Crystal and Molecular Structure of *trans*-6,8-Dibromo-1,2,3,4,4a,9a-hexahydro-4a,9-dimethylcarbazole†

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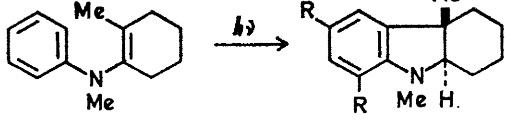
Summary The molecular structure of the title compound (**3**) has been elucidated by single crystal *X*-ray diffraction analysis.

The desire for additional mechanistic information regarding the recently discovered ready, nonoxidative synthesis of *trans*-2,3-dihydroindoles[1] as well as a lack of information regarding the stereochemistry of naturally occurring *trans*-indolines[2] prompted us to carry out the single crystal *X*-ray structure determination on *trans*-6,8-dibromo-1,2,3,4,-4a,9a-hexahydro-4a,9-dimethylcarbazole (**3**). The *trans*-2,3-dihydroindole (**2**) is formed in high yield photochemically from 1-(*N*-methylanilino)-2-methylcyclohexene(**1**). The photochemical product was brominated to facilitate *X*-ray analysis.



(1) (2) R = H;(3) R = Br

Clear hydroscopic plates, monoclinic; $a = 12{\cdot}53 \pm 0{\cdot}02$, $b = 15{\cdot}88 \pm 0{\cdot}02$, $c = 7{\cdot}21 \pm 0{\cdot}02$ Å; $\beta = 95{\cdot}59 \pm 0{\cdot}04°$: systematic extinctions $h0l$ $(h + l = 2n + 1)$ and $0k0$

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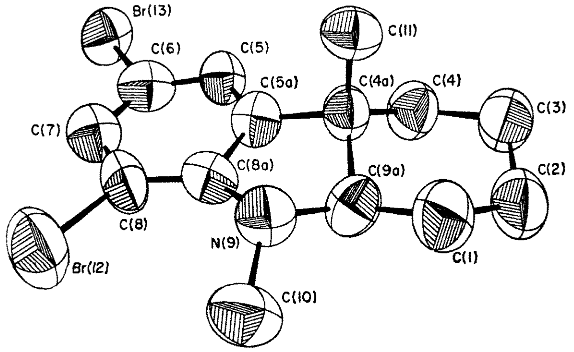
† Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

($k = 2n + 1$) and a density measurement fixed the space-group at $P2_1/n$ with $Z = 4$. Intensity data ($2\theta \leq 110°$) were collected on an automated Hilger–Watts diffractometer with Ni-filtered Cu (1·5418 Å) radiation. Of the 1806 reflections collected 1444 were judged observed after background and LP corrections. The two independent bromine atoms were located in the three-dimensional Patterson synthesis and the remaining 15 non-hydrogen atoms were located in the subsequent Br-phased electron-density map. Full-matrix least-squares in which all positional and anisotropic thermal parameters were varied lowered the discrepancy index to 0·089 for the observed reflections. Estimated standard deviations are ± 0·02 Å for bond lengths and ± 1·0° for bond angles (Figure). No peaks larger than 0·4e/Å^3 were found on a final electron density difference map. All bond angles and bond lengths compare favourably with generally accepted values.[3] No anomalously short intermolecular contacts were found.



FIGURE

As can be seen in the drawing the ring fusion is *trans*. The dihedral angle between planes (4,4a,9a) and (1,9a,4a) is 71° ± 2°. The angular methyl attached to C(4a) is in an axial orientation. The N(9) atom is clearly tetrahedrally hybridized and the C(10) methyl group is *trans* relative to C(1). The Br(12)–C(10) distance is 3·46 Å, substantially shorter than the sum of the van der Waals radii.

Two conclusions may be drawn from this structure. The first is that the photochemical ring closure occurs in a conrotatory fashion in view of the *trans*-fusion.[4] The second is that since the angular methyl group has not migrated a thermally allowed 1,4 sigmatropic hydrogen shift is favoured for product formation in this case.[4]

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[1] O. L. Chapman and G. L. Eian, *J. Amer. Chem. Soc.*, 1968, **90**, 5329.

[2] For pertinent examples, see "The Alkaloids, Chemistry and Physiology," ed. R. H. F. Manske, vol. XI, Academic Press, New York, 1968.

[3] L. E. Sutton, *Chem. Soc. Special Publ.* No. 11, 1958.

[4] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1968, **1**, 17.