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Synthesis of 2,3-Dibromobenzonorbornadiene and its Cyclotrimerization into 5,18:6,11:12,17-Trimethanotrinaphthylene†

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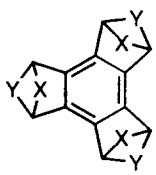
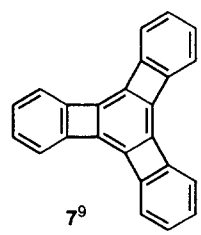
Abstract: The synthesis of 2,3-dibromobenzonorbornadiene **11** by high temperature bromination of 2-bromobenzonorbornadiene **9** allows the synthesis of the benzoannelated trimers, *syn*- and *anti*-5,18:6,11:12,17-trimethanotrinaphthylene **8**. The *syn* isomer is a basket shaped molecule that displays unusual geometric and electronic features including bond length fixation of the central benzene ring as shown by X-ray diffraction (exocyclic bond 1.41 Å, endocyclic bond 1.36 Å). © 1997 Elsevier Science Ltd.

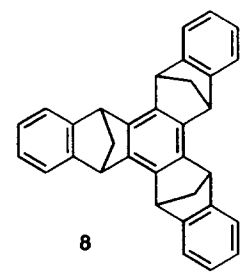
The recent discovery of fullerenes has spurred interest into the long standing topic of aromaticity. The mechanism of formation and the reactivity of these molecules still await for a convincing rational, although many aspects are certainly related with the phenomenon of bond length fixation of aromatic systems.[2] For example, while there is no substantial bond fixation in benzoannelated strained monocyclic rings (tricyclobutabenzene as an example), definite bond length alternation has been verified in **1-7**,[3-9] *i.e.* in molecules possessing either strained bicyclic rings (as especially manifested in **1**)[10] and/or π–π antiaromatic interactions (as in [3]phenylene **7**).[9] Here we report on the preparation of a new member in this series of molecules, 5,6,11,12,17,18-hexahydro-5,18:6,11:12,17-trimethanotrinaphthylene **8**, a structure made out of 5- and 6-membered rings, as in fullerenes, and that shows considerable bond length alternation in the central aromatic ring.



1[3] X = Y = CH_2
2[4] X = CH_2 Y = CH_2-CH_2
3[5] X = Y = CH_2-CH_2
4[6] X = CH_2 Y = CH=CH
5[7] X = O Y = CH=CH
6[8] X = Y = C_6H_4



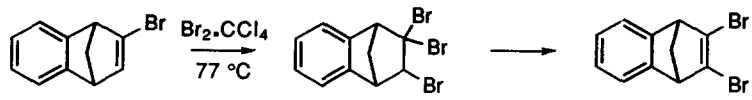
7[9]



8

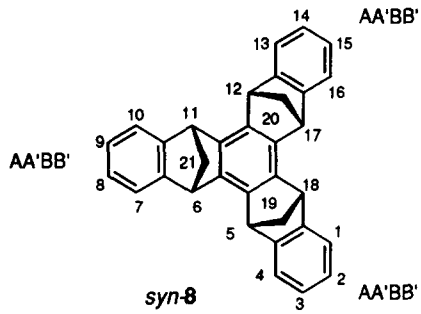
The triene **8** could be accessed by the availability of multigram quantities of 2,3-dibromobenzonorbornadiene **11**.[11] The bromination of 2-bromobenzonorbornadiene **9**[12] at high temperature[13] produces **10** in 90% yield and depresses the Wagner-Meerwein rearrangement which is the preferred reaction path under standard conditions. Dehydrobromination of **10** affords **11** in 91 % yield.

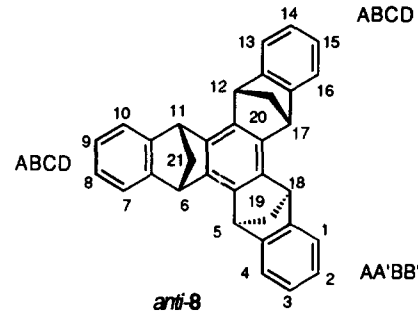
†Dedicated to Prof. Waldemar Adam in occasion of his 60th birthday.



9 **10** **11**

The cyclotrimerization was accomplished by treatment of **11** with *n*-butyllithium at -78 °C for 1 hour, followed by the addition of dry CuI and letting the mixture reach room temperature. Standard work up produced a mixture of the isomers *syn*-**8** and *anti*-**8**[14] in good yield (up to 50%). Short column chromatography allowed us to separate the trimers from impurities, but not to separate the *syn* from the *anti* form.





In the ^{1}H NMR spectrum of the mixture of the two isomers, three different AB systems, further split into triplets, can be recognized in the high field region. The two systems in the exact 1 : 2 integral ratio can be assigned to the methano bridges of *anti*-**8**, the third to the methano bridges of *syn*-**8**. The overall integration gives a 2.2 : 1 ratio of *anti*-**8** with respect to *syn*-**8**. The bridgehead protons of *anti*-**8** appear as a triplet at 4.28 ppm (H5 and H18) and as a multiplet at 4.31 ppm (H6, H17 and H11, H12, differentiated by the opposing orientations of the adjacent benzonorbornene units, and with a ^4J reciprocal coupling which shapes the multiplet into a pseudo sextet). The equivalent bridgehead protons of *syn*-**8** resonate as a triplet at 4.34 ppm. The coupling network of aromatic protons is deciphered by the COSY spectrum in Figure 1. The ABCD systems of *anti*-**8** are easily recognized at 6.88, 7.17 and 7.21 ppm. The comparison of accurate integration values allows to pick up the multiplets of the AA'BB' system of the same isomer at 6.98 and 7.31 ppm. The undifferentiated AA'BB' systems of *syn*-**8** resonate at 6.77 and 7.08 ppm.

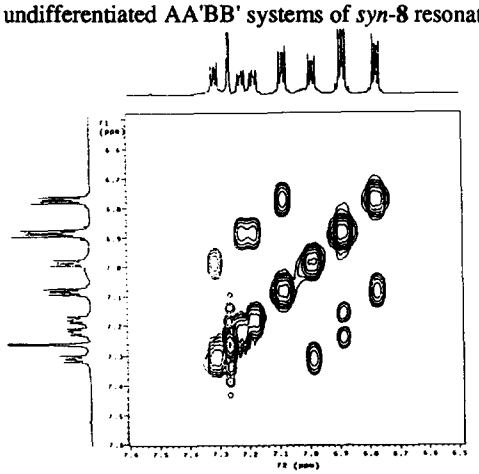


Figure 1. COSY spectrum of *syn*- and *anti*-**8**

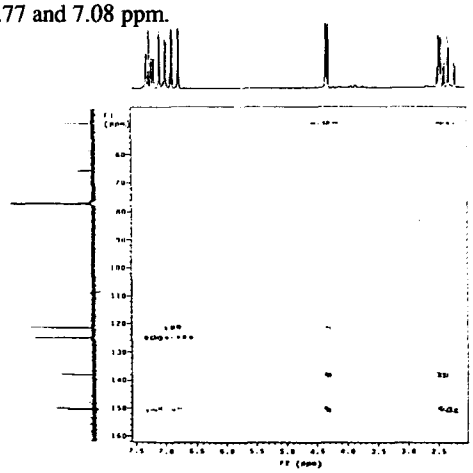


Figure 2. HMBC spectrum of *syn*- and *anti*-**8**

The mixture of *syn*-**8** and *anti*-**8**, in the approximate 1 : 2 ratio, gives rise to a ^{13}C spectrum characterized by signal bunches centered at 48.86, 65.40, 121.29, 124.83, 137.96 and 150.24 ppm, consisting of 4, 3, 4, 4, 4 and 4 lines respectively. From the symmetry of *syn*-**8** and *anti*-**8**, and from careful inspection of heterocorrelated HMQC and HMBC spectra, the bunches are attributed in the order to bridgehead carbons, to methano carbons, to ortho and meta carbons of the peripheral aromatic rings, to the carbons of the central ring, and to the ipso carbons of the peripheral rings. A closer look at the HMBC spectrum in Figure 2 allows the distinction between *endo* and *exo* methano protons on the basis of the Karplus rule.[15] The ^1H signals at 2.19, 2.30 and 2.44 ppm, correlating with the ipso carbons of peripheral rings, belong to the *endo* protons, the signals at 2.37, 2.43 and 2.48 ppm, correlating with the carbons of the internal ring, to the *exo* protons. The two isomers could be separated by slow recrystalization from THF/Et_2O. The *syn* isomer precipitated as a crystalline powder while the *anti* isomer remained in solution. Several experiments of X-ray diffraction analysis were unsuccessful, as the crystals melted before a sufficiently great set of data could be collected. Crystals of better quality could be grown from acetone/water. The isomer *syn*-**8** crystallized in the central P lattice.[16] The representation of *syn*-**8** based on X-ray coordinates is shown in Figure 3A. A similar representation of *anti*-**8** from *ab-initio* 3-21G* computations,[17] is reported in Figure 3B.

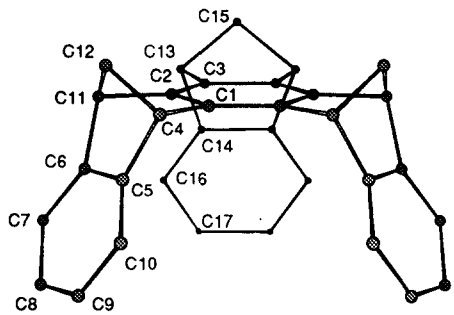


Figure 3A. Chem3D representation of *syn*-**8** based on the X-ray structure coordinates.

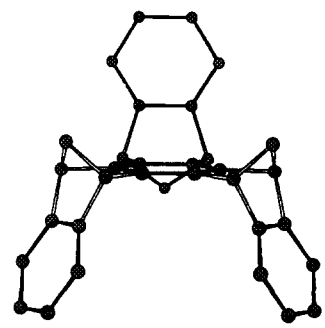


Figure 3B. Chem3D representation of *anti*-**8** based on the *ab initio* 3-21G* computations.

The central aromatic ring of *syn*-**8** shows bond length alternation, with the exocyclic bond shorter (1.36 Å) than the endocyclic one (1.41 Å). Table 1 reports a comparison between the available X-ray diffraction data and the results of *ab-initio* calculations at two different basis set levels for *syn*-**8** as well as similar molecules. Particularly significant appears the contribution of the phenyl rings in **8** with respect to **2**. Unfortunately, a comparison with **4** cannot be made because of the lack of X-ray data for the latter. However the Δ value appears to be reduced with respect to the oxa-bridged **5**.

Table 1. Bond lengths and difference in bond lengths from *ab initio* calculations and X-ray diffraction for compounds **1-5** and **8**.

#	3-21G*			6-31G*			X-Ray			Ref.
	endo, Å	*exo*, Å	Δ	*endo*, Å	*exo*, Å	Δ	*endo*, Å	*exo*, Å	Δ	
1	-	-	-	1.440	1.344	0.096	1.438	1.349	0.089	2
2	-	-	-	1.416	1.364	0.052	1.417	1.379	0.038	3
3	-	-	-	1.406	1.380	0.026	1.408	1.393	0.015	4
4[a]	1.434	1.343	0.091	-	-	-	-	-	-	5
5[b]	-	-	-	1.438	1.340	0.098	1.425	1.353	0.072	6
8[a]	1.427	1.348	0.079	-	-	-	1.412	1.360	0.052	*c*

[a] The computed values refer to the *syn*-isomer. No appreciable differences are noticed in the *anti*-isomer. [b]*Anti*-isomer. [c]This work.

The structure of *syn*-**8** is reminiscent of calixarenes and other types of host molecules. Indeed the X-ray analysis of this molecule was disturbed by the presence of disordered molecules of the solvent. This and other pecularities of **8** are actively studied.

Acknowledgements. The Italian laboratory thanks Dr. Richard Durr for preliminary experiments of cyclotrimerization. Work partially supported by CNR Rome. The contribution of the Regione Veneto, Department for Energy and Industry, for the purchase of Varian Unity 400 NMR spectrometer is also acknowledged. The Turkish laboratory are indebted to the Department of Chemistry (Atatürk University) and State Planning Organization of Turkey (DPT) for financial support.

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11. Dibromobenzonorbornadiene **11**: mp 74.5-75.5 °C (CH_2Cl_2-hexane). ^{1}H-NMR ($CDCl_3$, 200 MHz) δ (ppm): 7.36-7.29, 7.27-7.01 (4H, AA'BB', Ar), 3.94 (2H, t, *J* = 1.7 Hz), 2.75 (1H, dt, 1/2AB, *J* = 7.4, 1.7 Hz), 2.40 (1H, dt, 1/2AB, *J* = 7.4, 1.7 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 149.8, 135.8, 127.5, 124.1, 69.2, 60.8. IR (KBr) 3081, 3055, 3030, 2979, 2953, 1574, 1447, 1268, 1038, 757.
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14. *syn*-**8**: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.08 (6 H, m), 6.77 (6 H, m), 4.34 (6 H, t, *J* = 1.5 Hz), 2.48 (3 H, dt, *J* = 1.6, 7.8 Hz), 2.44 (3 H, dt, *J* = 1.6, 7.8 Hz). *anti*-**8**: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.31 (2 H, m), 7.22 (2 H, m), 7.18 (2 H, m), 6.98 (2 H, m), 6.88 (4 H, m), 4.31 (4 H), 4.28 (2 H, t, *J* = 1.5 Hz), 2.43 (2 H, dt, *J* = 2.4, 7.8 Hz), 2.37 (1 H, dt, *J* = 1.6, 7.8 Hz), 2.30 (2 H, dt, *J* = 1.6, 7.8 Hz), 2.19 (1 H, dt, *J* = 1.6, 7.9 Hz). *syn*-**8** and *anti*-**8**: ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): ipso external aromatics: 150.59 (*anti*-**8**: C4a, C18a), 150.18, 150.29 (*anti*-**8**: C6a, C10a, C12a, C16a), 149.80 (*syn*-**8**: C4a, C6a, C10a, C12a, C16a, C18a); internal aromatics: 138.15, 138.03, 137.92, 137.86; meta external aromatics: 124.96, 124.86, 124.80, 124.66; ortho external aromatics: 121.42 (*anti*-**8**: C1 and C4), 121.30 e 121.28 (*anti*-**8**: C7, C10, C13, C16), 121.14 (*syn*-**8**: C1, C4, C7, C10, C13, C16); apical: 6.64 (*syn*-**8**: C19, C20, C21), 65.40 (*anti*-**8**: C20 and C21), 45.19 (*anti*-**8**: C19); bridghead: 48.92, 48.90, 48.85, 48.83. UV (CH_2Cl_2, c = 1.7 10^{-4}) 236 (λ max), 256, 278 nm, A = 1.834, ε =11034.
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16. Orthorombic, space group *Pmnb*, No. 62. Unit cell parameters: *a* = 16.227(2), *b* = 16.510(2), *c* = 9.687(1) Å. $C_{33}H_{24}$; mw 420.56; *Z* = 4; *D* = 1.24 g/cm^3; centric P; λ (MoKα) = 0.7107Å. The structure was phased by SHELX 86 program and refined by blocked full matrix least squares using SHELX 76 program. The final conventional *R* factor for the 1656 considered observed reflections [$I \geq 2.7\sigma(I)$] was 0.084.
Bond distances (Å): C(1)-C(2) 1.412(5), C(1)-C(4) 1.527(5), C(2)-C(3) 1.360(5), C(2)-C(11) 1.528(5), C(3)-C(13) 1.530(5), C(4)-C(5) 1.530(5), C(4)-C(12) 1.554(6), C(5)-C(6) 1.407(6), C(5)-C(10) 1.363(6), C(6)-C(7) 1.373(6), C(6)-C(11) 1.519(6), C(7)-C(8) 1.386(7), C(8)-C(9) 1.370(8), C(9)-C(10) 1.398(7), C(11)-C(12) 1.554(6), C(13)-C(14) 1.521(6), C(13)-C(15) 1.544(6), C(14)-C(16) 1.364(6), C(16)-C(17) 1.395(7), C(1)S-C(3)S 1.39(2), C(2)S-C(3)S 1.47(2).
Bond angles (Degrees): C(2)-C(1)-C(4) 106.2(3), C(1)-C(2)-C(11) 106.8(3), C(1)-C(2)-C(3) 119.9(3), C(3)-C(2)-C(11) 133.4(4), C(2)-C(3)-C(13) 133.8(3), C(1)-C(4)-C(12) 98.5(3), C(1)-C(4)-C(5) 106.4(3), C(5)-C(4)-C(12) 98.7(3), C(4)-C(5)-C(10) 133.0(4), C(4)-C(5)-C(6) 106.5(3), C(6)-C(5)-C(10) 120.5(4), C(5)-C(6)-C(11) 106.7(3), C(5)-C(6)-C(7) 121.2(4), C(7)-C(6)-C(11) 132.1(4), C(6)-C(7)-C(8) 118.0(4), C(7)-C(8)-C(9) 120.9(5), C(8)-C(9)-C(10) 121.4(5), C(5)-C(10)-C(9) 118.0(4), C(2)-C(11)-C(6) 106.2(3), C(6)-C(11)-C(12) 98.7(3), C(2)-C(11)-C(12) 98.6(3), C(4)-C(12)-C(11) 94.3(3), C(3)-C(13)-C(15) 99.2(3), C(3)-C(13)-C(14) 105.0(3), C(14)-C(13)-C(15) 99.3(3), C(13)-C(14)-C(16) 132.7(4), C(14)-C(16)-C(17) 118.5(4), C(1)S-C(3)S-C(2)S 104.0(5).
17. Spartan Version 4.0, Wavefunction Inc., 18401 Karman Ave., #370, Irvine, CA 92715 U.S.A.

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