

The two C(carbonyl)—N bonds are significantly different [1.295 (4) and 1.336 (6) Å]. We ascribe this to the different environments around the two N atoms. Also, there is an asymmetric bend of the carbonyl O towards one of the nitrogens resulting in an N—C(1)—O angle of 126.8 (4)° for one side and 123.2 (2)° for the other. A similar asymmetry has also been reported for the pentakis(2-imidazolidinone)copper(II) perchlorate complex where the corresponding angles are 127.6 (6) and 124.7 (7)° (Majeste & Trefonas, 1974). The remaining C—N distances [1.442 (5) and 1.441 (6) Å] and C—C distance [1.498 (7) Å] are also similar to those reported for the copper(II) complex, where average distances of 1.43 and 1.50 Å, respectively, were reported.

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## Structure of 3-Benzyl-4-hydroxy-5-phenyl-1,2,4-triazole

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**Abstract.** C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>O, *M<sub>r</sub>* = 251.29, monoclinic, C2/*c*, *a* = 20.065 (3), *b* = 5.291 (1), *c* = 24.816 (5) Å, β = 101.83 (1)°, *V* = 2578.6 (1.5) Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.29 Mg m<sup>-3</sup>, λ(Cu Kα) = 1.5418 Å, μ = 0.64 mm<sup>-1</sup>, *F*(000) = 1056, *T* = 300 K, final *wR*(*F*) = 0.030 for 1247 observed reflections. The structure consists of an intermediate form between an *N*-hydroxytriazole and a triazole *N*-oxide. The molecules are connected into chains *via* strong hydrogen bonds between pairs of 4-hydroxy O atoms and 2-nitrogens, respectively. The chains thus formed run along [110] in *z* = 0 and along [110] in *z* = ½.

**Introduction.** The title compound is obtained by the reaction of hydrazides and hydroximates in methanol (Bel Hadj Amor & Baccar, 1988). As illustrated schematically in Fig. 1, a first reaction step leads to *N*<sup>3</sup>-hydroxy-*N*<sup>1</sup>-acylamidrazones which can then react to produce either an oxatriazine *A* or an *N*-hydroxytriazole *B*.

IR and <sup>1</sup>H NMR spectra and elemental analyses confirm the empirical formula of these heterocycles but cannot distinguish between the two isomers *A* and *B*.

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Therefore an X-ray study was undertaken on one compound obtained from this reaction.

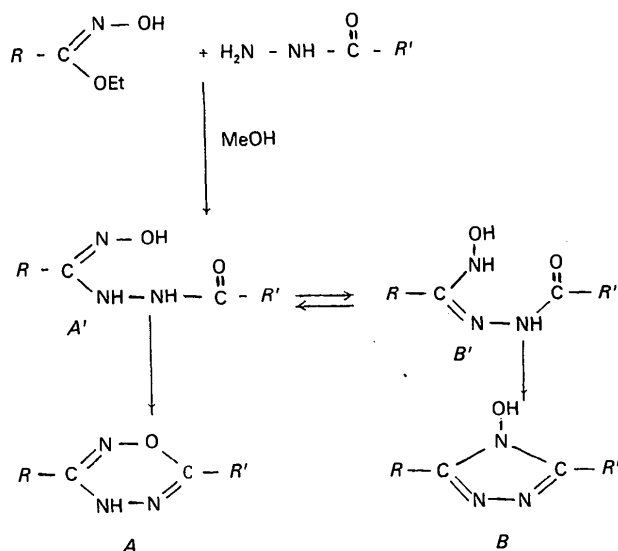


Fig. 1. Mechanism of action of hydrazides on hydroximates.

**Experimental.** Prismatic transparent crystals were grown by slow evaporation from a solution of the material in methanol. A needle of  $0.07 \times 0.04 \times 0.39$  mm was chosen for X-ray diffraction. Data were collected on an AED-2 four-circle diffractometer with graphite-monochromated Cu  $K\alpha$  radiation.

The final cell parameters were determined from the  $2\theta$  values of 36 reflections with  $10.5 < \theta < 31.8^\circ$ . Scan ratio  $\omega/2\theta = 1/1$  for intensity measurements. One hemisphere up to  $\theta = 50^\circ$ ,  $[(\sin\theta)/\lambda]_{\max} = 0.50 \text{ \AA}^{-1}$ , was explored; range of  $hkl$ :  $h: -19 \rightarrow 18$ ,  $k: 0 \rightarrow 5$ ,  $l: \pm 24$ . Three standard reflections measured every 90 min remained stable. A numerical absorption correction resulted in transmission factors ranging from 0.924 to 0.984. 3004 measured reflections after averaging yielded 1331 independent reflections ( $R_{\text{int}} = 0.015$ ). Of these 1247 had  $F > 2\sigma(F)$  and were used for the structure determination and refinement.

The structure was solved with *SHELX84* (Sheldrick, 1985) and refined with *SHELX76* (Sheldrick, 1976) to  $R(F) = 0.043$ ,  $wR = 0.030$  and  $S = 5.0$ . 173 parameters were refined. The weighting scheme was  $w(F) = 3.37/\sigma^2(F)$ ,  $(\Delta/\sigma)_{\max} < 0.002$  in the last cycle of refinement. All H atoms were found in the last Fourier map but during refinement all H atoms except H(N2) and H(O1) were located by geometrical calculation (C—H distance 1.08 Å) and not refined. The isotropic thermal parameters used for the H atoms were approximately 1.1 times the values of the attached atoms. Final difference Fourier map peaks were between  $-0.29$  and  $0.15 \text{ e \AA}^{-3}$ . Scattering factors and anomalous-dispersion coefficients from *International Tables for X-ray Crystallography* (1974). Calculations were performed on a MicroVAX II computer at Stoe & Cie, Darmstadt.

**Discussion.** The atomic coordinates are reported in Table 1, bond lengths and angles in Table 2.\* The molecular structure is shown in Fig. 2 and the packing of the molecules in the unit cell is presented in the projection along the  $b$  axis of Fig. 3.

The geometry of the title compound is that of isomer *B*. According to Fig. 1 this reaction requires a rearrangement of the  $N^3$ -hydroxy- $N^1$ -acylamidrazone *A'* to its tautomeric form *B'* before cyclization.

In this structure the geometry of the triazole ring is very similar to that observed in 3-methyl-5-phenyl-4-phenylamino-1,2,4-triazole (I) (Bois, Philoche-Levisalles & Chihaoui, 1983), 4-amino-3-(2-aminophenyl)-1,2,4-triazole (II) (Stam & van der Plas, 1976) and

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51551 (12 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 with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{1}{3}\pi^2 \sum_i \sum_j U_{ij} a_i a_j a_i^* a_j^*$$

	$x$	$y$	$z$	$B_{\text{eq}}(\text{\AA}^2)$
O(1)	0.4543 (1)	0.1552 (3)	0.4870 (1)	4.12 (12)
N(4)	0.3988 (1)	0.0752 (4)	0.5058 (1)	3.24 (13)
C(3)	0.3541 (1)	-0.1004 (5)	0.4807 (1)	3.60 (17)
N(2)	0.3064 (1)	-0.1189 (4)	0.5097 (1)	4.28 (15)
N(1)	0.3193 (1)	0.0427 (5)	0.5541 (1)	4.33 (15)
C(5)	0.3766 (1)	0.1592 (5)	0.5513 (1)	3.34 (17)
C(10)	0.4106 (1)	0.3431 (5)	0.5917 (1)	3.36 (16)
C(11)	0.4561 (1)	0.5212 (5)	0.5797 (1)	3.79 (17)
C(12)	0.4856 (1)	0.6925 (6)	0.6195 (1)	4.65 (19)
C(13)	0.4703 (1)	0.6885 (6)	0.6712 (1)	5.16 (21)
C(14)	0.4255 (1)	0.5112 (6)	0.6834 (1)	5.71 (22)
C(15)	0.3954 (1)	0.3382 (6)	0.6442 (1)	4.92 (20)
C(2)	0.3587 (1)	-0.2441 (5)	0.4303 (1)	4.12 (18)
C(23)	0.3439 (1)	-0.0860 (5)	0.3783 (1)	3.72 (18)
C(24)	0.3758 (1)	-0.1406 (6)	0.3351 (1)	4.66 (20)
C(25)	0.3609 (2)	0.0000 (7)	0.2867 (1)	5.49 (23)
C(26)	0.3149 (2)	0.1953 (7)	0.2813 (1)	5.66 (24)
C(27)	0.2834 (1)	0.2514 (6)	0.3241 (1)	5.54 (23)
C(28)	0.2973 (1)	0.1118 (6)	0.3720 (1)	4.66 (20)

Table 2. Bond lengths (Å) and angles ( $^\circ$ )

C(3)—N(4)	1.352 (3)	C(25)—C(26)	1.374 (4)
N(4)—C(5)	1.371 (3)	C(26)—C(27)	1.374 (4)
C(5)—N(1)	1.319 (3)	C(27)—C(28)	1.380 (4)
N(1)—N(2)	1.376 (3)	C(28)—C(23)	1.391 (4)
N(2)—C(3)	1.314 (3)	C(10)—C(11)	1.387 (3)
N(4)—O(1)	1.359 (2)	C(11)—C(12)	1.382 (3)
C(3)—C(2)	1.481 (3)	C(12)—C(13)	1.380 (3)
C(2)—C(23)	1.515 (3)	C(13)—C(14)	1.375 (4)
C(5)—C(10)	1.462 (3)	C(14)—C(15)	1.382 (4)
C(23)—C(24)	1.388 (3)	C(15)—C(10)	1.396 (3)
C(24)—C(25)	1.393 (4)		
N(4)—C(3)—N(2)	106.7 (2)	C(23)—C(24)—C(25)	120.3 (3)
C(3)—N(2)—N(1)	110.7 (2)	C(24)—C(25)—C(26)	120.4 (3)
N(2)—N(1)—C(5)	105.8 (2)	C(25)—C(26)—C(27)	119.7 (3)
N(1)—C(5)—N(4)	109.0 (2)	C(26)—C(27)—C(28)	120.4 (3)
C(5)—N(4)—C(3)	107.8 (2)	C(27)—C(28)—C(23)	120.9 (3)
C(3)—N(4)—O(1)	124.7 (2)	C(28)—C(23)—C(24)	118.4 (3)
C(5)—N(4)—O(1)	127.5 (2)	C(28)—C(23)—C(2)	121.4 (2)
N(4)—C(3)—C(2)	126.2 (2)	C(10)—C(11)—C(12)	119.8 (2)
N(2)—C(3)—C(2)	127.1 (2)	C(11)—C(12)—C(13)	120.7 (3)
C(3)—C(2)—C(23)	113.6 (2)	C(12)—C(13)—C(14)	119.7 (3)
N(4)—C(5)—C(10)	126.7 (2)	C(13)—C(14)—C(15)	120.5 (3)
N(1)—C(5)—C(10)	124.3 (2)	C(14)—C(15)—C(10)	119.8 (3)
C(2)—C(23)—C(24)	120.2 (3)	C(15)—C(10)—C(11)	119.5 (2)
C(5)—C(10)—C(11)	122.6 (2)	C(15)—C(10)—C(5)	117.9 (2)

1,2,4-triazole (III) (Goldstein, Ladell & Abowitz, 1969) as shown in Table 3.

The bonds C(3)—N(2) of 1.314 (3) Å and C(5)—N(1) of 1.319 (3) Å can be considered as double bonds but N(4)—C(3) and N(4)—C(5) of 1.352 (3) and 1.371 (3) Å respectively have an intermediate character between a single bond of 1.48 Å (Prusiner & Sundaralingam, 1976) and a double bond of 1.29 Å (Bel Hadj Amor, Kallel, Baccar, Driss & Gilmore, 1987). We therefore conclude that the electronic cloud in the heterocycle is rather delocalized. Torsion and dihedral angles of the triazole ring atoms are very small (Table

4), showing that the ring is essentially planar. N(4) is also coplanar with O(1), C(3) and C(5), as shown by best-plane calculation (Table 4). The phenyl ring linked to C(5) is twisted only  $23^\circ$  out of the heterocycle plane and that linked to C(2) is at an angle of  $92^\circ$  with this plane due to steric hindrance.

The title compound can be described in terms of two tautomeric forms (Fig. 4). Within the crystal an intermediate state between these two forms is realized: one H atom is shared by two O(1) atoms, the other by two N(2) atoms. The existence of this resonance form has already been suggested by Becker, Goermar, Haufe & Timpe (1972) for similar compounds from a UV study.

The shared H atoms have a high mobility. This explains the considerable acidity of *N*-hydroxytriazoles: Becker, Goermar & Timpe (1970) report a value of  $pK_a = 6$  for compounds of this type.

The H atoms which link neighbouring molecules together are at centres of symmetry. They build very short symmetrical hydrogen bonds: O(1)–H(O1)···O(1<sup>i</sup>) = 2.448 and N(2)–H(N2)···N(2<sup>ii</sup>) = 2.616 Å [(i)  $1-x, -y, 1-z$ ; (ii)  $\frac{1}{2}-x, -\frac{1}{2}-y, 1-z$ ]. The resulting chains of molecules extend along  $[1\bar{1}0]$  in  $z = 0$  and along  $[110]$  in  $z = \frac{1}{2}$ .

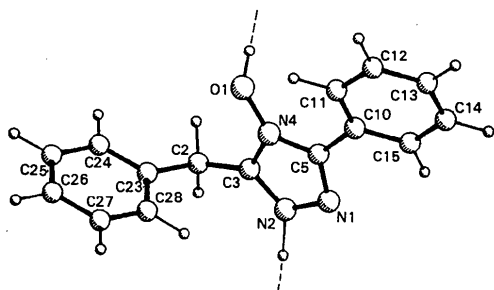


Fig. 2. Molecular structure and atom numbering.

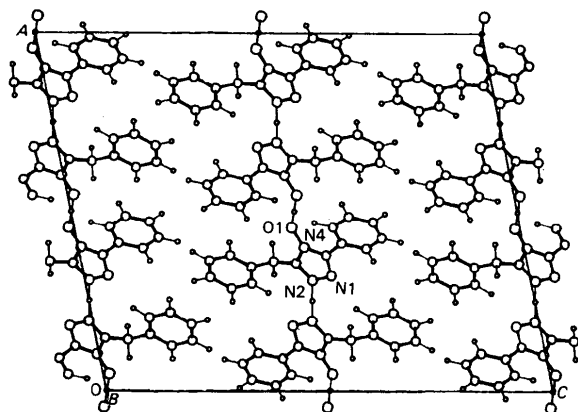


Fig. 3. Projection along the *b* axis showing the packing of the molecules in the unit cell.

Table 3. Comparison of bond lengths (Å) in triazole rings of various compounds

	Present work	Compound (I)	Compound (II)*	Compound (III)
N(1)–N(2)	1.376 (3)	1.39 (1)	1.390	1.359 (14)
N(2)–C(3)	1.314 (3)	1.31 (1)	1.304	1.323 (14)
C(3)–N(4)	1.352 (3)	1.36 (1)	1.358	1.359 (14)
N(4)–C(5)	1.371 (3)	1.38 (1)	1.370	1.324 (14)
C(5)–N(1)	1.319 (3)	1.32 (1)	1.311	1.331 (14)

\* Standard deviations were not reported by the authors.

Table 4. Torsion and dihedral angles ( $^\circ$ ) and best-plane calculation involving the triazole ring atoms

(a) Torsion angles (e.s.d.'s  $\approx 0.3^\circ$ )

N(4)–C(3)–N(2)–N(1)	0.0
C(3)–N(2)–N(1)–C(5)	0.0
N(1)–C(5)–N(4)–C(3)	–0.9

(b) Dihedral angles (e.s.d.'s  $\approx 0.5^\circ$ )

[N(4), N(2), N(1)]–[C(3), N(2), C(5)]	0.29
[N(2), N(1), C(5)]–[N(1), C(5), N(4)]	0.7

(c) Best-plane calculation for N(4), C(3), N(2), N(1), C(5) and O(1)  
Deviations of the atoms from the mean plane (Å)

N(4)	–0.014 (5)	N(1)	0.012 (5)
C(3)	–0.011 (5)	C(5)	–0.013 (5)
N(2)	0.009 (5)	O(1)	0.017 (5)

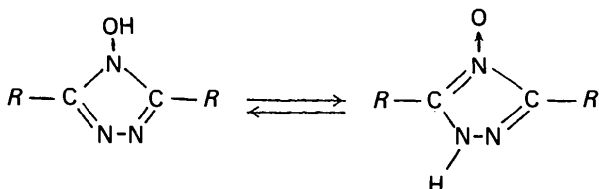


Fig. 4. The two tautomeric forms of the title compound.

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## Structure of (Phenyl)bis(4-hydroxybenzo-2H-pyran-2-one-3-yl)methane\*

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**Abstract.** A derivative of dicoumarol, C<sub>25</sub>H<sub>16</sub>O<sub>6</sub>, *M<sub>r</sub>* = 412.41, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 7.959 (2), *b* = 12.865 (3), *c* = 18.606 (6) Å, *V* = 1905.3 (22) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.44 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 0.965 cm<sup>-1</sup>, *F*(000) = 856, *T* = 293 K, final *R* = 0.042 for 2031 observations. The 4-hydroxycoumarins are intramolecularly hydrogen bonded between hydroxyls and carbonyls, O...O separations are 2.624 (3) and 2.718 (3) Å, a scheme which imparts a dissymmetry to the otherwise achiral molecule and underlies packing in a polar space group.

**Introduction.** During screening of a variety of coumarin compounds capable of H bonding, the title compound, which was not inherently chiral, was found to crystallize in a polar space group and have an unusually high density. Conveniently named phenyldicoumarol, in our hands the molecule was identified as a byproduct of the condensation of 4-hydroxycoumarin with 4-phenyl-3-buten-2-one (Bush & Traeger, 1983) although the original authors do not mention having isolated this molecule.

**Experimental.** Colorless blocks from 2-propanone, specimen: 0.51 × 0.38 × 0.54 mm, CAD-4 diffractometer, cell from 25 accurately centered higher-order intensities. Data measured to 2θ = 60° (*h*: 0–10, *k*: 0–18, *l*: 0–21), 2986 unique after elimination of systematic absences (*h*00, *h* ≠ 2*n*; 0*k*0, *k* ≠ 2*n*; 00*l*, *l* ≠ 2*n*), were corrected for coincidence, polarization; no decay noted, no absorption correction. An extinction

correction was applied later and refined, *g* = 3.2 (11) × 10<sup>-7</sup> (Zachariasen, 1963). Structure discovered with *MULTAN80* (Main, Fiske, Hull, Lesinger, Germain, Declercq & Woolfson, 1980). Non-H atom positions were refined with their *U*<sub>iso</sub>'s by full-matrix least squares minimizing ∑*w*(|*F<sub>o</sub>*| - |*F<sub>c</sub>*|)<sup>2</sup>, then with their *U*<sub>ij</sub>'s. Hydroxy H's located in difference Fourier map and positions refined with *B*<sub>iso</sub>'s, other H's fixed at 1.0 Å from their adjacent atoms with *B*'s fixed at 1.3 *B*<sub>eq</sub> for the attached carbon. Scattering factors were from *International Tables for X-ray Crystallography* (1974) except for H (Stewart, Davidson & Simpson, 1965). Final agreement factors: *R* = 0.042, *wR* = 0.053, GOF = 1.401 for the 2031 intensities with *I* > 2.5σ<sub>*I*</sub>. Least-squares weights were taken as 4*F<sub>o</sub>*<sup>2</sup>/σ<sup>2</sup>(*I*) where σ<sup>2</sup>(*I*) = σ<sup>2</sup>(*I*)<sub>*c*</sub> + 0.05(*I*)<sub>*c*</sub><sup>2</sup>; and the differences in structure factors were minimized for the 289 variables; maximum final |Δρ| excursions were less than +0.25 and -0.19 e Å<sup>-3</sup>; maximum Δ/σ in the final cycle 0.01. All programs were from the locally modified *SDP* package (Frenz, 1987). Positions and *B*<sub>eq</sub>'s for the non-H atoms in phenyldicoumarol are given in Table 1.†

**Discussion.** A plot (Johnson, 1976) of the molecular structure of phenyldicoumarol is given in Fig. 1. The structure is closely related to those of dicoumarol

† Lists of H-atom positions, anisotropic vibrational amplitudes and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51613 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* IUPAC name: 3,3'-benzylidenedi-4-hydroxycoumarin.