

(Z)-3,7-BISPHENYLSULFONYL-OCTABISVALENE
 IMPROVED SYNTHESIS AND X-RAY STRUCTURE ANALYSIS

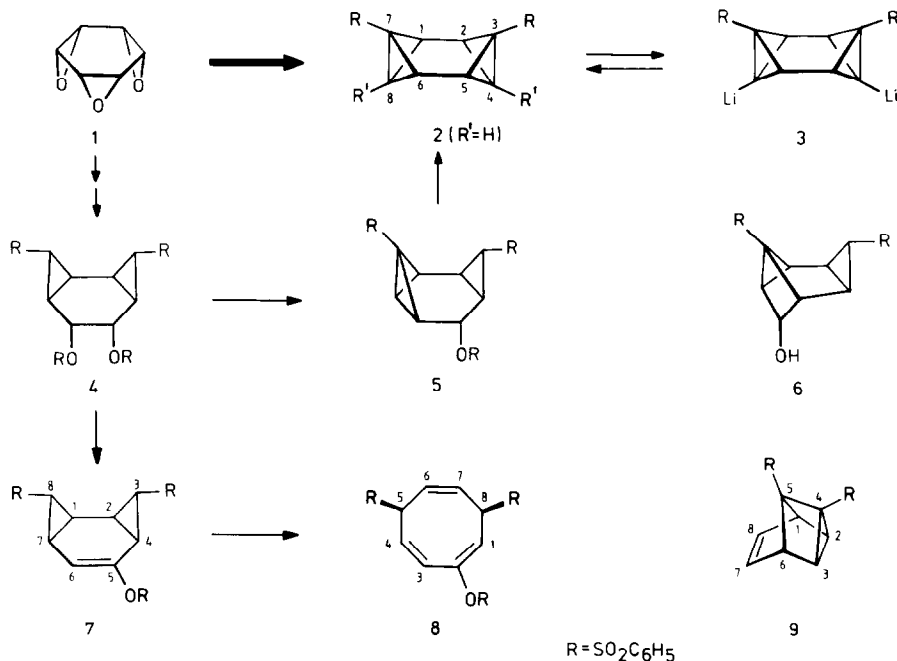
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SUMMARY: An improved eight-step synthesis of the title compound **2** starting from cis-benzenetrioxide and the X-ray structure analysis of **2** are reported.

The title compound **2** is the first derivative of "octabisvalene", the still unknown third saturated member of the $(CH)_8$ valence isomer family. In our recently reported eleven-step synthesis from cis-benzenetrioxide (**1**)¹⁾ the final step, a cumbersome silylation-desilylation procedure, was highly inefficient. In this paper we report a much improved version of this synthesis and the X-ray structure analysis of this unusual skeleton.

The synthesis of **2**, as depicted below²⁾, starts with the transformation of trioxide **1** into the tricyclic bis-benzenesulfonate **4** (70% overall yield).



Treatment of **4** with 1.2 equiv. of n-BuLi (THF, -78 → -30°C) yielded a mixture of tetracyclic sulfonate **5** (60%), alcohol **6** (25%) and only traces of **2**.

from which 6 was separated by chromatography. After stirring a solution of 5 in THF (0.5 mmole in 3.5 ml) with potassium hydride (3 equiv.) at room temperature for 3 days, 2 was isolated as the only monomeric product in 50-55% yield. On attempted scaling-up, however, this procedure proved much less satisfactory. KH was not very useful, on the other hand, for the conversion 4→5 or 4→2 (11%). The intricacies of the two base-induced CC bond formation steps 4→5 and 5→2, caused by competing deprotonation reactions, are manifested i. a. by the observation that on treating 4 with 2 equiv. of n-BuLi (THF, -78 → -40°C) ca. 7% 2, whilst upon raising the temperature to 0°C, 7% of the tetracyclic isomer 9³⁾ were produced. Similarly, when 4 was treated with 2 equiv. of KO^tBu (THF, -50°C, 1 h), neither 5 nor 2, but a mixture of cycloocta-1,3,6-triene 8 (60%) and the cis-bis-σ-homobenzene 7 (36%) was obtained. 7 slowly (20°C, 3 d) isomerized into 8. It is assumed that at low temperature (-50°C) the [$\pi 2 + \sigma 2 + \sigma 2$]-cycloreversion 7→8 occurs via the metallated species⁴⁾. With KO^tBu as a base, however, 5 is converted to 2 in 27% yield (3 equiv., 1 h, r.t.). Thus, while a rationalization of the differing impact of various bases is not obvious, a method of producing 2 in 100 mg batches from 4 is now at hand, using n-BuLi for the first step and KH for the second. The dilithio derivative 3 (2 equiv. of n-BuLi, -20°C, 5 min) is rather stable - up to 0°C (30 min) no isomerization into the COI²⁻ salt is observed - and can be used therefore for the preparation of additionally substituted derivatives of 2, e. g. R' = D, Si(CH₃)₃⁵⁾.

The X-ray structure determination of 2 was performed using a 0.5 x 0.45 x 0.2 mm³ crystal. 2 crystallizes in orthorhombic space group Pbca with unit cell dimensions a = 12.240(4), b = 15.404(4), c = 19.575(6) Å. The molecular structure of 2 (Figures 1 and 2) exhibits a close resemblance to the unsubstituted bicyclo[1.1.0]butane⁸⁾. The angles between the cyclopropane planes are 117.9(2)° for C2C3C4 and C3C4C5 and 118.0(1)° for C1C7C8 and C6C7C8, compared with 121.7° in the parent bicyclo[1.1.0]butane. Correspondingly the distances C2...C5 and C1...C6 are 2.231(3) and 2.232(2) Å long, compared with 2.265 Å in the parent structure^{8,9)}. The relatively long bonds C3-C4 and C7-C8 (Table 1) are in line with the known correlation between the bridge length and the interplanar angle¹⁰⁾; they are slightly longer than the corresponding bond in the adduct from octavalene and N-phenyl-triazolinedione (1.487(3) Å)¹¹⁾. The additional lengthening of these bonds in 2 is due to the electron withdrawing sulfonyl substituents which, in this respect, are similar to carbonyl groups¹²⁾. Thus the CC bonds distant to the sulfonyl groups are shorter than the vicinal (nonbridge) bonds by a mean of 0.017 Å. Likewise in correlation with the interplanar angle the angles S1-C3-C4 and S2-C7-C8 are widened to 120.9(1)° and 122.1(1)°, angles C3-C4-H4 and C7-C8-H8 to 128(1)° both¹⁰⁾. The R-substituted bridgehead C atoms exhibit a more pronounced inversion than the unsubstituted ones, the inversion parameters as defined by Wiberg¹³⁾ are C3 0.202, C7 0.184, C4 0.084, C8 0.083 [Å] or as defined by Allen⁹⁾ C3 161.9, C7 163.4, C4 170.4, C8 170.4 [°]. The bonds

connecting the bicyclobutane units (1.527 and 1.523Å) are longer than the corresponding bonds in benzvalene (1.503Å)¹⁴. This elongation is probably due to the fully eclipsed arrangement¹⁵.

Fig. 1.
Structure of 2

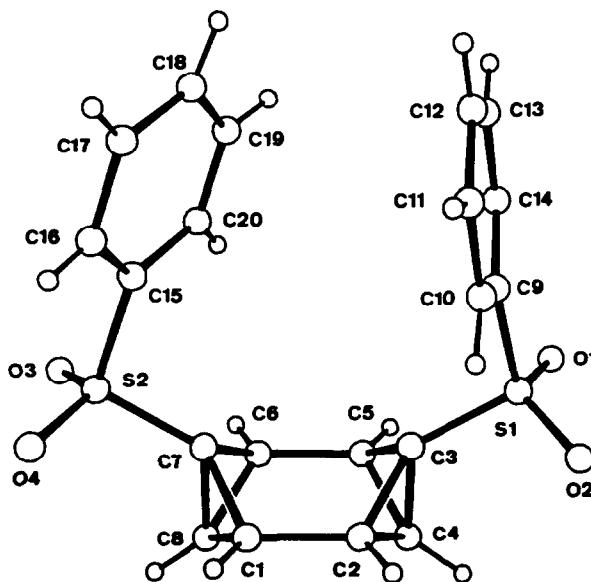
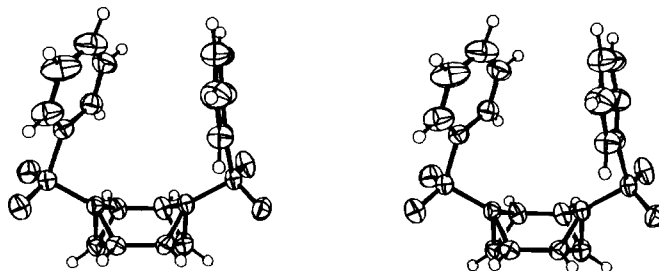


Table 1 Selected Bond Lengths [Å] and Bond Angles [°] in 2

C1-C2	1.527(3)	C4-C5	1.491(3)	C1-C2-C3	116.5(1)
C1-C7	1.506(3)	C5-C6	1.523(3)	C1-C2-C4	116.4(2)
C1-C8	1.502(3)	C6-C7	1.511(3)	C2-C3-C4	59.5(1)
C2-C3	1.515(3)	C6-C8	1.491(3)	C2-C3-C5	94.9(1)
C2-C4	1.497(3)	C7-C8	1.501(3)	C2-C4-C3	60.6(1)
C3-C4	1.505(3)	S1-C3	1.729(2)	C2-C4-C5	96.6(2)
C3-C5	1.514(2)	S1-C9	1.769(2)	C3-C2-C4	59.9(1)
				S1-C3-C2	130.1(1)
				S1-C3-C4	120.9(1)

Fig. 2.
Stereoview of 2

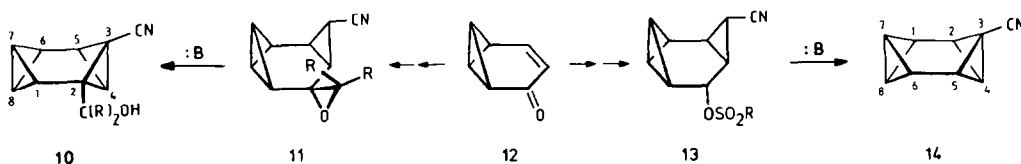


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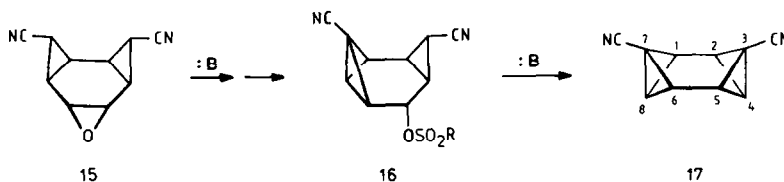
This paper is dedicated to Prof. Dr. HANS GRISEBACH on the occasion of his 60th birthday as an expression of our good wishes and a mark of our esteem.

REFERENCES AND NOTES

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- The structures of all new compounds are confirmed by elemental analysis and spectral data (250 MHz ^1H NMR, MS, IR), e.g.: ^1H NMR(CDCl_3): **2** ($\text{R}' = \text{Si}(\text{CH}_3)_3$): $\delta = 7.7\text{--}7.3$ (m, 10 H), 2.80 (s, 4 H), 0.17 (s, 18 H); **7**: 7.8–7.2 (m, 15 H), 5.59 (1 H), 2.60 (m, 1 H), 2.33 (m, 2 H), 2.20 (dd, 1 H), 1.88 (dd, 1 H), 1.66 (dd, 1 H); **8**: 7.9–7.4 (m, 15 H), 6.34 (ddd, 6-H), 6.16 (ddd, 7-H), 5.84 (dd, 4-H), 5.57 (d, 1-H), 5.13 (5-H), 5.11 (d, 3-H), 4.57 (dddd, 8-H), $J_{1,2} = 9.5$ Hz, $J_{3,4} = 11$, $J_{4,5} = 8.5$, $J_{5,6} = 5.5$, $J_{5,7} = 2$, $J_{5,8} = 2$, $J_{6,7} = 11.5$, $J_{6,8} = 2.5$, $J_{7,8} = 5$; **9**: 8.1–7.4 (m, 10 H), 5.80 (AA', 7(8)-H), 3.96 (BB', 1(6)-H), 3.12 (CC', 2(3)-H), $J_{1,2} = 2.86$, $J_{1,3} = 0.23$, $J_{1,6} = 0.69$, $J_{1,7} = 1.06$, $J_{1,8} = 2.70$, $J_{2,3} = 4.46$, $J_{2,6} = 0.23$, $J_{2,7} = -0.01$, $J_{2,8} = 0.00$, $J_{7,8} = 6.00$ (determined by computer simulation).
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- Because the synthesis beginning with **1** necessitates the two $\text{C}_6\text{H}_5\text{SO}_2$ substituents in **2**, more versatile substitution was sought in alternative approaches from norbornadiene (via quadricyclanone/tricyclic ketone **12**⁶) and from cyclooctatetraene (via the tetracyclic



dicyanoepoxide **15**⁷). After broad variations of bases and leaving groups, i.a. **10** ($\text{R} = \text{CH}_3$; ^1H NMR($\text{C}_6\text{D}_6/\text{CDCl}_3$ 1:1): $\delta = 2.53$ (d, 4-H), 2.35 (t, 5-H), 1.92 (m, 1-H), 1.88 (m, 6-H), 1.81 (ddd, 7-H)*, 1.69 (ddd, 8-H)*, 1.16 (s, CH_3), 1.14 (s, CH_3); $J_{1,6} = 5.0$, $J_{1,7} = J_{1,8} = 2.5$, $J_{4,5} = 3.5$, $J_{5,6} = 4.5$, $J_{6,7} = J_{6,8} = 2.5$, $J_{7,8} = 10.0$ Hz), **14** (^1H NMR(CDCl_3): $\delta = 2.80$ (dd, 2(5)-H), 2.75 (t, 4-H), 2.22 (m, 1(6)-H), 2.09 (dt, 7-H)*, 1.96 (dt, 8-H)*; $J_{1,2} = 5.0$, $J_{1,7} = J_{1,8} = 2.5$, $J_{2,4} = 3.0$, $J_{7,8} = 10.5$ Hz) and **17** (m.p. 232°C, ^{13}C NMR (CDCl_3): $\delta = 117.3$ (2 CN), 40.4 (C-1(2,5,6), $J = 165$ Hz), 23.5 (C-4(8), $J = 213$ Hz), 6.4 (C-3(7))) could be obtained (Ch. Rücker, D.-R. Handreck, B. Trupp, D. Hunkler and H. Prinzbach, in preparation).



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- Number of reflections used in least squares refinement = 2954. Final R-factor: 0.035. Further details of the X-ray structure analysis are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EM, UK. Any request should be accompanied by the full literature citation for this communication.

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