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Noncyclic Isobutenyl Compounds with Esters and Amides: Effect of Intramolecular Hydrogen Bonds Tuned by Tandem Claisen Rearrangement on the Two-dimensional Structures

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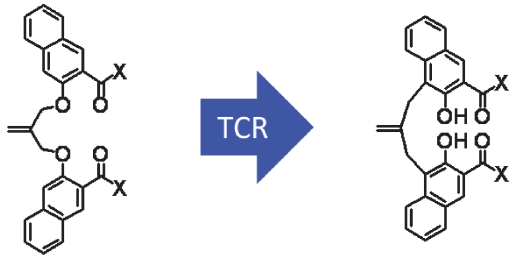
Two-dimensional structures of noncyclic isobutenyl compounds containing ester moieties were investigated by scanning tunneling microscopy. Folded alignment of the molecule was transformed into open extended-structure after a simple thermal reaction of tandem Claisen rearrangement. The drastic change in the two-dimensional structures was caused by the intramolecular hydrogen bonds.

Biological molecules, such as DNA, proteins, and enzymes, display elegant and complex structures via spontaneous self-assembly through noncovalent interactions.[1] In self-assembly systems, hydrogen bonding is a highly influential factor for determining molecular architecture and molecular arrangements.[2] For instance, both intra- and intermolecular hydrogen bonds play crucial roles for the formation of α-helix and β-sheet (β-turn) structures, resulting in the skeletal as well as functional positioning of amino acid sequences.[3]

Even in two-dimensional (2D) molecular arrays at solid surfaces, hydrogen bonds have acted as key interaction for the directional supramolecular arrangements of photonically and electronically active molecules.[4] Intermolecular hydrogen bonds have been a major topic for the stable orientation of functional molecules, while the 2D control by intramolecular hydrogen bonds have rarely been reported despite the fact that protein structure is dependent on both intra- and intermolecular interactions.[5]

In this contribution, we achieve the fabrication of "folded" and "extended" structures by tuning the intramolecular hydrogen bonds via the tandem Claisen rearrangement (TCR). These morphological appearances are similar to the chain-folded and extended-chain crystals of polymeric materials.[6] The TCR is a simple thermal reaction, which transform the ether function into hydroxy group in the isobutenyl compounds.[7] Indeed folded and unfolded structures on a surface have been achieved by chemically synthesizing appropriate compounds,[5a] but our present study is the first report on the formation of those structures using a sole compound, which can be transformed by the TCR. We prepared the isobutenyl diester compounds containing ether moieties and long alkyl chains (Scheme 1: **O-1**). Then, isobutenyl compounds possessing hydroxy groups are generated by TCR (Scheme 1: **O-2**). The 2D structures of both compounds are studied by scanning tunneling microscopy (STM) at a highly oriented pyrolytic graphite (HOPG)/1-phenyloctane interface. Furthermore, molecular arrangements of ester compounds are compared with those of amide compounds (Scheme 1: **N-1** and **N-2**)[8] to examine the effect of intramolecular hydrogen bonds on the 2D structures.



Scheme 1. Chemical structures of **O-1**, **O-2**, **N-1**, and **N-2**.

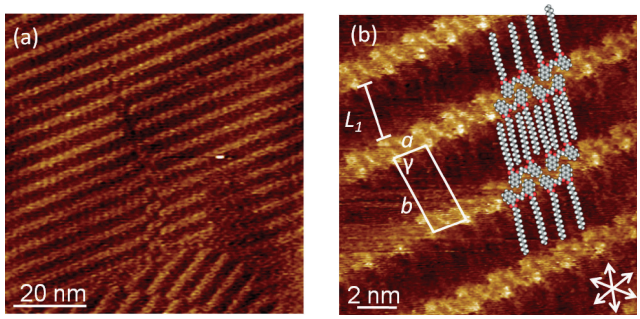


Figure 1. STM images of **O-1** physisorbed at a HOPG/1-phenyloctane interface. (a) Large-scale image. $I = 1.4$ pA, $V = -749$ mV. (b) High-resolution image. $I = 4.0$ pA, $V = -471$ mV, $L_1 = 2.4 \pm 0.1$ nm. A set of arrows indicates the underlying HOPG lattice direction. Tentative molecular models are superimposed in STM image.

Figure 1a shows the large-scale STM image of **O-1** physisorbed on HOPG surface. Some domain structures with different directionalities were observed, and the linear 2D structure was spontaneously formed at the HOPG/1-phenyloctane interface. The STM image shows the periodic bright and dark regions which correspond to the naphthalene and alkyl chain units, respectively. Figure 1b shows the high-resolution STM image of Figure 1a. In the bright area, pairs of oval dots were observed with an intervals of 1.7 ± 0.1 nm. These oval dots were seen in different image contrasts (see Supporting Information),[9] suggesting the unstable adsorption of naphthalene units

Table 1. Unit cell parameters of **O-1**, **O-2**, **N-1**, and **N-2**

	a/nm	b/nm	γ/degree
O-1	1.7 ± 0.1	4.3 ± 0.1	86 ± 1
O-2	1.0 ± 0.1	6.7 ± 0.1	88 ± 2
N-1	3.5 ± 0.1	5.4 ± 0.1	80 ± 1
N-2	1.0 ± 0.1	6.3 ± 0.3	80 ± 3

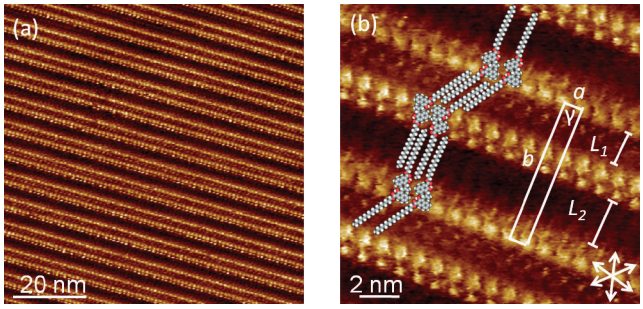


Figure 2. STM images of **O-2** physisorbed at a HOPG/1-phenyloctane interface. (a) Large-scale STM image. $I = 2.5$ pA, $V = -1000$ mV. (b) High-resolution STM image. $I = 2.5$ pA, $V = -1000$ mV, $L_1 = 1.5 \pm 0.1$ nm, $L_2 = 2.3 \pm 0.1$ nm. A set of arrows indicates the underlying HOPG lattice direction. Tentative molecular models are superimposed in STM image.

possibly due to the oblique orientation against the HOPG surface. In the dark spaces, parallel straight lines were visible at an ange of $79 \pm 2°$ against the bright line axis. The dark troughs have the width of $L_1 = 2.4 \pm 0.1$ nm which is almost identical to the length of octadecyl chains. From the STM image, a tentative model of the 2D arrangement is superimposed in Figure 1b. **O-1** exhibited folded structure alternately, where naphthalene units aligned in a head-to-head fashion and octadecyl chains were interdigitated. The unit cell parameters are summarized in Table 1.

The 2D structure of **O-2**, which was prepared through a TCR from **O-1**, was completely different from those of **O-1**. Figure 2a shows the large-scale STM image of **O-2** observed at HOPG/1-phenyloctane interface. Well-ordered linear alignment of **O-2** was formed over 100 nm × 100 nm. Figure 2b shows the high-resolution STM image of Figure 2a. The bright and dark regions were observed repeatedly. The bright areas were composed of both large and small oval dots, indicating that one of the naphthalene units has flat-on orientation (large dots) whereas that the other one is slightly tilting against the HOPG surface (small dots). Two types of dark troughs with different width were observed: $L_1 = 1.5 \pm 0.1$ nm and $L_2 = 2.3 \pm 0.1$ nm. The width of L_2 region is corresponding to the length of octadecyl chain. However, the width of L_1 region was shorter than that of L_2. This result suggests that the interdigitated octadecyl chains at L_1 and L_2 regions aligned with different angles against the columnar axis of the bright regions (naphthalene units). From the STM image, a tentative molecular model of **O-2** is superimposed in Figure 2b, and the unit cell parameters are summarized in Table 1. The naphthalene units of **O-2** directed opposite ways, and the molecules displayed open extended-structure. Therefore, it can be concluded that TCR enables the transformation of "folded" structures **O-1** into "extended" ones **O-2**.

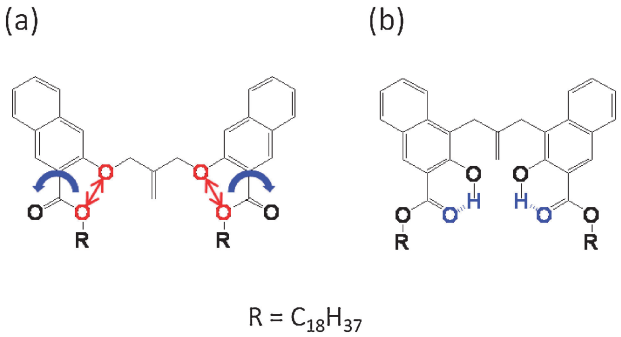


Figure 3. Molecular conformations and intramolecular interactions of **O-1** (a) and **O-2** (b).

The formation of folded and extended structures was explained in terms of alterations of molecular structures and resultant intramolecular hydrogen bonds by TCR. Molecular conformation and intramolecular hydrogen bonds of **O-1** and **O-2** are shown in Figure 3. The **O-1** has an electric repulsion between isobutenyl ether and residual carbonyl oxygen atoms (Figure 3a). Therefore, two naphthalene units form an angle, and cannot take flat geometry, which was evidenced by the unstable attachment of naphthalene units onto the HOPG surface (Figure 1b). Then, the space between alkyl chains was separated enough to interdigitate with each other.

Our previous studies[8] further emphasize the importance of intramolecular hydrogen bonds for the fabrication of consecutive folded structure of **O-1**. Comparing the isobutenyl diester compounds **O-1** with isobutenyl diamide compound **N-1** (NH–R instead of O–R in Figure 3), the naphthalene units of **O-1** located in head-to-head fashion, and the octadecyl chains were interdigitated. As stated above, there is repulsive interactions (isobutenyl ether and another carbonyl oxygen atoms), resulting in the deformation of naphthalene units from the HOPG flat surface. In contrast, wavy structures were formed by the naphthalene units of **N-1** and noninterdigitated alkyl chain units with head-to-tail alignment (Figure 4a). Therefore, the 2D structure seems as a parallel assembly of once folded objects. In this case, there is the intramolecular hydrogen-bonding site at the isobutenyl ether oxygen atom and the amide NH proton (Figure 4c). As a result, naphthalene and alkyl chain units can be fixed in the same plane. Despite the difference between the **O-1** and **N-1** is only oxygen atom and amide group, they exhibited different 2D arrangements as continuous and once folded structures, respectively. These results suggest that flatness of the molecular conformation and accompanying locations of alkyl chains determines the continuity of folded structures.

After the TCR of **O-1**, newly formed hydroxy and carbonyl groups interact via intramolecular hydrogen bonds, resulting in the flat-on orientation of naphthalene units (**O-2**). This is also the case for **N-2**, which was synthesized by the TCR of **N-1**. At the same time, intramolecular distance of naphthalene units are too close to accommodate at the same side, but flip into opposite direction (Figures 4b and 4d). Therefore, the **O-2** and **N-2** took almost the same molecular conformation and open extended-structures because the directions of two octadecyl chains were decided by the hydrogen bonds.

In conclusion, noncyclic isobutenyl compounds containing ester groups **O-1** and **O-2** were synthesized and STM observa-

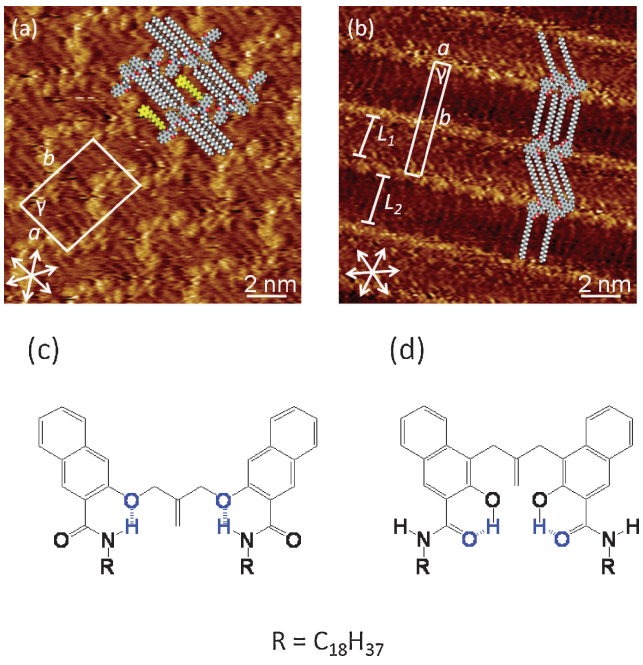


Figure 4. STM images of **N-1** (a) and **N-2** (b) physisorbed at a HOPG/1-phenyloctane interface and molecular conformations and intramolecular interactions of **N-1** (c) and **N-2** (d). (a) $I = 10$ pA, $V = -616$ mV. (b) $I = 3.9$ pA, $V = -499$ mV, $L_1 = 1.9 \pm 0.2$ nm, $L_2 = 2.2 \pm 0.1$ nm. A set of arrows indicates the underlying HOPG lattice direction.

tions of these compounds were performed at solid/liquid interface. The **O-1** adopted linear arrangements, in which the naphthalene and interdigitated alkyl chains exhibited folded structure. The **O-2** was synthesized from **O-1** via TCR, and showed straight array composed of extended molecules.

Only a single mutation of amino acid has influence on the structures and functions of proteins.[10] As with biological systems, subtle chemical change of isobutenyl ether compounds affected the formation of intramolecular hydrogen bond, and provided a drastic differences in 2D structures, namely, the "folded" structures **O-1** could change to "extended" ones **O-2** by modifying the molecular structures and intramolecular hydrogen bonds by TCR.

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References and Notes

1 a) A. Watzke, L. Brunsveld, T. Durek, K. Alexandrov, A. Rak, R. S. Goody, H. Waldmann, *Org. Biomol. Chem.* **2005**, *3*, 1157. b) J. H. Naismith, *Chem. Soc. Rev.* **2006**, *35*, 763. c) S. Pitchiaya, Y. Krishnan, *Chem. Soc. Rev.* **2006**, *35*, 1111. d) H. Kitagishi, Y. Kakikura, H. Yamaguchi, K. Oohora, A. Harada, T. Hayashi, *Angew. Chem.* **2009**, *121*, 1297. e) T. Hamada, M. Morita, Y. Kishimoto, Y. Komatsu, M. Vestergaard, M. Takagi, *J. Phys. Chem. Lett.* **2010**, *1*, 170.

2 a) F. Rakotondradany, A. Palmer, V. Toader, B. Chen, M. A. Whitehead, H. F. Sleiman, *Chem. Commun.* **2005**, 5441. b) S. Yagai, M. Higashi, T. Karatsu, A. Kitamura, *Chem. Commun.* **2006**, 1500. c) A.-P. Schaffner, G. Lena, S. Roussel, A. Wawrezinieck, A. Aubry, J.-P. Briand, C. Didierjean, G. Guichard, *Chem. Commun.* **2006**, 4069. d) M. J. Serpe, S. L. Craig, *Langmuir* **2007**, *23*, 1626. e) S. Yagai, S. Mahesh, Y. Kikkawa, K. Unoike, T. Karatsu, A. Kitamura, A. Ajayaghosh, *Angew. Chem., Int. Ed.* **2008**, *47*, 4691.

3 a) R. Ionov, A. El-Abed, M. Goldmann, P. Peretti, *J. Phys. Chem. B* **2004**, *108*, 8485. b) M. Khurram, N. Qureshi, M. D. Smith, *Chem. Commun.* **2006**, 5006. c) L. Liu, L. Zhang, X. Mao, L. Niu, Y. Yang, C. Wang, *Nano Lett.* **2009**, *9*, 4066.

4 a) S. Yoshimoto, N. Yokoo, T. Fukuda, N. Kobayashi, K. Itaya, *Chem. Commun.* **2006**, 500. b) J. M. MacLeod, O. Ivasenko, D. F. Perepichka, F. Rosei, *Nanotechnology* **2007**, *18*, 424031. c) F. Silly, A. Q. Shaw, M. R. Castell, G. A. D. Briggs, *Chem. Commun.* **2008**, 1907. d) A. Ciesielski, G. Schaeffer, A. Petitjean, J.-M. Lehn, P. Samorì, *Angew. Chem., Int. Ed.* **2009**, *48*, 2039. e) Y. Kikkawa, S. Kubota, T. Karatsu, A. Kitamura, M. Kanesato, S. Yagai, *J. Nanosci. Nanotechnol.* **2010**, *10*, 803. f) A. Ciesielski, S. Lena, S. Masiero, G. P. Spada, P. Samorì, *Angew. Chem., Int. Ed.* **2010**, *49*, 1963.

5 a) N. Schuurmans, H. Uji-i, W. Mamdouh, F. C. D. Schryver, B. L. Feringa, J. V. Esch, S. D. Feyter, *J. Am. Chem. Soc.* **2004**, *126*, 13884. b) A. S. Klymchenko, N. Schuurmans, M. V. D. Auweraer, B. L. Feringa, J. V. Esch, S. D. Feyter, *New J. Chem.* **2006**, *30*, 1420.

6 P. J. Barham, in *Structure and Properties of Polymers*, ed. by R. W. Cahn, P. Haasen, E. J. Kramer, VCH, Weinheim, **1993**, Vol. 12, Chap. 4, pp. 153–212.

7 a) K. Hiratani, M. Albrecht, *Chem. Soc. Rev.* **2008**, *37*, 2413. b) J. Hao, K. Hiratani, N. Kameta, T. Oba, *J. Inclusion Phenom. Macrocyclic Chem.* **2009**, *65*, 257.

8 K. Omori, Y. Kikkawa, H. Tokuhisa, M. Kanesato, K. Hiratani, *Colloids Surf., A* **2010**, *356*, 58.

9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

10 a) M. B. Tobin, C. Gustafsson, G. W. Huisman, *Curr. Opin. Struct. Biol.* **2000**, *10*, 421. b) S. Taguchi, Y. Doi, *Macromol. Biosci.* **2004**, *4*, 145. c) T. Hiraishi, S. Taguchi, *Mini-Rev. Org. Chem.* **2009**, *6*, 44.

