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THE MOLECULAR STRUCTURE OF DL-BI-O-TRIMETHYL-*CIS*-BRAZILANE

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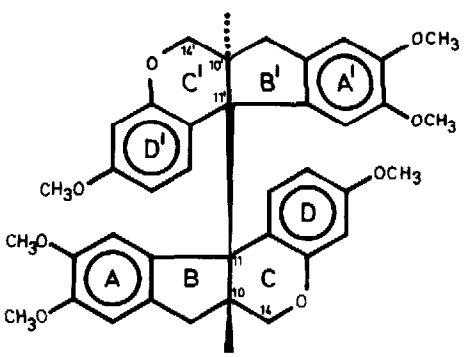
Bi-O-trimethyl-*cis*-brazilane, $C_{38}H_{38}O_8$, is a derivative of the natural product *d*-brazilin, $C_{16}H_{14}O_5$. The latter was first isolated in crystalline form by Chevreul in 1808 (2) from Brazil-wood, a tree occurring in various species of *Caesalpinia*, and has been the subject of extensive chemical study since late last century (3). The structure of brazilin has been known as a result of almost fifty years work by Perkin and Robinson (3,4). A recent synthesis of *dl*-brazilin starting with O-trimethyldeoxybrazilone involved synthesis of O-trimethylbrazilane as an intermediate (5). As this optically inactive compound was dimeric (6), bi-O-trimethyl-*cis*-brazilane shown here as (I), could form a racemate or a *meso* compound in which the two monomers comprising the molecule are of opposite chirality.



(I)

DL-Bi-O-trimethyl-*cis*-brazilane, $C_{38}H_{38}O_8$, forms monoclinic crystals belonging to the space group $P2_1/c$, with a = 16.701(6), b = 8.037(2), c = 23.600(9) Å, β = 93.10(2)° and Z = 4. The structure was solved by direct methods and refined with 2355 terms ($I > 4\sigma I$) measured on a Hilger and Watts four-circle diffractometer with CuKα radiation. Anisotropic refinement of the non-hydrogen atoms by block-diagonal least-squares has yielded a reliability index, $R = \Sigma\Delta F/\Sigma F_o$, of 0.10. No hydrogen atom parameters were included.

A view of the molecule given in Fig. 1 shows it to consist of two brazilanyl groups which are of the same chirality and which are linked by the bond C(11) - C'(11) into the dimer. The molecule has a non-crystallographic two-fold symmetry axis perpendicular to this bond, viewed down which the configuration is staggered. Apart from C(10), C(14) and the methyl carbons, the non-hydrogen atoms of the brazilanyl group lie nearly in two planes mutually inclined to render it approximately butterfly in shape. Consequently, ring B is envelope in form and ring C adopts a severely distorted boat (verging on a sofa) conformation. At the present stage of refinement, the distance between the calculated H positions at C(10) and C'(10) is 2.23 Å and the C(11) - C'(11) bond is 1.64 Å. Refinement is continuing and more accurate details will be presented later. The crystal is a racemate containing D and L molecules symmetry-related by the crystallographic symmetry.

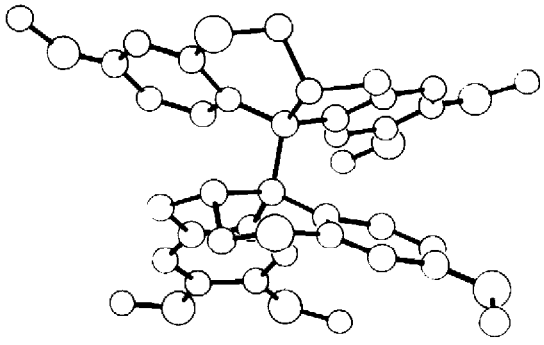


Fig. 1.

Acknowledgement

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FOOTNOTES AND REFERENCES

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