Pergamon

Tetrahedron Letters, Vol. 36, No. 8, pp. 1259-1262, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(94)02482-0

Synthesis, Photoreactivity and Fluorescence Properties of New bis -9-Anthryloxymethanes

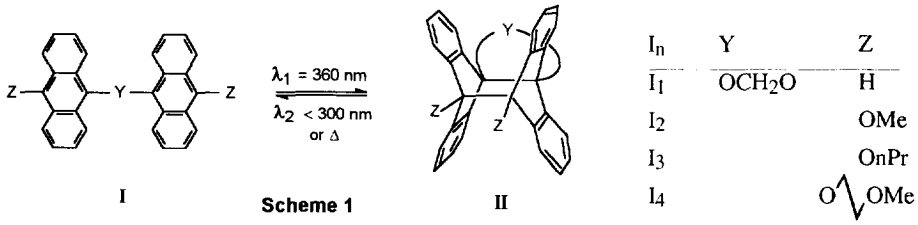
J.P. Desvergne*, M. Gotta#, J.C. Soulignac, J. Lauret and H. Bouas-Laurent.

Laboratoire de Photochimie Organique, associé au CNRS,
351 Cours de la Libération, 33405 Talence Cédex, France.

Abstract : The synthesis of new coloured anthryloxymethanes is described ; they are reversibly transformed upon irradiation into their colourless photocyclomers. Their high photoreactivity, accompanied by a weak fluorescence and short singlet excited lifetimes, originates in the great flexibility of the OCH_2O spacer.

Irradiation of yellow 9,9'- linked bisanthracenes (I) is usually accompanied by a blue shift (< 400 nm→ 300 nm) of the absorption spectrum of the starting material due to the saturation of the anthracene central ring in the photoproduct as shown in scheme 1. The colourless photocycloisomer ('intramolecular photodimer') (II) can be dissociated into the open form (I) upon heating or irradiation at wave lengths shorter than 300 nm.[1,2]

As the process was found to be reversible and can be repeated several times, bisanthracenes display concentration independent photochromic properties (within a concentration range not allowing intermolecular reactions).



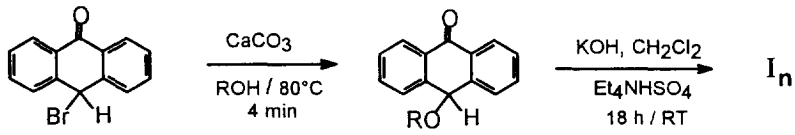
I **Scheme 1** II

I_n	Y	Z
I_1	OCH_2O	H
I_2		OMe
I_3		OnPr
I_4		O∧OMe

It has been shown that the dynamic properties of the spacer Y strongly affect the photochemical behaviour of the bisanthracenes and short chains (Y bearing 1 to 4 atoms), in which a minimum of conformational transitions is necessary, were found to significantly improve the closure efficiency.[3,4] Related to this, the highest photocyclomerization quantum yield (ϕ_R = 0.36) was recently obtained in our laboratory for Y = OCH_2O and Z = H (compound I_1), and for a reaction exclusively controlled by the singlet state.[4] However, the poor solubility of I_1 in organic media is a drawback for its potential application to information storage. Therefore, to improve the solubility in organic media, without affecting strongly the reactivity, we designed 10,10'- substituted (I_n) derivatives. In this letter, we describe the synthesis of these new bisanthracenes and report on their photochemical properties in various solvents.

Syntheses :

The synthesis of the parent molecule has already been reported.[4] The compounds I_n were prepared according to an improved procedure outlined in scheme 2.



III IV

The key intermediate 9- bromoanthrone III, which was obtained from anthrone as described in ref 5, readily reacts with the alcohols ROH in the presence of $CaCO_3$ at 80°C leading to the corresponding alkoxyanthrones (IV). The latter were transformed into I_n using KOH (or LiOH for I_4) pellets in suspension in CH_2Cl_2 with Et_4NHSO_4 as a Phase Transfer Catalyst at room temperature (Dehmlow procedure[6]). Compounds I_n were isolated as yellow solids, and were found to be more soluble in the usual organic solvents than the parent molecule I_1. The new compounds were characterized by the usual spectrometric techniques and gave satisfactory elemental analyses.[7]

Photochemical properties :

The substitution on the meso positions by alkoxy groups shifts (by ≈ 15 nm) the UV absorption in the visible range and gives bright yellow materials, whereas for n=1, paler yellow crystals were obtained (I_2, I_3 and I_4 display similar UV spectra).

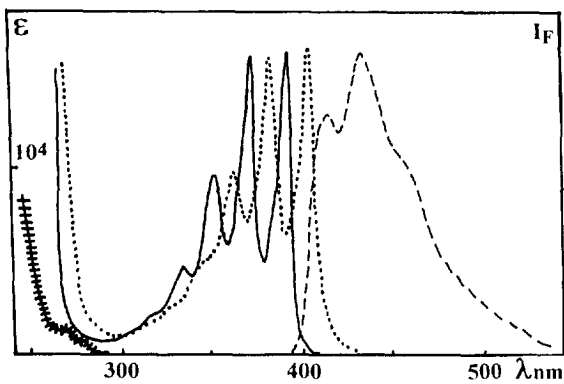


Fig.1 :

left : UV absorption spectra of I_1 (—), I_2 (....) and the photocycloisomer II_1 (xxxx) (Methylcyclohexane, RT, c ≈ 10^{-4}M). II_n display spectra similar to II_1.

right : Fluorescence emission spectum of I_2 (- - -) (Methylcyclohexane, RT, c ≈ 10^{-4}M, λ_{exc} 370 nm). I_3 and I_4 display similar spectra.

Irradiation of I_n (λ > 320 nm) in fluid solution gives the colourless photocyclomers II_n (see Fig.1) in quantitative yield and with a very high efficiency (Table 1). A significant enhancement of the reactivity is observed in methanol (for n=1, 2 and 3) compared with MCH (Methylcyclohexane), whereas the introduction of bulky alkoxy groups at the 10 position decreases, as expected, the reactivity. For CH_3OH and to a lesser extent CH_3CN, a provisional hypothesis to explain this unexpected polar effect for a cycloaddition between two identical halves, is that the solvent can be envisioned to induce specific folded conformations which are geometrically favourable to the photocycloaddition process.

Compounds	Solvent	ϕ_R	ϕ_F	τ (ns)	ϕ_{nr} $(1-\phi_F)$	α
I_1	MCH	0.38	0.040	0.4	0.96	0.39
	CH_3CN	0.43	0.003	*	0.99	0.43
	MeOH	0.54	0.005	*	0.99	0.54
I_2	MCH	0.33	0.070	1.2	0.93	0.35
	CH_3CN	0.31	0.002	*	0.99	0.31
	MeOH	0.42	0.007	< 0.3	0.99	0.42
I_3	MCH	0.24	0.113	1.6	0.89	0.27
	CH_3CN	0.22	0.003	*	0.99	0.22
	MeOH	0.27	0.008	< 0.3	0.99	0.27
I_4	MCH	0.21	0.110	1.6	0.89	0.24
	CH_3CN	0.17	0.003	*	0.99	0.17
	MeOH	0.19	0.007	< 0.3	0.99	0.19

* Lifetimes (too short) could not be determined with our equipment.

Table 1 : Quantum yields of photocycloisomerization (ϕ_R, 366nm), fluorescence emission (ϕ_F) and nonradiative deactivation of I_n at room temperature. Fluorescence lifetimes (τ) were measured using the single photon timing technique.[14] α is the partition coefficient derived from $\phi_R = \alpha\, \phi_{nr}$.

As mentioned in Table 1, the fluorescence intensity emissions are weak and the fluorescence lifetimes very short, underlining the remarkable efficiency of the nonradiative deactivation channels of the excited state. No excimer contribution was detected under our conditions, the structured fluorescence emission spectra of I_n being similar to that of a diluted solution of 9,10- dimethoxyanthracene and the fluorescence decays are singly exponential. These results reflect well the high reactivity of the bichromophores towards the photocyclomers II_n.

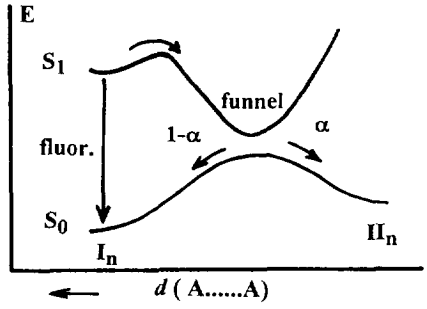


Fig. 2 :
Simplified energy profile (not scaled) for the singlet state (S_1) deactivation of compounds I_n. α denotes the partition coefficient and *d* (A...A) the distance between the meso carbons of the two anthracene rings. This calculation is valid only if internal conversion and intersystem crossing are negligible as observed for other bisanthracenes.[3,4]

Assuming, as proposed for other symmetrical bisanthracenes bearing short links,[3] that intersystem crossing is a minor deactivation channel, the nonradiative pathway ($\phi_{nr} = 1 - \phi_F$) could be essentially assigned to intramolecular interactions between the aromatic moieties on the route to the photoproduct II_n. As the reaction quantum yields (ϕ_R) are lower than ϕ_{nr}, this could indicate, according to Michl's model,[8] the efficiency with which the 'biradicaloid' intermediate in the funnel can generate the cycloadduct. The absence

of excimer fluorescence could be attributed to a high degree of symmetry in the intramolecular complex (k_F being low [9]) together with an efficient reactivity. The partition coefficients are in the range of those already found for other bisanthracenes [3,4], and strongly suggest the role of the substituent size on the ultimate photochemical step.

The photocyclomers II_n smoothly revert to the open form upon irradiation at 270 nm (ϕ_{diss} = 0.1 - 0.2) or upon heating. However, if several 'cycles : closure at 366 nm followed by thermal opening' could be performed without any apparent damage to the material, consecutive light monitored cyclomerization - dissociation steps are accompanied by some degradation [2] of I_n. This degradation is likely to originate in an homolytic α - scission ($ROAO\bullet + \bullet CH_2OAOR$) as suggested by CIDNP.[12]

These molecules are interesting models for improving our understanding of the mechanism of photodimerization, in particular the intriguing influence of solvent polarity.[13] This point is under current investigation.

REFERENCES AND NOTES :

ERASMUS student, T.H. Darmstadt, Germany.

1. H. Bouas-Laurent and J.P. Desvergne in *'Photochromism, Molecules and Systems'*, H. Dürr and H. Bouas-Laurent eds., Elsevier, **1990**, pp. 561-630.
2. J.P. Desvergne, H. Bouas-Laurent and A. Deffieux, *Mol. Cryst. Liq. Cryst.*, **1994**, *246*, 111.
3. J.P. Desvergne, N. Bitit, A. Castellan, M. Webb and H. Bouas-Laurent, *J. Chem.Soc. Perkin Trans. II*, **1988**, 1885.
4. J.P. Desvergne, H. Bouas-Laurent, F. Lahmani and J. Sepiol, *J. Phys. Chem.*, **1992**, *96*, 10616.
5. R. H. Baker, *J. Am. Chem. Soc.*, **1940**, *62*, 3305.
6. E. W. Dehmlow and J. Schmidt, *Tetrahedron Let.*, **1976**, 15.
7. I_n were synthesized as described as follows for I_4 : 9- bromoanthrone (2g, 7.3 mmol) and calcium carbonate (0.8g, 8 mmol) were added under stirring to nitrogen - purged methoxyethanol (100ml) and heated for 4 min. at 100°C. 9- methoxyethoxyanthrone (m : 72% yield) precipitated upon addition of water to the reaction mixture (m.p. 161°). δ ($CDCl_3$) ppm 3.2 (s,3H), 2.9-3.5 (m,4H), 5.8 (s,1H), 7.2-8.4 (m,8H). $\bar{\nu}$ cm^{-1} (KBr) : 1675, 1600, 1315, 1285, 1080, 830 and 700. m/z = 268 (M^+).
   9- methoxyethoxyanthrone (1.42g, 5.2 mmol), LiOH (1g, 41 mmol) and tetrabutylammonium hydrogenosulfate (Et_4NHSO_4) (3g, 8 mmol) were added to methylene chloride (20ml). The red mixture was stirred for 18 hr at room temperature under nitrogen. The yellow precipitate was filtered and purified by column chromotagraphy (neutral alumina, CH_2Cl_2/ pentane). I_4 was isolated as a yellow solid (m.p.120-3°C). (22 % yield). δ ($CDCl_3$) ppm : 3.5 (s,6H), 3.6-4;4 (m, 8H), 6.0 (s, 24), 7.2-8.6 (m,16H). $\bar{\nu}$ cm^{-1} (KBr) : 2920, 1620, 1415, 1370, 1340, 1170, 1100, 1040, 945, 765 and 675. m/z = 548 (M^+).
   I_2 : m.p ≈ 181°C (63% yield). δ $CDCl_3$ (ppm) : 4.2 (s, 6H), 6.1 (s, 2H), 7.3-8.6 (m, 16H).
   $\bar{\nu}cm^{-1}$ (KB_r) : 2920, 1620, 1430, 1350,1300, 1170, 1180, 1050 and 960. m/z = 460 (M^+).
   I_3 : m.p. : 114°C (15% yield). δ ($CDCl_3$) ppm : 1.25 (t, 6H), 2.2 0 (m, 4H), 4.20 (t, 4H) 6.1 (s, 2H) 7.2-8.4 (m, 16H). $\bar{\nu}$ cm^{-1} (KBr) : 2960, 2880, 1620, 1430, 1410, 1340, 1170, 1080, 1050, 985, 950, 765 and 665.
   m/z = 516 (M^+).
   9 - methoxyanthrone : m.p. 102°C (litt. [10] 102°C) (100% yield).
   9 - propyloxyanthrone : m.p. 135° (81% yield) δ ($CDCl_3$) ppm : 0.8 (t, 3H), 1.4 (m, 2H), 30 (t, 2H), 58 (s, 1H), 7.2-8.4 (m, 8H).$\bar{\nu}$ cm^{-1} (KBr) : 2960, 2930, 2885, 1665, 1600, 1455, 1315, 1060, 915, 805, 770 and 705. m/z = 252 (M^+).
8. N. Gerhartz, R.D. Poshusta and J. Michl, *J. Am. Chem. Soc.*, **1976**, *98*, , 6427.
9. B.F. Anderson, J. Ferguson, M. Morita and G.B. Robertson, *J. Am. Chem. Soc.*, **1979**, *101*, 1832.
10. W.R. Bergmark, G. Jones II, T.E. Reinhardt and A.M. Halpern, *J. Am. Chem. Soc.*, **1978**, *100*, 6665. K.H. Meyer, *Lieb. Ann. Chem.*, **1911**, *379*, 37.
12. M. Goez and M. Vogtherr, unpublished results.
13. L. E. Manring, K.S. Peters, G. Jones II and W.R. Bergmark, *J. Am. Chem. Soc.*, **1985**, *107*, 1485.
14. The DECAN 1.0 deconvolution programme was kindly provided by F. De Schryver. (T. De Roeck, N. Boens and J. Dockx, **1991**, K.U. Leuven).

(*Received in France* 21 *November* 1994; *accepted* 18 *December* 1994)