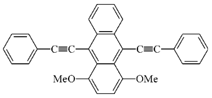
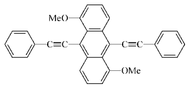
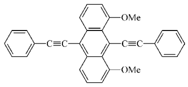
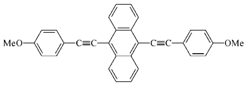
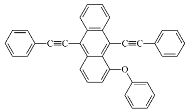
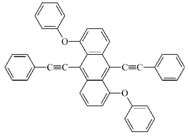
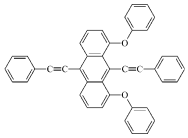
[a] Bond length.
[b] Bond resonance integral.
[c] Valance state ionization potential of atom Y.
[d] Electron affinity of atom Y.
[e] Core charge of atom Y.
[f] Excited state bond length used in fluorescence calculation.
[g] When two oxygen atoms were bonded with the same aromatic ring.
[h] When two chlorine atoms were bonded with the same aromatic ring.

Table 2
Experimental and calculated absorption and fluorescence spectral data

Compd.	Structure	Absorption $\lambda_{\max}$ (nm)		Fluorescence $\lambda_{\max}$ (nm)	
		Exp.	Calc.	Exp.	Calc.
1[a]		374	370	394	406
2[a]		385	376	402	409
3[a]		372	377	395	413
4[a]		411	413	449	433
5[b]		459	457	476	479
6[a]		552	515	563	527
7[b]		474	477	491	501
8[b]		464	465	480	486
9[a]		491	491	517	516
10[a]		472	460	487	481
11[b]		491	481	510	504
12[a]		499	481	528	506

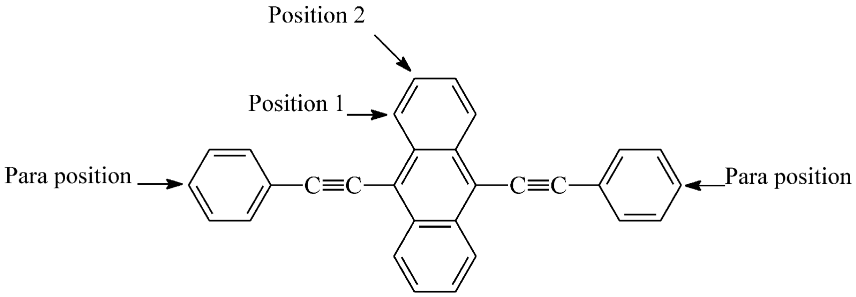
(continued on next page)

Table 2 (*continued*)

Compd.	Structure	Absorption λ_{max} (nm)		Fluorescence λ_{max} (nm)	
		Exp.	Calc.	Exp.	Calc.
13[a]		462	466	481	487
14[b]		474	476	494	493
15[a]		476	467	495	485
16[b]		481	481	500	507
17[a]		492	495	521	523
18[a]		492	523	562	565
19[b]		494	487	511	514
20[a]		500	488	529	514
21[a]		476	469	492	494
22[b]		473	480	497	502
23[b]		493	490	512	514
24[b]		500	492	522	516

[a] Absorption and fluorescence experimental data from [4–7].

[b] Absorption and fluorescence experimental data from [2,3].



obvious exceptions, which may be due to inadequate parameterization.

Certain features of the data in Table 2 are worthy of comment. The results showed that the PPP method could identify the influence of molecular structure on spectral properties. For example, for the three compounds with the same molecular weight, i.e., 9,10-bis(phenylethynyl)phenanthrene (**3** in Table 2), 9,10-bis(phenylethynyl)anthracene (**5**), 1,4-bis(phenylethynyl)anthracene (**4**), the calculated results gave the same wavelength sequence as the experimental data. This is probably due to the fact that in 9,10-bis(phenylethynyl)phenanthrene (**3**), the phenanthrene moiety forms an angular frame and the two phenylethynyl groups are substituted in the same ring at the ortho position, which lowers the conjugation of the π electrons of the molecule. As for 1,4-bis(phenylethynyl)anthracene (**4**), the two phenylethynyl groups at the 1,4 position of the anthracene may mean that the π electrons on the other side of the six-member ring participate less in conjugation of the whole molecule, making the spectra of the compound appear at shorter wavelengths than those of 9,10-bis(phenylethynyl)anthracene (**5**).

Another comment is that the PPP method predicted that substitutes at different positions of 9,10-bis(phenylethynyl)anthracene caused bathochromic effects in the sequence: position1 > position2 > *para* position, which may help in future molecule design.

It also can be seen by comparing the methoxy-substituted compounds with phenoxy-substituted ones (such as **16** and **22**, or **19** and **23**, or **20** and **24**) that the methoxy group and the phenoxy group exert nearly the same effect on the structure of 9,10-bis(phenylethynyl)anthracene. This may

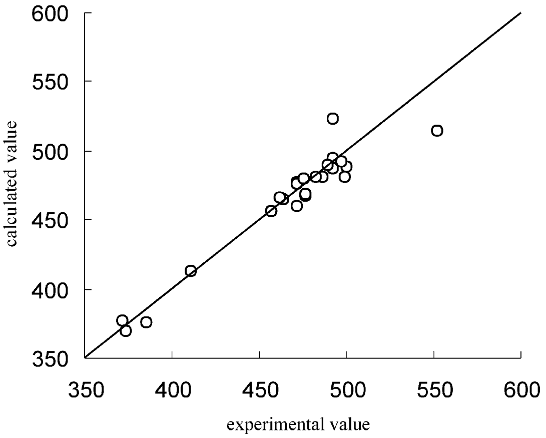


Fig. 1. Relationship between experimental and calculated absorption data.

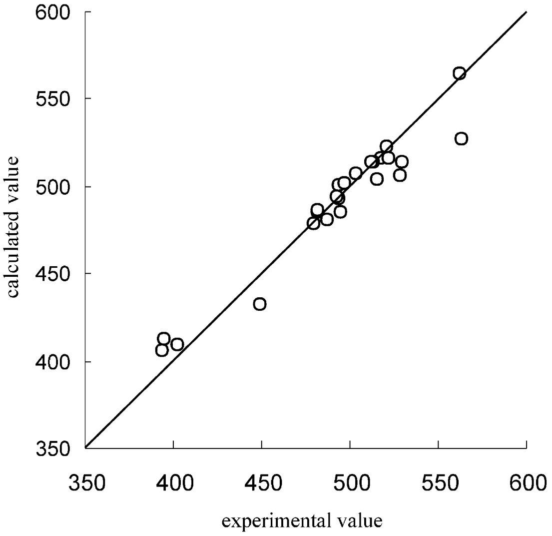


Fig. 2. Relationship between experimental and calculated fluorescence data.

lead to the conclusion that the π electrons on the benzene ring of the phenoxy group are not conjugated with the electrons of the molecule.

Although the PPP method proved to be generally good, there do exist some problems. For example, despite exhaustive parameterization, the calculated results of 1,5 and 1,8 substituted compounds (such as **11** and **12**, or **19** and **20**, or **23** and **24**) were very close, while the experimental values of 1,5 and 1,8 substituted compounds were quite different, with the 1,8 ones having $\lambda_{\max}$ values at much longer wavelength than the 1,5 compounds.

4. Conclusions

Reasonable agreement between the calculated and experimental absorption and fluorescence wavelengths was generally achieved using simple geometrical models and a generalized, empirically derived set of bond parameters. The PPP MO method proved to be reasonably good at describing aromatics with symmetrically substituted phenylethynyl groups.

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