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Journal of Photochemistry and Photobiology A: Chemistry 184 (2006) 44–49
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Different photochemical behavior of bis(biphenyl)ethylenes and ethenes in solution and in the solid-state: Structurally controlled Z/E-photoisomerization in the solid-state

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Received 2 December 2005; received in revised form 16 February 2006; accepted 18 March 2006
Available online 29 March 2006

Abstract

Several bis(biphenyl)ethylenes and ethenes were prepared and their photoisomerization both in solution and in the solid-state was investigated. While all ethylenes and ethenes gave the solutions containing both *E*- and *Z*-isomers in the manner of the mutual photoisomerization, the ethylenes having at least one hydrogen atom on the sp^2 carbons underwent unidirectional photoisomerization from the *Z*-isomers to the *E*-isomers in the solid-state even at low temperature. On the other hand, both the *E*- and *Z*-ethenes having no hydrogen atom on the double bonds did not change when irradiated in the solid-state even at room temperature. These different photochemical behaviors can be explained by the Hula-twist (HT) mechanism in such confined environments.

Keywords: Photoisomerization; Solid-state; Unidirectional isomerization; Hula-twist mechanism

1. Introduction

Among a number of photochemical molecular transformations, the *Z*/*E*-photoisomerization of olefinic compounds is the most fundamental and important process and this photochemical reaction in the confined environments has been extensively studied [1–6] in relation to the protein-bound visual chromophore. While the photoisomerization by conventional one-bond-flip (OBF) process, i.e., the 180° rotation around the double bond, is regarded to be difficult within the narrow space such as in a crystal or solid-state, the Hula-twist (HT) mechanism, a space-conserving isomerization process, was proposed by Liu et al. to explain such the phenomena [7–11]. Not only this hypothesis has sometimes been applied to the numerous examples of *Z*/*E*-photoisomerizations in the confined environments [5,12–15], but also several investigations have been undertaken to verify this process [16–20]. However, only the 1,2-disubstituted ethylenes were employed in almost all examples previously reported, but, to the best of our knowledge, the tri- and tetra-substituted alkenes have not been used for this type of investigation. In this paper, we investigated the *Z*/*E*-photoisomerization of some bis(biphenyl)ethenes and ethenes both in solution and in the solid-state, which provides a good field to apply the HT mechanism.

2. Experimental

2.1. General method

Melting points were determined on a hot stage microscope apparatus (Mitamura). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-400 at 400 and 100 MHz, respectively. The chemical shifts (δ) are reported in ppm downfield from TMS as internal standard or from the residual solvent peak. Coupling constants (*J*) are reported in Hz. Low resolution mass spectra (MS) were recorded by the JEOL JMS-K9 spectrometers. Elemental analysis was recorded on a Perkin-Elmer 2400CHN

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doi:10.1016/j.jphotochem.2006.03.022

elemental analyzer. Analytical TLC was carried out on precoated silica gel 60F-254 plates (E. Merck). Column chromatography was performed on silica gel (E. Merck).

2.2. Synthesis

2.2.1. (E)- and (Z)-4,4′-Diphenylstilbene 1

A suspension of a zinc powder (1.07 g, 16.5 mmol) in 1,4-dioxane (20 ml) was slowly added to a solution of *p*-phenylbenzaldehyde (1.00 g, 5.49 mmol) and $TiCl_4$ (1.04 g, 0.60 ml) in 1,4-dioxane (40 ml) at room temperature under a nitrogen atmosphere. After the reaction mixture was refluxed for 4 h, water was added and the product was extracted with ether. After drying over anhydrous Na_2SO_4, removal of the solvent gave the crude product, which was recrystallized from benzene to afford a colorless crystal of (*E*)-**1** (0.53 g, 58%). mp 299–300 °C (literature [21]: 300–302 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 2H), 7.33–7.37 (t, 2H, Ar–H, $J = 7.2$ Hz), 7.43–7.47 (t, 4H, Ar–H, $J = 7.6$ Hz), 7.61–7.64 (m, 12H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.31, 127.76, 129.19, 131.63, 135.78, 136.87, 137.12, 137.47, 143.36. MS: *m/z* 332 (M^+).

A solution of a mixture of *E*-**1** (0.30 g) in benzene was irradiated for 1 h to give a photostationary solution containing *E*- and *Z*-**1** in the ratio of 61:39, which were treated with hexane and the hexane insoluble *E*-**1** was removed off by filtration. The filtrate was concentrated to give a *Z*-**1** enriched powder. The recovered *E*-**1** was dissolved in benzene and subjected to the photoisomerization again. This operation was repeated. The corrected *Z*-**1** enriched powder was recrystallized from hexane to afford a white crystal of pure *Z*-**1** (0.10 g). mp 221–222 °C (literature [21]: 222–223 °C).^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (s, 2H), 7.31–7.35 (t, 2H, Ar–H, $J = 7.6$ Hz), 7.38 (d, 4H, Ar–H, $J = 8.2$ Hz), 7.41–7.44 (t, 4H, Ar–H, $J = 7.6$ Hz), 7.49 (d, 4H, Ar–H, $J = 8.2$ Hz), 7.60 (d, 4H, Ar–H, $J = 8.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.11, 127.28, 127.41, 127.68, 129.15, 129.75, 130.36, 136.70, 140.24. MS: *m/z* 332 (M^+).

2.2.2. (E)- and (Z)-2,3-Bis(biphenyl)propene 2

A solution of LiOEt (0.48 g, 9.27 mmol) in ethanol (20 ml) was slowly added to a solution of *p*-phenylbenzaldehyde (0.56 g, 3.08 mmol) and 1-phenylethyltriphenylphosphonium iodide (2.42 g, 4.64 mmol) in DMF (60 ml) at −5 °C under a nitrogen atmosphere for 8 h. After removal of DMF under a reduced pressure and addition of water, the product was extracted with ether. Drying over anhydrous Na_2SO_4 followed by removal of the solvent gave the mixture of *E*- and *Z*-**2**, which were isolated by recrystallization from petroleum ether. The petroleum ether soluble component is *Z*-**2**, which was recrystallized from hexane again to afford the white crystals (0.15 g, 14%). The petroleum ether-insoluble component is *E*-**2**, which was recrystallized from benzene to afford a yellow crystal (0.30 g, 28%). *E*-**2**: mp 211–212 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (d, 3H, Me, $J = 1.2$ Hz), 6.94 (s, 1H, C*H*=), 7.34–7.37 (t, 2H, Ar–H, $J = 8.0$ Hz), 7.44–7.48 (m, 6H, Ar–H), 7.62–7.65 (t, 10H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.96, 126.78, 127.26, 127.37, 127.42, 127.65, 127.71, 129.18, 130.03. MS: *m/z* 346 (M^+). *Z*-**2**: mp 122–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (d, 3H, Me, $J = 1.6$ Hz), 6.54 (s, 1H, C*H*=), 7.08 (d, 2H, Ar–H, $J = 8.4$ Hz), 7.28–7.40 (m, 8H, Ar–H), 7.42–7.45 (t, 2H, Ar–H, $J = 7.6$ Hz), 7.52–7.56 (t, 4H, Ar–H, $J = 7.2$ Hz), 7.62 (d, 2H, Ar–H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.50, 126.78, 126.93, 127.19, 127.34, 127.53, 127.64, 129.06, 129.14, 129.76, 134.03. MS: *m/z* 346 (M^+).

2.2.3. (E)- and (Z)-2,3-Bis(biphenyl)butene 3

A suspension of a zinc powder (1.10 g, 16.9 mmol) in 1,4-dioxane (20 ml) was slowly added to a solution of 4′-phenylacetophenone (1.10 g, 5.61 mmol) and $TiCl_4$ (1.06 g, 0.62 ml) in 1,4-dioxane (40 ml) at room temperature under a nitrogen atmosphere. After the reaction mixture was refluxed for 4 h, water was added and the product was extracted with ether. Drying over anhydrous Na_2SO_4 followed by removal of the solvent gave the mixture of *E*- and *Z*-**3**, which were separated by fractional recrystallization from hexane. The hexane soluble component is *Z*-**3**, which was recrystallized from methanol twice to afford the white crystals (0.52 g, 52%). The hexane-insoluble component is *E*-**3**, which was recrystallized from methanol to afford the light yellow crystals (0.12 g, 12%). *E*-**3**: mp 235–236 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 6H, Me), 7.33–7.38 (m, 6H, Ar–H), 7.43–7.47 (t, 4H, Ar–H, $J = 8.0$ Hz), 7.61–7.65 (t, 8H, Ar–H, $J = 8.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$), 22.94, 127.27, 127.42, 127.54, 129.13, 129.14, 133.28, 139.52, 141.40, 143.88. MS: *m/z* 360 (M^+). Found: C, 92.92; H, 6.92. Calc. for $C_{28}H_{24}$: C, 93.29; H, 6.71%. *Z*-**3**: mp 111–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 6H, Me), 7.07 (d, 4H, Ar–H, $J = 8.2$ Hz), 7.25–7.29 (t, 2H, Ar–H, $J = 7.2$ Hz), 7.34–7.39 (m, 8H, Ar–H), 7.53 (d, 4H, Ar–H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.94, 126.64, 127.22, 129.01, 129.14, 130.03, 130.06, 138.59, 141.22, 144.04. MS: *m/z* 360 (M^+). Found: C, 93.67; H, 6.91. Calc. for $C_{28}H_{24}$: C, 93.29; H, 6.71%.

*2.2.3.1. Crystal structure determination of Z-**3**.* Single crystals of Z-3 suitable for X-ray diffraction were selected directly from the analytical samples. The measurement was carried out at 93 K.

2.2.3.2. Crystal data. $C_{28}H_{24}$, $M_r = 360.50$, monoclinic, space group $P2_1/c$, $T = 93$ (1) K, $a = 10.889(2)$, $b = 35.553(6)$, $c = 10.902(2)$ Å, $\beta = 109.620(7)°$, $Z = 8$, $V = 3975(1)$ Å^3, $D_{Calc.} = 1.204$ g/cm^3, μ (Mo Kα) = 0.68 cm^{-1}. All the reflections were used in the refinement of 554 parameters. R_1 (calculated for 7169 reflections with $I > 2\sigma(I)) = 0.046$, R (for all reflections) = 0.075, wR_2 (for all reflections) = 0.099.

2.2.4. (E)- and (Z)-3,4-Bis(biphenyl)hexene 4

Prepared in a manner similar to the above procedure using a zinc powder (1.00 g, 15.4 mmol), 4′-phenylpropiophenone (1.06 g, 5.05 mmol), and $TiCl_4$ (0.96 g, 0.56 ml). The product was obtained as a mixture of *E*-**4** and *Z*-**4**, which were separated by fractional recrystallization from methanol as described above to give pure *E*-**4** (0.05 g, 4.7%) and *Z*-**4** (0.46 g, 47%). *E*-**4**: mp 282–283 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, 6H, CH_2CH_3, $J = 7.6$ Hz), 2.24 (q, 4H, CH_2CH_3, $J = 7.6$ Hz), 7.31 (d, 4H, Ar–H, $J = 8.2$ Hz), 7.35 (t, 2H, Ar–H, $J = 7.2$ Hz), 7.46

(t, 4H, Ar–H, $J = 7.2$ Hz), 7.61–7.67 (m, 8H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.84, 28.97, 127.11, 127.39, 127.50, 129.14, 129.57, 139.43, 139.48, 141.41, 142.07. MS: *m/z* 388 (M^+). Found: C, 92.98; H, 7.60. Calc. for $C_{30}H_{28}$: C, 92.74; H, 7.26%. *Z*-**4**: mp 141–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (t, 6H, CH_2CH_3, $J = 7.6$ Hz), 2.62 (q, 4H, CH_2CH_3, $J = 7.6$ Hz), 7.05 (d, 4H, Ar–H, $J = 8.2$ Hz), 7.26 (t, 2H, Ar–H, $J = 8.0$ Hz), 7.32–7.38 (m, 8H, Ar–H), 7.52 (d, 4H, Ar–H, $J = 8.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.41, 27.37, 126.08, 126.82, 126.91, 128.61, 130.21, 138.05, 138.99, 140.87, 142.29. MS: *m/z* 388 (M^+). Found: C, 92.92; H, 7.61. Calc. for $C_{30}H_{28}$: C, 92.74; H, 7.26%.

2.2.5. (E)- and (Z)-6,6′-Bis(phenyl)-1′-bisindanylidene **5**

Prepared similarly to the above procedure using a zinc powder (0.15 g, 0.2 mmol), 5-phenyl-indan-1-one (0.15 g, 0.72 mmol), and $TiCl_4$ (0.14 g, 0.08 ml). The product was obtained as an inseparable mixture of *E*-**5** and *Z*-**5**, which were recrystallized from ethyl acetate/hexane (0.04 g, 29%). The pure *E*-**5** was obtained by the photoisomerization in the solid-state and recrystallization from ethylacetate/hexane. *E*-**4**: mp 211–213 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.18 (m, 4H), 3.30 (m, 4H), 7.34–7.83 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.23, 32.74, 123.81, 125.61, 126.72, 127.46, 127.70, 129.16, 136.04, 140.24, 142.33, 144.23, 146.74. MS: *m/z* 384 (M^+). Found: C, 94.08; H, 6.26. Calc. for $C_{30}H_{24}$: C, 93.71; H, 6.29%. *E*- and *Z*-**5** as a mixture (*E*/*Z* = 87/13): ^{1}H NMR ($CDCl_3$) δ 2.89 (m, 0.52H, 2 and 2′-H for *Z*), 3.05 (m, 0.52H, 3 and 3′-H for *Z*), 3.18 (m, 3.48H, 2 and 2′-H for *E*), 3.30 (m, 3.48H, 3 and 3′-H for *E*), 7.19–7.24, 7.34–7.48, 7.62–7.65 (m, 14H, Ar–H for *E* and *Z*), 7.83 (s, 1.74H, Ar–H for *E*), 8.42 (s, 0.26H, Ar–H for *Z*).

2.2.6. (E)- and (Z)-1-Biphenyl-2-(4-benzoylphenyl) ethylene **6**

The Grignard reaction was carried out by addition of a solution of 4′-phenyl-4-styrylbenzaldehyde (0.50 g, 1.76 mmol) to a solution of phenylmagnesium bromide, prepared from bromobenzene (0.55 g, 3.50 mmol) and magnesium (0.10 g, 4.17 mmol) in ether (15 ml), and the usual workup gave 4-(4′-phenylstyrylphenyl)phenylmethanol in 75% yield. This alcohol (0.20 g, 0.55 mmol) was treated with a manganese(IV) oxide powder (1.00 g, 11.5 mmol) in benzene (60 ml) under reflux for 15 h. Removal of the solvent from the filtrate gave the crude product, which was recrystallized from benzene to afford the light green crystals (0.12 g, 58%). *E*-**6**: mp 236–237 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, 1H, $J = 16$ Hz), 7.29 (d, 1H, $J = 16$ Hz), 7.36 (t, 1H, Ar–H, $J = 7.2$ Hz), 7.44–7.52, 7.58–7.64, 7.80–7.85 (m, 17H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.64, 127.34, 127.66, 127.85, 127.89, 127.94, 128.67, 129.24, 130.32, 131.16, 131.29, 132.66, 136.18, 136.71, 138.27, 140.90, 141.43, 141.91, 196.45. MS: *m/z* 360 (M^+). Found: C, 89.61; H, 5.52. Calc. for $C_{27}H_{20}O$: C, 89.97; H, 5.59%.

A solution containing *E*- and *Z*-**6** in benzene was irradiated for 1 h to give a photostationary solution containing *E*- and *Z*-**6** in the ratio of 21:79. After removal of the solvent the residue was recrystallized from hexane to afford a light yellow crystal (0.05 g, 78%) of pure *Z*-**6**. *Z*-**6**: mp 100–101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (d, 1H, $J = 12$ Hz), 6.75 (d, 1H, $J = 12$ Hz), 7.32–7.35, 7.40–7.50, 7.55–7.60 (m, 14H, Ar–H), 7.71 (d, 2H, Ar–H, $J = 8.2$ Hz), 7.78–7.80 (m, 2H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.94, 127.02, 127.42, 128.27, 128.81, 129.29, 129.37, 129.93, 130.27, 131.92, 132.29, 135.68, 136.04, 137.76, 137.86, 140.32, 140.53, 141.83, 196.23. MS: *m/z* 360 (M^+). Found: C, 89.57; H, 5.50. Calc. for $C_{27}H_{20}O$: C, 89.97; H, 5.59%.

2.3. Photoisomerization

2.3.1. Photoisomerization of Z-**1** in solution: a typical procedure

A solution of *Z*-**1** (9 mg) in benzene (25 ml) was bubbled with a nitrogen gas for 30 min in a Pyrex glass-tube. The glass-tube was hung up with 3 cm away from a 500 W high-pressure mercury lamp ($\lambda > 300$ nm). After irradiation for each 10 min, a part of the solution was taken out and the solvent was removed. The ratio of the *E*- and *Z*-isomers was determined by the measurement of ^{1}H NMR spectrum. It took 1 h to reach the photostationary point.

In a similar manner to that described above, the photoreaction of all other alkenes in solution was carried out.

2.3.2. Photoisomerization of Z-**1** in the solid-state: a typical procedure

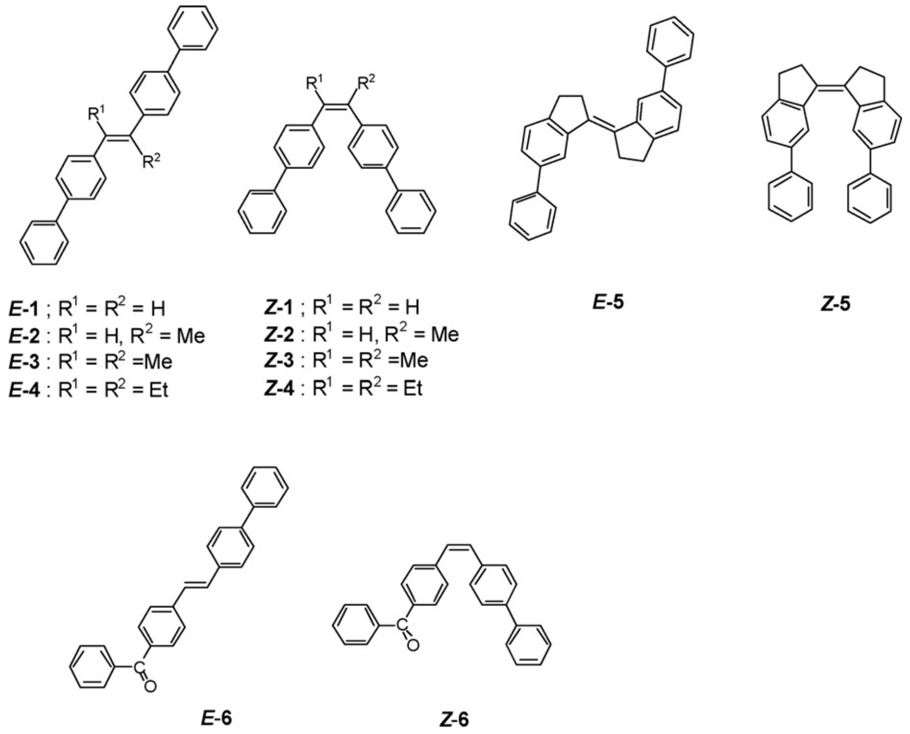
A powder of *Z*-**1** (30 mg) was put in a 30 ml Pyrex-flask under vacuum and the flask was cooled at −72 °C, which was irradiated with a 500 W high-pressure mercury lamp through a band-pass filter (HA 50) that passes only the light with the wavelength among 300–400 nm. After irradiation for 12 h, the powder was dissolved in deuterated chloroform and subjected to the measurement of the ^{1}H NMR spectrum.

This procedure was applied to all the solid-state photoreactions of other alkenes.

3. Results and discussion

3.1. Structure and spectra of alkenes (**1**–**6**)

The structures of the alkenes (**1**–**6**) used in the present study are arranged in Fig. 1, which all exist in the solid-state at room temperature. The NOE measurements as well as the X-ray crystallography (for *Z*-**3**) allowed us to unambiguously determine their geometries. For example, only the methyl protons of *E*-**2** provided the NOE between the opposite aromatic protons of the biphenyl groups, but not for *Z*-**2**. The geometry of **5** was determined by referencing the ^{1}H NMR chemical shifts of the previously reported structurally close compound [22]. Fig. 2 shows the X-ray analysis of *Z*-**3** measured at 93 K, which provides an unambiguous proof of the *cis*-structure of *Z*-**3** with an L shape as well as its characteristic feature with the almost plain ethylenic moiety but the benzene rings twisting as shown in Fig. 2. All compounds exhibited the absorptions within 310–350 nm in benzene, in which both the *E*- and *Z*-isomers absorbed almost same regions except for **1** and **6** (Table 1). The fluorescence stronger



***E*-1** ; $R^1 = R^2 = H$
***E*-2** : $R^1 = H$, $R^2 = Me$
***E*-3** : $R^1 = R^2 = Me$
***E*-4** : $R^1 = R^2 = Et$

***Z*-1** ; $R^1 = R^2 = H$
***Z*-2** : $R^1 = H$, $R^2 = Me$
***Z*-3** : $R^1 = R^2 = Me$
***Z*-4** : $R^1 = R^2 = Et$

***E*-5** ***Z*-5**

***E*-6** ***Z*-6**

Fig. 1. Structures of the crystalline alkenes **1**–**6**.

in the *E*-isomers than the *Z*-isomers was also observed in all alkenes.

3.2. Photoisomerization in solution and in the solid-state

The self-sensitized photoisomerization of both the *E*- and *Z*-isomers in benzene during irradiation by a 500 W high-pressure mercury lamp produced photostationary solutions of various contents as shown in Table 1. The ratios are independent of

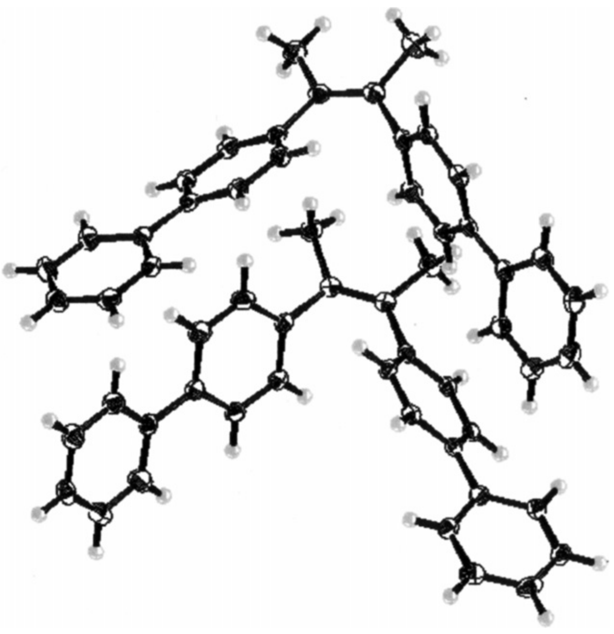


Fig. 2. Crystal structure of *Z*-**3**.

Table 1
Absorption spectral data and photostationary points during photoisomerization of alkenes **1**–**6** in solution

Alkenes	Absorption[a] (nm)	Photostationary point[b,c], *E*:*Z*[d]
1		
E	342	61:39[e]
Z	328	
2		
E	327	30:70
Z	323	
3		
E	314	92:8
Z	313	
4		
E	315	93:7
Z	314	
5		
E	354	78:22[g]
Z	–[f]	
6		
E	348	21:79
Z	329	

[a] Measured in benzene.
[b] Irradiated for 1 h.
[c] Both the *E*- and *Z*-isomers were used except for **5**.
[d] Determined by ^{1}H NMR spectrum.
[e] A slight side-reaction was detected.
[f] Not isolated.
[g] Either the pure *E*-**5** or a mixture of *E*-**5** and *Z*-**5** was used.

whether the *E*- or *Z*-isomers were employed, but highly dependent on the substitution pattern as well as the kind of substituents on the olefinic carbons, namely, **1** showed a medium *E*-preference, whereas the introduction of a methyl group afforded a converse ratio as shown in the case of **2**. The tetra-substituted alkenes **3** and **4** exclusively favored the *E*-forms, while the bis(indenyliden) derivative **5**, classified as a tetra-substituted alkene, had a medium *E*-preference. On the other hand, the alkene **6** containing a benzoyl group showed a *Z*-preference. Therefore, all the alkenes presented here underwent a mutual photoisomerization in solution.

Next, the photoreaction of these alkenes in the solid-state was investigated. After irradiation of the powdered samples of all the alkenes, the ^{1}H NMR spectra of the reactants were measured in $CDCl_3$ and then the contents were analyzed. Thus, *Z*-**1** was found to change into its *E*-isomer in a 50% conversion without any side-reaction, but no change was detected when *E*-**1** was irradiated under similar conditions, which revealed that *Z*-**1** isomerized in a unidirectional manner. Other alkenes, i.e., *Z*-**2** and *Z*-**6**, also changed into their *E*-isomers with 33 and 55% conversions, respectively, whereas their *E*-isomers showed no change under similar conditions. Therefore, both **2** and **6** also underwent a unidirectional photoisomerization in the solid-state, although they favored the *Z*-forms in solution. The spectral analysis of these isomerizations by ^{1}H NMR is shown in Fig. 3. The unidirectional photoisomerization in the solid-state observed here is probably due to the similar behavior of *cis*-1,2-di(1-naphtyl)ethylene previously investigated in detail [1,3]. To explain this unique photochemical behavior in the solid-state, it is useful to refer to the phase rebuilding, in which the new lattice of the photochemically formed *E*,*E*-isomer would no longer provide freedom for the reverse process because the *E*,*E*-molecules would be strongly interlocked.

On the contrary, neither the *E*- nor *Z*-isomers of **3**, **4**, and **5** changed at all in the solid-state even when irradiated at room temperature. A critical difference in the structure between the

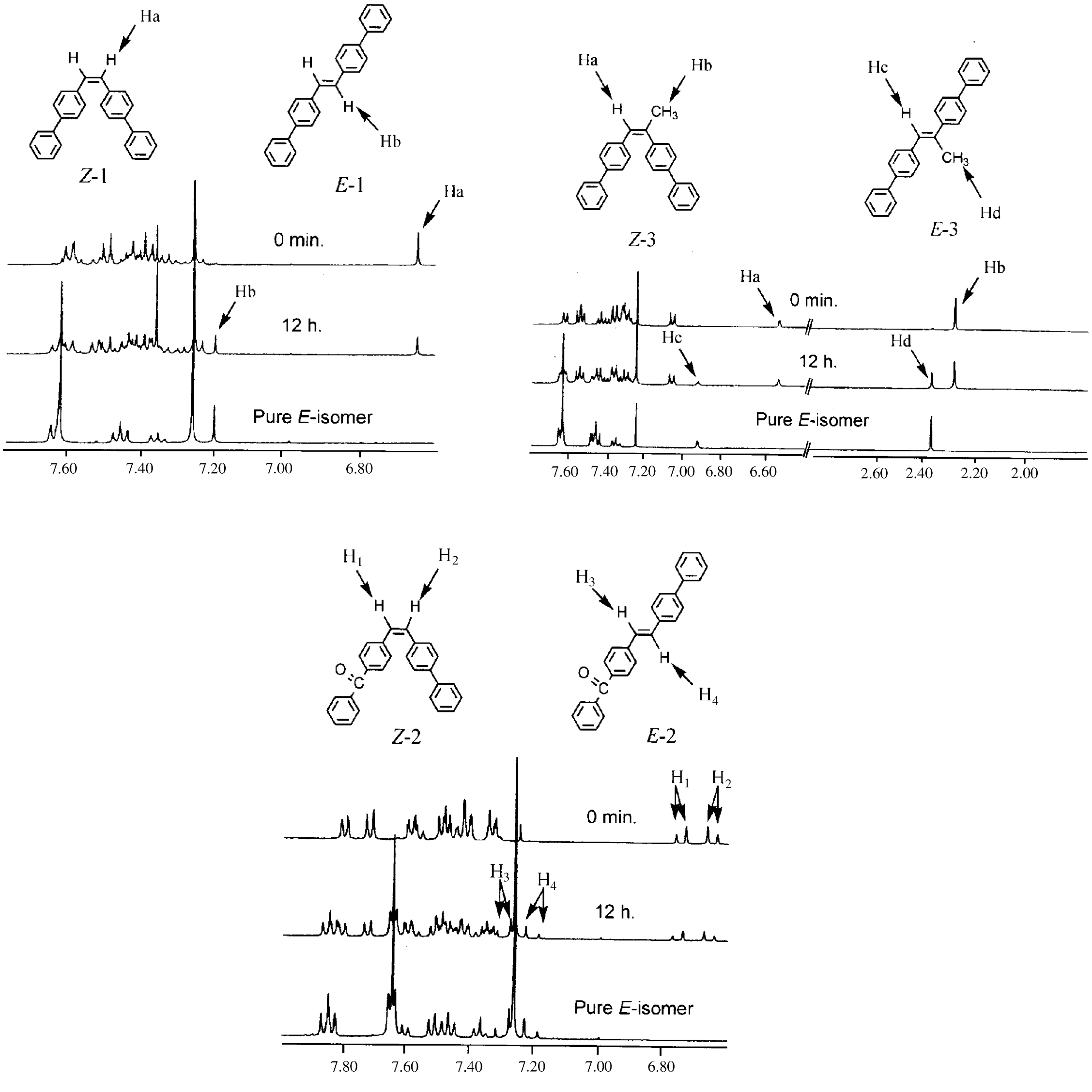


Fig. 3. Tracing ^{1}H NMR spectra of the photoisomerization of *Z*-**1**, **2**, and **6** in the solid-state. After irradiation for 12, the samples were dissolved in $CDCl_3$ for measurement.

alkenes that undergo the solid-state photoisomerization and those unreactive is whether or not they have at least one hydrogen atom on the central sp^2 carbons.

During the conventional OBF mechanism, one bond rotation around the central double bond demands a considerably large space, and therefore, such an isomerization in a confined environment is difficult to take place. According to the Hula-twist (HT) mechanism [7,9,10], the isomerization takes place not by the one bond rotation but by the concomitant twist of the double bond and the adjacent single bond to accomplish the double bond isomerization. In this mechanism, only one of the double bond C–H undergoes a space saving out-of-plane translocation, while the phenyl substituent at the same C essentially moves within its original plane. Different from a hydrogen atom, the alkyl groups attached to the sp^2 carbons of the double bonds would be incapable of revolving by means of the HT process due to steric factors, so that tetra-substituted olefins seem to be difficult to isomerize by this process in the solid-state. If the HT process is applied to the isomerization of the alkenes such as **3** and **4**, there is no space enough large for the corner flip of alkyl-substituted sp^2 carbons, which is the first and necessary motion for the HT process. Thus, steric repulsion with the adjacent molecules consequent in the solid-state prevents from undergoing *Z*/*E*-photoisomerization. Additionally, it is a matter of course that the ethene **5** cannot undergo an isomerization by the HT process because of its stiff structure [20] that inhibits the alkyl chain from twisting due to the linkage with the aromatic rings. Therefore, our experimental results that while the *Z*-**1**, **2**, and **6** underwent the unidirectional photoisomerization in the solid-state, *Z*-**3**, **4**, and **5** did not change under similar conditions in contrast to their mutual isomerization in solution are well explained when the HT mechanism is applied.

4. Conclusion

We have studied the *E*/*Z*-photoisomerization of some bis(biphenyl)ethylenes and ethenes both in solution and in the solid-state. While all these alkenes underwent the mutual photoisomerization in solution, those with at least one hydrogen atom on the central sp^2 carbon atoms isomerized in a unidirectional manner from the *Z*-forms to the *E*-forms in the solid-state. In contrast, both the *E*- and *Z*-isomers of the tetra-substituted alkenes no longer change in the solid-state. Consequently, the observed differentiation of the reaction modes in the solid-state depending on the structures can be explained by the Hula-twist mechanism.

Acknowledgements

This work was partially supported by the CLUSTER of the Ministry of Education, Culture, Sports, Science and Technology of Japan and the Grants-in-aid for the 21st Century COE Research. J.M. is also grateful for the financial support by the Grant-in-aid (16550122) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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