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THE GROUND STATE GEOMETRY OF A PENTATETRAENE

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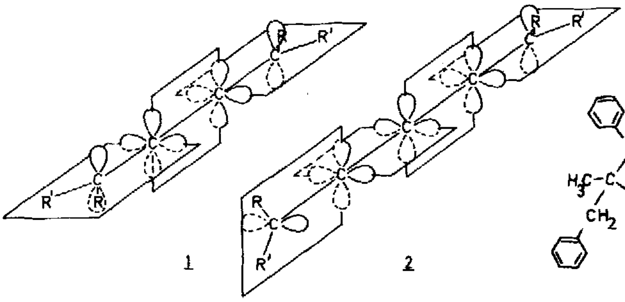
According to van't Hoff (1) the substituents of cumulenes with an even number of cumulated double bonds should be arranged in two planes vertical to each other, e.g.2, while in cumulenes with an uneven number of double bonds the substituents are expected to be in one plane, e.g.1. These predictions have been experimentally verified for many allenes (2,3), for butatrienes (4,5,6) and for one hexapentaene (7), but not for pentatetraenes, mainly probably because only four pentatetraenes seem to be described in literature (8,9,10). Quantum mechanical calculations (11,12) and experiments (6) indicate that for a given cumulene the differences in energy between conformations with the substituents in perpendicular planes (as 2) and with all substituents in one plane (like 1) decrease with increasing number of double bonds. Kuhn et al.(7) measured for the E-Z-isomerization of the butatriene 4 a Gibbs energy of activation $\Delta G^{\neq} \approx 125$ kJmol^{-1}. For the hexapentaene 5 $\Delta G^{\neq} \approx 84$ kJmol^{-1} was reported (7). For pentatetraene Dewar calculated barriers to rotation about the cumulated double bonds between 104 kJmol^{-1} and 127 kJmol^{-1} (13,14). According to these calculations the barrier of pentatetraene should be intermediate between those of butatriene and hexapentaene. On the other hand



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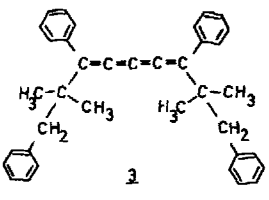

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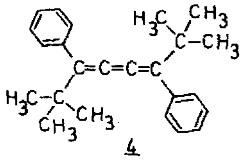

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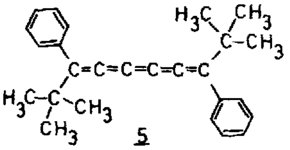

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extended Hückel calculations 15) predict for pentatetraene a barrier to rotation (74 $kJmol^{-1}$) lower than that of hexapentaene.

The pentatetraene 3 was prepared in 58% yield from the corresponding butatriene by addition of dichlorocarbene and carbene insertion 10). Compound 3 forms yellow needles, m.p. 134-135°C. The UV spectrum resembles that of 1.5-diphenyl-1.5-di-t.butyl-pentatetraene 16) (3: λ_{max}(cyclohexane): 252 nm (ε = 29700), 264 nm (34500), 290 nm(22300), 355 nm (1450)). On hydrogenation with Raney-Ni in ethyl acetate the cumulene 3 consumes 4 moles of hydrogen. Mass spectrum and microanalysis are consistent with the proposed structure. If the pentatetraene 3 had the dissymmetric C_2 geometry 2 with the substituents in perpendicular planes, the geminal methyl groups and the geminal benzylic protons would be diastereotopic. The ^{13}C nmr spectrum of 3 is shown in fig.1 (as for the assignments see 16)). This spectrum and also the 100 MHz proton resonance spectra show two non-equivalent methyl groups. But since in the 100 MHz spectra the CH_2 signal appears as a singlet, it can not be decided, whether the two methyl signals arise from diastereotopism (non-equivalent geminal methyl groups) or, for instance, from geometric isomerism (equivalent geminal methyl groups, but non-equivalent end groups in a Z- and E-form). The decision in favour of diastereotopism and consequently of geometry 2 came from the 360 MHz pmr spectrum (fig.2), which shows in addition to two methyl signals an AB quartet for the benzylic protons. Geometric isomerism should give two singlets for these protons, without any coupling. Van't Hoff's prediction 1) of an allene like structure (2) for pentatetraenes has thus been confirmed.

The non-equivalence of the methyl signals of 3 decreases linearly with increasing temperature in all solvents tried so far. Thus, although one observes coalescing methyl signals at temperatures differing from solvent to solvent, this is not a coalescence resulting from exchange of the chemical surroundings of the diastereotopic methyl groups through rotation about the cumulated double bonds. It was impossible therefore to measure the barrier to racemization of 3. But from the highest temperature (431 K, $\Delta\nu$ = 1 Hz at 100 MHz in DMSO-d_6), where separate signals could just still be observed, it follows that the free energy of activation $\Delta G^{\neq}$ must be larger than 106 kJmol^{-1}, that means: larger than the barrier of hexapentaene 5, as predicted by Dewar [13). Consequently, enantiomers of pentatetraene 3 should be stable enough at room temperature to permit separation. Experiments in this direction are in progress.

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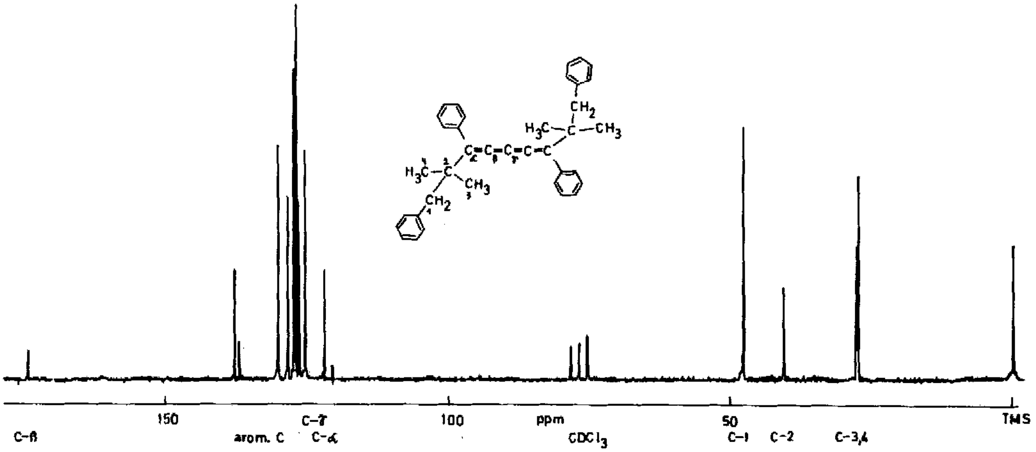

Fig.1: 22.63 MHz ^{13}C spectrum of compound 3 in $CDCl_3$ at 298 K.

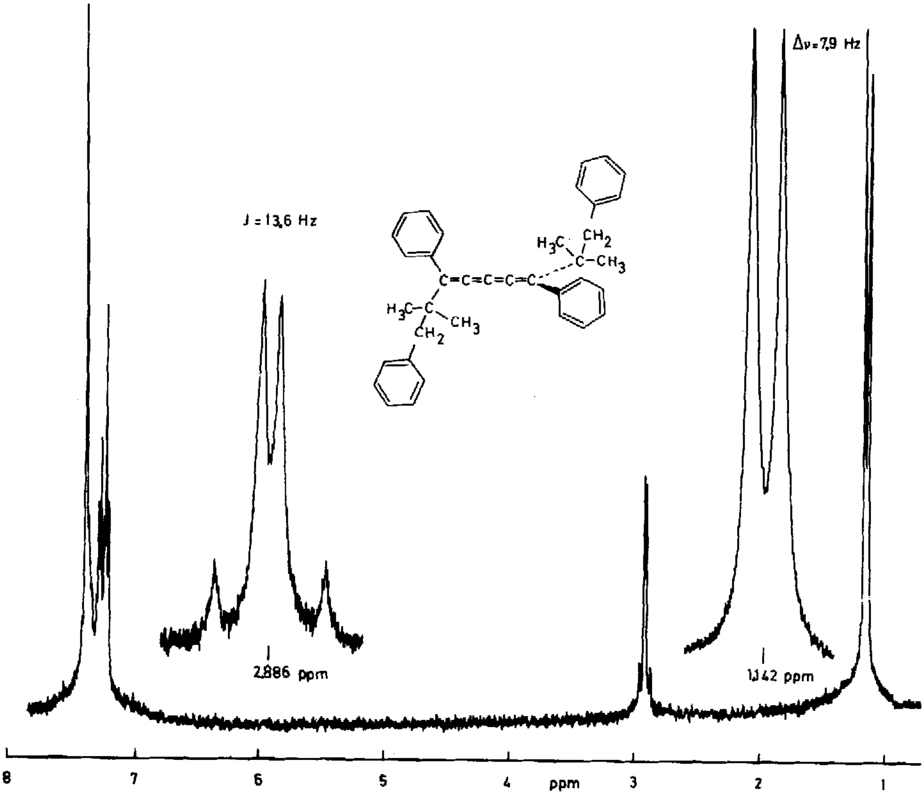

Fig.2: 360 MHz ^{1}H spectrum of 3 in $CDCl_2CDCl_2$ with TMS as internal reference at 298 K.