Substituent-dependency of *cis–trans*-Isomerization in Disubstituted Tetrabenzopentafulvalenes[1]

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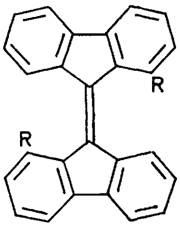
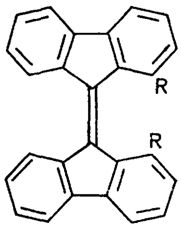
Summary The conformational behaviour of 1,1′-disubstituted tetrabenzopentafulvalene is strongly substituent-dependent; in the 2,2′-difluoro-derivative, the energy barriers associated with the *cis–trans*-isomerization did not prove to be low.

IN recent dynamic n.m.r. studies on the conformational behaviour of 1,1′-bisalkoxycarbonyltetrabenzopentafulvalenes (**1**; R = CO_2R')[2,3] "remarkably low energy barriers" ($\Delta G^{\ddagger}_{363}$ = 20—21 kcal mol^{-1}) for *cis–trans*-isomerizations have been observed.[2] We now show that this is not an intrinsic feature of the tetrabenzopentafulvalene system; its conformational behaviour is strongly substituent-dependent. In the 2,2′-difluoro-derivative (**2**), which strongly resembles the parent compound (**1**; R = H), the energy barriers associated with the *cis–trans*-isomerization are not at all low.

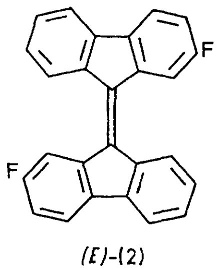
We used 2,2′-difluorotetrabenzopentafulvalene (**2**) (prepared according to Bergmann,[4] red needles, m.p. 225° from n-pentanol) as model because the environment around the "pinch", particularly the "overcrowding", is very similar to that in the parent compound (**1**; R = H). Moreover, the reported experimental dipole moment value (2·51 D in benzene)[4] does not contradict the presence of a mixture of the *cis*-isomer, (*Z*)-(**2**), and the *trans*-isomer, (*E*)-(**2**). Both the ^1H and the ^{19}F n.m.r. spectra served as probes for the study of the two possible geometrical isomers.† The ^{19}F spectrum of (**2**) in benzene consists of two distinctly separated sextets [Δν 34, *J* (F-1-H) 10, *J* (F-3-H) 9, *J* (F-4-H) 5 Hz] representing the two geometrical isomers, (*Z*)-(**2**) and (*E*)-(**2**), in the ratio of 1:1. In $CDCl_3$, CH_2Cl_2, 1-bromodecane, mesitylene, tetralin, and *m*-fluoroacetophenone, Δν becomes even smaller; the two multiplets partially overlap each other. The presence of the two isomers could be proved also by the multiplets in the low field region of the ^1H n.m.r. spectrum (in $CDCl_3$) of (**2**), which is characteristic of the protons *ortho* to the "pinch" of the tetrabenzopentafulvalene system.[5] It should be noted that the n.m.r. spectra of (**2**) in contrast to those of the 1,1′-difluoro-analogue, (**1**; R = F), do not give any indication of a "through space" 8-H–F coupling.[6]



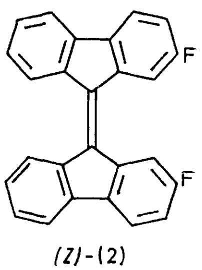
(*E*)-(1)



(*Z*)-(1)



(*E*)-(2)



(*Z*)-(2)

Neither the fluorine signals nor the proton multiplets in the low field region of (**2**) coalesced even at 220 °C. Although there were indications of an incipient *cis–trans*-isomerization process, the shift and the broadening of the absorptions with rising temperature pointed to considerably higher coalescence temperatures than 220 °C. The 1,1′-difluoro-isomer (**1**; R = F) showed similar behaviour. This behaviour contrasts sharply with the ease of the *cis–trans*-isomerization of 1,1′-disubstituted tetrabenzopentafulvalenes carrying bulky groups, *e.g.*, (**1**; R = CO_2R').[2] Our studies of the 1,1′-dimethyl- and 1,1′-dichloro-derivatives strengthen this point. The two methyl signals of *cis*- and *trans*-1,1′-dimethyltetrabenzopentafulvalene (**1**; R = Me) [1:5 ratio, 30 °C, δ ($CDBr_3$) 1·85 (Me, *cis*), 2·58 p.p.m. (Me, *trans*)] coalesce at 109 °C ($\Delta G^{\ddagger}_{382}$ 19 kcal mol^{-1}). The low field multiplet (8·36 p.p.m.) of *cis*-1,1′-dichlorotetrabenzopentafulvalene, (*Z*)-(**1**; R = Cl) population 0·25 mol fraction, 30 °C, $CDBr_3$, reach coalescence (7·85 p.p.m.) at *ca.* 140 °C. It appears that bulky substituents (CO_2R', Cl, Me) at positions 1 and 1′ increase the ground state strain and therefore lower substantially the activation energy for the *cis–trans*-isomerizations, whilst the small fluorine atoms do not have this effect. Undoubtedly, fluorine atoms at positions 2 and 2′ will not contribute much to the ground state strain and therefore will not favour *cis–trans*-isomerization. It is thus probable that the energy barriers associated with the degenerate isomerization of the parent compound (**1**; R = H), in spite of the "overcrowding" around the "pinch", are not remarkably low. The parent

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† The ^1H and ^{19}F n.m.r. spectra were recorded at 100 and 94·1 MHz, respectively. ^1H chemical shifts are reported in p.p.m. downfield from Me_4Si. ^{19}F chemical shifts are reported in Hz upfield from CCl_3F.

compound will not be able to "flip" through a form in which the two halves of the molecule are perpendicular to each other without considerable energy input which cannot be attained by the n.m.r. method.

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[1] For previous paper in the series see, I. Agranat, M. Rabinovitz, and M. Wiessman, *Tetrahedron Letters*, 1972, 273.

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[5] M. Rabinovitz, I. Agranat, and E. D. Bergmann, *Tetrahedron Letters*, 1965, 1265.

[6] I. Agranat, M. Rabinovitz, I. Gosnay, and A. Weitzen-Dagan, *J. Amer. Chem. Soc.*, in the press.