rillum rubrum<sup>18</sup> indicate that Ni is not present within the Fe-S cubane core since there was no evidence for Ni-Fe interactions. Further description of the linkage "X" between Ni and iron and the structure of this complex will require comparison of the properties of biomimetic models with those of CODH and further analyses of the properties of CODH.

Acknowledgment. We thank Professor Richard Dam for helpful comments in performing FTIR spectroscopy and Lifei Liu for preparing the copious amounts of CODH used.

(18) Tan, G. O.; Ensign, S. A.; Cuirli, S.; Scott, M. J.; Hedman, B.; Holm, R. H.; Ludden, P. W.; Korszun, Z. R.; Stephens, P. J.; Hodgson, K. O. Proc. Natl. Acad. Sci. U.S.A. 1992, 89, 4427-4431.

## **Blocked Photochromism of Diarylethenes**

Masahiro Irie,\* Osamu Miyatake, and Kingo Uchida

Institute of Advanced Material Study Kyushu University Kasuga-Koen 6-1, Kasuga, Fukuoka, Japan Received May 26, 1992

Photochromic molecules with a clasp, which undergo photoisomerization only when the clasp is freed by a switch molecule, were synthesized. Photochromism has attracted renewed interest because of the recent development of fatigue-resistant compounds. A classical photochromic molecule, 6-nitrospirobenzopyran, loses its photochromic property after 30-50 coloration/decoloration cycles, while several newly synthesized molecules can maintain performance through more than 10<sup>4</sup> repetitions of the cycle.<sup>1-4</sup> Among the molecules, 1,2-diarylethenes containing heterocyclic rings have the potential ability for many applications owing to an additional characteristic, namely, the thermal stability of both isomers.<sup>5</sup> Besides fatigue resistance and thermal irreversibility, a property that is strongly desired but still lacking in existing photochromic molecules is gated photochemical reactivity.<sup>6</sup> Gated reactivity is the property that irradiation with any wavelength causes no molecular change, while a photoreaction occurs when another external stimulation, such as an electric field or chemicals, is present.7 We designed and synthesized chemical-gated molecules by introducing substituents that have hydrogen-bonding ability into the 1,2-diarylethenes.

1,2-Bis(2-methylbenzo[b]thiophen-3-yl)perfluorocyclopentene derivatives with carboxyalkyl groups at the 6 and 6' positions, 1 and 2, were synthesized.<sup>8</sup> The perfluorocyclopentene moiety is

(1) (a) Hanazawa, M.; Sumiya, R.; Horikawa, Y.; Irie, M. J. Chem. Soc., Chem. Commun. 1992, 206. (b) Heller, H. G. IEE Proc. 1983, 130-1, 209. (2) Ichimura K. Saki T. Tamati T. Yanaki T. Tamati T. Tamati T. Yanaki T. Tamati T. Yanaki T. Tamati T. Tamati T. Yanaki T. Tamati T. Tamati T. Yanaki T. Tamati T. Yanaki T. Tamati T. Yanaki T. Yanaki T. Tamati T. Yanaki T. (2) Ichimura, K.; Seki, T.; Tamaki, T.; Yamaguchi, T. Chem. Lett. 1990,

1645.

(3) Uchida, K.; Nakayama, Y.; Irie, M. Bull. Chem. Soc. Jpn. 1990, 63, 1311.

(4) Chu, N. Y. C. In Photochromism. Molecules and Systems. Durr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; pp 493-509. (5) Irie, M. Jpn. J. Appl. Phys. 1989, 28, Suppl. 3, 215.

(6) Moerner, W. E. Jpn. J. Appl. Phys. 1989, 28, Suppl. 3, 221.

(7) Recently, a chemical-gated photochromic molecule was reported. Yokoyama, Y.; Yamane, T., Kurita, Y. J. Chem. Soc., Chem. Commun. 1991, 1722



Figure 1. Absorption spectra of 1 ( $2.5 \times 10^{-5} \text{ mol/L}$ ) (---) upon irradiation with 313-nm light in (a) cyclohexane and (b) ethanol; the absorption band around 525 nm (---) is due to the closed-ring form.

Scheme I



effective in increasing the durability of the molecules.<sup>1a</sup> The photochromic reaction of the 1,2-diarylethenes belongs to a 1,3,5-hexatriene to cyclohexadiene type reaction. According to the Woodward-Hoffmann rule based on  $\pi$ -orbital symmetries, a conrotatory cyclization is brought about by light.<sup>9</sup> When the aryl groups are heterocyclic five-membered rings, the molecule has two conformations, with the two rings in mirror and  $C_2$ symmetries,<sup>3,7</sup> and the conrotatory cyclization can proceed only from the conformation with the rings in  $C_2$  symmetry. This means that the photocyclization is prohibited if the heterocyclic rings are fixed to the mirror symmetry, or parallel orientation, while

<sup>(17) (</sup>a) Cramer, S. P.; Eidsness, M. K.; Pan, W.-H.; Morton, T. A.; Ragsdale, S. W.; DerVartanian, D. V.; Ljungdahl, L. G.; Scott, R. A. Inorg. Chem. 1987, 26, 2477-2479. (b) Bastian, N. R.; Diekert, G.; Niederhoffer, E. G.; Teo, B.-K.; Walsh, C. P.; Orme-Johnson, W. H. J. Am. Chem. Soc. 1988, 110, 5581-5582. (c) Scott, R. A.; Morton, T. A.; Ljungdahl, L. G. Unpublished data.

<sup>1722.</sup> (8) 1: mp 105–106 °C; <sup>1</sup>H-NMR (270 MHz,  $C_2D_3OD$ )  $\delta$  2.16 (3 H, s), 2.47 (3 H, s), 2.55 (2 H, t), 2.60 (2 H, t), 2.92 (2 H, t), 3.01 (2 H, t), 7.07 (1 H, d, J = 8.06 Hz), 7.29 (1 H, d, J = 8.06 Hz), 7.44 (1 H, d, J = 8.06 Hz), 7.56 (1 H, d, J = 8.06 Hz), 7.50 (1 H, s), 7.60 (1 H, s). Anal. Calcd for  $C_{29}H_{22}O_4S_2F_6$ : C, 56.85; H, 3.62. Found: C, 56.78; H, 3.72. 2: mp 219.5–220.5 °C; <sup>1</sup>H-NMR (270 MHz,  $C_{2D}OD$ )  $\delta$  2.21 (3 H, s), 2.49 (3 H) 2.60 (2 H c). 271 (2 H c). 714 (1 H d, J = 8.16 Hz), 7.44 (1 H, d, J = 8.16 Hz), 7.56 (1 H, d, J = 8.16 Hz), 7.56 (1 H, d, J = 8.16 Hz), 7.50 (1 H, s), 7.50 (1 H, s s), 3.62 (2 H, s), 3.71 (2 H, s), 7.14 (1 H, d, J = 8.18 Hz), 7.34 (1 H, d, J = 8.18), 7.50 (1 H, d, J = 8.18 Hz), 7.61 (1 H, d, J = 8.18 Hz), 7.59 (1 H, s), 7.69 (1 H, s). Anal. Calcd for C<sub>27</sub>H<sub>18</sub>O<sub>4</sub>S<sub>2</sub>F<sub>6</sub>: C, 55.48; H, 3.10. Found: C, 55.56; H, 3.46.

<sup>(9) (</sup>a) Nakamura, S.; Irie, M. J. Org. Chem. 1988, 53, 6136. (b) Laar-hoven, W. H. Reference 4, pp 270-313. (c) Whittal, J. Reference 4, pp 467-492.



Figure 2. NMR spectra of 1 in cyclohexane- $d_{12}$  and mixed solvents of cyclohexane- $d_{12}$  and ethanol- $d_6$ : (a) in cyclohexane- $d_{12}$ ; (b) in a cyclohexane- $d_{12}$ -ethanol- $d_6$  mixture (volume ratio, 98:2); (c) in a cyclohexane- $d_{12}$ -ethanol- $d_6$  mixture (volume ratio, 85:15).

the reaction is allowed when the conformation converts to the  $C_2$ symmetry, or antiparallel orientation, as shown in Scheme I.

Parts a and b of Figure 1 show the optical absorption spectra of 1 in cyclohexane and ethanol, respectively, upon irradiation with 313-nm light. The absorption band around 525 nm is due to the closed-ring form.<sup>1a</sup> Although the photocyclization proceeded in ethanol, it was completely prohibited in cyclohexane. This suggests that the conformation of 1 is fastened in parallel orientation in cyclohexane by intramolecular hydrogen bonding. If so, the hydrogen bonding is expected to be broken by ethanol or heating. In fact, the addition of a very small amount of ethanol activated the photoreactivity. In a mixed solvent of cyclohexane and ethanol (volume ratio, 98:2) the quantum yield of photocyclization was 0.29. It further increased with increasing ethanol content and reached a plateau value of 0.51 in the solvent containing 15 vol % ethanol. 1 became photoactive by the addition of not only alcohols but also other hydrogen-bond-breaking agents, such as propylamine. In decalin, the photoreaction occurred at temperatures higher than 100 °C.

In order to confirm the above reaction mechanism, <sup>1</sup>H NMR spectra of the molecule were measured in cyclohexane- $d_{12}$  and in mixed solvents of cyclohexane- $d_{12}$  and ethanol- $d_6$ , as shown in Figure 2. The methyl protons at the 2-position of the benzothienyl rings give information concerning the relative population of the two conformations. The protons give signals at different fields depending on the conformation, that is, whether the aryl rings are parallel or antiparallel.<sup>3</sup> The upper field signal is attributed to the protons in the parallel conformation, while the lower field signal points to the antiparallel conformation.

In cyclohexane the upper field signal was not observed, while it appeared upon the addition of ethanol. The <sup>1</sup>H NMR spectra clearly indicate that the molecule was in the parallel conformation in cyclohexane. It converted to the antiparallel conformation upon the addition of a small amount of ethanol. The absence of photocyclization in cyclohexane is explained by the clasped parallel conformation. Intramolecular hydrogen bonding fastened the molecule into the parallel conformation and made it photochemically inactive. Conversely, ethanol acted as a switch to unclasp the system. The dimethyl ester derivative of 1 did not show any such solvent dependence.

The contribution of intermolecular hydrogen bonding was considered to be negligible, because any upper field signal was not discerned in cyclohexane. When the carboxyethyl groups were replaced with carboxymethyl groups, compound 2, a weak 525-nm band appeared even in cyclohexane. This suggests that carboxymethyl groups did not fit to make rigid intramolecular hydrogen bonding, and intermolecular bonding existed to some extent.

Acknowledgment. This w k was supported by a Grant-in-Aid for New Program "Intellige: Molecular Systems with Controlled Functionality" (03NP0301 from the Ministry of Education, Science, and Culture of Ja\_ in.

Registry No. 1, 143619-58-3; 1 dimethyl ester, 143619-59-4; 1 closed-ring form, 143619-60-7; 2, 143619-61-8; ethanol, 64-17-5.

## **Design at Nanometric Dimensions To Enhance** Hydrophobicity-Induced pK, Shifts

D. W. Urry,\*,<sup>†</sup> D. C. Gowda,<sup>‡</sup> S. Q. Peng,<sup>†</sup> T. M. Parker,<sup>†</sup> and R. D. Harris<sup>‡</sup>

> Laboratory of Molecular Biophysics The University of Alabama at Birmingham, VH300 Birmingham, Alabama 35294-0019 Bioelastics Research, Ltd. 1075 South 13th Street Birmingham, Alabama 35205 Received June 24, 1992

With poly[4(GVGVP),(GEGVP)] (I) as a reference state, the polytricosapeptides, poly[3(GVGVP),2(GFGFP),(GEGFP)] (II), poly[2(GVGVP),2(GVGFP),(GFGFP),(GEGFP)] (III), poly-(GEGFPGVGVPGVGVPGVGVPGFGFPGFGFP) (IV), and poly(GEGFPGVGVPGVGFPGFGFPGVGVPGVGFP) (V), all having the same theoretical and essentially the same analytical amino acid compositions,1 were synthesized and designed for the specific purpose of testing the limits of hydrophobicity-induced pK<sub>a</sub> shifts in this system. Polymers I, II, III, IV, and V exhibited  $pK_a$  values for the Glu (E) residues of 4.3, 4.7, 6.3, 7.7, and 8.1, respectively. Due to the limited number of Glu residues, the structures themselves exclude the often invoked charge-charge interaction mechanism for  $pK_a$  shifts. The differences in  $pK_a$  values arise from the differences in proximity of the Glu (E) and Phe (F) residues within and between pentamers with optimal arranging of five nearest-neighbor Phe residues at nanometer distances from the Glu residue in IV and V. This remarkable increase of 3.8 pH units overall demonstrates a repulsive free energy of interaction between hydration processes of the Phe and Glu side chains of 5 kcal/mol. To our knowledge these are the largest  $pK_a$  shifts documented for the Glu residue, and the recently identified interactions responsible are considered to be important free energies of interaction in modulating protein structure and function.<sup>2</sup>

Polymers IV and V were designed on the basis of the working  $\beta$ -spiral structure of poly(GVGVP), shown schematically in Figure 1A.<sup>2,3</sup> For the  $\beta$ -spiral structure, the distance between turns is approximately 1 nm.<sup>4</sup> This results in the nanometer proximities of the Glu and Phe residues shown in Figure 1B. The polytricosapeptides were constructed by the sequential addition of pentamers. The composite pentamers were also mixed in the appropriate ratios and polymerized to obtain polymers II and III without fixed ordering of pentamers. A complete description of the syntheses will be presented elsewhere. The structures were verified by carbon-13 nuclear magnetic resonance and amino acid analyses. The resolved acid-base titration data, for one experiment of three, for each of the five polymers are given in Figure 2, and the standard deviations for three runs each for the polymers were less than  $\pm 0.1$  pH units.

Polymers of the composition  $poly[f_V(GVGVP), f_X(GXGVP)],$ where  $f_V$  and  $f_X$  are mole fractions with  $f_V + f_X = 1$  and where X can be any amino acid residue, undergo phase transitions, the

- The single-letter codes for the amino acid residues are Gly (G), Val
  (V), Pro (P), Glu (E), Phe (F), and Trp (W).
  (2) Urry, D. W. Prog. Biophys. Mol. Biol. 1992, 57, 23-57.
  (3) Urry, D. W.; Haynes, B.; Zhang, H.; Harris, R. D.; Prasad, K. U. Proc. Natl. Acad. Sci. U.S.A. 1988, 85, 3407–3411.
- (4) Chang, D. K.; Venkatachalam, C. M.; Prasad, K. U.; Urry, D. W. J. Biomol. Struct. Dyn. 1989, 6, 851-858.

<sup>\*</sup>To whom correspondence and reprint requests should be addressed.

<sup>&</sup>lt;sup>†</sup>The University of Alabama at Birmingham.

<sup>&</sup>lt;sup>‡</sup>Bioelastics Research, Ltd.