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Stereochemistry of a cubane-like photodimer of methyl 2-naphthoate

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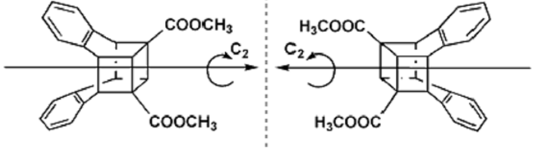
Abstract—A novel type of C_2-symmetric-chiral ligand, based on a cubane-like photodimer **1** of methyl 2-naphthoate, is reported in this work. Crystal analysis reveals that the methyl carboxylate functionality is in an *anti*-head-to-head conformation and **1** is highly rigid. The optically pure enantiomers of **1** can be obtained simply by HPLC resolution.

Photodimers of aromatic compounds have been known for over a century, but the first report of the isolation of a photodimer in the naphthalene series appeared only in 1963.[1] Since then photodimers have been obtained from several naphthalene derivatives.[2–11] Sasse's group[2–4] and our group[5–11] have established that irradiation of alkyl 2-naphthoate results in a 'cubane-like' *anti*-head-to-head photodimer as the unique product, although six isomeric dimers are formally possible. The selectivity originates from the fact that the photodimerization occurs only between the substituted rings, and the substitutes are in the head-to-tail orientation. Generally, the formation of a cubane-like photodimer of alkyl 2-naphthoate includes a two-step process.[4,11]

These photodimers were discovered 40 years ago,[1] but until now no detailed information is available with respect to their stereochemistry. At the same time, close inspection revealed that **1** has a C_2 axis (Scheme 1). Compound **1** and its mirror image cannot overlap with each other, implying **1** should possess chirality. In this letter, we report the chirality of C_2-symmetric photodimer **1** for the first time. The racemic mixture of **1** can be successfully resolved into its optically pure enantiomers by HPLC.

Irradiation of methyl 2-naphthoate[13] in degassed cyclohexane solution with a light wavelength longer than 280 nm for 8 h can produce photodimer **1**. Compound **1** was isolated by chromatographic column on silica eluted with petroleum ether/diethyl ether (10/1 in volume), followed by dichloromethane. Evaporation of the solvent afforded a white precipitate, which was further recrystallized from acetone to give a cubane-like photodimer **1** with 95% yield, based on the consumption of the starting material. The identity of **1** was confirmed by the ^{1}H NMR, MS (ESI) spectroscopies,[14] and the crystal structure analysis as well.[15]

Previously, the structure proposed for the 'cubane-like' photodimer mainly relied on its spectroscopic data.[2–11] In this work, we obtained the single crystal of **1**. The X-ray crystal structure analysis has confirmed the 'cubane-like' structure shown in Figure 1. Single crystals of **1** were obtained by recrystallization of **1** from acetone solution. A colorless single cuboid crystal with dimensions $0.20 \times 0.16 \times 0.14$ mm^3 was used for data



Scheme 1. The structure of *anti*-head-to-head photodimer **1**.

Keywords: Stereochemistry; C_2-symmetric ligand; Cubane-like photodimer; Methyl 2-naphthoate.

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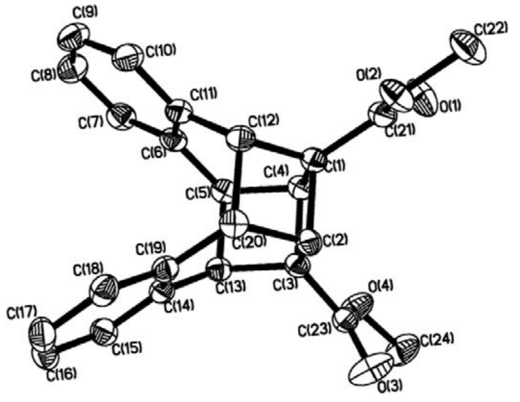

Figure 1. Perspective drawing of photodimer **1** with atomic numbering.

collection at 293 K on a Bruker Smart 1000 X-ray diffractometer. The molecular structure and perspective drawing of **1** are depicted in Figure 1. The crystal belongs to the orthorhombic crystal system of Pbca space group with unit cell parameters of $a = 11.9184(14)$ Å, $b = 16.992(2)$ Å, $c = 18.083(2)$ Å; $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$. The cubane-like structure was formed by the bonding of C_1, C_4, C_5, and C_{12} to C_2, C_3, C_{13}, and C_{20}, respectively. The dihedral angle formed by the aromatic rings is 73°, and torsion angles C_{21}–C_1–C_2–C_3 and C_{23}–C_3–C_4–C_1 are opened out to about 120°. As can be seen from Figure 1, the methyl carboxylate functionality is in an *anti*-head-to-head conformation, and the cubane-like photodimer **1** is highly rigid. The bond lengths in Table 1 are obtained by imposing the C_2 molecular axis of symmetry presented in **1**.

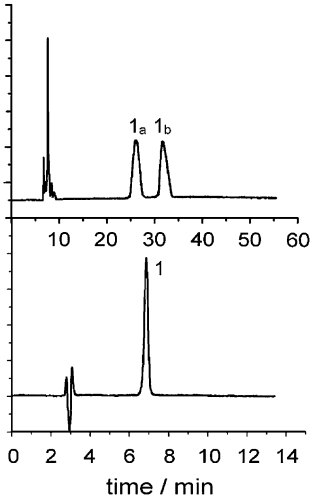

Figure 2. Typical HPLC chromatogram of **1** with chiralcel OT(+) column (top) and achiral HiQ sil C18V column (bottom), respectively.

It is of significance that the isolated racemic mixture of **1** can be successfully resolved, for the first time, into its optically pure enantiomers (first eluting $\mathbf{1_a}$ and second eluting $\mathbf{1_b}$) simply by high-performance liquid chromatography. The resolution was carried out with a JASCO-UV-1570 apparatus on a chiralcel OT(+), chiralcel OJ-H, chiralcel OJ-RH, and achiral HiQ sil C18V columns, respectively. The enantiomeric separation was performed by HPLC with the same apparatus on a chiralcel OJ-H semi-preparative column (Daicel Chemical Industries, Ltd., 10 × 250 mm; eluent: *n*-hexane/isopropyl alcohol = 9:1; at 20 °C; flow rate 1.0 ml/min; UV detection at 260 nm). The obtained fractions were analyzed by HPLC on a chiralcel OT(+) column (Daicel Chemical Industries, Ltd., 4.6 × 250 mm; eluent: *n*-hexane/2-propanol = 8:2; at 10 °C; flow rate 0.5 ml/min; UV detection at 260 nm).

Table 1. Important bond distance (Å) and angles (°) for photodimer **1**

Bond distance (Å)		Bond angle (°)	
C(1)–C(2)	1.574(3)	C(6)–C(5)–C(13)	117.97(17)
C(3)–C(4)	1.560(3)	C(4)–C(1)–C(12)	114.91(17)
C(5)–C(13)	1.589(3)	C(3)–C(2)–C(20)	115.95(17)
C(12)–C(20)	1.585(3)	C(21)–C(1)–C(2)	120.79(18)
C(13)–C(14)	1.494(3)	C(23)–C(3)–C(4)	123.39(18)
C(11)–C(12)	1.492(3)	C(21)–C(1)–C(2)–C(3)	120.3(2)
C(5)–C(6)	1.498(3)	C(23)–C(3)–C(4)–C(1)	−121.3(2)
C(19)–C(20)	1.495(3)	C(13)–C(5)–C(6)–C(11)	73.8(3)
		C(6)–C(11)–C(12)–C(20)	−71.7(3)

The chromatogram shows only one product peak when the reaction mixture is analyzed by HPLC using an achiral HiQ sil C18V column (Fig. 2). The optically pure enantiomers $\mathbf{1_a}$ ($[\alpha]_D^{20}$ −42.6 (*c* 0.23, CH_3OH)) and $\mathbf{1_b}$ ($[\alpha]_D^{20}$ +42.6 (*c* 0.12, CH_3OH))[16] were confirmed by analytical HPLC on a chiralcel OT(+) column.

The UV–vis absorption spectrum of **1** gives characteristic absorption bands centered at 225 nm and 265 nm in methanol solution, which are assigned to the E_2 transition and B transition of phenyl group, respectively. As expected, UV–vis absorption profiles of $\mathbf{1_a}$ and $\mathbf{1_b}$ are not distinguishable from each other and are the same as the spectrum of their racemic mixture. However, in the case of circular dichroism (CD) spectra[17] (Fig. 3),

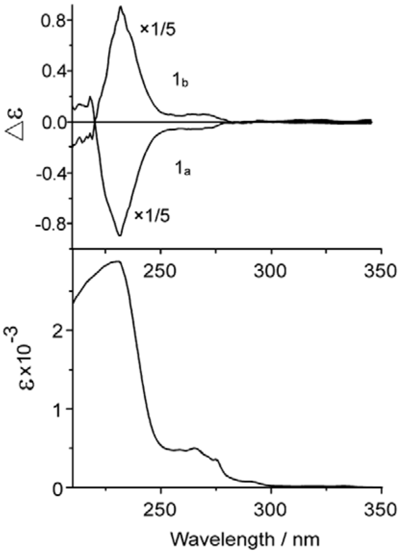

Figure 3. The circular dichroism (top) and absorption (bottom) spectra of enantiomers $\mathbf{1_a}$, $\mathbf{1_b}$ in methanol, respectively: $\mathbf{1_a}$ (4.4×10^{-4} M), $\mathbf{1_b}$ (4.2×10^{-4} M).

the two isolated enantiomers in methanol solution show near mirror image behavior, indicating opposite ground-state chirality and their enantiomeric relation.[12]

In summary, the chirality of C_2-symmetric **1** has been realized in this work and, for the first time, a racemic mixture of cubane-like photodimer **1** has been successfully resolved to yield the optical pure enantiomers $\mathbf{1_a}$ and $\mathbf{1_b}$. This new member of C_2-symmetric ligand, prepared by photochemical approach, will provide a potential backbone for chiral ligands and synthetic materials.

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Supplementary data

X-ray crystallographic data of photodimer **1**(CIF). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.04.112.

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13. Note: All the solvents were of gradient HPLC grade. Cyclohexane was dried before use. The identity of methyl 2-naphthoate was confirmed by ^{1}H NMR spectroscopy and MS spectroscopy; ^{1}H NMR ($CDCl_3$, ppm): 8.62 (s, 1H), 7.85–8.10 (m, 4H), 7.50–7.62 (m, 2H), 3.99 (s, 3H); MS-EI (M^+) 186.
14. Note: Irradiation of methyl 2-naphthoate in degassed cyclohexane solution with $\lambda > 280$ nm for 8 h can produce photodimer **1** in 95% yield, based on the consumption of the starting material. ^{1}H NMR spectroscopy of **1** (DMSO-d_6, ppm): 6.97–6.99 (m, 8H), 4.36–4.45 (m, 4H), 3.67 (s, 6H), 3.64 (d, 2H). MS-ESI (M^+) 372.
15. Note: X-ray analysis was performed on a Bruker Smart 1000 X-ray diffractometer. Crystallographic data for the structure of **1** have been deposited with Cambridge Crystallographic Data Center as a supplementary publication No. CCDC 281057.
16. Note: The values of specific rotation were measured on Perkin Elmer 341LC polarimeter.
17. Note: Circular dichroism spectrum was carried out on JASCO J-810 spectropolarimeter.