Stable Isomers of 1,6-Bis-(1-cyano-1-methylethyl)triptycenes

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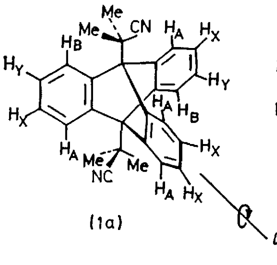
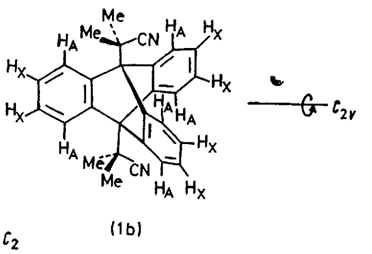
Summary The isomers (**1a**) and (**1b**) of 1,6-bis-(1-cyano-1-methylethyl)triptycene have been prepared and found to be stable to thermal (half-life of 115 min at 200°) and photochemical interconversions.

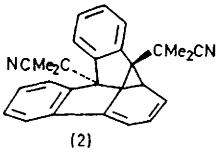
There has been considerable interest in triptycene and benzobarrelene derivatives in which the rotation around the sp^3 to sp^3 single bond between the bridgehead carbon atom and the substituent attached to it is restricted to give long-lived conformational isomers.[1] We now report on the conformational stability of isomeric 1,6-bis-(1-cyano-1-methylethyl)triptycenes which are resistant to both thermal and photochemical isomerization.



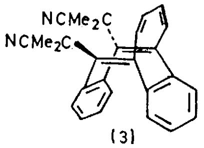
(1a)



(1b)



(2)



(3)

The triptycenes are prepared in good yield by the addition of benzyne to 9,10-bis-(1-cyano-1-methylethyl)anthracene, m.p. 195—198°,† obtained by dehydrobromination of 9-bromo-9,10-bis-(1-cyano-1-methylethyl)-9,10-dihydro-anthracene[2] in pyridine, and separated by column chromatography on alumina. The n.m.r. spectra of the less polar isomer (**1a**), m.p. 365—366° (decomp.), [δ ($CDCl_3$) 2·39 (2Me, s), 2·46 (2Me, s), and 7·0—8·3 (12ArH, m, analysed as A_2X_2 and 2 ABXY)] and of the more polar isomer (**1b**), m.p. 503—508° (decomp)., [δ 2·50 (4Me, s) and 7·0—8·2 (12ArH, m, 2 A_2X_2 and another A_2X_2)] are in accord with C_2 and C_{2v} symmetries, respectively.

Compounds (**1a**) and (**1b**) are exceptionally stable to thermal isomerization, but they isomerize at 200° in nitrobenzene, with a half-life of 115 min, to give an equilibrium mixture of (**1a**) and (**1b**) in the ratio 65·5 : 34·5. The temperature dependence of the rate of isomerization gives a rough estimate of the activation energy as 37·7 kcal mol^{-1} with a frequency factor of 10^{13} s^{-1}. The data represent the highest barrier to restricted rotation around the sp^3 to sp^3 hybridized pivot bond yet reported.

Irradiation of solutions of (**1a**) and (**1b**) in acetone, cyclohexane, or ether (0·05%) with a Pyrex-filtered high-pressure mercury source gives the common photoproduct (**2**), m.p. 162°, [δ ($CDCl_3$), 1·04, 1·24, 1·31, and 1·45 (4Me), 3·02 (1H d, J 6·0 Hz), 6·9—7·5(3 olefinic H); λ_{max} 248·5, 347 nm (log ϵ 4·23, 3·89)],[3] in a yield of 95% based on the rearranged triptycene. No isomerization between (**1a**) and (**1b**) is observed in the remaining triptycene fractions, nor are signals characteristic of a cyclo-octatetraene derivative detected. Once a cyclo-octatetraene derivative, *e.g.* (**3**), or its quadricyclene-type intermediate is formed, rotation of the CMe_2CN groups would be expected to occur as a result of decreased van der Waals interaction with the neighbouring *peri*-hydrogen atoms of the transition state. The present findings rule out the possibility of the unfavourable steady state established towards cyclo-octatetraenes which are often photoproducts of other barrelene derivatives.[4]

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† All new compounds analysed correctly.

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[4] H. E. Zimmerman and C. O. Bender, *J. Amer. Chem. Soc.*, 1970, **92**, 4366, and refs. therein.