Synthesis and Absorption/Emission Spectroscopic Properties of Bis(phenylethynyl)benzenes and 9,10-Bis(phenylethynyl)anthracenes

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A series of bis(phenylethynyl)benzenes 3 and 9,10-bis(phenylethynyl)anthracenes 4 was synthesized by bromination–dehydrobromination reaction or newly developed direct C≡C triple bond formation reaction from styrylstilbenes 1 or distyrylanthracenes 2. Subsequently systematic investigations were carried out on their absorption and fluorescence spectra, and their chemiluminescence properties. The following points are apparent; (a) a linear relationship between $\bar{v}$ and Hammett's σ_p of compounds 3 and 4 was observed, (b) a significant relationship between the Stokes' shift of 4 and σ_p was observed and (c) in the series of compounds 4 the electron-donating ability of the substituents has a pronounced effect on the chemiluminescence properties.

Our studies towards the development of new fluorescent and chemiluminescent probes for analytical and/or biological studies have been performed on a series of styrylstilbenes 1 and distyrylanthracenes 2.[1] We have further been interested in the synthesis of a series of bis(phenylethynyl)benzenes 3 or bis(phenylethynyl)anthracenes 4 in order to examine their absorption and emission spectroscopic properties. In this paper, we report on the synthesis, absorption, fluorescence and chemiluminescence spectroscopic properties together with some calculated results [Pariser–Parr–Pople selfconsistent field configurational interaction molecular orbital (PPP–SCF–CI–MO) calculations] on 3 and 4, and their comparison with the spectroscopic properties of styrylstilbenes 1 and distyrylanthracenes 2.

Results and Discussion

Synthesis of Bis(phenylethynyl)benzene and Bis(phenylethynyl)anthracene Derivatives.—Bis(phenylethynyl)benzenes (R = OMe, Me, H, Br) were prepared by dehydrobromination of the bromo-adduct of the alkene 1 with KOBuᵗ in THF (tetrahydrofuran). Their isolated yields ranged between 39 and 76%. On the contrary, no fruitful results were obtained in the case of R = NEt₂, NH₂, CO₂Et, CN, NO₂. Bis(phenylethynyl)anthracenes (R, R′ = OMe, Me, H and Cl) were afforded from the corresponding distyrylanthracenes[1] by the above method. However, the other acetylenes (R, R′ = NEt₂ and CN, and R = NO₂, R′ = OMe) could not be prepared by the classical method because a bromination reaction did not proceed to the corresponding alkenes. Fortunately, we have found that the acetylenes 4a, f, g were obtained at room temperature from the corresponding alkenes 2a, f, g by treatment with a large excess of KOBuᵗ in DMF (*N,N*-dimethylformamide) containing trace amounts of oxygen.[2] Moreover, the reaction occurred hardly at all in DMF degassed with nitrogen, but proceeded smoothly after bubbling oxygen into the above mixture. Since attempts to obtain the corresponding bis(phenylethynyl)anthracenes from the alkenes 2b–e have so far been impossible, it is supposed that the presence of such substituents leads to electronic perturba-
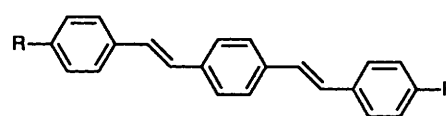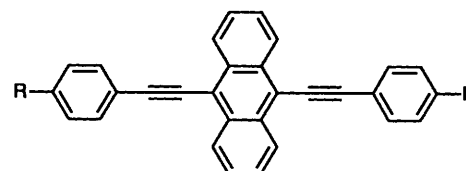

1
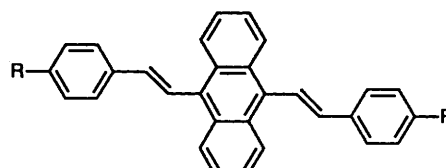
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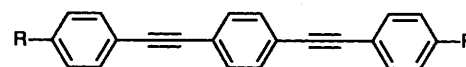
3a R = OMe
3b R = Me
3c R = H
3d R = Br

4a R,R′ = NEt₂
4b R = OMe
4c R = Me
4d R = H
4e R = Cl
4f R = CN
4g R = NO₂, R′ = OMe

tion on both benzene rings. The reaction mechanism of the oxidative dehydrogenation of the CH=CH bond to the triple bond is now being investigated by the use of EPR.‡

Absorption Spectroscopic Properties.—Table 1 summarizes the absorption spectroscopic data of the longest wavelength

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region of bis(phenylethynyl)benzenes **3** and bis(phenylethynyl)-anthracenes **4**. From these results, it was apparent that both electron-donating and electron-withdrawing groups in the *para*-
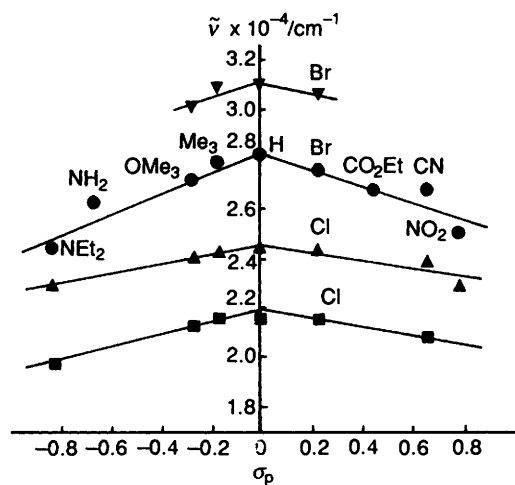

Fig. 1 Correlation diagram between wavenumber (absorption) and σ_p in chloroform [compounds **1** (●), compounds **2** (▲), compounds **3** (▼), compounds **4** (■)]

Table 1 Absorption spectra of compounds **3a–3d** and **4a–4g**

Compd.	R	σ_p	λ_{max}/nm ($\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1}) CHCl$_3$	Dioxane
3a	OMe	−0.27	332(5.82)	331(8.71)
3b	Me	−0.17	325(6.20)	324(6.79)
3c	H	0	322(4.98)	320(6.19)
3d	Br	0.23	327(7.37)	326(7.72)
4a	NEt$_2$	−0.83	490(4.98)	486(5.28)
			507(4.91)	505(5.19)
4b	OMe	−0.27	450(3.96)	450(4.13)
			471(3.94)	471(4.17)
4c	Me	−0.17	443(3.89)	441(3.83)
			466(4.00)	466(4.04)
4d	H	0	440(3.42)	438(3.46)
			462(3.62)	461(3.68)
4e	Cl	0.23	442(3.72)	441(3.77)
			465(3.51)	466(3.64)
4f	CN	0.66	455(4.47)	450(4.32)
			480(4.37)	477(4.49)
4g	NO$_2$, OMe		458(2.94)	455(3.17)

position of compounds **3** and **4** affect the absorption bathochromically as in the case of compounds **1** and **2**.

As shown in Fig. 1, the linear relationship between wavenumber and Hammett's σ_p of compounds **3** and **4** was observed as well as in the styryl series (**1** and **2**). Bathochromic shifts were observed for the absorption spectra of bis(phenylethynyl)anthracenes **4** compared with those of **1**,[1] **2**[1] and **3**.

Fluorescence Spectroscopic Properties.—In Table 2, the fluorescence spectroscopic data [excitation and emission maxima, relative fluorescence intensity (RFI) and Stokes' shift] of the compounds studied are summarized. In the bis(phenylethynyl)anthracene series **4**, the excitation maximum occurs at λ *ca.* 470 and emission maxima are at 475–560 nm; therefore a large bathochromic shift was observed in the emission spectra compared with **1**–**3** except for R = NO$_2$ in **1**[1] (Table 2).

Simultaneously, Stokes' shifts of 8–86 nm were observed in the bis(phenylethynyl)anthracene series; apparently the electronic character of the substituents seems to reflect these results. As regards RFI-values, it was obvious that the ratio of the RFI-values is 100:2:70:80 by comparison of the highest values in the four series **1**–**4**, *i.e.*, **1**; R = Br in dioxane (C), **2**; R = CN in dioxane (D), **3**; R = OMe in dioxane (A), **4**; R = H in CHCl$_3$ (B) (Table 2). Relative quantum yields for each compound were obtained using quinine sulfate as a standard.[1,4] The results are summarized in Table 3. In both series, the compounds except for **4** [with R = NEt$_2$, Cl, (NO$_2$, OMe)] proved to have comparable or larger values than quinine sulfate (0.55). It was also shown that the quantum yields of compounds **3** are comparable to those of compounds **1** and the series of compounds **4** have larger values than the series of compounds **2**. The reason of the discrepancy between ours and the reported quantum yields[11] on **4b**, **4d** and **4e** is not clear except for the difference in solvent used.

Table 3 Quantum yields of compounds **3a–3d** and **4a–4g** in CHCl$_3$

Compd.	R	Quantum yield, φ	Compd.	R	Quantum yield, φ
3a	OMe	0.59	**4a**	NEt$_2$	0.16[a]
3b	Me	0.93	**4b**	OMe	0.55[a](0.89[b])
3c	H	0.56	**4c**	Me	0.57[a]
3d	Br	0.54	**4d**	H	0.58[a](0.85[b])
			4e	Cl	0.45[a](0.82[b])
			4f	CN	0.83[a]
			4g	NO$_2$, OMe	0.0003[a]

[a] Apparent value. [b] Ref. 11 (in benzene).

Table 2 Fluorescence spectra of **3a–3d** and **4a–4g** [*]

Compd.	R	σ_p	λ_{ex}/nm CHCl$_3$	Dioxane	λ_{em}/nm CHCl$_3$(RFI[a])	Dioxane(RFI[a])	(λ_{em} − λ_{ex})/nm CHCl$_3$	Dioxane
3a	OMe	−0.27	334	333	368(0.67)	364(1.00)[c]	34	31
3b	Me	−0.17	328	327	357(0.69)	354(0.67)	29	27
3c	H	0	328	333[d]	370(0.54)	366(0.63)	42	33
3d	Br	0.23	330	328	358(0.64)	357(0.71)	28	29
4a	NEt$_2$	−0.83	472	471	558(0.24)	545(0.36)	86	76
			488	485	558(0.24)	545(0.35)	70	60
4b	OMe	−0.27	470	470	490(0.66)	488(0.80)	20	18
4c	Me	−0.17	468	468	481(0.84)	479(0.90)	13	11
4d	H	0	467	465	475(1.00)[b]	474(0.90)	8	9
4e	Cl	0.23	468	468	480(0.77)	479(0.85)	12	11
4f	CN	0.66	470	470	492(0.95)	487(0.93)	18	17
4g	NO$_2$, OMe		468[e]	468	530(0.01)	538(0.09)	62	70

[a] Relative fluorescence intensity. [b] Measured relative to compound **4d** (compound B in text). [c] Measured relative to compound **3a** (compound A in text). [*] Sample concentration was 10^{-7} mol dm^{-3}, except for [d] (10^{-8} mol dm^{-3}) and [e] (10^{-5} mol dm^{-3}).

Table 4 Experimental and calculated results for some representatives of series **3** and **4**

Compd.	R	Absorption, $\bar{v}/10^4$ cm^{-1}			Fluorescence, $\bar{v}/10^4$ cm^{-1}		
		CHCl$_3$	Dioxane	A[a]	CHCl$_3$	Dioxane	B[b]
3a	OMe	3.01	3.02	2.89	2.71	2.74	2.63
3c	H	3.11	3.12	2.97	2.70	2.73	2.65
4a	NEt$_2$	1.97	1.98	1.94	1.79	1.83	—
4b	OMe	2.12	2.12	2.11	2.04	2.05	—
4d	H	2.16	2.17	2.14	2.11	2.11	—
4f	CN	2.08	2.10	2.09	2.03	2.05	—

[a] Method A: Standard PPP-MO calculation [12] using the parameter sets proposed by Griffiths.[13] [b] Method B: Calculation of fluorescence using bond order–bond length relationship and bond length–resonance integral (β) relationship cited in the literature.[14] For **4a–f** see text.

Table 5 Relative chemiluminescence intensities of compounds **3a–3d** and **4a–4g**

Compd.	R	RCI[a]	Compd.	R	RCI[a]
DPA		1.00	**4a**	NEt$_2$	24.07
3a	OMe	nd[b]	**4b**	OMe	7.15
3b	Me	nd[b]	**4c**	Me	4.36
3b	H	nd[b]	**4d**	H	3.19
3d	Br	nd[b]	**4e**	Cl	2.32
			4f	CN	1.32
			4g	NO$_2$, OMe	nd[b]

[a] Relative chemiluminescence intensity; the RCI of DPA (9,10-diphenylanthracene) was arbitrarily taken as 1.0. [b] nd: non-detectable.

MO Calculations.—Molecular orbital calculations on some representatives of series **3** and **4** were carried out by the standard PPP method [12] using the parameters proposed by Griffiths [13] (values of $\beta = -2.80$ eV for the C≡C triple bond and $\beta = -2.33$ eV for the formal single bond adjacent to the acetylenic bond, respectively, were used). Fluorescence maxima of compounds **3** were obtained by the method proposed by one of us (W. F.).[14] The results of these calculations (wavenumbers $\bar{v}$ of the electronic transitions) are summarized in Table 4 together with the corresponding experimental data.

As can be seen from the data presented (Table 4) the agreement between calculation transition energies and experimental absorption maxima both for compounds **3** as well as compounds **4** is quite satisfactory. In particular, the substituent effects on UV–VIS spectra in both series are well reproduced by the calculations. In addition, the experimentally observed batho-chromic shifts of compounds **4** as compared to compounds **3** (as well as compounds **1** and **2**[1]) as also obtained using the calculations. It is interesting to note that in compounds **3** the methoxy group exerts a significant bathochromic effect on the absorption maximum whereas the fluorescence spectra are only marginally influenced by the presence of this substituent (see **3a** vs. **3c** in Table 4). Our calculations are in good agreement with this experimental finding. For compounds **4**, however, despite satisfactory results for absorption spectra, the calculated fluorescence maxima appeared rather unrealistic. Obviously, these types of compounds [Distyrylanthracenes **2**[1] and Bis(phenylethynyl)anthracenes **4**] present a limitation for the applicability of the proposed method for the calculation of fluorescence spectra.

Chemiluminescence Properties.—As in the previous paper,[1] we were very much interested in the chemiluminescence properties of the compounds in series **3** and **4** and their availability as chemiluminescent probes. For examination of the chemilum-inescence properties of the fluorescent compounds as enhancers, the peroxyoxalate chemiluminescent reaction system was used by the flow injection method developed in our laboratory[5] using bis(2,4,6-trichlorophenyl)oxalate (TCPO) as an oxalate, hydrogen peroxide, and 9,10-diphenylanthracene (DPA) as a standard fluorescent compound. Table 5 shows the relative chemiluminescence intensities (RCI) estimated from the calibration curve of each compound, where the RCI of DPA was arbitrarily taken as 1.0. The RCI-values (1–24) were observed in the series **4** except for **4g**.

On the other hand, RCI-values could hardly be detected in the series **3** or **2** (except when R = H). It was apparent that the high RCI-value (for the representative electron-donating substi-tuent, NEt$_2$) in the anthracene series **4** would reflect a high efficiency of the chemiluminescence reaction. The compound **4a** should be a promising candidate for an enhancer in the peroxyoxalate chemiluminescent reaction system.

Experimental

M.p.s were measured on a Yanagimoto MP-35 melting point apparatus and are uncorrected. UV–VIS spectra were recorded on a Shimadzu UV-250F or a Hitachi UV-250 spectrometer, IR spectra on a JASCO 810 spectrophotometer, ^{1}H NMR spectra on CDCl$_3$ solutions in a JEOL FX-90Q or a JEOL JNM-GX-400 spectrometer with SiMe$_4$ as the internal standard (*J* values are given in Hz), and mass spectra on a JEOL JMS-DX 303 instrument. Fluorescence spectra were recorded on a Hitachi 650-10S fluorescence spectrophotometer and were corrected by the method of Lippert *et al.* unless otherwise noted.[4]

1,4-Bis(phenylethynyl)benzene **3a**.—To a mixture of the styryl-stilbene **1a**[1] (0.30 g, 0.88 mmol) in CHCl$_3$ (120 cm^3) was added a solution of bromine (0.78 g, 9.7 mmol) in CHCl$_3$ (10 cm^3) and the mixture was stirred for 1 h. The resulting crystals were filtered, washed with ether, and then dried under reduced pres-sure (crude bromide, 0.49 g, 85%). After the crude crystals (0.20 g, 0.30 mmol) in dry THF (120 cm^3) had been stirred with KOBu^t (0.40 g, 3.6 mmol) for 30 min under reflux, the resulting solution was poured into water (100 cm^3). The organic layer was extracted with benzene, and the extract was washed with water and dried (MgSO$_4$). The colourless crystals [0.09 g, 90%; 77% (2 steps)] obtained by evaporation of extract were recrystallized from ether to give compound **3a**, m.p. 216–218 °C (Found: C, 85.0; H, 5.6. C$_{24}$H$_{18}$O$_2$ requires C, 85.2; H, 5.4%); v_{max}(KBr)/cm^{-1} 2200 (C≡C); δ_H(CDCl$_3$) 3.83 (6 H, s, OMe), 6.82–7.51 (8 H, m, ArH) and 7.46 (4 H, s, ArH); EI-MS (*m/z*) 338 (M$^+$).

Compounds **3b–3d** were prepared according to the above method.

Compound **3b**: Colourless crystals, 44%; m.p. 218–220 °C (lit.,[6] 215–216 C) (Found: C, 94.2; H, 6.0. C$_{24}$H$_{18}$ requires C, 94.1; H, 5.9%); v_{max}(KBr)/cm^{-1} 2200 (C≡C); EI-MS (*m/z*) 306 (M$^+$).

Compound **3c**: Colourless crystals, 47%; m.p. 186–188 °C (lit.,[7] 172–175 °C) (Found: C, 94.6; H, 5.6. C$_{22}$H$_{14}$ requires C, 94.9; H, 5.1%); v_{max}(KBr)/cm^{-1} 2200 (C≡C); δ_H(CDCl$_3$) 7.11–7.50 (10 H, m, ArH) and 7.35 (4 H, s, ArH); EI-MS (*m/z*) 278 (M$^+$).

Compound **3d**: Colourless crystals, 39%; m.p. 281–283 °C (Found: C, 60.4; H, 3.0. C$_{22}$H$_{12}$Br$_2$ requires C, 60.6; H, 2.8%); v_{max}(KBr)/cm^{-1} 2200 (C≡C); δ_H(CDCl$_3$) 7.23–7.45 (8 H, m, ArH) and 7.49 (4 H, s, ArH); EI-MS (*m/z*) 436 (M$^+$).

Bis(phenylethynyl)anthracenes **4**.—*Bromination–dehydrobro-mination method.* Compound **4b** was synthesized according to

the above procedure: orange crystals, 16% (2 steps); m.p. 244–246 °C (lit.,[8] 240–241 °C) (Found: C, 87.3; H, 5.3. $C_{32}H_{22}O_2$ requires C, 87.7; H, 5.4%); v_{max}(KBr)/cm^{-1} 2190 (C≡C); δ_H(CDCl$_3$) 3.89 (6 H, s, OMe), 6.98 (4 H, d, J 9.0, PhH), 7.56–7.76 (8 H, m, PhH and ArH) and 8.62–8.73 (4 H, m, ArH); EI-MS (m/z) 438 (M$^+$).

Compound 4c: yellowish orange crystals, 30%; m.p. 257–258 °C (Found: C, 94.4; H, 5.6. $C_{32}H_{22}$ requires C, 94.6; H, 5.5%); v_{max}(KBr)/cm^{-1} 2190 (C≡C); δ_H(CDCl$_3$) 2.43 (6 H, s, Me), 7.21–7.71 (8 H, m, PhH and ArH) and 8.63–8.74 (4 H, m, ArH); EI-MS (m/z) 406 (M$^+$).

Compound 4d: orange crystals, 10%; m.p. 251–253 °C (lit.,[9] 253–255 °C and lit.,[10] 249–250 °C) (Found: C, 94.5; H, 5.0. $C_{30}H_{18}$ requires C, 95.2; H, 4.8%); v_{max}(KBr)/cm^{-1} 2200 (C≡C); δ_H(CDCl$_3$) 7.40–7.84 (14 H, m, PhH and ArH) and 8.64–8.75 (4 H, m, ArH); EI-MS (m/z) 378 (M$^+$).

Compound 4e: yellowish orange crystals, 25%; m.p. 250–251 °C (lit.,[8] 258–260 °C) (Found: C, 80.3; H, 3.8; Cl, 16.2. $C_{30}H_{16}Cl_2$ requires C, 80.6; H, 3.6; Cl, 15.84%); v_{max}(Nujol)/cm^{-1} 2200 (C≡C); δ_H(CDCl$_3$) 7.43 (4 H, d, J 8.8, PhH), 7.59–7.70 (4 H, m, ArH), 7.71 (4 H, d, J 8.8, PhH) and 8.60–8.71 (4 H, m, ArH); EI-MS (m/z) 446 and 448 (M$^+$).

Direct formation of acetylenes 4 *from the corresponding ethylenes* 2. Compounds 4a, 4f and 4g were prepared according to the method recently reported.[2] Compound 4a: yellowish orange crystals, 28%; m.p. 258–260 °C (Found: C, 87.2; H, 7.0; N, 5.3. $C_{38}H_{36}N_2$ requires C, 87.7; H, 7.0; N, 5.4%); v_{max}(Nujol)/cm^{-1} 2200 (C≡C); δ_H(CDCl$_3$) 1.22 (12 H, t, J 7.0, Me), 3.43 (8 H, q, J 7.0, CH$_2$), 6.70 (4 H, d, J 9.0, PhH), 7.52–7.63 (4 H, m, ArH), 7.61 (4 H, d, J 9.0, PhH) and 8.63–8.74 (4 H, m, ArH); EI-MS (m/z) 520 (M$^+$).

Compound 4f: orange crystals; m.p. 324–325 °C (Found: C, 89.0; H, 4.0; N, 6.4. $C_{32}H_{16}N_2$ requires C, 89.7; H, 3.8; N, 6.5%); v_{max}(Nujol)/cm^{-1} 2210 (C≡C) and 2240 (C≡C); δ_H(CDCl$_3$) 7.63–7.92 (12 H, m, PhH and ArH) and 8.59–8.70 (4 H, m, ArH); EI-MS (m/z) 428 (M$^+$).

Compound 4g: orange crystals; m.p. 263–265 °C (Found: C, 81.6; H, 4.6; N, 3.1. $C_{31}H_{19}NO_3$ requires C, 82.1; H, 4.2; N, 3.1%); v_{max}(Nujol)/cm^{-1} 2200 (C≡C); δ_H(CDCl$_3$) 3.89 (3 H, s, OMe) and 6.94–8.76 (16 H, m, PhH and ArH); EI-MS (m/z) 453 (M$^+$).

Acknowledgements

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