THE SYNTHESIS AND STRUCTURE OF CHIRAL DI-N-p-TOLUENESULPHONYL DIAZACORONANDS DERIVED FROM L-TARTARIC ACID

Janusz Jurczak,[a*] Ryszard Ostaszewski,[a] Giovanni D. Andreetti,[b*] and Gianluca Calestani[b]

[a]Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland; [b]Istituto di Strutturistica Chimica, Università degli Studi di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, 43100 Parma, Italy

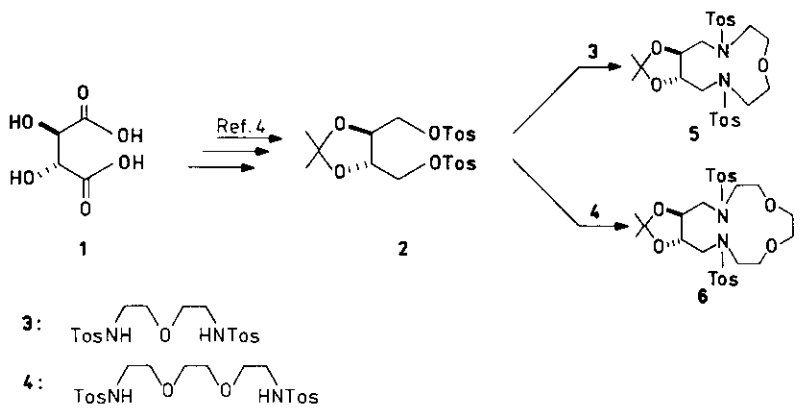
Abstract-Two chiral di-N-p-toluenesulphonyl diazacoronands **5** and **6**, derived from L-tartaric acid (**1**), were synthesized by the modified Richman-Atkins procedure. The structure of compound **5** was determined by X-ray analysis.

L-Tartaric acid (**1**), commonly used as a chiral building block in organic synthesis,[1] has found application as an excellent starting material for preparation of chiral macrocyclic ligands.[2,3]

This work was aimed at the synthesis and structure elucidation of diazacoronands containing the chiral unit derived from L-tartaric acid (**1**). Chiral bis-tosylate **2**, readily available from compound **1** by a known procedure,[4] was applied in the reaction with bis-tosylates **3** and **4** under standard Richman-Atkins conditions.[5] In both cases the reaction failed to afford the desired diazacoronands **5** and **6**. However, a modification of the Richman-Atkins procedure, consisting in the use of five equivalents of potassium carbonate and catalytic amounts of tetrabutylammonium chloride in dimethylformamide, allowed for successful carrying out of the reaction of the chiral derivative **2** with compound **3** or **4** (Scheme 1). When these reactions were performed under the above-mentioned conditions at 80°C during 12 h, the desired diazacoronands **5** and **6** were formed in 31 and 18% yield, respectively.[6]

Analysis of the ^{1}H and ^{13}C nmr spectra of chiral diazacoronands **5** and **6** testified to lower symmetry as compared with the previously obtained nonchiral di-N-p-

toluenesulphonyl diazacoronands.[7] Since diazacoronand 5 affords colorless single crystals suitable for X-ray measurements, we resolved to establish its structure by roentgenography. The structure was solved by direct methods and Fourier techniques[8] (Fig. 1).



Scheme 1

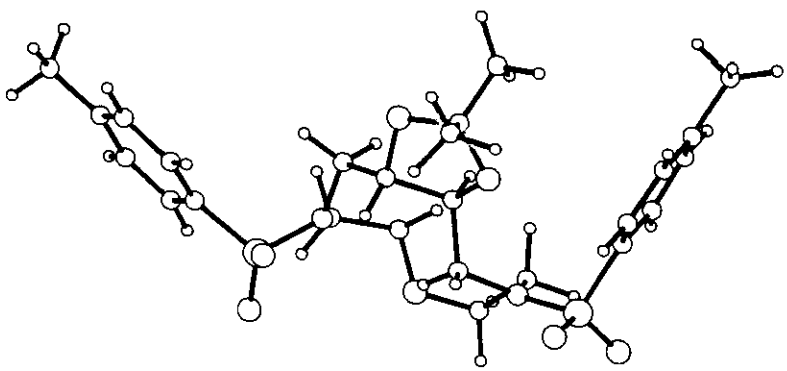


Fig. 1. Computer generating perspective drawing of diazacoronand 5

The molecule with the (S:S) absolute configuration on both chiral centers, shown in Fig. 1, exhibits the twist conformation of the acetal ring. This is in good agreement with the ^1H nmr data obtained for a $CDCl_3$ solution.[9] The macrocyclic ring displays the boat-like (syn) conformation since both phenyl rings are

situated on the same side of the diazacoronand. The dihedral angle between both phenyl rings amounts to 99.1°, this indicating that they are almost perpendicular.

Further studies of the synthesis and structure of other chiral di-N-p-toluenesulphonyl diazacoronands as well as of their complexation properties are in progress.

General procedure - To a heated (80°C) suspensions of potassium carbonate (13.8 g, 0.1 mol) in dimethylformamide (100 ml), containing tetrabutylammonium chloride (0.29 g, 0.001 mol), a solution of **2** (9.4 g, 0.02 mol) and **3** (8.2 g, 0.02 mol) in dimethylformamide (100 ml) was added dropwise. Heating was continued for additional 12 h, whereupon the reaction mixture was cooled and water (250 ml) was added. The mixture was extracted with chloroform (3x50ml), the combined extracts were washed with water (2x25ml) and dried ($MgSO_4$). After evaporation of solvents, the residue was crystallized from a mixture of ethyl acetate and hexane, to afford crystalline diazacoronand **5** in 31% yield.[6]

ACKNOWLEDGMENTS

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6. **5**: mp 146-147°C; $[\alpha]_D^{20}$ +36.8° (c 1.36, CH_2Cl_2); ^1H nmr (500 MHz), δ, 1.35 (s, 6 H), 2.44 (s, 6 H), 3.07-3.20 (m, 4 H), 3.48 (m, 4 H), 3.66 (m, 4 H), 4.31 (t, J = 3.8 Hz, 2 H), 7.32 (d, J = 8.2 Hz, 4 H), 7.72 (d, J = 8.2 Hz, 4 H); ^{13}C nmr (125.75 MHz), δ, 21.5, 27.4, 50.5, 54.4, 70.9, 78.3, 109.1,

127.5, 129.7, 135.4, 143.6. Anal. Calcd for $C_{25}H_{34}N_2S_2O_7$: C, 55.74; H, 6.36. Found: C, 55.79, H, 6.32.

6: oil; $[\alpha]_D^{20}$ -4.8° (c 1.09, CH_2Cl_2); ^1H nmr (500 MHz), δ, 1.31 (s, 6 H), 2.41 (s, 6 H), 3.27-3.40 (m, 4 H), 3.47-3.60 (m, 10 H), 3.74-3.85 (m, 2 H), 4.27 (m, 2 H), 7.28 (d, J = 8.2 Hz, 4 H), 7.72 (d, J = 8.2 Hz, 4 H); ^{13}C nmr (125.75 MHz), δ, 21.5, 27.5, 48.3, 51.9, 69.8, 71.3, 76.8, 110.1, 127.7, 129.5, 136.0, 143.3. Anal. Calcd for $C_{27}H_{38}N_2S_2O_8$: C, 55.65; H, 6.57. Found: C, 55.68, H, 6.50.

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8. Crystal data for compound **5**: $C_{25}H_{34}N_2S_2O_7$, orthorhombic, a = 28.743(1), b = 16.013(1), c = 5.796(1) Å, V = 2667.7(5) $Å^3$, space group $P2_12_12_1$, Z=4, D_x = 1.3412 gcm^{-3}. Intensity data were collected from a prismatic crystal (1.0 x 0.5 x 0.3 mm^3) on a Siemens AED diffractometer utilizing Ni filtered CuK_α radiation, θ-2θ scans, in the range $3<\theta<60°$. The structure was solved by direct methods and Fourier techniques using the CRYSRULER programs package. The final discrepancy indexes were R = 0.056, R_w = 0.061 for 3725 reflections and 411 parameters. The details of the crystal structure will be given in a full paper.

9. One of the acetal-ring protons is oriented inside and the second outside of the macrocyclic ring. This causes a nonequivalence of these protons in the ^1H nmr spectrum.

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