

Table 2. Geometric parameters (Å, °)

C1—C2	1.309 (7)	C9—O3	1.352 (5)
C1—C14	1.448 (7)	C10—C11	1.549 (6)
C2—C3	1.503 (7)	C11—C12	1.508 (6)
C2—C11	1.499 (6)	C11—C16	1.556 (7)
C3—C4	1.514 (7)	C12—C13	1.328 (6)
C3—N	1.475 (7)	C13—C14	1.479 (7)
C4—C5	1.520 (7)	C13—O4	1.371 (6)
C5—C6	1.387 (7)	C14—O1	1.214 (6)
C5—C10	1.408 (7)	C15—C16	1.521 (7)
C6—C7	1.361 (8)	C15—N	1.471 (7)
C7—C8	1.372 (8)	C17—O2	1.403 (7)
C8—C9	1.402 (7)	C18—O4	1.399 (7)
C8—O2	1.363 (6)	C19—N	1.469 (7)
C9—C10	1.387 (6)		
C2—C1—C14	123.0 (5)	C9—C10—C11	122.1 (4)
C1—C2—C3	122.9 (5)	C2—C11—C10	108.7 (4)
C1—C2—C11	123.7 (5)	C2—C11—C12	112.3 (4)
C3—C2—C11	113.3 (4)	C2—C11—C16	105.9 (4)
C2—C3—C4	106.9 (4)	C10—C11—C12	112.8 (4)
C2—C3—N	112.2 (4)	C10—C11—C16	108.4 (4)
C4—C3—N	114.2 (4)	C12—C11—C16	108.4 (4)
C3—C4—C5	114.6 (4)	C11—C12—C13	123.0 (4)
C4—C5—C6	117.1 (5)	C12—C13—C14	121.8 (5)
C4—C5—C10	122.9 (4)	C12—C13—O4	125.8 (5)
C6—C5—C10	120.0 (5)	C14—C13—O4	112.4 (4)
C5—C6—C7	121.2 (5)	C1—C14—C13	115.7 (5)
C6—C7—C8	119.3 (5)	C1—C14—O1	122.8 (5)
C7—C8—C9	121.1 (5)	C13—C14—O1	121.5 (5)
C7—C8—O2	124.6 (5)	C16—C15—N	114.2 (4)
C9—C8—O2	114.3 (4)	C11—C16—C15	110.7 (4)
C8—C9—C10	119.6 (4)	C3—N—C15	112.3 (4)
C8—C9—O3	119.2 (4)	C3—N—C19	109.8 (4)
C10—C9—O3	121.2 (4)	C15—N—C19	110.9 (4)
C5—C10—C9	118.4 (4)	C8—O2—C17	116.8 (4)
C5—C10—C11	119.3 (4)	C13—O4—C18	115.4 (4)

Data were corrected for Lorentz and polarization factors. A value for  $R_{\text{int}}$  is missing since a unique data set was collected. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985) and refined using *SHELX76* (Sheldrick, 1976). The positions of H atoms were generated from assumed geometry except that of H3' which was calculated using the program *MMX* (Allinger, Schäfer, Siam, Klimkowski & van Alsenoy, 1985) and refined isotropically. The positions of H atoms in CH<sub>3</sub> groups were checked on a  $\Delta\rho$  map. Non-H atoms were refined anisotropically. Several weighting schemes were tested and the best results were obtained with the unit weight. The overall isotropic temperature factor for H atoms was  $U_1 = 0.0575$  (50) Å<sup>2</sup> and for the methyl H atoms  $U_2 = 0.0868$  (73) Å<sup>2</sup>. Software used to prepare material for publication: *CSU* (Vicković, 1988). All calculations were carried out on a PC/AT computer.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55763 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1013]

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## 3-[1-(Ethylamino)ethylidene]-6-methyl-3H-pyran-2,4-dione

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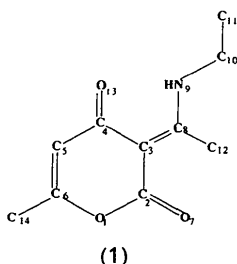
## Abstract

The structural results clearly indicate that 3-[1-(ethylamino)ethylidene]-6-methyl-3H-pyran-2,4-dione exists as a keto-enamine tautomer in the solid state. The H atom bonded to N(9) refines with a normal temperature factor and the bond distance of the keto group [C(4)—O(13)] of 1.263 (1) Å is elongated due to resonance. This resonance is also indicated by an averaging of the single bonds [C(2)—C(3), C(3)—C(4), C(4)—C(5) and C(8)—N(9)] and double bonds [C(3)—C(8) and C(4)—O(13)] in the crystal structure and by the fact that not only is the pyran ring planar [r.m.s. deviation 0.0212 (9) Å] but also there is

planarity for the whole molecule [r.m.s. deviation 0.074 (1) Å]. A strong intramolecular hydrogen bond is found between the 4-oxo group and the amine H atom.

### Comment

The title compound (1) was obtained as a by-product in the synthesis of benzyl *N*-ethyl-2,6-dimethyl-4-oxo-1*H*-pyridin-3-carboxylate from reaction of benzyl 2,6-dimethyl-4-oxo-4*H*-pyran-3-carboxylate with ethylamine (Dobbin, Hider, Venkatramani, Siripitayananon & van der Helm, 1992). Analogues of (1) are known commonly as Schiff bases of dehydroacetic acid (3-acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one), and are of interest as chelating agents (Rama Rao, Venkateswar Rao, Venkata Reddy & Ganorkar, 1987; Liu, Rettig & Orvig, 1991).



An *ORTEP* plot (Johnson, 1976) of the molecule (1) with numbering scheme is presented in Fig. 1. Final fractional coordinates and isotropic thermal parameters for non-H atoms are given in Table 1, while bond distances and angles are listed in Table 2. Crystallographic data for the *N*-phenyl analogue of (1) have previously been published (Zanotti, Filira & Del Pra, 1978), and in general the two structures compare well.

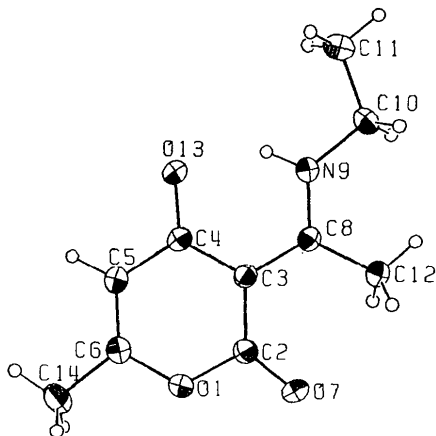


Fig. 1. An *ORTEP* view of the structure of compound (1).

The tautomerism of general *N*-aklyl/aryl analogues of (1) is illustrated in Fig. 2. Comprehensive NMR studies (Filira, Acampora, Giormani, Rothstein & D'Angeli, 1977; Tan, Ang, Jayachandran, Jones & Begg, 1982) have demonstrated the keto-enamine form (*a*) to be dominant over the enol-imine form (*b*) in  $\text{CDCl}_3$  solution. The structural results for (1) support these findings, only a low residual peak ( $0.14 \text{ e } \text{\AA}^{-3}$ ) close to O(13) being indicative of tautomer (*b*). The distances for C(2)—C(3), C(3)—C(4), C(4)—C(5) and C(8)—N(9) are clearly shorter than normal single bonds, while the distances for C(3)—C(8) and C(4)—O(13) are longer than normal double bonds. Also, the C(6)—O(1) and C(2)—O(1) distances are significantly different, and only the C(2)—O(7) distance is representative of a pure double bond. The above observations suggest resonance within the ring system in conjugation with the substituent groups at C(3) and C(4). This hypothesis is reinforced by the planarity of the molecule, which has an r.m.s. deviation of 0.074 Å for all non-H atoms.

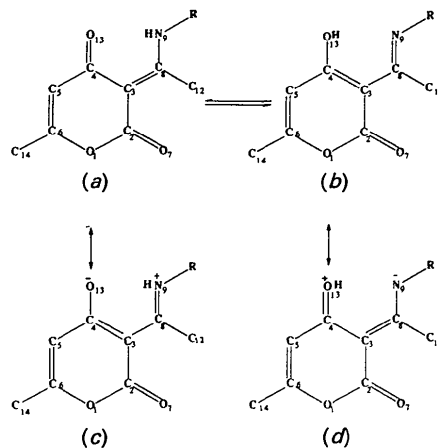
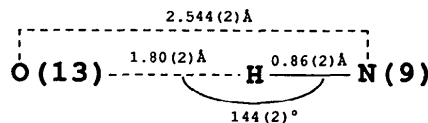


Fig. 2. Tautomerism equilibrium for compound (1).

An important feature of the molecule (1) is the strong intramolecular hydrogen bond formed between the 4-oxo group and the amine H atom.



Although it has been suggested that the stronger  $\text{NH}\cdots\text{O}$  bond relative to  $\text{O}\cdots\text{HO}$  is responsible for the predominance of the keto-enamine tautomer in general aromatic  $\alpha,\beta$ -unsaturated- $\beta$ -ketoamines (Brown & Nonhebel, 1968), a more likely explanation can be obtained from a consideration of

canonical forms (Fig. 2). In mesomer (c) a positive charge resides on N(9) and negative charge on O(13), while in mesomer (d) the situation is reversed. Clearly, the respective electronegativities of nitrogen and oxygen favour the charge distribution present in (c), and hence the stabilization effects of this mesomer on tautomer (a) are of greater importance. The significance of canonical form (c) is shown by the observed planarity of the three bonds around N(9): the sum of the three bond angles is  $360.0^\circ$ .

## Experimental

### Crystal data

$C_{10}H_{13}NO_3$

$M_r = 195.11$

Monoclinic

$P2_1/c$

$a = 5.0846$  (2) Å

$b = 27.374$  (1) Å

$c = 7.4008$  (3) Å

$\beta = 109.528$  (3) $^\circ$

$V = 970.8$  (8) Å<sup>3</sup>

$Z = 4$

$D_x = 1.34$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation

$\lambda = 1.54178$  Å

Cell parameters from 48 reflections

$\theta = 23-40^\circ$

$\mu = 0.73$  mm<sup>-1</sup>

$T = 138$  (2) K

Block

$0.50 \times 0.30 \times 0.20$  mm

Colourless

### Data collection

CAD-4 diffractometer

$\theta/2\theta$  scans

Absorption correction: none

2001 measured reflections

2001 independent reflections

1862 observed reflections

$[I \geq 2\sigma(I)]$

$\theta_{\max} = 75.0^\circ$

$h = 0 \rightarrow 6$

$k = 0 \rightarrow 34$

$l = -9 \rightarrow 9$

3 standard reflections

frequency: 120 min

intensity variation: 1.7%

### Refinement

Refinement on  $F$

Final  $R = 0.039$

$wR = 0.059$

$S = 2.60$

1862 reflections

179 parameters

All H-atom parameters refined

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.029$

$\Delta\rho_{\max} = 0.17$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.32$  e Å<sup>-3</sup>

Atomic scattering factors from *SHELXS86*

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
O(1)	0.0818 (2)	0.38372 (3)	0.7257 (1)	0.0267 (3)
C(2)	-0.1120 (2)	0.34864 (4)	0.6272 (1)	0.0240 (4)
C(3)	-0.3749 (2)	0.36544 (4)	0.4971 (1)	0.0213 (4)
C(4)	-0.4238 (2)	0.41726 (4)	0.4652 (2)	0.0245 (4)
C(5)	-0.2116 (3)	0.44994 (4)	0.5809 (2)	0.0277 (4)
C(6)	0.0262 (3)	0.43274 (4)	0.7054 (2)	0.0256 (4)
O(7)	-0.0304 (2)	0.30678 (3)	0.6643 (1)	0.0352 (3)
C(8)	-0.5871 (2)	0.33092 (4)	0.3978 (1)	0.0215 (4)

N(9)	-0.8162 (2)	0.34749 (4)	0.2704 (1)	0.0246 (3)
C(10)	-1.0550 (3)	0.31907 (5)	0.1500 (2)	0.0294 (4)
C(11)	-1.2832 (3)	0.35355 (5)	0.0377 (2)	0.0307 (4)
C(12)	-0.5596 (3)	0.27711 (4)	0.4351 (2)	0.0284 (4)
O(13)	-0.6419 (2)	0.43477 (3)	0.3445 (1)	0.0333 (3)
C(14)	0.2566 (3)	0.46229 (5)	0.8366 (2)	0.0355 (5)

Table 2. Geometric parameters (Å, °)

O(1)—C(2)	1.394 (1)	C(4)—O(13)	1.263 (1)
O(1)—C(6)	1.369 (1)	C(5)—C(6)	1.337 (2)
C(2)—C(3)	1.438 (2)	C(6)—C(14)	1.486 (2)
C(2)—O(7)	1.218 (1)	C(8)—N(9)	1.311 (1)
C(3)—C(4)	1.446 (2)	C(8)—C(12)	1.497 (2)
C(3)—C(8)	1.438 (2)	N(9)—C(10)	1.467 (2)
C(4)—C(5)	1.442 (2)	C(10)—C(11)	1.511 (2)
O(1)—C(2)—C(3)	117.80 (9)	C(3)—C(8)—N(9)	118.4 (1)
O(1)—C(2)—O(7)	113.7 (1)	C(3)—C(8)—C(12)	123.0 (1)
O(1)—C(6)—C(5)	121.8 (1)	C(4)—C(3)—C(8)	120.2 (1)
O(1)—C(6)—C(14)	111.9 (1)	C(4)—C(5)—C(6)	121.0 (1)
C(2)—O(1)—C(6)	122.26 (9)	C(5)—C(4)—O(13)	119.4 (1)
C(2)—C(3)—C(4)	119.6 (1)	C(5)—C(6)—C(14)	126.3 (1)
C(2)—C(3)—C(8)	120.2 (1)	C(8)—N(9)—C(10)	127.6 (1)
C(3)—C(2)—O(7)	128.5 (1)	N(9)—C(8)—C(12)	118.6 (1)
C(3)—C(4)—C(5)	117.3 (1)	N(9)—C(10)—C(11)	109.3 (1)
C(3)—C(4)—O(13)	123.4 (1)		

The title compound was crystallized from an ethyl acetate solution equilibrated with heptane at 277 K. Data were collected at 138 (2) K and corrected for Lorentz and polarization effects, but no absorption correction was performed. The structure was determined by direct methods using *SHELXS86* (Sheldrick, 1986) and refined by a full-matrix least-squares routine as in *SHELX76* (Sheldrick, 1976). All H atoms were located isotropically.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55744 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1027]

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