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*TRANS-15,16-DIMETHYLDIHYDROPYRENE: A NEW TYPE OF AROMATIC SYSTEM HAVING METHYL GROUPS WITHIN THE CAVITY OF THE π-ELECTRON CLOUD**

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For some time we have been concerned with the requirements for aromaticity in organic molecules and have undertaken the synthesis of molecules which might permit the solution of two classic problems: (1) the question of aromaticity in conjugated monocyclic polyenes larger than benzene; and (2) the question of whether the concept that an aromatic molecule has a doughnut-shaped π-electron cloud with a cavity in the center is actually valid. In this communication, we report the successful preparation of *trans*-15,16-dimethyldihydropyrene (III), a molecule whose properties provide a convincing affirmative answer to both these questions.

The reasons for choosing *trans*-15,16-dimethyldihydropyrene as a test molecule are readily apparent from an examination of a model of this molecule. As can be seen from Figure 1, the periphery is a 14-membered, conjugated polyene held planar by the internal butane unit. Since the butane unit has only saturated bonds, it should in theory have very little effect on the π-electron cloud but simply serve to maintain a nearly planar periphery. Further, in accord with theory, the

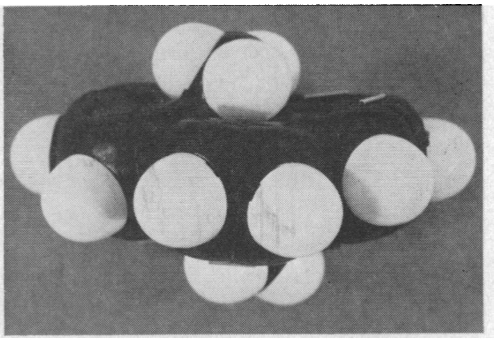
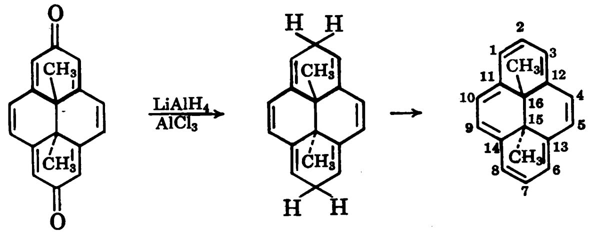


FIG. 1.—Side view of a Briegleb model of *trans*-15,16-dimethyldihydropyrene.

internal methyl groups should intrude into the cavity of the π-electron cloud and thus not interfere with the aromaticity of the molecule.

Recently, we reported on the synthesis of I and described its potential for the synthesis of 15,16-dihydropyrene derivatives.[1] We report now its conversion to *trans*-15,16-dimethyldihydropyrene. When an ether solution of the quinone I was added dropwise with stirring to a 1:1 mixture of lithium aluminum hydride and aluminum chloride in ether held at −80°, there could be isolated on work-up a hydrocarbon whose n.m.r. spectrum is in accord with structure II. Treatment of II with a palladium-on-charcoal catalyst in boiling cyclohexene led to an easy conversion to *trans*-15,16-dimethyldihydropyrene (III), the over-all yield from the quinone being 75 per cent.



I II III

Probably the simplest and best test for aromaticity is to determine whether the molecule develops a ring current in the presence of an outside magnetic field.[2] The n.m.r. spectrum of *trans*-15,16-dimethyldihydropyrene (III) shows signals at 1.33 τ (6 protons), 1.43 τ (2 protons), a multiplet at 1.77–2.02 τ (2 protons), and a sharp singlet at 14.25 τ (6 protons). The displacement of the ring protons to low field and the remarkable shift of the protons of the internal methyls to high field provide clear evidence of a strong ring current and establish III as an aromatic compound.

A full interpretation of the n.m.r. spectrum was accomplished by repeating the preparation of III using lithium aluminum deuteride in place of lithium aluminum hydride. In this case, III is obtained with deuterium labeling at the 2- and 7-positions. The n.m.r. spectrum of the deuterated sample lacks the multiplet at 1.77–2.02 τ (positions 2 and 7) and shows two sharp signals at 1.33 τ (4 protons, positions 4, 5, 9, and 10) and 1.43 τ (4 protons, positions 1, 3, 6, and 8) in addition to the protons of the internal methyls at 14.25 τ (6 protons).

Trans-15,16-Dimethyldihydropyrene is an emerald-green, crystalline compound, m.p. 119.0–119.5°, whose spectrum in cyclohexane shows absorption maxima at 337.5 (ε, 87,000), 377 (ε, 37,000), 463 (ε, 6000), 528 (ε, 58), 536 (ε, 58), 586 (ε, 110), 598 (ε, 150), 611 (ε, 210), 627 (ε, 230), 634 (ε, 210), and 641 mμ (ε, 330).

Theoretical calculations of the absorption spectrum to be expected for a 14 π-electron perimeter have been made by Simmons[3] and Heilbronner[4] and show very good agreement with these experimental values.

Although modern criteria for aromaticity relate to delocalization of π-electrons rather than the older concept of reactivity, it is of interest that *trans*-15,16-dimethyldihydropyrene also qualifies as an aromatic substance by the classical criterion of reactivity. Thus, III undergoes easy electrophilic substitution giving the expected products on nitration, bromination, and Friedel-Crafts acylation.[5] The n.m.r. spectra of these substitution products suggest that the 2- and 7-positions are involved in electrophilic attack. Although there is no obvious *a priori* basis for predicting attack at the 2- and 7-positions, it should be noted that our interpretation of the n.m.r. spectrum of the hydrocarbon III would suggest that, since the signal assigned to the 2- and 7-positions occurs at the highest field of the perimeter protons, the 2- and 7-carbon atoms are the centers of highest electron density.

Finally, it has been possible for Dr. A. W. Hanson to make an X-ray crystallographic examination of 2,7-diacetoxy-*trans*-15,16-dimethyldihydropyrene, one of our derivatives in this series.[1] His results confirm fully the assigned structure and establish that the perimeter is essentially planar.[6] Further, the bonds in the perimeter are typical benzenoid aromatic bonds, varying only between 1.384 and 1.403Å.

Thus, it is clear that *trans*-15,16-dimethyldihydropyrene is a typical aromatic molecule similar to benzene except that it has a fourteen-membered ring rather than a six. In many respects, III is very similar to the dehydro[14]annulenes synthesized by the elegant work of Sondheimer and his collaborators.[7, 8] The important respect in which III differs is the presence of the methyl groups intruding into the cavity of the π-electron cloud. This latter feature raises the possibility of extending this work through a whole range of studies dealing with the steric and electronic interaction of the aromatic π-electron cloud with various functional groups inserted into the cavity.

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