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Synthesis and chiroptical properties of enantiopure tricyclo[4.3.0.0^{3,8}]nonane-4,5-dione (twistbrendanedione)

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Abstract—The synthesis of chiral tricyclo[4.3.0.0^{3,8}]nonane-4,5-dione was accomplished starting from enantiomerically pure (+)-(1*S*,5*S*)-bicyclo[3.3.1]nonane-2,6-dione **1**. Ring contraction of the latter with thallium(III) nitrate proceeded with high stereoselectivity giving exclusively methyl (+)-(1*S*,4*S*)-(+)-*exo*,*exo*-bicyclo[2.2.1]heptan-2,5-dicarboxylate **2**. Inversion of the configuration of this diester to the required di-*endo* derivative was realized via the following reaction sequence. Bromination of the corresponding acid dichloroanhydride and subsequent reduction with zinc in acetic acid gave a diastereoisomeric mixture of esters, from which the *endo*,*endo*-ester **5** was isolated by column chromatography. Acyloin condensation of the latter with trimethylchlorosilane in toluene led to intramolecular ring closure, and subsequent oxidation of the enol silyl ether **7** in situ gave tricyclo[4.3.0.0^{3,8}]nonane-4,5-dione **8**. The chiroptical properties of this cage molecule were studied by electronic and vibrational circular dichroism spectroscopy. The (1*R*,3*R*,6*R*,8*R*) absolute configuration of the title structure was also unambiguously proved.

1. Introduction

Study of chiroptical phenomena in ketones gives insight into modes of interaction between the carbonyl group and perturbing substituents. Many examples of successful applications of the octant rule used to account for the Cotton effect (CE) observed in the electronic circular dichroism spectra are found in the literature.[1] A special case is chiral 1,2-diketones for which no clear rule is available. Only a few examples of the circular dichroism study in such systems are available[2] and the CE is difficult to predict since low energy n-π* transition above 350 nm is controlled by the both diketone chirality alone and adjacent substituents. Thus, 1,2-diketones with appropriate location of carbonyl groups in the molecule are of interest for chiroptical studies. Herein, the synthesis of chiral tricyclo[4.3.0.0^{3,8}]nonane-4,5-dione (twistbrendanedione), an α-diketone structure, was accomplished, and the chiroptical properties of this structure were studied by electronic (ECD) and vibrational circular dichroism (VCD) spectroscopy.

2. Results and discussion

2.1. Synthesis

Regarding the foregoing we considered that the synthesis of the chiral cage α-diketone structure, tricyclo-[4.3.0.0^{3,8}]nonane-4,5-dione **8** (twistbrendanedione) would afford a suitable model for the study of chiroptical properties of α-diketones. Although derivatives of this cage molecule have been synthesized,[3] it should be noted that only the synthesis of the monocarbonyl derivative has been reported.[3c] Thus, the synthesis of the α-dicarbonyl derivative of twistbrendane was elaborated based on transformation of (+)-(1*S*,5*S*)-bicyclo-[3.3.1]nonane-2,6-dione **1** (Scheme 1), which was obtained by kinetic resolution of the corresponding racemic diketone using baker's yeast according to a procedure described in the literature.[4] Oxidation of 1 mol of (+)-diketone **1** with 2 mol of thallium(III)nitrate (TTN) in methanol proceeded with oxidative rearrangement[5] and exclusively afforded methyl (+)-*exo*,*exo*-bicyclo[2.2.1]heptan-2,5-dicarboxylate **2** in good yield (85%). Analysis of the ^{1}H and ^{13}C NMR spectra of (+)-**2** proved the structure of the ring con-

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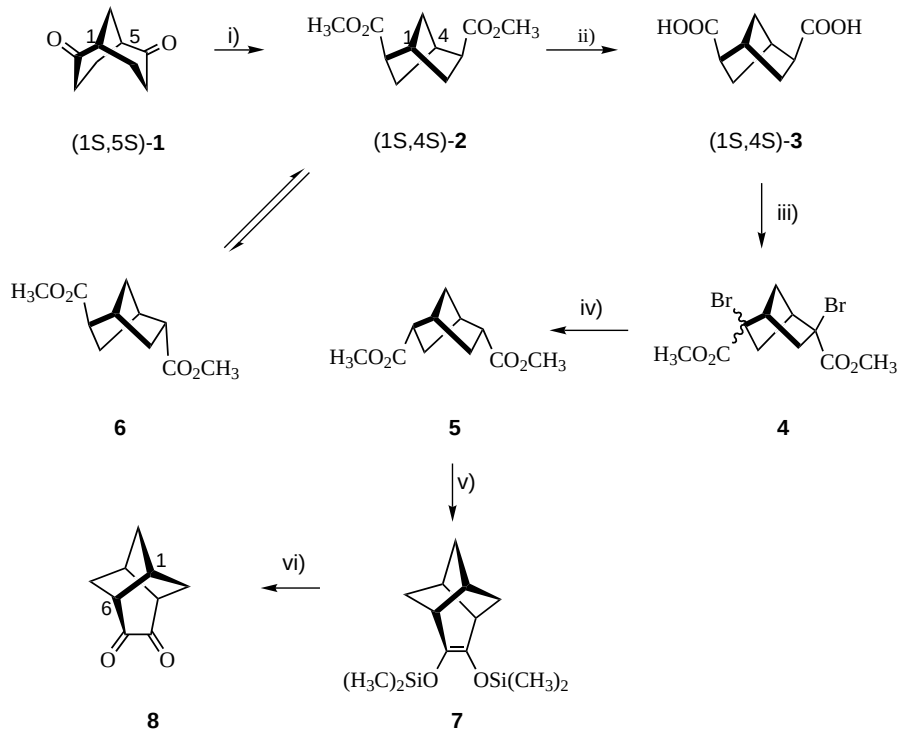

Scheme 1. *Reagents*: (i) $Tl(NO_3)_3$, CH_3OH; (ii) H^+/H_2O; (iii) $SOCl_2$, Br_2; (iv) Zn, AcOH; (v) $(CH_3)_3SiCl$, Na; (vi) Br_2/CCl_4.

traction product. The spin–spin coupling constants $^3J_{H2endoH3endo}$ and $^3J_{H2endoH3exo}$ are 9.0 and 5.5 Hz, respectively, and correspond to the calculated values by the Karplus equation, i.e. 10.8 and 6.1 Hz. Five carbon atom signals at 33.5, 34.2, 40.2, 45.2 and 51.3 were assigned to C-3(6), C-7, C-1(4), C-2(5) and the CH_3 group, respectively. The high stereoselectivity of this conversion is in accordance with earlier observations in the stereoselectivities of bicyclo[3.2.1]octan-2-one[6] and other ring contraction reactions of bicyclic ketones,[7] and agree with the general reaction mechanism proposed by McKillop.[8]

The *endo*,*endo*-diester was required to give the target tricyclic structure upon ring closure. An attempt to obtain the requested diastereoisomer by epimerization of **2** with sodium methoxide in methanol gave a mixture consisting of initial *exo*,*exo*-**2** and *exo*,*endo*-**6** diastereoisomers in the ratio 85:15. Calculations by semiempirical PM3 methods proved that the di-*exo* diastereoisomer is thermodynamically more stable by 2.2 kcal/mol compared to di-*endo* diastereoisomer. The successful inversion of configuration of diester (+)-**2** involved a reaction of the latter with thionyl chloride, subsequent addition of bromine and the esterification with methanol to yield a mixture of diastereoisomeric α-bromo methyl esters **4**. Reduction of bromine with zinc in acetic acid afforded a mixture of esters **5** and **6**. The predominance of the di-*endo* ester (+)-**5** in the mixture as shown by GC–MS analysis and the spin–spin coupling constants in the ^1H NMR spectrum. The latter diastereoisomer (+)-**5** was isolated by the column chromatography. The chemical shifts at 26.8, 40.3, 41.0, 45.5 and 51.3 in the ^{13}C NMR spectrum are strongly indicative of this di-*endo*-structure. The signals were assigned to C-3(6), C-1(4), C-7, C-2(5) and the CH_3 group, respectively. These values were calculated by the additivity scheme considering chemical shifts of bicyclo[2.2.1]heptane and the corresponding methyl esters of respective *exo*- and *endo*-bicyclo[2.2.1]heptane-2-carboxylic acids[9] and also by using ACDLabs software.[10] The enantiomerically pure *endo*,*endo*-diester (+)-(1*S*,4*S*)-**5** was used for synthesis of the target twistbrendanedione. Acyloin condensation of the *endo*,*endo*-diester **5** with trimethylchlorosilane in toluene led to the intramolecular ring closure to give enol silyl ether **7**. Oxidation of the enol silyl ether in situ with bromine gave (+)-tricyclo[4.3.0.$0^{3,8}$]nonane-4,5-dione **8**. The splitting of the carbonyl groups absorption at 1760 and 1743 cm^{-1} is observed in the IR spectrum of **8**. Three groups of proton signals and five distinct carbon atoms in the ^1H NMR and in the ^{13}C NMR spectra, respectively, are observed for **8**. The ^{13}C shifts at 36.4, 39.2, 41.1, 45.8 and 202.2 ppm correspond with the C_2 symmetry of the tricyclic structure **8**.

2.2. Chiroptical studies by ECD and VCD

In this work, the ECD and VCD spectroscopy was applied to study chiroptical properties of the diketone (+)-**8**. A complex ECD spectrum with a positive band below 235 nm, a negative band centered at 280 nm, and the positive band at 420 nm was observed for **8** (Fig. 1). The sign of the CE in the molecule (+)-**8** is determined by two carbonyl chromophores in this chiral structure. The contributions from two chromophores are assumed

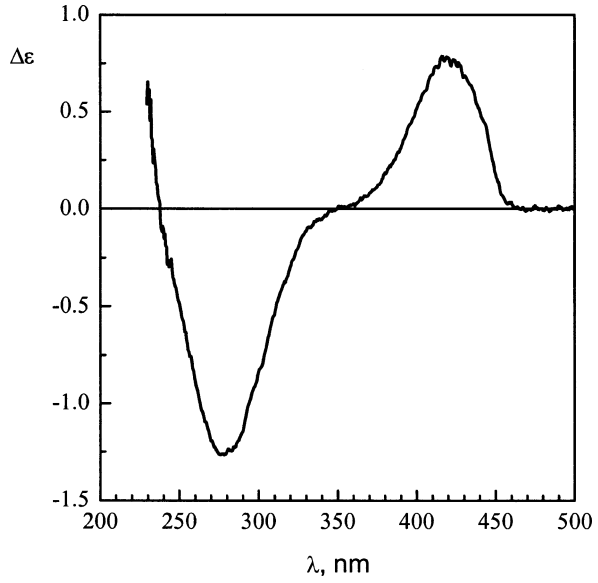

Figure 1. Experimental ECD spectrum of (+)-**8** in $CHCl_3$ ($c=7.8\times10^{-3}$ mol L^{-1}): λ_{max} ($\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1}) <235 (positive), 279 (−1.26), 419 (+0.78).

to be additive; however, the way in which different parts of a molecule interact to generate the resulting sign and magnitude of the CE is still debated. It was suggested that the sign of the long-wavelength CE for the planar α-diketone and related chromophores could be predicted by the antioctant sector rule.[2c]

Thus, the ECD of (+)-**8** spectrum exhibited the two low energy n-π* CD bands, one below 300 nm and the other above 400 nm as for other 1,2-diketones. This is a result of coupling and splitting of two n-π* transitions. The relevant band at 420 nm arises from the interaction of two carbonyl chromophores. The twisting of the HOMO of this molecule is shown in Fig. 3, where the angle between chromophores is approximately 17°. The relation of the helicity of the chromophores in 1,2-diketones has been considered.[11] In case of structure **8** the chirality of this 1,2-dione is right-handed when the CE sign of the n-π* transition above 400 nm is negative. Thus, following the above-mentioned relationship the 1*S*,3*S*,6*S*,8*S*-configuration should be assigned to (+)-**8**, which is in disagreement with the configuration assigned by chemical correlation. Consequently, this example demonstrates that semi-empirical rules should be employed very cautiously.

The absolute configuration of compound (+)-**8** was confirmed using VCD[12] spectroscopy. The commercial availability of the VCD technique in the last five years balanced the previous advantage of the more widespread ECD spectroscopy. VCD, which represents the application of circular dichroism to the vibrational transitions, has good theoretical background, which enables the assignment of the intensity features to individual vibration modes and, in the case of characteristic vibrations, to atoms of functional groups. Ab initio calculations of VCD spectra and the assignment of experimental VCD bands and their comparison with experimental spectra has been used for the determination of absolute configuration of small[13] as well as large[14] biomolecules.

Comparison of the experimental VCD and infrared absorption spectra of (+)-**8** with their corresponding simulations, which are based on ab initio calculations, are shown in Fig. 2. The optimized geometry used for ab initio calculation is shown in Fig. 3. Very good agreement for the signs as well as positions of the VCD patterns between experimental and simulated spectra clearly confirms the 1*R*,3*R*,6*R*,8*R*-configuration of the compound presented in Fig. 3. In addition, convincing agreement between experimental and calculated spectra enables the detailed assignment of vibrational bands (Table 1), which are based on the dynamic visualization of individual vibrational modes. A detailed inspection of Fig. 2 shows the advantage of VCD spectra: the existence of +/− signs causes better resolution of VCD bands as compared with IR absorption.

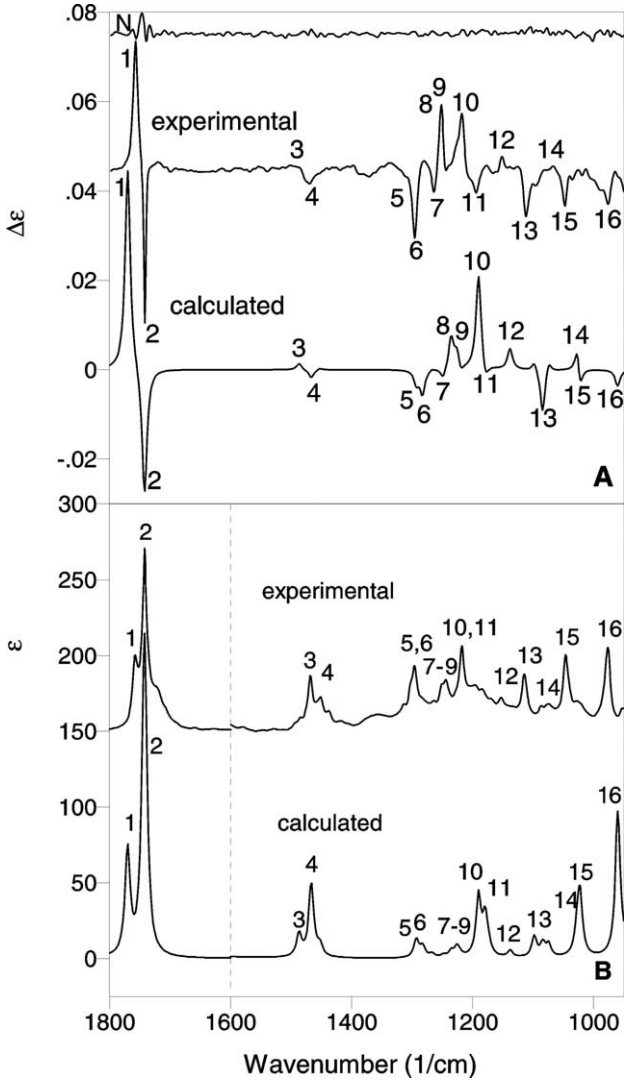

Figure 2. Experimental and calculated VCD (A), and absorption (B) spectra of (+)-**8**, noise spectrum (N). The intensity of the absorption spectra in the region 1800–1600 cm^{-1} is divided by 4.

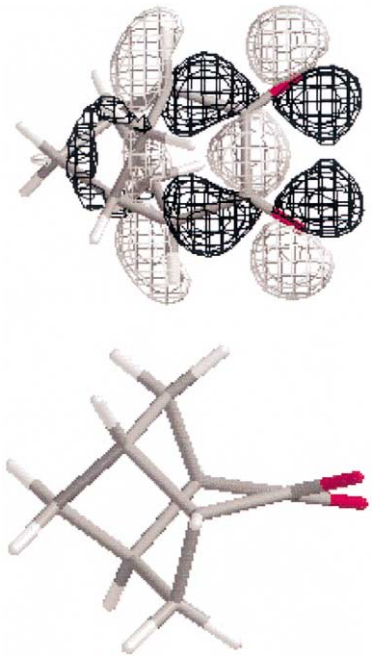

Figure 3. HOMO (top) and optimized geometry of (+)-**8** used for ab initio calculation.

Table 1. Assignment of VCD and absorption bands in the mid IR region, the mode labels are the same as in Fig. 2

Mode	VCD and absorption frequencies (cm^{-1})		Assignment
	Calculated	Experimental	
1	1771.2	1758	C=O of phase
2	1743.3	1743	C=O in phase
3	1487.6	1492	CH_2 scissoring
4	1467.5	1470	CH_2 scissoring
5	1293.7	1310	CH_2 wagging
6	1283.5	1295	CH_2 wagging
7	1249.5	1264	CH_2 wagging
8	1235.8	1255	CH_2 wagging
9	1226.3	1251	CH bend
10	1190.7	1218	C(O)–C(O) stretch
11	1179.8	1194	C–C stretch
12	1138.6	1153	CH_2 wagging
13	1084.6	1113	C–C stretch
14	1027.3	1064	CH bend
15	1022.8	1047	C(O)–C(O) stretch
16	960.2	977	C(O)–C(O) stretch

3. Conclusions

The synthesis of chiral (+)-tricyclo[4.3.0.0^{3,8}]nonane-4,5-dione was accomplished from enantiomerically pure (+)-(1*S*,5*S*)-bicyclo[3.3.1]nonane-2,6-dione. The chiroptical properties of this cage molecule were studied by ECD and VCD spectroscopy and the 1*R*,3*R*,6*R*,8*R* absolute configuration of the structure was proved.

4. Experimental and computations

Melting and boiling points are uncorrected. IR spectra were recorded in KBr pellets on a Perkin–Elmer Spectrum BX spectrometer. ^{1}H NMR spectra were recorded on Bruker (200 MHz) and Tesla BS-587A instruments in deuterated chloroform unless otherwise stated and are reported as chemical shifts (δ) in ppm relative to $(CH_3)_4Si$. Mass spectra were run by GC–MS on a Hewlett–Packard 6980 instrument with mass selective detector HP 5973 using Supelcowax capillary column (30 m×0.25 mm). GLC analysis was carried out on a Varian 3700 instrument (FID) by using 30 m long column (9% silicon on Chromosorb W-AW). A Perkin–Elmer Autosystem GC equipped with split/splitless injector and flame ionization detector was used for analytical separation on BetaDex 120 fused silica capillary column. The ECD spectra were recorded with a Jobin Yvon Mark V spectrometer at 20°C in a 0.1 cm cell using chloroform as a solvent ($c=7.8\times10^{-3}$ mol L^{-1}). Optical rotations were measured in a 10 cm cell on a polarimeter Polamat-A (Carl Zeiss) at 546 nm. Thin-layer chromatography was carried out on Kieselgel 60 F_{254} (Merck) sheets coated with silica gel and silica gel Kieselgel 60 (0.040–0.063 mm, Merck) was used for column chromatography. The VCD and infrared absorption spectra were measured at a resolution of 4 cm^{-1} using a Bruker FT-IR IFS 66/S spectrometer equipped with the VCD/IRRAS module PMA 37 as described in detail elsewhere.[15] The $CDCl_3$ solutions of samples were placed in a demountable cell A145 (Bruker, Germany) constructed from KBr windows separated by a 0.1 mm Teflon spacer. VCD spectra were obtained as an average of three blocks, each measured for 0.5 h as co-addition of 3320 interferometric scans. The VCD baseline was obtained as a spectrum of pure solvent. The noise spectra were calculated as a half of the difference between two blocks of scans. The concentration used for VCD measurements was 0.5 mol L^{-1}. Because of significantly higher molar absorptivity in carbonyl region (1800–1600 cm^{-1}), which is not favorable for VCD measurements, the carbonyl VCD pattern was proved also by measurements of solution with concentration of 0.1 mol L^{-1}.

A simulation of the VCD intensities based on the Gaussian program package[16] was performed for geometries optimized with the aid of the conformer searching routine implemented in the Spartan program.[17] Vibrational frequencies and intensities were calculated at the BPW91/6-31+G** DFT[18] level at the harmonic approximation using the MFP/GIAO theory[19] for VCD. Spectra were simulated using Lorentzian profiles with the 5 cm^{-1} bandwidth. Normal mode assignment is based on a visual inspection of the dynamic displacements.

4.1. (+)-(1*S*,5*S*)-Bicyclo[3.3.1]nonane-2,6-dione 1

Baker's yeast (6.0 g) and saccharose (72 g) were suspended in water (140 mL). Racemic bicyclo-[3.3.1]nonane-2,6-dione **2** (3 g) was added after 30 min and the mixture was stirred for 6 days. The yeast

was removed after centrifugation of the mixture and the products were isolated by continuous extraction with ether. The mixture of products was dissolved in dichloromethane and the butanedioic acid formed during the metabolism of yeast was filtered off. Column chromatography of the product with petrol ether–ethyl acetate (2:1) afforded (+)-**1** (1.75 g, 24%) with e.e. 93%, hydroxyketone (3.4 g), and diol (0.36 g). (+)-**1**: $[\alpha]_{546}^{18}$ +204.0 (dioxane, *c* 0.05) (lit.:[4] $[\alpha]_D$ +203.8 (dioxane), e.e. 93%).

4.2. (+)-(1*R*,2*S*,4*R*,5*S*)-*exo*,*exo*-Dimethylbicyclo[2.2.1]-heptan-2,5-dicarboxylate 2

A solution of (+)-**1** (1.75 g, 11.5 mmol) in anhydrous methanol (110 mL) was treated with a solution of TTN (9.1 g, 23.2 mmol) in methanol (60 mL). The reaction mixture was stirred for 16 h and the solid was filtered off. The major volume of methanol was evaporated and the residue was treated with acidified water (3 mL of HCl in 70 mL of H_2O). The resulting mixture was extracted with chloroform (3×70 mL). The solvent was evaporated and the residue distilled in vacuo yielding diester **2** (2.1 g, 85%), bp = 119–120°C/4 mmHg, n_D^{20} = 1.4760; $[\alpha]_{546}^{16}$ +40.0 ($CHCl_3$, *c* 0.1); IR ν_{max}/cm^{-1} 1728, 730; ^1H NMR: δ 1.40 (2H, m, C_7-H), 1.48 (2H, d, J = 9.0 Hz, $C_3(C_6)$-H_{endo}), 1.70–1.98 (2H, m, $C_3(C_6)$-H_{exo}), 2.1–2.28 (2H, dd, J = 5.5 and 9.0 Hz, $C_2(C_5)$-H), 2.45 (2H, d, J = 4 Hz, $C_1(C_4)$-H), 3.52 (6H, s, CH_3); ^{13}C NMR: δ 33.5, 34.2, 40.2, 45.2, 51.3, 175.7 (C=O), (all skeletal C). MS (relative intensity) *m*/*z* 212 (19), 180 (15), 152 (14), 120 (9), 86 (100). Anal. calcd for $C_{11}H_{14}O_4$: C, 62.26; H, 7.60. Found: C, 61.95; H, 7.56%.

4.3. Epimerization of (+)-*exo*,*exo*-dimethylbicyclo-[2.2.1]heptan-2,5-dicarboxylate

To a solution of (+)-**2** (0.3 g, 12.4 mmol) in anhydrous methanol (0.5 mL) was added sodium methoxide (0.15 g, 18.5 mmol) and the mixture was heated in sealed tube at 100–105°C for 40 h. The reaction mixture was cooled, the contents of the tube dissolved in water (5 mL) and extracted with ether (3×5 mL). The extracts were combined, washed with water and dried over Na_2SO_4, solvent evaporated and the residue distilled in vacuo (bp 119–120°C/4 mmHg) to yield a mixture of esters (0.28 g), consisting according to GC–MS of *exo*,*exo*- and *exo*,*endo*-isomers in ratio 85:15.

4.4. (+)-(1*R*,2*S*,4*R*,5*S*)-*exo*,*exo*-Bicyclo[2.2.1]heptan-2,5-dicarboxylic acid 3

A solution of (+)-**2** (1.7 g, 9 mmol) in dilute (1:1) hydrochloric acid (60 mL) was heated under reflux for 3 h. The reaction mixture was evaporated till dryness. The solid was recrystallized from ethanol–benzene yielding diacid **3** (1.4 g, 95%), mp 228–230°C; $[\alpha]_{546}^{16}$ +44.0 (C_2H_5OH, *c* 0.043); IR ν_{max}/cm^{-1} 1705, 3200 (br); ^1H NMR (CD_3OD) δ 1.33 (2H, s), 1.43 (2H, m, C_3 (C_6)-H_{endo}), 1. 81 (2H, m, C_3 (C_6)-H_{exo}), 2.26 (2H, m, C_2 (C_5)-H); 2.46 (2H, m, $C_1(C_4)$-H); ^{13}C NMR: δ 34.7, 35.4, 41.9, 179.1 (C=O), (all skeletal C). Anal. calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.72; H, 6.66%.

4.5. (+)-(1*R*,2*R*,4*R*,5*R*)-Dimethyl-*endo*,*endo*- and *endo*,*exo*-bicyclo[2.2.1]heptan-2,5-dicarboxylates 5 and 6

A mixture of dicarboxylic acid (1.26 g, 6.7 mmol) (+)-**3** and thionyl chloride (7 mL, 9.5 mmol) was heated under reflux for 2 h and then bromine (5.16 g, 32 mmol) was added. The reaction mixture was heated under reflux for 3 days. To a cooled reaction mixture, benzene (15 mL) was added and the mixture was evaporated in vacuo. The solid residue (2.25 g) was dissolved in anhydrous methanol (35 mL) and heated under reflux for 6 h. The solvent was evaporated and to the residue dissolved in glacial acetic acid (20 mL) zinc (6.5 g, 100 mmol) was added in portions during 1 h. The reaction mixture was stirred for 6 h, then water (100 mL) was added and the mixture was left overnight. The product was extracted into chloroform (3×35 mL), the combined organic phases were washed with sodium hydrocarbonate solution, dried over Na_2SO_4 and concentrated to yield a mixture of diesters **5** and **6**. Column chromatography on silica gel (elution with benzene) gave the individual esters.

5: (R_f = 0.64), yield 0.53 g (38%), bp 95–96°C/3 mmHg, $[\alpha]_{546}^{21}$ +32.5 ($CHCl_3$, *c* 0.08); IR ν_{max}/cm^{-1} 1735; ^1H NMR: δ 1.38–1.63 (6H, m), 2.38–2.75 (4H, m), 3.57 (6H, s); ^{13}C NMR: δ 26.8, 40.3, 41.0, 45.5, 51.3, 174.1 (C=O). Anal. calcd for $C_{11}H_{14}O_4$: C, 62.26; H, 7.60. Found: C, 62.22; H, 7.54.

6: (R_f = 0.45), yield 0.33 g (26%), mp 64–66°C, IR ν_{max}/cm^{-1} 1730; ^1H NMR: δ 1.23–1.87 (6H, m), 2.13–2.75 (4H, m), 3.50 (6H, s); ^{13}C NMR: δ 29.4, 32.0, 38.4, 40.3, 41.6, 45.7, 51.6, 51.7, 175.0, 176.0 (C=O). Anal. calcd for $C_{11}H_{14}O_4$: C, 62.26; H, 7.60. Found: C, 62.18; H, 7.63%.

4.6. (+)-(1*R*,3*R*,6*R*,8*R*)-Tricyclo [4.3.0.0^{3,8}]nonane-4,5-dione 8

A solution of trimethylchlorosilane (1.95 g, 18 mmol) and diester **5** (0.33 g, 1.55 mmol) in toluene (15 mL) was added dropwise to a boiling and vigorously stirred mixture of sodium (0.31 g, 13.5 mmol) in dry toluene (50 mL). The reaction mixture was refluxed and stirred for 3 h under a nitrogen atmosphere, filtered and solvent evaporated. The residue was dissolved in tetrachloromethane (40 mL) and an excess of 5% solution of bromine in CCl_4 was added in portions. The reaction mixture was concentrated and the obtained oily product was purified by column chromatography (eluent chloroform) to yield 0.07 g (30%) mp 72–74°C. $[\alpha]_{546}^{16}$ +207.5 ($CHCl_3$, *c* 0.07); CD: λ_{max} ($\Delta\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) <235 (positive), 279 (–1.26), 419 (+0.78); IR ν_{max}/cm^{-1} 1760, 1743; ^1H NMR: δ 1.38–1.63 (6H, m), 2.38–2.75 (4H, m), 3.57 (6H, s); ^{13}C NMR: δ 26.8, 40.3, 41.0, 45.5, 51.3, 174.1 (C=O). Anal. calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 72.31; H, 7.05%.

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