

Structure of the 4-Oxo-2-butenic Acid Alkyl Ester Moiety. IV.* Methyl-4-(3-Oxo-1-piperazinyl)-4-oxo-2-butenate

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Abstract. $C_9H_{12}N_2O_4$, $M_r = 212.2$, monoclinic, $P2_1/c$, $a = 17.022(2)$, $b = 6.161(1)$, $c = 10.031(2)$ Å, $\beta = 103.92(1)^\circ$, $V = 1021.1$ Å³, $Z = 4$, $D_x = 1.38$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, Ni filter, $\mu = 0.89$ mm⁻¹, $F(000) = 448$, $T = 293$ K, $R = 0.066$ and $wR = 0.074$ for 1247 observed intensities. Intermolecular hydrogen bonds join molecules related by a 2_1 axis to form infinite chains running in the $[010]$ direction, with butenoate groups perpendicular to the chain.

Experimental. The compound crystallized from chloroform as large transparent plates. Data collection and accurate cell determination ($9 < \theta < 16^\circ$, 25 reflections) were performed on a CAD-4 diffractometer. The crystal size was $0.31 \times 0.20 \times 0.04$ mm. 1942 independent intensities [1247 considered observed with $I \geq 3\sigma(I)$] were measured using the $\omega/2\theta$ scan technique ($\theta_{\max} = 75^\circ$, $-21 \leq h \leq 21$, $0 \leq k \leq 7$, $0 \leq l \leq 12$). Three standards monitored during data collection showed no significant change in their intensities. The data were corrected for Lorentz and polarization effects, and for absorption according to Walker & Stuart (1983) (transmission factors between 0.434 and 0.979).

The structure was solved by direct methods (Sheldrick, 1986) and refined by full-matrix least squares (Sheldrick, 1976) with anisotropic temperature factors for non-H atoms, isotropic temperature parameters for H atoms and an isotropic extinction parameter $g = 0.009(2)$ (Larson, 1967). Non-H and H atom parameters were refined in separate blocks. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(F_o) + 0.00225 F_o^2$. The refinement converged to a maximum shift/e.s.d. of 0.03 and 0.04 for non-H and H atom blocks comprising 137 and 50 variables, respectively. The final $R = 0.046$, $wR = 0.053$, $S = 0.874$. The maximum and minimum peaks in the final difference Fourier synthesis were 0.26 and -0.25 e Å⁻³. All calculations were carried out on an AMSTRAD 1512 microcomputer. Scattering factors were taken from *SHELX*.

* Part III: Glowka (1991).

The molecular conformation and atomic labeling scheme are shown in Fig. 1. The atomic coordinates are given in Table 1 and selected bond distances and angles for non-H atoms are in Table 2.*

Related literature. A number of piperazides, 2-methylpiperazides, 2,5-dimethylpiperazides, piperazine-2,5-diones, hydrazines, ethylenediamines and ureas of 4-oxo-2-butenates have been synthesized and tested against transplantable neoplasms (Groszkowski, Najman & Sienkiewicz, 1972;

* Lists of anisotropic thermal parameters for non-H atoms, structure factors and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54250 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

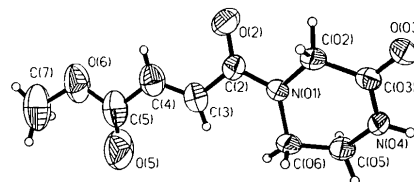


Fig. 1. A view of the molecule with the atomic labeling scheme (Johnson, 1976).

Table 1. Final atomic coordinates of non-H atoms and equivalent isotropic temperature factors (Å²)

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_i a_i^* a_j^* a_i a_j$$

	x	y	z	B_{eq}
C(2)	0.7683 (2)	0.2904 (7)	0.7432 (4)	3.62 (10)
O(2)	0.7573 (2)	0.0929 (5)	0.7263 (3)	4.98 (9)
C(3)	0.7226 (3)	0.4474 (8)	0.6403 (4)	4.51 (11)
C(4)	0.6788 (3)	0.3792 (9)	0.5223 (4)	4.94 (14)
C(5)	0.6377 (3)	0.5279 (13)	0.4130 (5)	6.35 (18)
O(5)	0.6461 (3)	0.7216 (10)	0.4166 (4)	9.69 (19)
O(6)	0.5931 (2)	0.4207 (8)	0.3081 (3)	7.24 (13)
C(7)	0.5564 (4)	0.5452 (14)	0.1861 (6)	9.83 (25)
N(01)	0.8241 (2)	0.3671 (5)	0.8534 (3)	3.25 (8)
C(02)	0.8752 (2)	0.2039 (6)	0.9363 (4)	3.69 (11)
C(03)	0.9267 (2)	0.2761 (7)	1.0717 (4)	3.23 (9)
O(03)	0.9699 (2)	0.1405 (5)	1.1449 (3)	4.40 (8)
N(04)	0.9244 (2)	0.4835 (5)	1.1061 (3)	3.51 (9)
C(05)	0.8680 (3)	0.6396 (7)	1.0280 (5)	4.56 (12)
C(06)	0.8518 (3)	0.5919 (6)	0.8754 (4)	4.01 (12)

Table 2. Bond lengths (Å), valency angles (°) and selected torsional angles (°)

N(01)—C(02)	1.453 (5)	C(2)—O(2)	1.237 (5)
C(02)—C(03)	1.496 (5)	C(2)—C(3)	1.490 (6)
C(03)—O(03)	1.232 (5)	C(3)—C(4)	1.307 (6)
C(03)—N(04)	1.327 (5)	C(4)—C(5)	1.470 (8)
N(04)—C(05)	1.448 (5)	C(5)—O(5)	1.201 (10)
C(05)—C(06)	1.517 (6)	C(5)—O(6)	1.317 (7)
C(06)—N(01)	1.463 (5)	O(6)—C(7)	1.452 (7)
N(01)—C(2)	1.357 (4)		
C(02)—N(01)—C(06)	116.2 (3)	O(2)—C(2)—N(01)	120.5 (4)
C(02)—N(01)—C(2)	115.5 (3)	C(3)—C(2)—N(01)	119.0 (4)
C(06)—N(01)—C(2)	126.1 (3)	O(2)—C(2)—C(3)	120.5 (4)
N(01)—C(02)—C(03)	117.0 (3)	C(2)—C(3)—C(4)	120.5 (4)
C(02)—C(03)—N(04)	118.4 (3)	C(3)—C(4)—C(5)	122.7 (5)
C(02)—C(03)—O(03)	118.3 (4)	C(4)—C(5)—O(5)	124.4 (5)
O(03)—C(03)—N(04)	123.3 (4)	C(4)—C(5)—O(6)	111.3 (6)
C(03)—N(04)—C(05)	123.8 (3)	O(5)—C(5)—O(6)	124.3 (5)
N(04)—C(05)—C(06)	110.7 (4)	C(5)—O(6)—C(7)	117.2 (5)
C(05)—C(06)—N(01)	108.0 (3)		
C(02)—N(01)—C(2)—O(2)	7.6 (5)		
C(02)—N(01)—C(2)—C(3)	-170.2 (4)		
C(06)—N(01)—C(2)—O(2)	170.3 (4)		
C(06)—N(01)—C(2)—C(3)	-7.6 (6)		
N(01)—C(2)—C(3)—C(4)	168.4 (4)		
O(2)—C(2)—C(3)—C(4)	-9.4 (7)		
C(2)—C(3)—C(4)—C(5)	-175.1 (5)		
C(3)—C(4)—C(5)—O(5)	6.9 (9)		
C(3)—C(4)—C(5)—O(6)	-175.7 (5)		
C(4)—C(5)—O(6)—C(7)	-173.1 (5)		
O(5)—C(5)—O(6)—C(7)	4.3 (9)		

Andrzejewska-Golec, Broda & Najman, 1977; Graczyk, Pakulska, Groszkowski & Najman, 1980; Groszkowski & Najman, 1986, and references therein). Some showed promising activity in mice. The —CH=CH—C=O fragment which is also present in butenoates is supposed to be responsible for the cytostatic activity of acrylates (Lee, Kim, Piantadosi, Huang & Geissman, 1974; Loeffler, Sajadi & Hall, 1977). Therefore we started an X-ray study on the 4-oxo-2-butenate moiety (Głowska & Iwanicka, 1990; Głowska, Iwanicka & Najman, 1991; Głowska, 1991).

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Structure of Tris(5-acetyl-3-thienyl)methane:Ethyl Acetate Inclusion Compound

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Abstract. C₄₂H₄₀O₈S₆, $M_r = 865.1$, triclinic, $P1$, $a = 12.329$ (5), $b = 11.229$ (5), $c = 8.229$ (5) Å, $\alpha = 98.42$ (5), $\beta = 106.43$ (5), $\gamma = 99.05$ (5)°, $U = 1057$ (1) Å³, $Z = 1$, $D_x = 1.36$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 3.23$ cm⁻¹, $F(000) = 452$, $T =$

The bond lengths and angles in the present structure agree with the previous results to within 3σ limits. In the crystal, the molecules are linked in infinite chains by means of intermolecular N(04)—H \cdots O(03) [$2 - x, y - \frac{1}{2}, \frac{5}{2} - z$] hydrogen bonds with N \cdots O and H \cdots O distances of 2.872 (4) and 2.04 (2) Å, respectively and an N—H \cdots O angle of 168 (3)°. The chains run along the 2_1 axis.

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