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A SIMPLE SYNTHESIS OF A DOUBLY-BRIDGED [16]ANNULENE

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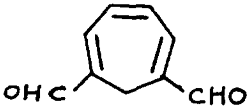
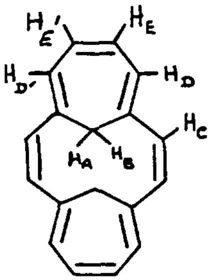
Reductive coupling of cycloheptatriene-1,6-dialdehyde using a low-valent titanium reagent provides a one-step route to a paratropic bismethano [16] annulene.

The annulenes play a central role in bridging theoretical and experimental organic chemistry.Largely due to the work of Sondheimer,[1a] Boekelheide[1b] and Vogel,[1c] a variety of [*N*]annulenes and their bridged counterparts is now available to test extant theories and criteria of aromaticity,anti-aromaticity and non-aromaticity.[2] The bridged [*N*]annulenes have very recently been the subjects of renewed theoretical interest.[3] However,the synthesis of these important compounds is usually no simple task,often involving lengthy synthetic sequences.We now wish to report a one-step synthesis of a doubly-bridged [16]annulene *(2)*,*i.e.* 1,6:9,14-bismethano[16]annulene.Most probably,*(2)* exists as an equilibrium mixture of double bond isomers,*(2a)* and *(2b)*,isomer *(2a)* being assumed to be favoured thermodynamically.

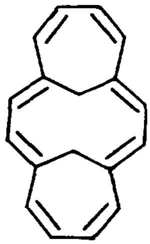


(1)



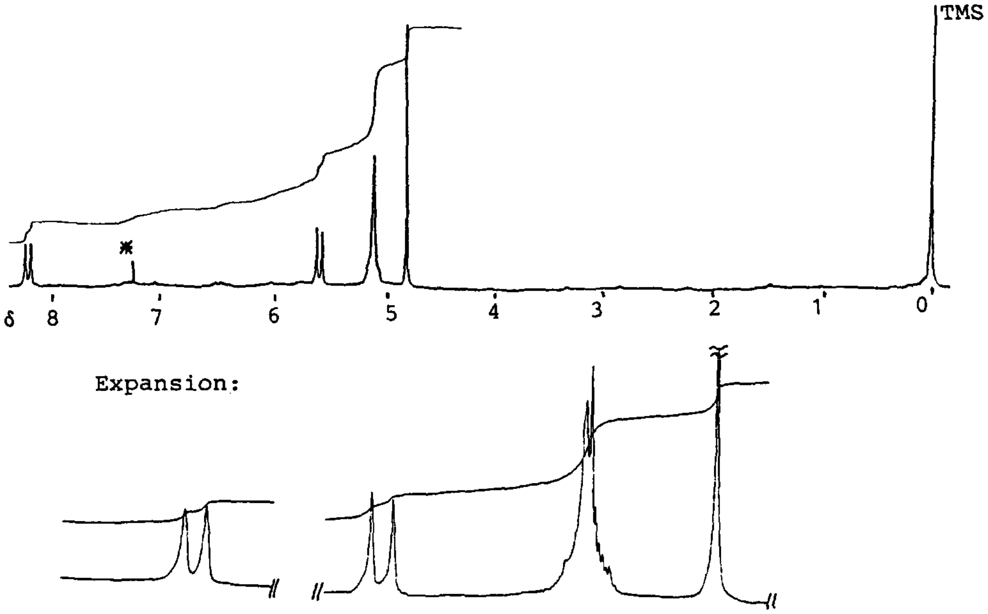
(2a)

⇌



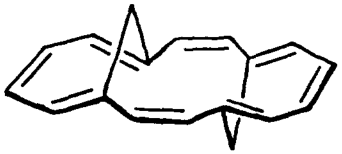
(2b)

The annulene *(2)* is readily available *via* the reductive coupling of cycloheptatriene-1,6-dialdehyde *(1)*[4] using the low-valent titanium species obtained from titanium tetrachloride and zinc.[5] Yields of the annulene thus obtained vary from 2 to 5%,a typical procedure being the following.A 500 ml three-necked flask fitted with a reflux condenser, Schlenk-type dropping funnel and an argon inlet was charged with dry THF (250 ml) and cooled to -78°C.$TiCl_4$ (20 mmol) was then added slowly, followed by zinc powder (40 mg-atom) and dry pyridine (1 ml).The resultant black mixture was refluxed under argon for one hour and a solution of the dialdehyde (2 mmol) in dry THF (150 ml) was then added dropwise to the stirred mixture over 24 hours.After reflux for a further 12 hours,the reaction mixture was ice-cooled and quenched (10% aqueous K_2CO_3).The grey precipitate was filtered off and both filter-cake and filtrate extracted thoroughly with dichloromethane.The combined organic phases were washed with water,dried ($MgSO_4$) and the solvent evaporated to give a blood-red semi-solid residue.Rapid chromatography on a short silica gel column (hexane/dichloromethane 8:1) yielded *(2)* as air-stable golden-brown needles,m.p. 163°C (dec.).UV(cyclohexane):λ_{max} 286 nm (ε 29,100),296(sh) (25,000),310 (14,380),326 (13,700). MS(50eV):*m/e* 232 (M^+,100%),217(25),216 (33),215(45),203(23),202(51),165(25).Only peaks stronger than 20% of the base peak are listed.Abs.mass:232.124±0.005, calc. for $C_{18}H_{16}$ 232.125. The 270 MHz ^{1}H NMR spectrum of *(2)* is shown below.($CDCl_3$/TMS,the peak marked with an asterisk being due to the solvent).



The spectrum is in accordance with the proposed structure,the annulene protons H_C giving rise to a sharp singlet at δ 4.80 and $H_{DD'EE'}$ appearing as a near-*AA'BB'* pattern centred on δ5.10 whereas the methylene bridge protons H_A and H_B give rise to an *AX* system (J = 14 Hz) at δ 5.58 and 8.20. The relatively high-field shifts of the annulene protons (H_C,$H_{DD'EE'}$) and the low-field shifts of the bridge protons (H_A,H_B) imply that *(2)* is a paratropic species.

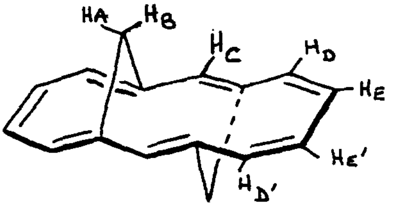
One important structural feature which cannot be deduced from the NMR spectrum alone is the relative geometry of the bridging methylene groups. Two arrangements are possible, *anti* (C_{2h}) and *syn* (C_{2v}) as shown below.



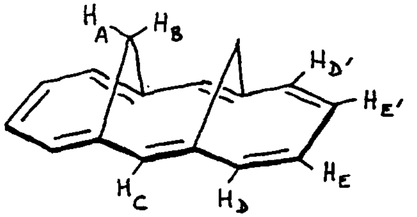
anti

syn

Inspection of CPK models reveals that extensive conjugation should be possible in both isomers, interconversion of the two *via* "flipping" of the methylene groups being, apparently, sterically hindered. A comparison of the ^{1}H NMR shifts of *(2)* with those of the non-aromatic (*i.e.* polyolefinic) *anti* species *(3)*^{6} and the diatropic (aromatic) *syn* species *(4)*^{6} is given in the Table below:



(3)



(4)

Compound		^{1}H NMR, δ		
	Methylene H	H_C	$H_{DD'EE'}$	
(2)	5.58, 8.20	4.80	5.03 *to* 5.15	*paratropic*
(3)	1.88, 2.48	6.33	6.20	*polyolefin*
(4)	−1.20, 0.90	7.90	7.00 *to* 7.80	*diatropic*

For compound *(4)* the lower-field half of the *AX* pattern due to the methylene protons is assigned to the "inner" protons (H_B) and the shift difference between H_A and H_B ascribed mainly to the "proximity effect"^{6}.

The extreme low-field shift of one half of the methylene *AX* system in *(2)*, δ 8.20, could thus be analogously rationalised as being due to a combination of the paramagnetic ring current and such a proximity effect. In the *anti* isomers, such steric effects are absent.

At a mercury drop electrode in dry DMF containing tetraethylammonium perchlorate as supporting electrolyte, compound *(2)* undergoes two fullyreversible one-electron reductions, the half-wave potentials being -1.31 V and -1.59 V *vs.* SCE (*i.e.* $\Delta E_{1/2}$ = 280 mV). The relevant electrochemical processes are thus reduction to the radical anion and the dianion, respectively, and the observed behaviour is rather similar to that found in [16]annulene[7] for which the corresponding values are -1.23 V and -1.52 V (*i.e.* $\Delta E_{1/2}$ = 290 mV).

Acknowledgements

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