Extremely Deformed Hydrocarbon Skeleton of a Clamped Biphenylene

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The highly strained and distorted ketone 1,2,3-trihydrocyclohepta[3,4,5,6-def]biphenylene-2-one 5 is prepared in 17% yield by cyclization of 1 with TsCNMe (Ts = p-Me-$C_6H_4SO_2$); the X-ray analysis of 5 exhibits an extremely elongated C(4a)–C(4b) bond (156.4 pm) and a strong alternation of bond lengths in both benzene rings.
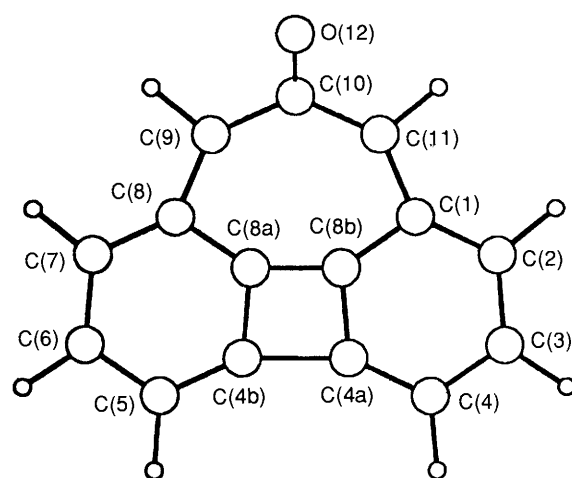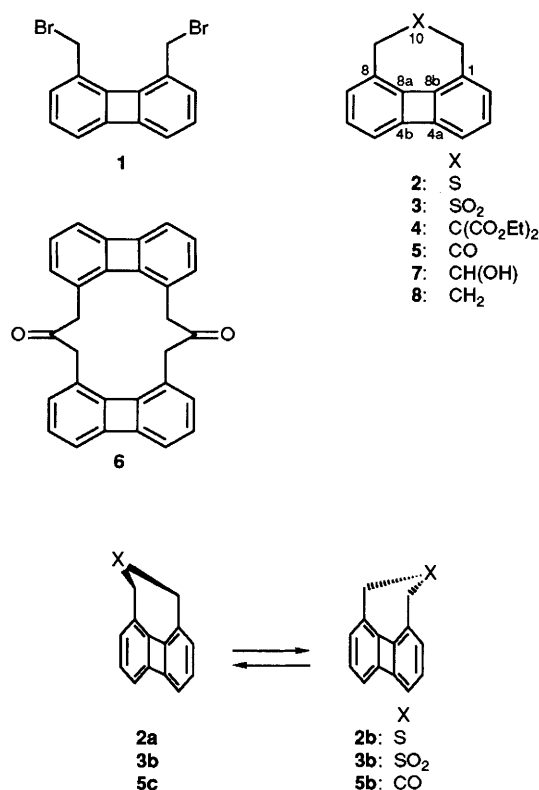
Biphenylene as a planar and rigid hydrocarbon presents a challenge to raise its strain energy further. Since the synthesis of the sulfur-bridged biphenylenophane 2 was successful[1,2] under dilution conditions[3] and by use of the 'caesium effect'[4] we were encouraged to increase the trapezoidal distortion of the four-membered 'cyclobutene' ring. As MM2 and MNDO†

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† SCF-MNDO (closed shell, singlet, RHF (Restricted Hartree–Fock) calculations; cf. C. C. J. Roothaan, Rev. Mod. Phys., 1951, 23, 69, and W. Thiel, J. Mol. Struct., 1988, 163, 415); quadratic search via fast-step-minimization, [MNDO '89, version 2.3 (W. Thiel, Universität Wuppertal, 1989) on CONVEX C220, Sonderforschungsbereich SFB 334 of Deutsche Forschungsgemeinschaft] gave for 2, 5 and 8 C(4a)–C(4b) bond lengths of 150.4, 150.8 and 150.8 pm, C(8a)–C(8b) bond lengths of 146.1, 145.2 and 145.2 pm and total energies of −2157, −2377 and −2084 eV, respectively; MM2/MMP1 calculations on HP 9000/825 SRX with MOLEK 9000, version Feb. '91, P. Bischof, ISKA, Bensheim, gave for 5 and 8 C(4a)–C(4b) bond lengths of 156.0 and 159.0 pm, C(8a)–C(8b) bond lengths of 149.8 and 158.6 pm and 'steric energies' of 264.4 and 239.3 kJ mol⁻¹; cf. M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc., 1977, 99, 4899, 4907.

calculations showed, this should be achieved by shortening of the bond lengths in the CH_2–X–CH_2 bridge at positions 1 and 8 of the biphenylene. We therefore attempted to substitute the sulfur atom in 2 by a carbon atom, by incorporation of groups X where X = $C(CO_2Et)_2$, CO, C(OH)H or CH_2.

Attempted preparation of the tetracyclic carbon species 4 by reaction of the dibromo compound 1 [as a mixture of 1,5- and 1,8-bis(bromomethyl)biphenylene in a ratio of 44:56 according to the integration of ¹H NMR signals] with diethyl malonate was unsuccessful.[5] However cyclization of 1 with p-tosylmethyl isocyanide (TsCNMe)[6a] yielded the ketone 5 (after chromatographic work up) in 17% yield [referring to 1,8-bis(bromomethyl)biphenylene], as well as equal amounts of the dimeric compound 6.[7] In this reaction an equimolar mixture of 1 and TsCNMe in diethyl ether–dimethyl sulfoxide (2.5:1) was treated under argon with slightly more than two equivalents of an NaH suspension in diethyl ether. Subsequent hydrolysis[6] delivers the ketones 5 and 6 along with unidentified by-products.

Compound 5 melts without decomposition (m.p. 137–138 °C) and in the solid state is stable under normal conditions,

1

X
2: S
3: SO₂
4: C(CO₂Et)₂
5: CO
7: CH(OH)
8: CH₂

6

2a   2b: S
3b   3b: SO₂
5c   5b: CO

Fig. 1 A view of molecule 5 with numbering scheme. Selected bond distances (pm) and angles (°): C(1)–C(2) 141.3, C(2)–C(3) 138.0, C(3)–C(4) 141.7, C(4)–C(4a) 135.8, C(4a)–C(8b) 140.2, C(4a)–C(4b) 156.4, C(8a)–C(8b) 145.1, C(8b)–C(1) 133.9, C(1)–C(11) 151.7, C(11)–C(10) 153.6, C(10)–O(12) 121.6; C(4)–C(4a)–C(4b) 153.3, C(4a)–C(4b)–C(5) 154.2, C(8a)–C(4b)–C(5) 118.2, C(4b)–C(5)–C(6) 115.1, C(5)–C(6)–C(7) 124.7, C(6)–C(7)–C(8) 120.4, C(7)–C(8)–C(8a) 112.7, C(8)–C(8a)–C(4b) 128.9, C(8a)–C(8)–C(9) 116.9, C(8)–C(9)–C(10) 111.8, C(9)–C(10)–C(11) 123.3.

although in solution decompositon occurs slowly. The 'normal' reactivity of the carbonyl group is lost as evident from the failure to obtain hydrazones with either 4-nitro- or 2,4-dinitrophenylhydrazine, and the starting ketone 5 could not be recovered.‡

The room-temperature ¹H NMR spectrum (200 MHz, CDCl₃, SiMe₄) of 5 shows besides the multiplet for the aromatic protons at δ 6.50–6.72 a sharp singlet at δ 3.73 arising from the methylene protons of the bridge. Temperature-dependent ¹H NMR experiments show neither broadening or splitting of this singlet down to −76 °C in the solvent used (CD₂Cl₂). In contrast to the sulfur analogue 2 we therefore could not evaluate the energy barrier for the ring interconversion 5a ⇌ 5b, which is suspected to be of too low energy to evaluate via usual NMR spectroscopy.

In the ¹³C NMR spectrum (62.89 MHz, CDCl₃) of 5 the expected eight signals for the eight anisochronous carbon atoms are observed. The resonance for the carbonyl carbon is not unusually shifted (δ 204.6). The infrared spectrum of 5 exhibits an intense absorption at 1693 cm⁻¹ due to v(C=O). An intense double band (at 753 and 756 cm⁻¹) is assigned to the out-of-plane oscillation of the aromatic skeleton.§

The formal substitution of sulfur in 2 or 3, by carbon in 5 leads to a strongly enhanced distortion of the aromatic framework as established by X-ray crystallography.¶ A view of the molecule with the numbering scheme is shown in Fig. 1 and a van der Waals stereoplot is shown in Fig. 2. The bond distances and angles in the cyclobutene ring and in the benzene rings are highly distorted (see Table 1) and in addition a small but definite deviation from coplanarity occurs to give a boat conformation (Fig. 3). Deviation of the aromatic rings A and C from the plane of the cyclobutene ring B are 2.5(2) and 3.4(2)° (Fig. 1). In the less strained compound 2 the corresponding angles are ca. 1.5 and 2.3°.

This enhanced distortion of 5 is reflected in the greater elongation (1.5 pm) of the bond C(4a)–C(4b) relative to that found for 2, whereas C(8a)–C(8b) is ca. 0.8 pm shorter in the carbonyl compound. Thus compound 5 compensates the additionally imposed strain relative to 2 by shortening of the bridge at positions 1 and 8 of the biphenylene achieving this by stretching of the C(4a)–C(4b) bond rather than shortening of C(8a)–C(8b) (see Table 1). The C(4a)–C(4b) bond is con-
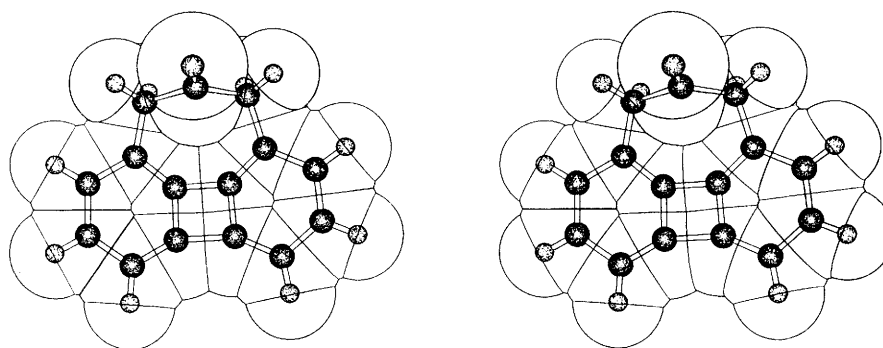
Fig. 2 A van der Waals stereoplot of **5**

Table 1 Comparison of important bond distances (pm) and angles (°) based on X-ray analysis of biphenylene, the sulfide **2** and the ketone **5**

	Biphenylene[a]	2[b]	5[c]
C(1)–C(8b)	137.2(9)	135.6(3)	133.9(3)
C(1)–C(2)	142.0(9)	140.9(4)	141.3(3)
C(1)–C(11)	—	150.1(4)	151.7(3)
C(2)–C(3)	138.0(9)	138.4(4)	138.0(3)
C(3)–C(4)	142.1(9)	142.2(3)	141.7(3)
C(4)–C(4a)	137.1(9)	135.5(4)	135.8(3)
C(4a)–C(8b)	142.5(9)	140.9(4)	140.2(3)
C(4a)–C(4b)	151.3(9)	154.9(3)	156.4(3)
C(8a)–C(8b)	150.9(9)	145.9(3)	145.1(3)
C(2)–C(1)–C(8b)	115.3(8)	113.2(2)	112.4(2)
C(1)–C(2)–C(3)	121.9(8)	121.2(2)	120.4(2)
C(2)–C(3)–C(4)	122.8(8)	123.6(3)	124.7(2)
C(3)–C(4)–C(4a)	114.9(8)	115.2(2)	114.7(2)
C(1)–C(8b)–C(4a)	122.6(8)	127.1(2)	129.2(2)
C(4a)–C(8b)–C(8a)	90.0(8)	92.2(2)	92.2(2)

[a] Ref 8. [b] Ref. 2. [c] This work.

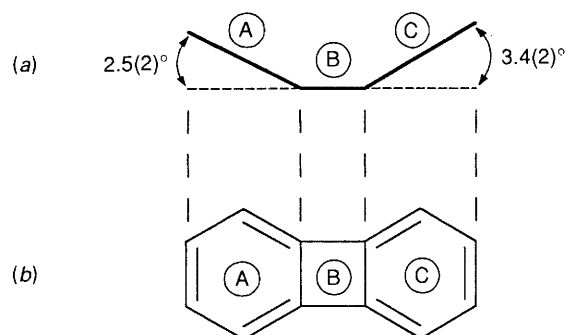**Fig. 3** Deviation from planarity of the biphenylene framework of **5**: (*a*) side view; (*b*) top view

siderably longer than found in biphenylene whereas bond length C(8a)–C(8b) is intermediate between a C–C single and a C=C double bond length as previously observed, albeit less dramatically, in the less strained sulfur derivative **2**. To our knowledge the C(4a)–C(4b) bond in **5** is the longest C–C single bond between two formally sp[2] carbon atoms.

The distinct alternation of the C⋯C bond lengths in both benzene rings of **5** is conspicuous and points to partial localization of the double bonds and a degree of reduction of aromaticity.

The dramatic enlargement of the angles at the opposite side of the carbonyl group is remarkable. The angles C(4)–C(4a)–C(4b) and C(4a)–C(4b)–C(5), 153.3(2) and 154.2(2)° respectively, are to our knowledge the largest angles associated with formally sp[2] carbons. The far-reaching distortion of the biphenylene framework in **5** is also reflected clearly in other bond lengths and angles (see Table 1) in the molecule relative to biphenylene.[8]

References

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