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SYNTHESIS AND STRUCTURE OF A 2,7 DIMETHYL-PERHYDROPYRENE STEREOISOMER

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The catalytic hydrogenation on Pd at high temperature of dodecahydrotriphenylene not only yields the trans-anti-trans-anti-trans isomer of perhydrotriphenylene (corrected melting point 128°C), but also a low melting compound (A)(m.p. 20-25°C), which also has the formula $C_{18}H_{30}$ (1). This constitutes another stereoisomer or a mixture of stereoisomers of perhydrotriphenylene because it can be converted into the isomer melting at 128°C by treatment with Pd and H_2 at 300°C.

When looking for other methods to perform this isomerization, we have studied the reaction products obtained from (A), in the presence of $AlCl_3$, which is an effective catalyst in the isomerization from cis- to trans-decalin (2). By treating (A) with $AlCl_3$ (40 hrs at 80°C), a product (B) with a 40% yield was obtained, having a saturated character and formula $C_{18}H_{30}$ (calculated: C 87.73%; H 12.27%; M.W. 246; found: C 87.93%; H 12.31%; M.W. (V.P.O.) 254), melting at 190°C.

It is impossible to attribute the formula of perhydrotriphenylene to (B); in fact the compound melting at 128°C, which,owing to its conformation completely equatorial and unstrained (1, 3), represents the most stable stereoisomer having this structure, is also transformed into compound (B), by treatment with $AlCl_3$.

The IR examination of (B) shows intense absorption bands at 3.40 and 7.25 μ, which can be attributed to the presence of methyl groups, also indicated by a strong peak at m/e = 231 equal to P-15 in the mass spectrum.

The X-ray analysis of a single crystal of (B) showed its space group to be $P2_1/\underline{c}$. It was deduced from the examination of the reciprocal lattice symmetry and of the systematic extinctions of the reflections, whose indexes satisfy the relationships: $(0\underline{k}0)$, $(\underline{k}=2\underline{n}+1)$ and $(\underline{h}0\underline{l})$, $(\underline{l}=2\underline{n}+1)$(4).

The values of the unit cell constants are:

$\underline{a} = 9.68 \pm 0.04$ Å; $\underline{b} = 15.89 \pm 0.07$ Å; $\underline{c} = 5.58 \pm 0.02$ Å;
$\beta = 120.0° \pm 30'$; N = 2.

The number of molecules present in the unit cell was deduced from the value of the experimental density ($d_{exp.} = 1.10$ g/cm^3; $d_{calc.} = 1.12$ g/cm^3, by assuming MW = 246).

Since the $P2_1/\underline{c}$ space group contains 4 general positions, each molecule must be centered on a crystallographic inversion point, and therefore must possess a centrosymmetric conformation. This first result, together with energetical considerations and hypotheses on the reaction mechanism, suggested the presence of the perhydropyrenic nucleus with two methyl groups in centrosymmetric positions.

Moreover, the presence of a very short axis in the unit cell ($\underline{c}$ = 5.58 Å) favoured very strongly the hypothesis of a completely equatorial molecular conformation: in fact, any other conformation should result in a too thick molecular shape for two parallel molecules being repeated at so short a distance.

Thus the choice of the molecular structure is limited to the three different isomers of dimethylperhydropyrene, with equatorial and centrosymmetric disposition of the methyl groups, represented in fig.1.

These three possibilities were investigated by the combined application of packing criteria among the molecules and by examination of the agreement factor between observed and calculated structure factors.

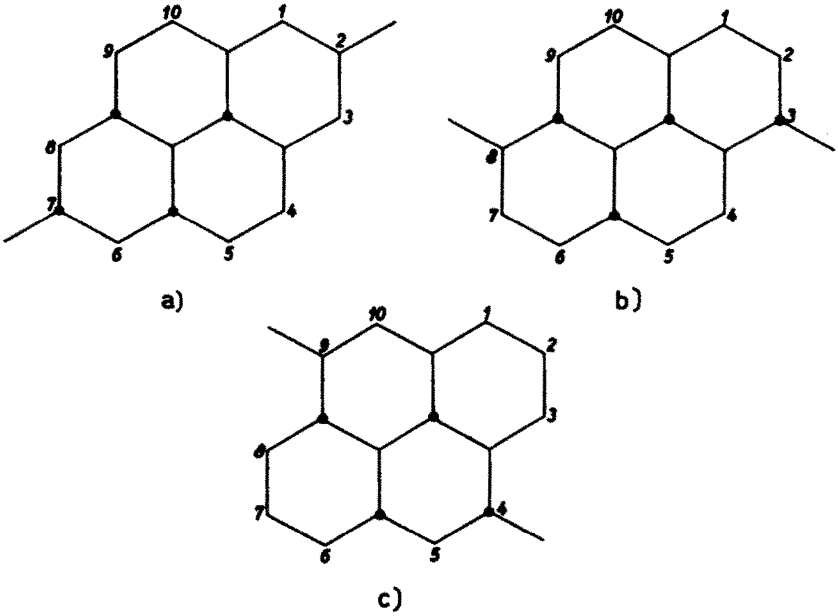

Fig.1 – Three possible formulas of centrosymmetric equatorial dimethyl-perhydropyrene.

From among the possible projections of the structure along rational axes, we have chosen that corresponding to the c axis: in fact, along this short axis, superpositions among molecules belonging to the same cell are impossible. Therefore we have carried out the first part of the X-ray structural analysis, which allowed us to assess the molecular conformation, on the reflections of the reciprocal section (hk0), corresponding to the structural projection along the c axis.

A preliminary comparison between the values of the c axis of (B) and of the c axis (4.78 Å) normal to the average molecular plane, determined in the structure of perhydrotriphenylene with included linear molecules (3), led us to the conclusion that the average molecular plane of (B) most probably was inclined by about 60° with respect to the c axis. In fact with this orientation in both cases the same distance ($\sim$4.78 Å) between the average planes of the molecules occurs: since (B), as perhydrotriphenylene does, should consist of fused cyclohexanic rings with an equatorial conformation, in both cases the same interatomic distances among molecules repeating along c should be present.

The presence of a glide plane perpendicular to the b axis, which connects molecules translated by 2.79 Å among themselves, in the c direction, severely binds the possible orientation of the perhydropyrenic nucleus (fig.2).

In particular, it can be observed that the most rational mode of packing between the two nuclei connected by the glide plane is obtained by the dispositions of fig. 2 a) or b): the orientation of each perhydropyrenic nucleus is obtained by arranging firstly its average plane perpendicular to the c axis, then by rotating it by +30° or -30° around the b axis (see fig.2 for the adopted convention of signs). Thus, by attributing the values usually accepted in analogous compounds to the bond distances and valency angles, the shortest (C-C) distance between the nuclei connected by the glide plane is 4.10 Å, and corresponds to the equal distances between the (1) and (10) C atoms, and the symmetrically related ones.

Since this value is very near to the mean Van der Waals distance in analogous cases, we have assumed the orientation of the perhydropyrenic nucleus represented in figs. 2 a) and b), as the starting point for the subsequent analysis.

Analogous considerations of packing between the molecules and a detailed analysis of the Fourier transform of the two molecules present in the unit cell, to be reported in another paper (5), led us to the conclusion that the only available positions for the methyl groups correspond to those in (2,7) and (4,9) (see fig.2).

The crystallographic possibilities therefore have been reduced to 4, and result from the combination of two types of alternatives: (i) the rotation angle φ (see fig.2) can assume the two values of ± 30°, and (ii) the methyl groups can be in the equatorial positions corresponding to (2,7) or to (4,9). The structure factor calculations in the considered projection ((hk0) reflections) allowed us to make a rapid choice from among these possibilities: the resulting molecular conformation corresponds to the highest possible symmetry, that is with methyl groups in the (2,7) positions, and the φ angle resulted to be +30° (see fig. 2a). Thus, the resulting molecular structure corresponds to the one indicated in fig.1a).

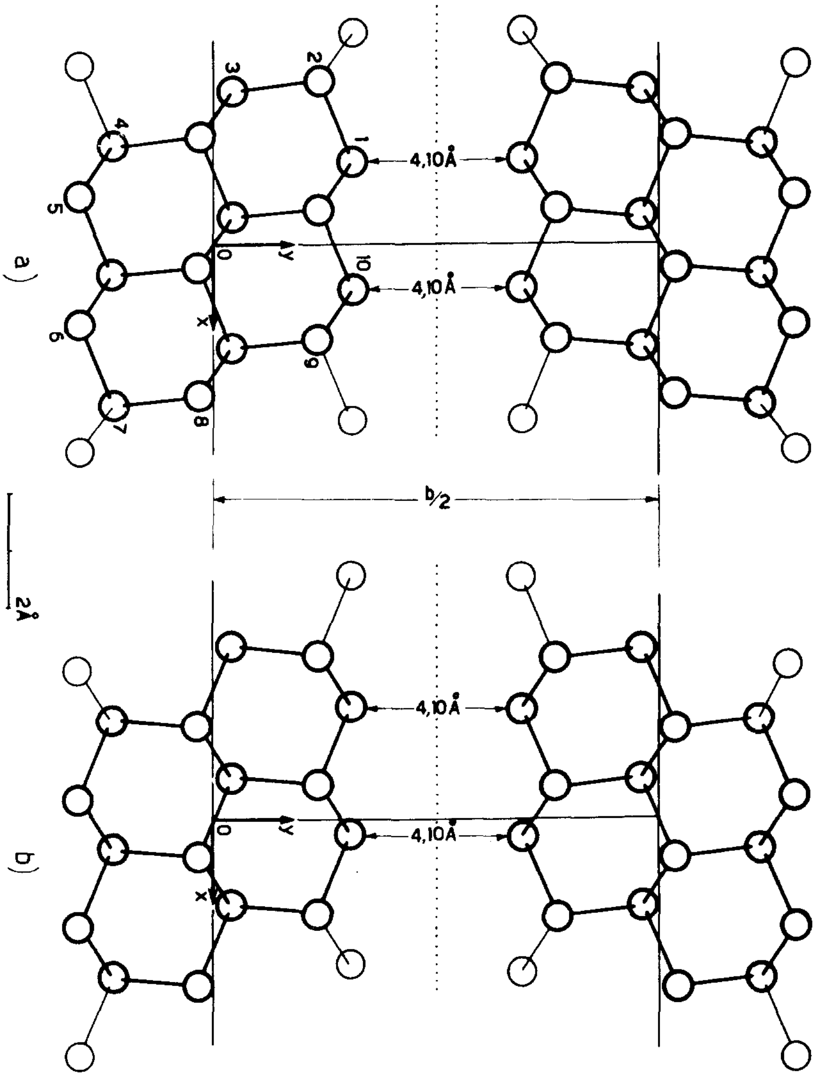

Fig.2 – Optimum packing between two molecules related by the glide plane (projection along the c axis). a) and b) correspond respectively to a rotation of φ = +30° and −30° around axes parallel to b. The possible positions of methyl groups are indicated by thin lines.

The agreement factor R between calculated and observed structure factors at the end of the structural refinement, performed on the reciprocal sections (hk0), (0kl) and (1kl), has assumed the average value of R = 0.10; isotropic thermal factors, different for non equivalent atoms, have been introduced.

The values of the resulting bond distances and valency angles, which will be discussed in detail in another paper (5), are near to those usually accepted, and the same results for the lowest values of the interatomic distances between adjacent molecules.

Fig.3 shows the projection of the electron density along the c axis. It can be easily observed that the drawing of the molecule thus obtained is in good agreement with that schematically reported in fig. 2a) (methyl groups in (2,7) positions).

The above results are in agreement with a qualitative analysis of the internal energy involved in the intramolecular interactions : in fact, the resulting disposition of methyl groups with respect to the nucleus gives rise to the minimum number of (C–C–C–C) successions in "gauche" conformation.

In our opinion this paper describes a typical example of structural determination of a new molecule, in which the preliminary information obtained by chemical and physical-chemical methods narrowed the range of the possible structural hypotheses, among which the X-ray crystallography allowed to make a definite choice.

The determination of the structure of(B)was already nearing completion, when a proof of the above reported conclusions was obtained by catalytic dehydrogenation. By treating(B)with Pd on carbon at 300°C in the presence of 1-octene for 200 hrs, it was obtained, with a 1% con-

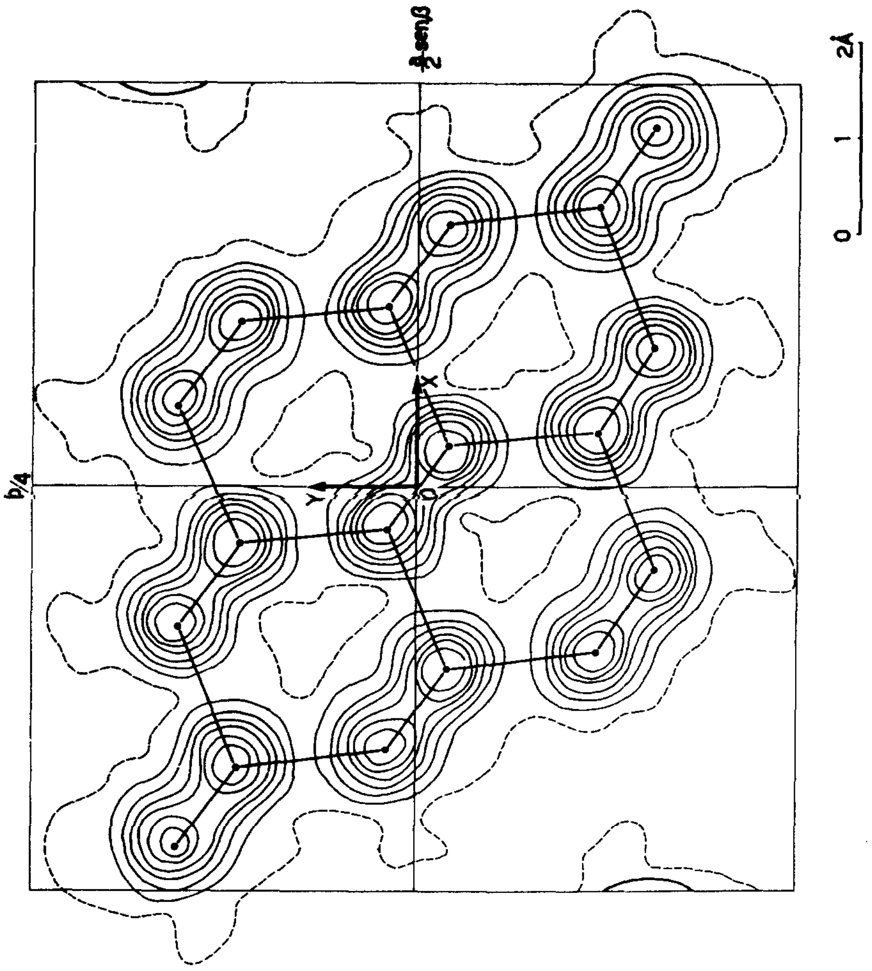

Fig.3 - Projection of the electron density of 2,7 dimethyl-perhydropyrene along the <u>c</u> axis. Levels are drawn at 1 (dashed line), 2, 3...el/Å^2.

version, an aromatic product, which, after repeated crystallizations, showed a melting point of 228-230°C and an U.V. spectrum characterized by absorption maxima at 238, 247, 267, 278, 310, 324, 340 mμ. The general features of the spectrum, as well as the melting point value, agree with those reported in literature for 2,7 dimethylpyrene(6)(7).

The obtainment of 2,7 dimethylperhydropyrene starting from perhydrotriphenylene constitutes an interesting example of isomerization of cycloparaffins in the presence of Friedel-Crafts catalysts: the study here reported is a contribution to a better knowledge of the course of such reaction in polycyclic systems.

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