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Novel chiral norbornadiene–quadricyclane systems: substituent effect on chiroptical properties and stereochemical consequence of photochemical interconversion

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Abstract

For efficient absolute asymmetric synthesis (AAS) by circularly polarized light (CPL), a series of 3-substituted 2-methoxycarbonylnorbornadiene (**N**) and -quadricyclane (**Q**) derivatives (R = H, Me, Ph, 4-biphenylyl, 1- and 2-naphthyl) were prepared and optically resolved, and the chiroptical properties of the enantiomeric pairs were determined in hexane and acetonitrile. All of the **N** and **Q** derivatives gave moderate to large circular dichroism intensities ($\Delta\varepsilon$) and specific rotations ($[\alpha]_D$). In particular, aromatic **N**s (R = 4-biphenylyl and 2-naphthyl) gave high $[\alpha]_D$ values of 216° and 206°, while non-aromatic **Q**s (R = H and Me) afforded high $[\alpha]_D$'s of 322° and 271°. Depending on the nature of the substituent introduced at the 3-position, the maximum anisotropy factor ($g = \Delta\varepsilon/\varepsilon$) varied over a wide range from 0.0141 (R = H) to 0.0022 (R = 1-naphthyl) in the **N** series and from 0.0091 (R = Me) to 0.0012 for (R = 2-naphthyl) in the **Q** series. Thus, non-aromatic **N**/**Q** pair is absolutely advantageous for the CPL-induced AAS reactions. The relatively high g_{max} values observed for non-aromatic **N**s and **Q**s may be rationalized by the contribution of the n, π^* transition of the ester chromophore to the **N** and **Q** chromophores. Stereochemical consequence of the photochemical interconversion of the chiral **N** and **Q** was also revealed; all of the (−)-**N**s examined photoisomerized to the corresponding (+)-**Q**s without any side reactions.

Keywords: Chiroptical property; Anisotropy factor; Circular dichroism; Specific rotation; Absolute asymmetric synthesis; Norbornadiene; Quadricyclane

1. Introduction

Not requiring any chiral reagent or catalyst, absolute asymmetric synthesis (AAS) is a unique photoprocess to produce optically active compounds through the preferential excitation of one over another enantiomer by circularly polarized light (CPL). The efficiency of AAS is determined exclusively by the anisotropy, or g factor, which was first defined by Kuhn and coworkers [1–7] as the relative difference of molar extinction coefficients of an optically pure compound (enantiomer) toward l- and r-CPL at a given wavelength:

$$g = \frac{\varepsilon_l - \varepsilon_r}{\varepsilon} = \frac{\Delta\varepsilon}{\varepsilon}$$

where ε represents the conventional molar extinction coefficient for unpolarized light and $\Delta\varepsilon$ the circular dichroism; $\varepsilon = \frac{1}{2}(\varepsilon_l + \varepsilon_r)$ and $0 \leq |g| < 2$.

For more than 70 years since Kuhn's work [1], practically only three types of AAS have been known to exist, i.e., (a) asymmetric photodestruction, (b) photochemical deracemization, and (c) photochemical asymmetric fixation [3–5]. Recently, we have proposed a new category of absolute asymmetric synthesis (NAAS) [8–10], in which both the reactant and product are chiral and photochemically interconvertible, but thermally each enantiomer never interconverts or racemizes at ambient temperature (Scheme 1). It differs from the photochemical deracemization which never produces the chiral product. It has been revealed also that, in NAAS, even the simultaneous enantiomeric enrichment in both reactant and product can be accomplished by CPL irradiation, provided that the sign of the product g factor is opposite to that of the reactant at the irradiation wavelength and the product/reactant ratio at the photostationary state is below unity. Thus, the chiroptical properties of the relevant reactant and product play the central role in NAAS. In the first experimental verification of NAAS [8–10], we employed the photochemically reversible, chiral norbornadiene (**N**)–quadricyclane (**Q**) system, i.e.,

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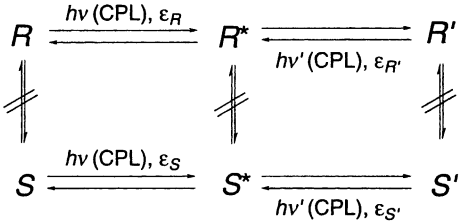
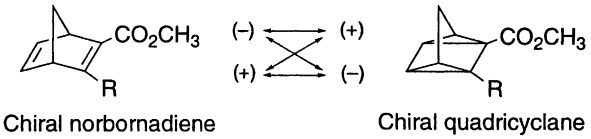


Scheme 1. Basic concept of reversible absolute asymmetric synthesis (NAAS), where both the reactant and product are chiral.

methyl bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**1a**) and methyl tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1-carboxylate (**1b**), but their chiroptical properties had not been reported at that time. Similarly, the chiroptical properties of other chiral **N** and **Q** derivatives have not been elucidated so far except for a few compounds [8,11,12], although they are essential for the evaluation of the NAAS process.

The NAAS may be extended in general to the other photocyclization/reversion reactions of chiral substrates. However, the chiroptical properties of the relevant compounds are rarely reported and the photoreactions do not necessarily proceed in high quantum and/or chemical yields [11,12]. In the **N**–**Q** system, **Q** is readily prepared by the intramolecular [2 + 2] photocycloaddition of **N**, which are recovered in turn by photolysis or thermolysis of the resulting **Q** [13–19]. The photochemical interconversion between **N** and **Q** is one of the most clean, efficient and durable NAAS systems, which affords good to excellent quantum yields (ca. 0.1–1.0) [20–22] without accompanying any side reactions and possesses a sufficient thermal stability at ambient temperature [21]. In this context, the extended survey of the chiroptical properties of substituted **N**–**Q** systems, as well as their photochemical and stereochemical behavior, are essential for further understanding and development of the NAAS.

In the present study, we first examine the chiroptical properties of a series of 3-alkyl- or 3-aryl-2-methoxycarbonylnorbornadiene (**1a**–**6a**) and -quadricyclane (**1b**–**6b**) derivatives (R = H, Me, Ph, 4-biphenylyl, 1- and 2-naphthyl), shown



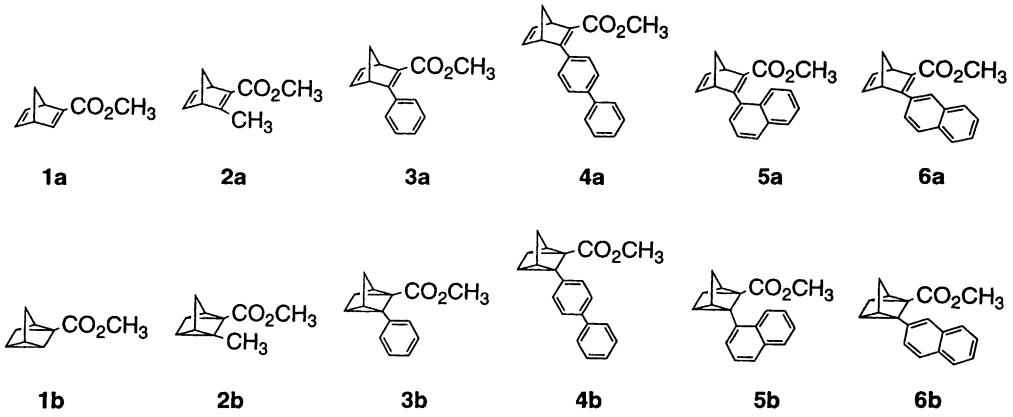
Scheme 3. Possible stereochemical routes of photochemical interconversion between chiral norbornadiene and quadricyclane.

in Scheme 2. The stereochemical consequence of the photochemical interconversion (Scheme 3) are also elucidated from the circular dichroism (CD) spectral changes during the photointerconversion. Based on these experimental results, we will discuss possible strategies for obtaining a chiral **N**–**Q** system with a large *g* factor and optimizing the efficiency of the NAAS system.

2. Experimental

2.1. General procedures

^{1}H and ^{13}C NMR spectra were recorded in chloroform-*d* at room temperature on a JEOL EX-400 instrument at 400 and 100 MHz, respectively. All chemical shifts (δ) are reported in ppm from a TMS internal standard (0.00 ppm) and coupling constants (*J*) values are reported in Hz. Mass spectra were obtained on a JEOL JMS-DX303 mass spectrometer using FAB ionization (Xe atoms, energy 6 keV, accelerating voltage 3 kV) in NBA matrix and the EI ionization (energy 70 eV, 300 μA, accelerating voltage 3 kV), IR spectra were recorded on JEOL JIR-6500 or JASCO FT/IR-230 spectrometer. UV and CD spectra were recorded on JASCO V-560 and J-720WI spectrometer, respectively. Optical rotations were determined at the wavelength (589.3 nm) of the D-line of a sodium resonance lamp with a Perkin Elmer 341 polarimeter. The reported molar CD intensities ($\Delta\varepsilon$) and specific rotations ($[\alpha]_D^{20}$) were corrected for the enantiomeric excess (ee) of the isolated enantiomers determined by chiral HPLC analysis.



Scheme 2. Chiral norbornadienes (**1a**–**6a**) and quadricyclanes (**1b**–**6b**) employed in this study.

2.2. Materials

Hexane (Merck spectrograde) and acetonitrile (Merck spectrograde) used as solvents were used without further purification. Norbornadiene, methyl acrylate, and methyl cyclopropanecarboxylate were distilled prior to use.

2.2.1. Synthesis of methyl bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**1a**)

1a was prepared according to the procedure reported in a previous paper [8]: ^{1}H NMR ($CDCl_3$) δ: 7.65 (d, 1H, J = 2.9), 6.91 (dd, 1H, J = 4.4, 3.4), 6.73 (dd, 1H, J = 4.4, 3.4), 3.90 (bs, 1H), 3.73 (s, 3H), 3.71 (bs, 1H), 2.15 (d, 1H, J = 6.4), 2.12 (d, 1H, J = 6.4). Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.96; H, 6.72.

2.2.2. Synthesis of methyl 3-methylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**2a**)

Diels-Alder reaction of cyclopentadiene (1.90 g, 0.029 mol) and tertrolic acid methyl ester (2.80 g, 0.029 mol) in 50 ml of dry benzene was performed at 160 °C for 18 h in a stainless steel autoclave. Purification of the resultant mixture by column chromatography (toluene eluent) on silica gel, followed by distillation under a reduced pressure, gave **2a** (3.15 g, 0.019 mol) in 66.1% yield: b.p. 52.0–53.5 °C/2 Torr; ^{1}H NMR ($CDCl_3$) δ: 6.89 (dd, 1H, J = 3.9, 2.9), 6.73 (dd, 1H, J = 3.9, 2.9), 3.88 (bs, 1H), 3.71 (s, 3H), 3.40 (bs, 1H), 2.22 (s, 3H), 2.05 (d, 1H, J = 6.4), 1.96 (d, 1H, J = 6.4); ^{13}C NMR ($CDCl_3$) δ: 170.0, 166.2, 144.0, 140.3, 138.1, 71.0, 58.1, 51.1, 51.0, 17.3; IR (NaCl) ν: 2976, 2947, 1707, 1630, 1435, 1340, 1318, 1296, 1238, 1194, 7112 cm^{-1}; FAB-MS (*m*-nitrobenzyl alcohol) *m/z* 165 (M^+), 149, 133, 105; UV (hexane): λ_{max} (log ε) 205 (4.00), 226 (3.54), 262 nm (3.35). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.12; H, 7.44.

2.2.3. Syntheses of methyl 4-biphenylylacrylate (**4c**), 3-(1-naphthyl)propenoate (**5c**) and 2-naphthylacrylate (**6c**)

According to the procedure reported by Koo et al. [23], **5c** was synthesized. In a 1 l round-bottomed flask, fitted with a reflux condenser and a thermometer, was placed malonic acid (204.0 g, 1.96 mol), 1-naphthaldehyde (102.0 g, 0.98 mol), and 400 ml of dry pyridine. After the malonic acid was dissolved in the pyridine solution, piperidine (11 ml) was added. The mixture was heated to 80 °C, kept at that temperature for 1 h, then at 85 °C for another 1 h, and further heated to reflux for 4 h. After being cooled, the reaction mixture was poured into ice-water. The resultant mixture was acidified by concentrated hydrochloric acid until the solution became highly acidic. The white yellow powder was separated by suction filtration and washed several times with cold water. The crude product was dried under vacuum for a week. The crude powder obtained (48.4 g) was dissolved in 400 ml of dry methanol and the solution was refluxed with a catalytic amount of sulfuric acid for 8 h. After removal of the methanol by evaporation, ether was added to the residue, and the resultant solution was neutralized with aqueous sodium hydrogen carbonate and was washed several times with water. The ether extract was dried over magnesium sulfate and evaporated to leave crude product, which was then distilled in vacuo to give pure **5c**: 34.2 g (0.160 mol), yield 16%; b.p. 173–174 °C/2 Torr; ^{1}H NMR ($CDCl_3$) δ: 8.53 (d, 1H, J = 15.3), 8.18 (d, 1H, J = 8.3), 7.87 (dd, 2H, J = 8.3, 7.3), 7.74 (d, 1H, J = 7.3), 7.59–7.45 (m, 3H), 6.33 (d, 1H, J = 15.3), 3.85 (s, 3H). Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.16; H, 5.72.

4c and **6c** were prepared by similar procedures described above. **4c**: yield 92.5%; m.p. 154–154.5 °C; ^{1}H NMR ($CDCl_3$) δ: 7.74 (d, 1H, J = 16.1), 7.63 (d, 2H, J = 7.6), 7.61 (d, 2H, J = 7.6), 7.61 (d, 2H, J = 6.1), 7.46 (dd, 2H, J = 7.3, 6.1), 7.38 (tt, 1H, J = 7.3, 1.7), 6.48 (d, 1H, J = 16.1), 3.82 (s, 3H). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.45; H, 5.88 [24].

6c: yield 49%; m.p. 94–94.5 °C; ^{1}H NMR ($CDCl_3$) δ: 7.94 (s, 1H), 7.88–7.51 (m, 2H), 7.84 (d, 1H, J = 8.3), 7.67 (dd, 1H, J = 8.3, 1.5), 7.53–7.51 (m, 2H), 7.84 (d, 1H, J = 16.1), 6.56 (d, 1H, J = 16.1), 3.83 (s, 3H). Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.20; H, 5.70 [25].

2.2.4. Syntheses of methyl 3-(4-biphenylyl)-2,3-dibromopropanoate (**4d**), 3-(1-naphthyl)-2,3-dibromopropanoate (**5d**), and 3-(2-naphthyl)-2,3-dibromopropanoate (**6d**)

5d was synthesized by the procedure of Wajack et al. [26]. Bromine (8 ml) was added dropwise to **5c** (30.4 g, 0.143 mol) dissolved in 200 ml of dry carbon tetrachloride under photoirradiation by a halogen lamp (Eikosha). The excess bromine was evaporated with carbon tetrachloride from the solution and the residue was recrystallized twice from benzene (49.4 g, 92.8% yield): m.p. 125.5–126 °C; ^{1}H NMR ($CDCl_3$) δ: 7.61 (dd, 2H, J = 7.1, 5.9), 7.61 (d, 1H, J = 7.1), 7.48–7.43 (m, 3H), 7.38 (d, 1H, J = 7.1), 5.41 (d, 1H, J = 11.9), 4.89 (d, 1H, J = 11.9), 3.92 (s, 3H) [25].

4d was similarly prepared by the reaction of **4c** and bromine: yield 82.3%, m.p. 148–148.5 °C; ^{1}H NMR ($CDCl_3$) δ: 7.63–7.59 (m, 4H), 7.48–7.43 (m, 4H), 7.37 (tt, 1H, J = 5.3, 1.3), 5.41 (d, 1H, J = 11.7), 4.89 (d, 1H, J = 11.7), 3.92 (s, 3H).

6d was similarly prepared by the reaction of **6c** and bromine: yield 85%, m.p. 144–144.5 °C; ^{1}H NMR ($CDCl_3$) δ: 8.15 (s, 1H), 7.98 (d, 1H, J = 8.8), 7.95–7.93 (m, 2H), 7.76 (d, 1H, J = 8.8), 7.57 (d, 1H, J = 6.4), 7.56 (d, 1H, J = 6.4), 5.69 (d, 0.5H, J = 11.7), 5.68 (d, 0.5H, J = 11.7), 5.36 (d, 0.5H, J = 11.7), 5.30 (d, 0.5H, J = 11.7), 3.88 (s, 3H).

2.2.5. Syntheses of methyl 3-(4-biphenylyl)propiolate (**4e**), 3-(1-naphthyl)propiolate (**5e**), and methyl 3-(2-naphthyl)propiolate (**6e**)

5e was synthesized by the procedure of Wajack et al. [26]. Potassium hydroxide (45.2 g, 0.806 mol) was dissolved in 400 ml of ethanol and the temperature was held at 50 °C.

Keeping the temperature under 60 °C, the powder of methyl 3-(1-naphthyl)-2,3-dibromopropanoate (56.0 g, 0.151 mol) was gradually added to the solution with stirring. After the addition of **5d**, the temperature of the solution was raised up to 70 °C and was held at the temperature for 1 h. After being cooled, the reaction mixture was poured into 200 ml of water, and the mixture was acidified by concentrated hydrochloric acid until it showed strong acidity. The ethanol was evaporated from the mixture, and the product was extracted from the mixture by ether. The ether extract was dried over magnesium sulfate, and the ether was evaporated. The obtained crude acid was dissolved in 200 ml of dry methanol and the solution was refluxed with a catalytic amount of sulfuric acid overnight. The solution was poured into water and was washed with sodium hydrogen carbonate solution. The crude methyl ester was extracted from the neutralized solution with ether. The ether extract was washed with water several times and dried over sodium carbonate, and the ether was evaporated. The residue was purified by column chromatography (hexane:toluene = 3:1) on silica gel to give **5e** (19.2 g, 0.091 mol, yield 61%); ^{1}H NMR ($CDCl_3$) δ: 8.33 (d, 1H, J = 7.8), 7.96 (d, 1H, J = 8.3), 7.88 (d, 1H, J = 8.3), 7.87–7.84 (m, 1H), 7.65–7.63 (m, 2H), 7.62–7.45 (m, 1H), 3.90 (s, 3H).

4e was similarly prepared by the reaction of **4d** and potassium hydroxide in ethanol and recrystallized from methanol. Yield 77%; m.p. 76–76.5 °C; ^{1}H NMR ($CDCl_3$) δ: 7.66 (d, 2H, J = 8.6), 7.61 (d, 2H, J = 8.6), 7.60 (d, 2H, J = 7.1), 7.47 (dd, 2H, J = 7.3, 7.1), 7.39 (tt, 1H, J = 7.3, 1.3), 3.83 (s, 3H).

6e was similarly prepared by the reaction of **6d** and potassium hydroxide in ethanol and recrystallized from methanol (12.5 g, 0.0595 mol, 77% yield); ^{1}H NMR ($CDCl_3$) δ: 7.94 (s, 1H), 7.88–7.51 (m, 2H), 7.84 (d, 1H, J = 16.1), 6.56 (d, 1H, J = 16.1), 3.83 (s, 3H).

*2.2.6. Syntheses of methyl 3-phenylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**3a**), 3-(4-biphenylyl)bicyclo [2.2.1]hepta-2,5-diene-2-carboxylate (**4a**), 3-(1-naphthyl)-bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**5a**), and 3-(2-naphthyl)-bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**6a**)*

5a (2.79 g, 0.010 mol, 31.3% yield) was synthesized by the Diels-Alder reaction of cyclopentadiene (2.60 g, 0.039 mol) and **5e** (6.81 g, 0.032 mol) in 60 ml of dry benzene at 175 °C in a stainless steel autoclave for 18 h and was purified by column chromatography (toluene) on silica gel and subsequent recrystallization from ethanol: m.p. 94.5–95.0 °C; ^{1}H NMR ($CDCl_3$) δ: 7.86 (d, 1H, J = 8.1), 7.80 (d, 1H, J = 8.3), 7.52–7.43 (m, 3H), 37.44 (d, 1H, J = 8.1), 7.13–7.11 (dd, 2H, J = 4.6, 1.5), 6.97 (br. s, 1H), 4.19 (s, 1H), 3.82 (s, 1H), 3.43 (s, 3H), 2.56 (s, 1H), 2.22 (dt, 1H, J = 6.6, 1.5); ^{13}C NMR ($CDCl_3$) δ: 167.5, 165.6, 144.0, 142.5, 141.5, 135.7, 133.5, 130.6, 128.4, 128.1, 125.9, 125.8, 125.6, 125.1, 123.8, 72,1, 59.8, 52.2, 51.1; IR (KBr) 3067, 3046, 2999, 2977, 2949, 1689, 1436, 1242 cm^{-1}; FAB-MS (*m*-nitrobenzyl alcohol) *m/z* 276 (M^+), 245, 210; UV (hexane): λ_{max} (log ε) 211.5 (4.02), 224.5 (4.68), 284 (3.79), 297 nm (3.82). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.47; H, 5.74 [27].

3-Arylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylates **3a**, **4a**, and **6a** were similarly synthesized by the Diels-Alder reactions of cyclopentadiene and the corresponding methyl 3-arylpropiolate.

3a: yield 76%; m.p. 123.0–123.5 °C; ^{1}H NMR ($CDCl_3$) δ: 7.53 (d, 2H, J = 7.3), 7.35 (dd, 2H, J = 7.3, 6.8), 7.31 (d, 2H, J = 6.8), 6.98 (d, 1H, J = 2.9), 6.93 (d, 1H, J = 2.9), 4.06 (s, 1H), 3.86 (bs, 1H), 3.67 (bs, 3H), 2.25 (d, 1H, J = 6.8), 2.07 (dt, 1H, J = 6.8, 1.5); ^{13}C NMR ($CDCl_3$) δ: 165.9, 143.6, 140.8, 139.9, 135.5, 135.5, 128.5, 128.3, 127.7, 70.5, 58.4, 53.0, 51.2; FAB-MS (*m*-nitrobenzyl alcohol) *m/z* 226 (M^+), 211, 167, 66; IR (KBr) 3062, 3030, 2952, 1735, 1438, 1254 cm^{-1}. UV (hexane): λ_{max} (log ε) = 221.5 (3.81), 293.5 nm (3.93). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.64; H, 6.39 [28].

4a: yield 32.6%; m.p. 76.5–77.0 °C; ^{1}H NMR ($CDCl_3$) δ: 7.66–7.59 (m, 2H), 7.62 (d, 2H, J = 8.1), 7.61 (d, 2H, J = 8.1), 7.45 (t, 2H, J = 7.6), 7.35 (t, 1H, J = 7.6), 7.00 (ddd, 1H, J = 4.9, 1.5, 1.5), 6.94 (ddd, 1H, J = 4.9, 1.5, 1.5), 4.08 (bs, 1H), 3.91 (bs, 1H), 3.71 (s, 3H), 2.27 (d, 1H, J = 6.6), 2.09 (d, 1H, J = 6.6); ^{13}C NMR ($CDCl_3$) δ: 166.5, 143.7, 143.6, 143.6, 141.3, 140.7, 140.6, 138.9, 134.4, 128.8, 128.3, 127.0, 126.4, 70.5, 58.4, 53.1, 51.3; FAB-MS (*m*-nitrobenzyl alcohol) *m/z* 302 (M^+), 271, 243, 236; IR (KBr) 3075, 3033, 3010, 2993, 2968, 2942, 1699, 1429, 1293 cm^{-1}. UV (hexane): λ_{max} (log ε) 247 (4.08), 315 nm (4.26). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.16; H, 6.08.

6a: yield 77%; ^{1}H NMR ($CDCl_3$) δ: 7.97 (s, 1H), 7.87–7.80 (m, 2H), 7.80 (d, 1H, J = 8.8), 7.64 (dd, 1H, J = 8.8, 2.0), 7.49–7.46 (m, 2H), 7.02 (dd, 1H, J = 5.0, 2.9), 6.99 (dd, 1H, J = 5.0, 2.9), 4.11 (dd, 1H, J = 2.9, 1.6), 3.98 (bs, 1H), 2.32 (dt, 1H, J = 5.0, 1.6), 2.12 (dt, 1H, J = 5.0, 1.6). ^{13}C NMR ($CDCl_3$) δ: 167.1, 143.7, 143.7, 139.2, 133.2, 133.2, 132.8, 127.1, 127.0, 127.0, 126.9, 126.5, 126.1, 125.9, 125.9; IR (KBr)13058, 2997, 2947, 1707, 1706, 1434, 1233 cm^{-1}; FAB-MS (*m*-nitrobenzyl alcohol) *m/z* 276 (M^+), 245, 210; UV (hexane): λ_{max} (log ε) 218 (4.56), 268 (4.11), 316 nm (4.05). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.53; H, 5.99.

*2.2.7. Syntheses of methyl tetracyclo[3.2.0.0^{2,7}.0^{4,6}] heptane-1-carboxylate (**1b**) and 3-methyltetracyclo [3.2.0.0^{2,7}.0^{4,6}]heptane-1-carboxylate (**2b**)*

1b was prepared according to the previous paper: ^{1}H NMR ($CDCl_3$) δ: 3.67 (s, 3H), 2.42 (ddd, 1H, J = 2.4, 1.5, 1.5), 2.27 (dd, 1H, J = 4.8, 1.5), 2.17 (ddd, 1H, J = 11.7, 1.5, 1.5), 2.09 (ddd, 1H, J = 11.7, 1.5, 1.5), 2.00 (ddd, 1H, J = 2.4, 2.4, 1.5), 1.67 (ddd, J = 5.8, 4.8, 2.4), 1.58 (ddd, 1H, J = 5.8, 2.4, 2.4). Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.92; H, 6.75 [8].

2b (3.77 g, 0.023 mol, 82.3% yield) was synthesized by the Diels-Alder reaction of cyclopentadiene (1.90 g, 0.029 mol) and tertrolic acid methyl ester (2.80 g, 0.029 mol) in 50 ml of dry benzene at 160 °C in a stainless steel autoclave for 18 h and was purified by column chromatography (toluene) on silica gel and was distillated under vacuum: b.p. 52.0–53.5 °C/2 Torr; ^{1}H NMR ($CDCl_3$) δ: 3.63 (s, 3H), 2.41 (dd, 1H, J = 4.8, 2.4), 2.27 (d, 1H, J = 4.0), 1.15 (d, 1H, J = 11.2), 1.96 (d, 1H, J = 11.2), 1.53 (dd, 1H, J = 4.8, 2.4), 1.41 (s, 3H), 1.27 (d, 1H, J = 3.6); ^{13}C NMR ($CDCl_3$) δ: 173.5, 51.0, 37.5, 31.3, 30.0, 29.9, 29.4, 24.6, 18.8, 13.7; IR (NaCl) 2951, 2930, 2860, 1717, 1439, 1389, 1304, 1219, 1103 cm^{-1}; EI-MS *m/z* 164 (M^+), 149, 133, 105, 66, 59; UV (hexane): λ_{max} (log ε) 221 nm (3.44). Anal. Calcd for $C_9H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.15; H, 7.45.

2.2.8. Syntheses of methyl 5-phenyltetracyclo [3.2.0.0^{2,7}.0^{4,6}]heptane-1-carboxylate (**3b**), 5- (4-biphenylyl)-tetracyclo[3.2.0.0^{2,7}.0^{4,6}] heptane-1-carboxylate (**4b**), 5-(1-naphthyl)-tetracyclo [3.2.0.0^{2,7}.0^{4,6}]heptane-1-carboxylate (**5b**), and 5-(2-naphthyl)-tetracyclo[3.2.0.0^{2,7}.0^{4,6}] heptane-1-carboxylate (**6b**)

5b (1.21 g, 0.00438 mol, 81% yield) was prepared from the photolysis of **5a** (1.5 g, 0.00543 mol) in acetonitrile (160 ml) through a Pyrex filter and was purified by column chromatography (toluene) on silica gel [27], and was recrystallized by hexane (m.p. 112.5–113.0 °C); ^{1}H NMR ($CDCl_3$) δ: 7.94 (bs, 1H), 7.83 (dd, 1H, J = 6.4, 2.4), 7.74 (d, 1H, J = 7.3), 7.49–7.44 (m, 2H), 7.40–7.34 (m, 2H), 3.22 (s, 3H), 2.69 (dd, 1H, J = 4.8, 2.4), 2.63 (d, 1H, J = 11.7), 2.60 (m, 1H), 2.36 (dd, 1H, J = 4.8, 2.4), 2.32 (d, 1H, J = 11.7), 1.77 (d, 1H, J = 3.9); ^{13}C NMR ($CDCl_3$) δ: 172.2, 134.3, 133.7, 133.3, 128.2, 127.4, 126.3, 125.5, 125.4, 125.4, 125.1, 50.8, 37.2, 32.6, 31.9, 31.6, 31.1, 29.0, 19.7; IR (KBr) 3068, 3042, 2956, 2929, 1696, 1110 cm^{-1}; FAB-MS (*m*-nitrobenzyl alcohol) *m/z* 276 (M^+), 245, 210; UV (hexane): λ_{max} (log ε) = 225 (4.82), 284.5 nm (3.90). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.41; H, 5.82.

5-Aryltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1-carboxylates such as **3b**, **4b**, and **6b** were similarly prepared from the photoirradiation of the corresponding 3-arylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylates **3a**, **4a** and **6a**, respectively.

3b: yield 71.3%; m.p. 92.5–93.0 °C; ^{1}H NMR ($CDCl_3$) δ: 7.27–7.25 (m, 4H), 7.19 (tt, 1H, J = 9.2, 3.8), 3.53 (s, 3H), 2.56 (ddd, 1H, J = 4.8, 2.4, 1.0), 2.46 (ddd, 1H, J = 4.8, 4.8, 1.0), 2.38 (dd, 1H, J = 10.3, 1.0), 2.24 (ddd, 1H, J = 4.8, 2.4, 1.0), 2.15 (dd, 1H, J = 10.3, 1.0), 1.72 (ddd, 1H, J = 4.8, 4.8, 1.0); ^{13}C NMR ($CDCl_3$) δ: 172.1, 136.7, 134.0, 127.3, 125.8, 50.8, 36.9, 32.6, 31.9, 31.4, 31.1, 28.9, 20.1; FAB-MS (*m*-nitrobenzyl alcohol) *m/z* 226 (M^+), 211, 167, 66; IR (KBr) 3085, 3061, 3030, 2947, 2924, 1699, 1197 cm^{-1}. UV (hexane): λ_{max} (log ε) < 200 nm. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.34; H, 6.24 [28].

4b: yield 67.3%; m.p. 64.5–65.0 °C; ^{1}H NMR ($CDCl_3$) δ: 7.56 (d, 2H, J = 7.3), 7.49 (d, 2H, J = 8.3), 7.38 (dd, 2H, J = 7.3, 7.3), 7.32 (d, 2H, J = 8.3), 7.28 (dd, 1H, J = 7.3, 1.5), 3.52 (s, 3H), 2.55 (dd, 1H, J = 4.8, 2.4), 2.45 (m, 1H), 2.36 (d, 1H, J = 11.5), 2.22 (dd, 1H, J = 4.8, 2.4), 2.12 (d, 1H, J = 11.5), 1.71 (m, 1H); ^{13}C NMR ($CDCl_3$) δ: 172.4, 141.1, 138.9, 136.2, 129.1, 128.89, 128.7, 127.0, 126.4, 51.1, 51.1, 37.2, 33.2, 33.1, 32.0, 21.3, 21.2; FAB-MS (*m*-nitrobenzyl alcohol) *m/z* 302 (M^+), 271, 243, 236; IR (KBr) 3059, 3026, 2946, 1705, 1175 cm^{-1}. UV (hexane): λ_{max} (log ε) 201 (4.66), 264 nm (4.33). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.12; H, 6.08.

6b: yield 60.7%; m.p. 80–80.5 °C; ^{1}H NMR ($CDCl_3$) δ: 7.78–7.74 (m, 2H), 7.75 (d, 1H, J = 8.8), 7.65 (bs, 1H), 7.45–7.38 (m, 2H), 7.40 (d, 1H, J = 8.8), 3.51 (s, 3H), 2.63 (dd, 1H, J = 4.8, 2.0), 2.50 (dd, 1H, J = 3.4, 2.0), 2.43 (d, 1H, J = 11.7), 2.35 (dd 1H, J = 4.8, 2.0), 2.19 (d, 1H, J = 11.7), 1.79 (dd, 1H, J = 3.4, 2.0); ^{13}C NMR ($CDCl_3$) δ: 172.4, 134.7, 133.2, 132.2, 127.7, 127.5, 126.9, 126.2, 126.1, 125.8, 125.3, 51.2, 33.3, 33.1, 32.5, 31.8, 21.1, 21.1; IR (KBr) 3057, 2950, 2933, 2859, 1716, 1172 cm^{-1}; FAB-MS (*m*-nitrobenzyl alcohol) *m/z* 276 (M^+), 245, 210;. UV (hexane): λ_{max} (log ε) 222.5 (4.77), 268 (3.77), 278 nm (3.78). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.94; H, 6.10.

2.2.9. Synthesis of methyl 3-(1-naphthyl)-bicyclo[2.2.1] hept-2-ene-2-carboxylate (**5aH**)

5aH (0.378 g, 0.00136 mol, yield 62.7%) was synthesized by the catalytic hydrogenation of **5a** (0.600 g, 0.00217 mol) over 10% palladium-activated carbon (0.487 g) in 60 ml of dry methanol and was recrystallized from hexane; m.p. 105.5–106 °C; ^{1}H NMR ($CDCl_3$) δ: 7.84 (d, 1H, J = 9.3), 7.78 (d, 2H, J = 8.0), 7.45 (d, 1H, J = 8.0), 7.43 (d, 1H, J = 9.3), 7.40 (d, 1H, J = 7.7), 7.11 (bs, 1H), 3.51 (d, 1H, J = 1.6), 3.42 (s, 3H), 3.23 (d, 1H, J = 2.0), 1.94 (dd, 2H, J = 9.5, 9.5), 1.84 (dd, 1H, J = 9.5, 9.5), 1.53 (dd, 1H, J = 9.5, 9.5), 1.37 (bs, 1H), 1.35 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ: 165.5, 136.0, 134.3, 133.4, 131.1, 128.3, 128.0, 125.9, 125.6, 125.3, 124.9, 124.7, 51.5, 50.9, 47.2, 44.6, 42.2, 26.1, 25.2; IR (KBr) 2995, 2962, 2948, 2870, 1692, 1505, 1435, 1357, 1280, 1240, 1189, 1088, 800, 781 cm^{-1}; EI-MS *m/z* 278 (M^+), 250, 218, 191; UV (hexane): λ_{max} (log ε) 224.5 (4.74), 294 (3.91), 292.5 nm (3.90). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.94; H, 6.60 [27].

2.3. Enantiomer separation

All enantiomers were resolved by HPLC (Japan Analytical Industry LC-908) on appropriate preparative chiral columns. Enantiomers of **1a** and **1b** were resolved by the procedure described in our previous paper [8], while the

Table 1
Preparative chiral HPLC columns and eluents employed in the optical resolution of norbornadiene (**1a**–**6a**) and quadricyclane derivatives (**1b**–**6b**)

Compound	Column	I.D. × length (mm)	Eluent (2-propanol:hexane)
1a	Chiracel OD	20.0 × 250	1:100
(−)-**2a**	Chiralpack AD	20.0 × 250	1:1000
(+)-**2a**	Chiracel OD	20.0 × 250	1:1000
3a	Chiracel OD	20.0 × 250	1:99
4a	Chiracel OD	20.0 × 250	2:98
5a	Chiracel OD	20.0 × 250	0.5:99.5
6a	Chiracel OD	20.0 × 250	1:99
1b	Chiralpack AS	4.6 × 250	1:200
2b	Chiralpack AD	4.6 × 250	1:1000
3b	Chiralpack AS	4.6 × 250	0.5:95.5
4b	Chiracel OD	20.0 × 250	10:90
5b	Chiracel OD	20.0 × 250	1:99
6b	Chiracel OD	20.0 × 250	1:99

other norbornadiene and quadricyclane derivatives, except for **2b**, were resolved chromatographically on Daicel Chiracel OD, Chiralpack AD or AS with 2-propanol/hexane eluent under the conditions shown in Table 1. The enantiomeric excesses (ees) of the isolated enantiomers were determined by HPLC (JASCO Gulliver) on appropriate analytical chiral columns under the conditions shown in Table 2. The CD intensity and $[\alpha]_D$ value reported for each enantiomer are corrected for the ee determined by this method.

However, the optical resolution of **2b** by preparative HPLC on Daicel Chiracel OD, OJ, or Chiralpack AD was not very successful, and the enantiomers obtained were not pure enough to examine the chiroptical properties. Hence, enantiopure (+)- and (−)-**2a**, resolved by preparative chiral HPLC, were photoisomerized to the relevant enantiomers of **2b**, with which the chiroptical properties were determined.

Table 2
Chiral HPLC columns and eluents for the evaluation of the enantiomeric excess of norbornadiene (**1a**–**6a**) and quadricyclane derivatives (**1b**–**6b**)

Compound	Column	I.D. × length (mm)	Eluent (2-propanol:hexane)
1a	Chiracel OD	4.6 × 250	1:200
2a	Chiracel OD	4.6 × 250	1:1000
3a	Chiracel OD	4.6 × 250	1:99
4a	Chiralpack OJ	4.6 × 250	10:90
5a	Chiracel OD	4.6 × 250	0.5:99.5
6a	Chiracel OD	4.6 × 250	0.5:99.5
1b	Chiralpack AS	4.6 × 250	1:200
2b	Chiracel OD[a]	4.6 × 250	1:300
3b	Chiralpack AS	4.6 × 250	1:99
4b	Chiracel OD	4.6 × 250	5:95
5b	Chiracel OD	4.6 × 250	0.5:99.5
6b	Chiracel OD	4.6 × 250	0.5:99.5

[a] Incomplete separation; not used in the determination of ee.

2.4. Specific rotation

All of the specific rotations, except for (+)- and (−)-**1b** and (+)- and (−)-**2b**, were measured at 589.3 nm in hexane by using a Perkin Elmer 341 Polarimeter equipped with a sodium resonance lamp, while those of (+)/(−)-**1b** and (+)/(−)-**2b** were measured in acetonitrile due to the low solubilities in hexane.

2.5. UV and CD spectra

All of the UV and CD spectra of chiral norbornadiene and quadricyclane derivatives were measured in hexane and acetonitrile with JASCO V-560 and J-720WI spectrometer, respectively.

2.6. Photolysis

A hexane solution of norbornadiene or quadricyclane derivative in 0.0176–0.1126 mM concentration was introduced in a rectangular Suprasil cell (10 × 10 × 40 mm), bubbled with argon gas, and sealed under an argon atmosphere. The solution was irradiated by linearly polarized light (LPL) from the monochromatic light source, which was originally designed in-house and made by JASCO as a CPL source [8] but used as an LPL source in the present case. In the apparatus, the light beam from a 500 W xenon arc lamp (Ushio) placed behind an elliptical mirror was made paralleled by two mirrors, made monochromatic with a grating monochromator (JASCO CT-10), and then collimated with a fused silica lens. The light beam was linearly polarized with a polarizer (Melles Griot, 03PTA403) which was placed in front of a Soleil-Babinet's compensator (Shimadzu, 691-02013-02). The full width at half-maximum (FWHM) of irradiated light was 15 nm at the irradiation wavelength. The sample cell placed in the cell holder was irradiated by the monochromatic light.

2.7. Product analysis

The photolyzed solutions were spectroscopically and chromatographically analyzed by UV and CD spectrometers and by chiral HPLC on the appropriate column used for the determination of the ee of each enantiomer.

3. Results and discussion

3.1. Chiroptical properties of chiral norbornadienes and quadricyclanes

The chiral norbornadienes examined possess ethylenic and acrylate moieties as common chromophores that interact through space with each other, while the aromatic group, if introduced, behaves as an additional chromophore

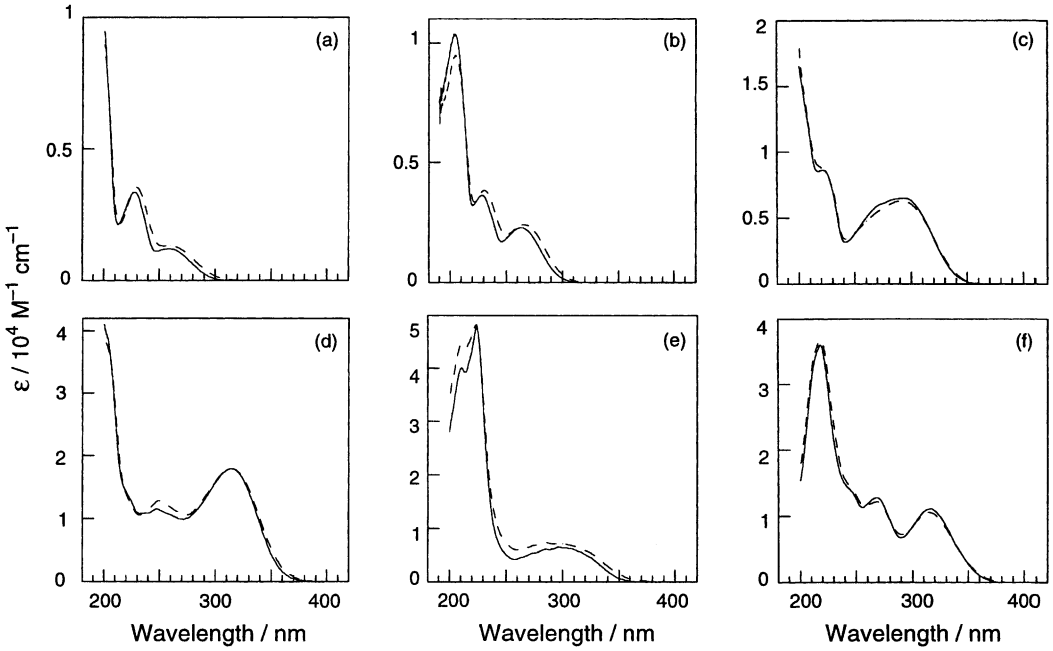


Fig. 1. UV spectra of chiral norbornadienes in hexane (solid line) and in acetonitrile (dashed line): (a) **1a**, (b) **2a**, (c) **3a**, (d) **4a**, (e) **5a**, and (f) **6a**.

in conjugation with the acrylate moiety. In contrast, the quadricyclanecarboxylate skeleton by itself appears to behave as a chromophore, which conjugates with the aromatic substituent, if exist.

3.1.1. UV spectra

The electronic spectra of 3-alkyl- and 3-arylnorbornadiene-2-carboxylates **1a**–**6a** were measured in hexane and acetonitrile, and the results are shown in Fig. 1a–f. Possessing the ethylenic and acrylate chromophores, the non-aromatic norbornadienecarboxylates **1a** and **2a** gave two common absorption bands at 227 and 260 nm (in hexane), along with an intense band at <200 nm for **1a** or at 205 nm for **2a** (Fig. 1a and b). The strong absorption around 200 nm is most probably assigned to the π, π^* transition of ethylenic moiety, judging from the peak position and high molar absorption coefficients (ε) of up to 10,000 M^{-1} cm^{-1}, as well as the bathochromic shift upon methylation (**2a** versus **1a**) and increasing solvent polarity (acetonitrile versus hexane) [29]. [1] The less-intense common bands at 227 and 260 nm in hexane are also red-shifted by changing the solvent to acetonitrile. The absorption band at 227 nm is also observed in aromatic norbornadienes **3a** and **4a** as shoulders (Fig. 1c and d) with ε of several thousands, which would be attributable to the methyl acrylate chromophore. On the other hand, the lowest-energy transition of non-aromatic norbornadienes, such as **1a** and **2a**, is known to involve the through-space interaction of the homoconjugated double bonds [21,30]. Since the spectrum of either unsubstituted norbornadiene or methyl acrylate does not show any absorption tail extended to 290 nm,[1] the longest absorption bands in **1a** and **2a** at 260 nm (hexane) are thought to originate from the through-space interaction between the ethylenic and acrylate chromophores.

The spectra of aromatic norbornadienes **3a–6a** are mostly dominated by the intense bands of the aromatic group introduced, but are significantly different in shape from those of the isolated aromatic chromophores. Phenyl derivative **3a** gave absorption peaks of moderate intensities at 222 and 294 nm in hexane (Fig. 1c). The lowest-energy peak at 294 nm is red-shifted than that in typical cinnamates and shows an appreciable bathochromic shift in acetonitrile, which may be attributed, respectively, to the through-space interaction with the ethylenic moiety and to the n, π^* character of the lowest-energy transition. In contrast, the absorption bands of **4a** at 247 and 315 nm in hexane shifted only slightly to longer wavelengths in acetonitrile (Fig. 1d). The shape and relative intensity of the E_2 and E_1 band of **4a** are similar to those of 2,2′,6,6′-tetramethylbiphenyl rather than unsubstituted biphenyl [31], suggesting a twisted biphenyl conformation. Judging from the very high ε's of up to 50,000 M^{-1} cm^{-1}, the intense peaks of **5a** at 211 and 225 nm in hexane (Fig. 1e) are assigned to the π, π^* transitions of ethylenic and 1-naphthyl chromophores [29,31,32], which is confirmed below through the spectral comparison with partially hydrogenated **5aH** (Fig. 2). The absorption tail of **5a** is obviously extended to longer wavelengths in acetonitrile (Fig. 1e) than in hexane, indicating the π, π^*

[1] ε_{max} in hexane: norbornadiene ε_{max} < 200 nm (ε_{200} = 2200 M^{-1} cm^{-1}), methyl acrylate 2040 M^{-1} cm^{-1} (206 nm), methyl cyclopropanecarboxylate 180 M^{-1} cm^{-1} (205 nm). Tail of absorbance in hexane: norbornadiene <270 nm, methyl acrylate <260 nm, methyl cyclopropanecarboxylate <280 nm.

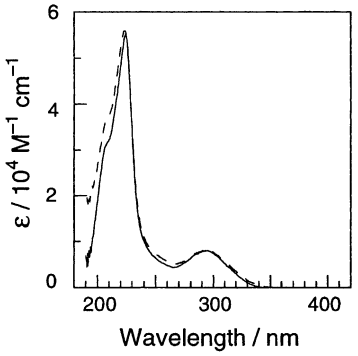


Fig. 2. UV spectra of **5aH** in hexane (solid line) and in acetonitrile (dashed line).

nature. The vibrational fine structures of the aromatic chromophores are preserved in the lowest-energy bands of **4a** and **5a** (Fig. 1d and e), which is consistent with the assignment to the π, π* transition. Similarly, the absorption bands of **6a**, showing little shifts in both hexane and acetonitrile, are reasonably assigned to the π, π* transition of the 2-naphthyl group.

In order to assess more closely the contribution of the through-space interaction to the spectrum, we synthesized the norbornene derivative **5aH** as a reference compound of **5a**. Lacking the ethylenic double bond, **5aH** gave a distinctly different absorption spectrum, shown in Fig. 2, where no peak is found at 211 nm and the lowest-energy peak shows much clear vibrational fine structures with significant hypsochromic shifts. The absence of the 211 nm peak is reasonable if this band arises from the π, π* transition of the ethylenic chromophore, while the diffused and bathochromically shifted lowest-energy band of **5a** clearly indicates the significant contribution of the through-space interaction. In view of the common norbornadiene-2-carboxyalte structure shared by **1a–6a**, it is most probable that the lowest-energy transition is more or less affected by the through-space interaction between the ethylenic and alkyl/aryl-acrylate chromophores [21].

UV spectra of the relevant quadricyclanecarboxylate derivatives **1b–6b** in hexane and acetonitrile are shown in Fig. 3a–f. Aliphatic quadricyclanecarboxylates **1b** and **2b**, carrying no functional group other than cyclopropane and methoxycarbonyl, gave a moderate intensity peak or shoulder around 220 nm. The peaks are significantly red-shifted and the magnitudes of ε's ($\sim$3000 M^{-1} cm^{-1}) are much larger than those observed for typical aliphatic carboxylic esters, cyclopropanes, or cyclopropanecarboxylates. For example, methyl cyclopropanecarboxylate does not shown any clear peak above 200 nm (hexane) and the ε is in the order of 10^2 M^{-1} cm^{-1}.[1] Hence, the absorption band around 220 nm cannot be attributed to the methoxycarbonyl, cyclopropane, or even cyclopropanecarboxylate chromophore, but rather assigned to the quadricyclane chromophore in conjugation with the methoxycarbonyl, which possesses some charge-transfer (C-T) character, as judged from the bathochromic shift observed in acetonitrile [8].

In the spectra of aromatic quadricyclanecarboxylates **3b–6b**, the original transition of moderate intensity, which is assigned to the quadricyclanecarboxylate chromophore, is almost hidden under the overriding intense aromatic transitions. However, the spectra are not identical to those of the corresponding isolated aromatic chromophores, accompanying evident bathochromic shifts and diffused peak shapes observed particularly for **3b** and **4b**. Thus, the absorption peaks of **3b** ($\sim$230 nm), **4b** (260 nm), **5b** (285 nm),

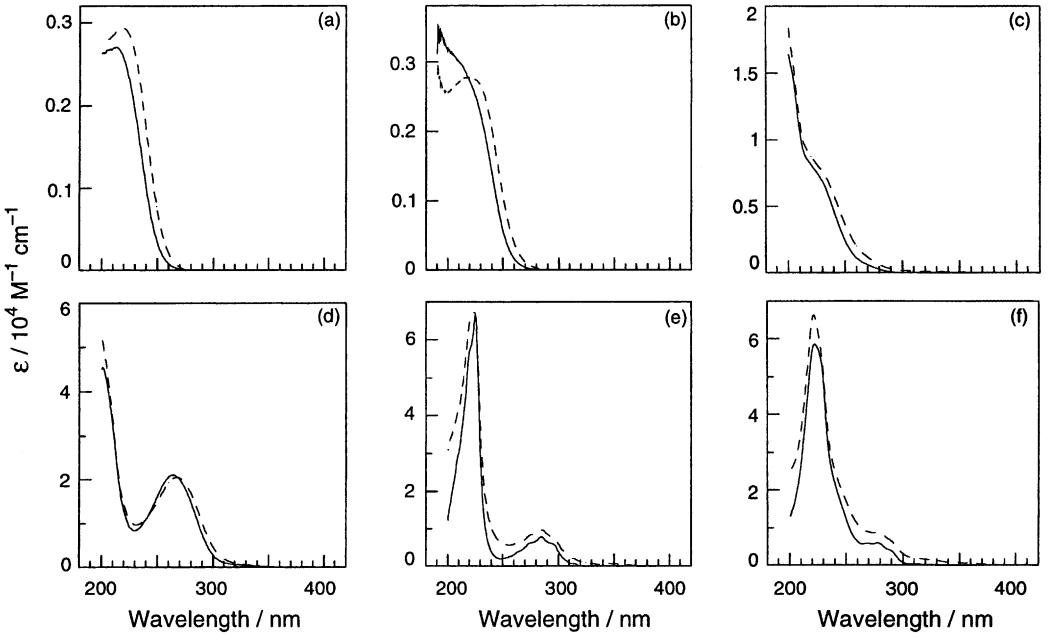


Fig. 3. UV spectra of chiral norbornadienes in hexane (solid line) and in acetonitrile (dashed line): (a) **1b**, (b) **2b**, (c) **3b**, (d) **4b**, (e) **5b**, and (f) **6b**.

and **6b** (275 nm) in hexane are located in general at longer wavelengths than the original E_2 band of the relevant aromatic compound. In contrast, the aromatic E_1 band of **5b** at 220 nm ($\varepsilon > 60,000\,M^{-1}\,cm^{-1}$) is very similar in peak position and intensity to that of 1-methylnaphthalene [31]. It is noted that the lowest-energy bands of not only aliphatic (**1b** and **2b**) but also aromatic quadricyclanecarboxylates (**3b–6b**) show appreciable bathochromic shifts in acetonitrile, indicating a consistent participation of the C-T interaction between the (alkyl/aryl)quadricyclane and methoxycarbonyl moieties.

3.1.2. CD spectra

Fig. 4 illustrates the CD spectra of a series of the enantiomeric pairs of norbornadienes **1a–6a** in hexane and in acetonitrile.

As can be seen from Figs. 1a and 4a, **1a** gives well-correlated UV and CD extrema. In accordance with the UV spectral assignment of **1a** mentioned above [21,30], the lowest-energy CD band at 268 nm (in hexane) with a moderate $\Delta\varepsilon$, displaying a bathochromic shift in acetonitrile, is assigned to the C-T transition arising from the through-space interaction between the ethylenic and acrylate moieties. The CD bands at <200 and 227 nm (in hexane) are assigned to the π, π^* transitions of the ethylenic and acrylate moieties, respectively.

Introducing an additional methyl to **1a** at the 3-position led to global bathochromic shifts in the UV and CD spectra of **2a**, as shown in Figs. 1b and 4b. The CD extrema observed at 205 and 273 nm (in hexane) are similarly assigned to the ethylenic π, π^* transition and the through-space C-T transition, respectively. On the other hand, the origin of the bisignated couplet at 224 and 242 nm (in hexane) is not simply assigned to the crotonic π, π^* transition but would be related to the weak exciton coupling between the ethylenic and crotonic chromophores or alternatively assigned to a hidden weak transition.

The aromatic norbornadienes **3a–6a** gave distinctly different CD spectra, which are dominated by the aromatic chromophores introduced. The full assignment of all transition bands appears difficult due to the overlap of the aromatic transitions on the original ethylenic and acrylic transitions. Nonetheless, it may be interesting to point out the common feature in the CD spectra of **3a**, **5a** and **6a**, the sign of which shows the same alternating profile with a positive–negative–negative–positive, or the opposite, pattern. The shortest-wavelength CD bands, which appear at 207 nm for **3a**, 210 nm for **5a** and ≤210 nm for **6a** in hexane, may be assigned to the ethylenic π, π^* transition at 200–205 nm of non-aromatic norbornadienes **1a** and **2a**. The CD bands at longer wavelengths are related to the original and conjugated transitions of the acrylate and aromatic moieties, and the lowest-energy CD bands of the aromatic norbornadienes are undoubtedly assigned to the through-space C-T transitions. However, these overlapped transitions make the complete analysis and assignment of these complicated CD bands difficult.

CD spectra of chiral quadricyclanes **1b–6b** in hexane and acetonitrile are shown in Fig. 5a–f. The non-aromatic quadricylanes **1b** and **2b** give very similar CD spectra in shape and intensity, displaying only one CD band at 213–214 nm in hexane and at 216–218 nm in acetonitrile. As discussed above in the UV spectral examinations, the bathochromic shift observed in the polar solvent is ascribed

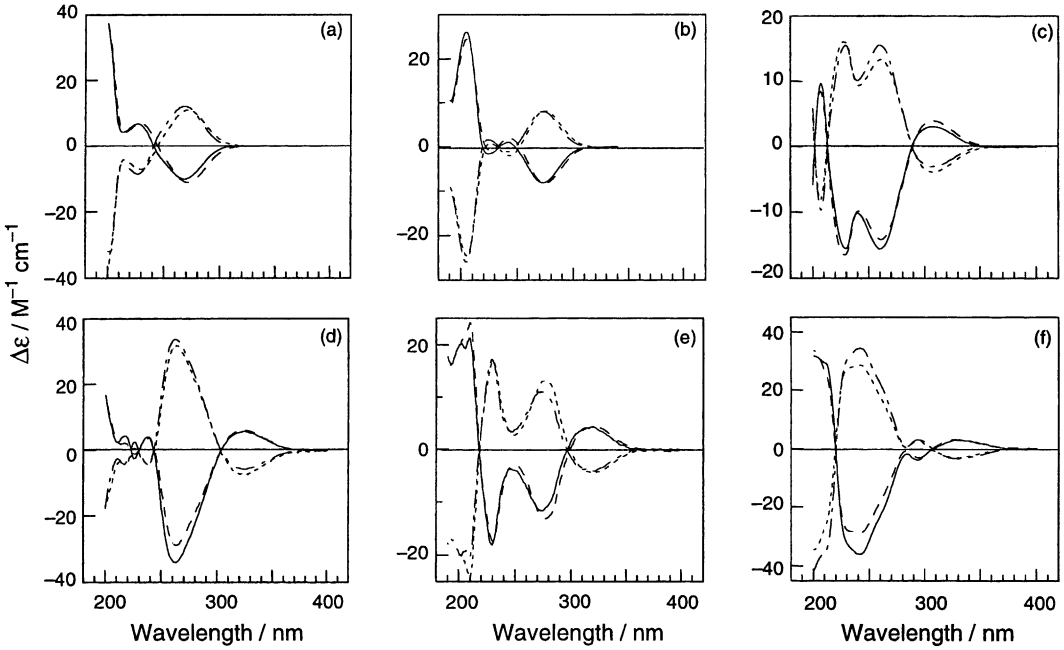


Fig. 4. CD spectra of (−)- and (+)-norbornadienes in hexane (solid and chain, respectively) and in acetonitrile (dash and short dash, respectively): (a) **1a**, (b) **2a**, (c) **3a**, (d) **4a**, (e) **5a**, and (f) **6a**.

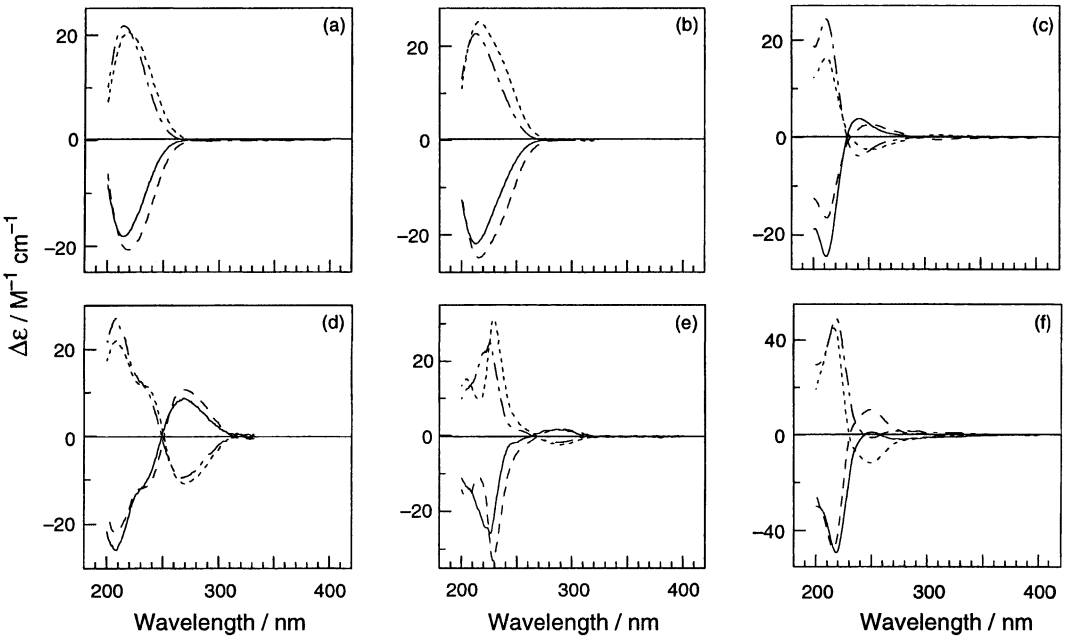


Fig. 5. CD spectra of (−)- and (+)-quadricyclanes in hexane (solid and chain, respectively) and in acetonitrile (dash and short dash, respectively): (a) **1b**, (b) **2b**, (c) **3b**, (d) **4b**, (e) **5b**, and (f) **6b**.

to the C-T character of this transition from the quadricyclane to acrylate/crotonate moiety. Accompanying a sign inversion in the wavelength range employed, the CD spectra of quadricylanes **3b–6b** are dominated by the aromatic moieties introduced. In the cases of **3** and **4**, the lowest-energy band shifts more or less to the longer wavelength in acetonitrile due to the C-T character, while the higher-energy transition(s) are not appreciably influenced by the solvent polarity. These CD spectral changes in polar solvent are consistent with those observed in the UV spectra. However, the solvent effects on the CD spectra of naphthylquadricylanes **5b** and **6b** are substantially different from those observed in the UV spectra. Thus, not only the lowest-energy band but also the band(s) at shorter wavelength(s) show appreciable bathochromic shifts, probably as a result of the C-T interactions.

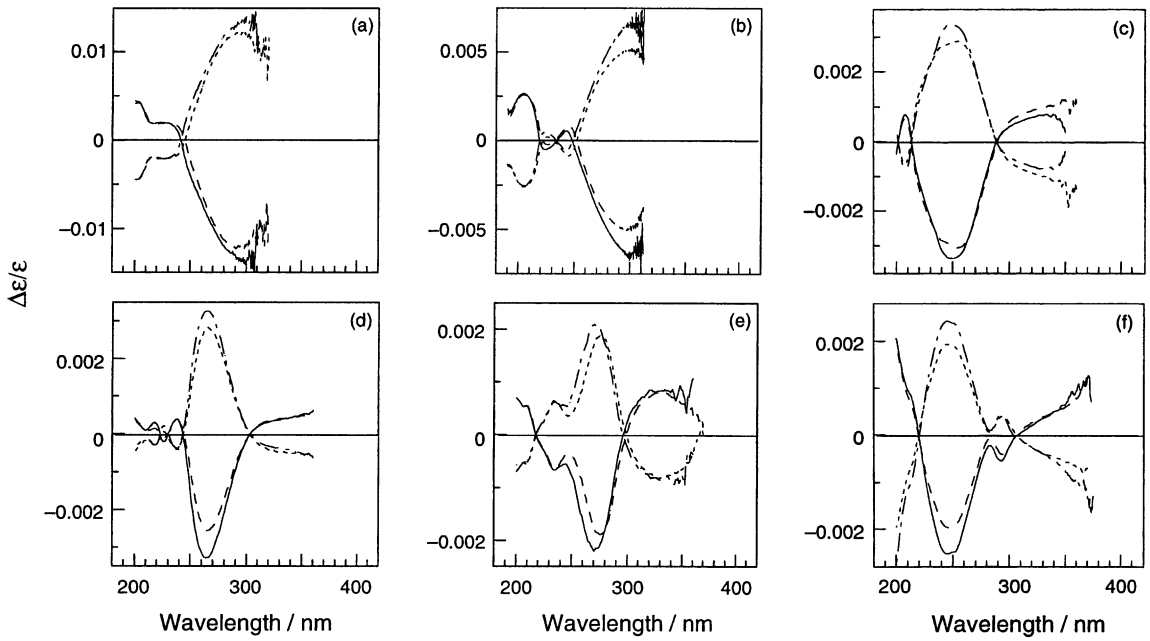


Fig. 6. Anisotropy (*g*) factors of (−)- and (+)-norbornadienes in hexane (solid and chain, respectively) and in acetonitrile (dash and short dash, respectively): (a) **1a**, (b) **2a**, (c) **3a**, (d) **4a**, (e) **5a**, and (f) **6a**.

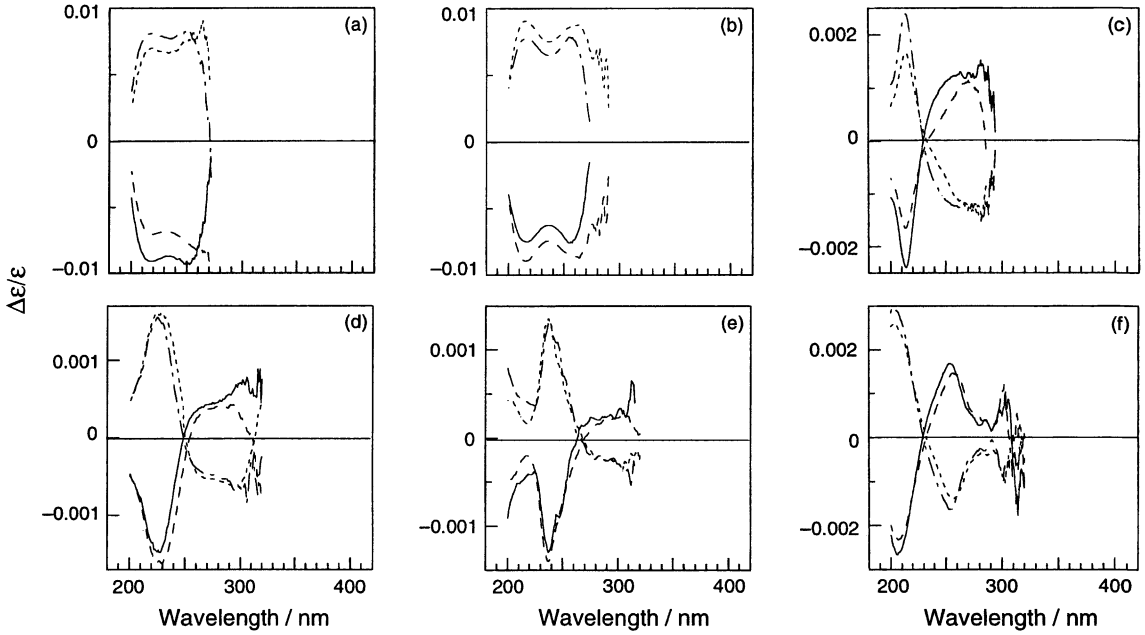


Fig. 7. Anisotropy (g) factors of (−)- and (+)-quadricyclanes in hexane (solid and chain, respectively) and in acetonitrile (dash and short dash, respectively): (a) **1b**, (b) **2b**, (c) **3b**, (d) **4b**, (e) **5b**, and (f) **6b**.

3.1.3. Anisotropy factor

In NAAS reactions using CPL, the relative rate of excitation of antipodal reactants, and therefore the ee's of the remaining reactant and formed product, are determined exclusively by the anisotropy factor ($g = \Delta\varepsilon/\varepsilon$) [8–10]. In the present study, the g factors of all enantiomeric norbornadiene and quadricyclane derivatives examined (**1a–6a** and **1b–6b**) were determined for the first time. The g factors obtained are plotted against the wavelength in Figs. 6 and 7.

As can be readily recognized from the comparison of the relevant UV and CD spectra of norbornadienes shown in Figs. 4 and 6 and of quadricyclanes shown in Figs. 5 and 7, the g factor as a function of wavelength, or "anisotropy spectrum", is very much different in relative intensity from the corresponding CD spectrum, although the positions of the relevant g and CD extrema show good agreement, except for the lowest-energy peak. For example, the non-aromatic norbornadienes **1a** and **2a** give moderate g factors of 0.014 (**1a** in hexane) and 0.007 (**2a** in hexane), which are unusually large for a simple π, π* transition but are reasonable as a C-T band incorporating the n, π* transition of the acrylate chromophore. In contrast, aromatic norbornadienes **3a–6a** afford substantially lower g factors of 0.002–0.003, which are however, appreciably larger than the typical values (10^{-3}–10^{-4}) reported for an allowed π, π* transition [33], probably due to the contribution from the n, π* transition of acrylate.

Quadricyclane derivatives **1b–6b** share a common tendency in the anisotropy spectra, where the g factor of the lowest-energy peak is specifically exaggerated. In the cases of **1b** and **2b** (Fig. 7a and b), the existence of the lowest-energy transition with a C-T character, which is hidden in the tail of the shorter-wavelength peak in the CD spectrum, is clearly recognized as an independent peak at 250–260 nm in the anisotropy spectrum. Even in the aromatic quadricyclanes **3b–6b**, the relative importance of the g factor is clearly enhanced for the lowest-energy peak. The highest g factors thus obtained for non-aromatic and aromatic quadricyclanes are 0.0091 (**2b** in acetonitrile) and 0.0024 (**3b** in hexane).

3.1.4. Specific rotation

Optical rotations of these enantiopure norbornadienes and quadricyclane derivatives were measured in hexane or acetonitrile to give the specific rotations $[\alpha]_D^{20}$ listed in Table 3. Although, these values, varying widely from 6.55° to 322°, do not show any apparent general trend or direct relationship

Table 3
Specific rotation ($[\alpha]_D^{20}$) of enantiopure norbornadienes (**1a–6a**) and quadricyclanes (**1b–6b**)

Compound	Solvent	$[\alpha]_D^{20}$ (c)
(−)-**1a**	CH_3CN	−43.5 (0.0624)
(−)-**2a**	Hexane	−86.3 (0.105)
(−)-**3a**	Hexane	−158 (0.650)
(−)-**4a**	Hexane	−216 (0.189)
(−)-**5a**	Hexane	−110 (0.465)
(−)-**6a**	Hexane	−206 (0.0302)
(+)-**1b**	CH_3CN	322 (0.00375)
(+)-**2b**	Hexane	271 (0.177)[a]
(+)-**3b**	Hexane	13.6 (0.177)
(+)-**4b**	Hexane	63.4 (0.202)
(+)-**5b**	Hexane	137.2 (0.0198)
(+)-**6b**	Hexane	63.9 (0.144)

[a] Specific rotation of (+)-**2b** prepared photochemically from (−)-**2a**.

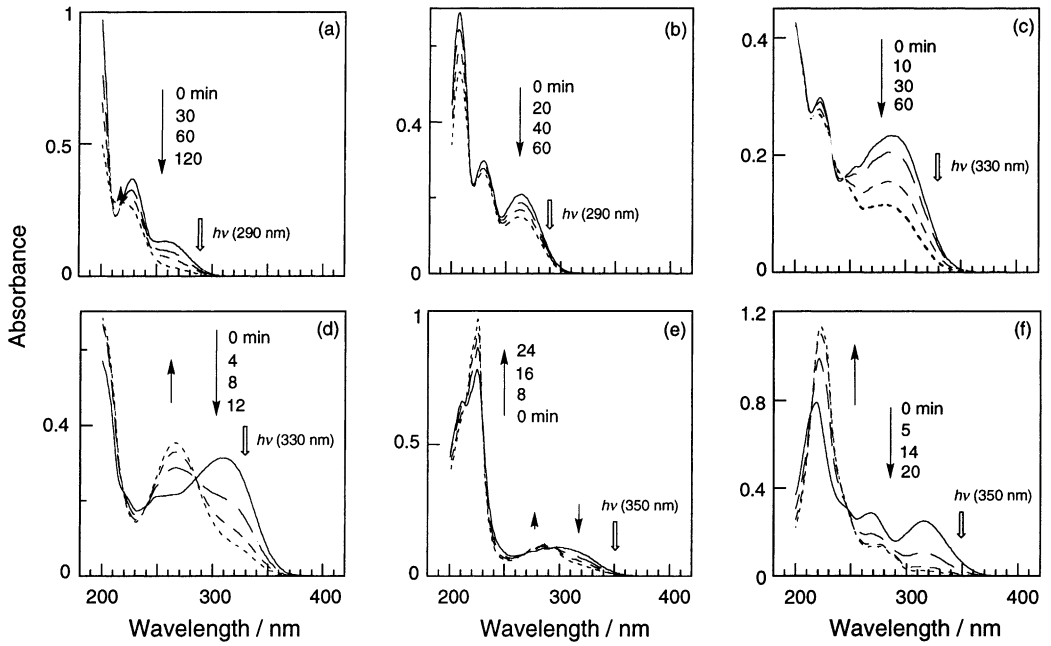


Fig. 8. UV spectral changes of (−)-norbornadienes in hexane upon irradiation near the absorption edge (double arrow): (a) (−)-**1a**, (b) (−)-**2a**, (c) (−)-**3a**, (d) (−)-**4a**, (e) (−)-**5a**, and (f) (−)-**6a**.

to the structural features, (−)-**4a**, (−)-**6a**, (+)-**1b** and (+)-**2b** afford fairly large $[\alpha]_D^{20}$ of up to −216°, −206°, 322° and 271°, respectively.

3.2. Stereochemical consequences of photoconversion from norbornadienes to quadricyclanes

The stereochemical relationships between the norbornadiene (**1a–6a**) and quadricyclane derivatives (**1b–6b**) are elucidated through the analyses of UV and CD spectral changes upon photochemical valence isomerization between the relevant optically active isomeric pairs.

3.2.1. UV spectral changes upon irradiation

A series of (−)-norbornadienes were irradiated near the absorption edge where the light is not absorbed by the quadricyclanes produced. As can be seen from the UV

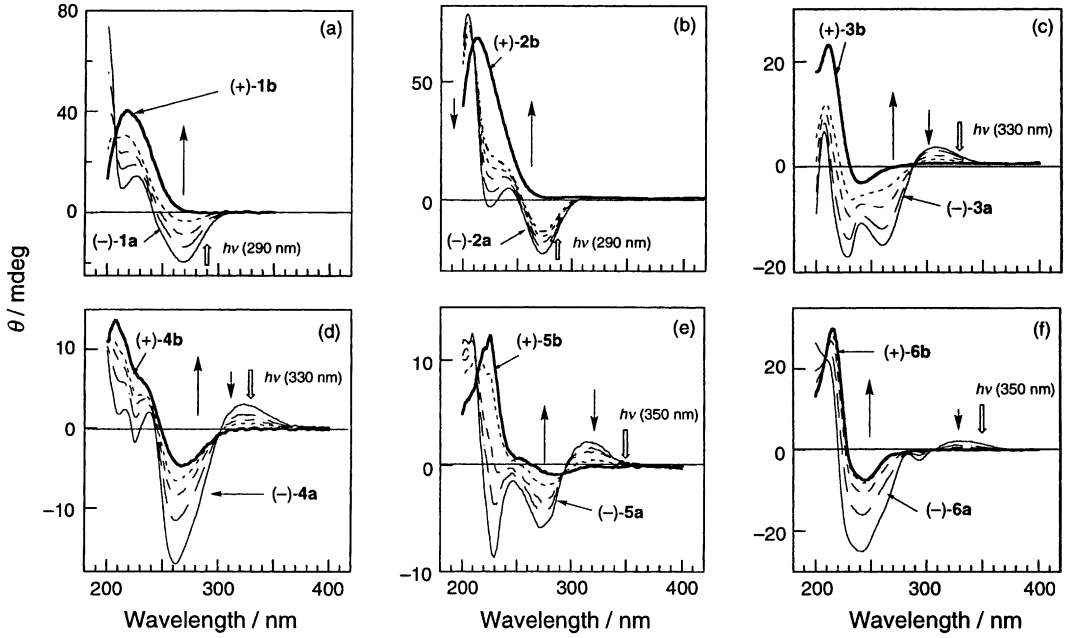
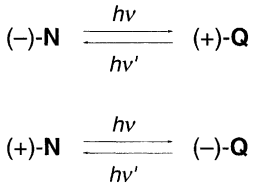


Fig. 9. CD spectral changes of (−)-norbornadienes in hexane upon irradiation near the absorption edge (double arrow): (a) (−)-**1a**, (b) (−)-**2a**, (c) (−)-**3a**, (d) (−)-**4a**, (e) (−)-**5a**, and (f) (−)-**6a**.



Scheme 4. The stereochemical consequences determined for the photochemical interconversion between optically active norbornadiene and quadricyclane.

spectral changes upon irradiation shown in Fig. 8, all of the norbornadienes examined (**1a–6a**) smoothly isomerized to the corresponding quadricyclane derivatives (**1b–6b**), exhibiting the isosbestic points. These results clearly indicate that the photocyclization of non-aromatic and aromatic norbornadienes **1a–6a** to quadricyclanes **1b–6b** is a clean and quantitative process, which is best suitable for the CD spectral examination of the stereochemical consequence of photocyclization.

3.2.2. CD spectral changes upon irradiation

The CD spectral changes upon irradiation of norbornadienes **1a–6a** near the absorption edge are illustrated in Fig. 9.

Upon prolonged irradiations, all of the (−)-norbornadienes employed were completely converted to the corresponding quadricyclanes, as illustrated in Fig. 9a–f. From the CD spectral profiles of the resultant solutions, the quadricyclanes produced are assigned as the (+)-enantiomers in all cases. The photolyzed solutions were also examined by chiral HPLC to confirm that each (−)-norbornadiene isomerizes to the corresponding (+)-quadricyclane. Quadricyclanes isomerizes to the corresponding norbornadienes if the irradiation wavelength is suitable [22]. We reported in our recent papers that (+)-**1b** isomerized to (−)-**1a** [10]. Thus, the stereochemical consequences of the photoconversion between enantiomeric norbornadiene and quadricyclane pairs are summarized in Scheme 4.

4. Conclusions

In search of photochemically reversible systems with high anisotropy (g) factors for NAAS by CPL, we synthesized and optically resolved a series of chiral 3-alkyl/aryl-norbornadiene-2-carboxylates and the relevant quadricyclanecarboxylates, and elucidated their chiroptical properties for the first time. Both of the norbornadienecarboxylates and quadricyclanecarboxylates prepared showed fairly strong CD bands ($\Delta\varepsilon_{max}$ = 20–30 $M^{-1}\,cm^{-1}$) and moderate to high anisotropy factors (g_{max} = 0.002–0.014) particularly for the lowest-energy transitions, for which the intramolecular C-T interaction involving the ester n, π^* transition is most probably responsible.

The photochemical conversions of the norbornadienecarboxylates to the corresponding quadricyclanecarboxylates proceeded quantitatively without accompanying any side reactions. The stereochemical consequence of the photoconversion between the norbornadiene and quadricyclane pairs was also revealed unambiguously by examining the CD spectral changes upon irradiation of the enantiopure norbornadiene reactants; thus (−)-norbornadienes are consistently correlated to (+)-quadricyclanes.

Such spectral, chiroptical, and photochemical features make these norbornadiene–quadricyclane pairs best suitable systems for the new absolute asymmetric synthesis using circularly polarized light, which we proposed recently [8–10].

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