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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF trans-syn-trans-syn-trans PERHYDRONAPHTHACENE

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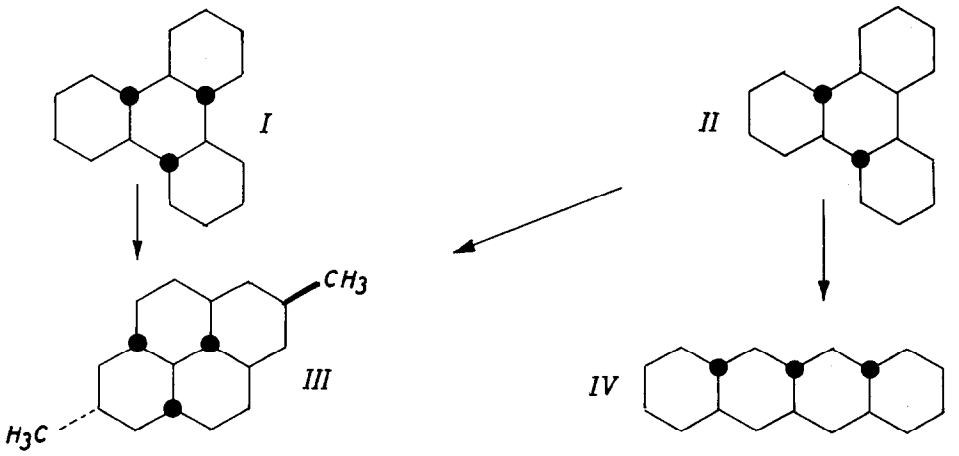
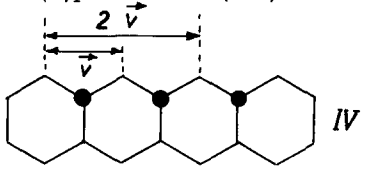
In a previous paper (1) we showed that aluminum trichloride promotes a skeletal isomerization both of the high-melting isomer of perhydrotriphenylene (or anti-trans-anti-trans-anti-trans isomer)(I) (2) and of a low-melting mixture of isomers of the same compound predominantly consisting of the syn-trans-anti-trans-anti-cis isomer(II) (3). The main isomerization product (m.p. 191°C) was identified by X-ray analysis as the completely equatorial stereoisomer of 2,7-dimethylperhydropyrene (III) (1).

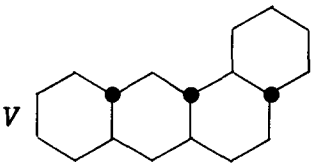
Isomerizations from II to III were carried out with re-sublimed $AlCl_3$ at 100°C: no particular care was taken to remove traces of moisture. When runs were repeated with high-vacuum techniques in sealed vials (100°C, 40 h) with accurately purified reagents, the least soluble product, which may be easily obtained by crystallization, showed a melting point of 206°C and a structure completely different from III. It is still a $C_{18}H_{30}$ hydrocarbon (elemental analysis: calculated C 87.73 %, H 12.27 %; found C 87.70 %, H 12.23 %; molecular weight 246, by mass spectrography); as it will be shown hereinafter, it corresponds to trans-syn-trans-syn-trans perhydronaphthacene (IV).



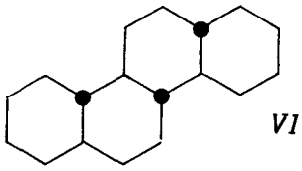
The presence of methyl groups and of unsaturations may be certainly excluded by instrumental analyses (nmr, ir, mass). Hence, for the subsequent structural analysis, we took into account the possible tetracyclic structures $C_{18}H_{30}$ with ortho-fused rings, i.e. perhydronaphthacene(IV), perhydrobenzo(a)anthracene(V), perhydrocrysene(VI) and perhydrobenzo(c)phenanthrene(VII).



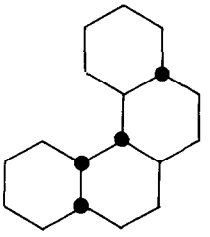
IV



V



VI



VII

IV-VII represent the stables stereoisomers of each skeleton, IV-VI are completely equatorial and with trans junctions, whereas VII has a cis junction to eliminate a strong steric interaction between the C1 and C12 atoms.

Among these structures, the nmr analysis strongly supports structure IV due to the very close analogies between the spectrum of our compound and that of perhydroanthracene having m.p. 90°C, to which the trans-syn-trans structure has been attributed (4).

Attempts for the chemical and catalytic dehydrogenation carried out under very drastic conditions were unsuccessful; consequently, for a definitive attribution of the structure, we subjected our compound to X-ray analysis. From a set of single crystal X-ray spectra, carried out by the usual rotating crystal and equatorial Weissenberg methods, we deduced the following parameters of the triclinic unit cell:

$a \sin \gamma = 5.26 \pm 0.02$ Å; $b = 5.42 \pm 0.03$ Å; $c \sin \alpha = 12.60 \pm 0.05$ Å; $\beta^* = 91.2 \pm 0.3°$;

$V = 359 \pm 4$ Å^3

$D_{calc.} = 1.15$ g/cm^3 (for $Z = 1$)

which demonstrate the existence of a single molecule in the cell.

The choice of the molecular model was made first of all on the basis of packing considerations, then with the use of Patterson and Fourier methods. The existence of at least one repetition axis shorter than 5.5 Å induced us to exclude model VII; its conformation remarkably deviates from planarity, thus preventing the packing among molecules

repeating at so short a distance. The Patterson map in the a c projection shows the existence of two parallel interatomic vectors, by far the most intense, having length $\simeq 2.5$ and $\simeq 5$ Å, and relative weights about 3:2 respectively. This finding is in good agreement with both models IV and V, in which the interatomic vectors indicated by $\vec{v}$ (of length 2.5 Å) and $2\vec{v}$ occur 14 and 10 times (IV) and 12 and 7 times (V) respectively. The two above-mentioned Patterson maxima, instead, are not adequately explained for model VI; therefore it was discarded.

Finally the choice between models IV and V was made by Fourier methods and by structure factors calculation.

By first accepting model IV, which is centrosymmetrical, we placed the molecule in its more plausible conformation in the unit cell in such a way that its average plane is nearly perpendicular to the b axis - due to the shortness of this last - and that vector $\vec{v}$ is oriented as in the Patterson projection. The centre of the molecule was made to coincide with the origin of the cell (space group $P\bar{1}$). By subsequent projections of the electron density, the orientation of the molecule was adjusted by trial, until obtaining the value of the disagreement factor:

$$R = \sum \left| F_{calc.}(h0l) \right| - \left| F_{obs.}(h0l) \right| \Big/ \sum \left| F_{obs.}(h0l) \right| = 0.21$$ (88 observed reflections).

An analogous precedure adopted with model V led to much higher values of the disagreement factor (> 0.35); therefore we assumed that the isomer obtained by us corresponds to model IV.

The purpose of the X-ray analysis being the determination of the molecular structure, the X-ray refinement was stopped at this point.

The reaction pathway of perhydrotriphenylene to III and to IV is analogous to what occurs in the isomerization of perhydrophenanthrene, where perhydroanthracene and 2-methylperhydrophenalene are the main products (5). The most extensive isomerization observed under non strictly anhydrous conditions (I or II $\longrightarrow$ III) is to be connected with the well known promoting effect of water in the Friedel-Crafts reactions.

A more detailed study on the acid isomerization of perhydrotriphenylene will be published in the near future.

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