Tetrahedron Letters Vol. 21, pp 541 - 544 0040-4039/80/0201-0541$02.00/0

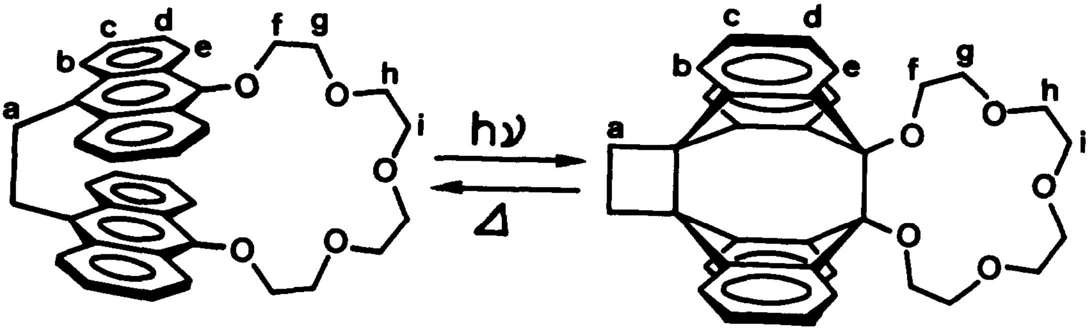
SYNTHETIC MACROCYCLIC LIGANDS. II.[1)]
SYNTHESIS OF A PHOTOCHROMIC CROWN ETHER

Isamu YAMASHITA, Mieko FUJII, Takahiro KANEDA, and Soichi MISUMI*
The Institute of Scientific and Industrial Research, Osaka University
Suita, Osaka 565, Japan

Tetsuo OTSUBO
Department of Applied Chemistry, Faculty of Engineering
Hiroshima University, Sendamachi, Hiroshima 730, Japan

Abstract: A photochromic crown ether with two anthracene nuclei is synthesized and the metal ion dependence of its photo and thermal reactions is studied.

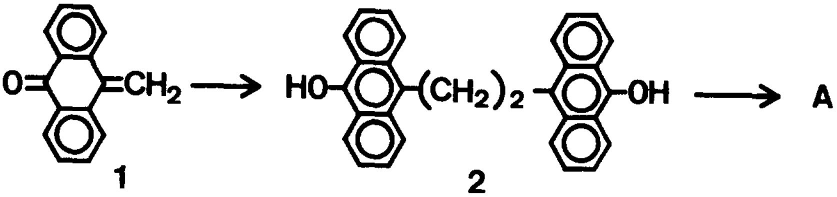
A wide variety of macrocyclic polyethers bearing aromatic nuclei have been reported to complex with metal ions as well as ammonium salts.[2)] However, most of them are photochemically inactive host molecules. A photochromic crown ether in which a macrocyclic polyether is bonded to a photochromic molecule and the cavity of the polyether moiety is changeable in photochromic or reversible process, is of interest for the following reasons: 1) the complexation with metal ions of different sizes is photo-controlled, 2) the reversible process is usable for selective metal ion transportation. In this regard a few host molecules, to our knowledge, have been reported.[3)] This paper is concerned with the synthesis of and the alkali metal ion complexation of a photochromic crown ether where two anthracene moieties are closely linked each other in a crown ether.



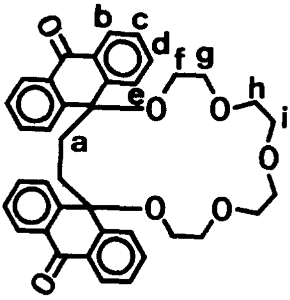
A

P

The preparation of 1,2-bis(10-hydroxy-9-anthryl)ethane **2**, which was extremely air-sensitive in solution, was carried out by reductive dimerization of 10-methyleneanthrone **1**.4) Co-cyclization of diol **2** with tetraethylene glycol ditosylate under a nitrogen atmophere gave a 3.8% yield of macrocyclic polyether **A** (**A**: greenish yellow columns from alcohol, mp 170-171°C).5) When nitrogen exchange in the reaction vessel was incomplete and sodium hydride was used as a base, undesired cyclic polyether **3** was obtained in an 18% yield in place of compound **A** (**3**: colorless columns from diethyl ether, mp 217-218°C).5)



On irradiation of compound **A** in benzene-d_6, the ^{1}H NMR spectra showed the appearance of new signals containing a sharp singlet (2.68 ppm) assigned to cyclobutane protons while the signals assigned to compound **A** were completely missing. This indicates the formation of a photoisomer, 15-crown-5 derivative **P**.5) When heated the colorless solution thus obtained at 40-50°C in the dark, the original signals of **A** were restored with the same intensity as before irradiation. Such a quantitative interconversion between compounds **A** and **P** was also confirmed by rise and fall of the long wavelength band (340-440 nm) associated with the anthracene chromophore in the electronic spectra.



3

$$\begin{tikzcd}
A \arrow[d, shift right, "k_1\,(h\nu)"'] & + \; M^+ \arrow[r, shift left, "K_A"] & AM^+ \arrow[l, shift left] \arrow[d, shift right, "k_2\,(h\nu)"'] & \cdots\cdots(3) \\
P \arrow[u, shift right, "k_{-1}\,(\Delta)"'] \arrow[d, dash, dotted] & + \; M^+ \arrow[r, shift left, "K_P"] & PM^+ \arrow[l, shift left] \arrow[u, shift right, "k_{-2}\,(\Delta)"'] \arrow[d, dash, dotted] & \cdots\cdots(4) \\
(1) & & (2) &
\end{tikzcd}$$

The complexation of compounds A and P was examined next. When a metal ion coexists in the above-stated reversible process (equation 1), another photochromic process (eq. 2) may be possible through two complexation equilibria (eq. 3 and 4). In order to examine the effect of metal ion on photochromic process eq.(1), half-lives of compound A in the photo-reaction and of compound P in the thermal reaction were measured with and without metal ions, using the time dependence of absorbance at 385 nm of the anthracene chromophore in the electronic spectra. The results are summarized in the Table.

Table Half-lives of compounds A and P$^{a)}$

Thermal reaction$^{b)}$			Photo-reaction$^{c)}$		
$M^{+d)}$	M^+/P	$t^{1/2}$(min)	$M^{+d)}$	M^+/A	$t^{1/2}$(min)
ion free	—	9.6	ion free	—	12
Li^+	1.6	11	Li^+	1000	12
	890	2100			
Na^+	1.6	26	Na^+	1000	12
K^+	1.6	12			

a) solvent: dry THF. b) at 30°C. c) at 4°C; the thermal reaction does not proceed at this temperature. d) as perchlorate.
e) solvent: 1% aq. THF.

As shown in the Table, the half-life of the dark reaction is prolonged in the presence of metal ion compared to that of ion-free case, and the ion dependence of half-life is in the order: $Na^+ > K^+ > Li^+$. The longest half-life for Na^+ is understood by lowering of the concentration of compound P due to the formation of stable P-Na^+ complex, considering that the parent crown ether of P, 15-crown-5, forms the most stable complex with Na^+ compared to those with other alkali metal ions.[6)] Furthermore, the half-life of the dark reaction increases with an increase of ion concentration as seen in the case of lithium perchlorate. This fact suggests the rate constant, k_{-1}, of the dark reaction in eq.(1) to be larger than k_{-2} of the corresponding reaction in eq.(2), providing that the complexation of compound P attains equilibrium rapidly as same as in that of parent 15-crown-5. In other words, the dark reaction proceeds, also in the presence of metal ions, through the photochromic process of eq.(1), but not eq.(2).

On the other hand, the photo-reaction shows no dependence on metal ions in contrast to the dark reaction. The Table shows that all the photo-reactions have the same half-life even in the presence of large excess of metal perchlorate. This may be attributed to much larger energy of the photo-transition than the stabilization energy due to the ion complexation.

Further studies on the title compound as well as the corresponding compounds with different crown rings are under way.

References and Notes

1) Part I: N. Kawashima, T. Kawashima, T. Otsubo, and S. Misumi, *Tetrahedron Lett.*, 5025 (1978).

2) G. W. Gokel and H. D. Durst, *Synthesis*, 168 (1976); D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, **11**, 8 (1978); J.-M. Lehn, *ibid.*, **11**, 49 (1978); R. M. Izatt and J. J. Christensen, "Synthetic Multidentate Macrocyclic Compounds", Academic Press, New York (1978); R. M. Izatt and J. J. Christensen, "Progress in Macrocyclic Chemistry", Vol. 1, John Wiley & Sons, New York (1979).

3) J.-P. Desvergne and H. Bouas-Laurent, *J. Chem. Soc., Chem. Commun.*, 403, (1978); A. Ueno, H. Yoshimura, R. Saka, and T. Osa, *J. Am. Chem. Soc.*, **101**, 2779 (1979); A. Ueno, R. Saka, and T. Osa, *Chem. Lett.*, 841 (1979).

4) H.-D. Becker and D. Sanchez, *Tetrahedron Lett.*, 3745 (1975).

5) Compounds A and 3 show satisfactory elemental analyses and spectral properties. A: ^{1}H NMR (100 MHz, $CDCl_3$) δ 8.11 (d, J=9 Hz, 4H, He), 7.63 (d, J=9 Hz, 4H, Hb), 7.3-6.8 (m, 8H, Hc and Hd), 4.18 (s, 4H, Ha), 3.99 (t, J=5 Hz, 4H, Hf), 3.75-3.5 (m, 12H, Hg, Hh, and Hi); λmax (log ε) in THF, 255 nm (5.22), 262 (5.18), 367 (4.00), 385 (4.13), 409 (4.00); MS m/e 572 (M^+), 206 (1^+). P: ^{1}H NMR (100 MHz, C_6D_6) δ 7.65-7.55 (m, 4H, Hb), 7.1-6.7 (m, 12H, Hc, Hd, and He), 4.05-3.75 (A_2B_2, 8H, Hf and Hg), 3.55-3.35 (A_2B_2, 8H, Hh and Hi), 2.68 (s, 4H, Ha). 3: ^{1}H NMR (100 MHz, $CDCl_3$) δ 8.18 (d, J=8 Hz, 4H, Hb), 7.8-7.3 (m, 12H, Hc, Hd, and He), 4.05-3.8 (A_2B_2, 8H, Hf and Hg), 3.64-3.5 (m, 4H, Hh or Hi), 3.2-3.02 (m, 4H, Hi or Hh), 1.87 (s, 4H, Ha); λmax (log ε) in CH_2Cl_2, 276 nm (4.49); IR (nujol mull), 1664 cm^{-1} ($\nu_{C=O}$); MS m/e 604 (M^+), 576 (M-CO), 206 (1^+).

6) H. K. Frensdorff, *J. Am. Chem. Soc.*, 93, 600 (1971).

(Received in Japan 20 November 1979)