

The First Out-of-plane Deformed Biphenylene

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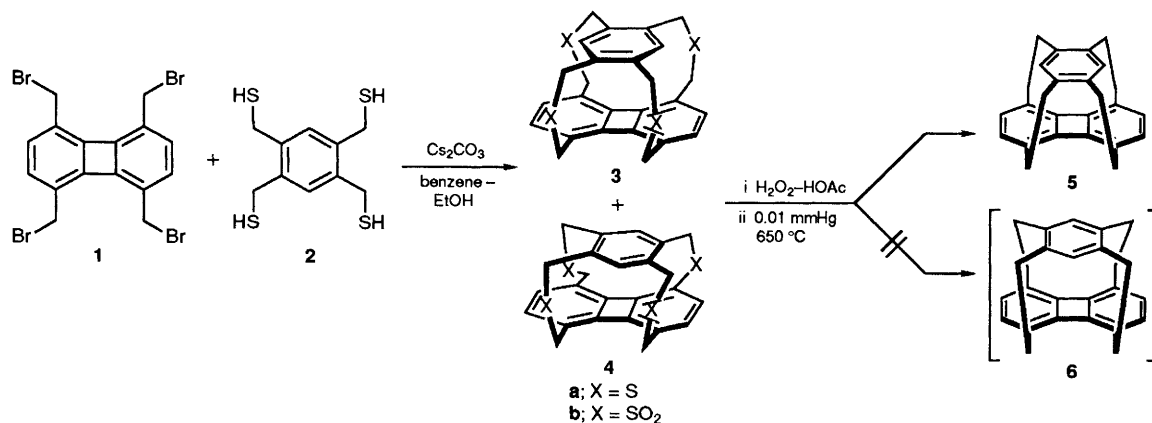
The fourfold clamped title hydrocarbon **5**, the biphenylene unit of which is strongly deformed out of plane, was obtained in 13% yield *via* sulfone pyrolysis; the X-ray analysis demonstrates that the framework of the biphenylene unit is bent out of planarity up to 18.7° due to transannular repulsion, whereas the C–C bonds of the four ethano bridges are elongated compared with reference compounds.

Recently, we described the most deformed biphenylene framework.¹ The distortion in that 2-oxo[3](1,8)biphenylenophane was related to angles and bond lengths in the plane of the biphenylene; the deviation from planarity of the biphenylene was only small (max. 3.44°). Now we report the first successful synthesis of a new fourfold clamped biphenylene hydrocarbon, the [2₄]benzenobiphenylenophane **5**.

The [2₄](1,2,4,5)cyclophane **7**² that has been known since 1975 was the first representative of this type of framework and it was the starting-point for studies of more than threefold bridgedphanes.³ Whereas, in the following years mainly benzene rings and simple heteroaromatic compounds were bridged fourfold,⁴ the biphenylene unit incorporated in **5** brings along a (4*n*)-π-electron perimeter and a considerable contribution to strain energy.

The preparation of the [2₄](1,2,4,5)benzeno(4,5,8,1)biphenylenophane **5** succeeded by use of the caesium effect⁵ in high dilution⁶ and subsequent sulfone pyrolysis (650 °C, 0.01 mmHg).⁷ By reaction of 1,4,5,8-tetrakis(bromomethyl)biphenylene **1** with 1,2,4,5-tetrakis(mercaptomethyl)benzene **2** by use of four equivalents of Cs₂CO₃, the mixture of the two tetrathia[3₄]phanes **3** and **4** was obtained in 39% yield. According to the ¹H NMR spectra the ratio of **3** and **4** is 1:4. After oxidation of this mixture with H₂O₂–glacial acetic acid yielding the tetrasulfones and subsequent sulfone pyrolysis only one isomer, the title compound **5**, was obtained in which the protons of the fourfold substituted benzene ring are located right over the two benzene rings of the biphenylene unit.

The ¹H NMR spectrum of **5** (400 MHz, CDCl₃) shows the



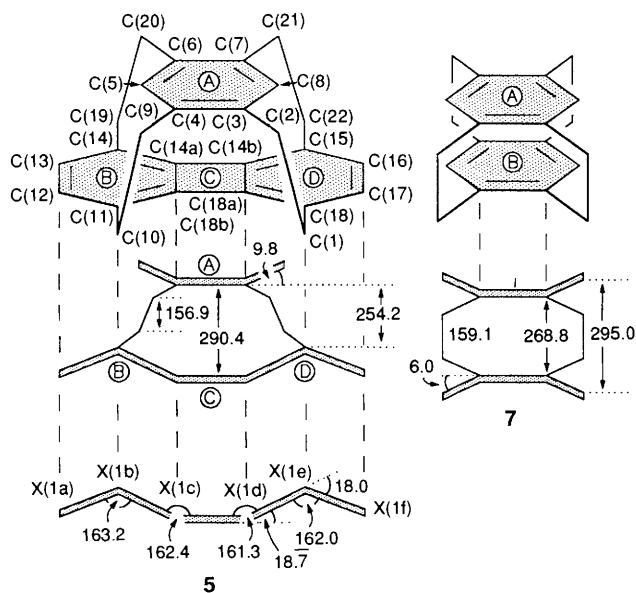


Fig. 1 Results of the X-ray analysis of the title hydrocarbon **5** and, for comparison, of **7** (side views); angles ($^{\circ}$) and bond lengths (pm) shown are exaggerated for easy recognition of the bending of the aromatic skeleton. Selected bond lengths (pm) and angles ($^{\circ}$) interatomic distances (pm) and molecular angles ($^{\circ}$) in **5**: C(16)–C(17) 138.1(6), C(17)–C(18) 141.0(6), C(18)–C(18a) 137.2(6), C(18a)–C(14b) 142.2(5), C(14b)–C(15) 136.2(6), C(15)–C(16) 140.8(7), C(15)–C(22) 150.4(5), C(22)–C(21) 156.9(5), C(21)–C(7) 151.8(5), C(7)–C(8) 140.2(6), C(8)–C(3) 138.7(5), C(3)–C(4) 139.2(6), C(4)–C(5) 140.0(6), C(5)–C(6) 138.4(5), C(6)–C(7) 139.6(6), C(15)–C(7) 280.4, [C(18a)–C(18b)–C(14a)–C(14b)]–[C(3)–C(4)–C(6)–C(7)] 290.4, [C(3)–C(4)–C(6)–C(7)]–[C(4)–C(5)–C(6)] 9.5, [C(3)–C(4)–C(6)–C(7)]–[C(3)–C(7)–C(8)] 9.8, [C(3)–C(4)–C(6)–C(7)]–[C(18a)–C(18b)–C(14a)–C(14b)] 0.3, X(1a)–X(1b)–X(1c) 16.8, X(1d)–X(1e)–X(1f) 18.0, X(1b)–X(1c)–X(1d) 17.6, X(1c)–X(1d)–X(1e) 18.7.

expected four signals (ddd) of the four anisochronous methylene protons at δ 2.2, 2.75, 2.97 and 3.1; the protons of the biphenylene unit appear at the usual chemical shift, whereas the two aromatic protons of the fourfold clamped benzene ring are distinctly shifted upfield (δ 5.95, s).⁸ As expected, in the ¹³C NMR spectrum of **5** the seven signals (δ 31.6, 34.0, 130.2, 132.7, 133.0, 138.4 and 146.0) of the non-equivalent carbon atoms appear.

As expected from the simplicity of the ¹H NMR spectra the X-ray analysis[†] of **5** exhibits (almost perfect) C_{2v} symmetry. In the side view of Fig. 1 the strong deformation of the biphenylene framework is to be seen. The bond lengths and angles of **5** are in the range of what is found for the also fourfold bridged **7** (see Fig. 1 caption).⁹

As can be seen in all manifold bridged phanes the ethano clamps show the increasing distances of the central C–C bond of each bridge. Compared to the ideal C(sp³)–C(sp³) bond

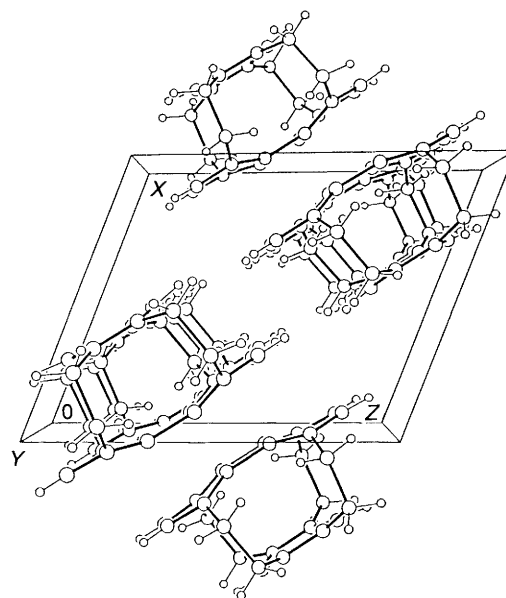


Fig. 2

length of 154.0 pm elongated distances between 156.7 and 157.2 pm in **5** are found. These CH₂–CH₂ bonds are consequently about 2 pm shorter than in **7**. The two almost coplanar aromatic planes C(14a)–C(14b)–C(18a)–C(18b) and C(3)–C(4)–C(6)–C(7) exhibit an interplanar distance of 290.4 pm which is ca. 21 pm longer than in **7** (see Fig. 1 caption and Fig. 2). These two differences reflect the higher flexibility of the more extended biphenylene framework, which helps to evade the transannular repulsion of both aromatic units.

If one places dummy atoms [X(1a–f)] in the middle of lines drawn from the atoms C(16) to C(17), C(18) to C(15), C(18a) to C(14b), C(18b) to C(14a), C(11) to C(14) and C(12) to C(13) (numbering of the atoms as in Fig. 1) and connects these atoms in the direction of the biphenylene axis, the deviation of angles, up to 18.7 $^{\circ}$ out of planarity of the biphenylene framework, can be recognized (cf. Fig 1 caption and Fig. 2).

The hydrocarbon **5** thus represents the first crystalline biphenylene derivative that exhibits distinct deviations from ideal planarity of the aromatic framework.

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[†] *Crystal structure analysis of 6*: C₂₆H₂₂, M_r = 334.4; triclinic, space group P1; a = 892.0(3), b = 916.6(2), c = 1088.1(3) pm, α = 85.15(2), β = 68.20(2), γ = 86.30(2) $^{\circ}$; V = 822.5(4) Å³; Z = 2; D_c = 1.350 g cm⁻³; MoK α (λ = 0.71073 Å); μ = 0.076 mm⁻¹; F(000) = 356, T = 293 K; crystal dimensions, 0.25 \times 0.25 \times 0.9 mm³, yellow needles; Siemens R3m/V diffractometer; 2 θ = 3.0 to 50.0 $^{\circ}$; hkl range: h = -9 \rightarrow 10, k = -10 \rightarrow 10, l = 0 \rightarrow 12; 3081 measured reflections, 2915 unique (R_{int} = 0.070), 1847 observed reflections [F > 3.0 σ (F)]. The structure was solved using Siemens SHELXTL PLUS by direct methods, non H-atoms refined anisotropically (full-matrix least-squares); H atoms refined using a riding model with fixed isotropic U; 236 refined parameters; final R (obs. data): R = 0.064 [R_w = 0.069, w⁻¹ = $\sigma^2(F) + 0.0005 F^2$]. An extinction correction was applied. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.