

## Preparation of Photoresponsive Cyclobutane-1,2-dicarbonyl-capped 2.*n* Diazacrown Ethers by Intramolecular [2 + 2] Photocycloaddition, and their Highly Selective Complexation with Lithium Cation

Sadatoshi Akabori,<sup>a\*</sup> Takeshi Kumagai,<sup>a</sup> Yoichi Habata,<sup>a</sup> and Sadao Sato<sup>b</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Toho University, Funabashi-shi, Chiba 274, Japan

<sup>b</sup> Analytical Metabolic Research Laboratories, Sankyo Co. Ltd., 1-2-58 Hiromachi, Shinagawa-ku, Tokyo 140, Japan

Photoresponsive cyclobutane-1,2-dicarbonyl-capped 2.*n* diazacrown ethers were prepared by the intramolecular [2 + 2] photocycloaddition of *p,p'*-trimethylene dicinnamoyl-capped 2.*n* diazacrown ethers; the cyclobutane-1,2-dicarbonyl-capped 2.1 diazacrown ether showed a highly selective complexing ability for the lithium cation.

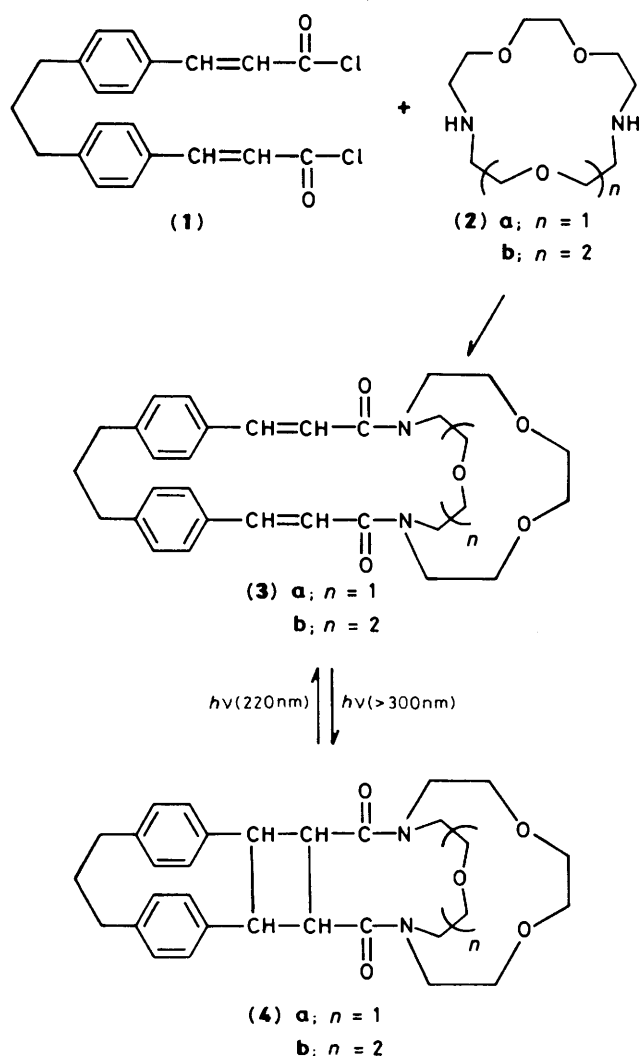
Recently, many kinds of photoresponsive crown ethers have been reported.<sup>1</sup> Cyclobutanocrown ethers formed by intramolecular [2 + 2] photocycloaddition have received much attention from the viewpoint of the synthesis of crown ethers in this respect.<sup>2</sup> However, the possibility of photoreversible cleavage of the cyclobutanocrown ethers has not been considered. In concert with the cyclobutanocrown ethers, we have reported the syntheses of cyclobutanocrown ethers by the intramolecular [2 + 2] photocycloaddition of  $\alpha,\omega$ -dicinnamoyl polyethylene glycol derivatives and their photoreversible reactions.<sup>3</sup> The extraction abilities of the cyclobutanocrown ethers toward alkali metal cations were found to be very low or negligible as a result of the structures being in the  $\delta$ -form, containing ester groups in the macrocycle, a disadvantageous feature for complexation.

As a consequence of this reaction, we have studied the syntheses of photoresponsive cyclobutane-1,2-dicarbonyl-capped 2.*n* diazacrown ethers (**4**) by the intramolecular [2 + 2] photocycloaddition of *p,p'*-trimethylene dicinnamoyl-capped 2.*n* diazacrown ethers (**3**) and their properties. Condensation of (**1**)<sup>4</sup> with (**2a**) and (**2b**) gave (**3a**) (m.p. 228.5–230.5 °C) and (**3b**) (m.p. 202.0–203.5 °C) in 15 and 14.1% yields, respectively.<sup>†</sup>

The intramolecular [2 + 2] photocycloaddition of (**3**) and its photoreversible reaction was carried out as follows. Irradiation of (**3a**) and (**3b**) in acetonitrile for 1.5 h under a nitrogen atmosphere at running-water temperature (Pyrex filter with a 450 W high-pressure mercury lamp) in the absence of a sensitizer gave (**4a**) (m.p. 255.0–257.0 °C) and (**4b**) (m.p. 300.0–302.0 °C) in 91.7 and 31.6% yields, respectively. X-Ray analysis<sup>‡</sup> of (**3a**) shows that the two double bonds lie in the same direction and that the distance between the two double bonds is *ca.* 4.7–4.8 Å. This distance is much longer

<sup>‡</sup> Crystal data for (**3a**): C<sub>31</sub>H<sub>38</sub>N<sub>2</sub>O<sub>5</sub>, *M* = 518.6, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 18.359(1), *b* = 10.391(3), *c* = 15.477(1) Å,  $\beta$  = 108.84(1)°, *U* = 2794.2 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.23 g cm<sup>-3</sup>,  $\mu$ (Cu-K $\alpha$ ) = 6.8 cm<sup>-1</sup>; for (**5**): C<sub>32</sub>H<sub>28</sub>LiN<sub>3</sub>O<sub>5</sub>S, *M* = 583.7, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 16.442(15), *b* = 14.949(12), *c* = 12.841(11) Å,  $\beta$  = 111.89(6)°, *U* = 2928.6 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.30 g cm<sup>-3</sup>,  $\mu$ (Cu-K $\alpha$ ) = 13.3 cm<sup>-1</sup>. Intensity data for 2 $\theta$  < 128° were recorded on a Rigaku AFC-5R diffractometer with graphite monochromated Cu-K $\alpha$  irradiation. Of 4655 and 4825 independent reflections measured, only 3384 and 2461 were considered as observed with *F*<sub>o</sub> > 2 $\sigma$ (*F*<sub>o</sub>) for (**3a**) and (**5**), respectively. All intensities were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods using MULTAN84,<sup>8</sup> and refined by block-diagonal least-squares methods. For (**5**) the central carbon atom of the trimethylene moiety is disordered over two sites, approximately 1 Å apart, and occupancies for the split atoms [C(27) and C(27')] were set at 0.5 and not varied. The positions of the hydrogen atoms were estimated using standard geometry, and the final refinements with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperatures for the hydrogen atoms were lowered *R* values 0.085 [*R*<sub>w</sub> = 0.047, *w* = 1/ $\sigma^2$ (*F*<sub>o</sub>)] and 0.175 [*R*<sub>w</sub> = 0.161, *w* = 1/ $\sigma^2$ (*F*<sub>o</sub>)] for (**3a**) and (**5a**), respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

<sup>†</sup> Satisfactory spectroscopic, microanalytical, and/or high resolution mass spectroscopic data were obtained for all new compounds. <sup>1</sup>H n.m.r. (400 MHz): (**3b**): (CDCl<sub>3</sub>),  $\delta$  7.47 (d, *J* 15.4 Hz, 2H, C-H), 7.16–6.57 (m, A<sub>2</sub>B<sub>2</sub> pattern, 8H, aromatic H), 6.66 (d, *J* 15.4 Hz, 2H, C-H), 4.07–3.36 (m, 24H, -NCH<sub>2</sub>- and -OCH<sub>2</sub>-), 2.90–2.52 (m, 4H, -CH<sub>2</sub>-), 2.40–2.06 (m, 4H, -CH<sub>2</sub>-); (**4b**): (CDCl<sub>3</sub>),  $\delta$  6.67–6.28 [m, (2 × A<sub>2</sub>B<sub>2</sub>), 8H, aromatic H], 4.56–4.53 (q, *J* 3.5 Hz, 1H, -NCH<sub>2</sub>-), 4.52–4.50 (q, *J* 3.5 Hz, 1H, -NCH-), 4.45–4.44 (m, 2H, C-H), 4.27–4.25 (m, 2H, C-H), 3.96–3.42 (m, 20H, -OCH<sub>2</sub>- and -NCH<sub>2</sub>-), 2.74–2.68 (m, 6H, -CH<sub>2</sub>- and -NCH-), 2.17–2.02 (m, 2H, -CH<sub>2</sub>-).



Scheme 1

than that observed for olefinic compounds (4.0 Å) in which intermolecular [2 + 2] photocycloaddition can occur in the crystalline state.<sup>5</sup> Therefore, the intramolecular [2 + 2] photocycloaddition of (3) must have occurred after the two double bonds approached within 4.0 Å of each other, made possible by the molecular flexibility of (3) in solution. The respective configurations of (3a) and (3b) were elucidated by a comparative n.m.r. spectrum with the corresponding starting materials and a 2D COSY n.m.r. study of (4b). Since in compounds (4a) and (4b) the bridged chain is too short to allow the formation of a  $\delta$ -isomer, these intramolecular [2 + 2] photoadducts should be the  $\beta$ -isomer. Indeed, this was substantiated by the fact that, in the n.m.r. spectra, the aromatic protons absorb at a higher field where they are deshielded by the opposite aromatic group, thus differing from the spectra of the starting materials (3a) and (3b). Compound (4b) is sterically very crowded and shows interesting properties: for example, in the 2D COSY <sup>1</sup>H n.m.r. spectrum of (4b) the chemical shift of one proton of the methylene group adjacent to the nitrogen atom is *ca.* 0.82 p.p.m. further downfield from that of the starting materials (3b), whereas the other proton on the same carbon atom is generally found upfield (*ca.* 1.00 p.p.m.) from that of (3b). As expected from the Corey-Pauling-Koltun (CPK) model, the

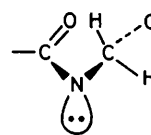


Figure 1

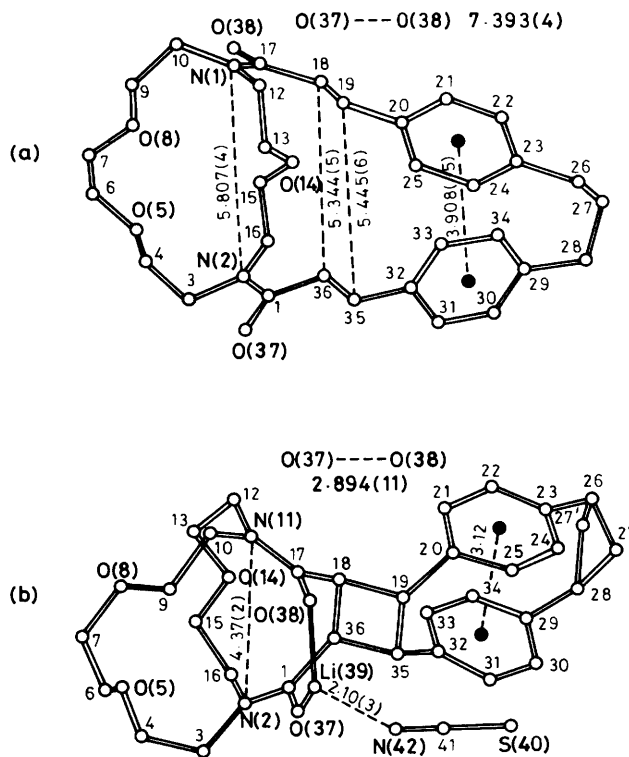


Figure 2. The molecular structures of (a) (3a) and (b) (5) with selected interatomic distances (Å) and the atom-numbering scheme. A filled circle (●) denotes the centroids of the phenyl rings.

upfield and downfield shifts of the methylene protons can be attributed to the steric compression between the carbonyl group and the methylene proton adjacent to the nitrogen atom, Figure 1.

Acetonitrile solutions of (4a) and/or (4b) (*ca.*  $4 \times 10^{-5}$  mol/l) were irradiated with 220 nm u.v. light using a grating monochromator with a 500 W Xenon lamp. The absorption band at 275 nm increased with u.v. irradiation of the solution, and a steady state was attained for 3 h. The structures of the irradiated products were confirmed by direct comparison of the  $R_F$  values from t.l.c. and spectral data with those of the authentic samples. The photoreversible cleavage of (4a) and (4b) proceeded in 44.8 and 39.1% yields, respectively. Measurement of the extraction ability was carried out by the method described in a previous paper.<sup>6</sup> It was found that (4a) extracts  $\text{Li}^+$  most efficiently among alkali metal ions, although (3a) did not show any extraction ability toward them. The extraction ability of (4a) was found to be:  $\text{Li}^+$  (39%) >  $\text{Cs}^+$  (33%) >  $\text{K}^+$  (27%) >  $\text{Rb}^+$  (25%)  $\geq$   $\text{Na}^+$  (24%). Furthermore, (4a) showed a high extraction ability toward the silver(I) cation (39%). Compounds (3b) and (4b) showed poor extraction efficiency with alkali metal ions (less than 1%). These findings are in contrast to the results obtained by Vögtle *et al.*<sup>7</sup> That is, they suggest the selective complexing ability of

the *p*-xylyl-capped 2.2 diazacrown ethers with sodium ion amongst alkali metal ions. Furthermore, a 1:1 complex (**5**) (m.p. 300.0–304.0°C) of (**4a**) with LiSCN was obtained. The molecular structures of (**3a**) and (**5**) are illustrated in Figure 2. In (**3a**) the alkene–alkene distances [C(19)–C(35) and C(18)–C(36)] are 5.445(6) and 5.344(5) Å, respectively. The distance between the centroids of the two phenyl groups is 3.908(5) Å and the dihedral angle of the two phenyl groups is 28.2(1)°. The intramolecular distance between the N(2) and N(11) atoms is 5.807(4) Å. In (**5**) no special disorder was observed for the guest molecule and the other part of the host molecule except the trimethylene group. Trimethylene groups are notoriously difficult to refine owing to the potential for disorder. The complexing manner differs completely from the general aspect of the complexes of crown and azacrown ethers with metal ions in which the metal ions are incorporated into the cavity of the macrocyclic moiety of the host molecule. In complex (**5**), the lithium ions are complexed by co-ordination to the oxygen atoms of the two amide groups. The bond distances between Li+–O(37), Li+–O(38), and Li+–N(42) are 1.93(2), 1.90(2), and 2.10(3) Å, respectively. These distances are in fair agreement with the sums of the ionic radius of Li+ (0.60 Å) and the van der Waals radii of the oxygen atom (1.4 Å) and nitrogen atom (1.5 Å). The distance (3.12 Å) between the centroids of the two phenyl groups and the dihedral angle [8.4(6)°] of the two phenyl groups are smaller than those in (**3a**). Furthermore, the intramolecular distance between O(37) and O(38) of the amide groups is 2.894(11) Å, extremely short compared with that in (**3a**).

In conclusion the differences in the extraction abilities and the photoreversible reaction between (**3a**) and (**4a**) suggest

that the photoreversible reaction can control the extraction abilities toward alkali metal cations, especially the lithium cation, by changes in the wavelength of the irradiating u.v. light. More detailed structural studies are in progress.

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