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# THE MOLECULAR STRUCTURE OF 1,5,6,1′,3′-PENTAMETHYL-3-OXOPIPERAZINE-2-SPIRO-5′-HYDANTOIN

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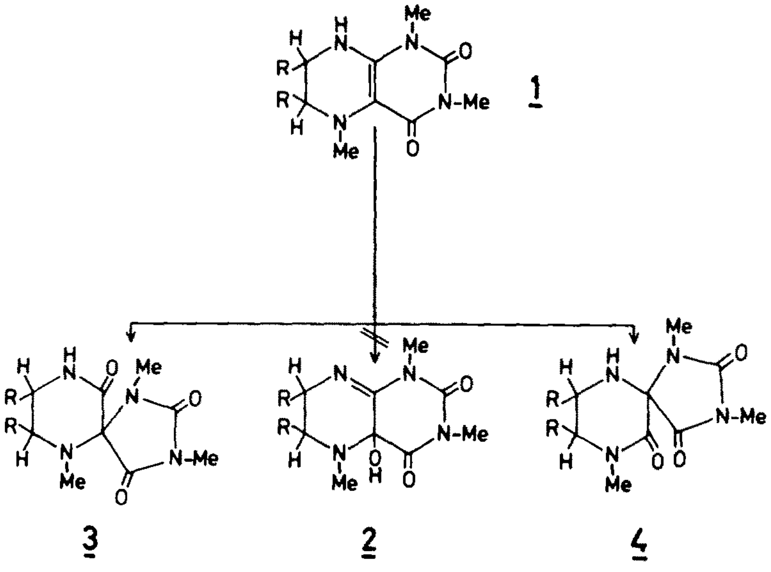
**Abstract**—The autoxidation product of 1,3,5,6,7-pentamethyl-5,6,7,8-tetrahydrolumazine has been studied by X-ray analysis. The final R-index is 5.0% using 1969 non-zero reflexions. The compound was identified as a new spirohydantoin. In the oxopiperazine ring the oxygen is double bonded to the ring C atom; there is no Me group bonded to the adjacent N atom.

## INTRODUCTION

In Scheme 1 the autoxidation of 1,3,5,6,7-pentamethyl-5,6,7,8-tetrahydrolumazine (1, R = – Me) is considered. From the literature[1] one would expect structure 2 being the main reaction product. The structure 3 or 4 (R = – Me) is proposed starting from a different point of view concerning the reaction mechanism.



Scheme 1.

To determine the actual configuration of the main reaction product this X-ray analysis was undertaken.

## EXPERIMENTAL

A sample of the compound $C_{11}H_{18}N_4O_3$, was kindly provided by Mager from the Biochemical and Biophysical Laboratory of the Delft University of Technology.

Crystals were grown from water. The crystals are monoclinic, space group $P2_1/c$ with $a = 10.946(4)$, $b = 8.143(3)$, $c = 16.653(7)$ Å, $\beta = 116.55(3)°$ and $Z = 4$. Three dimensional intensity data were collected with the CAD3-Nonius diffractometer using $CuK_\alpha$ radiation and the $\theta/2\theta$-scan mode with a maximum $\theta$-value of 68.10°. High intensities were reduced by Ni filters. No correction for absorption was made. The crystal had approximate dimensions of $0.15 \times 0.50 \times 0.10$ mm in the a, b and c direction respectively and was mounted about the b-axis.

## STRUCTURE DETERMINATION

The structure was solved using direct methods. The E-map revealed all, but one of the heavy atoms. After three cycles of blocked full-matrix refinement the remaining heavy atom and the H atoms were obtained by a difference synthesis. The last cycle of blocked full-matrix anisotropic least-squares refinement, with fixed isotropic thermal parameters for the H atoms, converged to the conventional $R = 5.0\%$ using 1969 observed (non-zero) reflections. The final difference map did not show any special features. The final atomic coordinates, the temperature factors and their standard deviations (e.s.d's) as calculated from the refinement are given in Table 1. A list of $F_0$ and final $F_c$ values is available from the laboratory.

All calculations were done using the "X-ray-system".[2]

## RESULTS

Figure 1 shows the bond distances and bond angles in the molecule. For the sake of clarity the bond angles involving H atoms are not included. The CO distances indicate a double bond character of the CO bonds. Therefore, a single bonded OH group can be decisively excluded. The O atom in the oxopiperazine ring is double

Table 1. Final parameters with e.s.d.'s in parentheses. The fractional atomic coordinates are multiplied by $10^4$ for the non-hydrogen atoms and by $10^3$ for the hydrogen atoms. The expression for the anisotropic thermal parameters ($Å^2 \times 10^3$) is

$$\exp[-2\pi^2(ha^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + a^*b^*khU_{12}V{:} + b^*c^*klU_{23} + c^*a^*lhU_{31}]$$

The isotropic factors (U) are in $Å^2 \times 10^3$.

| Atom | x/a | y/b | z/c | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| N1 | 4293(2) | 477(3) | 5822(1) | 43(1) | 52(1) | 35(1) | 24(1) | 22(1) | 12(1) |
| N2 | 2153(2) | 2218(3) | 5874(1) | 32(1) | 45(1) | 28(1) | 14(1) | 13(1) | 0(1) |
| N3 | 1314(2) | 2573(3) | 4296(1) | 32(1) | 44(1) | 27(1) | 7(1) | 6(1) | 1(1) |
| N4 | 2236(3) | 5021(3) | 4347(2) | 64(2) | 35(1) | 47(1) | 11(1) | 26(1) | 8(1) |
| C1 | 2509(2) | 2593(3) | 5155(1) | 30(1) | 35(1) | 26(1) | 7(1) | 9(1) | -1(1) |
| C2 | 3588(2) | 1425(3) | 5121(2) | 34(1) | 36(1) | 34(1) | 9(1) | 16(1) | 1(1) |
| C3 | 4036(3) | 303(4) | 6609(2) | 37(1) | 49(2) | 28(1) | 13(1) | 15(1) | 7(1) |
| C4 | 3384(3) | 1875(4) | 6728(2) | 35(1) | 49(2) | 23(1) | 7(1) | 10(1) | -2(1) |
| C5 | 1214(3) | 3944(4) | 3805(2) | 47(2) | 51(2) | 39(2) | 21(1) | 22(1) | 7(1) |
| C6 | 3056(3) | 4347(3) | 5158(2) | 52(2) | 35(1) | 43(2) | 5(1) | 21(1) | -2(1) |
| C7 | 3245(4) | -1263(4) | 6527(2) | 72(2) | 52(2) | 55(2) | 8(2) | 35(2) | 9(2) |
| C8 | 3027(4) | 1699(5) | 7514(2) | 62(2) | 81(2) | 30(1) | 19(2) | 24(1) | -0(2) |
| C9 | 1252(4) | 3482(5) | 5955(2) | 62(2) | 76(3) | 54(2) | 38(2) | 32(2) | 5(2) |
| C10 | 2459(5) | 6635(5) | 4051(3) | 116(4) | 41(2) | 87(3) | 11(2) | 54(3) | 18(2) |
| C11 | 557(4) | 1082(5) | 3900(2) | 55(2) | 65(2) | 42(2) | -13(2) | 8(2) | -3(2) |
| O1 | 3776(2) | 1475(3) | 4447(1) | 61(1) | 65(1) | 40(1) | 31(1) | 34(1) | 18(1) |
| O2 | 382(2) | 4228(3) | 3041(1) | 62(1) | 86(2) | 34(1) | 27(1) | 12(1) | 20(1) |
| O3 | 4029(2) | 4978(3) | 5766(1) | 74(2) | 49(1) | 56(1) | -16(1) | 10(1) | -9(1) |
| H1 | 491(3) | -13(4) | 580(2) | 29 | | | | | |
| H31 | 496(3) | 19(4) | 710(2) | 25 | | | | | |
| H41 | 414(3) | 281(4) | 665(2) | 25 | | | | | |
| H71 | 329(3) | -141(4) | 708(2) | 43 | | | | | |
| H72 | 365(3) | -236(4) | 640(2) | 43 | | | | | |
| H73 | 231(4) | -111(4) | 600(2) | 43 | | | | | |
| H81 | 279(3) | 280(4) | 770(2) | 39 | | | | | |
| H82 | 389(3) | 130(4) | 807(2) | 39 | | | | | |
| H83 | 215(3) | 96(4) | 741(2) | 39 | | | | | |
| H91 | 75(3) | 297(4) | 634(2) | 42 | | | | | |
| H92 | 42(3) | 351(4) | 537(2) | 42 | | | | | |
| H93 | 173(4) | 453(5) | 609(2) | 42 | | | | | |
| H101 | 231(4) | 744(5) | 438(3) | 53 | | | | | |
| H102 | 145(4) | 690(5) | 337(3) | 53 | | | | | |
| H103 | 332(4) | 668(5) | 403(3) | 53 | | | | | |
| H111 | -24(4) | 134(4) | 323(2) | 49 | | | | | |
| H112 | 36(4) | 50(5) | 435(2) | 49 | | | | | |
| H113 | 105(4) | 41(5) | 366(2) | 49 | | | | | |

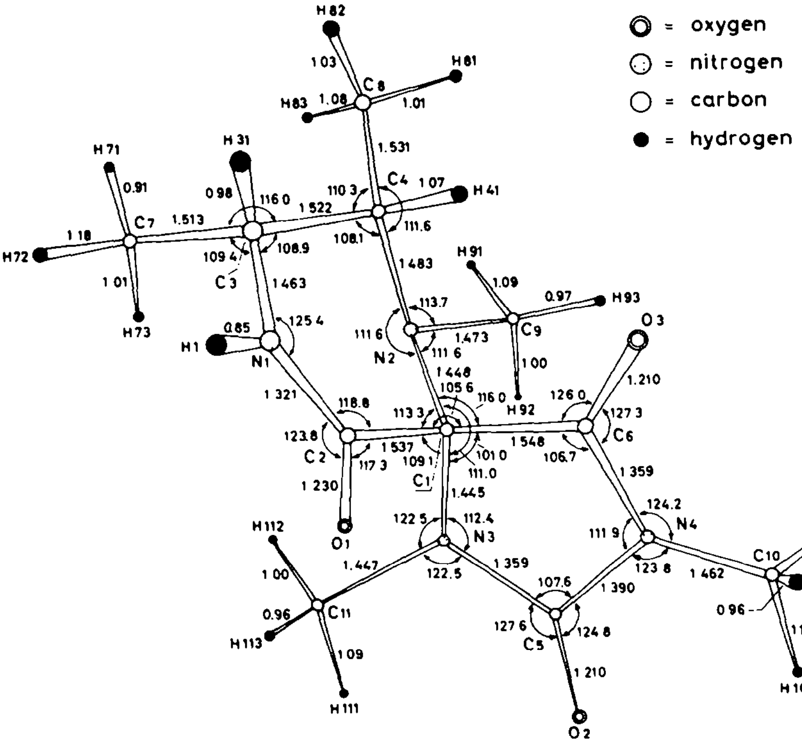


Fig. 1.

bonded to the C2 atom; a Me group is bonded to the N2 atom and not to the N1 atom (Fig. 1). Therefore structure 3 (R = – Me) is the autoxidation product of the reaction in aqueous solution shown in Scheme 1.

## REFERENCES

[1] See: H. I. X. Mager, Discussion in previous paper. To be published.

[2] The X-ray System, *Tech. Rep.* TR-192 of the Computer Science Center, University of Maryland (June 1972).