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6a-Methoxycarbonyl-3-ethoxycarbonyl-4-oxofuro[3,4-*c*]-2-pyrazoline*

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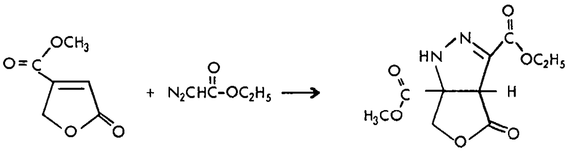
Abstract. $C_{10}H_{12}N_2O_6$, M.W. 256·22, m.p. 96–97°C, orthorhombic, *Pbca*, $a=20{\cdot}130(3)$, $b=13{\cdot}835(2)$, $c=8{\cdot}833(1)$ Å, $Z=8$, $D_x=1{\cdot}384$, $D_m=1{\cdot}385$ g cm^{-3}. The title compound was synthesized as a precursor to a substituted butenolide. The refined structure ($R=0{\cdot}044$, $R_w=0{\cdot}045$) is shown to be a 2-pyrazoline. Among the potential hydrogen-bond acceptors, only the ethoxycarbonyl C=O oxygen is found to participate in hydrogen bonding. This carbonyl group is also found to assume the s-*cis* conformation relative to the C–N double bond.

Introduction. In the course of an investigation of a general synthesis of substituted butenolides (Pelletier, Djarmati, Mićović & Lajšić, 1974; Pelletier, Djarmati, Lajšić, Mićović & Yang, 1975), the title compound was prepared by the following reaction:



The second step of the butenolide synthesis involves the loss of N_2 by thermal decomposition. Because the structure of the substituted butenolide could be unambiguously deduced from the structure of the furopyrazoline intermediate, rigorous knowledge of this structure was essential. Appropriate model compounds could not be found in the literature, and so the title compound was selected for crystallographic study to provide a known reference structure.

Large colorless tabular crystals of the title compound were grown from ether. Precession photographs showed that the crystals were orthorhombic. Systematic absences ($0kl$ for $k=2n+1$, $h0l$ for $l=2n+1$, $hk0$ for $h=2n+1$) established the space group as *Pbca*. Precise measurements of 2θ were made for 15 general reflexions in the range of 28–50° 2θ. Least-squares refinement of the unit-cell dimensions gave $a=20{\cdot}130(3)$, $b=13{\cdot}835(2)$, $c=8{\cdot}833(1)$ Å ($\lambda=1{\cdot}5418$ Å for Cu $K\alpha$). The density of the crystals was measured by flotation in benzene/CCl_4. Integrated intensities were measured by ω–2θ scans for all reflexions, including systematic absences, on an Enraf-Nonius CAD-4 diffractometer, using Cu $K\alpha$ radiation (graphite monochromator). Of the systematically absent reflexions, 10 showed a net intensity greater than the $3\sigma(I)$ threshold. With the exception of 301 (discussed below), all these measurements exceeded the threshold by a sufficiently small amount that they could reasonably be considered to result from noise in the detector electronics. Of the 2541 reflexions accessible to a 2θ limit of 150°, 1557 (61·3%) were observed at the $3\sigma(I)$ level of significance. On the basis of the final refinement, 96 of the 'observed' reflexions were reclassified to 'unobserved' because of an apparent underestimation of the standard deviation based on counting statistics. Repeated measurements of 301 and the symmetrically related $30\bar{1}$ showed significant ($I>5\times$ the $3\sigma(I)$ threshold) diffracted intensity. Acceptance of this reflexion as truly 'observed' would have required that the space group be lowered to the noncentrosymmetric $Pb2_1a$ (an alternate setting of $Pca2_1$). This alternative was rejected on the basis of the observed density (which would have then required two independent molecules in the asymmetric unit) and the chemical knowledge that the sample was a racemic mixture. The statistical distribution of the E's conformed closely to that expected for a centrosymmetric space group, supporting the choice of *Pbca*. The source of the apparent diffraction for 301 was not investigated further. Renninger enhancement cannot be excluded, but the fact that the crystal was mounted in a random orientation would seem to make this event unlikely.

MULTAN (Germain, Main & Woolfson, 1971) was used to determine phases for 298 reflexions with $|E|\geq 1{\cdot}5$, with the best starting set of phases yielding an absolute figure of merit of 1·16. An E map based on these phases revealed 19 peaks, of which 17 could be related to a molecule of the anticipated geometry. The two remaining peaks were distinguished by the fact that they participated in every interatomic distance and angle which was out of the range of reasonable values, hence they were considered spurious. The positions of the 17 atoms from the E map were refined by full-matrix least-squares calculations, and the missing non-hydrogen atom [C(63)] was found from a difference map. Hydrogen atoms were located from a subsequent difference map and varied in the final cycles of the refinement. Five of the largest observed structure amplitudes were found to have

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$|F_c|$ much greater than $|F_o|$, and were assumed to be affected by secondary extinction. These reflexions were removed from the later cycles of refinement. The final R values were 0·044 (unit weights) and 0·045 (weighted, $w=1/\{1+[(|F_o|-20)/10]^2\}^{1/2}$), based on 1456 observed reflexions.* Of the 1080 unobserved reflexions, only 133 had calculated structure amplitudes greater than the threshold value; the latter were included in the least-squares refinement with unit weights. Analytic approximations to the atomic scattering factors were used for C, N and O (Cromer & Mann, 1968), and the values of Stewart, Davidson & Simpson (1965) were used for H. All calculations other than the phase determination were carried out with the X-RAY System (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on a CDC 6400 computer. A diagram of the molecule, numbered in accordance with *The Ring Index* (Patterson, Capell & Walker, 1960; ring system RRI 939), is shown in Table 1, along with the final values of the atomic positional and thermal parameters. Distances, angles, and torsion angles between non-hydrogen atoms are given in Table 2. Fig. 1 shows a perspective drawing (Johnson, 1965) of the molecule.

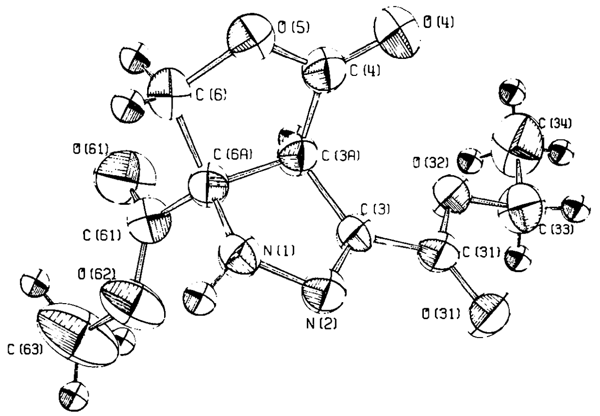
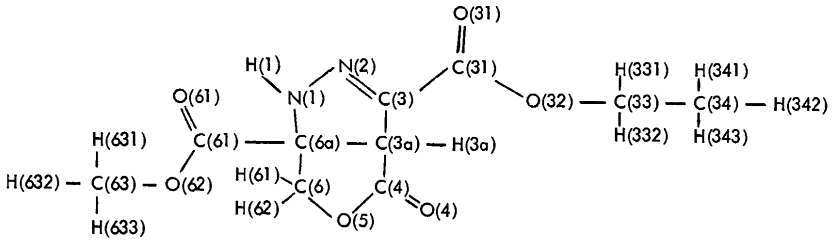


Fig. 1. A perspective view of the molecule.

Table 1. *Numbering scheme, atomic positional* ($\times 10^4$) *and thermal* ($\times 10^3$) *parameters*

$T=\exp[-2\pi^2(h^2a^{*2}U_{11}+\ldots+2klb^*c^*U_{23}+\ldots]$



	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	7142 (1)	4970 (2)	5688 (2)	36 (1)	65 (1)	41 (1)	8 (1)	4 (1)	2 (1)
N(2)	7043 (1)	5128 (2)	7203 (2)	39 (1)	62 (1)	43 (1)	4 (1)	−1 (1)	2 (1)
C(3)	6446 (1)	5462 (2)	7385 (3)	33 (1)	59 (2)	37 (1)	4 (1)	3 (1)	1 (1)
C(3a)	6081 (1)	5536 (2)	5908 (3)	37 (1)	54 (2)	38 (1)	5 (1)	−1 (1)	3 (1)
C(4)	5683 (1)	4622 (2)	5586 (3)	42 (1)	68 (2)	44 (1)	−2 (1)	−3 (1)	4 (1)
O(4)	5261 (1)	4256 (2)	6356 (2)	54 (1)	91 (2)	60 (1)	−18 (1)	8 (1)	8 (1)
O(5)	5879 (1)	4227 (1)	4268 (2)	55 (1)	66 (1)	48 (1)	−12 (1)	3 (1)	−7 (1)
C(6)	6359 (1)	4837 (2)	3520 (3)	52 (1)	62 (2)	43 (1)	−5 (1)	7 (1)	0 (1)
C(6a)	6650 (1)	5470 (2)	4769 (3)	41 (1)	53 (2)	40 (1)	2 (1)	2 (1)	5 (1)
C(31)	6191 (1)	5676 (2)	8896 (3)	37 (1)	69 (2)	44 (1)	3 (1)	0 (1)	3 (1)
O(31)	6486 (1)	5524 (2)	10073 (2)	51 (1)	118 (2)	36 (1)	15 (1)	−3 (1)	4 (1)
O(32)	5589 (1)	6060 (1)	8825 (2)	41 (1)	79 (1)	43 (1)	12 (1)	2 (1)	−2 (1)
C(33)	5289 (2)	6339 (3)	10263 (4)	60 (2)	94 (3)	56 (2)	9 (2)	14 (2)	−14 (2)
C(34)	4629 (2)	6771 (4)	9897 (6)	79 (3)	118 (4)	88 (3)	40 (3)	22 (3)	1 (3)
C(61)	6878 (1)	6450 (2)	4163 (3)	52 (1)	58 (2)	51 (2)	−2 (1)	3 (1)	2 (1)
O(61)	6529 (1)	6965 (2)	3418 (3)	92 (2)	81 (2)	98 (2)	−11 (1)	−24 (1)	39 (2)
O(62)	7486 (1)	6662 (1)	4586 (3)	53 (1)	56 (1)	121 (2)	−10 (1)	−1 (1)	9 (1)
C(63)	7746 (3)	7579 (4)	3997 (11)	84 (3)	70 (3)	218 (8)	−27 (2)	4 (4)	29 (4)

	X/a	Y/b	Z/c	U_{iso}		X/a	Y/b	Z/c	U_{iso}
H(1)	7558 (16)	4940 (21)	5422 (32)	60 (8)	H(341)	4769 (24)	7361 (42)	9343 (67)	156 (23)
H(3a)	5808 (11)	6089 (17)	5774 (27)	34 (6)	H(342)	4352 (26)	6395 (42)	9267 (63)	159 (24)
H(61)	6701 (14)	4437 (20)	3068 (33)	58 (8)	H(343)	4408 (21)	6954 (33)	10854 (50)	120 (14)
H(62)	6114 (14)	5244 (22)	2724 (34)	70 (9)	H(631)	7529 (51)	7598 (69)	2862 (116)	319 (60)
H(331)	5254 (17)	5759 (27)	10964 (44)	97 (13)	H(632)	7544 (32)	8085 (46)	4766 (69)	189 (27)
H(332)	5556 (17)	6825 (26)	10775 (38)	82 (11)	H(633)	8194 (27)	7587 (39)	4429 (57)	149 (19)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31095 (22 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances, angles and torsion angles*

(*a*) Interatomic distances (Å)

N(1)—N(2)	1·371 (3)	C(6)—C(6a)	1·526 (4)
N(1)—C(6a)	1·455 (3)	C(6a)–C(61)	1·528 (4)
N(2)—C(3)	1·298 (3)	C(31)–O(31)	1·215 (3)
C(3)—C(3a)	1·500 (3)	C(31)–O(32)	1·325 (3)
C(3)—C(31)	1·461 (4)	O(32)–C(33)	1·458 (4)
C(3a)–C(4)	1·524 (4)	C(33)–C(34)	1·492 (6)
C(3a)–C(6a)	1·526 (3)	C(61)–O(61)	1·197 (4)
C(4)—O(4)	1·200 (3)	C(61)–O(62)	1·313 (4)
C(4)—O(5)	1·346 (3)	O(62)–C(63)	1·468 (6)
O(5)—C(6)	1·443 (4)		

(*b*) Interatomic angles (°)

C(6a)–N(1)—N(2)	111·7 (2)	C(6)—C(6a)–C(3a)	102·9 (2)
N(1)—N(2)—C(3)	108·2 (2)	C(6)—C(6a)–C(61)	111·8 (2)
N(2)—C(3)—C(3a)	111·7 (2)	N(1)—C(6a)–C(3a)	99·9 (2)
N(2)—C(3)—C(31)	120·7 (2)	N(1)—C(6a)–C(61)	114·4 (2)
C(3a)–C(3)—C(31)	127·5 (2)	C(3a)–C(6a)–C(61)	113·8 (2)
C(3)—C(3a)–C(4)	111·3 (2)	C(3)—C(31)–O(31)	125·1 (2)
C(3)—C(3a)–C(6a)	101·6 (2)	C(3)—C(31)–O(32)	111·1 (2)
C(4)—C(3a)–C(6a)	102·8 (2)	O(31)–C(31)–O(32)	123·8 (2)
C(3a)–C(4)—O(4)	128·1 (3)	C(31)–O(32)–C(33)	116·3 (2)
C(3a)–C(4)—O(5)	110·1 (2)	O(32)–C(33)–C(34)	106·6 (3)
O(4)—C(4)—O(5)	121·8 (3)	C(6a)–C(61)–O(61)	123·0 (3)
C(4)—O(5)—C(6)	110·8 (2)	C(6a)–C(61)–O(62)	112·2 (2)
O(5)—C(6)—C(6a)	105·2 (2)	O(61)–C(61)–O(62)	124·8 (3)
C(6)—C(6a)–N(1)	113·1 (2)	C(61)–O(62)–C(63)	115·1 (3)

(*c*) Selected torsion angles (°)

C(61)–C(6a)–C(3a)–C(3)	−98·8 (2)
C(61)–C(6a)–C(3a)–C(4)	−146·0 (2)
N(1)—C(6a)–C(3a)–C(3)	23·5 (3)
N(1)—C(6a)–C(3a)–C(4)	−91·8 (2)
C(6)—C(6a)–C(3a)–C(3)	140·1 (2)
C(6)—C(6a)–C(3a)–C(4)	24·8 (2)
O(31)–C(31)–C(3)—N(2)	−3·7 (4)
O(31)–C(31)–C(3)—C(3a)	173·1 (3)
O(31)–C(31)–O(32)–C(33)	2·3 (4)
C(31)–O(32)–C(33)–C(34)	178·6 (3)
O(61)–C(61)–C(6a)–N(1)	−178·2 (3)
O(61)–C(61)–C(6a)–C(6)	51·7 (3)
O(61)–C(61)–O(62)–C(63)	−3·8 (5)

Discussion. The bond between N(2) and C(3) is clearly a double bond on the basis of its length. This, together with the hydrogen atom bonded to N(1), established the molecular structure as a 2-pyrazoline. Atoms N(1), N(2), C(3) and C(3a) are coplanar within 0·006 Å, as required by the double bond. In addition, atoms C(3a), C(4), O(5) and C(6) all lie within 0·03 Å of their least-squares plane, with the carbonyl oxygen O(4) 0·07 Å from the plane. The dihedral angle formed by the two planes is 107°. Thus, both five-membered rings are in the envelope conformation, C(6a) being the 'flap' of the envelope in both cases. This appears to be sufficient to absorb the strain of the ring fusion. Any unrelieved stress would be expected to appear in a distortion of bond angles at C(6a). However, the interior angles N(1)–C(6a)–C(3a) and C(6)–C(6a)–C(3a) are not noticeably different from the corresponding angles at C(3a).

All six oxygen atoms, as well as N(2), may be considered as potential acceptors for a hydrogen bond from N(1), which possesses the only H atom available for hydrogen bonding. Although this variety of potential acceptors led us to anticipate the possibilities of bi- or tri-furcated hydrogen bonding, only the carbonyl oxygen of the ethoxycarbonyl group lies close enough to H(1) to allow the inference of a hydrogen bond [O(31)···H(1′)=2·05(3), O(31)···N(1′)=2·897(3) Å, ∠O(31)-H(1′)-N(1′)=163°; $x'=\frac{3}{2}-x, y'=1-y, z'=\frac{1}{2}+z$]. There are no other intermolecular contacts less than 2·6 Å which involve H(1).

Both alkoxycarbonyl groups are found in the expected extended conformation. The ethoxycarbonyl C=O eclipses the neighboring C(3)–N(2) double bond, while the methoxycarbonyl C=O is staggered with respect to the adjacent bonds C(6a)–C(3a) and C(6a)–C(6). Similar s-*cis* conformations have been reported for methyl acrylate, both in the solid (Brown, Gillbro & Nilsson, 1971) and vapour phases (Williams, Owen & Sheridan, 1971), and methyl *m*- and *p*-bromocinnamate (Leiserowitz & Schmidt, 1965). The hydrogen-bond formation by the ethoxycarbonyl C=O group thus appears to be a result, rather than a cause, of the carbonyl orientation.

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