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PATHWAYS FOR THERMAL Z,E ISOMERIZATION IN TETRABENZOPENTAFULVALENES: TRANSITION-STATE STABILIZATION COMBINED WITH GROUND-STATE DESTABILIZATION[1]

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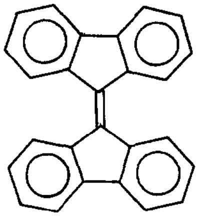
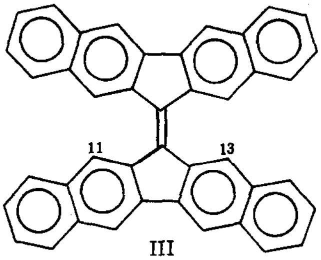
Tetrabenzopentafulvalene (I) has evoked intense theoretical and experimental interest.[2-3] With the advent of dynamic nmr spectroscopy, attention has been focused on the conformational behaviour of this highly overcrowded ethylene.[4,5] The tetrabenzopentafulvalene system plays a prominent role in the study of the mechanisms of uncatalyzed thermal Z,E isomerizations around carbon-carbon double bonds.[6,7] The remarkably low rational barriers for Z,E isomerizations about the "pinch" of 1,1'-disubstituted derivatives of I carrying bulky groups have been attributed mainly to ground-state destabilization due to steric overcrowding.[4-6] However, this is not an intrinsic feature of the tetrabenzopentafulvalene system: the corresponding barriers in the 1,1'-difluoro- and 2,2'-difluoro-derivatives of I, in spite of the overcrowding around the "pinch", are not low.[5,8] We submit that low energy barriers for Z,E isomerization in tetrabenzopentafulvalenes may be realized through the stabilization of a diradical transition-state. This mechanism, in which steric considerations are not necessarily decisive, appears to operate in the Z,E isomerization of $\Delta^{11,11'}$-bis(11H-benzo[b]fluorenylidene) (II).

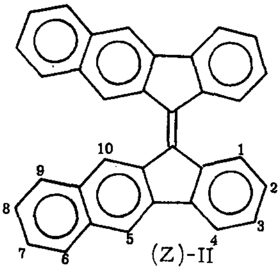
We used II as model because in the ground-state, the electronic properties as well as the steric environment around the "pinch", particularly the overcrowding, closely resemble those prevailing in the parent compound (I). Both I and II are hydrocarbons lacking any substituents which might polarize the "pinch" (through an inductive or a conjugative mechanism). In contrast to I, II may exhibit geometrical isomerism, and thus may be liable to a dynamic nmr investigation. II was prepared by dehydrobromination of 11-bromo-11H-benzo[b]fluorene[9] with



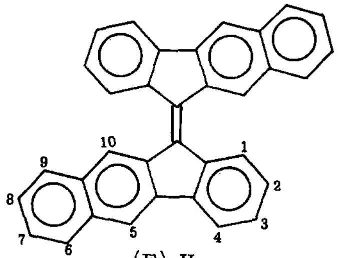
I



III



(Z)-II



(E)-II

Triton B (40% in methanol) in dry acetone at 24° and was obtained as red-purple crystals: mp 240° (from benzene)[10] (lit.,[9] mp 239-241°); $\lambda_{max}^{CH_2Cl_2}$ (log ϵ) 272 nm (5.08), 306 (4.67), 319s (4.36), 362 (4.04), 508 (4.37), and 530 (4.38). II exists in two geometrical forms, the cis isomer ((Z)-II) and the trans isomer ((E)-II) as revealed by the ^{1}H nmr spectrum:[11] δ^{CDBr_3} (30°C) 9.01 (s, *ca.* 0.9 H), 8.80 (s, *ca.* 1.1 H), 8.54 (broad d, *ca.* 1.1 H), 8.36 (broad d, *ca.* 0.9 H), 8.05 (s, 2H), 7.77 (m, 6H), and 7.34 ppm (m, 8H). The downfield ^{1}H absorptions at δ 8.36, 8.54, 8.80, and 9.01 ppm are characteristic of the protons ortho to the "pinch" of the tetrabenzopentafulvalene system.[12] The broad doublets at 8.36 and 8.54 ppm represent H-1 (and H-1') of (Z)-II and (E)-II, respectively, while the singlets at 9.01 and 8.80 ppm represent H-10 (and H-10') of (Z)-II and (E)-II, respectively. The downfield shift is most pronounced in H-10 of (Z)-II (δ 9.01 ppm). This assignment is supported by the pmr spectrum of $\Delta^{12,12'}$-bis(12H-dibenzo[b,h]fluorenylidene) (III). The linearly annelated tetranaphthopentafulvalene III, which resembles (Z)-II rather than (E)-II, was synthesized in the following manner: LAH reduction of 12H-dibenzo[b,h]fluoren-12-one[13] in boiling Et$_2$O gave the corresponding alcohol which was converted by boiling CH$_3$COBr to 12-bromo-12H-dibenzo[b,h]fluorene. Treatment of the latter with Triton B (40% in methanol) in dry acetone at 24° afforded III as purple crystals: mp > 360° (from xylene)[10] (total yield, 55%); $\lambda_{max}^{CH_2Cl_2}$ (log ϵ) 303 nm (5.17), 331 s (4.75), 396 (4.95), 525 s (4.30), and 546 (4.33); nmr,[11] δ^{CDBr_3}

(30°C) 9.12 (s, 4H), 8.29 (s, 4H), 7.91 (broad d, 4H), 7.71 (broad d, 4H), and 7.40 ppm (m, 4H). The downfield ^1H singlet at 9.12 ppm represents H-11, H-13, H-11' and H-13' of III; it resembles the singlet at 9.01 ppm due to H-10 and H-10' of (Z)-II. The pmr spectrum of II[14] points to a mixture of 45% of (Z)-II and 55% of (E)-II. The above interpretation was supported by the separate nmr spectrum of each of the two geometrical isomers.[15]

A study of the temperature-dependent nmr spectrum of II revealed that in contrast to the 1,1'-difluoro- and 2,2'-difluoro-derivatives of I,[5,8] the energy input attained by the nmr method can overcome the barriers for the Z,E isomerization of II. The two downfield singlets representing H-10 (and H-10') (ν((Z)-II) $-$ ν((E)-II) = 19 Hz in 1-bromodecane solution) coalesced at 180°. The two downfield doublets representing H-1 (and H–1') showed similar behaviour. The application of the usual coalescence approximation[16,17] leads to the low value of $\Delta G^{\ddagger}_{453°}$ 23.5 kcal mole^{-1}.

The remarkably low energy barriers associated with the Z,E isomerization of II, which are unusual for an ethylenic hydrocarbon, cannot be interpreted solely in terms of ground-state destabilization due to steric strain.[6] They are probably to a significant extent a consequence of an excellently stabilized diradical transition-state.[4] Effective delocalization of the unpaired electrons in the transition-state is favoured by the extensive conjugation in each of the two orthogonally accommodated aromatic benzo[b]fluorenyl units. The unusually rapid Z,E isomerization of II (relative, e.g., to the presumed rate of the Z,E topomerization of I), substantiates the prediction that "isomerization becomes faster, the more stable the corresponding biradical of the olefin."[7]

References

1. Fulvenes and Thermochromic Ethylenes. Part 84. For Part 83, see I. Agranat and D. Avnir, J. Chem. Soc., Perkin I, in the press.
2. E. D. Bergmann, Progr. Org. Chem., **3**, 81 (1955).
3. N. A. Bailey and S. E. Hull, Chem. Comm., 960 (1971).
4. I. R. Gault, W. D. Ollis, and I. O. Sutherland, Chem. Comm., 269 (1970).

5. I. Agranat, M. Rabinovitz, A. Weitzen-Dagan, and I. Gosnay, *J. C. S. Chem. Comm.*, 732 (1972).

6. I. O. Sutherland, *Ann. Reports*, N.M.R. Spectroscopy, **4**, 71 (1971).

7. H.-O. Kalinowski and H. Kessler, in "Topics in Stereochemistry", N. L. Allinger and E. L. Eliel, Eds., Vol. 3, Interscience, New York, 1973, p. 295.

8. I. Agranat, M. Rabinovitz, I. Gosnay, and A. Weitzen-Dagan, *J. Amer. Chem. Soc.*, **94**, 2889 (1972).

9. E. D. Bergmann, E. Fischer, Y. Hirshberg, D. Lavie, Y. Sprinzak, and J. Szmuszkovicz, *Bull. Soc. Chim. Fr.*, 798 (1953).

10. Compounds II and III have been fully characterized (combustion analyses, ir, uv, mass spectra).

11. The ^{1}H spectra were recorded at 100 MHz. ^{1}H chemical shifts are reported in parts per million downfield from Me$_4$Si.

12. M. Rabinovitz, I. Agranat, and E. D. Bergmann, *Tetrahedron Letters*, 1265 (1965).

13. R. H. Martin, *J. Chem. Soc.*, 679 (1941); *Helv. Chim. Acta*, **30**, 620 (1947).

14. The singlet at 8.15 ppm represents H-5 and H-5' (in both isomers). The multiplet at 7.77 ppm represents the angular protons H-4 and H-4' and the α-naphthalene protons H-6, H-9, H-6' and H-9', while the multiplet at 7.34 ppm represents H-2, H-3, H-2', H-3', and the β-naphthalene protons H-7, H-8, H-7', and H-8' (in both isomers).

15. Almost pure (E)-II precipitated directly from the reaction mixture. The nmr spectrum of almost pure (Z)-II was obtained by heating a CDBr$_3$ solution of (Z)-II and (E)-II in an nmr pressure tube at 240°C followed by quick cooling.

16. H. Kessler, *Angew. Chem. Internat. Ed.*, **9**, 219 (1970).

17. D. Kost, E. H. Carlson, and M. Raban, *Chem. Comm.*, 656 (1971).