

## Even-Odd Effect on the Monolayer Behavior of Azobenzene Derivatives Containing Urea Head Group

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Monolayers of azobenzene (Az)-containing long chain having a urea head group on water show a characteristic packing structure in which the trans-to-cis photoisomerization is completely hindered (Seki et al., *Bull. Chem. Soc. Jpn.*, **71**, 2807 (1998)). Such a characteristic feature is probably derived from the formation of bifurcated hydrogen bonds among the urea heads. In this paper, we prepared a series of homologous derivative changing the alkylene spacer length connecting between the Az moiety and the urea head group. It is found here that the spreading behavior of these amphiphiles on water and UV-visible absorption spectral features on a quartz substrate change regularly depending on the even/odd carbon number of the spacer.

Key words: urea, azobenzene, monolayer, even-odd effect, spacer length

### 1. INTRODUCTION

The urea moiety provides a particularly useful building block<sup>1)</sup> in supramolecular chemistry.<sup>2), 3)</sup> The urea group is able to form bifurcated NH...O hydrogen bond with two NH groups with neighboring another urea group (see Fig. 1), and these paired hydrogen bonds afford a robust and highly directional intermolecular joint. The spreading behavior of the Langmuir monolayers of long chain alkylureas at the air-water interface is also a subject of great interest.<sup>4)</sup> The monolayer of alkylureas, unlike other amphiphiles, exhibits a sudden contraction at an intrinsic transition temperature on heating. It is interpreted that the bifurcated hydrogen bonds among the urea heads are responsible for this thermal change in the molecular packing.

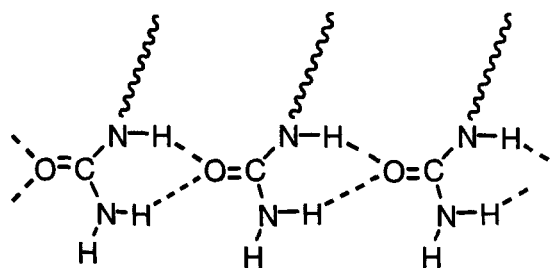


Fig. 1 Schematic representation of the bifurcated hydrogen bonds between the urea units.

Our recent work using an azobenzene (Az)-containing long chain urea showed that this monolayer on the water surface takes a characteristic packing structure in which the trans-to-cis photoisomerization is completely prevented.<sup>5)</sup> More interestingly, when the monolayer is transferred onto a hydrophilic substrate, the stacking

state and photoisomerization behavior of Az is obviously switched by the isothermal atmospheric change.<sup>6)</sup> We report herein a new aspect on the molecular design of the Az-urea monolayer system. It is found here that the carbon parity (even-odd number) of the alkylene spacer connecting the urea and the Az unit leads to alternations of the spreading behavior and the molecular packing nature. Examples of even-odd effects affecting to the thermal properties in thermotropic liquid crystals are widely known.<sup>7)</sup> In the two dimensional monolayer or bilayer assembly systems, various surface-mediated phenomena such as wetting of liquid,<sup>8)</sup> ice nucleation,<sup>9)</sup> liquid crystal alignment<sup>10)</sup> and electrochemical properties<sup>11)</sup> are altered by the carbon parity. As mentioned below, the results presented here should give new insight into the photochromic monolayer.

### 2. EXPERIMENTAL

A series of Az-urea compounds, *N*-(*n*-{4-[(4-hexylphenyl)azo]phenoxy})alkylurea (6Az<sub>*n*</sub>-urea, *n*=3-7), used in this work is shown in Fig. 2. These compounds were synthesized in the similar manners as described in reference 5 for *n*=10.<sup>5)</sup> The corresponding Az-containing carboxylic acid derivatives (6Az<sub>*n*</sub>-COOH), the starting compounds, were converted to isocyanates and then a following reaction with ammonia gas was performed (Scheme 1). The melting points were measured on a Yanaco MP-S3 melting-point apparatus, and are uncorrected. <sup>1</sup>H-NMR spectra were recorded on a Bruker AC-200 spectrometer (at 200 MHz), and chemical shifts are denoted in  $\delta$  units relative to CDCl<sub>3</sub> and converted to the Me<sub>4</sub>Si scale  $\delta$ =7.26.

The spreading behavior of Az-containing monolayers was evaluated on pure water (Milli-Q grade, 18 M $\Omega$  cm<sup>-1</sup>, pH=5.8) using a Lauda FW1 film balance in subdued red light. The temperature of subphase was

maintained  $20 \pm 0.5$  °C by water circulation. The 6Az<sub>n</sub>-urea and 6Az<sub>n</sub>-COOH were spread from a chloroform solution ( $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>). After evaporation of chloroform, 6Az<sub>n</sub>-urea and 6Az<sub>n</sub>-COOH monolayers were compressed at a speed of 30 cm<sup>2</sup> min<sup>-1</sup>. The surface pressure was recorded *versus* the molecular area.

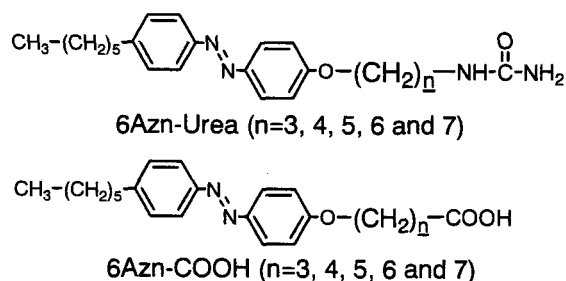


Fig. 2 The chemical structure of the Az-amphiphiles used in this study.

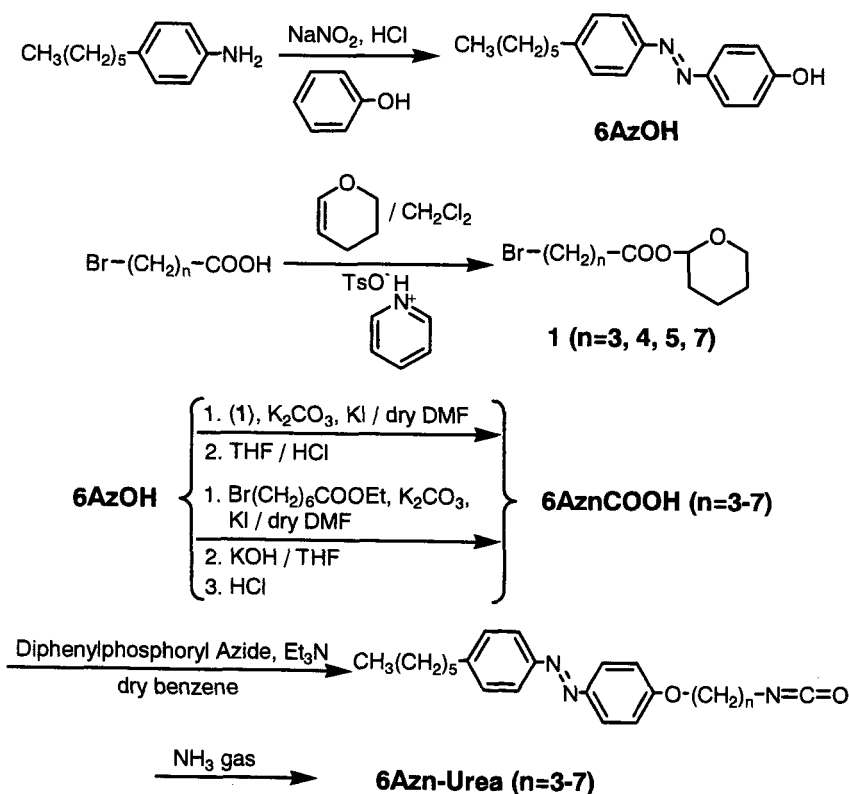
Table I. Yields and melting points of 6Az<sub>n</sub>-Urea (n=3–7).

Carbon number of spacer (n)	Yield (%)	Melting point (°C)
3	63	163–165
4	81	154–156
5	85	148–149
6	69	154–155
7	61	141–143

Quartz plates were treated with a saturated sodium hydroxide ethanol solution and pure water (Milli-Q). The static contact angle of water on this surface was  $10 \pm 2$  °. Single layers of 6Az<sub>n</sub>-urea on water were deposited onto a clean quartz plate by vertical lifting at 20 mN m<sup>-1</sup>. The transfer ratio was  $1.0 \pm 0.1$  in all cases. The lifting speed was 5 mm min<sup>-1</sup>. The absorption spectra were taken on a JASCO MAC-1 spectrophotometer that was principally designed for low absorbance measurements. UV-visible absorption spectra of the monolayers of 6Az<sub>n</sub>-urea on both sides of the quartz plate were measured in a dry state.

### 3. RESULTS AND DISCUSSION

Figure 3 shows the surface pressure-area ( $\pi$ -A) isotherms of 6Az<sub>n</sub>-urea monolayers in the *trans* form. As indicated, the limiting area per molecule, which was estimated by extrapolating the steepest slope to zero pressure, indicated a systematic alternation with respect to the carbon number of the spacer (Fig. 4). For the compounds of odd numbered spacer (n=3, 5 and 7), the limiting area ranged 0.29–0.30 nm<sup>2</sup>. In contrast, the monolayers of 6Az<sub>n</sub>-urea having the even numbered spacer (n=4 and 6) showed significant area expansions with higher compressibility. Since the cross section of vertically aligned Az is 0.25 nm<sup>2</sup> from the X-ray diffraction data of crystals,<sup>12</sup> it can be interpreted that the molecules in these monolayers are tilted with respect to the surface normal. The degree of molecular tilt for the even numbered carbon spacer should be greater than that of the odd numbered ones.



Scheme 1. Synthetic routes of the Az-urea derivatives.

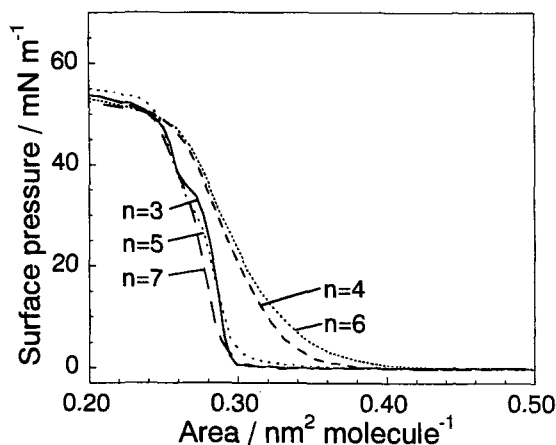


Fig. 3 Surface pressure-area isotherms of monolayers of 6Azn-Urea ( $n=3\sim 7$ ) on pure water at 20 °C.

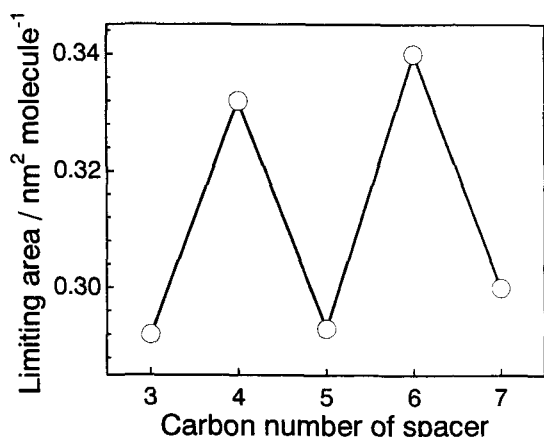


Fig. 4 The limiting occupying area as a function of the alkylene spacer length. ( $n$ ).

The shape of  $\pi$ -A curves also showed regular changes with carbon number of spacer. The even numbered ( $n=4$  and  $6$ ) compound gave a continuous smooth slope in the  $\pi$ -A curves. On the contrary, the monolayers of odd carbon series ( $n=3, 5$  and  $7$ ) showed a shaper increase in the curve, indicative of the lower compressibility. Furthermore, a characteristic inflecting region around  $33 \text{ mN m}^{-1}$  was observed only for the odd number series. We have not yet elucidated the process involved in this phase transition.

As the control experiments,  $\pi$ -A isotherms of the series of carboxylic acid derivatives (6Azn-COOH) monolayers were taken. As shown,  $\pi$ -A isotherms gave completely different results. The  $\pi$ -A isotherms of 6Azn-COOH monolayers in the *trans* form at 20 °C are indicated in Fig. 5. In the inset, the limiting occupying area is plotted against the alkylene spacer of carbon number. In this case, odd-even regular change of the limiting area was not observed. Therefore, the even-odd number effect is the characteristic spreading behavior for the monolayers having the urea head group.

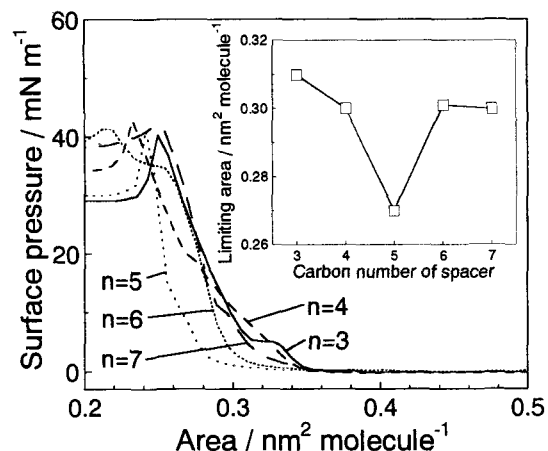


Fig. 5 Surface pressure-area isotherms of monolayers of 6Azn-COOH ( $n=3\sim 7$ ) on pure water at 20 °C. In the inset, the limiting occupying area is plotted against the alkylene spacer length. ( $n$ ).

Figure 6 shows the transmission UV-visible absorption spectra of the monolayers of 6Azn-urea on quartz plate. The carbon number altered the aggregation state of Az. The peak position of the  $\pi$ - $\pi^*$  band attributed to the long axis transition of Az ( $\lambda_{\text{max}}$ , 300–400 nm), which indicates the aggregation state of the chromophore,<sup>13</sup> showed a zigzag change with increase of carbon number (see open triangles of the Fig. 7). The Az unit in the transferred monolayers formed H-aggregates in all cases judging from the considerable hydrochromic shifts of  $\lambda_{\text{max}}$  (317–327 nm) from that in a chloroform solution at 352 nm.<sup>5</sup> As the general tendency,  $\lambda_{\text{max}}$  shifted to the shorter wavelengths with increasing the spacer length, indicating that the stronger H-type aggregation is formed in the monolayer with the longer spacer due to the stronger van der Waals interaction. Among them,  $\lambda_{\text{max}}$  for the odd number series showed significant hypsochromic shifts. In this way, the packing state of Az is influenced in the altered manner with respect to the odd or even number of the spacer.

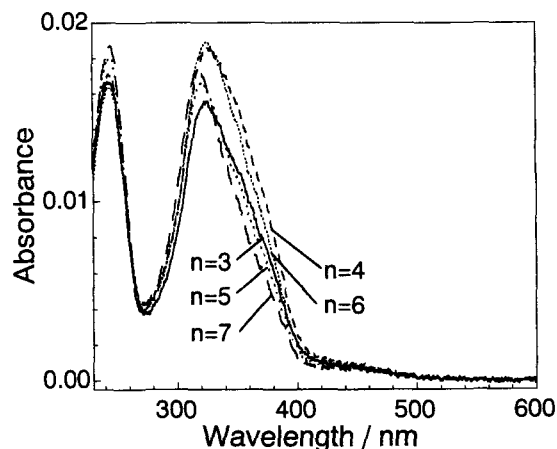


Fig. 6 UV-Vis absorption spectra of monolayers of 6Azn-Urea ( $n=3\sim 7$ ) transferred at  $20 \text{ mN m}^{-1}$  onto both sides of a quartz plate.

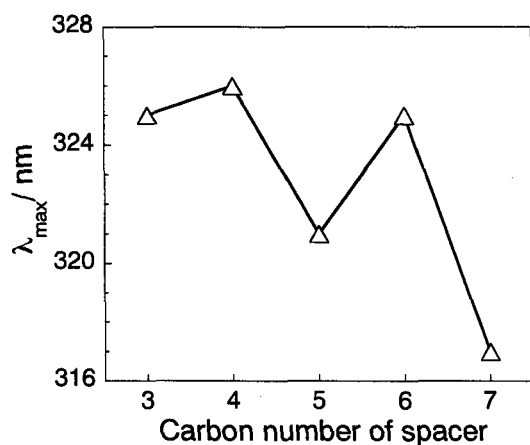


Fig. 7  $\lambda_{\max}$  as a function of the alkylene spacer length ( $n$ ).

#### 4. CONCLUSION

This work revealed the new carbon parity effect observed in the packing state of photochromic Az unit in the monolayer assembly. To our knowledge, this is the first example that the packing state of the floating monolayer on water surface was obviously influenced by the carbon parity. Probably, the formation of the bifurcated hydrogen bonds firmly fixes orientation, and the molecular motion thereby will be highly hindered. When the alkylene spacer chain takes the all-trans-zigzag conformation, then the orientation of the Az moiety should be affected alternately by the carbon parity. Since the packing state of Az governs the trans-to-cis photoisomerization behavior,<sup>9)</sup> the findings observed here may provide new implications for the design of various photochromic functions.

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