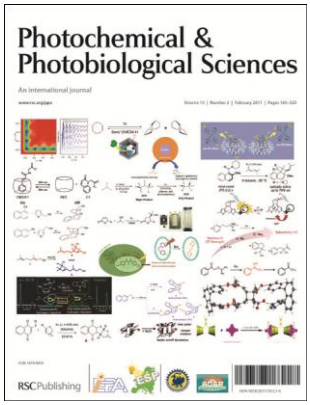

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PAPER

Competitive photocyclization/rearrangement of 4-aryl-1,1-dicyanobutenes controlled by intramolecular charge-transfer interaction. Effect of medium polarity, temperature, pressure, excitation wavelength, and confinement†

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A series of 4-aryl-1,1-dicyanobutenes (**1a–1f**) with different substituents were synthesized to control the intramolecular donor–acceptor or charge-transfer (C–T) interactions in the ground state. Photoexcitation of these C–T substrates led to competitive cyclization and rearrangement, the ratio being critically controlled by various environmental factors, such as solvent polarity, temperature and static pressure, and also by excitation wavelength and supramolecular confinement (polyethylene voids). In non-polar solvents, the rearrangement was dominant (>10 : 1) for all examined substrates, while the cyclization was favoured in polar solvents, in particular at low temperatures. Selective excitation at the C–T band further enhanced the cyclization up to >50 : 1 ratios. More importantly, the cyclization/rearrangement ratio was revealed to be a linear function of the C–T transition energy. However, the substrates with a sterically demanding or highly electron-donating substituent failed to give the cyclization product.

Introduction

Despite the significant developments in mechanistic organic photochemistry in recent decades, the precise control of regio- and stereoselectivities is still one of the most intriguing and challenging tasks in photochemistry.[1] In contrast to the conventional thermochemical counterparts, photochemical transformations occurring in the excited states are more susceptible to environmental variants, enabling us to manipulate the selectivities by temperature, solvent polarity, pressure and other factors.[2] Additionally, the properties and reactivity of excited or reactive species can be modulated by using various techniques such as singlet/triplet sensitization and energy/electron transfer, and also by directly altering excitation wavelength.[3] Recently, weak non-covalent interactions, such as hydrogen bonding,[4] cation–π,[5] donor–acceptor[6] and hydrophobic interactions, have also been used to control photoreactions in the solid and solution phases. Thus, a wide variety of cavities, supercages, voids or receptor sites of cyclodextrins, cucurbiturils, zeolites, polymer matrices, metal–organic frameworks, organic cages, dendrimers, micelles and biomolecules have also been exploited to manipulate the photochemical outcomes, the choice of which may depend on the nature of the targeted reactions.[7]

The photochemistry of donor–acceptor systems has been studied mostly from the electron transfer point of view. The rate of electron transfer is dependent on the strengths of both donor and acceptor molecules, and usually governed by the Marcus equation.[8] The effect of donor–acceptor interaction has thus been discussed in terms of the rate of electron transfer and the lifetime of charge-separated state, where the resulting charge-separated state is eventually quenched by the back electron transfer, reverting to the initial state. Although the selective excitation of the charge–transfer (C–T) band by irradiating at the absorption edge is feasible,[9] less attention has been paid to the photochemical transformation of donor–acceptor molecules and the studies are rather limited. We have recently investigated the effects of excitation wavelength on the product's (dia)stereoselectivity in several chiral donor–acceptor systems.[10–12] Thus, the direct (or local) excitation of one of the components in chiral fumarate-stilbene[10,11] or chiral benzoate-diphenylethene[12] systems leads to the formation of a conventional exciplex *via* the excited singlet state. In contrast, the selective C–T band excitation of a ground-state complex affords a distinctly different excited species, *i.e.*, excited C–T complex, accordingly providing quite different product distributions.

In this study, we investigated the photoreaction of a series of 4-aryl-1,1-dicyanobutenes (**1a–1f**) with varying degrees of intramolecular C–T interaction. In addition to the donor/acceptor abilities, steric bulk is known to critically affect the donor–acceptor interaction.[13] Hence, we examined the steric effect on the photoreactions by using more sterically congested substrates (**1d** and **1e**). The photolysis of **1** afforded the cyclization and rearrangement products in almost quantitative manner (Scheme 1), the ratio

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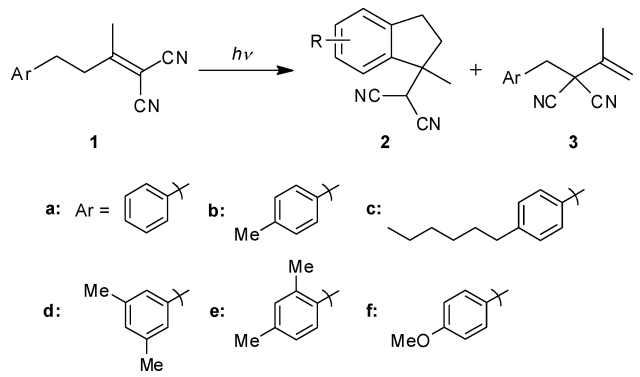


Scheme 1 Photoreactions of 4-aryl-1,1-dicyanobutenes (**1a–1f**).

of which was shown to be a critical function of environmental factors such as medium polarity, temperature, pressure, as well as excitation wavelength. We will demonstrate how and to what extent the strength of C–T interaction affects the product distribution, and reveal that the combined use of multiple factors (*e.g.*, solvent, temperature and pressure) significantly enhances the product selectivity.

Experimental

Instrumentation

UV-vis absorption spectra were recorded on a JASCO V-550 or V-560 spectrometer fitted with an ETC-505T temperature controller. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ on JEOL GX-400 or JNM-ECP400, and chemical shifts are reported in ppm relative to Me_4Si. Gas chromatographic (GC) analyses were performed on Shimadzu GC-2014, and the reactant conversion and product yield were determined on a capillary column ZB-5 (30 m × 0.25 mm i.d. × 0.25 μm d.f.). GC peaks were integrated on a Shimadzu GC Solution (version 2.3). GC-MS was obtained on a Hewlett Packard HP 5890 Series II fitted with an HP 5971A mass-selective detector at an applied voltage of 70 eV. Elemental analyses were performed at the Center for Chemical Analyses, Osaka University. Column chromatography was performed on silica gel 60 (230–400 mesh ASTM) with a Yamazen PREP UV-10V detector and pump Model 540 or by GPC (JAIGEL-H column) on JAI LC-908.

Materials

Solvents (Aldrich or Wako, spectrophotometric grade) and reagents – benzylbromide (Wako, 98% purity), acetylacetone (Kanto, 99.5%), potassium carbonate (Wako, 99.5%), malononitrile (Wako, 98%), acetic acid (Wako, 99.7%), ammonium acetate (Kanto, >97%), *p*-methylbenzyl bromide (Wako, 98%), 3,5-dimethylbenzylbromide (Alfa Aesar, 98%), *m*-xylene (Wako, 98%), paraformaldehyde (Kanto, 92%), hydrobromic acid (Wako, 47–49%), 1-phenylhexane (Wako), 4-(4-methoxyphenyl)-2-butanone (Aldrich) – were used as received.

General procedures for preparing 4-aryl-1,1-dicyanobutenes

4-Aryl-1,1-dicyanobutenes were prepared from the corresponding butenones, which were obtained by the condensation of appropriate benzyl bromides with acetylacetone. The benzyl bromides needed for the preparation of **1c** and **1e** were prepared by the literature procedures.[14,15] 4-Methoxyphenyl-2-butanone (for preparation of **1f**) and other benzyl bromides (for **1a**, **1b**, and **1d**) were commercially available.

(a) 4-Substituted 2-butanones. These compounds were prepared by procedures similar to those described in the literature.[16] A mixture of benzylbromide (8.0 mmol), acetylacetone (0.80 g, 8.0 mmol), and anhydrous potassium carbonate (1.10 g, 8.0 mmol) in methanol (20 mL) was refluxed for 16 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and the solvent was removed under a reduced pressure. The resulting residue was treated with ethyl acetate (20 mL) and water (20 mL), and the organic layer was collected. The aqueous layer was further extracted with ethyl acetate (3 × 15 mL). The combined organic phase was washed with brine (3 × 15 mL), dried over anhydrous sodium sulfate, and the solvent was removed under a reduced pressure. The resulting oily material was chromatographed on silica gel using an 8 : 2 mixture of hexane and ethyl acetate as eluent to give the corresponding butanones as oil in 29–64% yield.

(b) 4-Aryl-1,1-dicyanobutenes. These were prepared by procedures similar to those in the literature.[17] 4-Substituted 2-butanone (5.1 mmol), malononitrile (0.34 g, 5.1 mmol), acetic acid (0.30 mL, 5.1 mmol) were dissolved in toluene (25 mL). Ammonium acetate (0.11 g, 1.4 mmol) was added and the mixture was refluxed with a Dean–Stark apparatus for 16 h under nitrogen. The solution was cooled to room temperature and the resulting mixture was washed with saturated aqueous sodium hydrogen carbonate (3 × 20 mL) and dried over anhydrous sodium sulfate. The solution containing the crude product was filtrated, concentrated *in vacuo* and chromatogrammed on silica gel with hexane–ethyl acetate (8 : 2) eluent to give the corresponding 4-aryl-1,1-dicyanobutenes in 28–95% yield.

1,1-Dicyano-2-methyl-4-phenyl-1-butene (1a).

4-Phenyl-2-butanone. (0.77 g, 64%). ^{1}H NMR (lit.[18]): δ 2.16 (3H, s), 2.78 (2H, t, J = 7.6 Hz), 2.92 (2H, t, J = 7.6 Hz), 7.19–7.23 (3H, m) and 7.27–7.32 (2H, m).

*1,1-Dicyano-2-methyl-4-phenyl-1-butene (**1a**).* (0.86 g, 85%). ^{1}H NMR (lit.[17]): δ 2.26 (3H, s), 2.90 (4H, s), and 7.18–7.35 (5H, m).

1,1-Dicyano-2-methyl-4-(4-methylphenyl)-1-butene (1b).

4-(4-Methylphenyl)-2-butanone. (0.80 g, 62%). ^{1}H NMR (lit.[18]): δ 2.14 (3H, s), 2.31 (3H, s), 2.74 (2H, t, J = 7.6 Hz), 2.86 (2H, t, J = 7.6 Hz) and 7.06–7.10 (4H, m).

*1,1-Dicyano-2-methyl-4-(4-methylphenyl)-1-butene (**1b**).* (0.99 g 95%). ^{1}H NMR: δ 2.25 (3H, s), 2.34 (3H, s), 2.86–2.89 (4H, m), 7.06 (2H, d, J = 8.1 Hz) and 7.13 (2H, d, J = 8.1 Hz); ^{13}C NMR: δ 21.1, 22.8, 33.3, 39.7, 86.5, 111.6, 111.9, 128.1, 129.5, 135.3, 136.6 and 181.4; MS (EI): m/z = 210 (M^+, 7%), 106 (10), 105 (100); EA: Found: C, 79.88; H, 6.58; N, 13.10%. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32%.

1,1-Dicyano-2-methyl-4-(4-hexyllphenyl)-1-butene (1c).

4-Hexylbenzylbromide. (3.47 g, 71%). ^{1}H NMR (lit.[14]): δ 0.88 (3H, t, J = 6.9 Hz), 1.30 (6H, bs), 1.55–1.66 (2H, m), 2.59 (2H, t, J = 7.8 Hz), 4.49 (2H, s), 7.17 (2H, d, J = 7.2 Hz) and 7.27 (2H, d, J = 7.2 Hz).

4-(4-Hexylphenyl)-2-butanone. (0.91 g, 29%). ^{1}H NMR: δ 0.88 (3H, t, J = 6.9 Hz), 1.30 (6H, bs), 1.54–1.61 (2H, m), 2.14 (3H, s), 2.56 (2H, t, J = 7.6 Hz), 2.75 (2H, t, J = 7.6 Hz), 2.86 (2H, t, J = 7.6 Hz) and 7.07–7.11 (4H, m). ^{13}C NMR: δ 14.2, 22.8, 29.2, 29.5, 30.2, 31.7, 31.9, 35.7, 45.5, 128.3, 128.7, 138.2, 140.9 and 208.3; MS (EI): m/z = 232 (M^+, 76%), 175 (48), 161 (100), 147 (31), 104 (33); EA: Found: C, 82.59; H, 10.48%. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41%.

1,1-Dicyano-2-methyl-4-(4-hexylphenyl)-1-butene (***1c***). (0.95 g, 86%). ^{1}H NMR: δ 0.88 (3H, t, J = 7.0 Hz), 1.25–1.36 (6H, m), 1.55–1.63 (2H, m), 2.25 (3H, s), 2.58 (2H, t, J = 7.9 Hz), 2.83–2.91 (4H, m), 7.08 (2H, d, J = 8.1 Hz) and 7.14 (2H, d, J = 8.1 Hz); ^{13}C NMR: δ 22.1, 22.9, 39.3, 46.3, 87.0, 111.8, 126.6, 127.3, 129.0, 143.5 and 180.5; MS (EI): m/z = 280 (M^+, 4%), 176 (15), 175 (100), 104 (11); EA: Found: C, 81.44; H, 8.69; N, 10.09%. Calcd for $C_{19}H_{24}N_2$: C, 81.38; H, 8.63; N, 9.99%.

1,1-Dicyano-2-methyl-4-(3,5-dimethylphenyl)-1-butene(1d).

4-(3,5-Dimethylphenyl)-2-butanone. (0.82 g, 55%). ^{1}H NMR (lit.[19]): δ 2.14 (3H, s), 2.28 (6H, s), 2.73 (2H, t, J = 7.7 Hz), 2.82 (2H, t, J = 7.7 Hz), 6.80 (2H, s) and 6.83 (1H, s).

1,1-Dicyano-2-methyl-4-(3,5-dimethylphenyl)-1-butene (***1d***). (0.52 g, 50%). M.p. 126 °C. ^{1}H NMR: δ 2.25 (3H, s), 2.34 (3H, s), 2.78–2.90 (4H, m), 7.06 (2H, d, J = 8.1 Hz) and 7.13 (2H, d, J = 8.1 Hz); ^{13}C NMR: δ 21.3, 22.9, 33.7, 39.8, 87.0, 111.7, 112.0, 126.1, 128.8, 138.4, 138.6 and 181.4; MS (EI): m/z = 224 (M^+, 12%), 120 (9), 119 (100); EA: (Found: C, 80.32; H, 7.23; N, 12.39%. Calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49%).

1,1-Dicyano-2-methyl-4-(2,4-dimethylphenyl)-1-butene (1e).

2,4-Dimethylbenzylbromide. (2.64 g, 70%). ^{1}H NMR (lit.[15]): δ2.30 (3H, s), 2.38 (3H, s), 4.51 (2H, s), 6.99–7.00 (2H, m) and 7.19 (1H, d, J = 7.5 Hz).

4-(2,4-Dimethylphenyl)-2-butanone. (1.23 g, 54%). ^{1}H NMR: δ2.14 (3H, s), 2.28 (6H, s), 2.73 (2H, t, J = 8.0 Hz), 2.82 (2H, t, J = 8.0 Hz), 6.93–7.01 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ19.2, 20.9, 26.7, 30.0, 44.1, 126.8, 128.5, 131.1, 135.7, 135.8, 136.0 and 208.2; $C_{12}H_{16}O$ (176.1201) HRMS: 176.1207.

1,1-Dicyano-2-methyl-4-(2,4-dimethylphenyl)-1-butene (***1e***). (0.44 g, 28%). M.p. 63 °C. ^{1}H NMR: δ 2.30 (6H, s), 2.32 (3H, s), 2.88–2.87 (4H, m), 6.97 (2H, d, J = 1.1 Hz) and 7.00 (1H, br s); ^{13}C NMR: δ 19.2, 21.1, 23.1, 31.2, 38.9, 86.6, 111.7, 111.9, 127.2, 128.9, 131.7, 133.8, 135.8, 137.0 and 181.4; MS (EI): m/z = 224 (M^+, 6%), 120 (10), 119 (100); EA: Found: C, 80.34; H, 7.03; N, 12.44%. Calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49%.

1,1-Dicyano-2-methyl-4-(4-methoxyphenyl)-1-butene (1f). (3.77 g, 83%). M.p. 89 °C. ^{1}H NMR: δ 2.25 (3H, s), 2.84–2.87 (2H, m), 3.80 (3H, s), 6.86 (2H, d, J = 8.6 Hz) and 7.09 (5H, d, J = 8.6 Hz); ^{13}C NMR: δ23.0, 33.1, 40.0, 55.4, 111.7, 111.9, 114.4, 129.4, 130.5, 158.8 and 181.3; MS (EI): m/z = 226 (M^+, 5%), 122 (9), 121 (100); EA: Found: C, 74.31; H, 6.24; N, 12.38%. Calcd for $C_{14}H_{14}N_2O$: C, 74.39; H, 6.23; N, 12.40%.

Irradiation procedures

A 0.1 mM solution of 4-aryl-1,1-dicyanobutene in acetonitrile or other appropriate solvent was placed in a 1 cm quartz cell and purged with nitrogen for 10 min. This was irradiated typically at 20 °C with a 300 W xenon lamp (Asahi Spectra, MAX-301) fitted with a UV mirror module and HQBP254/280/290/300-UV band-pass filter. After a certain period of time, the photolyte was directly analyzed by GC.

Irradiation under high pressure was conducted in a pressure vessel fitted with sapphire windows and connected to a plunger pump. A 0.15 mL quartz cuvette (light path, 0.2 cm) filled with a sample solution under air was placed in the high-pressure vessel, which was thermostatted by circulating water through the reactor body. The pressure was applied with the pump, and its magnitude was measured by a pressure gauge. The sample solution was photoirradiated through one of the sapphire windows. After the photolysis, the pressure was released and the resulting photolyte was directly analyzed by GC.

Typical procedures for photoreaction in a cavity of polyethylene film were described elsewhere.[20] Briefly, cleaned and doped polyethylene film was placed in a 1 cm quartz cell capped with a rubber septum, and was purged with nitrogen for 20 min. After the photoirradiation, the film was successively immersed in a series of dichloromethane aliquots (50 mL) until no absorption was detected in the UV spectrum of the last aliquot. The combine extract was concentrated *in vacuo* and the residue was analyzed by GC.

In preparative-scale photolyses, a 1–5 mM acetonitrile solution of 4-aryl-1,1-dicyanobutene (250 mL) in a donut-shaped flask was irradiated for 6–35 h under nitrogen atmosphere with a 30 W low-pressure mercury lump (λ_{ex} = 254 nm). After irradiation, the photolyte was concentrated and separated and purified by repeated GPC with $CHCl_3$ as eluent.

1-Dicyanomethyl-1,5-dimethylindane (2b). Yield: 31%; ^{1}H NMR: δ 1.64 (3H, s), 2.18 (1H, td, J = 8.5, 13.8 Hz), 2.37 (3H, s),2.40 (1H, td, J = 8.5, 13.8 Hz), 2.91–3.06 (2H, m),3.72 (1H, s) and 7.10–7.26 (3H, m); ^{13}C NMR: δ 21.4, 24.1, 29.2, 33.7, 38.0, 50.5, 112.1, 112.2, 123.7, 125.1, 130.0, 137.1, 139.8 and 143.3; $C_{14}H_{14}N_2$(210.1157) HRMS: 210.1155.

3,3-Dicyano-2-methyl-4-(4-methylphenyl)-1-butene (3b). Yield: 8%; ^{1}H NMR:δ 2.05 (3H, q, J = 0.7 Hz), 2.37 (3H, s), 3.26 (2H, s), 5.28 (1H, q, J = 0.7 Hz), 5.44 (1H, bs), 7.19 (2H, d, J = 8.1 Hz) and 7.25 (2H, d, J = 8.1 Hz); ^{13}C NMR: δ 19.0, 21.3, 43.2, 45.7, 114.3, 118.6, 128.9, 129.7, 130.2, 135.1 and 138.9; $C_{14}H_{14}N_2$(210.1157) HRMS: 210.1149.

1-Dicyanomethyl-5-hexyl-1-methylindane (2c). Yield: 24%; ^{1}H NMR: δ 0.88 (3H, t, J = 7.1 Hz), 1.25–1.36 (6H, m), 1.56–1.62(2H, m), 2.13–2.21 (1H, m), 2.36–2.42 (1H, m), 2.61 (2H, t, J = 7.8 Hz), 2.91–3.06 (2H, m), 3.71 (1H, s),7.12 (1H, d, J = 8.7 Hz), 7.16 (1H, s) and 7.17 (1H, d, J = 8.7 Hz); ^{13}C NMR: δ 14.2, 22.7, 24.1, 29.1, 29.4, 31.8, 31.8, 33.9, 36.0, 38.2, 50.7, 112.3, 112.3, 123.2, 125.2, 129.5, 140.1, 142.5 and 143.4; $C_{19}H_{24}N_2$(280.1939) HRMS: 280.1937.

3,3-Dicyano-2-methyl-4-(4-hexylphenyl)-1-butene (3c). Yield: 9%; ^{1}H NMR: δ 0.88 (3H, t, J = 7.1 Hz), 1.26–1.35 (6H, m), 1.56–1.64(2H, m), 2.04 (3H, q, J = 0.7 Hz), 2.61 (2H, t, J = 7.9 Hz), 3.26 (2H, s), 5.28 (1H, q, J = 0.7 Hz), 5.43 (1H, s), 7.19 (2H, d, J = 8.1 Hz) and 7.26 (2H, d, J = 8.1 Hz); ^{13}C NMR: δ 14.2, 19.0, 22.7, 29.1, 31.4, 31.8, 35.8, 43.3, 45.7, 114.3, 118.6, 129.0, 129.1, 130.2, 135.1 and 143.9; $C_{19}H_{24}N_2$(280.1939) HRMS: 280.1937.

3,3-Dicyano-2-methyl-4-(3,5-dimethylphenyl)-1-butene (3d). Yield: 8%; ^{1}H NMR: δ 2.04 (3H, q, J = 0.7 Hz), 2.33 (6H, s),

3.20 (2H, s), 5.28 (1H, q, J = 0.7 Hz), 5.46 (1H, bs), 6.96 (2H, s) and 7.26 (1H, s); ^{13}C NMR: δ19.0, 21.4, 43.4, 45.6, 114.3, 118.4, 128.1, 130.6, 131.9, 135.3 and 138.5; $C_{15}H_{16}N_2$(224.1313) HRMS: 224.1308.

1-Dicyanomethyl-1,5,7-trimethylindane (2e). Yield: 33%; ^{1}H NMR:δ 1.63 (3H s), 2.17 (1H, ddd, J = 4,7, 7.3, 13.9 Hz), 2.23 (3H, s), 2.33 (3H, s), 2.39 (1H, ddd, J = 4,7, 7.3, 13.9 Hz), 2.87–2.91 (2H, m), 3.71 (1H, s), 6.95 (1H, s) and 6.98 (1H, s); ^{13}C NMR: δ19.1, 21.4, 24.5, 28.1, 34.1, 37.8, 50.9 112.3, 112.3, 121.1, 131.0, 134.6, 137.5, 138.8 and 143.3; $C_{15}H_{16}N_2$(224.1313) HRMS: 224.1312.

3,3-Dicyano-2-methyl-4-(2,4-dimethylphenyl)-1-butene (3e). Yield: 19%; ^{1}H NMR: δ 2.08 (3H, q, J = 0.7 Hz), 2.32 (3H, s), 2.40 (3H, s), 3.32 (2H, s), 5.32 (1H, q, J = 0.7 Hz), 5.51 (1H, bs), 7.03–7.06 (2H, m) and 7.25–7.27 (1H, m); ^{13}C NMR: δ19.1, 20.0, 21.2, 39.7, 45.2, 114.5, 118.3, 127.2, 127.6, 130.9, 132.1, 135.7, 137.4 and 138.8; $C_{15}H_{16}N_2$(224.1313) HRMS: 224.1311.

3,3-Dicyano-2-methyl-4-(4-methoxyphenyl)-1-butene (3f). Yield: 7%; ^{1}H NMR: δ 2.04 (3H, q, J = 0.7 Hz), 3.24 (2H, s), 3.82 (2H, s), 5.28 (1H, q, J = 0.7 Hz), 5.43 (1H, bs), 6.90 (2H, d, J = 8.6 Hz) and 7.28 (2H, d, J = 8.6 Hz); ^{13}C NMR: δ 19.0, 42.9, 45.8, 55.4, 114.4, 118.6, 123.9, 129.5, 131.6, 135.0 and 160.1; $C_{14}H_{14}N_2O$ (226.1106) HRMS: 226.1102.

Results and discussion

Ground-state donor–acceptor interactions of 4-aryl-1,1-dicyanobutenes

Intramolecular donor–acceptor interactions of **1a–1f** in the ground state were investigated by absorption spectroscopy. The UV spectra of **1a–1f** showed a long-wavelength band, ascribable to the charge–transfer (C–T) band. This band was not observed in the spectrum of donor (*p*-xylene) or acceptor (1,1-dicyano-2-methylpropene) component of **1b** (Fig. 1a). The degree of donor–acceptor interaction was dependent on the nature of substituent, and the absorption edge of the C–T band of **1a–1f** was gradually shifted to the red, as the donor strength of the aryl group increased (Fig. 1b). Table 1 summarizes the excitation energies of the deconvoluted C–T bands and the oxidation potentials of

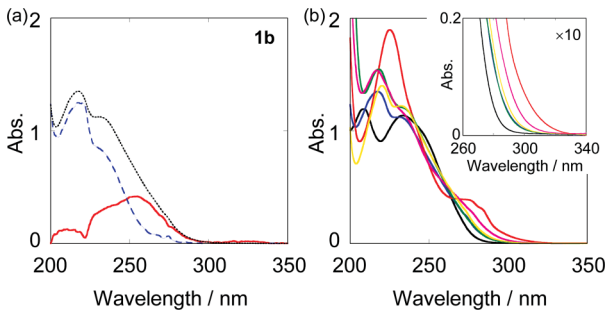


Fig. 1 (a) UV spectral examinations of donor–acceptor interaction of **1b**; black: spectrum of **1b**, blue: spectral sum of *p*-xylene and 1,1-dicyano-2-methylpropene, red: difference spectrum (black – blue). All experimental spectra were obtained for 0.1 mM solution in acetonitrile at 20 °C. (b) UV spectra of 0.1 mM of **1a–1f** in acetonitrile at 20 °C. black: **1a**, blue: **1b**, green: **1d**, yellow: **1c**, pink: **1e**, red: **1f**. Inset: expansion of the C–T band region.

Table 1 Charge-transfer band maxima and oxidation potentials of **1a–1f**

Substrate	λ_{CT}/nm, E_{CT}/eV[a]	E_{ox}/V *vs.* SCE[b]	ΔG_{ET}/eV[c]
1a	266, 4.66 (264, 4.70)	2.37	–0.29
1b	270, 4.59 (269, 4.61)	2.11	–0.39
1c	270, 4.59 (270, 4.59)	2.14	–0.34
1d	271, 4.58 (270, 4.59)	2.09	–0.41
1e	273, 4.54 (273, 4.54)	1.98	–0.40
1f	277, 4.48 (278, 4.46)	1.63	–0.61

[a] C–T band maxima (in acetonitrile) determined by deconvolution of the UV spectra of **1a–1f**. The values in parentheses were obtained in methylcyclohexane. [b] Oxidation potentials obtained in acetonitrile using n-$Bu_4N^+PF_6^-$ as a supporting electrode. [c] Free energy change for (intramolecular) electron transfer in the excited singlet state of **1**, calculated by using the Rehm–Weller equation.[23] The following values were used in the estimation of ΔG_{ET}. E_{red} = –1.69 V (1,1-dicyano-2-methylpropene),[24] A = –0.06 V (acetonitrile). The 0-0 transition energies upon singlet excitation were estimated from those of the C–T band (at the wavelength of ε_{CT} = 100).

1a–1f. The excitation energy (E_{CT}) of the C–T band was found to be a linear function of the oxidation potential (Fig. 2a; slope = 0.24, intercept = 4.08, r = 0.99). The fact that the degree of C–T interaction evaluated from its excitation energy is linearly proportional to the donor strength of the molecule indicates insignificant contribution of the steric effects upon ground-state C–T interaction at least in**1a–1f**.

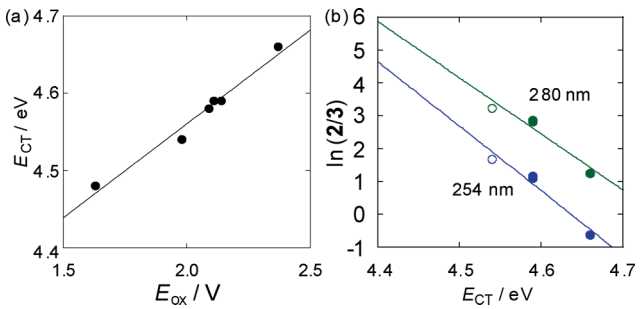


Fig. 2 (a) Relationship between the excitation energy of the deconvoluted C–T band (E_{CT}) and the oxidation potential of **1**. (b) Relationship between the logarithm of **2**/**3** ratio and E_{CT}upon excitation at 254 nm (blue) and 280 nm (green) in acetonitrile at 20 °C. The values for **1e** (open circles) are doubled for statistical corrections. See text.

The solvent effect on the intramolecular C–T interaction was rather small, as the λ_{CT} value was slightly shifted by 0–2 nm, by changing from polar acetonitrile to non-polar methylcyclohexane. The opposite shift observed for **1f** may indicate possible mixing of some n–π* character.

The ground-state donor–acceptor interaction of 4-aryl-1,1-dicyanobutenes arises from the through-space interaction in folded conformation(s) as well as the through-bond interaction in extended conformation(s).[21] Fig. 3 illustrates the ground-state geometries of **1b** optimized by dispersion-corrected density functional theory calculations.[22] Three conformations were found stable upon rotation around the C3–C4 bond; *i.e.*, *gauche*$^+$, *gauche*$^-$ and *trans* conformers. The relative energies of these conformers were 0, 2.5 and 5.4 kJ mol^{-1}, respectively, at the DFT-D-B97-D/TZV2P level in the gas phase. The cyclization in the excited state appears to be possible only from the *gauche* (or related

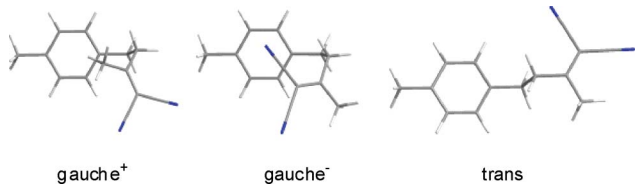


Fig. 3 Optimized geometries of three most stableconformations of **1b** optimized at the DFT-D-B97-D/TZV2P level.

syn-periplanar) conformations, as the bond-forming carbon–carbon distance is not suitable in the *trans* (anti-periplanar) conformation.

Photochemistry of 4-aryl-1,1-dicyanobutenes

(a) Effects of irradiation period on product selectivity. Photoreaction of 4-aryl-1,1-dicyanobutenes (**1**) affords cyclization and rearrangement products, as shown in Scheme 1. The photochemistry of 4-phenyl-1,1-dicyanobutene **1a** was extensively investigated by Cookson *et al.* in early 1980s.[17] Although the pronounced wavelength dependence was observed for the product ratio upon high-energy excitation in the photoreaction of **1a**, the irradiation at short wavelengths may evoke secondary photoreaction(s) of the primary products.

Hence, we first examined the time course of the product distribution in the photoreaction of **1b** at two different excitation wavelengths (Fig. 4). The formation of both **2b** and **3b** gradually became slower as the reaction proceeded (simply due to the internal filter effect of the photoproducts), but no apparent formation of byproducts was observed on GC even after 2 h of irradiation at 254 and 280 nm. The **2/3** ratio was virtually kept constant at 2.8–3.1 upon irradiation at 254 nm and at 14–17 at 280 nm at least for up to 30 min. Thereafter, the photoreaction was gradually slowed down and the ratio appreciably deviated from the initial value upon prolonged irradiations. We therefore employ the data at conversions lower than 15% (typically 6–10 min irradiation) in the following discussion to avoid any complexities, except for the photoreaction in polyethylene films, where the cyclization was observed only after prolonged irradiations.

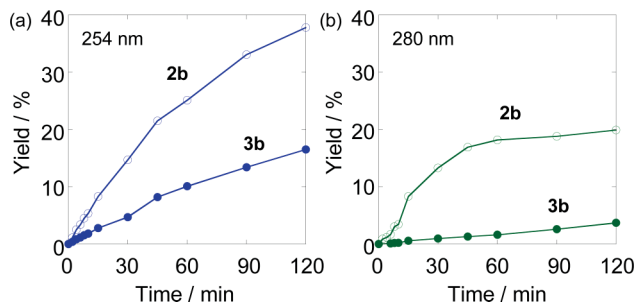


Fig. 4 Yields of **2b** (open circles) and **3b** (closed circles) upon irradiation of **1b** at (a) 254 or (b) 280 nm in acetonitrile at 20 °C.

The product distribution was not affected very much upon irradiation in the presence of air (**2/3** = 2.9 under air or 3.0 under nitrogen, with 254 nm in acetonitrile at 20 °C for **1b**), supporting that the reaction proceeds through the singlet manifold. A weak broad fluorescence was observed for **1b** in acetonitrile at long wavelengths (λ_{max} = 434 nm) with a large Stokes shift of 14 000 cm^{-1}, indicating the formation of a highly polarized excited species stabilized in polar acetonitrile. The fluorescence quantum yield of **1b** in acetonitrile was determined as 0.007, by using *p*-xylene as a reference.

(b) Effects of C–T interaction on product selectivity. The local excitation of non-substituted **1a** at 254 nm in acetonitrile at 20 °C afforded rearranged **3a** as the major product, together with a smaller amount of cyclized **2a**, the **2/3** ratio being 0.5 (Table 2).[17] In contrast, the substrates of stronger C–T character predominantly photocyclized under the same conditions. For instance, the photoirradiation of methyl- and hexylphenyl derivatives **1b** and **1c** afforded the corresponding cyclization products with **2/3** ratios of 3.0 and 3.1, respectively. Despite the increased C–T character, 2,4-dimethylphenyl derivative **1e** afforded a lower **2/3** ratio of 2.6, which however should be doubled, as one of the *ortho* positions to be attacked upon cyclization is blocked by the methyl substituent. Indeed, the logarithm of **2/3** ratio plotted against the C–T excitation energy (E_{CT}) gave a linear relationship, as shown in Fig. 2b (where the values for **1e** were statistically corrected (doubled) for the number of available *ortho* position). The nice linear plot indicates that the rearrangement and cyclization are competing (trade-off) processes and the cyclization is accelerated as the intramolecular C–T interaction becomes stronger. Unfortunately, 3,5-dimethylphenyl derivative **1d** did not afford any cyclization product, probably due to the steric hindrance of the methyl groups at adjacent *meta* positions. The failure of **1f** to give the cyclization product would be ascribed to the efficient back electron transfer in the geminate radical ion pair generated upon photoexcitation, formation of which is supported by the highly negative free energy change (Table 1).

(c) Effects of solvent polarity on product selectivity. In nonpolar methylcyclohexane, the photorearrangement was the dominant pathway, irrespective of the substituent introduced. The reaction of **1b** was examined also in dichloromethane and diethyl ether, but only a small amount of **2b** (cyclization) was obtained. However, the formation of cyclization product became substantial in polar acetonitrile (Table 2). The possible reaction mechanism for photoreaction of 4-aryl-1,1-dicyanobutenes is shown in Scheme 2. The electron transfer (ET) from the aromatic donor of **1** to the dicyanoethylene acceptor is initiated by the photoexcitation of **1**. The intramolecular electron transfer is energetically feasible in acetonitrile, as judged from the negative free energy change (ΔG_{ET}) for this process (Table 1). The ET process is prohibited in non-polar solvent due to the lack of effective solvation. Instead, another possible reaction channel, *i.e.*, the rearrangement process starts to occur, as this sigmatropic benzyl shift is a concerted process and does not involve any polar intermediate.[25] Although the formation of **3** is claimed to occur through the extended (*trans*) conformer, we do not rule out the possibility of its formation from the other conformers.

(d) Effects of excitation wavelength on product selectivity. The cyclization/rearrangement (**2/3**) ratio was a critical function of the irradiation wavelength and significantly increased upon excitation at longer wavelengths. For example, the **2/3** ratio was enhanced from 0.5 to 6.3 in the case of **1a** by changing the irradiation wavelength from 254 to 290 nm (in acetonitrile at 20 °C). Thus, an exclusive formation of cyclization product **2b** was achieved in

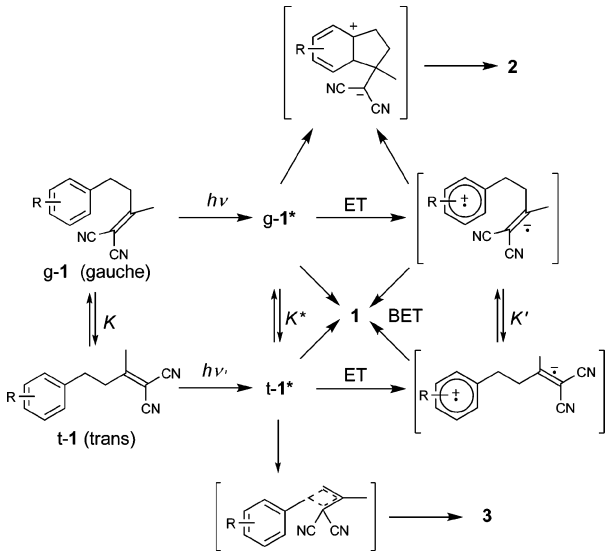
Table 2 Product distributions in the photoreaction of **1a–1f**[a]

Substrate	Solvent	Temperature/°C	λ_{ex}/nm[b]	t/min[c]	Conversion (%)	Yield of **2** (%)	Yield of **3** (%)	**2**/**3** ratio
1a	CH_3CN	20	254	16	7	1.1	2.1	0.5 (0.5)[f,g]
			280	50	6	1.7	0.5	3.4
			290	180	6	1.9	0.3	6.3 (8.1)[f]
			300	240	[e]			
		–40	254	16	6	1.6	1.2	1.3
			280	50	5	1.7	0.2	8.5
	MCH[d]	20	254	6	9	< 0.01	5.6	< 0.01
			280	40	7	< 0.01	2.1	< 0.01
1b	CH_3CN	20	254	8	6	4.5	1.5	3.0
			280	8	7	3.0	0.2	15
			300	60	8	5.0	< 0.01	> 50
		0	254	8	6	3.3	0.7	4.7
			280	8	6	1.6	0.07	23
		–20	254	8	6	3.5	0.6	5.8
			280	8	6	1.7	0.05	34
		–40	254	8	6	3.7	0.5	7.4
			280	8	6	1.8	0.04	45
	CH_2Cl_2	20	254	10	4	< 0.01	2.3	< 0.01
			280	10	3	< 0.01	0.5	< 0.02
	Et_2O	20	254	6	4	< 0.01	1.4	< 0.01
			280	20	3	0.3	0.9	0.3
	MCH[d]	20	254	6	9	0.6	6.2	0.1
			280	6	4	0.1	1.4	0.1
1c	CH_3CN	20	254	8	5	2.8	0.9	3.1
			280	8	6	2.4	0.1	24
			300	60	8	5.1	< 0.01	> 50
		–40	254	8	5	2.9	0.5	5.8
			280	8	5	1.0	0.03	33
	MCH[d]	20	254	6	9	0.6	6.5	0.1
			280	6	4	0.1	1.2	0.1
1d	CH_3CN	20	254	60	11	< 0.01	9.5	< 0.01
			280	120	6	< 0.01	1.0	< 0.01
			300	240	[e]			
	MCH[d]	20	254	6	2	< 0.01	0.4	< 0.01
			280	20	2	< 0.01	0.2	< 0.01
1e	CH_3CN	20	254	8	4	2.1	0.8	2.6
			280	8	7	2.5	0.2	13
			300	60	9	6.9	< 0.01	> 50
	MCH[d]	20	254	6	10	< 0.01	3.5	< 0.01
			280	6	6	< 0.01	1.9	< 0.01
1f	CH_3CN	20	254	60	14	< 0.01	1.9	< 0.01
			280	120	[e]			
			300	240	[e]			
	MCH[d]	20	254	10	2	< 0.01	0.9	< 0.01
			280	120	[e]			

[a] Solutions of **1a–1f** (0.1 mM) were irradiated at 254, 280, 290 or 300 nm under nitrogen. [b] Excitation wavelength. [c] Irradiation period. [d] MCH = methylcyclohexane. [e] Not detected. [f] Ref. 17. [g] Irradiated at 250 nm.

acetonitrile upon excitation of **1b** at the C–T band edge (300 nm). Considering the fact that both folded (*gauche*) and extended (*trans*) conformations are possible for 4-aryl-1,1-dicyanobutenes (*vide supra*), we may conclude that the folded conformer is selectively excited when irradiated at longer wavelengths to give the cyclization product (Scheme 2). The theoretical calculations for the electronic transition of these three conformers of **1b** at the TD-DFT-BH-LYP/TZV2P level[26] revealed that the *gauche* conformers possess the C–T band at longer wavelengths than the *trans* conformer, *i.e.*, 250 and 263 nm for $g^{\pm}$ conformations and 249 nm for *t* conformation. The upward-shifted linear ln (**2**/**3**) *versus* E_{CT} plot for the 280 nm excitation, compared to the 254 nm excitation (Fig. 2b), supports this conclusion, indicating the higher population of folded C–T conformer absorbing at the longer wavelength.

(e) Effects of temperature on product selectivity. The temperature effects on chemo-, regio- and stereoselectivity have been investigated in a wide variety of photochemical reactions.[2] We also examined the temperature effects on the photoreaction of **1a–1c**. In all the cases examined, the **2**/**3** ratios increased with decreasing temperature (Table 2). Somewhat unexpectedly, the temperature effect on **2**/**3** ratio was appreciably smaller for hexyl derivative **1c** than for methyl derivative **1b**, possibly due to the greater freedoms of **1c** that make the folded structure less favorable.



Scheme 2 Mechanism for photoreaction of 4-aryl-1,1-dicyanobutenes.

The product ratios obtained in the variable-temperature photoreactions of **1b** at both 254 and 280 nm (Fig. 5a) were subjected to the Eyring analysis. Thus, the ln (**2b**/**3b**) values were plotted against the reciprocal temperature to afford a good straight line in each case, indicating that the product selectivity is determined in a single step (at least in the temperature range examined). The differential activation enthalpy ($\Delta\Delta H^{\ddagger}$) and entropy ($T\Delta\Delta S^{\ddagger}$; T = 293 K) were calculated from the slope and intercept of the plot as –8.0 and –5.2 kJ mol^{-1} for the local excitation at 254 nm and –9.5 and –2.5 kJ mol^{-1} for the C–T excitation at 280 nm, respectively, indicating that the enthalpic factors are more favorable for cyclization in both excitation modes. We presume that the ground-state equilibrium (K), rather than that in the excited state, plays the critical roles in determining the product ratio and it temperature dependence, although the other possibilities cannot be rigorously ruled out and remain to be elucidated (Scheme 2). In any case, the combined use of excitation wavelength and temperature enabled us to further enhance the product selectivity. Indeed, the **2**/**3** ratio obtained in the photoreaction of **1b** dramatically leaped from 3.0 upon local excitation (254 nm) at 20 °C up to 45 upon C–T excitation (280 nm) at –40 °C.

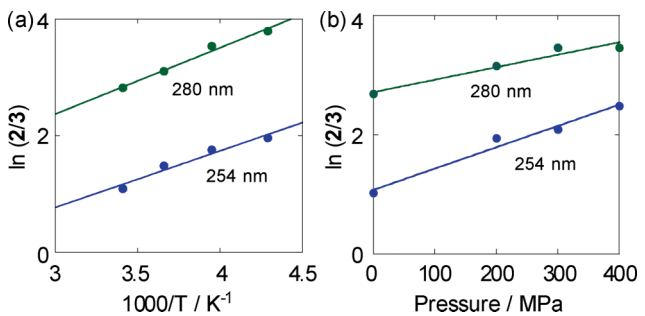


Fig. 5 (a) Temperature and (b) pressure dependence of the **2b**/**3b** ratio obtained upon irradiation of **1b** in acetonitrile at 254 (blue) and 280 nm (green).

(f) Effects of pressure on the product selectivity. Although using pressure as a tool for modifying thermodynamics and kinetics of a (photo)chemical process is less common, applying static pressure is known to alter the chemo- and stereoselectivity, provided that an appreciable difference exists in activation and/or reaction volume between the relevant competing processes.[27] Indeed, the **2**/**3** ratio was considerably increased by applying pressure of up to 400 MPa to the photoreaction of **1a–1c** (Table 3). Thus, the plots of ln (**2b**/**3b**) against pressure gave good straight lines for the photoreaction of **1b** at 254 and 280 nm, as shown in Fig. 5b. From the slopes of the plots, the differential activation volumes were determined as $\Delta\Delta V^{\ddagger}_{2/3} = -8.7$ and -5.1 cm^3 mol^{-1} for 254 and 280 nm excitation, respectively. These values are at least one order of magnitude larger than those found in the intermolecular donor–acceptor system.[11] The negative differential activation volumes indicate that the transition state for **2b** is more compact than that for **3b**, which may be consistent with the smaller volume of **2b** than that of **3b** (the van der Waals volumes were calculated for **1b**, **2b**, and **3b** as 128, 125, and 128 cm^3 mol^{-1}, respectively).

(g) Photoreactions in polyethylene films. The confinement effect on photoreaction has been extensively explored. Among various supramolecular systems used for that purpose, polymer matrices are rather unique, putting a passive pressure on the substrate accommodated in polymer void, and hence frequently utilized for controlling photochemical behavior.[20] The nature of polymer, such as crystallinity and branching, affects the passive pressure and therefore the photochemical outcomes. Polyethylene films are particularly intriguing in their templating effect, as the cavity shape is preserved for a certain period of time during the course of reaction. Hence, we investigated the photoreaction of **1a–1c** in selected polyethylene films of different crystallinities (**PE0–PE74**) (Table 4). The photolysis of **1a** or **1c** in both **PE0** and **PE46** matrices afforded only the rearrangement product, probably due to the nonpolar nature of the matrices. Quite interestingly, the photoreaction of **1b** in **PE0** afforded a much larger amount of cyclization product, the **2**/**3** ratio being 0.1 and 0.7 upon local (254 nm) and C–T (280 nm) excitations, respectively. This behavior is quite a contrast to the fact that the photochemical behavior of **1b** and **1c** (*i.e.*, methyl *versus* hexyl) resembles to each other in solution phase. This may be explained by assuming that the folded (*gauche*) conformations are slightly more favored in this polymer matrix for **1b** than for **1c** (with a lengthy hexyl chain), leading to the increased formation of cyclization product. Thus, it is shown that the cavity of polyethylene film is sensitive to the shape of substrate, right matching of which is essential for controlling the product selectivity in polyethylene matrices. However, further detailed studies of the photoreaction of **1** in polymer matrices was not feasible, as the material balance was rather low in these media, accompanying formation of considerable amounts of unidentified products.

Conclusion

In this study, we investigated the photochemistry of charge-transfer 4-aryl-1,1-dicyanobutenes under a variety of conditions to demonstrate that the product selectivity, cyclization/rearrangement ratio, can be critically controlled from practically zero to over 50 by manipulating solvent polarity, temperature, pressure, and excitation wavelength.

Table 3 Effect of pressure on photoreaction of **1a–1c**[a]

Substrate	λ_{ex}/nm[b]	t/min[c]	Pressure/MPa	Conversion (%)	Yield of **2** (%)	Yield of **3** (%)	**2**/**3** ratio
1a	254	16	0.1	7	1.3	2.3	0.6
		16	400	7	2.3	1.0	2.3
	280	50	0.1	5	0.5	0.2	2.5
		50	400	6	1.6	0.2	8.0
1b	254	8	0.1	9	2.6	0.9	2.9
		8	200	9	3.1	0.4	7.8
		8	300	9	4.4	0.5	8.8
		8	400	7	4.7	0.4	12
	280	30	0.1	7	3.7	0.3	12
		30	200	7	6.3	0.3	21
		30	300	12	8.9	0.3	30
		30	400	11	8.9	0.3	30
1c	254	8	0.1	8	2.4	0.9	2.7
		8	400	8	3.9	0.5	7.9
	280	30	0.1	7	3.9	0.2	20
		30	400	10	3.6	0.1	36

[a] Irradiations were performed at 254 or 280 nm under air in a high-pressure vessel. [b] Excitation wavelength. [c] Irradiation time.

Table 4 Photoreaction of **1a–1c** in polyethylene films[a]

Substrate	Media	λ_{ex}/nm[b]	Conversion (%)	Yield of **2** (%)	Yield of **3** (%)	**2**/**3** ratio
1a	**PE0**	254	61	< 0.1	9.8	< 0.01
		280	52	< 0.1	35.7	< 0.01
	PE46	254	28	< 0.1	19.2	< 0.01
		280	64	< 0.1	13.0	< 0.01
1b	**PE0**	254	61	1.6	11.6	0.1
		280	74	7.3	10.3	0.7
	PE46	254	70	< 0.1	4.4	< 0.01
		280	62	< 0.1	12.1	< 0.01
	PE50	254	20	< 0.1	18.0	< 0.01
		280	18	< 0.1	18.0	< 0.01
	PE68	254	63	< 0.1	2.0	< 0.01
		280	80	< 0.1	11.2	< 0.01
	PE74	254	52	< 0.1	14.7	< 0.01
		280	71	< 0.1	21.2	< 0.01
1c	**PE0**	254	23	< 0.1	13.1	< 0.01
		280	56	< 0.1	26.2	< 0.01
	PE46	254	77	< 0.1	9.3	< 0.01
		280	86	< 0.1	11.7	< 0.01

[a] Irradiation of **1a–1c** was performed in polyethylene films at 254 (2 h) or 280 nm (4 h) and at ambient temperature (23–25 °C). Numbers in the acronyms are the % crystallinities from X-ray diffraction measurement. For details of polyethylene films, see ref. 20. [b] Excitation wavelength.

The cyclization was favored in polar solvents at lower temperatures and upon selective C–T excitation at longer wavelengths. Mechanistically, the cyclization involves the initial electron transfer from the donor to acceptor moiety and the subsequent combination of the resulting radical ion pair in the folded (*gauche*) conformation to give a zwitterion, which eventually leads to the product. Such a process is accelerated in polar solvents as the electron transfer becomes energetically more feasible. The folded conformers with stronger C–T character absorb at longer wavelengths and can be selectively excited, and the subsequent cyclization reaction is much faster than the relaxation in the excited state. Changing the temperature should shift the equilibrium in both ground and excited states. However, the linear relationships found upon the Eyring treatment of the data obtained at 254 and 280 nm revealed that the ground-state equilibrium plays a major role in determining the product selectivities. The static and passive pressures can also be used as independent environmental variants for altering the product selectivity. It is more important that the cyclization/rearrangement ratio strongly depends on the magnitude of C–T interaction and its logarithmic value is proportional to the C–T excitation energy. Thus, the quantitative adjustment of C–T interaction can be used as an additional tool for precisely controlling the photochemical outcomes in donor–acceptor systems. The combined use of multiple controlling factors, such as solvent, temperature, pressure, wavelength, and C–T strength, is a convenient, effective method to improve the product selectivity. Accordingly, the exclusive cyclization (*cf.* the **2**/**3** ratio being >50 with 300 nm at 20 °C in acetonitrile or 45 with 280 nm at –40 °C) or rearrangement (*cf.* **2**/**3** ratio being <0.01 in polymer matrices and in most of non-polar solvents) was achieved

just by tuning the reaction conditions. This strategy is currently being applied to a wide variety of asymmetric photoreactions both in solution and in supramolecular systems, and the results will be reported in due course.

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