

# 1,6:9,14-BISMETHANO[16]ANNULENE - A NEW BRIDGED [4n]ANNULENE

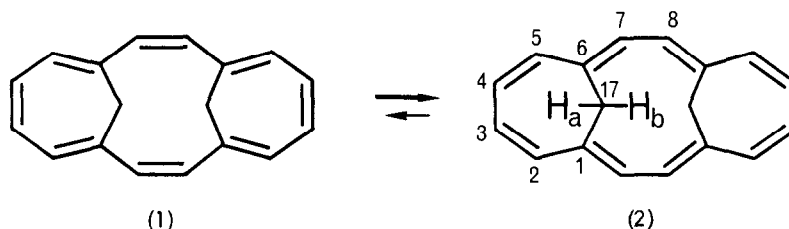
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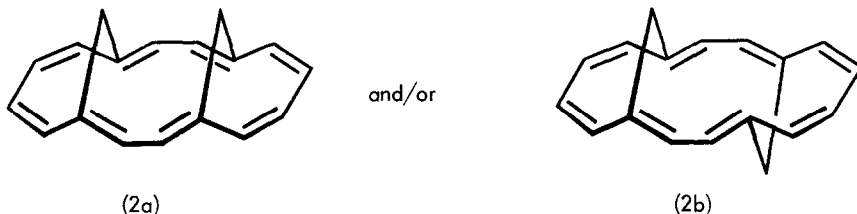
**Summary:** The molecular structure and dynamic behaviour of the bridged [4n]annulene 1,6:9,14-bismethano-[16]annulene is unravelled by NMR and X-ray investigations, combined with force field calculations.

In a recent publication we reported on the synthesis of 1,6:9,14-bismethano[16]annulene [(1) and/or (2)]<sup>1</sup>, a new bridged [4n]annulene, by reductive coupling of cycloheptatriene-1,6-dialdehyde<sup>2</sup>, but did not elaborate on the structural details of the compound. As [4n]annulenes, other than cyclobutadiene<sup>3</sup> and cyclooctatetraene<sup>4</sup>, are far less well-known than their [4n+2]annulene counterparts, it was of obvious interest to subject 1,6:9,14-bismethano[16]annulene to closer physical and chemical scrutiny. Evidence as to the double bond configuration, stereochemistry and dynamic behaviour of this annulene has now been obtained.

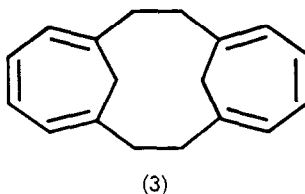


The <sup>1</sup>H NMR spectrum [300 MHz (CD<sub>2</sub>Cl<sub>2</sub>)] of 1,6:9,14-bismethano[16]annulene, similar to that of the parent [16]annulene<sup>5</sup>, is indicative of the presence of a paramagnetic ring current, for the resonances of the annulene protons occur at relatively high field [AA'BB'-system at δ= 5.03 (H-3,4) and 5.09 (H-2,5) with J<sub>2,3</sub> = 10.73, J<sub>2,4</sub> = 0.61, J<sub>2,5</sub> = 0.95, J<sub>3,4</sub> = 8.74 Hz and singlet at δ= 4.77 (H-7,8), J<sub>7,8</sub> = 7.05 Hz] whereas those of the bridge protons appear at relatively low field [AX-system at δ= 5.68 (H-17a) and 8.30 (H-17b) with J<sub>17a,17b</sub> = 13.44 Hz]. The assignment of the spectrum rigorously follows from decoupling experiments. Deeper insight into the nature of the 16π-electron system of the compound is provided by an examination of the vicinal coupling constants J<sub>2,3</sub> and J<sub>3,4</sub>. The pronounced alternation of these couplings not only demonstrates the presence of localized π-bonds but, due to the relationship J<sub>2,3</sub> > J<sub>3,4</sub>, also permits the safe conclusion that one is dealing with the double bond isomer (2)<sup>6</sup>.

If (2) is in rapid equilibrium with (1) (as seems likely) the concentration of the latter must be below 5 % (detection limit of the method).



The stereochemical question of whether (2) has the bridges in a syn or anti arrangement [(2a) and (2b), respectively] escapes a clear-cut answer on the basis of the NMR spectrum. An argument in favour of (2a) can be construed on the assumption that the marked difference in the chemical shift of the bridge protons (2.6 ppm) arises from a steric compression of the inner bridge protons<sup>7</sup>. Such an explanation, however, is hard to reconcile with the fact that 7,8,15,16-tetrahydro-1,6:9,14-bismethano[16]annulene (3), which exists as a single conformer (syn or anti), is so flexible as to undergo a fast degenerate bridge inversion ( $\Delta G^\ddagger = 15.4$  kcal/mol)<sup>8,9</sup>.



An investigation of the temperature dependence of the NMR spectrum of (2) shows that, starting at 40°C, the AX-system of the bridge protons broadens until coalescence is observed at 132°C (90 MHz). Significantly, the parameter  $N (= J_{2,3} + J_{2,4})$ <sup>10</sup> remains essentially constant over the entire range of temperature (-80° to 150°C) studied, indicating that the changes in the spectrum do not originate from a shift of the supposed equilibrium (2)  $\rightleftharpoons$  (1) towards (1). By analogy to the situation with the aforementioned tetrahydro derivative (3), the dynamic process of (2) responsible for the temperature dependent NMR spectrum must be a degenerate bridge inversion of either the syn conformer (2a) or the anti conformer (2b). From the coalescence temperature the  $\Delta G^\ddagger$  value of this process is estimated to be 18 kcal/mol.

An X-ray structural analysis of 1,6:9,14-bismethano[16]annulene<sup>11</sup>, apart from confirming the presence of (2) with alternating single and double bonds (Figure 1a), demonstrates that, at least in the crystalline state, (2) exists as the anti conformer (2b). Although the annulene ring of (2b) is grossly planar, conjugation of the  $\pi$ -system is hindered to some extent, since the torsional angle at the single bonds which connect the two seven-membered rings measures no less than 46°. As regards the position of the bridge protons with respect to the annulene ring, it seems interesting to note that the inner protons reside directly above the center of the ring whilst the outer bridge protons point away from the ring (Figure 1b). These spatial features of the solid state conformation (2b) of (2), obviously, allow for a more convincing explanation of the difference in chemical shift of the inner and outer bridge protons

than the compression effect, invoked originally, and hence justify the assumption that the anti conformation (2b) is also true for the molecule in solution.

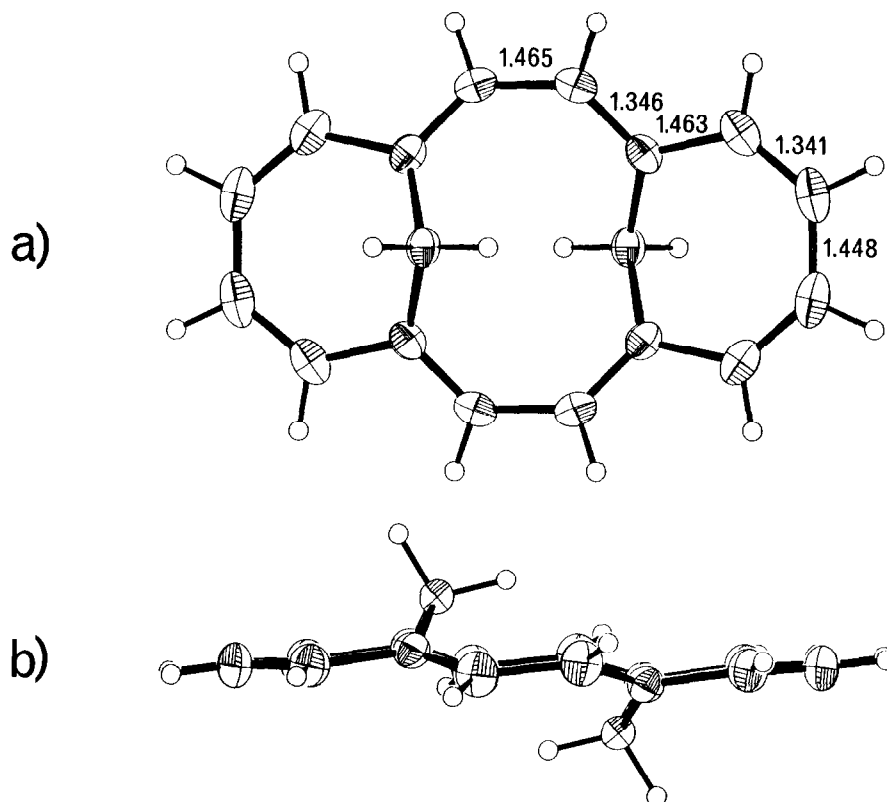
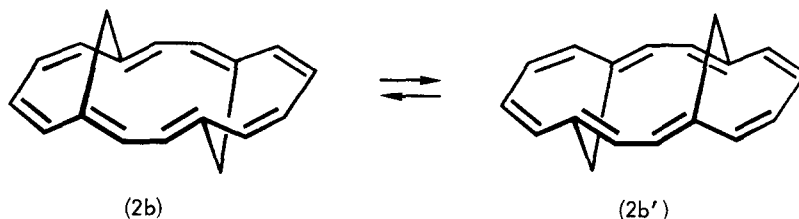


Figure 1. molecular structure of 1,6:9,14-bismethano[16]annulene

a) top view of the molecule, bond lengths [Å]

b) side view

Molecular mechanics calculations<sup>12</sup> on 1,6:9,14-bismethano[16]annulene, which almost exactly reproduced the results of the X-ray structural analysis, indeed, show (2b) to be the double bond isomer and conformer of lowest energy. Not too surprisingly, the cycloheptatriene-type double bond isomer with anti bridges is found to differ from (2b) by only 1.3 kcal/mol. Particularly pertinent to the steric problem in question is the fact that the calculations place the syn conformer (2a) higher in energy than the anti conformer (2b) by as much as 19 kcal/mol<sup>13</sup>. This energy value rules out (2a) beyond reasonable doubt.



In summary, the experimental and theoretical findings on 1,6:9,14-bismethano[16]annulene prove the compound to be represented (in solution) by the rapid degenerate equilibrium (2b)  $\rightleftharpoons$  (2b'). It will require a more sophisticated investigation to delineate the mechanistic pathway along which this inversion process proceeds.

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11. Crystal data: (2), orthorhombic, space group P n n m,  $a = 4.306(1)$ ,  $b = 11.321(1)$ ,  $c = 12.932(1)$  Å,  $Z = 2$ ,  $R = 0.035$  and  $R_w = 0.037$  for 582 unique reflections. Crystallographic data have been deposited with the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen, FRG. Any request should be accompanied by the full literature citation for this communication and the reference number CSD 51280.
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13. The syn conformer of the cycloheptatriene-type double bond isomer (1) is calculated to be 5.1 kcal/mol higher in energy than (2b).

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