

2-Acetyl-4(3H)-quinazolinone, C₁₀H₈N₂O₂

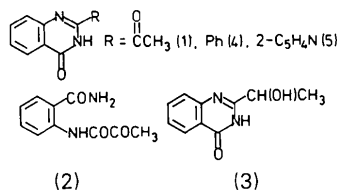
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Abstract. $M_r = 188.06$, triclinic, $P\bar{1}$, $a = 8.44$ (2), $b = 10.19$ (2), $c = 5.25$ (2) Å, $\alpha = 102.4$ (1), $\beta = 90.0$ (1), $\gamma = 101.2$ (1)°, $U = 431.3$ Å³, $Z = 2$, $D_x = 1.49$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 0.873$ mm⁻¹, $F(000) = 196$, $T = ca$ 293 K. Final $R = 0.044$ for 822 unique reflexions. The title compound was obtained from extracts of the fungus *Alternaria citri* and its structure established by diffraction measurements.

Introduction. The title compound (1) (m.p. 478–479 K) was isolated from the liquor extract of the fungus *Alternaria citri* via column chromatography (SiO₂, CHCl₃/MeOH 95:5) and further purified by preparative, thin-layer chromatography. Structure determination by X-ray measurements was undertaken because spectroscopic methods proved inadequate for the task: in particular, it was not possible to establish the positions of the N atoms or the substitution pattern reliably. Subsequent to the structure determination, it emerged that the compound had previously been isolated from the fungus *Fusarium culmorum* (Blight & Grove, 1974). The biosynthesis presumably involves cyclization of the pyruvoylaminobenzamide (2) arising from anthranilic acid and pyruvate. The related compound chrysogine (3) (Suter & Turner, 1967) has been obtained from the *Alternaria citri* mycelium (Easton & Johnstone, unpublished results).



Experimental. Crystals suitable for X-ray analysis obtained by slow evaporation of the solvent from a solution in ethyl ethanoate, reflexion intensities measured by the SERC Microdensitometer Service, Daresbury Laboratory, from Weissenberg photographs of layers $h0l$ to $h8l$ for a crystal of dimensions $0.3 \times 0.2 \times 0.2$ mm, equivalents merged ($R_{\text{int}} = 0.036$) yielding 822 unique data which were used for structure solution and refinement, cell dimensions determined from precession photographs and interlayer

scale factors, initially, from exposure times; structure solved (with difficulty) in space group $P\bar{1}$ by direct methods (*MULTAN* 80, Main *et al.*, 1980) the common method of locating reasonable structural fragments, but misplaced in the cell, being repeatedly encountered; success finally achieved by insertion of one such fragment as a group of known orientation, but random position, into the program and manipulation of the parity-group scale factors; structure refined satisfactorily on F values by full-matrix least squares (XRAY system, Stewart, Kruger, Ammon, Dickinson & Hall, 1972), ratio of least-squares shift to error in final refinement cycle = 0.0001 (maximum) and 0.00003 (average); at an intermediate stage positions of H atoms located from a difference map and subsequently refined with isotropic temperature factors, all other atoms refined with anisotropic thermal parameters; in final stages interlayer scale factors refined individually and an extinction correction ($g = 7.04 \times 10^{-3}$) applied, maximum and minimum peak heights in final difference map were 0.15 and -0.16 e respectively.

Discussion. Positional and mean thermal parameters are given in Table 1.* The atomic-numbering system, molecular and crystal structures are depicted in Figs. 1 and 2 and the bond lengths, bond angles and torsion angles (not involving H) are listed in Fig. 3.

A search of the Cambridge Crystallographic Database reveals (1) to be the simplest example of the quinazolinone system for which accurate geometric data are available. Other simple, substituted derivatives whose structures are known reliably include the 2-phenyl analogue (4) (Holm, Christophersen, Ottersen, Hope & Christensen, 1977) and the 2-pyridyl analogue (in chelation with Cu^{II}) (5) (Battaglia, Corradi, Nardelli, Pelizzi & Tani, 1976): the structure found for (1) is closely comparable with the structures of (4) and (5). In particular, the ten-membered, bicyclic ring system is close to planarity, maximum deviations

* Lists of structure factors and anisotropic thermal parameters (for C, N and O atoms) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38266 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

from the least-squares plane through the ten atoms occurring for C(2) (0.022 Å) and N(2) (−0.031 Å), with slightly smaller values for N(1) (0.019 Å) and C(8) (−0.021 Å).

There is considerable bond-length variation around the heterocyclic ring redolent of substantial bond fixation. However, a close comparison of the structures of (1), (4) and (5) reveals small (but significant) trends in bond-length variation which presumably reflect differing degrees of π -electron delocalization. Thus, the 2-substituent is in extended conjugation with the

Table 1. Atomic coordinates and mean isotropic temperature factors ($\times 10^4$; $\times 10^3$ for H) with e.s.d.'s in parentheses

	x	y	z	$\bar{U}(\text{\AA}^2)$
N(1)	6793 (3)	4835 (3)	1334 (6)	330 (17)
N(2)	8463 (3)	4735 (3)	−2239 (5)	305 (16)
O(1)	7532 (3)	1995 (2)	−3164 (5)	514 (17)
O(2)	10047 (3)	6608 (2)	−3241 (5)	401 (15)
C(2)	7430 (4)	4149 (3)	−622 (6)	295 (20)
C(4)	9043 (4)	6120 (3)	−1880 (7)	290 (19)
C(5)	8801 (4)	8356 (3)	904 (8)	385 (22)
C(6)	8143 (5)	9112 (3)	2996 (8)	431 (23)
C(7)	7031 (5)	8435 (4)	4444 (7)	453 (25)
C(8)	6579 (4)	7050 (3)	3897 (7)	386 (22)
C(9)	7253 (4)	6254 (3)	1797 (6)	308 (21)
C(10)	8341 (4)	6934 (3)	321 (6)	304 (20)
C(11)	7042 (4)	2623 (3)	−1209 (7)	342 (20)
C(12)	6080 (5)	1930 (4)	661 (8)	468 (24)
H(3)	874 (5)	414 (4)	−360 (8)	70 (11)
H(5)	963 (4)	882 (4)	3 (8)	70 (11)
H(6)	840 (4)	1003 (3)	326 (6)	42 (8)
H(7)	651 (4)	902 (3)	583 (6)	41 (8)
H(8)	575 (5)	645 (4)	485 (8)	80 (13)
H(121)	504 (4)	216 (3)	84 (7)	53 (10)
H(122)	678 (6)	215 (5)	222 (10)	111 (16)
H(123)	575 (5)	93 (4)	9 (8)	74 (12)

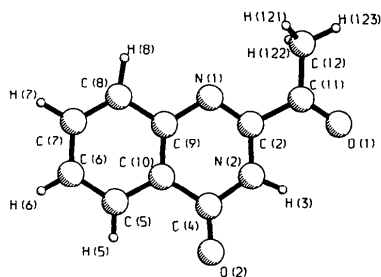


Fig. 1. A view of (1) drawn by the program *PLUTO 78* (W. D. S. Motherwell).

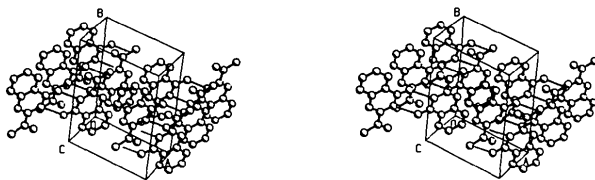


Fig. 2. Stereoscopic view of the crystal structure of (1) (drawn by *PLUTO 78*), showing the hydrogen-bonded dimerization.

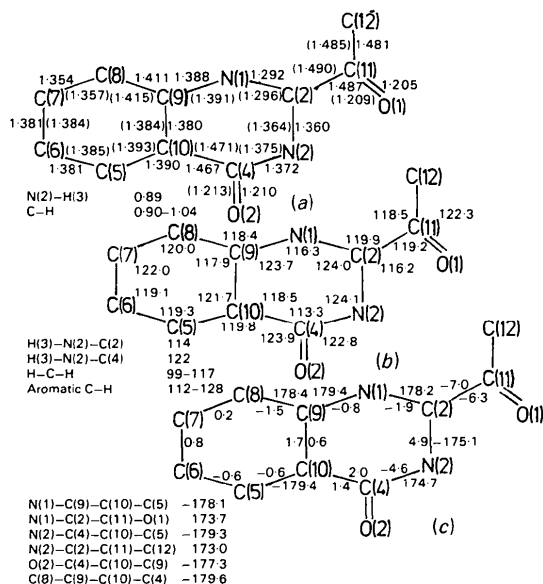


Fig. 3. (a) Bond lengths (Å), (b) bond angles ($^{\circ}$) and (c) torsion angles ($^{\circ}$). E.s.d.'s are ca 0.005 Å for bond lengths, 0.3 $^{\circ}$ for bond angles and >0.3 $^{\circ}$ for torsion angles, not involving H atoms. Bond lengths in parentheses are corrected for the effects of rigid-body thermal motion (see text).

benzenoid ring in all cases *via* the C(9)–N(1)–C(2) conjugation pathway: whereas the C(9)–N(1) bond length decreases in the order (4) [1.442 (8)] > (1) [1.388 (4)] > (5) [1.384 (4) Å], the N(1)–C(2) bond length increases in the same order [1.273 (7) < 1.292 (4) < 1.302 (3) Å], and perhaps related to this is the decrease in the C(2)–N(2) bond length also in the same order [1.385 (8) > 1.360 (4) > 1.358 (3) Å]. These values suggest a comparable measure of electron delocalization between the quinazolinone system and the acetyl and 2-pyridyl substituents, with less interaction when the substituent is phenyl. This is supported by the values of the angle between the mean planes of the 2-substituents and the ten-membered ring, which are 14.4 in (4), 8.5 in (1) and 3.3 $^{\circ}$ in (5) (mean of two values). The remaining bond distances in the heterocyclic ring common to the three molecules are the same to within experimental errors with the exception of the bond common to the heterocyclic and benzenoid rings in (5), which comprised part of a constrained group during the refinement. There are significant differences in the carbonyl-group bond distances in the three molecules [(1), 1.205 (4); (4), 1.267 (8); (5), 1.233 (4) Å] which may partly reflect the extent to which the group contributes to hydrogen bonding [(1) and (4)] or Cu^{II} chelation (5), and partly the extent of amide-type conjugation with N(2) [there does seem to be a coupling of carbonyl bond lengthening with N(2)–C(4) bond shortening, although as noted above, the extent of N(2)–C(4) bond-length variation in these molecules is not large].

The carbonyl group of the acetyl substituent in (1) is disposed in a *transoid* sense with respect to the N(1)–C(2) double bond, which is not surprising in view of the preference of methyl vinyl ketone for such a *transoid* conformation (Liljefors & Allinger, 1976).

This structure determination definitively establishes that N(2) bears an H atom, *i.e.* that the structure is as shown in Fig. 3 and not one of the alternative tautomeric forms [4-hydroxyquinazoline or 4(1H)-quinazolinone]. The amide system indulges in intermolecular hydrogen bonding with a neighbouring molecule [N(2)···O(2) 2.889 Å] forming dimers. It is, perhaps, noteworthy that the position found for H(8) implies a considerable bond-angle distortion from ideality [C(7)–C(8)–H(8) 128 (2), C(9)–C(8)–H(8) 112 (2)°] in the sense that would relieve *ortho*-interactions between H(7) and H(8). Although this distortion may be an artefact of the limited data set available, it is significant that structures (4) and (5) display a similar pattern of distortion, though to a reduced extent.

Analysis of thermal vibrational ellipsoids for non-H atoms in terms of rigid-body motion (Cruickshank, 1956; Schomaker & Trueblood, 1968) leads to fair agreement between observed and calculated U_{ij} values ($\langle \Delta U_{ij}^2 \rangle^{1/2} = 34 \times 10^{-4} \text{ \AA}^2$), maximum discrepancies occurring for the carbonyl group in the acetyl substituent.

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Structure of 5-Bromo-2',3'-O-isopropylideneuridine, C₁₂H₁₅BrN₂O₆

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Abstract. $M_r = 363.17$, orthorhombic, $P2_12_12_1$, $a = 5.251$ (4), $b = 14.962$ (5), $c = 19.112$ (5) Å, $U = 1501.41$ Å³, $Z = 4$, $D_x = 1.61$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 3.02$ mm⁻¹, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, final $R = 7.0\%$ for 1091 reflections with $F_o > 2\sigma(F_o)$. The glycosidic torsion angle χ_{CN} is 13.1 (12)°. The ribose has a C(3')-*exo*, C(4)-*endo* twist geometry. The dioxolane ring assumes an envelope conformation with O(3') displaced by 0.453 (10) Å from the plane of the other four atoms. The conformation about the C(4')–C(5') bond is *gauche-gauche*. The structure is stabilized by two hydrogen bonds between screw-axis-related molecules. The crystal packing and the conformation of the

molecule are very similar to those found in the structure of 2',3'-O-isopropylideneuridine which lacks the Br atom at the 5-position.

Introduction. We report here the structure of the title compound (I). This is part of a systematic study of nucleosides where the ribose is cyclized at O(2') and O(3') by an isopropylidene group. We have previously obtained the structures of 2',3'-O-isopropylideneuridine, (Katti, Seshadri & Viswamitra, 1981) and 5'-deoxy-5',6-epithio-5,6-dihydro-2',3'-O-isopropylidene-3-methyluridine (Gautham, Ramakrishnan, Seshadri, Viswamitra, Salisbury & Brown, 1982).