

Ethyl α -Phenylhydrazono-2-furanpropionate

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(Received 5 March 1981; accepted 18 August 1981)

Abstract. $C_{15}H_{16}N_2O_3$, $M_r = 272.14$, orthorhombic, $Pca2_1$, $a = 11.115$ (1), $b = 8.170$ (1), $c = 15.341$ (1) Å, $Z = 4$, $d_m = 1.290$, $d_c = 1.293$ Mg m $^{-3}$, $\mu(Cu K\alpha) = 0.713$ mm $^{-1}$, m.p. = 348 K. The structure was solved by direct methods and refined to an R value of 0.041 for 1033 observed reflections. The structure conforms to the non-hydrogen-bonded α form. The hydrazine moiety is planar with sp^2 hybridization at the N and neighboring atoms. Intermolecular N—H...O hydrogen bonds link the molecules into chains along a .

Introduction. The title compound is an intermediate for the synthesis of indole and pyrazole derivatives which have antitubercular activity (Ambekar & Siddappa, 1965). The compound belongs to the general family of ethyl pyruvate phenylhydrazones which have different forms due to hydrogen bonding (Fig. 1a and b). The compound is synthesized *via* a Japp–Klingemann reaction (Holla, 1979).

The compound in powder form was obtained from S. Y. Ambekar, University of Mysore, Mysore, India. Brown crystals, stable in air and in the X-ray beam, were grown from a benzene solution. The preliminary data for the compound were collected with a Weissenberg camera using Cu $K\alpha$ radiation. The compound crystallizes in the orthorhombic system. The systematic absences, $h0l$, $h = 2n + 1$; $0kl$, $l = 2n + 1$, indicate the non-centrosymmetric space group $Pca2_1$ with $Z = 4$ since the molecule has no mirror or center of symmetry. The density was measured by flotation using bromoform and kerosene. The lattice parameters were refined using 54 high-angle reflections from a crystal

mounted on the NRC PDP-8e controlled four-circle diffractometer.

The intensity data were collected using the θ – 2θ scan technique and profile analysis (Grant & Gabe, 1978). One unique set was collected to $2\theta_{max} = 100^\circ$ with graphite-monochromatized Cu $K\alpha$ [$\lambda(K\alpha_1) = 1.5406$ Å] radiation giving 1088 valid reflections of which 1033 were considered significant at the $I_{net} > 2\sigma(I_{net})$ level. 155 systematic absences were also measured of which nine were considered significant at the same level.

The structure was solved using the general direct-method program in *SHELX 76* (Sheldrick, 1976) and independently using *MULTAN* (Germain, Main & Woolfson, 1971). Non-H atoms were located from the E map and the subsequent difference Fourier synthesis. Successive block-diagonal least-squares refinement cycles using anisotropic thermal parameters reduced the R value to 0.07. At this stage the positions of H atoms were fixed from geometric considerations and difference Fourier synthesis, and they were assigned isotropic temperature factors corresponding to the heavy atom to which they are attached. Positional and isotropic thermal parameters of the H atoms were refined. Final refinement gave an R value of 0.041 for 1033 observed reflections, 0.042 including unobserved reflections. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$ and $\sigma^2(F)$ were derived from counting statistics. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Final positional parameters and B_{eq} values are given in Table 1. Computations in the initial stages of refinement were performed with *SHELX 76* (Sheldrick, 1976) and the IISc crystallographic programs (Shiono & Reddy, 1968) and in the final stages with the NRC PDP-8e package (Larson & Gabe, 1978).*

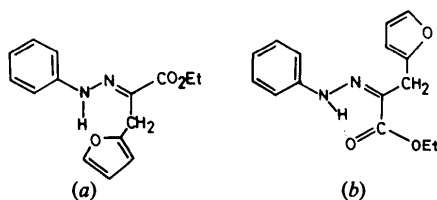


Fig. 1. (a) Non-hydrogen-bonded (α form) and (b) hydrogen-bonded (β form) molecules.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36246 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

	x	y	z	B_{eq}^*
O(1)	0.99689 (22)	0.6742 (3)	0.46119 (18)	5.54 (13)
O(2)	1.12801 (19)	0.7996 (3)	0.37269 (16)	4.88 (12)
O(3)	0.68287 (18)	0.9308 (3)	0.55747 (18)	5.69 (14)
N(1)	0.96780 (21)	1.0445 (3)	0.35461 (18)	3.90 (14)
N(2)	0.89072 (22)	1.1671 (3)	0.34139 (18)	4.20 (14)
C(1)	1.0304 (3)	0.7933 (4)	0.40692 (25)	4.32 (18)
C(2)	0.9340 (3)	0.9149 (4)	0.39603 (24)	3.71 (16)
C(3)	0.8097 (3)	0.8841 (4)	0.43097 (24)	4.07 (17)
C(4)	0.7935 (3)	0.9520 (4)	0.52094 (24)	3.83 (17)
C(5)	0.8636 (3)	1.0304 (5)	0.5750 (3)	5.54 (21)
C(6)	0.7970 (3)	1.0583 (4)	0.6536 (3)	5.30 (21)
C(7)	0.6908 (3)	0.9976 (5)	0.6394 (3)	5.64 (21)
C(8)	1.0785 (4)	0.5296 (5)	0.4707 (3)	6.24 (23)
C(9)	1.1806 (4)	0.5736 (5)	0.5268 (3)	7.2 (3)
C(10)	0.9263 (3)	1.3053 (4)	0.2948 (3)	3.95 (16)
C(11)	1.0336 (3)	1.3091 (5)	0.2494 (3)	5.24 (20)
C(12)	1.0633 (3)	1.4514 (5)	0.2038 (3)	6.49 (25)
C(13)	0.9892 (4)	1.5865 (5)	0.2049 (3)	6.18 (24)
C(14)	0.8828 (4)	1.5792 (5)	0.24931 (25)	5.49 (22)
C(15)	0.8509 (3)	1.4410 (4)	0.2945 (3)	4.75 (19)
H(N2)	0.8227 (21)	1.163 (3)	0.3674 (17)	3.7 (7)
H(3A)	0.754 (3)	0.928 (3)	0.3973 (18)	3.0 (6)
H(3B)	0.8002 (22)	0.771 (3)	0.4343 (18)	3.3 (7)
H(5)	0.943 (3)	1.060 (4)	0.5689 (25)	8.5 (11)
H(6)	0.820 (3)	1.114 (4)	0.7043 (20)	5.6 (8)
H(7)	0.610 (3)	0.997 (3)	0.6651 (22)	6.2 (8)
H(8A)	1.105 (3)	0.483 (4)	0.4108 (20)	6.1 (9)
H(8B)	1.0406 (21)	0.418 (3)	0.4981 (17)	3.8 (7)
H(9A)	1.208 (4)	0.441 (5)	0.536 (4)	17.0 (19)
H(9B)	1.131 (3)	0.627 (5)	0.571 (3)	9.2 (11)
H(9C)	1.233 (4)	0.665 (5)	0.505 (3)	11.7 (13)
H(11)	1.0872 (25)	1.210 (4)	0.2490 (19)	6.1 (9)
H(12)	1.125 (3)	1.453 (3)	0.1840 (23)	6.5 (9)
H(13)	1.013 (3)	1.687 (4)	0.166 (3)	7.6 (10)
H(14)	0.829 (3)	1.667 (4)	0.2548 (23)	9.4 (11)
H(15)	0.770 (3)	1.432 (3)	0.3224 (21)	5.9 (9)

* B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoids.

Discussion. The structure conforms to the non-hydrogen-bonded α form. The atomic numbering, bond lengths and angles for non-H atoms are shown in Fig. 2(a) and (b), and a stereoview of the molecule in Fig. 3. The e.s.d.'s for these bonds and angles are in the range 0.003–0.006 \AA and 0.2–0.4°. The C–H bond lengths vary from 0.752 to 1.088 \AA with e.s.d.'s in the range 0.023–0.043 \AA .

The important feature of the structure is that the hydrazine moiety with its neighbors C(2), C(1), O(1) forms an almost planar extended zig-zag chain with bond angles typical of sp^2 hybridization. The bond lengths in the hydrazine moiety differ from those reported earlier by Furberg & Solbaak (1969) in the case of the *p*-bromophenylhydrazone of mannose. In the present structure there is a slight elongation of the C(10)–N(2) bond and shortening of the N(1)–N(2) bond. Similar results have been observed by Hvoslaf & Nordensle (1976) in the case of the *p*-bromophenylhydrazone derivative of monomeric dehydroascorbic

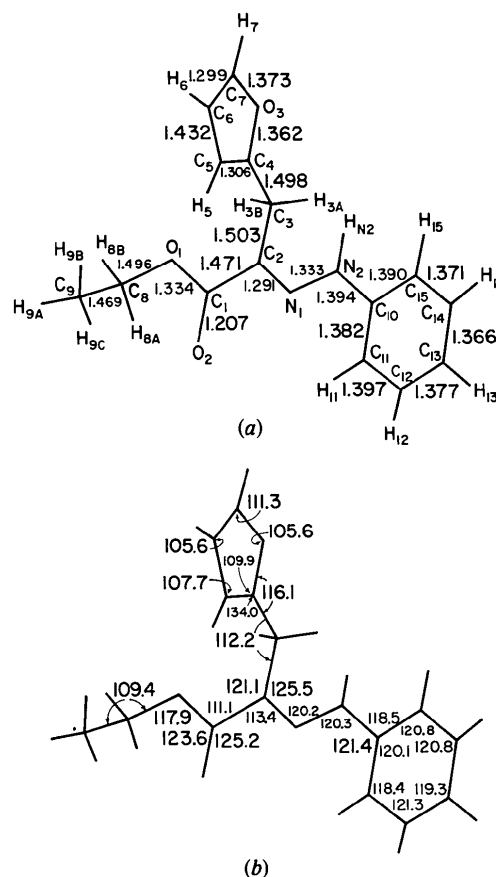


Fig. 2. (a) Atomic numbering and bond distances (\AA). (b) Bond angles ($^\circ$).

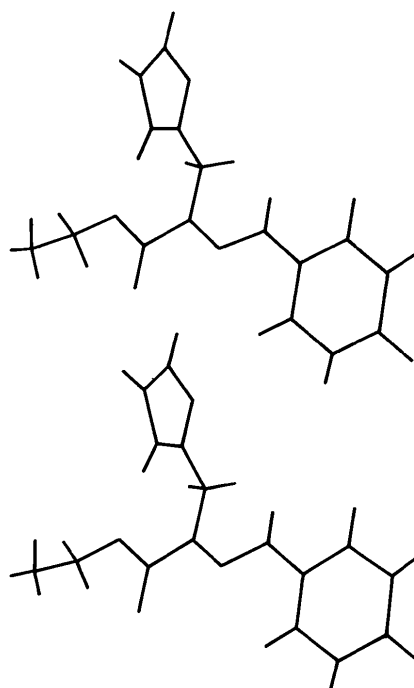


Fig. 3. A stereoview of the molecule.

acid. The apparent change in the bond lengths of the ethyl group might be due to the strong thermal vibrations of C(8) and C(9). The ester moiety is *cis* to the C=O about the C—O bond and the phenylhydrazone group is in the *anti* position to the ethyl group about the N(1)—C(2) bond; the C(10)—N(2)—N(1)—C(2) torsion angle is $-178.4(3)^\circ$.

The bond lengths in the propionate group are normal and agree with the standard values associated with C(sp^2)—C(sp^3) single-bond, C(sp^2)—C(sp^2) single-bond and C(sp^2)—O single-bond distances. The geometry of the benzene and furan rings is normal and they are essentially planar. The dihedral angle between the two planes is $82.4(4)^\circ$.

The molecules are held by hydrogen bonding along a between N(2) and O(2) of the molecule at $\frac{1}{2} + x, \bar{y}, z$ [N(2)···O(2) = 2.971 \AA and N(2)—HN(2)···O(2) = 143°]. All other contacts are of van der Waals type.

Table 2. Intermolecular contacts less than 3.6 \AA

Symmetry code: (i) x, y, z ; (ii) $\bar{x}, \bar{y}, \frac{1}{2} + z$; (iii) $\frac{1}{2} + x, \bar{y}, z$; (iv) $\frac{1}{2} - x, y, \frac{1}{2} + z$; (v) $x, 1 + y, z$.

C(13)—C(9 ⁱⁱ)	3.569 (6)	C(13)—C(1 ^v)	3.559 (6)
C(12)—C(15 ⁱⁱⁱ)	3.596 (5)	C(13)—O(2 ^v)	3.469 (5)
C(15)—O(2 ⁱⁱⁱ)	3.382 (4)	C(14)—C(2 ^v)	3.593 (5)
C(5)—O(3 ⁱⁱⁱ)	3.573 (4)	C(14)—C(1 ^v)	3.405 (5)
C(3)—O(2 ⁱⁱⁱ)	3.399 (4)	C(14)—O(1 ^v)	3.574 (5)
C(4)—O(2 ⁱⁱⁱ)	3.562 (4)	C(15)—O(1 ^v)	3.578 (5)
N(2)—C(7 ^{iv})	3.513 (5)		

Acta Cryst. (1982). **B38**, 694–696

(1 β ,9 β)-1-Methoxypicras-12-en-16-one

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(Received 27 May 1981; accepted 21 August 1981)

Abstract. C₂₁H₃₂O₃, $M_r = 332.484$, monoclinic, $P2_1/n$, $a = 8.522(2)$, $b = 22.773(4)$, $c = 10.190(2) \text{ \AA}$, $\beta = 111.32(2)^\circ$, $U = 1842.4(6) \text{ \AA}^3$, $Z = 4$, $d_m = 1.22$ (by flotation), $d_c = 1.20 \text{ Mg m}^{-3}$, $F(000) = 728$. The structure was solved by direct methods. Full-matrix least-squares refinement converged to $R = 0.056$ for 1713 observed reflections. (1 β ,9 β)-1-Methoxypicras-12-en-16-one has the tetracyclic framework of quassinoids (e.g. quassin) and, with the exception of the

The intermolecular contacts less than 3.6 \AA are given in Table 2.

The authors wish to thank Professor K. N. Kuchela for his encouragement and interest in the work. They thank Professor S. Y. Ambekar for providing the powder sample and University Grants Commission for the financial assistance.

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configuration at C(9), six of the seven chiral centers found in quassin.

Introduction. The synthesis of (1 β ,9 β)-1-hydroxypicras-12-en-16-one and its derivative (1 β ,9 β)-1-methoxypicras-12-en-16-one (1) has been described by Grieco, Vidari, Ferriño & Haltiwanger (1980). Subsequently, Grieco, Ferriño & Vidari (1980) have reported the total synthesis of (\pm)-quassin in which (1)