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# GEOMETRICAL ISOMERISM IN THE DIBENZOPENTAFULVENE SERIES. ATTEMPTS OF THERMAL TOPOMERIZATION AND ISOMERIZATION[1]

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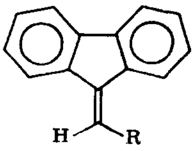
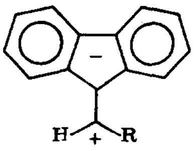
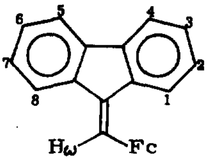
Recent dynamic nmr studies on the conformational behaviour of the highly overcrowded 1,1'-disubstituted tetrabenzopentafulvalenes have revealed a strong substituent dependency of cis-trans isomerizations.[2] Bulky substituents, in particular, favoured low energy barriers for these isomerizations. The steric effect, which appeared to govern the ease of these thermal processes, could be substantially diminished in the analogous dibenzopentafulvene series, especially when one of the substituents of the "fulvenic" double bond is hydrogen (I). In such cases, lower energy barriers could be obtained through an electronic effect, by introducing suitable substituents which may increase the contribution of the dipolar "aromatic" structure (Ia). An attractive substituent is the ferrocenyl group (Fc), which may qualify for this purpose by delocalizing the positive charge of (Ia) through "metal participation".[3] We wish to report the phenomenon of cis-trans isomerism in asymmetric $\omega$-ferrocenyldibenzopentafulvene derivatives. These systems proved to be suitable substrates for dynamic nmr studies. However, neither the topomerization[4] of the parent compound 9-(ferrocenylmethylene)fluorene (II), nor the geometrical isomerization of its derivatives could be detected, even at 220°C. In spite of the non-negligible dipolar character of these systems, substantial energy barriers were probably



(I)



(Ia)

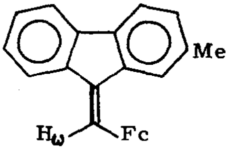


(II)

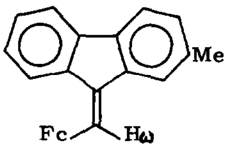
associated with their isomerizations.

The parent system (II) was synthesized in 90% yield by a direct Wittig condensation of tributylfluoren-9-ylidenephosphorane[5] and ferrocenecarboxaldehyde in boiling benzene[6]; red needles: mp 145° (cyclohexane).[7] Uv, $\lambda_{\max}^{\text{cyclohexane}}$ (log $\epsilon$) 235 nm (4.53), 250 (4.64), 300 (4.02), 337 (4.19), and 464 (3.40). Nmr,[8] $\delta$ ($CDCl_3$) 4.07 ppm (s, 5H, Fc), 4.41 (t, J <1 Hz, 2H, Fc), 4.66 (t, J< 1 Hz, 2H, Fc), 7.06-7.42 (m, 4H, $H_2$, $H_3$, $H_6$, $H_7$), 7.44 (s, 1H, $H_\omega$), 7.48-7.46 (m, 3H, $H_4$, $H_5$, $H_8$), 8.16 (q, $J_1$ = 8 Hz, $J_2$< 1 Hz, $H_1$). The dipole moment of (II)[9] (1.54D, $\alpha'$ = 5.21, $\beta'$ = -2.08, $P_{2\infty}$ = 153.1 $cm^3$, $MR_{calc}$ = 105.4 $cm^3$) indicate a certain contribution of a dipolar structure (e.g., (Ia) R = Fc) in the ground state.

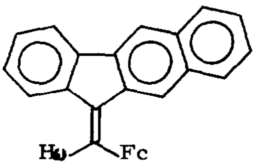
The existence of cis-trans isomerism in the dibenzopentafulvene series was revealed in the following two derivatives of (II): 2-methyl-9-(ferrocenylmethylene)fluorene (III) and 11-(ferrocenylmethylene)-11H-benzo[b]fluorene (IV) (III) was prepared analogously to (II) in three steps from 9-bromo-2-methylfluorene[10] (through the respective phosphonium salt and phosphorane) and was obtained as a 1 : 1 mixture of (Z)-(III) and (E)-(III), red needles, mp 115° (EtOH).[7] Nmr,[8] $\delta$ ($CDCl_3$) 2.30 ppm (s, 1.5H, $CH_3$), 2.42 (s, 1.5H, $CH_3$), 4.11 (s, 5H, Fc), 4.38 (t, J< 1 Hz, 2H, Fc), 4.66 (t, J<1Hz, 2H, Fc), 7.00-7.36 (m, 3H, $H_3$, $H_6$, $H_7$), 7.40 (broad s, 1H, $H_\omega$), 7.48-7.78 (m, 3H, $H_4$, $H_5$, $H_1$ of (E)-(III), $H_8$ of (Z)-(III), 7.97 (broad s, 0.5H, $H_1$ of (Z)-(III)), 8.10 (q, $J_1$ = 8 Hz, $J_2$ < 1 Hz, 0.5H, $H_8$ of (E)-(III)). (IV) was prepared in a similar manner starting from 11-bromo-11H-benzo[b]fluorene,[11] and was obtained as a 1 : 1 mixture of (Z)-(IV) and (E)-(IV), red needles, mp 160-162° (PrOH).[7] Nmr,[8] $\delta$ ($CDCl_3$) 4.01 ppm (s, 5H, Fc), 4.41-4.58 (m, 2H, Fc), 4.69-4.86 (m, 2H, Fc), 7.26-7.56 (m, 4.5H, $H_3$, $H_4$, $H_8$, $H_9$, $H_\omega$ of (Z)-(IV)), 7.58 (s, 0.5H, $H_\omega$ of (E)-(IV)), 7.70-8.00 (m, 3.5H, $H_2$, $H_5$, $H_7$, $H_{10}$ of (Z)-(IV)), 8.08 (s, 1H, $H_6$), 8.10-8.22 (m, 0.5H, $H_{10}$ of (E)-(IV)), 8.18 (s, 0.5H, $H_1$ of (E)-(IV)), 8.66 (s, 0.5H, $H_1$ of (Z)-(IV)). The most



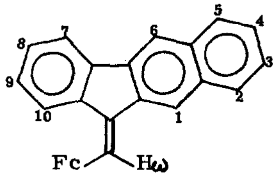
(Z)-(III)



(E)-(III)



(Z)-(IV)



(E)-(IV)

striking feature in the nmr spectra of (II), (III), and (IV) was the absorptions in the low field of the aromatic region ((II): 8.16 (q, 1H); (III): 7.97 (s, 0.5H), 8.10 (q, 0.5H); (IV): 8.66 (s, 0.5H), 8.10-8.22 (m, 0.5H)). On the basis of their chemical shifts, relative intensities and different patterns, these signals must be assigned (in each case) to the protons ortho to the "pinch" and cis to the ferrocenyl group. In the case of (IV), the singlet at 8.66 ppm was due to only one half proton; thus, it must represent a proton of only one geometrical isomer ((Z)-(IV)). In the case of (III), the geometrical isomerism is exhibited not only in the low field aromatic region but also by the two methyl singlets.

Neither the methyl signals of (III), nor its low field aromatic signals coalesced even at 220°C. The absence of any indication of even an incipient cis-trans isomerization process pointed to considerably higher coalescence temperatures than 220°C and thus to "normal" energy barriers. The parent compound (II) behaved similarly: the low field quartet remained unaltered at 220°C. Thus, the diastereotopomerization of the type (Z)-(II) $\rightleftharpoons$ (E)-(II) could not be achieved with the energy input available (at present) by the nmr method. As expected, topomerization could not be affected in 9-benzylidene-2,7-dimethylfluorene[12]: the two methyl signals in the nmr spectrum (2.19, 2.42 ppm) failed to coalesce at 220°C, indicating again a high barrier of rotation around the fulvenic double bond. Systems with considerably higher dipolar character (than (II)) are apparently needed in order to turn the static isomerism in the dibenzopentafulvene series into the dynamic phenomena of thermal isomerizations (at 220°C).

Finally a word of caution. In various dipole moment studies in the fulvene series, the possibility of geometrical isomerism has been overlooked. It is now evident that the previously reported 5-benzylidene- and 5-chlorobenzylidene-5H-benzo[a]naphtho[2,1-d]cycloheptene ((V) and (VI), respectively)[13] were in fact 1 : 1 mixtures of the respective two geometrical isomers, as indicated (in each case) by the two vinylic signals in the nmr spectrum ((V): 6.52 and 6.57 ppm; (VI): 6.38 and 6.43 ppm). This interpretation is consistent with the difference in dipole moment values between (V) and (VI) (2.03 D - 1.02 D = 1.01 D) compared with the respective difference obtained for the corresponding derivatives of the 5H-dibenzo[a,d]cycloheptene series (2.05 D - 1.58 D = 0.47 D). The results reported here emphasize the need to consider the possibility of geometrical isomerism when evaluating experimental or theoretical dipole moment data, especially in cases where the overall dipole moment values are low.

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