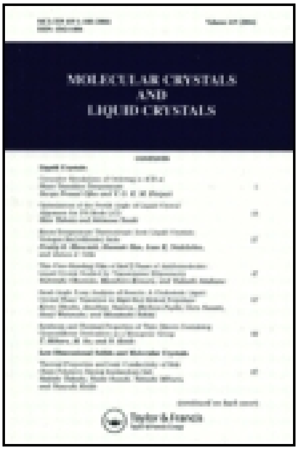

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Spironaphthoxazine-Linked Crown Ethers: Synthesis, Photochromic and Ionophoric Properties

Mohammed El Maloulibibout [a] , Lekbir Noussi [a] , Pierre Lareginie [b] , André Samat [b] & Robert Guglielmetti [b]

[a] Faculté des Sciences Am Chock., Dept. Chimie, B. P.5366, Maarif, Casablanca, Maroc

[b] Faculté des Sciences de Luminy, GCOBO, URA CNRS 1320, Case 901, 13288, Marseille, France

Version of record first published: 24 Sep 2006.

To cite this article: Mohammed El Maloulibibout , Lekbir Noussi , Pierre Lareginie , André Samat & Robert Guglielmetti (1994): Spironaphthoxazine-Linked Crown Ethers: Synthesis, Photochromic and Ionophoric Properties, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 177-181

To link to this article: http://dx.doi.org/10.1080/10587259408037809

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 177–181
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

SPIRONAPHTHOXAZINE- LINKED CROWN ETHERS : SYNTHESIS, PHOTOCHROMIC AND IONOPHORIC PROPERTIES.

Mohammed EL MALOULI BIBOUT *, Pierre LAREGINIE **,
Lekbir NOUSSI *, André SAMAT **, Robert GUGLIELMETTI **

* Faculté des Sciences Ain Chock., Dept. Chimie, B.P.5366 Maarif, Casablanca, Maroc.
** Faculté des Sciences de Luminy, GCOBO, URA CNRS 1320, Case 901, 13288 Marseille- France.

Abstract : Two new spironaphthoxazine-linked crown-ethers were synthesized, in which photoinduced structural changes and alkali-metal cations recognition have been investigated. Complexation of the crown entity does not give rise to any change in the photochromic behaviour.

INTRODUCTION

Photoresponsive systems linked crown-ethers are interesting for usefull applications, as photoinduced ionic conductivity switching, or transfer of light energy to the crown-ether moiety.[1] Up to now, investigations on this field, using photochromic compounds, were particularly carried out on spirobenzopyran series [1b,c] but also on spirooxazine series.[2] The latter show a great improvement of photoresistance. [3]

We report herein the preliminary results obtained for spironaphthoxazines bearing a benzo-crown ring as recognition site. The purpose of our work was to study the own properties of each function and eventually to determine interactions between the two moieties, i.e. photochromic behaviour of spironaphthoxazine moiety after complexation of cations and the eventual changes in the recognition ability of the crown ether part.

SYNTHESIS

The new spironaphthoxazine-linked crown ethers **3** and **4** were prepared in three steps from 2,7-dihydroxy-naphtalene (figure 1). Among the numerous methods available in the literature, Hassner's esterification[3] revealed to be a convenient procedure; indeed, the last step of the reaction is performed under mild conditions,using dicyclohexylcarbodiimide and catalytic amount of pyrrolidino-pyridine, with relatively good yields (60-70 % in our case).

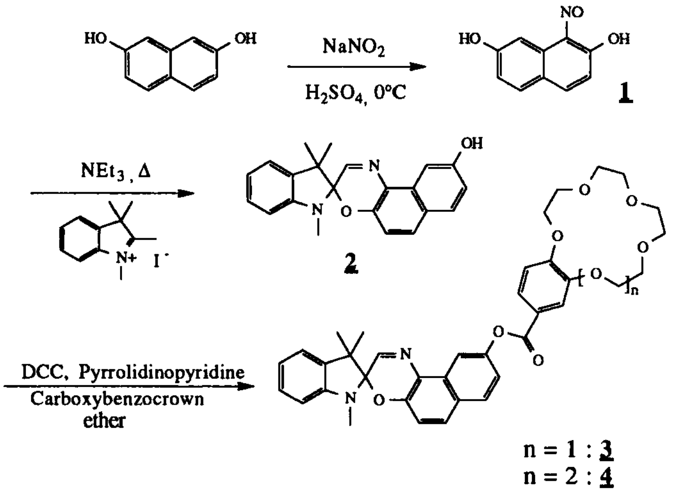

FIGURE 1

PHOTOCHROMIC BEHAVIOUR

Preliminary spectrokinetic studies on spironaphthoxazines **3** and **4** in acetonitrile gave results very close to those obtained in the case of spiro[indoline-naphthoxazine] without crown-ether (Table 1). Addition of alkali-metal iodides to these solutions did not lead to any substantial change in the maximum absorptions. A decrease of the bleaching constant with NaI saturated solutions is observed in all the cases, showing that the complexation of the crown ether is not responsible of this phenomenom.

These results are in accordance with those observed in some cases by Inoue[5], and may suggest that the crown moiety located at the 9'-position of the spironaphthoxazines might keep the complexed cation away from the quinoid part of the photomerocyanine.

COMPLEXATION

In order to estimate cation complexing capacities of the resulting crowned spironaphthoxazines **3** and **4**, cation extraction was carried out from an aqueous alkali-metal picrate solution with a crowned spironaphthoxazine in chloroform solution under dark conditions.[6] The results are summarized in figure 2 (percent extraction is given as a measure of cation complexing ability)

TABLE 1 Salt effects on spectrokinetic parameters of **3** and **4** (toluene, 25°C, $C = 2.5 \cdot 10^{-5}$ mol/l).

Compound	Salt in acetonitrile	λmax (nm)	A0	k_Δ (s^{-1})
1,3,3-trimethyl spiro[indoline-naphthoxazine]	none	593	1	1.6
	KI saturated solution	593	0.57	1.7
	NaI saturated solution	600	0.49	0.5
3	none	592	0.76	0.81
	KI saturated solution	593	0.80	0.77
	NaI saturated solution	598	0.48	0.26
4	none	590	1.2	0.75
	KI saturated solution	592	0.82	0.72
	NaI saturated solution	594	0.77	0.41

The shapes of the curves observed for Li$^+$, Rb$^+$ and Cs$^+$ are omitted for clarity. Cation-complexing properties of compounds **3** and **4** are comparable with those of the free methyl-carboxybenzocrown under the same conditions . The order of extraction ability is : Na$^+$> K$^+$> Rb$^+$> Cs$^+$> Li$^+$ for (**3**), and K$^+$> Na$^+$> Rb$^+$> Li$^+$ > Cs$^+$ for (**4**).

Thus, the cation complexing behaviour of crowned spironaphthoxazines originates essentially from their crown entity.

TRANSPORT

Transport of alkali-metal ions was carried out in a U-type cell with stirring at room temperature.[7] The amounts of the transported alkali-picrate ions from the aqueous solution through a chloroformic phase containing the synthetic ionophores **3** and **4** were measured by spectrophotometry . Figure 3 shows that potassium ion was preferentially transported by (**4**) and sodium by (**3**). Lithium, rubidium and cesium ions are also carried but more slowly . The overall orders of selectivity observed in each case are quite similar to the results obtained for extraction process.

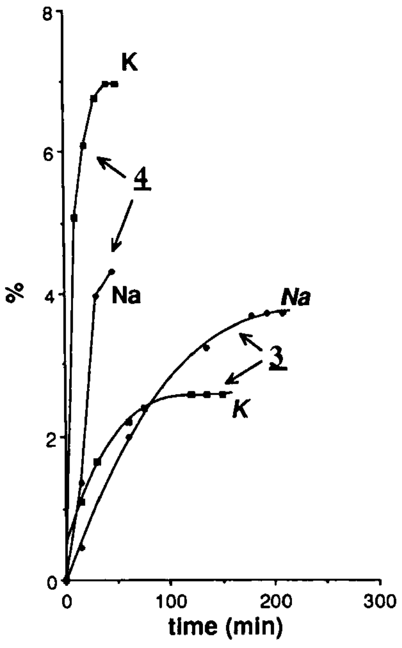

FIGURE 2 Extraction (%) of Na^+ and K^+ from an aqueous to a chloroformic phase vs time.

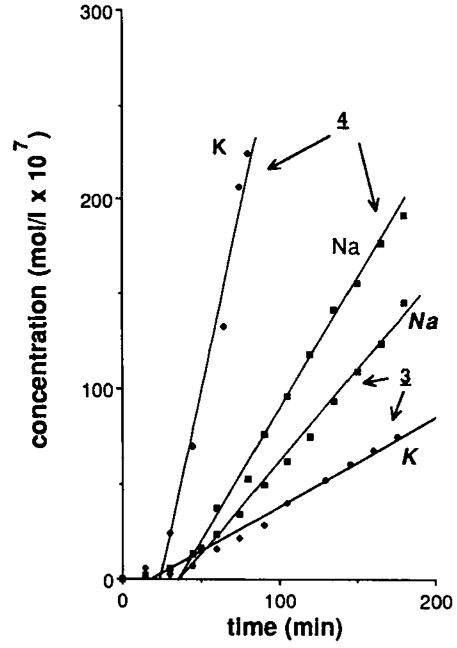

FIGURE 3 Na^+ and K^+ transport through a chloroformic phase (picrate concentration in the aqueous phase vs time).

CONCLUSION

Preliminary results on spectrokinetic studies of the photochromic properties have shown no influence of the crown ether part, even complexed. Concerning the crown ether moieties, the results obtained for transport and complexation of alkali-metal cations can be compared with their parent free benzo-crown compounds.

EXPERIMENTAL :

2,7- dihydroxy-1-nitrosonaphtalene (1) was synthesized almost quantitatively from 2,7-dihydroxynaphtalene.[8]

a) 1,3,3-trimethyl-9'-hydroxyspiro[indoline-naphthoxazine] (2) :

To a 100 ml round bottomed flask equipped with a condenser, and an addition funnel, are added 6.0g (33mmol) of 2,7-dihydroxy-1-nitrosonaphtalene, and 60ml of absolute ethanol.

The mixture is gently refluxed and stirred, while a solution of 10,5g (36mmol) of 1,2,3,3-tetramethyl-3H-indoleninium iodide, 5,4 ml of triethylamine and 36 ml of absolute ethanol is added over a 30 min period. The mixture is refluxed for 2h and evaporated under vacuum. The crude product was chromatographied on silica gel column with dichloromethane as eluent. Recrystallization from ethanol gave 4,2g (37%) of the pure compound. m.p . 167-173°C (Lit.[9] 167-173 °C).^{1}H n.m.r.($CDCl_3$, TMS) ; (δ p.p.m., J (Hz)) : 1.35 (s) ; 2.76 (s); 5.85 (s); 6.57 (d, 7.7) ; 6.84 (d, 8.8) ; 6.90 (dd, 7.4) ; 7.02 (dd, 8.8, 2.5) ; 7.08 (d, 7.1); 7.21 (dd,7.6) ; 7.58 (d, 8.8) ; 7.65 (d, 8.8) ; 7.71 (s) ; 7.88 (d, 2.5) .

b) 1,3,3-trimethyl-9'-carboxybenzo-15-crown-5-spiro[indoline-naphthoxazine] (3) :
A solution mixture of 0,22g (0,77mmol) of 4-carboxybenzo-15-crown-5, 0,35g (0,77mmol) of (2), 0,16g (0,7mmol) of N,N- dicyclohexylcarbodiimide, and10mg (0,07mmol) of 4-pyrrolidinopyridine in 30ml of anhydrous dichloromethane, was stirred at room temperature for 24 h. The N,N- dicyclohexylurea was filtered, and the filtrate washed with water (3x50ml), 5% acetic acid solution (3x50 ml) and finally with water (3x50 ml), dried over $MgSO_4$, and evaporated under vacuum.The crude product was chromatogaphied on silica gel column with dichloromethane / ethylacetate (90/10) as eluent. The last fraction was isolated to give 0,30g (67%) of (3). m.p. 129°C . ^{1}H n.m.r. ($CDCl_3$, TMS) ; (δ p.p.m., J (Hz)) : 1.35 (s) ; 2.76 (s) ; 3.70 (m) ; 3.79 (s) ; 3.90 (m) ; 3.94 (m) ; 4.20 (m) ; 4.23 (m) ; 6.57 (d, 7.7) ; 6.90 (dd, 7.30); 6.94 (d, 8.4) ; 7.00 (d, 8.9) ; 7.09 (dd, 6.4) ; 7.22 (dd, 7.6) ; 7.26-7.36 (dd, 8.8, 2.2); 7.67 (d, 8.9); 7.72 (d, 2.0); 7.76 (s); 7.78 (d, 8.9) ; 7.89 (dd, 8.4); 8.35 (d, 2.3) .

c) 1,3,3-trimethyl-9'-carboxybenzo-18-crown-6-spiro[indoline-naphthoxazine] (4) :
Similar procedure gave (4) in 60% yield; m.p. 113-114 °C.1H n.m.r. ($CDCl_3$, TMS) ; (δ p.p.m., J (Hz)) : 1.39 (s) ; 2.80 (s) ; 3.70 (m) ; 3.74 (s) ; 3.79 (d) ; 3.90 (m) ; 4.00 (m) ; 4.29 (m) ; 4.30 (m) ; 6.61 (d, 7.60); 6.93 (dd, 7.60) ; 7.74 (s) ; 7.93 (dd, 8.4) ; 8.39 (d, 2.1).

REFERENCES

1.a) H. Sakai, A. Ueno, J. Anzai, T. Osa , Bull.Chem.Soc.Jpn, 59, 1953 (1986).
   b) S. Shinkai, T. Ogawa, O. Manabe, J.Am.Chem.Soc , 104, 1960 (1982).
   c) M. Inouye, M. Ueno and T. Kitao , J.Org. Chem., 57, 1639 (1992).
2. K. Kimura , T. Yamashita and M. Yokoyama , J.Chem. Soc. Chem. Commun., 969 (1992) .
3. a) N.Y.C. Chu," Photochromism : Molecules and Systems"; eds. H. Dürrr, H. Bouas-Laurent, Elsevier, Amsterdam, 493 (1990), Chap. 10.
   b) J.C. Crano, W.S. Kwak, C.N.Welch, "Applied Photochromic Polymer Systems", ed. C.B. McArdle, Blackie, London, 31 (1992), Chap. 2
   c) N.Y.C. Chu, Can.J.Chem, 61, 300 (1983).
4. A. Hassner, V. Alexanian, Tetrahedron Lett., 46, 4475 (1978)
5. M. Inoue , M. Ueno and T. Kitao , J. Am. Chem.Soc., 112 , 8977 (1990).
6. J. Pedersen , Fed. Proc., 27, 1305 (1968).
7. A. Samat, M. El Malouli Bibout, J. Elguero, J.Chem. Soc. Perkin.Trans.1 , 1717 (1985)
8. C.S. Marvel, P.K. Porter, Org.Synth. Coll , 1, 411 (1941) .
9. B. Osterby, R.D. McKelvy, L.Hill , J.Chem. Educ., 68, 425 (1991) .