J. Chem. Research (S), 1998, 302–303
J. Chem. Research (M), 1998, 1389–1397

Syntheses and Photoreactivity of New Bisanthracenes Incorporating One or Two Nitrogen Atoms in the Linkage

Souad Lahlou,[a] Najib Bitit*[a] and Jean-Pierre Desvergne*[b]

[a]Université Sidi Mohamed Ben Abdellah, Faculté des Sciences Dhar El Mehraz, Département de Chimie, Fes, Marocco
[b]Laboratoire de Photochimie Organique, CNRS UMR 5802, Université Bordeaux 1, 351 cours de la Libération, 33405 Talence Cedex, France

Three new bisanthracenes (**1**–**3**) incorporating one or two nitrogen atoms in the linkage exibit low photoreactivity towards intramolecular dimerization which is assigned to an intramolecular electron-transfer from the amino group towards the excited anthracene, and to the poor flexibility of the chain tethering the chromophores.

Non-conjugated bisaromatic systems joined by a flexible linker are of interest to study, at low concentrations, interactions between chromophores.[1] In this context, bisanthracenes have been investigated because they display, in addition to photodimerization and photochromic properties, a dual fluorescence emission of excimer and monomer-type in the visible range.[2]

It has been shown that oxygen atoms bring conformational mobility to the chain tethering the anthracenes and facilitate the intramolecular interaction and thus photocycloaddition.[3] The highest reactivity has been registered with the three-membered acetal[3] sequence in agreement with Hirayama rules.[4] Such an influence of the chain on the photoreactivity of bisanthracenes encouraged us to inspect systems incorporating nitrogen atoms in the linkage, in order to delineate the role of heteroatoms in the photophysics under both neutral and acidic conditions.

In this short paper we report on the syntheses of new bisanthracenes (**1**–**3**), which incorporate one or two nitrogens in the chain, and on some of their photochemical and spectroscopic properties. The two secondary amine intermediates (**4** and **5**) in the preparation of **1**–**3** were used as reference monochromophoric materials for the spectroscopic studies.

A_9-(CH_2-NH-CH_2)$_2$-A_9 (**1**), (A_9-CH_2)$_2$N-CH_2-Ph (**2**),
(A_9-CH_2)$_2$N-CH_3 (**3**), A_9-CH_2-NH-CH_3 (**4**),
A_9-CH_2-NH-CH_2Ph (**5**) (A_9 = 9-anthryl)

The compounds were prepared by reduction of the corresponding imines, which were obtained by condensation of 9-anthraldehyde and the appropriate amines (Scheme 1).

The new products were purified by chromatography on silica gel and/or recrystallization from various solvents. The chemical yields, not optimized, ranged from 12 to 45%. The structures of **1**–**5** were fully established by the usual spectrometric techniques and elemental analysis (see Experimental section).

The electronic absorption spectra of compounds **1**–**5** were recorded, at room temperature, in cyclohexane and acetonitrile. The spectral regions characteristic of the anthracene chromophore[5] display a structured band between 300 and 400 nm (^1L_a band) and a higher energy transition between 220 and 300 nm (^1B_b band). Some changes are discernible both on the ^1L_a band (redshifted by 2–3 nm) and on the ^1B_b band (redistribution of intensity of its two components) for **1**–**3** compared with the reference molecules (**4** and **5**), these are attributed to intramolecular interactions between the two anthracene rings. This presumably reflects some degree of alignment of the chromophores in the ground state.[6] In solution, for both bi- and monochromophoric compounds, addition of trifluoracetic acid to the acetonitrile solutions induces some weak batho- and hypochromic shifts for the ^1L_a band (the ^1B_b band being masked by the absorption of the acid).

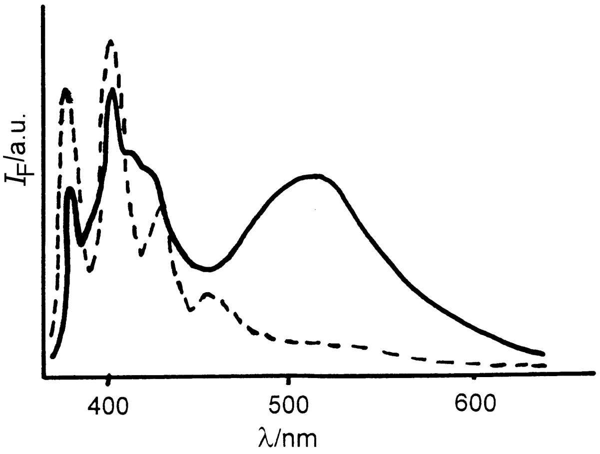


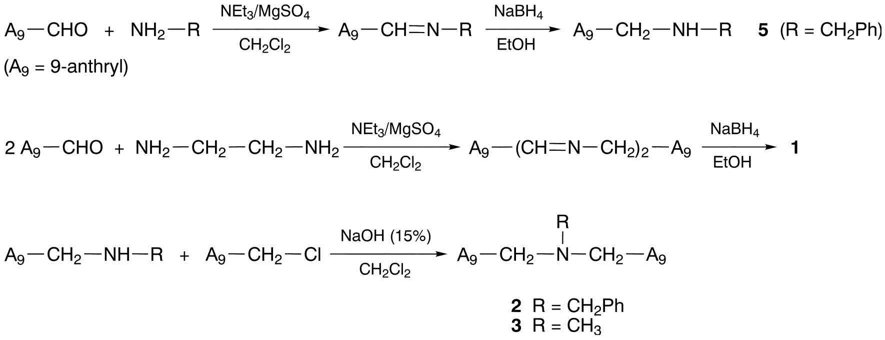
Fig. 1 Corrected fluorescence emission spectra of 1 in cyclohexane (—) and acetonitrile (– – –) at room temperature (λ_{exc} 370 nm, conc. *ca.* 10^{-5} mol dm^{-3}). Fluorescence quantum yields, ϕ_F: 0.16 (cyclohexane) and 0.004 (acetonitrile). In acetonitrile no clear exciplex emission band is observed

The fluorescence emission spectra recorded in acetonitrile or acetonitrile and trifluoroacetic acid display a structured band assignable to the radiative deactivation of a locally excited state species (pure anthracene-type emission, no excimer contribution). In cyclohexane, the spectrum is dual: in addition to the 'pure anthracene-type' emission band, a redshifted and non-structured band emerged. This emission, which is also present for the reference materials (**4** and **5**), probably proceeds from an exciplex between anthracene and a nitrogen lone pair, and disappears upon addition of acid to the solution (Fig. 1). The fluorescence quantum yields are very weak (Table 1), especially for **1** and **2** in acetonitrile, where the exciplex band is absent (the polar solvent may induce an electron transfer between anthracene and nitrogen); fluorescence revival is observed on the addition of a drop of trifluoroacetic acid. Compound **1** behaves similarly to bis-9-anthrylmethylamine, which has been recently studied by Mori[7] (Table 1).

When solutions of **1**, **2** and **3** were irradiated (conc. *ca.* 10^{-5}–10^{-6} mol dm^{-3}, in degassed cyclohexane, acetonitrile or acetonitrile and a few drops of trifluoroacetic acid) at room temperature (λ_{irrad} *ca.* 365 nm), cyclomers **1c**, **2c** or **3c** were formed, respectively (Scheme 2). The occurrence of an intramolecular [4 + 4] cycloaddition was demonstrated as

---

*To receive any correspondence.



$$\mathrm{A_9{-}CHO + NH_2{-}R \xrightarrow[CH_2Cl_2]{NEt_3/MgSO_4} A_9{-}CH{=}N{-}R \xrightarrow[EtOH]{NaBH_4} A_9{-}CH_2{-}NH{-}R}\quad \mathbf{5}\ (\mathrm{R = CH_2Ph})$$

(A_9 = 9-anthryl)

$$\mathrm{2\,A_9{-}CHO + NH_2{-}CH_2{-}CH_2{-}NH_2 \xrightarrow[CH_2Cl_2]{NEt_3/MgSO_4} A_9{-}(CH{=}N{-}CH_2)_2{-}A_9 \xrightarrow[EtOH]{NaBH_4}}\ \mathbf{1}$$

$$\mathrm{A_9{-}CH_2{-}NH{-}R + A_9{-}CH_2{-}Cl \xrightarrow[CH_2Cl_2]{NaOH\ (15\%)} A_9{-}CH_2{-}\overset{R}{\overset{|}{N}}{-}CH_2{-}A_9}$$

2 R = CH_2Ph
3 R = CH_3

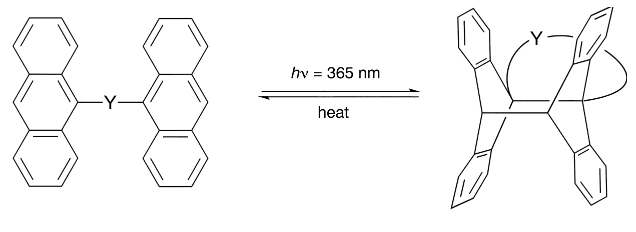
Scheme 1

Table 1 Quantum yields of fluorescence (ϕ_F) and cyclomerization (ϕ_R) of compounds **1–5** in various solvents, at room temperature

	Cyclohexane		Acetonitrile		Acetonitrile/acid	
Compounds	ϕ_F	ϕ_R[a]	ϕ_F	ϕ_R	ϕ_F	ϕ_R
A_9–(CH_2–NH–CH_2)$_2$–A_9 (**1**)	0.163	0.03	0.004 (383 nm)[b]	0.02	0.22 (388 nm)[b]	0.02
(A_9–CH_2)$_2$N–CH_2–Ph (**2**)	0.094	0.05	0.004 (390 nm)[b]	0.07	0.031 (394 nm)[b]	0.08
(A_9–CH_2)$_2$N–CH_3 (**3**)	0.026	0.05	0.018 (387 nm)[b]	0.06	0.012 (392 nm)[b]	0.03
A_9–CH_2–NH–CH_3 (**4**)	0.096	–[c]	0.019	–[c]	0.44	–[c]
A_9–CH_2–NH–CH_2Ph (**5**)	0.090	–[c]	0.020	–[c]	0.40	–[c]
A_9–CH_2–NH–CH_2–A_9 (Ref. 7)	0.16[d]	0.17[d]	0.015	0.05	0.53[e]	0.28[e]

[a]For comparison, some other bisanthracenes were found to give in methylcyclohexane (MCH) the following ϕ_R: –OCH_2O– (0.36);[2] –CH_2OCH_2– (0.32),[2] –(CH_2)$_3$– (0.14),[2] –(CH_2)$_4$– (0.06),[2] –Si(CH_3)$_2$–CH_2–Si(CH_3)$_2$– (0.02).[9] [b]λ_{max} For the ^1L_a band (electronic absorption spectrum). [c]Irradiation gave the classical intermolecular (9,9′,10,10′)-photodimers. [d]In MCH. [e]In HCl/EtOH–H_2O.

the quantum yields (ϕ_R) did not vary with concentration. The structure of the photoproducts was established from their ultraviolet absorption spectra, which resemble that of 9,10-dihydroanthracene[8] without any indication of an absorption band above 300 nm (involving a lateral ring in a dissymmetrical photocycloaddition[2]). The colourless photoproducts, stable at room temperature, are thermally degraded at $T > 100$ °C to give back the starting (deep yellow) bisanthracenes. The photocycloaddition quantum yields are very low (they do not exceed 0.08). This very low reactivity could be related to the poor flexibility of the azamethylenic sequence in addition to a possible electron-transfer quenching of the reactive excited state (ΔG_{ET} could be estimated[10] and ~0.4 eV). Although an enhancement of fluorescence intensity was recorded for **1** and **2** under acidic conditions (acetonitrile), the reaction efficiency was not significantly improved (measurements were repeated several times), contrary to data reported by Mori[7] for bisanthrylmethylamine (in that case, a molecular folding owing to hydrophobic effects cannot be excluded since the experiments were carried out in aqueous ethanol).



1 Y = —(CH_2—NH—CH_2)$_2$—

2 Y = $\mathrm{{-}CH_2{-}\underset{CH_2Ph}{\underset{|}{N}}{-}CH_2{-}}$

3 Y = $\mathrm{{-}CH_2{-}\underset{CH_3}{\underset{|}{N}}{-}CH_2{-}}$

1c
2c
3c

Scheme 2

This study underlines the poor flexibility of the amino chains incorporated in compounds **1**, **2** and **3** compared with –OCH_2O–, –CH_2OCH_2– or –$CH_2CH_2CH_2$– sequences which produce photocyclomers in higher quantum yields.[2] However, their conformational mobility is apparently greater than that displayed by the –Si(CH_3)$_2$–Si(CH_3)$_2$– ($\phi_R = 0.22$) linkage,[9] for which even poorer quantum yields have been recorded.

We are indebted to Professor Henri Bouas-Laurent and Dr Dario Bassani for helpful discussions.

Techniques used: IR, elemental analysis, ^1H NMR, UV

References: 10

Received, 1st December 1997; Accepted, 12th January 1998
Paper E/7/08628H

References

1 F. C. De Schryver, N. Boens and J. Put, *Adv. Photochem.*, 1977, **10**, 359.
2 H. Bouas-Laurent, J.-P. Desvergne and A. Castellan, *Pure Appl. Chem.*, 1980, **52**, 2633.
3 J.-P. Desvergne, H. Bouas-Laurent, F. Lahmani and J. Sepiol, *J. Phys. Chem.*, 1992, **96**, 10616 and refs therein.
4 F. Hirayama, *J. Chem. Phys.*, 1965, **42**, 3163.
5 R. P. Steiner and J. Michl, *J. Am. Chem. Soc.*, 1978, **100**, 686.
6 J. Ferguson, *Chem. Rev.*, 1986, **86**, 957.
7 Y. Mori and K. Maeda, *Bull. Chem. Soc. Jpn*, 1997, **70**, 869.
8 R. A. Friedel and M. Orchin, in *U.V. Spectra of Aromatic Compounds*, Wiley, New York, 1951, p. 114.
9 J.-P. Desvergne, N. Bitit, J. P. Pillot and H. Bouas-Laurent, *J. Chem. Res.* (*S*), 1989, 146.
10 A. Weller, *Z. Phys. Chem.* (*Wiesbaden*), 1982, **133**, 93; G. Kavarnos, '*Fundamentals of Photoinduced Electron Transfer*', VCH, New York, 1993.