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THE STRUCTURE OF HELLER'S DIMER

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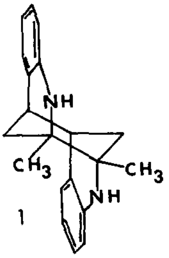
In an earlier communication a constitution was provisionally advanced for the dihydroquinoline dimers of the type originally investigated by Heller (1,2). These dimeric compounds were prepared by reduction of quinaldine with zinc in hydrochloric acid solution. The gross structural features were established primarily by NMR, and the head-to-head nature of the dimer was suggested by relative pKa-values for both the dimer and the monoacetyl derivative. The sterochemistry, represented in I, was accepted *faute de mieux:* beyond the appearance of two equivalent ABX patterns associated with the 2,2,4-trisubstituted-1,2,3,4-tetrahydroquinoline ring systems, there were no discernable couplings of protons to permit further stereochemical assignments. In the choice of *cis* or *trans* isomers, models and conformational arguments indicated the *trans* form to be sterically preferable.



I

The lack of rigorous proof for the stereochemical details of structure, together with some problems that arose in studying comparative configurations in another series of "dihydroquinoline dimers" from electrolytic reduction of quinaldine in alkaline medium,[3] prompted a fuller investigation initially of Heller's dimer.

A dibromo derivative of Heller's dimer was synthesized by two routes: one was by reductive dimerization of 6-bromoquinaldine, and the other was by bromination of Heller's dimer. Both synthetic processes yielded the same brominated dimer (m.p. 199-200). Analysis: Calculated for $C_{20}H_{20}N_2Br_2$: C, 53.59; H, 4.50; N, 6.25. Found: C, 53.95; H, 4.77; N, 6.23.

The structure of Heller's dimer was unambiguously established by a single crystal X-ray analysis of the above dibromo derivative. Suitable crystals were grown from acetonitrile by sl evaporation. The resulting plate-like crystals were cut to a size of 0.2 x 0.3 x 0.3 mm and wer surveyed using a precession camera. The survey indicated the crystals were monoclinic and belong to space group $P2_1/c$. The density, measured by flotation, was 1.61 g/cc; the density calculated on the basis of four molecules per unit cell was 1.645 g/cc.

Cell dimensions were obtained on a Syntex $P\bar{1}$ diffractometer using a least-squares fit of eight high angle reflections (2θ>50°). The cell dimensions were as follows: a = 16.218 Å±0.009, b = 11.515 Å±0.006, c = 9.702 Å±0.006, beta = 92.99 deg.±0.03.

One angstrom intensity data (maximum $\sin\theta/\lambda = 0.5$) were collected on the Syntex $P\bar{1}$ diffractometer using copper radiation which had been passed through a graphite monochromator. A θ-2θ scan technique was employed, the scan rate was 2° per minute in 2θ, and the background was counted for half the scan time at each end of the scan. A single check reflection was monitored every 30 reflections; this reflection indicated no crystal damage and was reproducible well within counting statistics.

The diffractometer output was processed using subprograms of the CRYM crystallographic computer system (4). The processing included corrections for background and for Lorentz and polarization effects (monochromator included). The data was placed on an absolute scale by means of Wilson (5) statistics.

The trial structure was obtained by the usual Patterson and Fourier techniques and refined smoothly to an acceptable R index. The refinement procedure included a full matrix least-square treatment of coordinates, anisotropic temperature factors, and scale factors. Hydrogen atoms were located by difference Fourier techniques and were added to the structure factor calculations in the latter stages of refinement. Hydrogen parameters were not refined. The quantity minimized by the least-squares procedure was $\sum w(F_o^2 - F_c^2)^2$, where $w=1/\sigma^2(F_o^2)$. The final R index was 0.073. A final difference Fourier revealed no missing or misplaced atoms.

The structure obtained was stereographically plotted (Fig.1) using the ORTEP program of C.K. Johnson (6). The results of the X-ray analysis established that Heller's dimer is the *trans* isomer.

The standard deviations in the coordinates, derived from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle, correspond to positional uncertainties of about 0.001 Å for the bromine atoms and about 0.01 Å for the C,N atoms. Uncertainties in the C,N,Br bond distances are about 0.015 Å. Uncertainties in the bond angles involving non hydrogen atoms are approximately 0.9 degree. All bond distances and angles were as expected. Due to limitations of space, further pertinent X-ray data cannot be presented here. F-tables, atomic coordinates, and bond distances and angles may be obtained from the author (Bordner).

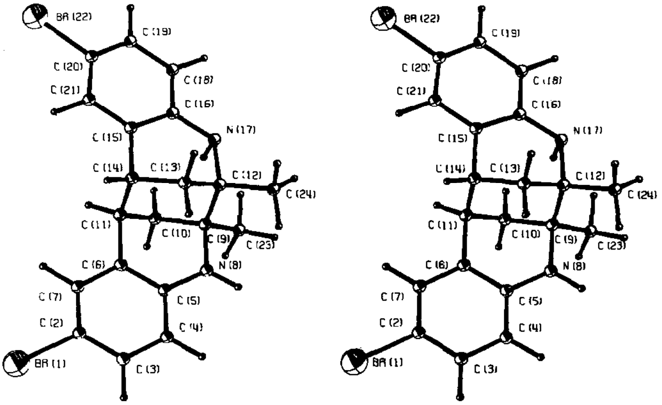


Figure 1

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