Resolution and Optical Stability of Tetrabenzocyclo-octatetraene Derivatives

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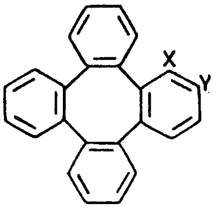
Summary The tetrabenzocyclo-octatetraene derivative (**2**) has been partially resolved, and a lower limit for the barrier to racemization of 45 kcal mol^{-1} has been determined.

We have previously shown[1] that the tetrabenzocyclo-octatetraene derivative (**1**) exists as a mixture of diastereomers which do not interconvert rapidly on the n.m.r. time scale at 98° ($\Delta G^{\ddagger}_{98} > 21$ kcal mol^{-1}).† In order to obtain a more meaningful estimate of the barrier to ring inversion in such compounds, we have prepared optically active (**2**), and studied its optical stability at elevated temperatures.



(**1**) X=H,Y=CH(OH)Me
(**2**) X=H,Y=CO$_2$H
(**3**) X=H,Y=CHO
(**4**) X=CHO,Y=H

Treatment of tetraphenylene with titanium tetrachloride and dichloromethyl methyl ether in methylene chloride gave a mixture of (**3**) and (**4**), which were separated by fractional crystallization from methylene chloride–hexane.[1] Oxidation of (**3**) with silver oxide in ethanol, followed by acidification, yielded racemic (**2**), m.p. 281—284°.‡ Partial resolution of (**2**) by fractional crystallization of the brucine salt from ethanol gave (+)-(**2**), m.p. 285—287°, $[\alpha]_{320}$ $+23{\cdot}3°$ (*c* 0·45 in EtOH), and (−)-(**2**), m.p. 287—288°, $[\alpha]_{320}$ $-8{\cdot}4°$ (*c* 0·57 in EtOH). A sample of (+)-(**2**) showed no change in rotation within experimental error (*ca.* ±10%) after heating at 251° for 36·0 h (0·038 molal solution in biphenyl). This result yields a lower limit to racemization, and hence a lower limit to ring inversion, of $\Delta G^{\ddagger}_{251} > 45$ kcal mol^{-1}.

A comparison of the barrier for ring inversion in (**2**) with the barriers reported for less sterically hindered cyclo-octatetraene derivatives[1] is a striking confirmation of our thesis that non-bonded interactions constitute the major source of structural rigidity exhibited by such systems.[1]

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† *Added in proof.* Independently, A. Rosdahl and J. Sandström (*Tetrahedron Letters*, 1972, 4187) have reported a lower limit to ring inversion of 26 kcal mol^{-1} for another derivative of tetrabenzocyclo-octatetraene.

‡ Satisfactory elemental and mass spectral analyses were obtained for (**2**). N.m.r. spectral data were in agreement with the structure assigned.

[1] G. H. Senkler, jun., D. Gust, P. X. Riccobono, and K. Mislow, *J. Amer. Chem. Soc.*, 1972, **94**, 8626.