Synthesis and Absorption/Emission Spectral Properties of Styrylstilbene and Distyrylanthracene Derivatives

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A series of *para*-substituted styrylstilbenes **I** and 9,10-distyrylanthracenes **II** was synthesized by Wittig or Arbusov–Horner reaction as a key step. Subsequently, systematic investigations were carried out on their absorption and fluorescence spectra, and their chemiluminescence properties. It has become apparent that substituent effects are present in each π-electron system. Pariser–Parr–Pople self-consistent field configurational interaction molecular orbital (PPP-SCF-CI-MO) calculations on some representatives of each series **I** and **II** were put into practice by considering the geometry of excited states, and the values obtained were well correlated with the experimental results.

Organic luminescent materials are widely used in the basic as well as applied research fields and various kinds of organic luminescent materials are now known.[1] During the course of our studies to develop new fluorescent as well as chemiluminescent probes for analytical and/or biological studies, we have prepared some heterocyclic fluorescent compounds, *i.e.*, benzofuran,[2] benzothiazole,[3] pyrylium,[4] or pyrimidopyrimidine[5] derivatives and also reported on their analytical applications. Moreover, we have recently reported the fluorescence spectral characteristics of α,ω-di-1- and 9-anthrylpolyynes.[6] We have been further interested in the synthesis of series of styrylstilbenes **I**, distyrylanthracenes **II**, bis(phenylethynyl)benzenes **III** or bis(phenylethynyl)anthracenes **IV** in order to examine their absorption and emission spectral properties. In this paper, we report on their synthesis, absorption, fluorescence and chemiluminescence spectral properties together with calculated results (PPP-SCF-MO) on a series of *para*-substituted styrylstilbene **I** and distyrylanthracene derivatives **II**. Furthermore, we plan to report our results on the synthesis and properties of compounds of types **III** and **IV** in the near future.

Results and Discussion

Synthesis of Styrylstilbene and Distyrylanthracene Derivatives.—Styrylstilbenes are a well known class of compounds showing high fluorescence activity[7] and some synthetic methods are already known for their preparation. We have prepared a series of *para*-substituted styrylstilbenes **5a–l** by the method of Campbell and Macdonald[8] by using a Wittig reaction as shown in Scheme 1. Campbell and Macdonald reported on the synthesis of a series of *para*-substituted styrylstilbenes (R = NH_2, MeO, Me, H, CN, NO_2) by Wittig reaction using lithium ethoxide as base, and we have also prepared these compounds by the same method (except R = NH_2, see Experimental section), as well as those derivatives with R = NEt_2, Br, CO_2Et; C_6H_4R = 1-anthryl, 9-anthryl and biphenyl-4-yl. Their isolated yields ranged between 30–80% and the compounds obtained had almost exclusively the *E,E*-configuration suggested from ^1H NMR spectroscopic analysis. Interestingly, a *trans*-esterification reaction was encountered with the *p*-methoxycarbonylbenzaldehyde **4g**, yielding not the methyl ester but instead the ethyl ester derivative of styrylstilbene, compound **5g**. For the preparation of the distyrylanthracene series, we tried at first to prepare the bisphosphonium salt[9] of 9,10-bis(chloromethyl)anthracene[10] corresponding to compound **3** in Scheme 1 but since the desired salt was only poorly obtained in our hands, we then pursued other approaches. Anthracene-9,10-dicarboxaldehyde **6**,[11] easily available from 9,10-bis(chloromethyl)anthracene, was subjected to Wittig reaction with various *para*-substituted benzylphosphonium salts **7** (R = MeO, Me, H, Cl) to afford the desired distyrylanthracenes in 55–71% yield. When the *p*-nitrobenzylphosphonium halide was treated with dialdehyde **6**, the half-condensed product **9** was exclusively precipitated and it could be used to prepare unsymmetrically substituted distyrylanthracenes (Scheme 2).

Owing to the fruitless results obtained by this method in the cases of R = NMe_2, CN or NO_2, we then used the method of Okazaki *et al.*,[12] *i.e.*, Arbusov–Horner reaction to prepare the bisphosphonate **12** from dihalide **10**. The reaction using MeONa as base in dimethylformamide (DMF) afforded the desired compounds of type **II** (R = CN, NO_2 or 9-anthryl) (Scheme 3). When R = NMe_2, the reaction proceeded with Bu^{t}OK as base in DMF to afford compound **13**‡ as by-product (Scheme 3).

Absorption Spectroscopic Properties.—Table 1 summarizes the absorption spectroscopic data of the longest wavelength region of styrylstilbenes **I** as well as of distyrylanthracenes **II**. From the results, it is apparent that both electron-donating and electron-withdrawing groups in the *para*-position affect the absorption bathochromically and no significant solvent effect was observed between the two solvents studied. The linear relationship between wavenumber and Hammett's σ_p of the compounds was observed as indicated in Fig. 1 and the substituent effect observed was larger in the styrylstilbene series than in the distyrylanthracene series. Bathochromic shifts were observed for the absorption spectra of distyrylanthracenes compared with those of the corresponding styrylstilbenes.

Fluorescence Spectroscopic Properties.—The fluorescence spectroscopic data of the compounds studied are summarized in Table 2. In the styrylstilbene series, the excitation maxima are at 360–400 nm, the emission maxima are at 415–460 nm in both solvents and only for R = NO_2 in $CHCl_3$ does the

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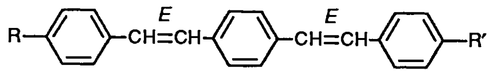
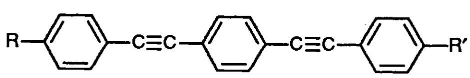
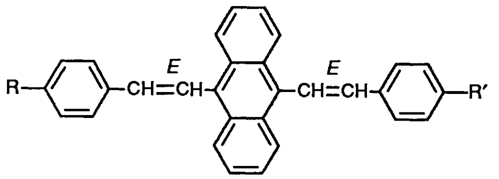
‡ Presumably the oxidation of a double bond to form a triple bond had occurred. We are now investigating the scope of such reactions.



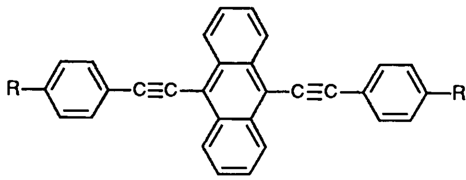
I



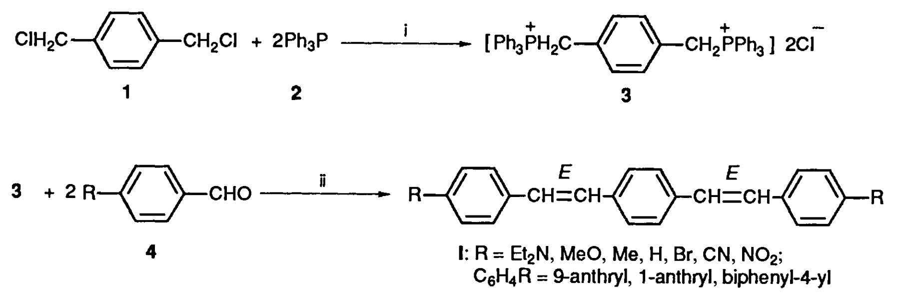
III



II

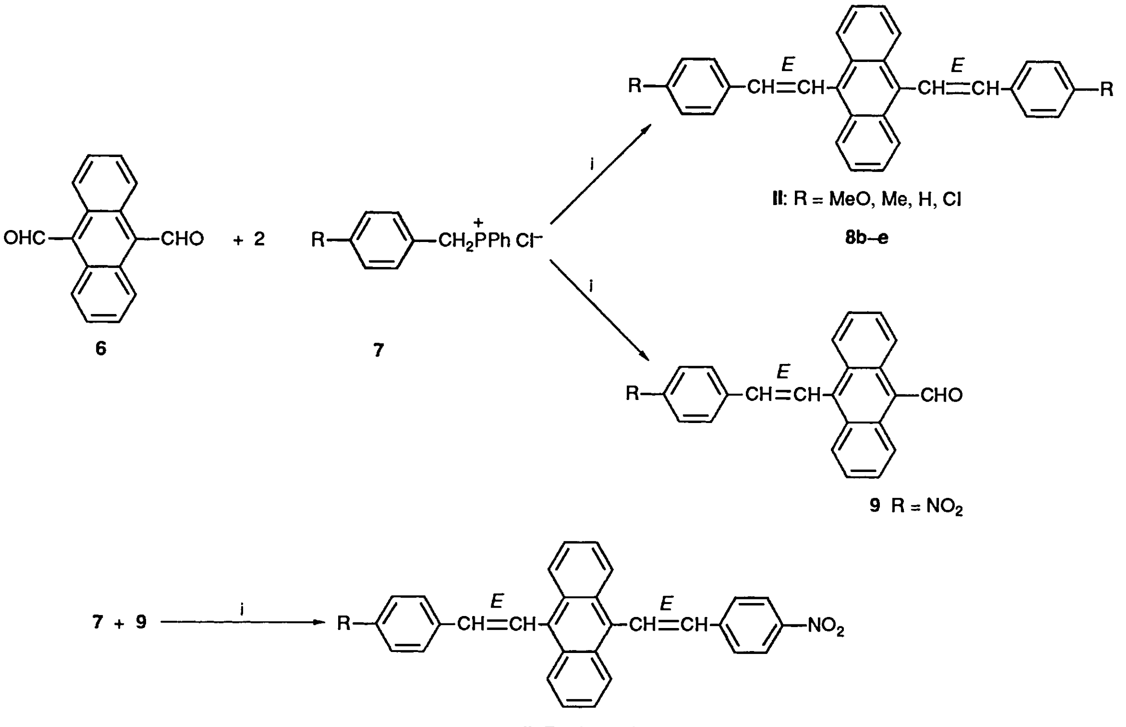


IV



5a, c-f, h-l

Scheme 1 *Reagents and conditions:* i, heat; ii, EtOLi, EtOH

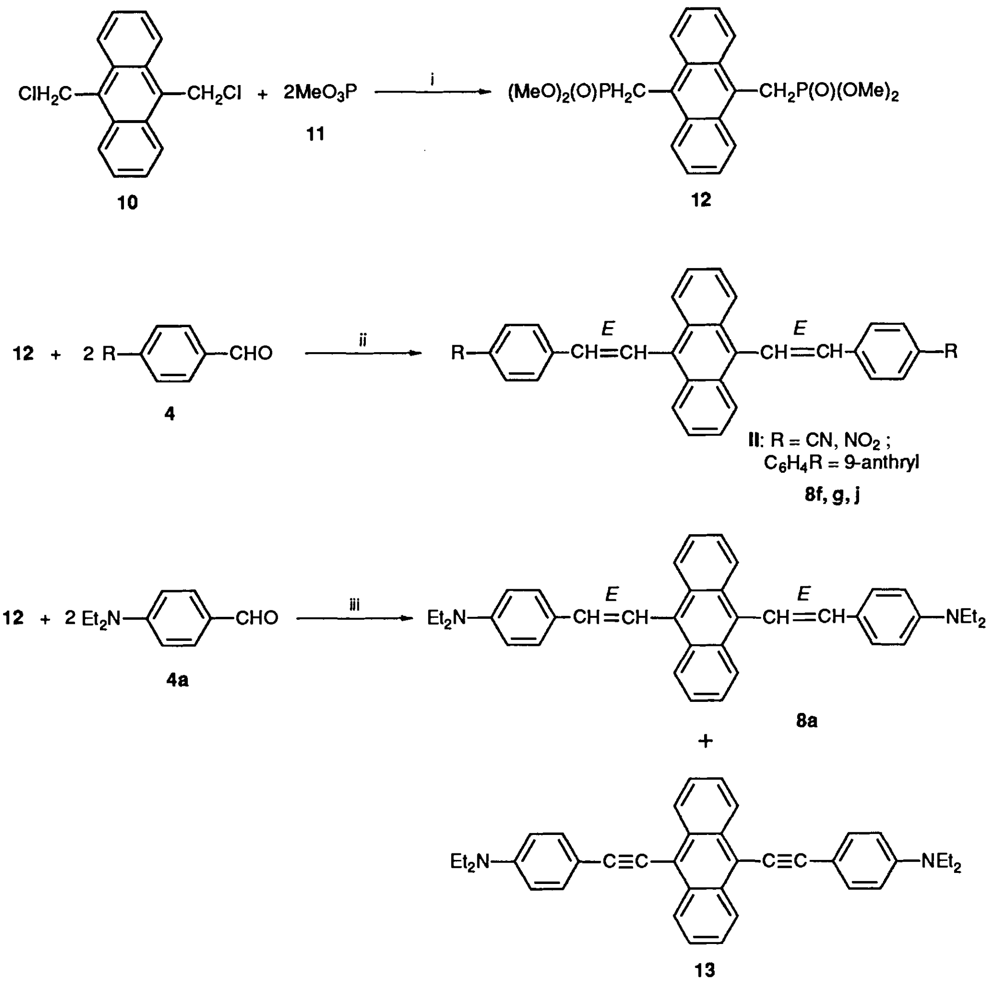


8h, i

Scheme 2 *Reagents:* i, MeOLi, DMF

emission maximum move to exceptionally long wavelength. An enhanced solvent effect was observed for R = NO_2 as well as for R = NMe_2; this effect was also observed, although to a lesser extent, in the distyrylanthracene series. In the distyrylanthracene series, excitation maxima occur at ~420 nm and emission maxima are at 550–570 nm; hence a large bathochromic shift was observed, especially in the emission spectra, compared with the styrylstilbene series (Fig. 2). At the same time, large Stokes' shifts were evidently observed in the distyrylanthracene series compared with the styrylstilbenes, again with R = NO_2 as the sole exception.

In Table 1 and Table 2 are compared the relative fluorescence intensity (RFI)-values of the compounds under investigation. Although no straightforward relationship was observed, the derivatives with small σ_p-values have, in general, higher RFI-values and relatively large solvent effects were observed for each value. By comparison of the highest values in both series (**I** and **II**), *i.e.*, **I**; R = Br in dioxane with **II**; R = CN in dioxane, it was



Scheme 3 *Reagents and conditions*: i, heat; ii, MeONa, DMF; iii, Bu^{t}OK, DMF

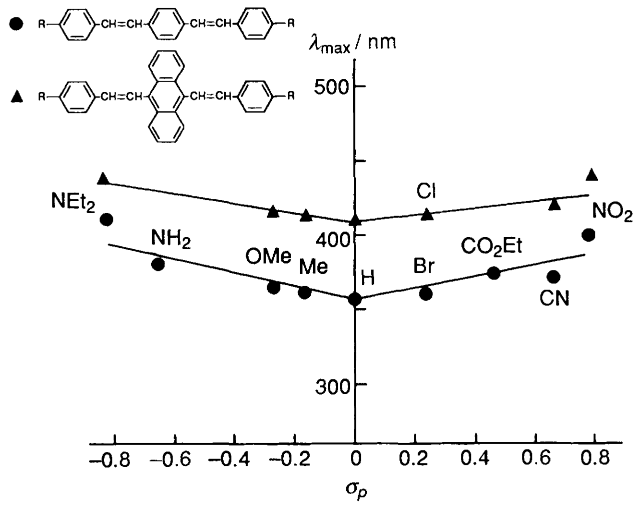


Fig. 1 Correlation diagram between λ_{max} (absorption) and σ_p, in chloroform

apparent that styrylstilbenes have RFI-values about 50-times larger than those of distyrylanthracenes.

In correlation with the RFI-values, we have measured relative quantum yields for each compound by using quinine sulphate as a standard.*[13] The results are summarized in Table 3. The general tendency observed in the RFI-values is consistent in

Table 1 Absorption spectra of compounds **I** (**5a**–**5l**) and **II** (**8a**–**8j**)

			λ_{max}/nm (ε/10^4 dm^3 mol^{-1} cm^{-1})	
Compd.	R	σ_p	$CHCl_3$	Dioxane
5a	NEt_2	−0.83	410 (8.13)	407 (7.68)
5b	NH_2	−0.66	381 (6.79)	386 (6.92)
5c	MeO	−0.27	367 (5.17)	367 (5.71)[a]
5d	Me	−0.17	360 (6.42)	360 (6.81)[b]
5e	H	0	356 (6.74)	355 (6.39)[c]
5f	Br	0.23	362 (5.70)	362 (7.45)
5g	CO_2Et	0.45	374 (7.51)	373 (6.18)
5h	CN	0.66	372 (6.21)	371 (6.81)
5i	NO_2	0.78	400 (6.11)	395 (5.28)
5j	C_6H_4R = 9-Anthryl		404 (3.94)	405 (2.78)[d]
5k	C_6H_4R = 1-Anthryl		414 (3.28)	415 (3.05)
5l	C_6H_4R = Biphenyl-4-yl		376 (3.24)	377 (1.58)
8a	NEt_2	−0.83	437 (2.67)	437 (2.81)
8b	MeO	−0.27	416 (1.92)	415 (2.05)
8c	Me	−0.17	413 (1.93)	411 (2.08)
8d	H	0	410 (1.69)	410 (1.76)
8e	Cl	0.23	412 (1.92)	411 (2.05)
8f	CN	0.66	420 (2.23)	418 (2.28)
8g	NO_2	0.78	438 (2.31)	431 (2.17)
8h	MeO, NO_2		428 (1.80)	424 (2.05)
8i	Me, NO_2		438 (2.31)	431 (2.32)
8j	C_6H_4R = 9-Anthryl		422 (*e*)	423 (*e*)

[a] lit.,[7a] 368 nm (7.30). [b] lit.,[7a] 359 nm (5.80); lit.,[7b] 358 nm. [c] lit.,[7a] 357 nm (5.70); lit.,[7b] 354 nm. [d] lit.,[7a] 404 nm (solvent dioxane). [e] Insoluble.

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* The method employed here was that of Parker and Barns, where the emission strength of each sample at 365 nm in $CHCl_3$ was compared with that of quinine sulphate.

Table 2 Fluorescence spectra of compounds **I** (**5a**–**5l**) and **II** (**8a**–**8i**)

Compd.	R	σ_p	λ_{ex}/nm		λ_{em}/nm		$(\lambda_{em} - \lambda_{ex})$nm	
			$CHCl_3$	Dioxane	$CHCl_3$ (RFI[a])	Dioxane (RFI[a])	$CHCl_3$	Dioxane
5a	NEt_2	−0.83	361	406	420 (0.06)	458 (0.92)	59	52
5b	NH_2	−0.66	372	385	421 (0.17)	439 (0.58)	49	54
5c	MeO	−0.27	368	368	432 (0.34)	454 (0.78)[b]	64	86
5d	Me	−0.17	362	361	420 (0.32)	418 (0.08)[c]	58	57
5e	H	0	361	360	414 (0.73)	410 (0.97)[d]	53	50
5f	Br	0.23	364	364	421 (0.46)	421 (1.00)[A]	57	57
5g	CO_2Et	0.45	374	374	439 (0.64)	436 (0.82)	65	62
5h	CN	0.66	373	372	438 (0.37)	433 (0.63)	65	61
5i	NO_2	0.78	404	364	523 (0.10)	415 (0.03)	119	51
5j	C_6H_4R = 9-Anthryl		394	378	480 (<0.01)	428 (0.01)[e]	86	50
5k	C_6H_4R = 1-Anthryl		399	348	432 (0.01)	453 (0.01)	33	105
5l	C_6H_4R = Biphenyl-4-yl		378	380	422 (0.28)	418 (0.22)	44	38
8a	NEt_2	−0.83	415	435*	555 (0.52)	562 (0.03)	140	136
8b	MeO	−0.27	415*	418*	562 (0.08)	564 (0.20)	147	146
8c	Me	−0.17	416	416	560 (0.37)	560 (0.89)	144	144
8d	H	0	415	414	560 (0.57)	550 (0.85)	145	136
8e	Cl	0.23	416	415	560 (0.64)	558 (0.91)	144	143
8f	CN	0.66	415	420	556 (0.64)	560 (1.00)[B]	141	143
8g	NO_2	0.78	468*	438	575 (0.03)	568 (0.78)	107	130
8h	MeO, NO_2		422**	430*	562 (<0.01)	570 (0.02)	140	140
8i	Me, NO_2		438	427*	473 (0.23)	565 (0.05)	35	138

[a] Relative fluorescence intensity; RFI *vs.* A or B; RFI, A:B 50:1. Each sample concentration was 10^{-7} mol dm^{-3}, except for * (10^{-6} mol dm^{-3}) and ** (10^{-5} mol dm^{-3}). [b] Lit.,[7a] 428, 453 nm. [c] Lit.,[7a] 414, 440 nm; lit.,[7b] 418, 443sh nm. [d] Lit.,[7a] 414, 435 nm; lit.,[7b] 411.5, 430sh nm. [e] Lit.,[7a] 470 nm (solvent dioxane).

Table 3 Quantum yields of compounds **I** (**5a**–**5i**) and **II** (**8a**–**8i**)

Compd.	R	Quantum yield	Compd.	R	Quantum yield
5a	NEt_2	0.26	**8a**	NEt_2	0.003[a]
5b	NH_2	0.22	**8b**	MeO	0.003[a]
5c	MeO	0.53	**8c**	Me	0.012[a]
5d	Me	0.66	**8d**	H	0.021[a]
5e	H	0.77 (0.91[b])	**8e**	Cl	0.019[a]
5f	Br	0.65	**8f**	CN	0.028[a]
5g	CO_2Et	0.61	**8g**	NO_2	0.001[a]
5h	CN	0.46	**8h**	MeO, NO_2	<0.001[a]
5i	NO_2	0.22[a]	**8i**	Me, NO_2	<0.001[a]

[a] Apparent value. [b] Ref. 7*b*.

both series and some of compounds of series I (with R = Me, H, Br, CO_2Et) proved to have larger values compared with that of quinine sulphate (0.55).

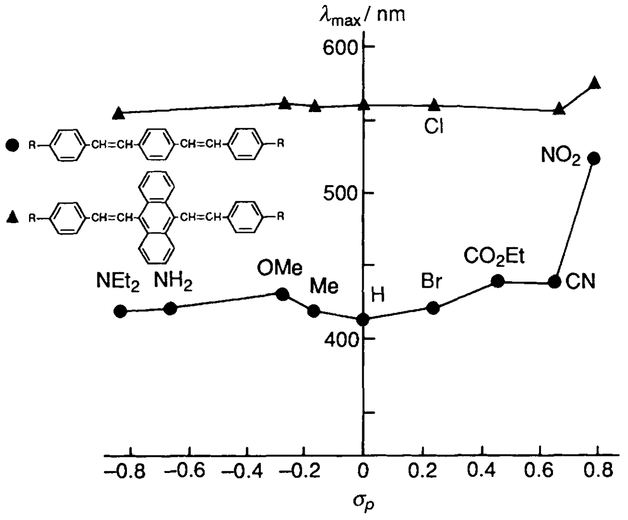

Fig. 2 Correlation diagram between λ_{max} (emission) and σ_p, in chloroform

Chemiluminescence Properties.—Together with the previously described surveys on the fundamental absorption and emission spectroscopic properties of the compounds studied, we were very much interested in their chemiluminescence properties. The chemiluminescence properties of the fluorescent compounds as enhancers in the peroxyoxalate chemiluminescent reaction system were examined by the flow injection method developed in our laboratory[14] using bis(2,4,6-trichlorophenyl) oxalate (TCPO) as an oxalate, hydrogen peroxide, and 9,10-diphenylanthracene (DPA) as a standard fluorescent compound. The chemiluminescence efficiency was estimated from the calibration curve of each compound. Each calibration curve showed a good correlation coefficient with *r*-values of 0.9785–0.9999 and the slope of the calibration curve afforded the relative chemiluminescence intensity (RCI). The results are summarized in Table 4, where the RCI of DPA was arbitrarily taken as 1.0. The following points were apparent from the data. The electron-donating ability of substituents has a serious effect on the styrylstilbenes I, i.e., the stronger the electron-donating ability of the substituent the higher the RCI-value. The RCI-value of compound I; R = NEt_2 was over 100-times larger than that of DPA. On the other hand, the RCI-values of a distyrylanthracene series **II** were very small and/or could hardly be detected. The high RCI-values (for R = NEt_2 or NH_2) in the styrylstilbene series **I** would reflect a high

Table 4 Relative chemiluminescence intensities of compounds **I** (**5a**–**5i**) and **II** (**8a**–**8i**)

Compd.	R	RCI[a]	Compd.	R	RCI[a]
DPA		1.00	**8a**	NEt_2	nd
5a	NEt_2	111.38	**8b**	MeO	nd
5b	NH_2	10.69	**8c**	Me	nd
5c	MeO	1.24	**8d**	H	0.09
5d	Me	0.47	**8e**	Cl	nd
5e	H	0.18	**8f**	CN	nd
5f	Br	0.16	**8g**	NO_2	nd
5g	CO_2Et	0.10	**8h**	MeO, NO_2	nd
5h	CN	0.04	**8i**	Me, NO_2	nd
5i	NO_2	nd			

[a] Relative chemiluminescence intensity; the RCI of DPA was arbitrarily taken as 1.0. nd: non-detectable.

efficiency of the peroxyoxalate chemiluminescent reaction with these derivatives. They were excited by lower energies compared with other derivatives and the efficiency of their emission of light should also be higher than for other derivatives.

MO Calculations.—The MO calculations were carried out by the PPP method (either standard or variable β) and the QCFF/PI program including a CI refinement (for relevant references see footnotes in Table 5). For the calculation of fluorescence maxima besides the QCFF/PI program we also used the method reported by one of us (W. F.).[15] The results will be discussed separately.

(1) *Styrylstilbenes.* The results are shown in Table 5. For the calculations a planar *E,E*-conformation was postulated. QCFF/PI Calculation with non-planar conformations led to higher total energy values. A recent publication using the newly developed semiempirical AM1 method also suggests the *E,E*-isomer for *p*-styrylstilbene with a nearly planar conformation as the most stable one.[16] The agreement of the calculated results with experimental values was satisfactory. The calculation by method A with standard parameter sets predicted the experimental values of the absorption maxima fairly well. The experimental values of the fluorescence maxima were, in turn, best predicted by method D taking the geometries of excited states into account. The three methods investigated could predict the general tendencies of both absorption and fluorescence spectra of the derivatives relatively well.

(2) *Distyrylanthracenes.* The calculated results are shown in Table 6. We met difficulties with this class of compounds because of nonplanarity.[17] By the QCFF/PI method, we found the best results as shown in Table 6, *i.e.*, the dihedral angle of the twisted geometry between the ethylene and anthracene groups was ~45° in the ground state and ~30° in the excited state, respectively, while the coplanarity between the ethylene group and the phenyl group was retained. For the standard PPP-calculation the value of β was multiplied by cos φ (φ = dihedral angle). Again, the best results for prediction of absorption maxima were obtained by the standard method (method A). With method C we encountered difficulty in reproducing the absorption maximum of compound **II**; R = H. To reproduce the emission maxima turned out to be even more problematic because of the large Stokes shifts observed. Even though the results obtained by QCFF/PI are cited in Table 6, the resolution of these discrepancies will be the subject of future research.

In conclusion, we have prepared series of styrylstilbenes and distyrylanthracenes. Linear relationships between their absorption spectra (λ_{max}) and σ_p-values of the substituents have been found, which could be satisfactorily reproduced by PPP-SCF-CI-MO calculations with the assumption of planarity. Systematic investigations have been made of their fluorescence spectroscopic properties, their Ex_{max}-, Em_{max}-, RFI-values and their quantum yields in two different solvent systems to show their emission properties. Anomalous Stokes shifts of the distyrylanthracene series were poorly predicted by PPP-MO calculations even by postulating a twisted, non-planar conformation. Chemiluminescence measurements by the peroxyoxalate method were carried out, and showed that electron-donating substituents at the *para*-position of styrylstilbenes afforded strong chemiluminescence, above all when R = NEt_2.

Experimental

M.p.s were measured on a Yanagimoto MP-53 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, ^1H NMR spectra on $CDCl_3$ solutions in a JEOL JNM-FX-90Q 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.[13]

Synthesis of the Styrylstilbene **5a**.—To a mixture of *p*-phenylenedimethylenebis(triphenylphosphonium chloride) **3** (1.00 g, 5.64 mmol) and *p*-diethylaminobenzaldehyde **4a** (2.00 g, 2.86 mmol) in EtOH (10 cm^3) was added 0.2 mol dm^{-3} EtOLi (20 cm^3, 4.0 mmol) and the mixture was stirred overnight. The resulting reaction mixture was poured into water to give a precipitate which was filtered off, washed with EtOH, dried under reduced pressure and then recrystallized from benzene containing a trace of iodine to afford pure *compound* **5a** as yellow crystals (0.44 g, 39%); m.p. 242–246 °C (Found: C, 84.9; H, 8.6; N, 6.3. $C_{30}H_{36}N_2$ requires C, 84.9; H, 8.5; N, 6.6%); ν_{max}(Nujol)/cm^{-1} 1600 (C=C) and 965 (*E* CH=CH); δ_H 1.18 (12 H, t, *J* 7, Me), 3.38 (8 H, q, *J* 7, CH_2) and 6.7–7.42 (16 H, m, ArH and olefinic H); EI-MS (*m*/*z*) 424 (M^+). Other derivatives (except **5b**) were prepared similarly. Compound **5b** was obtained by reduction of *p*-nitro derivative **5i** in the usual way although the yield was very low.

Compound **5b**: pale yellowish brown crystals; m.p. 292–294 °C (lit.,[8] 303 °C); ν_{max}(Nujol)/cm^{-1} 3420, 3300 (NH_2), 1600 (C=C) and 970 (*E* CH=CH); EI-MS (*m*/*z*) 312 (M^+).

Compound **5c**: pale yellowish green crystals (35%), m.p. 299–302 °C (lit.,[8] 310–310.5 °C;[12] 272–275 °C); ν_{max}(Nujol)/cm^{-1} 1610 (C=C) and 980 (*E* CH=CH); EI-MS (*m*/*z*) 342 (M^+).

Compound **5d**: pale yellowish green crystals (66%); m.p. 301–303 °C (lit.,[8] 307–308 °C); ν_{max}(Nujol)/cm^{-1} 970 (*E* CH=CH); δ_H 1.18 (6 H, s, Me), 7.00–7.30 (12 H, m, ArH and olefinic H) and 7.41 (4 H, s, ArH); EI-MS (*m*/*z*) 310 (M^+).

Compound **5e**: pale yellowish green crystals (30%); m.p. 260–262 °C (lit.,[8] 268–268.5 °C); ν_{max}(Nujol)/cm^{-1} 970 (*E* CH=CH); δ_H 7.11–7.51 (14 H, m, ArH and olefinic H) and 7.51 (4 H, s, ArH); EI-MS (*m*/*z*) 282 (M^+).

Compound **5f**: pale yellow crystals (71%); m.p. 316–318 °C (Found: C, 59.6; H, 3.7. $C_{22}H_{16}Br_2$ requires C, 60.03; H, 3.36%); ν_{max}(Nujol)/cm^{-1} 1585 (C=C) and 975 (*E* CH=CH); δ_H 6.53–7.52 (16 H, m, ArH and olefinic H); EI-MS (*m*/*z*) 339 and 441 (M^+).

Compound **5g**: pale yellow crystals, m.p. 241–247 °C (Found: C, 78.85; H, 6.2. $C_{28}H_{26}O_4$ requires C, 78.85; H, 6.14%); ν_{max}(Nujol)/cm^{-1} 1720 (C=O), 1600 (C=C) and 965 (*E* CH=CH); δ_H 1.41 (6 H, t, *J* 7, Me), 4.39 (4 H, q, *J* 7, CH_2), 7.19–8.08 (12 H, m, ArH and olefinic H) and 7.54 (4 H, s, ArH); EI-MS (*m*/*z*) 426 (M^+).

Compound **5h**: yellow crystals (87%); m.p. 279–281 °C (lit.,[18] 277–278 °C); ν_{max}(Nujol)/cm^{-1} 2230 (C≡N), 1595 (C=C) and

Table 5 Experimental and calculated results for some representatives of compound type **I**

		Absorption[a]					Fluorescence[a]				
Compd.	R	$CHCl_3$	Dioxane	A[b]	B[c]	C[d]	$CHCl_3$	Dioxane	B[c]	C[d]	D[e]
5a	NEt_2	2.44	2.46	2.51		2.64[f]	2.38	2.18		2.22[f]	2.41
5b	NH_2	2.62	2.59	2.66	3.01	2.83	2.38	2.28	2.65	2.37	2.54
5c	MeO	2.72	2.72	2.78	*g*	2.95[f]	2.31	2.20	*g*	2.46[f]	2.48
5e	H	2.81	2.82	2.84	3.05	3.02	2.42	2.44	2.68	2.50	2.60
5h	CN	2.69	2.69	2.66	*g*	2.88[h]	2.28	2.31	*g*	2.44[h]	2.54
	CHO[i]				2.80	2.86			2.52	2.45	

[a] $\nu/10^4$ cm^{-1}. [b] Method A: standard PPP-MO calculation (ref. 20) using the parameter sets proposed by Griffiths (ref. 21). [c] Method B: QCFF/PI calculation (ref. 22). [d] Method C: PPP-MO calculation using QCFF/PI-optimized geometry and geometry dependence of resonance integral β_{ij} under consideration (*cf.* ref. 23): $\beta_{ij} = \beta^0{}_{ij}\cdot\cos\varphi\cdot\exp[-A(R_{ij} - R^0{}_{ij})]$; φ = torsion angle; $R^0{}_{ij}$ = 140 pm; $A = 2.5 \times 10^{-2}$ pm^{-1}; $\beta^0{}_{ij} = -2.318$ eV. [e] Method D: calculation of fluorescence using bond order–bond length relationship and bond length–resonance integral (β) relationship cited in the literature.[15] [f] Owing to [g], this was calculated using the geometry of **I**; R = NH_2. [g] No QCFF/PI potential parameter is available. [h] Owing to [g], this was calculated using the geometry of **I**; R = CHO. [i] A model for acceptor-substituted derivative.

Table 6 Experimental and calculated results for some representatives of compound type **II**

		Absorption[a]					Fluorescence[a]		
Compd.	R	$CHCl_3$	Dioxane	A[b]	B[c]	C[d]	$CHCl_3$	Dioxane	B[c]
8a	NEt_2	2.29	2.29	2.20			1.80	1.78	
	NH_2			2.30	2.46				2.14
8b	MeO	2.40	2.41	2.32			1.78	1.77	
8d	H	2.44	2.44	2.34	2.45	2.61	1.79	1.82	2.11
8f	CN	2.38	2.39	2.27			1.80	1.79	
	CHO				2.41				2.11

[a] $\nu/10^4$ cm^{-1}. [b] Method A: standard PPP-MO calculation. [c] Method B: QCFF/PI calculation. [d] Method C: PPP-MO calculation using QCFF/PI-optimized geometry and geometry dependence of resonance integral β_{ij} under consideration.

960 (*E* CH=CH); δ_H 7.16–7.62 (16 H, m, ArH and olefinic H); EI-MS (*m*/*z*) 332 (M^+).

Compound **5i**: orange crystals (89%); m.p. 289–291 °C (lit.,[8] 288–290 °C); ν_{max}(Nujol)/cm^{-1} 1590 (C=C) and 960 (*E* CH=CH); δ_H 7.22–8.23 (12 H, m, ArH and olefinic H) and 7.58 (4 H, s, ArH); EI-MS (*m*/*z*) 372 (M^+).

Compound **5j**: yellowish brown crystals (57%); m.p. 308–310 °C (lit.,[19] 308–310 °C; ν_{max}(KBr)/cm^{-1} 1620 (C=C) and 980 (*E* CH=CH); δ_H 6.29–8.38 (26 H, m, ArH and olefinic H); EI-MS (*m*/*z*) 482 (M^+).

Compound **5k**: yellow crystals (73%); m.p. 313–314 °C (Found: C, 94.8; H, 5.6. $C_{38}H_{26}$ requires C, 94.57; H, 5.43%); ν_{max}(KBr)/cm^{-1} 1610 (C=C) and 960 (*E* CH=CH); EI-MS (*m*/*z*) 482 (M^+).

Compound **5l**: pale yellowish green crystals (78%); m.p. >320 °C (Found: C, 93.6; H, 6.2. $C_{34}H_{26}$ requires C, 93.97; H, 6.03%); ν_{max}(KBr)/cm^{-1} 970 (*E* CH=CH); EI-MS (*m*/*z*) 434 (M^+).

Synthesis of the Distyrylanthracene **8b**.—To a stirred solution of *p*-methoxybenzyl(triphenyl)phosphonium chloride **7b** (10.74 g, 25.64 mmol) in MeOH (30 cm^3) was added under nitrogen 0.2 mol dm^{-3} MeOLi (200 cm^3, 40 mmol) and then a solution of dialdehyde **6** (2.00 g, 8.55 mmol) in DMF (230 cm^3). After the mixture had been stirred for 3.5 h and the resulting solution kept on an ice-bath, the precipitate was filtered off by suction, washed with hexane, dried under reduced pressure and recrystallized from CH_2Cl_2–hexane to give pure compound **8b** as yellow crystals (2.46 g, 65%); m.p. 261–262 °C (lit.,[12] 261.0–262.0 °C); ν_{max}(Nujol)/cm^{-1} 1629 (C=C) and 980 (*E* CH=CH); δ_H 3.88 (6 H, s, OMe), 6.86 (2 H, d, *J* 16, olefinic H), 6.99 (4 H, d, *J* 9, ArH), 7.40–7.51 (4 H, m, ArH), 7.63 (4 H, d, *J* 9, ArH), 7.79 (2 H, d, *J* 16, olefinic H) and 8.33–8.45 (4 H, m, ArH); EI-MS (*m*/*z*) 442 (M^+). In the same manner were prepared compounds **8c**, **8d** and **8e**.

Compound **8c**: yellow crystals (57%); m.p. 281–283 °C (lit.,[12] 274.0–274.5 °C); ν_{max}(Nujol)/cm^{-1} 970 (*E* CH=CH); δ_H 2.43 (6 H, s, Me), 6.89 (2 H, d, *J* 16, ArH), 7.25 (4 H, d, *J* 8, ArH), 7.39–7.50 (4 H, m, ArH), 7.58 (4 H, d, *J* 8, ArH), 7.87 (2 H, d, *J* 16, olefinic H) and 8.33–8.44 (4 H, m, ArH); EI-MS (*m*/*z*) 410 (M^+).

Compound **8d**: yellow crystals (71%); m.p. 278–280 °C (lit.,[12] 283.0–284.0 °C); ν_{max}(Nujol)/cm^{-1} 1600 (C=C) and 970 (*E* CH=CH); δ_H 6.93 (2 H, d, *J* 16, olefinic H), 7.38–7.65 (14 H, m, ArH), 7.93 (2 H, d, *J* 16, olefinic H) and 8.34–8.45 (4 H, m, ArH); EI-MS (*m*/*z*) 382 (M^+).

Compound **8e**: yellow crystals (55%); m.p. 278–280 °C (lit.,[12] 283.0–284.0 °C); ν_{max}(Nujol)/cm^{-1} 975 (*E* CH=CH); δ_H 6.88 (2 H, d, *J* 16, olefinic H), 7.36–7.66 (12 H, m, ArH), 7.91 (2 H, d, *J* 16, olefinic H) and 8.29–8.41 (4 H, m, ArH); EI-MS (*m*/*z*) 450 and 452 (M^+).

Reaction of p-*Nitrobenzyl*(*triphenyl*)*phosphonium Bromide with Compound* **6**.—To a stirred mixture of phosphonium salt (**7**, R = NO_2) (5.31 g, 11.1 mmol), MeOH (20 cm^3) and 0.2 mol dm^{-3} MeOLi (111 cm^3, 22.2 mmol) was added a solution of the dial **6** (2.00 g, 8.6 mmol) in DMF (230 cm^3) under nitrogen. After the reaction mixture had been stirred for 30 min and then stored in an ice-bath, the resulting orange precipitate was filtered off, washed with hexane and purified by column chromatography and recrystallization from CH_2Cl_2 to give a compound, orange crystals (1.45 g, 48%), with m.p. 272–273 °C, which was identified as compound **9** (Found: C, 78.2; H, 4.3; N, 4.0. $C_{23}H_{15}NO_3$ requires C, 78.18; H, 4.28; N, 3.96%); ν_{max}(Nujol)/cm^{-1} 1680 (C=O) and 1595 (C=C); δ_H 6.90–9.02 (14 H, m, olefinic H and ArH) and 11.54 (1 H, s, CHO); EI-MS (*m/z*) 353 (M^+). Prolongation of the reaction time to 12 h did not afford compound **8g** but again afforded compound **9** in lower yield (25%).

Preparation of the Unsymmetrical Distyrylanthracene **8h**.—To a stirred solution of phosphonium salt **7** (0.45 g, 1.1 mmol) in MeOH (10 cm^3) was added 0.2 mol dm^{-3} MeONa (20 cm^3, 4.0 mmol) under nitrogen, and this was followed by addition of aldehyde **9** (0.25 g, 0.71 mmol) in DMF (30 cm^3). An orange precipitate immediately appeared, which was filtered off after the mixture had been kept in an ice-bath for 0.5 h; the product was washed with hexane, purified by column chromatography and then recrystallized from CH_2Cl_2–hexane to give compound **8h** as orange crystals (0.12 g, 65%); m.p. 312–313 °C (Found: C, 81.5; H, 5.2; N, 3.1. $C_{31}H_{23}NO_3$ requires C, 81.38; H, 5.07; N, 3.06%); ν_{max}(Nujol)/cm^{-1} 1590 (C=C); δ_H 3.89 (3 H, s, OMe) and 6.78–8.48 (20 H, m, ArH and olefinic H); EI–MS (*m/z*) 457 (M^+).

In a similar manner compound **8i** was obtained as orange crystals (0.12 g, 48%); m.p. 312–313 °C (Found: C, 84.1; H, 5.25; N, 3.1. $C_{31}H_{23}NO_2$ requires C, 84.33; H, 5.21; N, 3.17%); ν_{max}(Nujol)/cm^{-1} 1595 (C=C); δ_H 2.44 (3 H, s, Me) and 6.81–8.47 (20 H, m, ArH and olefinic H); EI–MS (*m/z*) 441 (M^+).

Preparation of Compound **8f** *by Arbusov–Horner Reaction*.—2.3 Mol dm^{-3} MeONa (6 cm^3, 14 mmol) was added to a stirred solution of compound **12** (2.00 g, 4.74 mmol) in DMF (10 cm^3) under nitrogen, followed by a solution of compound **4f** (1.24 g, 9.47 mmol) in DMF (25 cm^3). After the reaction mixture had been kept in an ice-bath for 1 h, the resulting precipitate was washed successively with MeOH and light petroleum (40–70 °C), and recrystallized from CH_2Cl_2–benzene to give compound **8f** as orange crystals (1.38 g, 67%); m.p. >320 °C (lit.,[12] >320 °C); ν_{max}(Nujol)/cm^{-1} 2230 (C≡N), 1600 (C=C) and 960 (*E* CH=CH); EI–MS (*m/z*) 432 (M^+). In a similar manner were obtained compounds **8g** and **8f**.

Compound **8g**: orange crystals (89%); m.p. >320 °C (lit.,[12] >320 °C); ν_{max}(Nujol)/cm^{-1} 1590 (C=C); EI–MS (*m/z*) 72 (M^+).

Compound **8j**: yellow crystals (10%); m.p. >320 °C (lit.,[12] >320 °C); ν_{max}(KBr)/cm^{-1} 1620 (C=C); EI–MS (*m/z*) 581 (M^+).

*Preparation of 9,10-Bis(*p*-diethylaminostyryl)anthracene* **8a**.—Compound **12** (3.00 g, 7.1 mmol) was stirred with Bu^tOK (3.98 g, 35.5 mmol) under nitrogen. Compound **4a** (2.57 g, 14.5 mmol) in DMF (20 cm^3) was added to the solution and the mixture was stirred for 3 h. The resultant precipitate was filtered off and recrystallized from CH_2Cl_2 to give *compound* **8a** as yellow crystals (15.5 g, 42%); m.p. 284–285 °C (Found: C, 87.0; H, 7.8. $C_{38}H_{40}N_2$ requires C, 86.98; H, 7.64%); ν_{max}(Nujol)/cm^{-1} 1600 (C=C) and 960 (*E* CH=CH); δ_H 1.22 (12 H, t, *J* 7.0, Me), 3.43 (8 H, q, *J* 7.0, CH_2), 6.75 (4 H, d, *J* 9, ArH), 6.80 (2 H, d, *J* 16, olefinic H), 7.36–7.47 (4 H, m, ArH), 7.55 (4 H, d, *J* 9, ArH), 7.69 (2 H, d, *J* 16, ArH and olefinic H) and 8.36–8.48 (4 H, m, ArH); EI–MS (*m/z*) 524 (M^+).

Another experiment, with a longer reaction time (18 h), afforded, besides compound **8a** (18%), the bis(phenylethynyl)-anthracene derivative **13** (0.4%), identified from its mass spectral data [*m/z* 520 (M^+)].*

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* Presumably the oxidation of a double bond to form a triple bond had occurred. We are now investigating the scope of such reactions.