*Tetrahedron.* Vol. 29, pp. 3375 to 3377. Pergamon Press 1973. Printed in Great Britain

# THE MOLECULAR STRUCTURE OF 7,9a,10-TRIMETHYL-8-OXO-8,9,9a,10-TETRAHYDROALLOXAZINE.$H_2O$

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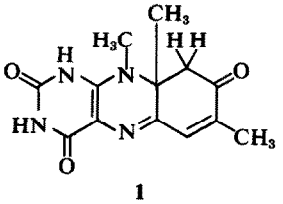
(*Received in the UK* 19 *April* 1973; *Accepted for publication* 13 *June* 1973)

**Abstract**—The proposed molecular structure of a reduced alloxazine has been confirmed by X-ray analysis. The structure was solved by direct methods and refined to a R index of 4·1% using 1780 non-zero reflexions. The closed ring system contains three CO groups and three Me groups. One Me group is bonded to the C(9a)-atom. The greater part of the molecule is planar.

## INTRODUCTION

In a recent paper[1] Addink and Berends assign, from spectroscopic measurements and chemical behaviour, structure **1** to a product (hereafter referred to as TOTA) which was isolated after a condensation reaction of dimeric diacetyl with 5-amino-6-(methylamino)pyrimi-2,4-dione at pH < 3. To confirm this assignment this X-ray structure investigation was started.



**1**

## EXPERIMENTAL

A sample of the compound, $C_{13}H_{14}N_4O_3.H_2O$, was kindly provided by Dr Addink from the biochemical and biophysical Laboratory of the University of technology, Delft.

Monoclinic crystals of TOTA, space group $P2_1/c$ with $a = 9{\cdot}431(3)$, $b = 15{\cdot}064(5)$, $c = 10{\cdot}945(4)$Å and $\beta = 122{\cdot}24(3)°$, were obtained by recrystallization from water.

Intensities were collected up to $\theta = 69{\cdot}00°$ with the CAD3-Nonius diffractometer using $CuK_\alpha$ radiation. In reduction of the intensities to F and E values no absorption correction was made.

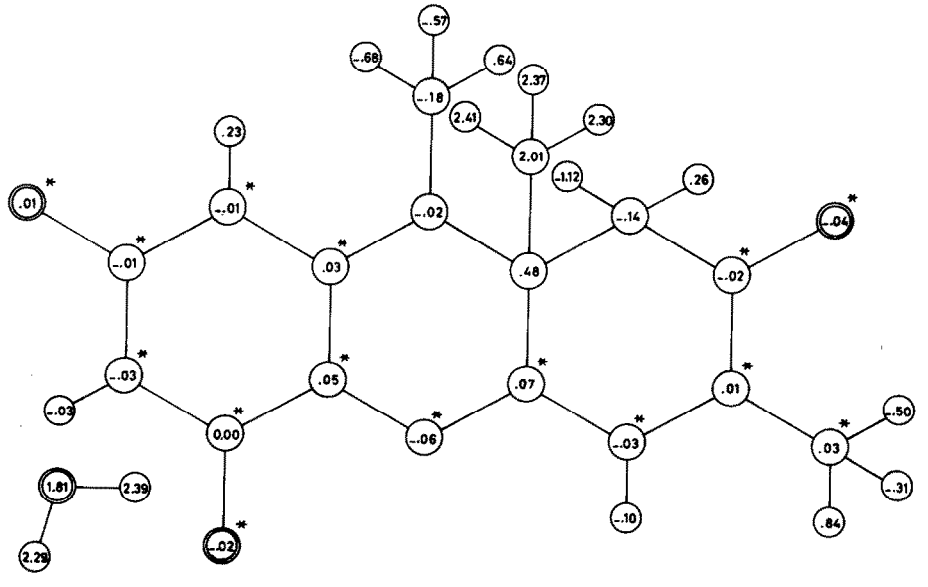



Fig 1. Deviation (in Å) of the atoms from the least squares plane through the starred atoms. A negative deviation means: the atom is above the plane of the paper.

Table 1. Final fractional atomic coordinates ($\times 10^4$ for the non-hydrogen atoms and $\times 10^3$ for the hydrogen atoms) and their estimated standard deviations in parenthesis.

| | x/a | y/b | z/c | | x/a | x/b | z/c |
|---|---|---|---|---|---|---|---|
| O(1) | 413(2) | 3888(1) | −337(2) | C(19) | 8066(3) | 3192(2) | 3800(3) |
| O(2) | 2443(3) | 1942(1) | 1209(2) | C(20) | 5511(3) | 2503(2) | 523(3) |
| O(41) | 4078(2) | 6155(1) | 1847(2) | H(1) | 305(5) | 150(3) | 178(4) |
| O(81) | 11807(2) | 3058(1) | 2967(2) | H(2) | 216(5) | 228(3) | 174(4) |
| N(1) | 3123(2) | 3641(1) | 421(2) | H(11) | 292(4) | 304(2) | 32(3) |
| N(3) | 2266(3) | 5018(1) | 736(2) | H(31) | 141(4) | 538(2) | 62(3) |
| N(5) | 6754(2) | 5122(1) | 2215(2) | H(61) | 975(4) | 559(2) | 336(3) |
| N(10) | 5932(2) | 3378(1) | 1210(2) | H(91) | 848(4) | 330(2) | 94(3) |
| C(2) | 1846(3) | 4174(2) | 241(3) | H(92) | 895(4) | 252(2) | 208(3) |
| C(4) | 3882(3) | 5380(2) | 1456(3) | H(191) | 731(4) | 350(2) | 408(3) |
| C(4a) | 5164(3) | 4781(1) | 1654(2) | H(192) | 928(4) | 330(2) | 460(3) |
| C(5a) | 7933(3) | 4567(2) | 2485(2) | H(193) | 785(4) | 250(2) | 371(3) |
| C(6) | 9609(3) | 4919(2) | 3088(3) | H(201) | 624(4) | 234(2) | 20(3) |
| C(7) | 10932(3) | 4432(2) | 3338(2) | H(202) | 438(4) | 245(2) | −25(4) |
| C(71) | 12688(3) | 4794(2) | 4096(3) | H(203) | 562(4) | 206(2) | 116(4) |
| C(8) | 10656(3) | 3519(2) | 2813(2) | H(711) | 1331(4) | 452(2) | 366(4) |
| C(9) | 8886(3) | 3160(2) | 1956(3) | H(712) | 1271(4) | 547(2) | 407(4) |
| C(9a) | 7710(3) | 3571(2) | 2360(2) | H(713) | 1330(4) | 459(2) | 499(4) |
| C(10a) | 4764(3) | 3923(2) | 1119(2) | | | | |

*Structure determination.* The structure was solved by the direct phase determining method based on the symbolic addition method for centrosymmetrical structures.[2] The E-map revealed all the heavy atoms in the asymmetric unit. Full-matrix anisotropic least-squares refinement, using 1785 observed (non-zero) reflexions, converged to $R(=\Sigma||Fo|-|Fo||/\Sigma|Fo|\times 100)=12\%$. At this stage H atom positions were obtained from a difference Fourier synthesis. Continued refinement, with fixed isotropic thermal parameters for the H atoms and with omission of 5 very strong low-order reflexions reduced R to 4·1%. The final atomic coordinates and their estimated standard deviations are given in Table 1. The temperature factors and a list of F(obs) and final F(calc)-values is available from the laboratory.

## RESULTS

A least squares plane was calculated through all non-H atoms except N(10), C(20), C(9a), C(19), and

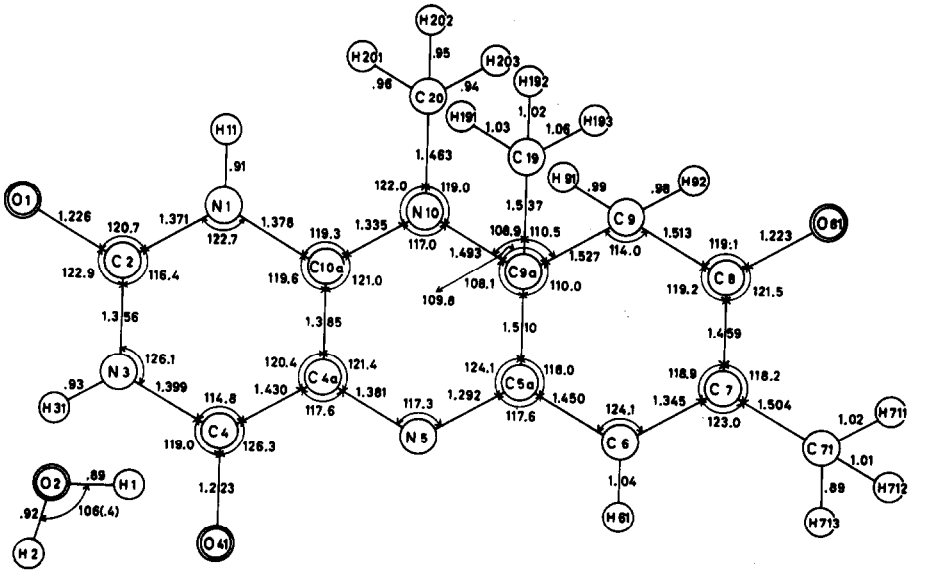



Fig 2. Bond lengths (Å) and bond angles (°) in TOTA. The estimated standard deviations (e.s.d's) are 0·004 Å for distances between non-hydrogen atoms and 0·05 Å for distances to hydrogen atoms. The bond angles involving hydrogen atoms are omitted for clarity. The e.s.d's of the angles given are around 0·2°.

C(9). The greater part of the molecule is planar within 0·1 Å. The deviation of any atom from this plane is shown in Fig. 1.

The dimensions of the molecule are given in Fig. 2. The O(2)···· O(81) distance is 2·850 Å and the O(2)-H(2)···· O(81) angle is nearly 180° indicating a very weak hydrogen bond between TOTA and the water molecule. The three C-O distances are equivalent within experimental error and are normal values for a carbonyl bond in this kind of compounds (e.g. 3, 4, 5). A methyl group on C(9a) has been determined unequivocally. The assignment from spectroscopic measurements by Addink and Berends[1] has thus been confirmed.

## REFERENCES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