

As a result of this conformationally rigid arrangement the O atom of the ester aminal function becomes locked into a configuration where cleavage of the N(3)–C(4) bond is no longer stereoelectronically allowed since the O(4) electron pair is no longer antiperiplanar to the N(3) atom (Fig. 2). The N(3)–C(4) bond is still longer than the C(4)–N(9) bond, but the O(4) atom with an electron pair now antiperiplanar to the C(4)–N(9) bond has a larger O(4)–C(4)–N(9) angle than the N(3)–C(4)–O(4) angle of the ester aminal function. It can be readily seen that this variation in bond lengths and angles is very simply related to the stereoelectronic effects and the rates of regiospecific ring openings of uric acid glycol ethers (Poje & Vicković, 1987*a,b*). An inspection of molecular models shows that the propellane molecule has no reasonable accessible conformation to develop a proper electron-pair orientation, and the remarkable stability of the ester aminal grouping under mild-acid conditions can be explained on the same stereoelectronic grounds.

We thank the Croatian Republic Research Fund for financial support. We also thank M. Bruvo, MSc, for data collection.

References

- JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- POJE, M. & VICKOVIĆ, I. (1987*a*). *Acta Cryst.* C43, 539–542.
- POJE, M. & VICKOVIĆ, I. (1987*b*). *Acta Cryst.* C43, 547–549.
- STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY76* system. Tech. Rep. TR-466. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- VICKOVIĆ, I. (1985). *CSU*. Crystal structure utility – highly automatic and selective program for chemical connectivity relationships and their e.s.d.'s. 9th Eur. Crystallogr. Meet., Torino, Italy, Abstr. 1–048, p. 81.

Acta Cryst. (1987). C43, 547–549

Stereoelectronic Effects in Oxidative Transformations of Purines. IV. Structure of 4,5-Dihydro-4,5-dimethoxy-1,3,7-trimethyluric Acid*

BY MIRKO POJE

Laboratory of Organic Chemistry, Faculty of Science, University of Zagreb, PO Box 153, 41001 Zagreb, Yugoslavia

AND IVAN VICKOVIĆ

University Computing Centre, University of Zagreb, Engelsova b.b., 41000 Zagreb, Yugoslavia

(Received 7 February 1986; accepted 17 September 1986)

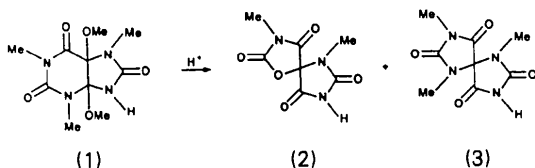
Abstract. C₁₀H₁₆N₄O₅, $M_r = 272.26$, triclinic, $P\bar{1}$, $a = 8.780$ (4), $b = 8.260$ (5), $c = 8.997$ (5) Å, $\alpha = 91.77$ (3), $\beta = 89.65$ (5), $\gamma = 103.54$ (4)°, $V = 634.1$ (5) Å³, $Z = 2$, $D_x = 1.426$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 1.24$ cm⁻¹, $F(000) = 288$, room temperature, $R = 0.043$ for 2678 observed reflections. The *cis*-fused bicyclic system has a ring-twisted conformation which is defined by the bridgehead torsion angle N(3)–C(4)–C(5)–N(7) of 91.4 (1)°. The nearly orthogonal N(3)–C(4)–N(9)–C(8) array [–93.5 (1)°] with N(9) antiperiplanar to the 4-methoxy group allows stereoelectronically controlled N(3)–C(4) bond breaking in the ring contractions to spiro[4.4]nonane systems.

Introduction. Uric acid glycol ethers offer an attractive means of determining stereochemistry and interactions which relate to structure and reactivity of tetrahedral intermediates in oxidative transformations of purines. Dramatic conformational changes effected by substitution at N atoms have been ascribed to repulsive Me↔O interactions, and at the same time the molecular structures indicated that the bond lengths and angles of the ester aminal function show strong stereoelectronic conformational dependence in complete agreement with the stereoelectronic principle (Poje & Vicković, 1987*a,b,c*). On the basis of this principle, the regiospecific ring-opening processes, involving two ring-twisted conformations of a *cis*-fused system, become intelligible.

More extensively alkylated uric acids, having both N(1) and N(7) alkylated, undergo an interesting

* Uric acid is 7,9-dihydro-1*H*-purine-2,6,8(3*H*)-trione.

oxidative ring contraction to spiro[4.4]nonane systems, *viz* caffolides (2) and spirodihydantoin (3) (Biltz, 1936).



Rearrangement of a model uric acid glycol ether on acidic hydrolysis is exemplified by that of (1) which gave a mixture of spiro[4.4]nonanes (2) and (3) (Fischer, 1907). This result suggested that similar conformational and stereoelectronic effects may be involved in pyrimidine ring openings and pyrimidine ring contractions. To test this idea and to develop a general concept of stereoelectronic control in oxidative ring transformations of purines, it was of interest to investigate in detail the structure of 4,5-dihydro-4,5-dimethoxy-1,3,7-trimethyluric acid (1).

Experimental. The title compound was prepared by chlorination of caffeine in methanol. Recrystallization from methanol gave prismatic crystals. Crystal dimensions 0.20 × 0.29 × 0.36 mm, Philips PW 1100 diffractometer, graphite-monochromatized Mo K α radiation, lattice parameters from 18 reflections ($5 \leq \theta \leq 11^\circ$); θ - 2θ mode, scan width 1.6° , scan speed $0.04^\circ \text{ s}^{-1}$ ($2 \leq \theta \leq 30^\circ$). Three standard reflections monitored every 2 h showed no significant variation in intensity. From 2790 independent intensities ($0 \leq h \leq 12$, $-11 \leq k \leq 11$, $-12 \leq l \leq 12$), 84 reflections with $I \leq 3\sigma(I)$, 17 reflections with $F_o \leq 0.04(F_o)_{\text{max}}$ and poor F_o/F_c agreement, and 11 reflections (10 $\bar{1}$, 20 $\bar{1}$, 01 $\bar{1}$, 1 $\bar{1}$ 0, 3 $\bar{1}$ 0, 200, 001, 101, 201, 011, 022) due to

secondary extinction were ignored; data corrected for Lorentz and polarization effects but not for absorption. Structure was solved using *MULTAN80* (Main *et al.*, 1980). All H atoms were found in ΔF map; 2678 observed intensity data and 237 parameters in full-matrix least-squares refinement using F magnitudes. Coordinates of all atoms, anisotropic thermal parameters for non-H and isotropic for H atoms were refined in the last cycle; ureide H atoms relocated by a ΔF synthesis perfectly agreed with those refined. Final $R = 0.043$, $wR = 0.058$, $S = 2.1$, $(\Delta/\sigma)_{\text{max}} = 1.0$, $(\Delta/\sigma)_{\text{av}} = 0.09$ for all atoms, $\Delta\rho_{\text{max}} = 0.33 \text{ e } \text{\AA}^{-3}$.

Table 2. Bond lengths (Å) and angles ($^\circ$) and geometry of the hydrogen bond (*e.s.d.*'s in parentheses)

N(1)—C(1)	1.475 (2)	O(4)—C(10)	1.433 (2)
N(1)—C(2)	1.404 (2)	C(5)—O(5)	1.399 (1)
N(1)—C(6)	1.361 (2)	C(5)—C(6)	1.529 (2)
C(2)—O(2)	1.215 (2)	C(5)—N(7)	1.441 (1)
C(2)—N(3)	1.351 (2)	O(5)—C(11)	1.425 (2)
N(3)—C(3)	1.465 (2)	C(6)—O(6)	1.206 (2)
N(3)—C(4)	1.453 (2)	N(7)—C(7)	1.450 (2)
C(4)—O(4)	1.388 (1)	N(7)—C(8)	1.367 (2)
C(4)—C(5)	1.570 (2)	C(8)—O(8)	1.221 (2)
C(4)—N(9)	1.435 (1)	C(8)—N(9)	1.364 (2)
C(1)—N(1)—C(2)	117.9 (2)	C(4)—C(5)—C(6)	115.7 (1)
C(1)—N(1)—C(6)	117.1 (2)	C(4)—C(5)—N(7)	100.4 (1)
C(2)—N(1)—C(6)	125.0 (1)	O(5)—C(5)—C(6)	104.1 (1)
N(1)—C(2)—O(2)	119.5 (2)	O(5)—C(5)—N(7)	114.2 (2)
N(1)—C(2)—N(3)	118.0 (1)	C(6)—C(5)—N(7)	110.0 (1)
O(2)—C(2)—N(3)	122.5 (2)	C(5)—O(5)—C(11)	117.6 (1)
C(2)—N(3)—C(3)	117.6 (1)	N(1)—C(6)—C(5)	116.6 (1)
C(2)—N(3)—C(4)	126.7 (1)	N(1)—C(6)—O(6)	122.1 (2)
C(3)—N(3)—C(4)	115.7 (1)	C(5)—C(6)—O(6)	121.2 (2)
N(3)—C(4)—O(4)	111.3 (1)	C(5)—N(7)—C(7)	124.6 (1)
N(3)—C(4)—C(5)	111.2 (1)	C(5)—N(7)—C(8)	111.6 (1)
N(3)—C(4)—N(9)	110.9 (1)	C(7)—N(7)—C(8)	122.1 (1)
O(4)—C(4)—C(5)	114.6 (1)	N(7)—C(8)—O(8)	125.5 (1)
O(4)—C(4)—N(9)	107.1 (1)	N(7)—C(8)—N(9)	108.0 (1)
C(5)—C(4)—N(9)	101.3 (1)	O(8)—C(8)—N(9)	126.6 (2)
C(4)—O(4)—C(10)	115.3 (1)	C(4)—N(9)—C(8)	110.9 (1)
C(4)—C(5)—O(5)	112.8 (1)		

N—H...O	N—H	H...O	N...O	N—H...O
N(9)—H(9)...O(8) [†]	0.86 (2) Å	2.02 (2) Å	2.872 (2) Å	173 (2) $^\circ$

Symmetry code: (i) 1-x, -y, 1-z.

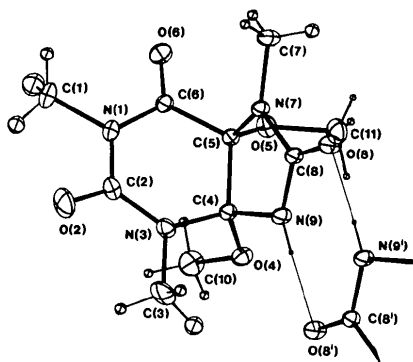


Fig. 1. Molecular conformation of the title compound (*R,R*-configuration).

Table 1. Fractional atomic coordinates ($\times 10^4$) and U_{eq} ($\text{\AA}^2 \times 10^3$) values

	x	y	z	U_{eq}^\dagger
N(1)	7495 (2)	2176 (2)	-319 (1)	44 (<1)
C(1)	7587 (4)	2403 (3)	-1940 (2)	77 (1)
C(2)	7232 (2)	546 (2)	194 (2)	42 (<1)
O(2)	6853 (2)	-626 (2)	-683 (2)	75 (<1)
N(3)	7480 (2)	349 (1)	1651 (1)	38 (<1)
C(3)	7409 (3)	-1343 (2)	2139 (3)	67 (1)
C(4)	7755 (1)	1643 (2)	2816 (1)	29 (<1)
O(4)	9204 (1)	1796 (1)	3484 (1)	39 (<1)
C(5)	7454 (1)	3315 (2)	2236 (1)	27 (<1)
O(5)	8445 (1)	4726 (1)	2895 (1)	40 (<1)
C(6)	7686 (2)	3575 (2)	567 (2)	36 (<1)
O(6)	7935 (2)	4949 (2)	65 (1)	60 (<1)
N(7)	5824 (1)	3113 (1)	2612 (1)	30 (<1)
C(7)	4865 (2)	4232 (2)	2182 (2)	41 (<1)
C(8)	5381 (2)	1991 (2)	3710 (2)	31 (<1)
O(8)	4129 (1)	1728 (1)	4365 (1)	44 (<1)
N(9)	6595 (1)	1263 (2)	3964 (1)	36 (<1)
C(10)	10511 (2)	2041 (3)	2486 (3)	57 (<1)
C(11)	8137 (3)	5145 (3)	4397 (2)	54 (<1)

$^\dagger U_{\text{eq}} = \frac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^*\cos\gamma + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha]$.

Function minimized $\sum w(|F_o| - |F_c|)^2$, $w = \sigma^{-2}(F_o)$ (derived from counting statistics). Geometrical considerations by *CSU* program (Vicković, 1985); atomic scattering factors and anomalous-dispersion coefficients as defined by *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). All calculations performed on a Univac 1110/42 computer at the University Computing Centre, Zagreb.

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1,* main bond lengths and angles and hydrogen-bond geometry in Table 2. An *ORTEP* view (Johnson, 1971) of the molecule is shown in Fig. 1 with the numbering scheme and the hydrogen-bonding pattern.

The ring-twisted conformation of the *cis*-fused bicyclic system [N(3)—C(4)—C(5)—N(7) 91.4 (1)°] and important conformational features of (1), defined by the torsion angles (Table 3, deposited), are reminiscent of those found in 4,5-dihydro-4,5-dimethoxy-3,7-dimethyluric acid (Poje & Vicković, 1987b); moreover, there is a coincidental short N(3)···C(10) intramolecular contact of 2.796 (3) Å. The N(7) and N(9) atoms also showed a distinct pyramidalization; the distances from the planes through their three adjacent atoms are 0.107 (1) and -0.157 (1) Å, respectively.

A nearly orthogonal N(3)—C(4)—N(9)—C(8) array of -93.5 (1)° along with the suitably oriented non-bonded electron pair on O(4) weaken the N(3)—C(4) bond of the ester aminal function (Fig. 2). The ring contractions can again be rationalized on the basis of the arguments derived from the principles of stereo-electronic control in the hydrolysis of uric acid glycol ethers, and results are consistent only if these are taken into consideration. The difference in behaviour of

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H atoms and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43421 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1987). C43, 549–552

The 1:1 Complex of Pyrene with 2,4,6-Trinitrotoluene

BY JOHN C. BARNES AND WIGAN GOLNAZARIANS

Chemistry Department, The University, Dundee DD1 4HN, Scotland

(Received 25 July 1986; accepted 7 October 1986)

Abstract. C₁₆H₁₀·C₇H₅N₃O₆, $M_r = 429.4$, triclinic, $P\bar{1}$, $a = 8.046$ (1), $b = 15.067$ (1), $c = 16.433$ (3) Å, $\alpha = 82.03$ (1), $\beta = 89.10$ (1), $\gamma = 87.52$ (1)°, $U =$

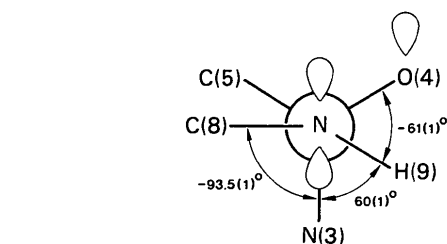


Fig. 2. The Newman projection along the N(9)—C(4) axis showing the alignment of non-bonded electron pairs and the N(3)—C(4) bond; N and O electron escorts are pictured as sp^2 - and sp^3 -hybridized, respectively.

ring-opening products can, however, be readily explained by the effect of substitution at N(1) imposing restrictions on the stable orientation of the ureide side chain (Poje, Paulus & Ročić, 1980).

We thank the Croatian Republic Research Fund for financial support and M. Bruvo, MSc, for data collection.

References

- BILTZ, H. (1936). *J. Prakt. Chem.* **145**, 65–228.
 FISCHER, E. (1907). *Untersuchungen in der Puringruppe*, pp. 85–135. Berlin: Springer.
 JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
 POJE, M., PAULUS, E. F. & ROČIĆ, B. (1980). *J. Org. Chem.* **45**, 65–68.
 POJE, M. & VICKOVIĆ, I. (1987a). *Acta Cryst.* **C43**, 539–542.
 POJE, M. & VICKOVIĆ, I. (1987b). *Acta Cryst.* **C43**, 542–545.
 POJE, M. & VICKOVIĆ, I. (1987c). *Acta Cryst.* **C43**, 545–547.
 STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
 VICKOVIĆ, I. (1985). *CSU*. Crystal structure utility – highly automatic and selective program for chemical connectivity relationships and their e.s.d.'s. 9th Eur. Crystallogr. Meet., Torino, Italy, Abstr. 1–048, p. 81.

0108-2701/87/030549-04\$01.50

© 1987 International Union of Crystallography