Synthesis of Allene Derivatives and their Photophysical Processes

Takashi Yamashita, Takuto Nishiguchi, Jun Kato, Yusa Muroya, Yosuke Katsumura,

*Department of Pure and Applied Chemistry, Faculty of Science and Technology,
Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan*

Allenes, one of the compounds with cumulative double bonds, are attracting much interests due to the characteristics of their twisted π -conjugated bonds. Several allenes were synthesized to characterize their electronic features by their ground-state absorption, transient absorption and emission spectra to be found that they increase conjugation length in the excited state due to their conformational change. Photophysical process and active species were determined by laser flash photolysis and electron beam pulse radiolysis to find that intramolecular charge transfer of an allene is induced upon electron beam irradiation.

Keywords: allene, cumulene, charge transfer, transient absorption, photophysical processes.

1. Introduction

Recently, π conjugated organic compounds have been attracting much attention as photonics materials. Stilbenes are one of the fundamental structures which are often used in photochromic reactions isomerizing between *trans* and *cis* forms upon photoirradiation. The photoisomerization rate¹⁾ is known as fast as $1.5 \times 10^{10} \text{ s}^{-1}$ which is applicable to high speed optical switching.

The π -conjugated system is also utilized as the key structure in electron conductivity, charge transfer (CT) spacer, luminescent materials²⁾, 3-D micro photo-fabrication³⁾ via two-photon absorption, and so on. Thus conjugation along co-planer π -conjugated system is important. Controlling or switching the π -conjugation is attractive phenomena because that can control opt-electronic properties described above. One of the methods perturbing the π -conjugated system is twisting the π system⁴⁾ introducing bulky substituents as the side-chain, for example.

Recently we are interested in the compounds with cumulative double bonds, because their π -electrons are twisted and they may become co-planer each other by the similar way to the chemistry of stilbenes. Changing the conformation of the cumulenes can change the π -conjugation length and so the opt-electronic properties

The twisted conformation of substituted allenes

may be the chiral axis,^{5,6)} which means that allenes are potential materials for photo-induced asymmetric control.⁷⁾ Allenes have been used as the materials for cyclization via Diels-Alder reactions, meaning that the cumulative double bonds are very reactive, which can apply for the synthesis of allotrope, carbene⁸⁾, the next generation compounds of fullerenes or carbon nanotubes.

Optical properties of cumulenes are not sufficiently known up to now, so we prepared three substituted allens (Scheme 1) to investigate the spectral properties using laser flash photolysis, and electron beam pulse radiolysis.

Scheme 1 Allene derivatives

2. Experimental

2.1 Materials

Phenylacetylene and 4-cyanobenzaldehyde were purchased from Sigma-Aldrich Co., and were used without purification. Benzaldehyde was purchased

from Wako Pure Chemical Industries, Ltd., and was washed by sodium carbonate aqueous solution, dried over sodium sulphate, distilled in vacuo (87°C, 40mmHg) and stored under Ar atmosphere. 4-Methoxy-benzaldehyde was purchased from Wako Pure Chemical Industries, Ltd., and was washed with sodium carbonate aqueous solution, dried over sodium sulphate, distilled in vacuo (96°C, 5mmHg) and stored under Ar atmosphere. Triethylsilane, boron-trifluoride-ethylether complex and *n*-butyllithium (hexane solution, 1.6M) were purchased from Wako Pure Chemical Industries, Ltd., and were used without purification. Tetra-*n*-hexylammonium bromide was purchased from Tokyo Kasei Kogyo Co. Ltd., and was used without purification. Benzene, THF and diethyl ether were purchased from Wako Pure Chemical Industries, Ltd., and were dried over calcium chloride and then sodium wire, distilled and stored over sodium wire. Acetonitrile and methylenechloride were purchased from Wako Pure Chemical Industries, Ltd., and were dried over calcium chloride and then calcium hydride, distilled and stored over molecular sieves 3A.

2.2. Measurements

¹H-NMR spectra were obtained using a JEOL JNM-ECP500 NMR system. Infrared spectra were recorded on a JASCO FT/IR-410 spectrometer. UV-vis spectra were recorded on a JASCO UV-560 spectrophotometer. Emission and excitation spectra were measured with a JASCO FL-6200 spectrophotometer.

2.3 Synthesis of allene derivatives

General procedures

Allene derivatives were synthesized following to

Scheme 2. ⁹⁻¹¹⁾

A 300ml three-necked round-bottom flask was charged with 80ml of dry diethyl ether and

11ml(0.12mol) of phenylacetylene under Ar atmosphere and added 63ml(0.10mol) of *n*-butyllithium (hexane solution, 1.6M) at -78°C using an acetone-dry ice bath. After stirring for 10 minutes, the solution was allowed to warm to 0°C using an ice bath. After 15min., a solution of 11.6g (0.11mol) of benzaldehyde in diethyl ether (8ml) was slowly added at 0°C using a dropping funnel. After stirring for 2 hours, the solution was quenched with a saturated ammonium chloride aqueous solution. The organic layer was extracted 5 times with diethyl ether, which was dried over magnesium sulphate. After filtration and evaporation of the solvent the raw product was distilled in vacuo (130°C, 1mmHg), to give propargyl alcohol **1a** yield 15.5g, 75%. A 300ml, three-necked round-bottom flask was charged with 50ml of dry Acetonitrile, 8.03g(0.039mol) of **1a** and 20ml(0.13mol) of triethylsilane under N₂ atmosphere and added 10ml (0.079mol) of borontrifluoride-ethylether complex solution at -78°C using an ice bath. After stirring for 15 minutes, the solution was quenched with a saturated potassium carbonate aqueous solution. The solution was extracted 5 times with diethyl ether, and the organic layer was dried over magnesium sulphate. After filtration, and evaporation of the solvent the raw product was purified by flash column chromatography (CH₂Cl₂:Hexane=1:5) to give **2a**: yield 6.09g, 82%. A 100ml round-bottom flask was charged with 15ml of toluene, 2.01g (10.4mmol) of **2a** and 0.45g (1.04mmol) of THAB, and added 0.59g (10.5mmol) of potassium hydroxide at room temperature. After stirring for 2 hours, the solution was quenched with water. The organic layer was extracted 5 times with toluene, which was dried over sodium sulphate. After filtration and evaporation of the solvent, the raw product was purified by flash column chromatography (CH₂Cl₂:Hexane=1:5) to give allene **3a**: yield 1.56g, 78%.

1,3-Diphenylprop-2-yne-1-ol (**1a**)

¹H-NMR(500MHz, CDCl₃): δ 2.31(s, 1H, OH), 5.70(s, 1H, CH), 7.29-7.35(m, 4H, ArH), 7.38-7.41(d, *J*=7.00, 2H, ArH), 7.46-7.47(m, 2H, ArH), 7.60-7.62(d, *J*=7.00, 2H, ArH). ¹³C-NMR(500MHz, CDCl₃): δ 65.1, 86.6, 88.7, 122.4, 126.7, 128.3, 128.4, 128.5, 128.6, 131.7, 140.6. Yellow oil: yield 75%.

1-Phenyl-3-(*p*-methoxyphenyl)prop-2-yne-1-ol (**1b**)

¹H-NMR(500MHz, CDCl₃): δ 2.27(d, *J*=6.00Hz, 1H, OH), 3.82(s, 1H, OCH₃), 5.64(d, *J*=6.00Hz, 1H, CH), 6.93(d, *J*=8.50Hz, 2H, ArH), 7.31-7.33(m, 3H, ArH), 7.46-7.48(m, 2H, ArH), 7.54(d, *J*=8.50Hz, 2H, ArH). ¹³C-NMR(500MHz, CDCl₃): δ 55.4, 64.8, 86.5, 88.9, 114.0, 122.5, 128.2, 128.3, 131.8, 133.0, 159.8, 190.9. White powder: yield 75%.

1-Phenyl-3-(*p*-cyanophenyl)prop-2-yne-1-ol (**1c**)

$^1\text{H-NMR}$ (500MHz, CDCl_3): δ 2.70(s, 1H, OH), 5.74(s, 1H, CH), 7.30-7.37(m, 3H, ArH), 7.44-7.46(m, 2H, ArH), 7.67(d, $J=9.00\text{Hz}$, 2H, ArH), 7.72(d, $J=9.00\text{Hz}$, 2H, ArH). $^{13}\text{C-NMR}$ (500MHz, CDCl_3): δ 64.2, 87.5, 112.0, 118.7, 121.8, 127.3, 128.4, 129.0, 131.8, 132.5, 145.6. Yellow powder: yield 74%.

1,3-Diphenylprop-1-yne (2a)

$^1\text{H-NMR}$ (500MHz, CDCl_3): δ 3.84(s, 2H, CH_2), 7.27-7.30(m, 4H, ArH), 7.34(t, $J=8.00\text{Hz}$, 2H, ArH), 7.41-7.46(m, 4H, ArH). $^{13}\text{C-NMR}$ (500MHz, CDCl_3): δ 82.7, 87.5, 119.4, 123.7, 126.6, 127.8, 128.0, 128.2, 128.6, 131.7, 136.8. Yellow oil: yield 82%.

1-Phenyl-3-(*p*-methoxyphenyl)prop-1-yne (2b)

$^1\text{H-NMR}$ (500MHz, CDCl_3): δ 3.77(s, 2H, CH_2), 3.80(s, 3H, OCH_3), 6.88(d, $J=9.00\text{Hz}$, 2H, ArH), 7.28-7.36(m, 5H, ArH), 7.43-7.44(m, 2H, ArH). $^{13}\text{C-NMR}$ (500MHz, CDCl_3): δ 24.9, 55.3, 82.4, 88.0, 114.0, 123.7, 127.7, 128.2, 128.8, 128.9, 131.6, 158.4. Yellow oil: yield 85%.

1-Phenyl-3-(*p*-cyanophenyl)prop-1-yne (2c)

$^1\text{H-NMR}$ (500MHz, CDCl_3): δ 3.89(s, 1H, CH_2), 7.31-7.33(m, 3H, ArH), 7.44-7.46(m, 2H, ArH), 7.53(d, $J=8.00\text{Hz}$, 2H, ArH), 7.63(d, $J=8.00\text{Hz}$, 2H, ArH). $^{13}\text{C-NMR}$ (500MHz, CDCl_3): δ 25.9, 83.7, 85.5, 110.7, 118.8, 123.0, 128.2, 128.3, 128.7, 131.6, 132.3, 142.3. Yellow oil: yield 64%.

1,3-Diphenylallene (3a)

$^1\text{H-NMR}$ (500MHz, CDCl_3): δ 6.59(s, 2H, CH), 7.22(t, $J=7.25\text{Hz}$, 2H, ArH), 7.30-7.36(m, 8H, ArH). $^{13}\text{C-NMR}$ (500MHz, CDCl_3): δ 98.41, 126.99, 127.30, 128.72, 133.61, 207.79. IR(NaCl, cm^{-1}): 1935($\text{C}=\text{C}=\text{C}$), 3025, 3060, 3079(Ar C-H). FAB MS : m/z 192(M^+). Yellow oil: yield 78%.

1-Phenyl-3-(*p*-methoxyphenyl)allene (3b)

$^1\text{H-NMR}$ (500MHz, CDCl_3): δ 3.79(s, 3H, OCH_3), 6.57(s, 2H, CH), 6.85(d, 2H, $J=14\text{Hz}$, ArH), 7.28-7.35(m, 7H, ArH). $^{13}\text{C-NMR}$ (500MHz, CDCl_3): δ 55.7, 98.3, 114.7, 126.2, 127.4, 127.6, 128.5, 128.7, 129.1, 134.4, 159.5, 207.6. IR (NaCl, cm^{-1}): 1032($\text{C}-\text{O}-\text{C}$), 1935($\text{C}=\text{C}=\text{C}$), 2835, 2931(Ar C-H), 3001, 3028, 3060(Ar C-H). FAB MS : m/z 222(M^+). Yellow oil: yield 72%.

1-Phenyl-3-(*p*-cyanophenyl)allene (3c)

$^1\text{H-NMR}$ (500MHz, CDCl_3): δ 6.60(d, 1H, $J=6.4\text{Hz}$, CH), 6.68(d, 1H, $J=6.4\text{Hz}$, CH), 7.27(t, 1H, $J=4.3\text{Hz}$, ArH), 7.33-7.34(m, 4H, ArH), 7.42(d, 2H, $J=8.1\text{Hz}$, ArH), 7.59(d, 2H, $J=8.1\text{Hz}$, ArH). $^{13}\text{C-NMR}$ (500MHz, CDCl_3): δ 97.7, 99.3, 110.5, 118.9, 127.1, 127.4, 127.9, 128.3, 128.9, 132.5, 138.8, 209.2. IR(NaCl, cm^{-1}): 1936($\text{C}=\text{C}=\text{C}$), 2227($\text{C}-\text{N}$), 3032, 3062, 3084(Ar C-H). EI MS : m/z 217(M^+). Yellow oil: yield 66%.

2.4 Electron beam pulse radiolysis

Transient absorption spectra of the samples during pulsed electron beam irradiation were measured by using a linear accelerator (LINAC, acceleration energy of 35MeV, pulse duration of 10ns) as beam source, a pulsed Xe lamp as monitor light, and a PIN photodiode (Hamamatsu Photonics, 1722-01) as a detector. Transient absorption was recorded on a transient digitizer (Tektronics, SCD-1000). The sample solutions were prepared in 2-cm fused silica cells, and they were degassed by argon bubbling before the measurements.

2.5 Laser flash photolysis

Sample solutions were excited by the forth harmonics (266nm) of Nd:YAG laser (HOYA continuum, 10Hz, 5ns), monitored with the light of a Xe-lamp (HAMAMAYSU, CW Xe arc lamp) through a filter Y-25 which cut the light below 250nm off. The monitoring light through the cut filter was monochromated and detected with a photomultiplier, whose output signal was recorded on a digitizing oscilloscope (SONY Tektronix TDS 3012). All sample solutions were degassed by freeze-pump-thaw cycles for 10 times and sealed in 1-cm quartz cells.

3. Results and Discussion

3.1 The absorption and emission spectra of allenes

Absorption and emission spectra were measured to compare the ground state conjugation between stilbene and allene **3a**. Fig.1 shows the absorption spectra of stilbene and **3a** in CH_2Cl_2 solution, and Fig.2 shows their emission spectra in CH_2Cl_2 . Absorption of **3a** blue shifts much compared to that of stilbene, shown in

Fig. 1 Absorption spectra of **3a** and stilbene in CH_2Cl_2

Fig. 2 Emission spectra of **3a** and stilbene in CH_2Cl_2

Fig.1, due to the existence of π -conjugation in stilbene in the ground state. The weaker emission intensity of **3a** is possibly due to fast conformational change in the photoexcited state of **3a**.

In order to compare the substituent effect on the absorption and emission of allenes, absorption and emission spectra of allenes (**3a**, **3b**, **3c**) in CH_2Cl_2 were measured, shown in Fig.3 and Fig.4, respectively. The absorption of those with substituent shifts to the longer wavelength region compared to that without substituents due to the existence of intramolecular charge transfer induced by the substituents. Large Stokes shift is observed for **3c** in Fig.4, which is thought to be due to large conformational change in the photoexcited state, which make the π -system coplanar to increase both in conjugation and charge transfer from the electron donating group to the electron accepting group at the end of the phenyl groups. Thus, stilbenes become twisted in the photoexcited state to decrease the π -conjugated system of ground state, while the twisted state of allenes does increase the π -conjugated system.

3.2 The photophysical processes of an allene **3a**

Transient absorption spectra in several solvents during electron beam pulse radiolysis were measured to investigate photophysical processes of allenes (**3a**, **3b**, **3c**). Measuring transient absorption during electron beam irradiation is a powerful tool to determine the active species, because these methods can selectively generate radical cations, radical anions or electronically excited species. For example, electronically excited state of benzene is produced after ionization upon

Fig. 3 Absorption spectra of **3a**, **3b** and **3c** in CH_2Cl_2

Fig. 4 Emission spectra of **3a**, **3b** and **3c** in CH_2Cl_2

electron beam irradiation in benzene solution and consequent fast geminate ion recombination, which transfer the excited energy to produce an electronic excited state of substrate. In CH_2Cl_2 solution, radical cation of the dichloromethane is produced upon electron beam irradiation, followed by the electron transfer from substrate to the cation make a radical cation of the substrate. In THF solution, rubbed electron is solvated by THF to generate solvated electrons, which are transferred to substrate to generate radical anion of substrate.

Fig.5 shows the transient absorption spectra of 12mM **3a** in benzene solution, and 1.2mM **3a** solution in the presence of O_2 or triethylamine (TEA) as quenchers. Two absorption bands are observed at 400nm and 580nm in benzene solution. The absorption at 580nm is quenched by addition of TEA, while the absorption at 400nm is quenched by addition of oxygen.

Fig.6 shows the transient absorption of **3a** in CH_2Cl_2 solution obtained by exciting at 266nm. Weak absorption is observed at 400nm, which can be assigned as the T-T absorption of **3a**. Thus, the absorption at 400nm observed in Fig.5 can be assigned as the electronically excited state, and the absorption at 580nm as radical cation of **3a**. Generation of the electronically excited state of **3a** even in CH_2Cl_2 solution by the electron beam pulse radiolysis is thought due to the electron accepting characteristics of **3a**.

Fig. 5 Transient absorption spectra of **3a** in benzene solution without quencher, with O_2 and with TEA during electron beams pulse radiolysis acceleration energy of 35MeV.

Fig. 6 Transient absorption spectra of **3a** in CH_2Cl_2 solution. Excited wavelength was 266nm.

Fig.7 (a) shows decays of **3a** in benzene solution at 420nm, and Fig.7 (b) shows the decays of **3a** at 580nm pumped with pulsed electrons from a linear accelerator. Addition of oxygen to **3a** decrease the lifetime of decaying component at 420nm from $0.98\mu\text{s}$ to $0.054\mu\text{s}$, while it increase the lifetime at 580nm does from $1.9\mu\text{s}$ to $8.1\mu\text{s}$. On the other hand, addition of TEA to **3a** decrease the lifetime of the decay both at 420nm (from $0.98\mu\text{s}$ to $0.14\mu\text{s}$) and at 580nm (from $1.9\mu\text{s}$ to $0.03\mu\text{s}$). This observation supports the assignment of the transient absorption of **3a** as described above.

Fig.8 shows the transient absorption spectra of 12mM **3a** in CH_2Cl_2 solution, and 1.2mM **3a** solution in CH_2Cl_2 in the presence of quenchers pumped with pulsed electrons from a linear accelerator. The

Fig. 7 Decays of transient absorption of **3a** in benzene solution at (a)420nm and (b)580nm without quencher, with O_2 and with TEA during electron beams pulse radiolysis acceleration energy of 35MeV.

Fig. 8 Transient absorption spectra of **3a** in CH_2Cl_2 solution without quencher, with O_2 and with TEA during electron beams pulse radiolysis acceleration energy of 35MeV.

absorption of the radical cation of **3a** is clearly seen at

Fig. 9 Decays of transient absorption of **3a** in CH_2Cl_2 solution at 580nm without quencher, with O_2 and with TEA during electron beams pulse radiolysis acceleration energy of 35MeV.

580nm, which is quenched by the addition of TEA, while which is not quenched with oxygen.

Fig.9 shows the decays of **3a** in CH_2Cl_2 solution at 580nm. Addition of oxygen increases the lifetime from $1.5\mu\text{s}$ to $2.9\mu\text{s}$, while addition of TEA decreases it from $1.5\mu\text{s}$ to $0.03\mu\text{s}$, showing the formation of radical cation of **3a**.

Fig.10 shows the transient absorption spectra of 12mM **3a** in THF solution, and that of 1.2mM solution in the presence of quenchers pumped with pulsed electrons from a linear accelerator. Absorptions are observed at 580nm both with or without quenchers (oxygen and TEA) observed, and really observed at 580nm. Addition of oxygen decreases the lifetime of

Fig. 10 Transient absorption spectra of **3a** in THF solution without quencher, with O_2 and with TEA during electron beams pulse radiolysis acceleration energy of 35MeV.

Fig. 11 Decays of transient absorption of **3a** in THF solution at 580nm without quencher, with O_2 and with TEA during electron beams pulse radiolysis acceleration energy of 35MeV.

the absorption at 580nm (from $0.09\ \mu\text{s}$ to $0\ \mu\text{s}$), while addition of TEA increases (from $0.09\ \mu\text{s}$ to $0.3\ \mu\text{s}$), showing that the absorption at 580nm observed for **3a** in THF can be assigned to the radical anion of **3a**.

Thus both radical anion and radical cation of **3a** have the same transient absorption at 580nm, while T-T absorption is at 400nm.

3.3 Substituent Effect on the Photophysical processes of Allenes

Fig.12 shows the transient absorption spectra of 12mM **3b**, which has a methoxy group at one phenyl ring of **3a**, in benzene solution pumped with pulsed electrons from a linear accelerator, and those of 1.2mM **3b** in the presence of quenchers. Two absorption bands are observed at 450nm and 650nm, whose absorption at 450nm can be assigned as T-T absorption of **3b** by the laser flash photolysis experiment in Fig.13, in which triplet state absorption is also observed at 450nm.

Fig.14 shows the transient absorption spectra of 12mM **3b** in CH_2Cl_2 or THF solutions pumped with pulsed electrons from a linear accelerator. Absorption of radical anion of **3b** is observed in THF at 580nm, and radical cation of **3b** in CH_2Cl_2 is observed at 640nm. Based on the assignment in Fig. 14, the absorption at 640nm, which is observed in benzene solution in Fig. 12, can be also assigned to the absorption of radical cation of **3b**.

Fig.15 shows the transient absorption spectra of 12mM **3c** in benzene solution pumped with pulsed

Fig. 12 Transient absorption spectra of **3b** in benzene solution during electron beams pulse radiolysis acceleration energy of 35MeV.

Fig. 13 Transient absorption spectra of **3b** in CH_2Cl_2 solution. Excited wavelength was 266nm.

Fig. 14 Transient absorption spectra of **3b** in CH_2Cl_2 solution and in THF solution during electron beams pulse radiolysis acceleration energy of 35MeV.

electrons from a linear accelerator, and Fig.16 is the transient absorption of **3c** obtained by the laser flash photolysis pumped at 266nm. The absorption at 380nm is observed both in the electron pulse radiolysis and in the laser flash photolysis, showing that the absorption can be assigned to T-T absorption. and that the absorption at 600nm is either radical cation or radical an.

Fig.17 shows the transient absorption of **3c** in THF solution pumped by pulsed electrons, showing that the absorption of radical cation of **3c** is observed at 580nm.

Fig.18 shows the transient absorption spectra of 12mM **3c** in THF solution. Two absorption bands are observed at 600nm and 640nm. The absorption at 600nm decays fast within $2.5\ \mu\text{s}$ and the absorption at

Fig. 15 Transient absorption spectra of **3c** in benzene solution during electron beams pulse radiolysis acceleration energy of 35MeV.

Fig. 16 Transient absorption spectra of **3c** in CH_2Cl_2 solution. Excited wavelength was 266nm.

Fig. 17 Transient absorption spectra of **3c** in CH_2Cl_2 solution during electron beams pulse radiolysis acceleration energy of 35MeV.

640nm remains even after 5 μs . In order to confirm the active species, transient absorption of **3c** was measured in the presence of TEA (Fig.19). In the presence of TEA, absorption at 640nm built up after electron beam pulse radiolysis, while the absorption at 600nm was not quenched so much. These results show that the absorption at 640nm can be assigned to radical anion of **3c**, which had been assigned in Fig. 17. The absorption at 600nm seems similar with the absorption of radical cation of **3c** in Fig.17, however, the absorption at 600nm observed in THF solution is not same as the radical cation. Fig. 20 (b) shows decays of **3c** in THF solution at 640nm. It is

Fig.20 (a) shows decays of the transient absorption of **3c** in THF solution at 600nm during electron beam pulse radiolysis, that addition of TEA increases the formation of **r** and Fig. 20(b) easily seen radical anion of **3c** in Fig. 20 (b), whose lifetime also increased from

Fig. 18 Transient absorption spectra of **3c** in THF solution during electron beams pulse radiolysis acceleration energy of 35MeV.

Fig. 19 Transient absorption spectra of **3c** in THF solution with TEA during electron beams pulse radiolysis acceleration energy of 35MeV.

Fig. 20 Decays of transient absorption of **3c** in THF solution at (a)600nm and (b)640nm without quencher and with TEA during electron beams pulse radiolysis acceleration energy of 35MeV.

2.5 μs to 4.3 μs . On the other hand, addition of TEA does to quench the decay of the absorption at 600nm, meaning that the absorption is neither radical cation nor electronically excited state. We assigned the absorption as the intramolecular charge transfer state of (ICT) **3c**. The ICT state should be a mixed state of radical cation and radical anion, but the electronically neutral intermediate. And so the ICT state is not thought to be quenched by the TEA, while the **3c** has larger Stokes shift compared to the other allenes.

4. Conclusion

Three allenes (**3a**, **3b**, **3c**) were synthesized, and their absorption, emission, transient absorption were compared with stilbene to find the conjugation length has changed upon photoirradiation due to conformational change. Influences of substituent effect were also found. Especially allenes with cyano group if found to form intramolecular charge transfer state upon electron beam irradiation in THF solution. These materials are one of potential and powerful photofunctional unit for opto-electronic control of next generation technology.

Acknowledgment

The authors are grateful to Assistant Professor Shigeru Arai of Graduate school of pharmaceutical Sciences, Chiba University for his kind advice on our synthesizing allene derivatives.

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