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[2.2](4,4´)TRANS-STILBENOPHANE

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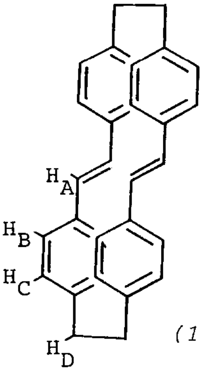
The title compound has been synthesised by a reductive coupling of bibenzyl-4,4´-dicarbaldehyde and its dynamic properties and photo-induced isomerisations are briefly described.

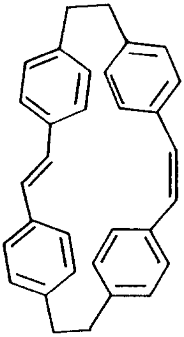
Cis- and *trans*-stilbene have been the subjects of numerous investigations and their structures,properties and isomerisation are now well understood. Linking together two 4,4´-stilbene units by two -CH_2-CH_2- bridges to form a [2.2](4,4´)stilbenophane makes it possible to investigate some novel properties of the stilbene system.Since the layered and more rigid *trans, trans*-isomer is strained,while the *cis,cis*-isomer can be relatively planar and strain-free,the thermodynamical equilibrium between the *trans* and *cis* isomers may be shifted in the stilbenophane case.Moreover,the facile dynamic processes in the simple stilbenes,the rotation of the benzene rings and the *trans* vinylene group,should be more hindered and might become separable and measureable in the cyclophanes.

The photoisomerisation of *cis-* and *trans*-stilbenes must occur *via* rotation about the double bond.It could be argued that the steric effects in strained *trans*-stilbenophanes such as *(1)* should prevent such isomerisations to the *cis*-isomers[1],a proposal which can now be tested on the title compound.

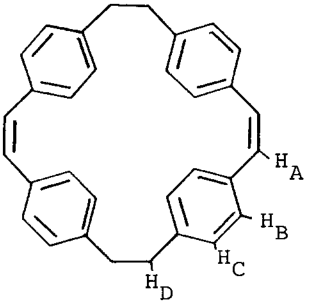
[2.2](4,4´)*trans*-Stilbenophane *(1)* can be prepared from bibenzyl-4,4´-dicarbaldehyde using the low-valent titanium species obtained from titaniumtetrachloride and zinc.[2] A solution of $TiCl_4$ (20 mmol) in dry THF (30 ml) was ice-cooled under argon in a three-necked flask fitted with a reflux condenser and a Schlenk-type dropping funnel.Zinc powder (40 mg-atom) was then added carefully in small portions to the magnetically stirred solution,followed by dry pyridine (2 ml).The resultant black mixture was then refluxed for one hour and a solution of bibenzyl-4,4´-dicarbaldehyde[3] (2 mmol) in dry THF (100 ml) added dropwise over a period of several hours.After reflux overnight,the reaction mixture was cooled



(1)



(2)



(3)

and then quenched by addition of 10% aqueous potassium carbonate.The grey precipitate was filtered off,the filtrate extracted thoroughly with dichloromethane,and the combined organic phases washed with water,dried ($MgSO_4$) and the solvent evaporated.Care was taken to protect the solutions from light.Rapid chromatography of the residue on a short silica gel column yielded 93 mg (23%) of crude [2.2](4,4´)*trans*-stilbenophane *(1)*. Recrystallisation from chloroform/methanol gave colourless crystals (56 mg, 16%) which showed no melting up to 290°C,whereafter they decomposed. UV (ethanol): λ_{max} 295 nm, ε 63,500; IR (KBr): 3010(m), 2920(m), 2850(m), 1510(s), 1460(m), 960(s) and 800(s) cm^{-1}.MS (50eV):*m/e* 412 (M^+, 100%), 206 (87), 205 (19) and 191 (14).Abs. mass 412.219; calc. for $C_{32}H_{28}$ 412.219. ^1H NMR (270 MHz, $CDCl_3$): δ 6.88 (8H, m, H_B or H_C), 6.65 (8H, m, H_C or H_B), 6.54 (4H, s, H_A) and 2.99 (8H, s, H_D).

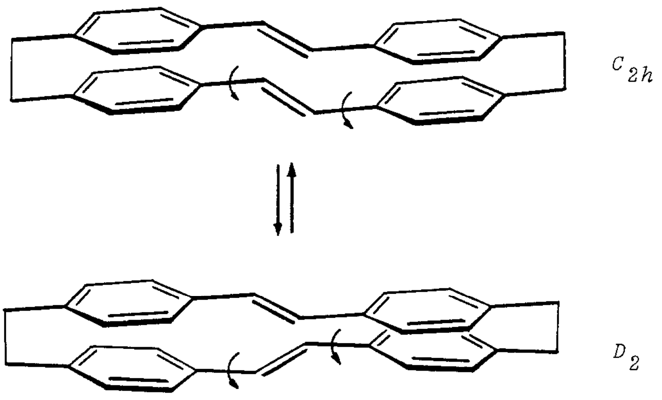
From careful chromatography on silica gel of the mother liquors from recrystallisation and of the other fractions from the crude separation, only the *cis,cis*-isomer *(3)* was isolated[4]. The ^1H NMR spectrum of the original crude reaction product had shown only trace amounts of this isomer,which must then have been formed on contact with silica gel.

Upon irradiation in a Rayonet reactor with light of maximum intensity around 300 nm,the *trans,trans*-isomer *(1)*, (1.6×10^{-2}M, benzene-d_6, pyrex NMR-tube) isomerised smoothly to the *cis,cis*-isomer *(3)*. A low steady-state concentration of a third compound was observed.Its ^1H NMR spectrum was consistent with that of the *cis,trans*-isomer *(2)* (two AA´XX´ patterns for the aromatic protons,two singlets for the olefinic protons, one of which must coincide with a more intense peak,and a complex pattern for the methylene protons).The same isomerisation process could be observed by UV spectroscopy.Exposure of the UV sample of the *trans,trans*-isomer *(1)* to daylight caused a rapid isomerisation to the *cis,cis*-isomer *(3)* with the *cis,trans*-isomer *(2)* as a possible intermediate.A more careful investigation of the photoequilibria and properties of these stilbenophanes is under way.

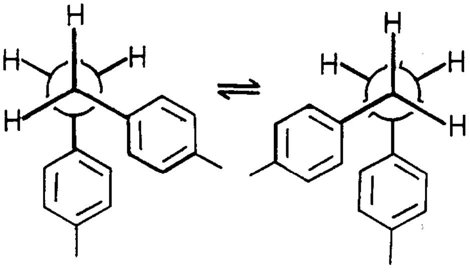
[2.2](4,4´)*trans*-Stilbenophane *(1)* is reduced at the same potential

(-2.43 V *vs.* SCE) as the *cis,cis*-isomer *(3)* at a mercury drop in dry DMF. Under these experimental conditions[5] both cyclophanes are reduced irreversibly in two-electron processes at considerably more negative potentials than *trans*- and *cis*-stilbene[6].

[2.2](4,4′)*cis*-Stilbenophane *(3)* has previously been prepared by a twofold Wittig reaction between bibenzyl-4,4′-dicarbaldehyde and the bistriphenylphosphonium salt from 4,4′-bis(bromomethyl)bibenzyl[4] and by constant potential electrolysis of $[2_4]$paracyclophanetetraene[7]. Isomer *(3)* has also been the subject of a variable-temperature ^{1}H NMR study[8]. The rotation or flipping of the benzene rings in *(3)* is fast,on the NMR timescale,down to 150 K whereas the torsional motion of the $-CH_2-CH_2-$ bridges takes place over a barrier of *ca.* 29 kJ mol^{-1}.In the *trans,trans*-isomer *(1)*,the latter barrier should also be present while the rotation of the benzene rings seems to be severely hindered from inspection of CPK molecular models.The rotation of the *trans* -CH=CH- group is sterically unhindered.Since the last-named process involves the loss of resonance stabilisation over the two benzene rings and the linking double bond,the process has a barrier of electronic origin which can be estimated only from quantum mechanical calculations.



The ^{1}H NMR spectrum of *(1)* remained unchanged down to 193 K.At lower temperatures,a broadening of the singlet for the methylene protons began to occur together with a less distinct broadening of one half of the aromatic signals.The olefinic singlet remained sharp down to 165 K (CD_2Cl_2 solution).From comparison with low-temperature spectra of *(3)* and from inspection of CPK molecular models,the following tentative conclusions can be drawn.*(i)* The rotation of the -CH=CH- groups in *(1)* is fast even at 165 K. *(ii)* The rotation of the benzene rings is hindered in *(1)* but fast in *(3)*. *(iii)* The one dynamic process observable by ^1H NMR methods is the same for both *(1)* and *(3)* and is identified as the interconversion of *gauche*$^+$ and *gauche*$^-$ conformations of the saturated bridges.



gauche$^+$ *gauche*$^-$

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References and notes.

1. This possibility was suggested to us by Prof. H.Rau of the University of Hohenheim,Stuttgart,in a personal communication.
2. D.Lenoir, Synthesis 1977 553.
3. Prepared from 4,4´-dibromobibenzyl by successive treatment with butyl--lithium,dry DMF,and dilute hydrochloric acid.
4. B.Thulin and O.Wennerström, to be published.The isomers *(1)* and *(3)* have near-identical MS but can be distinguished in a number of ways.The *cis,cis*-isomer *(3)* has m.p. 147-151^{0}C,absorbs at shorter wavelength (λ_{max} 265 nm, ε 23,600 in ethanol),has no distinct IR absorption at 960 cm^{-1} and shows small shift differences in the ^1H NMR spectrum as compared to *(1)* ($CDCl_3$ solution,the overall pattern of the spectra being the same for both isomers).The shift differences are much greater in the benzene-d_6 solvent used in the photochemical studies.
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