Structure of (Z)-5-Chloro-3,4-dihydro-1-methyl-4-phenacylidene-2(1H)-pyrimidinone

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Abstract. $C_{13}H_{11}ClN_2O_2$, $M_r = 262 \cdot 70$, orthorhombic, *Pbca*, $a = 6 \cdot 821$ (8), $b = 23 \cdot 486$ (27), $c = 14 \cdot 798$ (16) Å, $V = 2370 \cdot 61$ Å^3, $Z = 8$, $D_x = 1 \cdot 472$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $\mu = 0 \cdot 313$ mm^{-1}, $F(000) = 1088$, $T = 130$ K, $R = 0 \cdot 0317$ ($R = 0 \cdot 0537$ including unobserved reflections), $wR = 0 \cdot 0292$ for 1752 independent reflections. The title compound consists of three essentially planar rings, with the phenyl ring 29° out of the plane of the two other rings. There are two hydrogen bonds present, one intramolecular between O(8) and H(1), and one intermolecular between C(4)–H(4) and O(8) [H(4)–O(8) = 2·21 Å], with an angle of 169°.

Introduction. 2(1*H*)-Pyrimidinones are of interest as cell proliferation inhibitors (Gacek, Undheim, Oftebro & Laland, 1979). In our continued studies (Rise & Undheim, 1985) it was necessary for our screening program to determine the exact configuration (*E* or *Z*) around the exocyclic double bond in the title compound and, for the same reason, the extent of inter- and intramolecular bonding. Since the title compound obviously has more hydrogen-bond acceptor sites than donor sites it may be expected to have strong interactions involving C–H···O. Such interactions, which may be termed hydrogen bonds, have recently been examined by Taylor & Kennard (1982). Investigations at our laboratory (Nordenson & Semmingsen, 1988) indicate that these interactions are more common than initially expected.

Experimental. Yellow crystal, 0·3 × 0·3 × 0·3 mm, from ethyl acetate (Rise & Undheim, 1985). Auto-mated Syntex *P*$\bar{1}$ diffractometer with graphite mono-chromator. Systematic absences: 0*kl*: $k = 2n+1$, *hk*0: $h = 2n+1$, *h0l*: $l = 2n+1$. The cell dimensions were determined from a least-squares fit to 2θ values for 20 reflections, in the range 15° <2θ< 34°. When collect-ing the data all unique reflections with 2θ < 50° were considered. The maximum values for *hkl* were $h = 8$, $k = 28$, $l = 17$. Standard reflections showed only random variations; no absorption correction. All reflections with $I > 3\sigma(I)$ were treated as observed giving 1752 observed reflections out of the 2241 accessible reflections in this region. The structure was solved by direct methods (Germain, Main & Woolf-son, 1971). After a few cycles of least-squares refine-ment (Groth, 1973; Willis & Pryor, 1975) all H atoms were located from a difference electron density map, and included in the least-squares refinement with isotropic thermal parameters. The weighting function was $w = 1/\sigma^2(F)$. In the last cycles 207 parameters were refined. These included positional parameters for all atoms, anisotropic thermal parameters for non-H atoms, isotropic thermal parameters for all H atoms as well as a scaling factor. The final maxima and minima on the difference map showed no features outside ±0·2 e Å^{-3}. The final least-squares cycle showed no shift larger than 0·05σ. As a check on the consistency of weights a normal probability plot (Abrahams & Keve, 1971) was made from $(F_{obs}-F_{calc})/\sigma(F_{obs})$.‡ The plot shows an essentially straight line with zero intercept and a slope of ∼1·5 in good correspondence

‡ Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms, details of libration corrections and a normal probability plot have been deposited with the British Library Document Supply Centre as Supplementary Publication No SUP 44854 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates and* B_{eq}/B_{iso} (Å^2) *as obtained from the refinement using all data*

E.s.d.'s in the last digit are given in parentheses. B_{eq} is calculated as

$$B_{eq} = \tfrac{8}{3}\pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}/B_{iso}
Cl	0·18970 (7)	0·06909 (2)	0·01984 (3)	2·080
O(2)	0·40293 (19)	−0·08855 (5)	0·30038 (8)	1·820
O(8)	0·22467 (19)	0·07596 (5)	0·38423 (8)	1·780
C(3)	0·42536 (34)	−0·12623 (9)	0·12652 (14)	1·960
N(1)	0·29068 (23)	−0·00084 (6)	0·25999 (10)	1·377
C(2)	0·35566 (26)	−0·05507 (7)	0·24124 (13)	1·460
N(3)	0·36388 (21)	−0·06840 (6)	0·15045 (10)	1·473
C(4)	0·30890 (28)	−0·02998 (8)	0·08556 (12)	1·627
C(5)	0·25189 (26)	0·02293 (8)	0·10667 (12)	1·497
C(6)	0·24155 (25)	0·04157 (7)	0·19902 (12)	1·370
C(7)	0·19378 (28)	0·09516 (8)	0·22819 (11)	1·407
C(8)	0·19453 (26)	0·11089 (7)	0·32177 (12)	1·400
C(9)	0·16782 (26)	0·17255 (7)	0·34679 (12)	1·407
C(10)	0·06162 (28)	0·21063 (8)	0·29356 (13)	1·640
C(11)	0·04449 (29)	0·26721 (8)	0·31831 (13)	1·817
C(12)	0·24329 (29)	0·28687 (8)	0·39609 (13)	1·970
C(13)	0·24329 (29)	0·24961 (9)	0·44910 (13)	1·940
C(14)	0·25847 (28)	0·19262 (8)	0·42500 (12)	1·670

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

Cl–C(5)	1·734 (1)	C(6)–C(7)	1·370 (2)
O(2)–C(8)	1·253 (2)	C(7)–C(8)	1·433 (2)
C(3)–N(3)	1·465 (2)	C(8)–C(9)	1·506 (2)
N(1)–C(2)	1·377 (2)	C(9)–C(10)	1·395 (3)
N(1)–C(6)	1·385 (2)	C(9)–C(14)	1·394 (3)
C(2)–N(3)	1·381 (2)	C(10)–C(11)	1·383 (3)
N(3)–C(4)	1·370 (2)	C(11)–C(12)	1·389 (3)
C(4)–C(5)	1·339 (3)	C(12)–C(13)	1·363 (3)
C(5)–C(6)	1·437 (2)	C(13)–C(14)	1·390 (3)
C(2)–N(1)–C(6)	127·7 (2)	C(5)–C(6)–C(7)	126·3 (2)
O(2)–C(2)–N(1)	122·5 (2)	C(6)–C(7)–C(8)	122·7 (2)
O(2)–C(2)–N(3)	122·8 (2)	O(8)–C(8)–C(7)	123·0 (2)
N(1)–C(2)–N(3)	114·8 (2)	O(8)–C(8)–C(9)	117·9 (2)
C(3)–N(3)–C(2)	117·2 (2)	C(7)–C(8)–C(9)	119·0 (2)
C(3)–N(3)–C(4)	121·3 (2)	C(8)–C(9)–C(10)	122·7 (2)
C(2)–N(3)–C(4)	121·5 (2)	C(8)–C(9)–C(14)	118·4 (2)
N(3)–C(4)–C(5)	121·8 (2)	C(10)–C(9)–C(14)	118·8 (2)
Cl–C(5)–C(4)	118·6 (1)	C(9)–C(10)–C(11)	120·7 (2)
Cl–C(5)–C(6)	120·2 (1)	C(10)–C(11)–C(12)	120·0 (2)
C(4)–C(5)–C(6)	121·3 (2)	C(11)–C(12)–C(13)	119·8 (2)
N(1)–C(6)–C(5)	112·9 (2)	C(12)–C(13)–C(14)	120·2 (2)
N(1)–C(6)–C(7)	120·9 (2)	C(9)–C(14)–C(13)	120·4 (2)
O(8)–C(8)–C(9)–C(10)	−154·1 (2)	C(7)–C(8)–C(9)–C(10)	28·8 (3)
O(8)–C(8)–C(9)–C(14)	28·0 (2)	C(7)–C(8)–C(9)–C(14)	−149·1 (2)
N(1)–C(6)–C(7)–C(8)	1·0 (3)	C(5)–C(6)–C(7)–C(8)	−177·4 (2)
N(1)–C(6)–C(7)–H(7)	176·8 (1·3)	C(5)–C(6)–C(7)–H(7)	−1·7 (1·4)
Cl–C(5)–C(6)–N(1)	178·3 (2)	C(4)–C(5)–C(6)–N(1)	−1·6 (3)
Cl–C(5)–C(6)–C(7)	−3·1 (3)	C(4)–C(5)–C(6)–C(7)	177·0 (2)

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the molecule.

Fig. 2. Schematic drawing of the hydrogen-bond-like interaction, C(4)–H(4)···O(8). Some H atoms have been omitted for clarity. The view is along the a axis.

with the goodness of fit, $S = 1·69$. Final coordinates and B values using all data are given in Table 1. Bond lengths and bond angles are given in Table 2, together with torsion angles for relevant parts of the molecule. The molecule with thermal ellipsoids is shown in Fig. 1. Atomic scattering factors from Stewart, Davidson & Simpson (1965) and Doyle & Turner (1968).

Discussion. The title compound is formed as an adduct between the lithium enolate of acetophenone and 5-chloro-1-methyl-2(1*H*)-pyrimidinone followed by dehydrogenation (Rise & Undheim, 1985). The crystal structure consists of sheets in the *bc* plane. The stacking

arrangement involves overlap between the quasi-rings formed by the intramolecular hydrogen bond, N(1)—H(1)···O(8). There is a well defined interaction between C(4)—H(4) and O(8), geometrically corresponding to a weak hydrogen bond (Fig. 2). Such interactions are described in recent literature (Taylor & Kennard, 1982), and may be an important factor in crystal structure arrangement involving highly conjugated compounds with hydrogen-bond acceptors (Nordenson & Semmingsen, 1988). The phenyl ring is tilted 29° with respect to the remaining part of the molecule, which is essentially planar. This is due to the repulsive interaction between H(7) and H(10), which could only be relieved by a rotation around either C(7)—C(8) or C(8)—C(9). The preference for the latter is probably caused by the intramolecular hydrogen bond and the accompanying conjugation. The difference in bonding distance between C(7)—C(8) and C(8)—C(9) may also be an effect of this conjugation.

All bonding distances and angles are within the range normally reported.

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Structure of Dicaesium Sodium Uranium Hexachloride

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Abstract. Cs_2NaUCl_6, $M_r = 739.55$, cubic, $Fm3m$, $a = 10.937$ (1) Å, $V = 1308.3$ (5) Å^3, $Z = 4$, $D_x = 3.754$ g cm^{-3}, $\lambda(Mo\,K\bar{\alpha}) = 0.71073$ Å, $\mu = 184.331$ cm^{-1}, $F(000) = 1260$, $T = 295$ (1) K, $R = 0.039$ for 79 observed reflections. Cs_2NaUCl_6 crystallizes with the 'ideal cryolite' arrangement. The trivalent uranium (site symmetry O_h) is octahedrally coordinated to six chloride ions, each at a distance of 2.723 (9) Å. The sodium (O_h) and the caesium (T_d) ions are respectively surrounded by six and twelve equidistant chloride ions.

Experimental. The compound was obtained by heating, under a high vacuum, stoichiometric amounts of the binary halides CsCl, NaCl and UCl_3 in a quartz tube (1070–1170 K). The UCl_3 used was prepared from metal by hydriding it at 470 K, converting it to trichloride with HCl (g) at 470 K and subliming it at *ca*

1170 K. CsCl and NaCl (Merck, > 99.5% purity) were dried under vacuum at 770 K. Gradient solidification from the melt (Morss, Siegal, Stenger & Edelstein, 1970) was used to grow the single crystal (~0.25 × 0.25 × 0.25 mm) used in this study. Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\bar{\alpha}$ radiation. Cell parameters refined by least squares from angle data of 25 reflections in range 17–25° (2θ). Space group unequivocally established from systematic absences. 2569 reflections collected (θ–2θ scan mode) in range $4 \le 2\theta \le 50°$, $h - 15/15$, $k - 15/15$, $l - 15/0$; 1767 reflections considered observed [$I \ge 2\sigma(I)$], averaged to 126 unique reflections ($R_{int} = 0.06$), 79 reflections with $I > 3\sigma(I)$ used in refinement. Intensities of three standard reflections measured at 30 min intervals, anisotropic decay correction applied (total decay 3.1%). Lorentz and polarization corrections. Empirical absorption corrections (trans-