

Synthesis and Crystal Structure of a Bis[6.3.3]propellane[☆]

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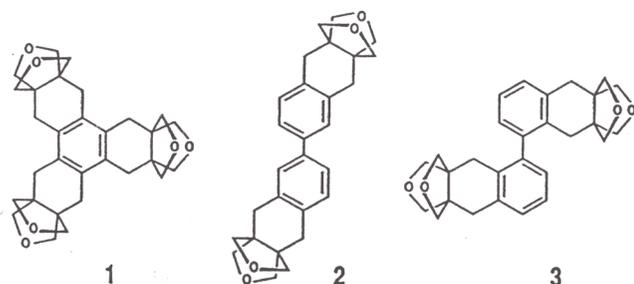
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The bis[6.3.3]propellane **6** derivative of 2,2',6,6'-tetramethylbiphenyl was, in the final stage, synthesized by dehydration, of octaalcohol **5**. X-ray structure analysis revealed the highly

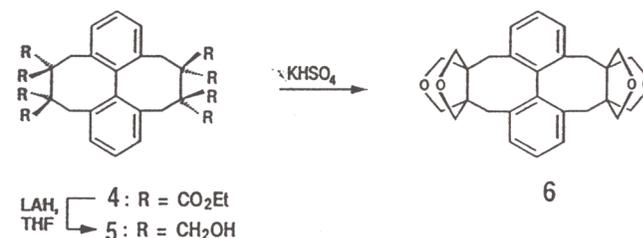
symmetric shape of the molecule and disordered oxygen atoms in the tetrahydrofuran rings. The dihedral angle between LSQ phenyl planes is 62.6(1)°.

Tricyclic molecular structures containing three rings which are conjoined along a common carbon-carbon bond between bridgeheads, were coined propellanes by Ginsburg^[1,2], because of their propeller-like three-dimensional shape. The chemistry of propellanes has been studied extensively from many points of view^[3,4]. Our interest in this field concerned tris- and bis[4.3.3]propellane **1**, **2**, **3** compounds containing a central benzene ring^[5] or a central biphenyl system, respectively^[6,7]. One of the main goals was to study how the arrangement of three rings along a common (conjoining) bond affects their conformation.



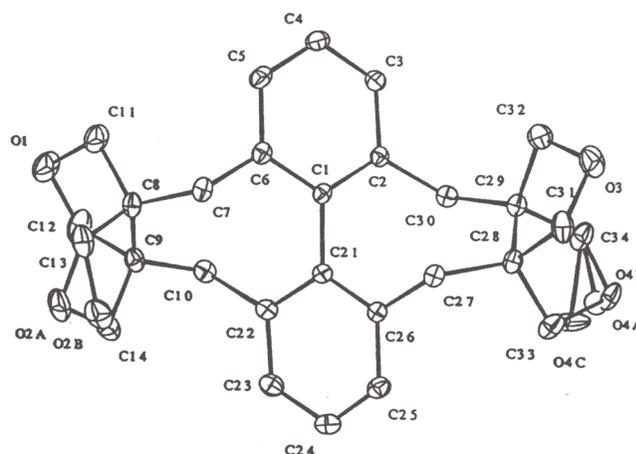
We now describe the first synthesis of bis[6.3.3]propellane **6**, conducted in a simple manner. As described earlier^[8], the reaction of 2,2',6,6'-tetrakis(bromomethyl)biphenyl with 1,1,2,2-tetrakis(ethoxycarbonyl)ethane gave tetraester **4**. This conformationally rigid biphenyl derivative was reduced with LiAlH₄ to octaalcohol **5**. Finally, treatment of **5** with KHSO₄ afforded bis(propellane) **6** as a stable, high-melting compound (365–366 °C).

In contrast to the previously described propellanes, compound **5** contains two eight-membered alicyclic rings. The conformation of these rings enforces rigid synclinal position of the vicinal hydroxymethyl groups. It probably promotes the process of dehydration of octaalcohol **5** to the bis(propel-



lane) **6**. The ¹H-NMR spectrum reveals a singlet δ = 2.56, arising from the methylene protons, two AB-systems of the tetrahydrofuran protons at δ = 3.37/3.90 (*J* = 8.7 Hz) and 3.85/3.95 (*J* = 8.8 Hz) and a multiplet at δ = 7.07–7.29 of the aromatic protons. As it was pointed out^[8], the parent ring system is conformationally static on the NMR time scale.

Figure 1. Molecular structure of bis(propellane) **6**



A perspective view of the molecule with the atoms numbering scheme is given in Figure 1. The dihedral angle be-

tween LSQ phenyl planes is 62.6(1)°. The molecule of bis(propellane) **6** exhibits D_2 pseudosymmetry with 3 twofold axes: one along the biphenyl bond (C1–C21), the second one passes through the centre of the biphenyl bond and the centres of the conjoining bonds (C8–C9, C28–C29) and the third one is orthogonal to both of them. The asymmetry parameters^[9] δC_2 calculated for the central part of the molecule, excluding the hetero rings which, due to disordered oxygen atoms, deviate more significantly from the symmetry, are 7.53, 7.54, and 1.82, respectively. Hence, the third twofold axis is the most "exact" one, which is also indicated by the chi-square value 10.24 (which should be less than 18.34 at 95% for 10 degrees of freedom), and has a well-defined [101] crystallographic orientation.

Both eight-membered rings have a slightly distorted conformation of a twisted boat-chair, as deduced from the values of relevant torsional angles. The conformation of the tetrahydrofuran rings requires some comment. For previously determined structures of bis[4.3.3]propellanes^[7,10], tetrahydrofuran rings have an envelope conformation with oxygen atoms in the respective mirror planes. In the present case of the bis[6.3.3]propellane the tetrahydrofuran rings also adopt an envelope-like conformation although the respective mirror planes never intersect the conjoining bonds and do not pass through the oxygen atoms. Moreover, the asymmetry parameters, which measure the deviation from the ideal conformation, have larger values than in the case of [4.3.3]propellanes. In two THF rings the oxygen atoms are disordered occupying alternative positions with occupancy factors of 0.42(1):0.58(1) for O2A and O2B, respectively, and 0.75(1):0.12(1):0.13(1) for O4A, O4B, and O4C, respectively. In spite of this disorder, the relatively high molecular symmetry correlates with the unusually high melting point of the newly synthesized bis[6.3.3]propellane **6**.

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Experimental

Melting points (uncorrected): Boëtius hot-stage microscope. – IR: Bruker IFS 48. – ¹H and ¹³C NMR: Bruker WM 500 (500 MHz). Chemical shifts are referenced to internal SiMe₄. – MS: Finnigan MAT 44S (EI, 70 eV).

1,2,3,4,8,9,10,11-Octahydro-2,2,3,3,9,9,10,10-octakis(hydroxymethyl)dibenzo[fg,mn]octalen (**5**): To a solution of octaester **4**^[8] (1.26 g, 1.50 mmol) in THF (50 ml) LiAlH₄ (12 ml of a 1 M solution in THF) was gradually added, and the mixture was heated at reflux for 150 h. After cooling, water (1 ml) and 10% NaOH (1 ml) were poured into the reaction mixture, a white solid was filtered off and extracted twice with pyridine. The solvent was evaporated and the residue recrystallized from methanol to give 140 mg (18%) of **5** as colorless crystals, m.p. 272–274 °C. – IR (KBr): $\tilde{\nu}$ = 3065 cm⁻¹, 2931, 1060, 1026. – ¹H NMR (CD₃OD): δ = 2.26/2.49 (AB, J = 13.6 Hz, 8H; CCH₂C), 3.34–3.86 (m, 16H, OCH₂), 4.85 (br. s, 8H, OH), 7.09–7.59 (m, 6H; arom.). – MS, m/z (%): 466 (3) [M⁺ – 2 H₂O], 448 (3) [M⁺ – 3 H₂O], 430 (5) [M⁺ – 4 H₂O], 81 (100). – C₂₈H₃₈O₈ · H₂O (520.6): calcd. C 64.60, H 7.74; found C 64.51, H 7.61.

4,8,12,16-Tetrahydro-1H,3H,9H,11H-3a,16a:8a,11a-bis(methanoxymethano)dibenzo[fg,mn]octaleno[3,4-c:9,10-c']difuran (**6**): A

mixture of octahydroxy compound **5** (100 mg, 0.20 mmol) and KHSO₄ (136 mg, 0.10 mmol) was heated at 160–170 °C for 1 h and then extracted with chloroform. After removal of the solvent the crude product was purified by high vacuum sublimation (1 Torr/260 °C) and subsequent crystallization from ethanol gave 13 mg (15%) of **6** as colorless crystals, m.p. 365–366 °C. – IR (KBr): $\tilde{\nu}$ = 3070 cm⁻¹, 3020, 3005, 2960, 2936, 2920, 2853, 1127, 1060. – ¹H NMR (CDCl₃): δ = 2.56 (s, 8H; CCH₂C), 3.37/3.90 (AB, J = 8.8 Hz, 8H; OCH₂), 3.85/3.95 (AB, J = 8.8 Hz, 8H; OCH₂), 7.07–7.29 (m, 6H, arom.). – ¹³C NMR (CDCl₃): δ = 36.1, 53.8, 82.6, 126.8, 129.6, 136.1, 140.0. – MS, m/z (%): 430 (81) [M⁺], 412 (71) [M⁺ – H₂O], 400 (23) [M⁺ – CH₂O], 81 (100). – C₂₈H₃₀O₄ (430.5): calcd. C 78.11, H 7.02; found C 77.90, H 6.95.

Crystal Structure Analysis: Empirical formula C₂₈H₃₀O₄, formula weight 430.52, temperature 293(2) K, wavelength 0.70926 Å, crystal system monoclinic, space group $P21/n$, unit cell dimensions determined from diffractometric measurements (graphite monochromated Cu-K α radiation, λ = 1.54178 Å: a = 12.678(2), b = 10.1310(11), c = 16.6870(12) Å, β = 97.320(10)°, volume 2125.8(4) Å³, Z = 4, density (calculated) 1.345 Mg/m³, absorption coefficient 0.089 mm⁻¹, min/max transmission 0.004/0.018, $F(000)$ = 920, crystal sample: transparent colorless platelet, crystal size 0.05 × 0.1 × 0.2 mm. Data collection^[11,12,13]: Mar Research 2D imaging plate detector, diameter 180 mm, single axis phi-rotation method, Mo-K α normal focus X-ray tube, 50 kV, 60 mA, graphite-monochromated. Two sets of data were collected to overcome the limitation of the dynamic range: with a crystal-to-plate distance of 100 mm and a 20-min exposure time, and with a crystal-to-plate distance of 170 mm and 2-min exposure time. A total of 180° of rotation was recorded for each set. Data reduction was performed by program DENZO, Lorentz and polarization corrections, no absorption correction. 2θ range for data collection 5.16 to 52.82°, index ranges $0 \leq h \leq 15$, $0 \leq k \leq 12$, $-20 \leq l \leq 20$, 4255 independent reflections collected. The structure was solved by direct methods and difference Fourier syntheses and refined by full-matrix least-squares on F^2 . All hydrogen atoms were located on a difference Fourier map and refined (positional, isotropic thermal parameters). The total of 440 parameters was refined against 4254 data with 1 restraint. All reflections were included in the refinement except (101) partly overshadowed by the primary beam stop, goodness-of-fit on F^2 1.026, final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0511, $wR2$ = 0.1211, R indices (all data) $R1$ = 0.0772, $wR2$ = 0.1477, largest diff. peak and hole 0.214 and -0.198 eÅ⁻³[14].

* Dedicated to Professor Richard Neidlein on the occasion of his 65th birthday.

- J. Altman, E. Babad, J. Itzchaki, D. Ginsburg, *Tetrahedron* **1966**, Suppl. 8, 279–304.
- D. Ginsburg, *Propellanes-Structure and Reactions*, Verlag Chemie, Weinheim, 1975; *Sequel I*, 1980, *Sequel II*, 1985, Department of Chemistry, Technion Haifa.
- Y. Tobe, Propellanes, in: *Carbocyclic Cage Compounds*, (Eds.: E. Osawa, O. Yonemitsu), Verlag Chemie, Weinheim, 1992, pp. 125–153.
- G. Szeimies, *Advances in: Strain in Organic Chemistry* (Ed.: B. Halton), 1992, 2, 1.
- J. Jamrozik, W. Żesławski, *Chem. Ber.* **1994**, *127*, 2471–2474.
- J. Jamrozik, W. Żesławski, *J. Prakt. Chem./Chem. Ztg.* **1993**, *335*, 482–484.
- J. Grochowski, J. Jamrozik, P. Serda, W. Żesławski, *Liebigs Ann. Chem.* **1995**, 1123–1125.
- K. Müllen, W. Heinz, F.-G. Klärner, W. R. Roth, I. Kindermann, O. Adamerak, M. Wette, J. Lex, *Chem. Ber.* **1990**, *123*, 2349–2371.
- W. L. Daux, D. A. Norton, *Atlas of Steroid Structures*, Plenum Press, New York, 1975, pp. 284–285.
- K. Stadnicka, W. Żesławski, *Acta Cryst. C* **1995**, *51*, 2377–2381.

- [11] J. Grochowski, P. Serda, Z. Dauter, *Univ. Jagellon. Folia Phys.* 1994, 36, 65–69.
- [12] U. W. Arndt, A. J. Wonacott, (Eds.), *The rotation method in crystallography*, North Holland, Amsterdam, 1977.
- [13] Z. Otwinowski, DENZO: A film processing program for macromolecular crystallography, 1992, Yale University, New Haven.
- [14] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344

Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-404579. Structure solution by SHELXS-86 (G. M. Sheldrick, A program for structure solution, 1986, University of Göttingen), structure refinement by SHELXL-93, (G. M. Sheldrick, Program for crystal structure refinement, 1993, University of Göttingen), plotting by SNOOPI (E. K. Davies, 1980, Univ. of Oxford, England).

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