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THE STRUCTURE AND STEREOCHEMISTRY OF JAMINE, $C_{21}H_{35}N_3$, BY X-RAY ANALYSIS

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The seeds of Ormosia panamensis Benth. and related species contain a number of related alkaloids[1]. Among them is ormosanine, $C_{20}H_{35}N_3$, also known as piptamine[2] and alkaloid A[3]. The formaldehyde adduct of $C_{20}H_{35}N_3$, which we shall designate as jamine, is identical to a naturally occurring alkaloid in Ormosia jamaicensis[4]. Crystals of jamine for the x-ray determination of the molecular structure were kindly supplied by Drs. H. A. Lloyd and P. Naegeli of the National Institutes of Health.

Jamine occurs naturally as a racemate, hence it may be expected that the material crystallizes in a centrosymmetric system. It was found

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[1] H. A. Lloyd and E. C. Horning, J. Am. Chem. Soc., 80, 1506 (1958); J. Org. Chem., 25, 1959 (1960); J. Org. Chem., 26, 2143 (1961).

[2] R. A. Konovalova, B. S. Diskina and M. S. Rabinovich, Zhur. Obschei Khim., 21, 773 (1951).

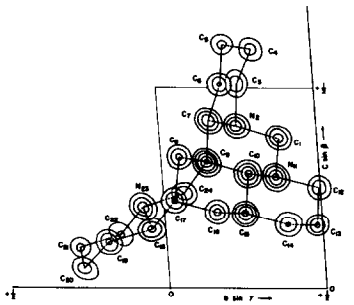
[3] C. H. Hassall and E. M. Wilson, Chem. & Ind., 1358 (1961).

[4] H. A. Lloyd, private communication.

that the unit cell is triclinic with the following cell dimensions: a = 6.79 Å, b = 10.61 Å, c = 13.41 Å, $\alpha = 95^{\circ}$, $\beta = 97^{\circ}\ 20'$ and $\gamma = 103^{\circ}\ 55'$. For two molecules in the unit cell, the computed density is 1.184. Statistical tests on the normalized structure factors derived from the x-ray intensities confirmed that the unit cell is centrosymmetric and that the space group is $P\bar{1}$.

The application of the symbolic addition method[5] to obtain the phases of the x-ray data resulted in the E-map from which the structure was obtained directly. The three-dimensional E-map (Fourier map using normalized structure factors as coefficients) was computed using 287 independent reflections or 16% of the total data. In Fig. 1, sections from the three-dimensional computation were projected down the a axis. A least squares refinement of the data (R = 16.9%) and subsequent electron density maps enabled identification of the three nitrogen atoms. The average C-C bond distance is 1.55 Å and the average C-N bond distance is 1.47 Å with standard deviations of at most 0.019 Å

Fig. 1.

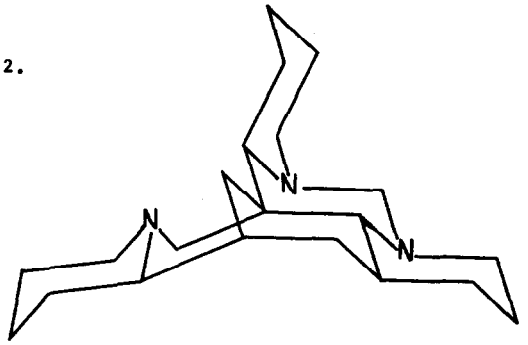


[5] I.L. Karle and J. Karle, Acta Cryst., in press.

for the individual bond lengths.

The molecule is composed of six six-membered rings, five of which have the chair configuration as illustrated in Fig. 2. The ring formed by

Fig. 2.



$C_{24}C_9C_8C_{17}C_{18}N_{23}$ has the boat configuration. The carbon atom marked C_9 is the only atom with four other carbon atoms bonded to it. The carbon atom C_1 is the atom which comes from formaldehyde and bonds to the two secondary nitrogens when the formaldehyde adduct of $C_{20}H_{35}N_3$ is formed[6].

A full description of the x-ray analysis will be published at a later date. An accompanying article in this journal describes the chemical aspects of the structure.

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[6] W. Eisner and F. Sorm, Coll.Czech.Chem.Comm. 24, 2348(1959).