triethylamine (0.1 mL) were added. Butyl (*Z*)-3-D-propenoate was added through a syringe. The vial was sealed, and the reaction mixture was stirred at ambient temperature for 17 h. The solvent was removed in vacuo, and the product was purified by filtration through a short plug of silica gel (diethyl ether) to afford butyl (*E*)-cinnamate (8.2 mg, 49 %). B.p. 280–284 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.99$ (3 H, t, $J = 7.3$ Hz; CH_3), 1.43 (2 H, m; CH_2), 1.72 (2 H, m; CH_2), 4.23 (2 H, t, $J = 6.7$ Hz; OCH_2), 6.48 (1 H, d, $J = 16$ Hz; H2), 7.40 (3 H, m; ArH), 7.53 (2 H, m; ArH), 7.77 (1 H, d, $J = 16$ Hz; H3); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 13.6$ (CH_3), 19.1 (CH_2), 30.6 (CH_2), 64.3 (OCH_2), 118.2 (C2), 127.9, 128.7, 130.1, 134.3, (Ar-C), 144.4 (C3), 167.0 (C1); UV/Vis: $\tilde{\nu}_{max}$ (MeOH) = 276 nm ($\varepsilon = 22\,000$); MS (CI +): *m*/*z* (%): 205 [MH^+].

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Enantiopure Double-Helical Alkynyl Cyclophanes

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Chiral π-conjugated molecules have been the subject of extensive investigation from the standpoints of structural chemistry and material science.[1] Double-helical molecules, in particular, are of great interest on account of their unique structural features as well as potential applications in optics and electronics. Several twisted alkynyl cyclophanes have been reported, but, unfortunately, they were obtained as racemates.[2, 3] To the best of our knowledge, only one nonracemic double-helical molecule has been prepared. Namely, a cyclophane was synthesized by connecting a (+)-2,15-diethynyl[6]helicene auxiliary with *ortho*-phenylene bridges.[4] However, this synthesis was rather lengthy, and only one enantiomer was obtained. Moreover, in the key coupling of the helicene with an *o*-diiodobenzene unit, the target molecule was obtained in less than 3 % yield. We report here on a rational synthesis and full characterization of double-helical alkynyl cyclophanes **1** of both enantiopure forms.[5]

The synthetic route is shown in Scheme 1. Separately (*R*)- and (*S*)-2,2′-diformyl-1,1′-binaphthyl (**2**)[6] underwent carbon–carbon coupling, and the resulting diethynyl compound **3** was converted to the monosilylethynyl derivative **4**. Exposure of this compound to an aryl iodide with the diethyltriazene function **5** afforded **6**. The triazene derivatives **6** were transformed into iodides **7** or desilylated to give **8**.[7] Sonogashira coupling[8] of **7** with **8** furnished **9**. After conversion of **9** to **11** via **10** through successive functional group transformations, intramolecular Sonogashira coupling provided the desired cyclophanes **1** in enantiopure form (Table 1). These compounds formed white needlelike crystals upon recrystallization, but none of them were suitable for X-ray analyses. Then, we prepared racemic **1b** by mixing equimolar amounts of (*R*,*P*)- and (*S*,*M*)-**1b**. Recrystallization of this mixture from CH_2Cl_2/hexane furnished crystals conducive to X-ray crystallographic analysis.[9]

As is evident from the ORTEP view depicted in Figure 1, the cyclophane skeleton is twisted, resulting in the double-helical motif. The C≡C bonds are slightly deformed from linearity. Notably, the two binaphthyl groups differ significantly in the dihedral angle defined by the naphthalene planes (68° and 78°, respectively). The space-filling model (Figure 2) indicates that the symmetrical structure places the inside hydrogen atoms of the phenylene rings very close to each other. The resulting ring strain is passed on unsymmetrically into the binaphthyl termini in the crystal.

In contrast to the solid-state molecular structure, ^{1}H and ^{13}C NMR spectra of **1** (Table 1) are compatible with a single

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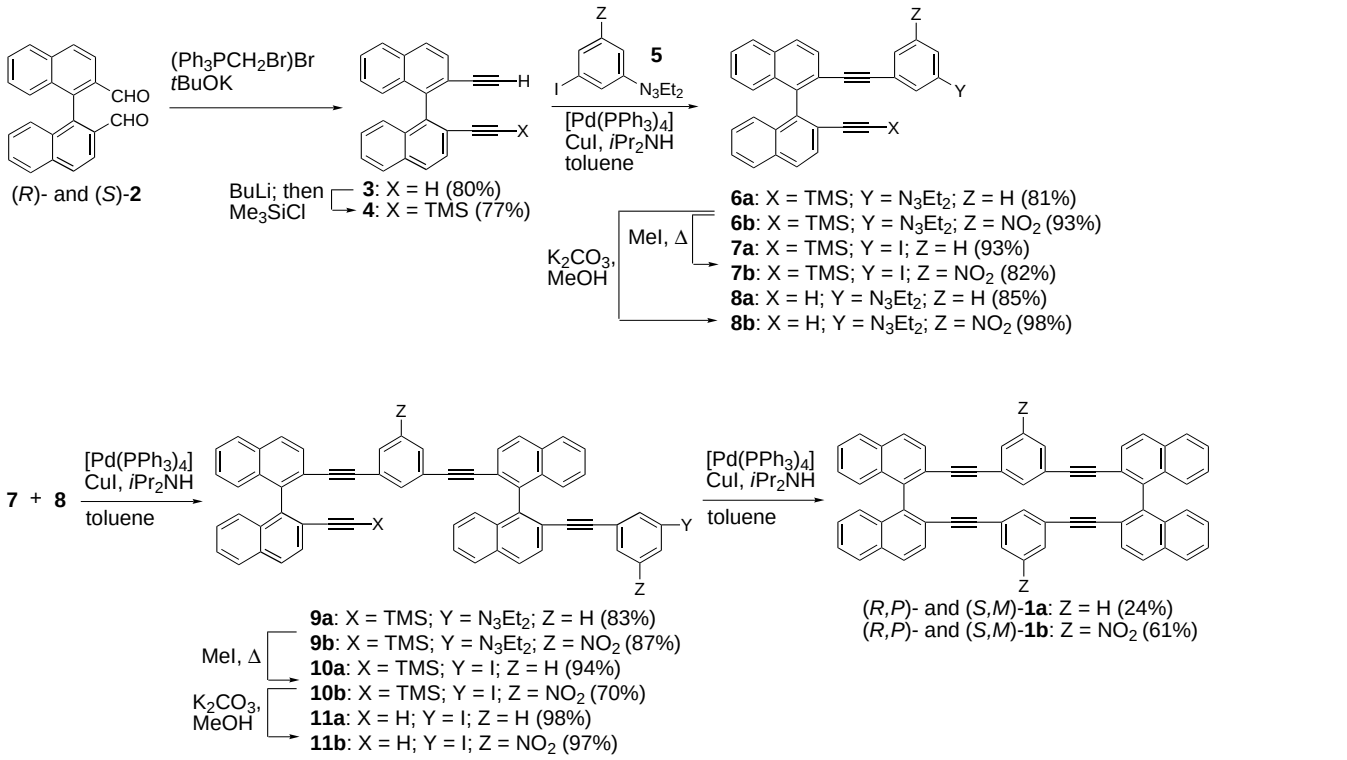

Scheme 1. Synthesis of **1**. TMS = trimethylsilyl.

Table 1. Selected physical data of compounds **1**.

1a: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.89-6.94$ (m, 6H), 7.05 (d, $J = 8.6$ Hz, 4H), 7.21 (t, $J = 7.0$ Hz, 4H), 7.42 (t, $J = 7.0$ Hz, 4H), 7.76 (d, $J = 8.6$ Hz, 4H), 7.86 (d, $J = 8.6$ Hz, 4H), 7.87 (d, $J = 8.6$ Hz, 4H), 7.92 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 90.4$, 92.1, 121.7, 123.6, 126.4, 126.7, 126.8, 128.1 (2C), 128.2, 129.2, 129.6, 132.7, 133.0, 136.9, 138.6; MS (positive-ion matrix-assisted laser desorption/ionization (MALDI)): $[M^+]$ calcd 752.25, found 752.3. (*R*) isomer: $[\alpha]_D^{29.6} = +690.4$ ($c = 1.0$ in $CHCl_3$); $[M]_D = +5198.2$; UV/Vis ($CHCl_3$, 2.7×10^{-6} M): λ_{max} (ε_{max}) = 240 (1.0×10^5), 255 (9.2×10^4), 278 (9.4×10^4), 302 nm (6.4×10^4); CD ($CHCl_3$, $c = 2.4 \times 10^{-6}$ M, 1.0-cm cell): 275 ($\theta = -13.5$, $\Delta\varepsilon = -171.4$), 301 nm ($\theta = 12.4$, $\Delta\varepsilon = 157.5$); solid-state CD (Nujol mull): 272 ($\theta = -13.9$), 301 nm ($\theta = 11.3$). (*S*) isomer: $[\alpha]_D^{29.2} = -713.2$ ($c = 0.89$ in $CHCl_3$); $[M]_D = -5369.3$; UV/Vis ($CHCl_3$, $c = 2.7 \times 10^{-6}$ M): λ_{max} (ε_{max}) = 240 (1.3×10^5), 254 (1.1×10^5), 278 (1.1×10^5), 303 nm (7.2×10^4); CD ($CHCl_3$, $c = 2.7 \times 10^{-6}$ M, 1.0-cm cell): 273 ($\theta = 19.3$, $\Delta\varepsilon = 220.1$), 300 nm ($\theta = -16.6$, $\Delta\varepsilon = -189.0$); solid-state CD (Nujol mull): 272 ($\theta = 13.4$), 301 nm (θ = -13.0)

1b: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.07$ (d, $J = 8.6$ Hz, 4H), 7.30 (t, $J = 7.5$ Hz, 4H), 7.52 (t, $J = 7.5$ Hz, 4H), 7.79 (d, $J = 8.6$ Hz, 4H), 7.83 (s, 4H), 7.96 (d, $J = 8.6$ Hz, 4H), 8.00 (d, $J = 8.6$ Hz, 4H), 8.04 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta =$ 89.5, 93.0, 120.3, 124.1, 125.2, 126.8, 127.0, 127.1, 128.2, 128.6, 128.7, 132.5, 133.2, 138.9, 141.7, 148.0; MS (electrospray ionization (ESI)): $[M^+]$ calcd 842.2, found 842.2. (*R*) isomer: $[\alpha]_D^{29.2} = +436.6$ ($c = 0.98$ in $CHCl_3$); $[M]_D = +3680.0$; UV/Vis ($CHCl_3$, $c = 2.4 \times 10^{-6}$ M): λ_{max} (ε_{max}) = 239 (1.3×10^5), 264 (1.1×10^5), 301 nm (6.4×10^5); CD ($CHCl_3$, $c = 2.7 \times 10^{-6}$ M, 1.0-cm cell): 254 ($\theta = -8.7$, $\Delta\varepsilon = -98.9$), 297 nm ($\theta = 6.7$, $\Delta\varepsilon = 76.7$); solid-state CD (Nujol mull): 242 ($\theta = -9.7$), 307 nm ($\theta = 3.2$). (*S*) isomer: $[\alpha]_D^{30.4} = -461.4$ ($c = 0.99$ in $CHCl_3$); $[M]_D = -3888.8$; UV/Vis ($CHCl_3$, 2.3×10^{-6} M): λ_{max} (ε_{max}) = 238 (1.2×10^5), 263 (1.1×10^5), 306 nm (6.7×10^4); CD ($CHCl_3$, $c = 1.2 \times 10^{-4}$ M, 0.2 mm cell): 255 ($\theta = 10.7$, $\Delta\varepsilon = 139.0$), 296 nm ($\theta = -7.6$, $\Delta\varepsilon = -98.6$)

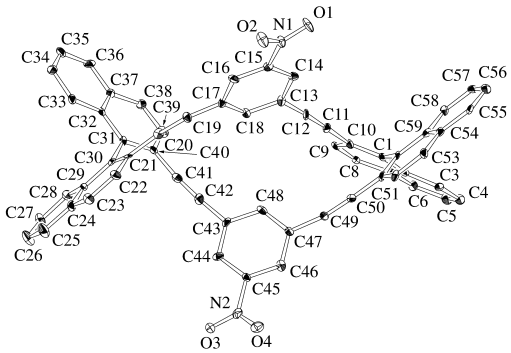

Figure 1. Structure of **1b** in crystals of **1b**·2 CH_2Cl_2; ellipsoids drawn at the 50% probability level. Hydrogen atoms and CH_2Cl_2 were omitted for clarity. Selected interatomic distances [Å] and angles[°]: C10-C11 1.446(8), C11-C12 1.229(8), C12-C13 1.427(8), C17-C19 1.423(8), C19-C20 1.239(9), C20-C21 1.423(8), C40-C41 1.441(9), C41-C42 1.199(9), C42-C43 1.427(9), C47-C49 1.431(8), C49-C50 1.220(8), C50-C51 1.430(8); C9-C10-C11 117.2(5), C10-C11-C12 176.2(6), C11-C12-C13 177.2(7), C12-C13-C14 120.6(5), C16-C17-C19 121.5(5), C17-C19-C20 170.4(6), C19-C20-C21 173.6(6), C20-C21-C22 118.0(6), C39-C40-C41 117.4(5), C40-C41-C42 174.5(6), C41-C42-C43 175.2(6), C42-C43-C44 120.7(5), C46-C47-C49 122.6(6), C47-C49-C50 170.5(6), C49-C50-C51 174.1(6), C50-C51-C52 116.3(5).

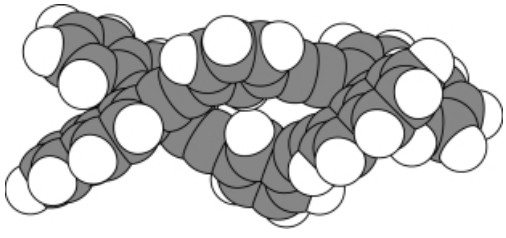

Figure 2. Space-filling model of double-helical cyclophane **1a**.

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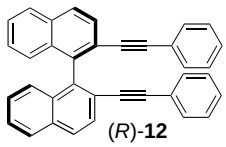
symmetrical species. With decreasing temperature, the ^{1}H NMR signals shift to lower field and broaden to some extent. No unsymmetrical patterns corresponding to the strained structure were observed, which is indicative of rapid fluctuation of the cyclophane frameworks in solution.


(*R*)-**12**

The chirality of **1** is reflected unambiguously by its optical properties. The $[\alpha]_D$ values of these compounds are totally different from that of the simple binaphthyldiyne **12** (Table 2). Upon formation of cyclic arylene – ethynylene skeletons, the sign of the optical rotation reverses and the absolute magnitude increases significantly. As expected, the circular dichroism (CD) spectra of the enantiomers of **1** are opposite in sign but equal in magnitude, and their profiles differ significantly from that of **12** (Figure 3a). The strong Cotton effect in **12** with a zero-point at 320 nm is not observed for **1**, rather a new Cotton effect with a zero-point at 283 nm is observed. The Cotton effect induced in **12** by the ethynylated binaphthyl chromophore is apparently overcompensated in **1** by the double-helix formation. This finds strong support from CD spectra in the solid state (Figure 3b).[10] The analogous profiles observed in the spectra given in Figure 3 imply no essential structural alteration in solution.

Table 2. Optical properties of **1** and a model compound.

Compound	$[\alpha]_D$	*c* [g per 100 mL]	*T* [°C]
(*R*)-**12**	− 6.91	1.01 ($CHCl_3$)	30.5
(*R*,*P*)-**1a**	+ 690.42	0.995 ($CHCl_3$)	29.7
(*S*,*M*)-**1a**	− 713.15	0.89 ($CHCl_3$)	29.2
(*R*,*P*)-**1b**	+ 436.59	0.98 ($CHCl_3$)	29.2
(*S*,*M*)-**1b**	− 461.36	0.99 ($CHCl_3$)	30.4

We have synthesized unique double-helical alkynyl cyclophanes in enantiopure form and have performed the first successful X-ray crystallographic analysis of this type of compound. Access to both enantiomers allowed full characterization of the chiral double-helical arylene – ethynylene moiety by CD spectra. The utility of solid-state CD spectroscopy is particulary noteworthy. The agreement between solution and solid-state spectra indicates that virtually the same structure occurs both in solution and in the solid state. Thus, once the crystal structure is available, the structure of the nonracemic molecule in solution can be unambiguously elucidated by comparison of CD spectra in both states.

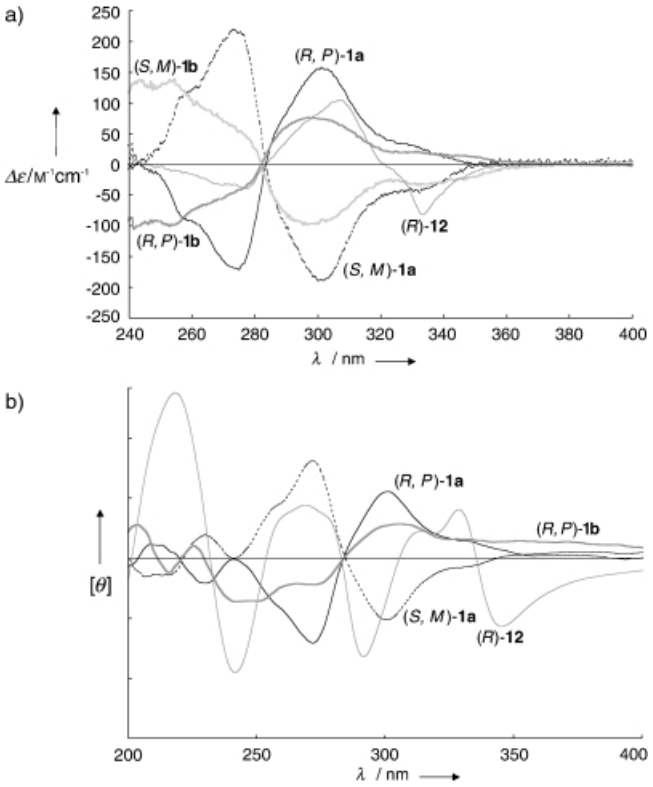


Figure 3. CD spectra of **1a**, **1b**, and **12** a) in $CHCl_3$, b) in Nujol mull.

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