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Synthesis and fluorescence properties of 9,10-bis(phenylethynyl)anthracences

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Abstract

9,10-Bis(phenylethynyl)anthracences (BPEA's) are of great interest as fluorescent emitters for peroxyoxalate chemiluminescence. A series of substituted BPEA's were synthesized by condensing phenylethynyl magnesium bromide with substituted anthraquinones followed by acid hydrolysis and reduction by stannous chloride. Fluorescent quantum yields of 0.72–0.87 were found among most of the compounds, with 1-iodo-BPEA at 0.47 and 1,8-diphenoxy-BPEA at 0.51 as exceptions. Absorption and fluorescent emission data for all compounds are presented.

Keywords: Synthesis; 9,10-Bis(phenylethynyl)anthracence; Peroxyoxalate chemiluminescence; Fluorescent quantum yields; Phenylethynyl magnesium bromide

1. Introduction

Chemiluminescence materials are used in a variety of fields, especially in analytical chemistry and biological engineering [1,2]. Peroxyoxalate chemiluminescence is far superior to other known chemiluminescence processes both in quantum yield and light efficiency. A variety of linear fused aromatics with symmetrically substituted phenyethynyl groups have been synthesized and their fluorescent properties have been studied. Among these compounds, 9,10-bis(phenylethynyl)anthracences (BPEA's) have exhibited exceptionally high fluorescent quantum yields and excellent chemiluminescent performance [3,4].

Since a close relationship exists between chemiluminescence and fluorescence properties, a study involving fluorescence was carried out prior to evaluating chemiluminescence behavior. In this paper, six BPEA's were prepared and their fluorescent properties were examined. Six previously reported dyes were also prepared to compare our synthetic method with that employed by others and to corroborate the accuracy of our work in the determination of spectral properties.

2. Experimental

Mass spectra were recorded on a Finnigan Mat 312/SS200 GC/MS spectrometer (EI-MS, direct probe method). UV/visible and fluorescence spectra were obtained on a Shimadzu UV-3100 spec-

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trophotometer and a RF-5000 spectrofluoro-photometer, respectively. Melting points were determined on Yanaco MP-500 melting point (prism scope type) apparatus and are uncorrected. Elemental analyses were conducted with a Carlo Erba 1106 element analyzer.

2.1. Material

THF was purified by distilling reagent grade solvent followed by heating under reflux with sodium for 8–10 h. The solvent was then fractionally distilled and stored in the presence of fresh sodium wire in the dark. Anthraquinone (AQ), 2-chloroanthraquinone, 1,5-dichloroanthraquinone were obtained as commercial samples and were recrystallized before use. 1-Methoxyanthraquinone and 1,5-dimethoxyanthraquinone were prepared from 1-nitro- and 1,5-dichloroanthraquinone, respectively, by reacting the latter with sodium methoxide. 1-Phenoxy-, 1,5-diphenoxy-, 1,8-diphenoxyanthraquinone were prepared from corresponding nitro-anthraquinones by reacting the latter with phenol in the presence of KOH. 1-Fluoro-, 1-chloro-, 1-bromo-, 1-iodo-AQ were prepared from 1-aminoanthraquinone by diazotization and then treatment with fluoroboric acid, cuprous chloride, cuprous bromide and potassium iodide, respectively. All intermediates were recrystallized to give high purity.

2.2. Synthesis of substituted BPEA's

A THF solution of ethyl magnesium bromide was prepared by adding a solution of ethyl bromide (1.3 g, 0.012 mol) in THF (5 ml) to a mixture of magnesium powder (0.3 g, 0.013 mol) and THF 5 ml at 45–50°C. A solution of phenylacetylene (1.3 g 0.013 mol) in THF (1.5 ml) was added dropwise. After evolution of ethane ceased, a suspension of 0.0015 mol substituted anthraquinone in THF (5 ml) was added quickly and the mixture was then stirred under reflux for 0.5–24 h. The time needed varied as shown in Table 1. Into the cooled mixture was added HCl (10 ml, 1N) and eventually two layers were formed. The upper layer containing 9,10-bis(phenylethynyl)-9,10-dihydroanthracence-9,10-diol was collected, and on treatment with a warm solution of stannous chloride (2.0 g, 0.009 mol) in acetic acid (15 ml, 50%), a yellow or orange precipitate of crude BPEA's were formed immediately. The product collected by filtration, was washed with cold methanol, and dried. The crude BPEA's were then purified by using preparatory thin layer chromatography (silica gel GF254, eluent: *benzene*/cyclohexane = 3/1), followed by recrystallization from *benzene*/light petroleum. Melting points are given in Table 1, along with data from previous reports. Element analysis for C, H was conducted and the results for compounds that had not been reported previously are as follows: 1,5-diphenoxy ($C_{42}H_{26}O_2$, Found: C, 90.02; H, 4.74%. Calcd.: C, 89.68; H, 4.63%); 1,8-diphenoxy ($C_{42}H_{26}O_2$, Found: C, 90.04; H, 4.65%. Calcd.: C, 89.68; H, 4.63%); 1-phenoxy ($C_{36}H_{22}O$, Found: C, 91.91; H, 4.85%. Calcd.: C, 91.91; H, 4.68%); 1-bromo ($C_{30}H_{17}Br$, Found: C, 78.37; H, 3.66%. Calcd.: C,78.77; H, 3.71%); 1-iodo ($C_{30}H_{17}I$, Found: C, 71.23; H, 3.23%. Calcd.: C, 71.42; H, 3.37%). EI mass spectra had the base peak as the molecular ion for all compounds.

Table 1
Yields and melting points of BPEA's

Subsitution	Reaction time (h)	Yields (%)	Yields (%) [5,6]	M.P. (°C)	M.P. (°C) [5]
None	24	55	66	253–254	253–255
1-Chloro	24	47	58	203–204	204–205
2-Chloro	24	54	57	226–227	226–227
1,5-Dichoro	48	43	50	230(dec.)	226–227
1-Methoxy	10	33	48	193–194	194–195
1,5-Dimethoxy	5	55	61	213–214	214
1-Phenoxy	3	50		178–179	
1,5-Diphenoxy	10	48		238–240(dec.)	
1,8-Diphenoxy	10	45		212–214	
1-Fluoro	2	30		230–231	
1-Bromo	5	45		185–187	
1-Iodo	0.5	35		167–169	

2.3. Fluorescence spectra and quantum yields

Fluorescent quantum yields were determined using previosuly published procedures [3,4], with quinine sulfate as the reference standard. The absorption and fluorescent emission spectra were

recorded on a Shimadzu UV-3100 spectrophotometer, with the slit width set at 8 nm, and a Shimadzu RF-5000 spectrofluorophotometer, with the emission slit width and excitation slit width set at 10 nm and 2.5 nm, respectively. For each compound stock solutions were made at concentraiton that gave an absorbance of 0.7 at the excitation wavelength. Thus, for BPEA's the concentration was about 20 μM and for quinine sulfate it was 68 μM. Stock solutions were diluted precisely 100 fold, 200 fold or 400 fold to enable maximum fluorescent emission intensity to fit within the spectrofluorophotometer's measurement range. Though solvents such as THF and dibutyl phthalate could have been selected, all measurements were conducted in benzene except for quinine sulfate (1N H_2SO_4 used), in order to generate data that could be compared directly with literature data in which benzene was used [4].

3. Results and discussion

3.1. Synthesis

The standard method for the preparation of BPEA's is a two-step synthesis [5]. In step 1, a solution of 9,10-bis(phenylethynyl)-9,10-dihydroanthracene-9,10-diol is formed by the addition of lithium phenylacetylide to the anthraquinone derivative in a solvent such as THF. The diol is isolated and purified prior to step 2 where it undergoes stannous chloride reduction to the target BPEA's. Modifications made to the standard method are shown in Scheme 1. The fact that phenylethynyl magnesium bromide is easier to prepare and handle than lithium phenylacetylide led us to develop a method employing the former instead of lithium phenylacetylide. The diols that was obtained by condensing phenylethynyl magnesium bromide with the anthraquinones, was treated directly by stannous chloride without isolating the diol. Using the revised method twelve BPEA's were prepared in overall yields of 30–55%. Although reaction time was found to be a key factor in determining reaction yields, no attempt was made to optimize the yields of individual compounds.

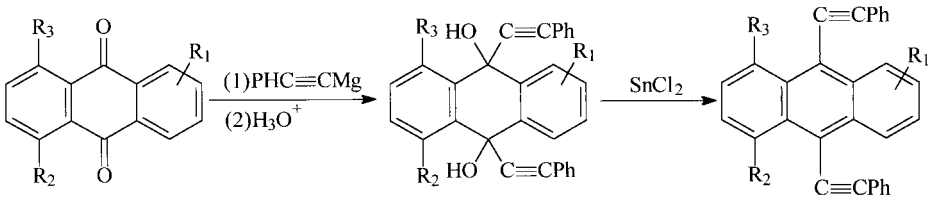
For the six previously reported compounds, yields and melting points obtained using the modified method were compared with published data (Table 1). We found that the melting points were in agreement, while the yields were generally lower than those from the standard method. However, due to its ease of operation, the modified method might still be a practical route to BPEA's on the laboratory scale.

3.2. Quantum yields

Quantum yields were calculated by use of the following equation:

$$Q_x = Q_r(A_r/A_x)(\lambda_r/\lambda_x)(A_{F,x}/A_{F,r})(\eta_x^2/\eta_r^2)$$

Here, subscript r and x refer to the unknown and the standard, respectively. Q is the quantum yield, A is the absorbance of the solution at the excitation wavelength (λ), A_F is the area of the corrected fluorescence spectrum, and η is the refractive index of solvent. The reference standard (quinine sulfate in 1.0 N H_2SO_4) had a quantum



R_1=F,Cl,Br,I,OMe,OPh
R_2=H,Cl,OMe,OPh
R_3=H,OPh

Scheme 1.

yield of 0.55. The absorbance was obtained from the dilution ratio of the absorbance solution, which in our operation was 1/100, 1/200 or 1/400. The term $\eta^2(\text{benzene})/\eta^2(1.0\text{N } H_2SO_4) = 1.26$ was used. The quantum yields obtained show minor deviation from those reported by Henhela [4]. The excitation wavelength recorded in each case is also listed in Table 2. Good agreement was found between our data and literature values for the previously reported. Among the six compounds whose fluorescence properties have not been reported, 1-fluoro and 1-bromo BPEA showed a high quantum yield (0.87). Heavy atom effect might be responsible for 1-iodo BPEA's low value of 0.47. Compared to the other methoxy or phenoxy BPEA's, the quantum yield of 1,8-diphenoxy BPEA (0.51) is surprisingly low.

Table 2
Quantum yields of BPEA's

Substitution	λ_{ex}[a] (nm)	Q	Q[4]
None	440	0.86	0.85
1-Chloro	451	0.84	0.87
2-Chloro	442	0.85	0.87
1,5-Dichoro	465	0.83	0.84
1-Methoxy	455	0.74	0.73
1,5-Dimethoxy	467	0.76	0.76
1-Phenoxy	455	0.85	
1,5-Diphenoxy	465	0.72	
1,8-Diphenoxy	470	0.51	
1-Fluoro	445	0.87	
1-Bromo	450	0.87	
1-Iodo	450	0.47	

[a] Wavelength at which Q values were calculated.

Table 3
Absorption and fluorescence spectroscopic data

	Absorption	Fluorescence		
	λ_{max}nm ($\varepsilon/10^4 dm^3 mol^{-1} cm^{-1}$)	λ_{ex}[a] (nm)	λ_{em} (nm)	($\lambda_{em} - \lambda_{ex}$) (nm)
None	457(3.59), 440(3,42)	459	476	17
1-Chloro	470(3.23), 451(3.01)	474	491	17
2-Chloro	461(3.17), 441(3.00)	464	480	16
1,5-Dichoro	487(3.28), 463(2.87)	491	510	19
1-Methoxy	478(2.97), 455(2.88)	481	500	19
1,5-Dimethoxy	493(3.14), 465(2.82)	494	511	17
1-Phenoxy	475(3.18), 456(3.19)	473	497	24
1,5-Diphenoxy	489(2.95), 470(2.88)	493	512	19
1,8-Diphenoxy	497(3.03), 473(3.04)	500	522	22
1-Fluoro	468(3.09), 445(2.89)	470	484	14
1-Bromo	472(3.28), 452(3.02)	474	494	20
1-Iodo	473(3.87), 454(3.55)	476	498	22

[a] λ_{ex} represents maxima of excitation spectra.

3.3. Absorption and fluorescence properties

Table 3 provides a summary of the visible absorption data and the fluorescence data (excitation and emission maxima and Stokes' shift) of BPEA's. From these results it was apparent that both electron-donating and electron-withdrawing groups have a bathochromic affect the visible and fluorescence spectra with 1,8-diphenoxy-BPEA giving a shift from 476 nm to 522 nm. It can also be seen that electron-donating phenoxy and methoxy groups give a greater bathochromic shift than fluorine, chlorine and bromine, while iodine causes a bathochromic shift that is comparable to the phenoxy group. Within the series of halogenated BPEA's, spectral shifts increase slightly in the order of I > Br > Cl > F.

4. Conclusions

1. A series of BPEA's were prepared with overall yields of 30–55% using a modified version of a previously reported method. In the new method, the intermediate diol was used without isolation.
2. Fluorescence yields of these BPEA's were found to range from 0.47 to 0.87.
3. Both electron-donating and electron-withdrawing groups have a bathochromic effect on the absorption and fluorescence spectra. A relatively small Stoke's shift (14–24 nm) was observed for all compounds.

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