The First Enantiomerically Pure Triangulane (*M*)-Trispiro[2.0.0.2.1.1]nonane Is a σ-[4]Helicene**

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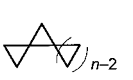
Dedicated to Professor Hans-Jürgen Quadbeck-Seeger on the occasion of his 60th birthday

Enantiomerically pure chiral compounds that do not show any optical activity in the ordinarily accessible UV/Vis spectral range (800–200 nm) have been termed cryptochiral.[1] As demonstrated by Wynberg et al. some 35 years ago,[2] chiral hydrocarbons with four different alkyl groups at their centers of chirality, even in neat form, do not exhibit any optical rotation and are thus cryptochiral. This is likely to be due to the conformational mobility in such acyclic hydrocarbons. In contrast, [*n*]triangulanes **1**[3]—that is, hydrocarbons which consist of spiro-annelated and thereby mutually orthogonal cyclopropane rings only—are completely rigid. Many of the higher [*n*]triangulanes **1** ($n \geq 4$) not containing any centers of chirality are chiral due to their symmetry (or lack thereof),[4] and they should not behave as cryptochiral, although they are saturated hydrocarbons.



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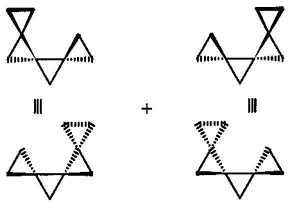
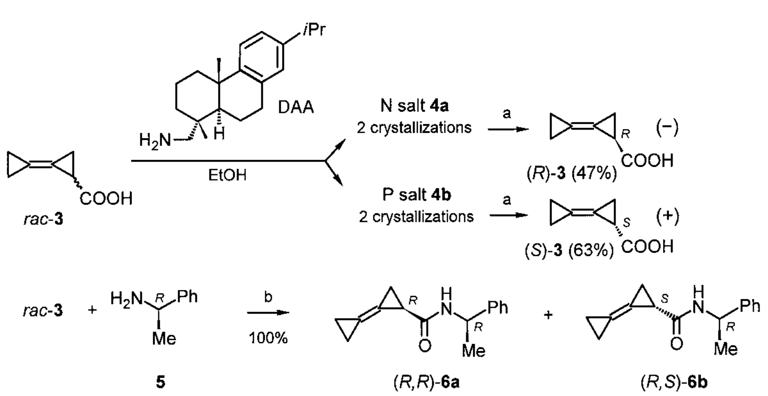
To test this hypothesis, we have developed a synthesis of enantiomerically pure (*M*)-[4]triangulane ((*M*)-**2**), the smallest chiral [*n*]triangulane.[4] Racemic [4]triangulane (*rac*-**2**) was first synthesized over 25 years ago,[5] and in the meantime improved syntheses[6] as well as spectral,[7] structural,[8] and thermochemical properties[9] of *rac*-**2** are sufficiently well documented. Essentially, the C_2-symmetric molecule of (*M*)-**2** is a section of a helix, so that the stereochemical descriptors for helicenes[10] should also be applicable to (*M*)-**2** and extended unbranched triangulanes **1**.



(*M*)-**2** (*P*)-**2**

Racemic bicyclopropylidenecarboxylic acid (*rac*-**3**), which is easily available from bicyclopropylidene[11] by deprotonation and carboxylation,[12] was resolved by crystallization of a mixture of its diastereomeric N and P[13] salts **4a** and **4b** with (+)-dehydroabietylamine (DAA, Scheme 1). Two crystallizations from ethanol and subsequent decomposition with aqueous sodium hydroxide and acidification with concentrated hydrochloric acid furnished enantiomerically pure (*R*)-(−)-**3** ($[\alpha]_D^{20} = -183.7$, $c = 1.00$, $CHCl_3$; 100% *ee*) and (*S*)-(+)-**3** ($[\alpha]_D^{20} = +183.2$, $c = 1.00$, $CHCl_3$; 100% *ee*).



Scheme 1. Resolution of *rac*-**3** and synthesis of amides (*R*,*R*)-**6a** and (*R*,*S*)-**6b**. a) 1. aq. NaOH, 2. conc. HCl, 3. crystallization; b) $Ph_2P(O)Cl$, Et_3N, EtOAc, −10 °C, 1 h.

The absolute configuration of (*R*)-**3** was assigned on the basis of the relative configuration of its (*R*)-(1-phenylethyl)amide (*R*,*R*)-**6a**. The amides (*R*,*R*)-**6a** and (*R*,*S*)-**6b** were prepared from the racemic acid *rac*-**3** and (*R*)-(1-phenylethyl)amine (**5**) applying a known procedure[14] (Scheme 1) and separated by column chromatography. The configurations were assigned by comparison with authentic samples prepared from the enantiomerically pure acids (*R*)-(−)-**3** and (*S*)-(+)-**3** after the absolute configuration of (*R*,*R*)-**6a** had been established[15] by an X-ray crystal structure analysis (Figure 1).[16]

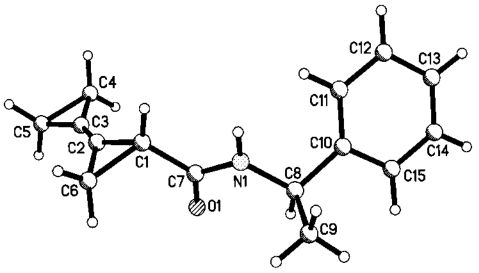


Figure 1. Structure of (*R*,*R*)-**6a** in the crystal.[16]

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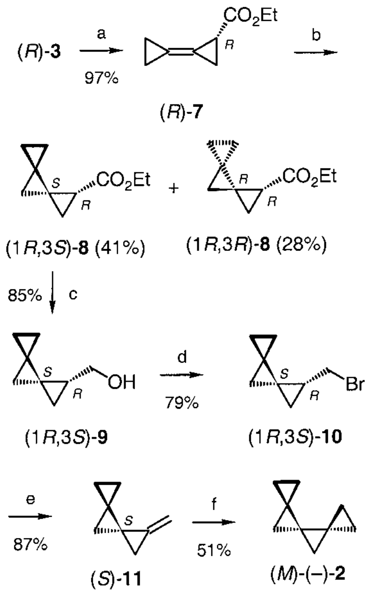
The enantiomerically pure acid (*R*)-**3** was first transformed to its ethyl ester ((*R*)-**7**),[12, 17] following a standard procedure,[18] which was then cyclopropanated with the Simmons–Smith reagent (CH_2I_2/Zn)[19] accelerated by ultrasonication[20] to give a mixture of ethyl *endo*-(1*R*,3*R*)- and *exo*-(1*R*,3*S*)-[3]triangulane-1-carboxylates ((1*R*,3*R*)-**8** and (1*R*,3*S*)-**8**, Scheme 2).[11a, 21] These diastereomers were easily separated by column chromatography and isolated in 28 and 41 % yield, respectively. Thus, enantiomerically pure (1*R*,3*S*)-**8** was obtained in 19 % yield from the racemic acid *rac*-**3**.



Scheme 2. Synthesis of (1*R*,3*S*)-**8** and (1*R*,3*R*)-**8** as well as (*M*)-(–)-**2**. a) $BF_3 \cdot Et_2O$, EtOH, 78 °C, 2 h; b) CH_2I_2, Zn, DME, ultrasound, 80 °C, 2 h; c) $LiAlH_4$, Et_2O; d) $Ph_3P \cdot Br_2$, pyridine, CH_2Cl_2, – 10 °C, 1.5 h, then 20 °C, 7 h; e) *t*BuOK, DMSO, 20 °C, 14 h; f) CH_2N_2, $Pd(OAc)_2$, Et_2O, – 5 °C.

The ester (1*R*,3*S*)-**8** could be transformed to enantiomerically pure (*M*)-(–)-**2** following a sequence of routine steps established for the preparation of triangulanes.[3] First, (1*R*,3*S*)-**8** was reduced to the alcohol (1*R*,3*S*)-**9**, which was converted into (bromomethyl)[3]triangulane ((1*R*,3*S*)-**10**) by treatment with triphenylphosphane/bromine (Scheme 2). Dehydrobromination of (1*R*,3*S*)-**10** with potassium *tert*-butoxide gave (*S*)-1-methylenedispiro[2.0.2.1]heptane ((*S*)-**11**), and cyclopropanation of (*S*)-**11** with diazomethane under $Pd(OAc)_2$ catalysis[22] furnished enantiomerically pure (*M*)-(–)-**2** in 51 % yield after gas-chromatographic separation in the last step. This corresponds to a 6 % overall yield from *rac*-**3**, with an enantiomeric excess of 99 %, as determined by gas chromatography on a chiral capillary column.[23]

Although (*M*)-(–)-**2** does not have a chromophore that would lead to any significant absorption above 200 nm, it has a remarkably high specific rotation even at 589 nm ($[\alpha]_D^{20} = -192.7$, $c = 1.18$, $CHCl_3$). The specific rotation increases drastically on going to shorter wavelengths ($[\alpha]_{578}^{20} = -201.3$, $[\alpha]_{546}^{20} = -229.7$, $[\alpha]_{436}^{20} = -400.2$, and $[\alpha]_{365}^{20} = -648.2$), indicating a strongly negative Cotton effect in the optical rotatory dispersion (ORD) below 200 nm.

For a better understanding of the remarkably high rotatory strength of (*M*)-**2**, ab initio computations were carried out at a reasonably high level of theory (B3LYP/6-31G(d)),[24–28] applying a full valence space single excitation configuration interaction treatment (DFT-SCI at B3LYP/TZVP) according to Grimme.[29] Indeed, the computed specific rotations over the whole range of wavelengths are in very good agreement with the experimental values, and thus confirm the strong negative Cotton effect in the ORD going along with a large ellipticity in the circular dichroism below 200 nm (Table 1).[30]

Table 1. A comparison of the measured and DFT/SCI-computed specific rotations of (*M*)-(–)-**2**.

λ [nm]	$[\alpha]_D^{20}$	
	measured	computed
589	– 192.7	– 241.0
578	– 201.3	– 250.2
546	– 229.7	– 283.8
436	– 400.2	– 466.0
365	– 648.2	– 703.7

This good agreement between experiment and theory for (*M*)-**2** not only provides confidence in the general applicability of this computational approach to the simulation of CD spectra, but also confirms that the rotatory power of (*M*)-**2** is an outflow of its helical arrangement of σ bonds. Thus [4]triangulane is a true "σ-[4]helicene", the first σ-bond analogue of the aromatic [*n*]helicenes, which have a helical arrangement of skeletal π bond and should therefore be termed π-[*n*]helicenes to distinguish them from these newly established σ-[*n*]helicenes.[35]

With the same type of computations it is predicted that the rotatory strength of the next higher analogue in the series of chiral triangulanes, (*M*)-[5]triangulane ((*M*)-**12**), should be about twice as large (by a factor of 1.8) as that of (*M*)-**2**, whereas the rotatory strength of (*M*)-[6]triangulane ((*M*)-**13**) would only be slightly larger (factor of 1.1) than that of (*M*)-**12**. This may have to do with the simple fact that the sum of interplanar angles between all adjacent pairs of spiro-fused cyclopropane rings reaches 360° in (*M*)-**12**, while it is 270° in (*M*)-**2**. This is indicated in Figure 2 by the yellow spiral connecting one methylene group of each of the terminal cyclopropane rings with those of the rings in between. In (*M*)-**12**, such a spiral completes exactly one turn of a helix, while in (*M*)-**13** it simply goes 90° beyond a complete turn. To test these computational predictions, it is well worth to prepare at least the two next higher members of this family of σ-[*n*]helicenes.

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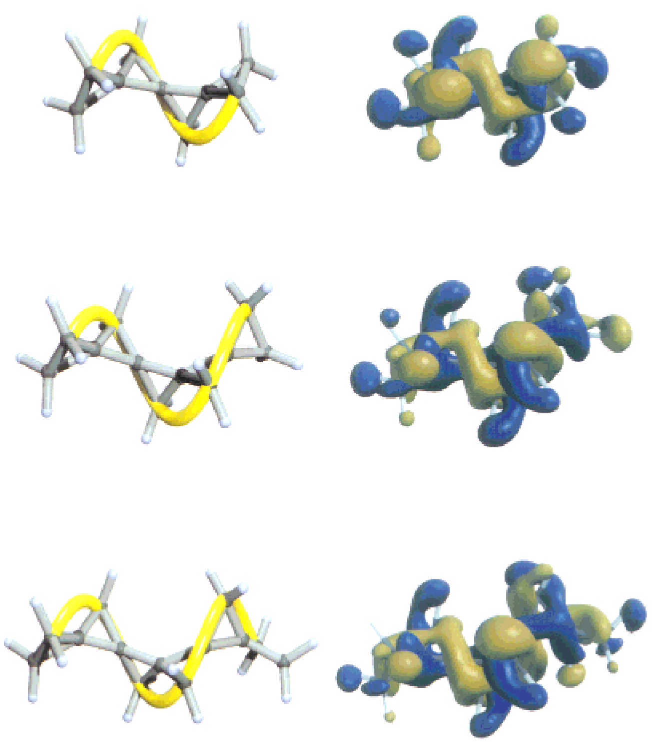

Figure 2. The helicity of (*M*)-**2** (top) and its higher analogues (*M*)-**12** (middle) and (*M*)-**13** (bottom). Left: Visualization by a spiral connecting one methylene group each of the two terminal cyclopropane rings with the methylene groups of the rings in between. Right: Lowest unoccupied orbital (LUMO) of each molecule according to DFT calculations at the B3LYP/6-31G(d) level of theory.

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[16] Crystal structure determination of (*R*,*R*)-**6a** ($C_{15}H_{17}NO$, $M_r = 227.30$): Suitable crystals were grown by slow concentration of a diluted solution of (*R*,*R*)-**6a** in hexane/diethyl ether. During cooling of the crystals, broadening of the reflection profiles occurred. The process is reversible and begins at about 250 K. Therefore the X-ray experiment was performed at room temperature. The data were collected on an automated Nonius CAD-4 four-circle diffractometer, graphite monochromator, $Mo_{K\alpha}$ radiation, $\omega/2\theta$ scan; monoclinic, space group $P2_1$, $a = 10.623(2)$, $b = 4.803(1)$, $c = 13.283(3)$ Å, $\beta = 96.00(3)°$, $V = 674.0(2)$ Å^3, $F(000) = 244$, $Z = 2$, $\rho_{calcd} = 1.120\ \mathrm{mg\,mm^{-3}}$, $\mu = 0.070\ \mathrm{mm^{-1}}$. In total, 1904 reflections were collected with $2.5 \leq \theta \leq 25°$, which gave 1631 independent reflections. The structure was solved by direct methods and refined by full-matrix least square on F^2. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined as "riding" atoms. Final $wR_2(F^2) = 0.141$ for all data (153 parameters), conventional $R(\mathrm{F}) = 0.0524$ for 587 reflections with $I \geq 2\sigma(I)$, GOF = 1.033. The absolute configuration was assigned on the basis of the known *R* configuration of **5**; the Flack parameter for the reported configuration is 0(5) and for the inverted model 1(5). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112810. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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gave the specific rotations in the ORD at the recorded wavelengths (Table 1). As the calculated data are for the gas phase, whereas the experimental ones are obtained for solutions, the computed values are systematically somewhat too large. Nevertheless, the agreement between experiment and theory is remarkably good and emphasizes the quality of the theoretical approach used here.[29]

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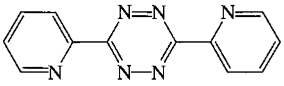
A One-Pot, High-Yield Synthesis of a Paramagnetic Nickel Square from Divergent Precursors by Anion Template Assembly**

Cristian S. Campos-Fernández, Rodolphe Clérac, and Kim R. Dunbar*

Self-assembly of metal cations with nitrogen heterocyclic bridging ligands is a central theme in supramolecular chemistry aimed at developing light-harvesting assemblies of electronically coupled metal centers.[1] The ability of these π-ligand systems to transmit electronic information between remote metal centers is well-documented,[1–4] but much less is known about their suitability for promoting strong superexchange between paramagnetic centers. The bis-chelating α-diimine ligand 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) with its low-lying π* orbitals is a particularly promising candidate for use as an electronic spacer,[5] as judged by the strong coupling observed between the metal centers in $[(NH_3)_4Ru(\mu\text{-bptz})Ru(NH_3)_4]^{4+}$ which exhibits a K_c value of 10^{15}.[5f]



bptz

Studies in our laboratories have revealed a new application for the bptz molecule, namely as a linking group in the formation of paramagnetic squares. The bptz ligand is ideally suited for this purpose for two reasons. First bptz is a rigid molecule with two bipyridine units on each end suitable for bridging two metals, and second two bptz ligands coordinated to an octahedral metal center are required to be *cis* to each other. These binding preferences are being capitalized upon in one-pot, high-yield reactions of unprotected solvated cations $[M(CH_3CN)_6]^{2+}$ with bptz in the presence of tetrafluoroborate anions. In this study we report an unusual, high-yield formation of a cyclic product from solutions of $[Ni(CH_3CN)_6][BF_4]_2$ and bptz in a 1:1 molar ratio [Eq. (1)].[6]

$$[Ni(CH_3CN)_6][BF_4]_2 + \text{bptz} \xrightarrow[\text{RT}]{\text{MeOH}} [Ni_4(\text{bptz})_4(CH_3CN)_8][BF_4]_8 \qquad (1)$$

Regardless of the ratio of bptz and $[Ni(CH_3CN_6)][BF_4]_2$, the reactions proceed at room temperature in MeOH to give a dark green solution with eventual deposition of a green solid (74 % yield). Single crystals of the product are easily obtained by diffusion of toluene into a solution of the compound in acetonitrile. The reactions are quite remarkable in that there is no evidence for polymer formation in spite of the lack of protective groups and the relatively high concentrations used for the reaction. Hupp and co-workers have reported similar observations for various octahedral based squares prepared under refluxing conditions in their laboratories, and it is clear from their detailed analyses that cyclic oligomers are thermodynamic products.[7]

An X-ray crystallographic study revealed the new compound to be the partially solvated molecular square $[Ni_4(\text{bptz})_4(CH_3CN)_8][BF_4]_8 \cdot 4\,CH_3CN$.[8] An ORTEP diagram is provided in Figure 1 (top) and a packing diagram is

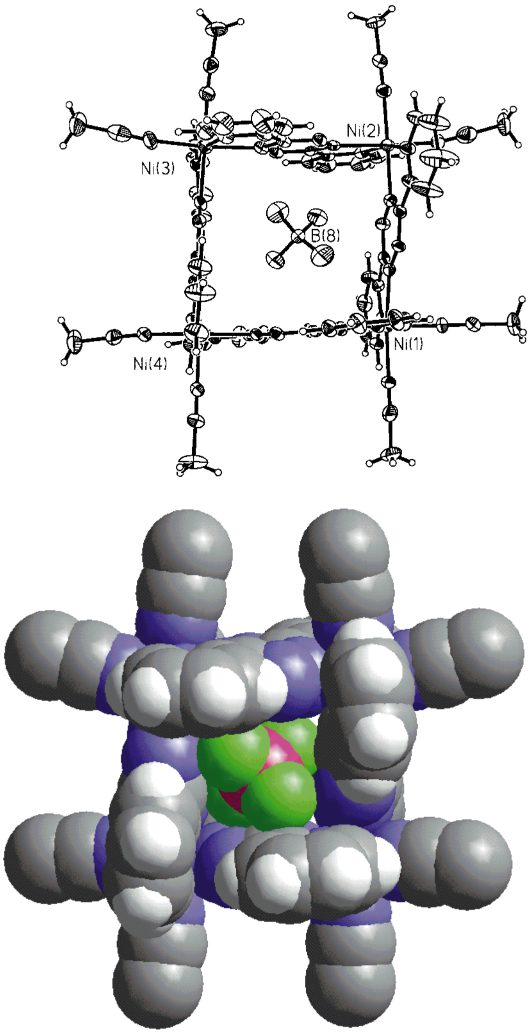


Figure 1. Top: ORTEP drawing of the molecular structure of the $[Ni_4(\text{bptz})_4(CH_3CN)_8]^{8+}$ ion. Thermal ellipsoids are drawn at the 50 % probability level; bottom: space-filling diagram of the molecular cation with the encapsulated $[BF_4]^-$ ion.

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