References

BELL, J. D., BLOUNT, J. F., BRISCOE, O. V. & FREEMAN, H. C. (1968). *Chem. Commun.* pp. 1656–1657.

CHU, S. S. C., NAPOLEONE, V., TERNAY, A. L. & CHANG, S. (1982*a*). *Acta Cryst.* B**38**, 2506–2508.

CHU, S. S. C., NAPOLEONE, V., TERNAY, A. L. & CHANG, S. (1982*b*). *Acta Cryst.* B**38**, 2508–2511.

CHU, S. S. C., NARAYANA, S. V. L. & ROSENSTEIN, R. D. (1984). *Acta Cryst.* C**40**, 1281–1283.

CHU, S. S. C. & VAN DER HELM, D. (1974). *Acta Cryst.* B**30**, 2489–2490.

CHU, S. S. C. & VAN DER HELM, D. (1975). *Acta Cryst.* B**31**, 1179–1183.

CHU, S. S. C. & VAN DER HELM, D. (1976). *Acta Cryst.* B**32**, 1012–1016.

CHU, S. S. C. & YANG, H. T. (1977). *Acta Cryst.* B**33**, 1892–1896.

CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197–204.

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

FRENZ, B. A. (1978). In *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64–71. Delft Univ. Press.

JOHNSON, C. K. (1976). *ORTEP*, 3rd revision. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MALMSTROM, M. C. & CORDES, A. W. (1973). *J. Heterocycl. Chem.* **10**, 715–720.

MALREAU, J. P. & PULLMAN, B. (1964). *Theor. Chim. Acta*, **2**, 293–301.

MARSAU, P. & BUSETTA, B. (1973). *Acta Cryst.* B**29**, 986–991.

MARSAU, P. & CAM, Y. (1973). *Acta Cryst.* B**29**, 980–986.

MARTIN, A. R., HALLBERG, A., KRAMER, T. H., SVENSSON, A., BATES, R. B. & ORTEGA, R. B. (1984). *Acta Cryst.* C**40**, 2113–2116.

PHELPS, D. W. & CORDES, A. W. (1976). *J. Heterocycl. Chem.* **13**, 625–627.

SVENSSON, A. & MARTIN, A. R. (1985). *Heterocycles*, **23**, 357–363.

Acta Cryst. (1985). C**41**, 1807–1810

Two Polymorphs of 4,5-Dichloro-6(1*H*)-pyridazinone

BY V. M. LYNCH AND S. H. SIMONSEN

The Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, *USA*

AND M. J. MUSMAR AND G. E. MARTIN

Department of Medicinal Chemistry and Pharmacognosy, The University of Houston, Houston, Texas 77004, *USA*

(*Received* 22 *February* 1985; *accepted* 19 *June* 1985)

Abstract. $C_4H_2Cl_2N_2O$, $M_r = 164{\cdot}99$; form (I): monoclinic, $P2_1/c$, $a = 5{\cdot}1967$ (12), $b = 9{\cdot}046$ (2), $c = 12{\cdot}901$ (3) Å, $\beta = 100{\cdot}090$ (15)°, $V = 597{\cdot}1$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}84$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 9{\cdot}93$ cm^{-1}, $F(000) = 328$, $T = 163$ K, $R = 0{\cdot}028$ for 1552 reflections; form (II): monoclinic, $P2_1/c$, $a = 5{\cdot}3384$ (7), $b = 13{\cdot}827$ (2), $c = 7{\cdot}9107$ (12) Å, $\beta = 94{\cdot}397$ (14)°, $V = 582{\cdot}20$ (14) Å^3, $Z = 4$, $D_x = 1{\cdot}88$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 10{\cdot}18$ cm^{-1}, $F(000) = 328$, $T = 163$ K, $R = 0{\cdot}025$ for 1597 reflections. The compound, in each form, exists in the oxo form and crystallizes as hydrogen-bonded dimers. Infinite layers of dimers result from C—H···O- and C—H···Cl-type H bonds for forms (I) and (II), respectively [H···O 2·25 (2), C···O 3·076 (2); H···Cl 2·74 (2), C···Cl 3·534 (1) Å]. There are only minor differences in the bond distances and angles of the two forms.

Introduction. Syntheses of many heterocyclic systems containing a pyridazine ring rely on the pivotal and highly versatile starting material 4,5-dichloro-6(1*H*)-pyridazinone. For example, syntheses of 2,3-diazaphenothiazines (Yoneda, Ohtaka & Nitta, 1965, 1966; Scapini, Duro & Pappalardo, 1968; Maki, Suzuki, Toyota & Takaya, 1973) and the isosterically related phenoxathiins (Womack, Martin, Martin & Smith, 1982; Musmar, Martin, Lynch & Simonsen, 1985) have been based on this precursor. Electronically, the 4-halo substituent is the most readily displaced, and the molecule behaves like a β-halovinyl ketone (Benson & Pohland, 1964). Interestingly, when 4,5-dichloro-6(1*H*)-pyridazinone was reacted with the disodium salt of 2-mercaptophenol (Womack *et al.*, 1982) both of the possible phenoxathiins, 1-oxo-1,2-dihydro- and 4-oxo-3,4-dihydro-2,3-diazaphenoxathiin, were formed. The pathway for the reaction was hypothesized to be *via* a Smiles rearrangement (Truce, Kreider & Brand, 1970) which would require the pyridazinone to be in the oxo form throughout the reaction rather than in its hydroxy tautomeric form. In an effort to support partially the proposed reaction pathway, we report the crystal

0108-2701/85/121807-04$01.50

© 1985 International Union of Crystallography

structures of the title compound. In an attempt to obtain a suitable sample, we observed two different crystalline modifications. The structures were determined for the two modifications because of the possibility that several of the different tautomeric forms had crystallized.

Experimental. The title compound was synthesized according to the procedure of Mowry (1953). Form (I): colorless, block-like crystal, 0·31 × 0·24 × 0·46 mm, from ethanol. Form (II): faintly pink plate-like crystal, 0·24 × 0·58 × 0·56 mm, from chloroform. Identical experimental conditions for both form (I) and form (II). Syntex $P2_1$ diffractometer, graphite monochromator, Syntex LT-1 low-temperature delivery system. Lattice parameters from least-squares refinement of setting angles of 45 reflections [2θ range 22·7–29·6° for form (I) and 24·0–29·9° for form (II)]. Space group uniquely determined from systematic absences. ω-scan technique [1754 unique reflections for form (I) and 1695 unique reflections for form (II)], 2θ range 4–60°, 1° ω scan at 3–6° min^{-1} [h 0 to 7, k 0 to 12, l −18 to 17 for form (I); h 0 to 7, k 0 to 19, l −11 to 11 for form (II)]. Four reflections [020, 00$\bar{6}$, $\bar{1}2\bar{1}$, 100 for form (I) and 040, 400, 111, 002 for form (II)] remeasured after every 96 reflections to monitor instrument and crystal stability. Decay correction on I of <0·02 for form (I) (Henslee & Davis, 1975). No decay correction for form (II). Data corrected for Lp effects and absorption [based on crystal shape; transmission-factor range 0·75–0·82 for form (I) and 0·61–0·82 for form (II)]. Data reduction described in Riley & Davis (1976). Reflections having $F_o < 4\sigma(F_o)$ considered unobserved [202 for form (I) and 98 for form (II)]. Structures solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by full-matrix least-squares procedures with anisotropic thermal parameters for non-H atoms. H atoms located from a difference map and refined with isotropic thermal parameters. 90 parameters refined. $\sum[w(|F_o|-|F_c|)^2]$ minimized, where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = 0{\cdot}5(kI)^{-1/2}\{[\sigma(I)]^2 + (0{\cdot}04I)^2\}^{1/2}$. Intensity, I, given by $(I_{\text{peak}}-I_{\text{background}})$ (scan rate); 0·04 is a factor used to downweight intense reflections and to account for instrument instability and k is the correction due to Lp effects, absorption and decay. $\sigma(I)$ estimated from counting statistics; $\sigma(I) = (\text{scan rate})(I_{\text{peak}} + I_{\text{background}})^{1/2}$. Final $R = 0{\cdot}028$ for 1552 reflections,* with $wR = 0{\cdot}040$ ($R_{\text{all}} = 0{\cdot}033$, $wR_{\text{all}} = 0{\cdot}041$) and a goodness of fit of 1·50 for form (I), while for form (II) the final $R = 0{\cdot}025$ for 1597 reflections, $wR = 0{\cdot}042$ ($R_{\text{all}} = 0{\cdot}027$, $wR_{\text{all}} = 0{\cdot}043$) and goodness of fit of 1·75. Max $|\Delta/\sigma|$ <0·01 in the final refinement cycle for both structures and the min. and max. peaks in the final difference map were −0·30 and 0·42 e Å^{-3}, respectively, for form (I) and −0·28 and 0·56 e Å^{-3}, respectively, for form (II). Scattering factors for the non-H atoms from Cromer & Mann (1968) with anomalous-dispersion corrections from Cromer & Liberman (1970), while scattering factors for the H atoms from Stewart, Davidson & Simpson (1965); linear absorption coefficient was calculated using values from *International Tables for X-ray Crystallography* (1974). The least-squares-planes program was supplied by Cordes (1983); other computer programs are listed in reference (II) of Gadol & Davis (1983).

Table 1. *Positional and thermal parameters for atoms of both forms of* 4,5-*dichloro*-6(1*H*)-*pyridazinone*

For anisotropic atoms $U_{\text{eq}} = \frac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\text{eq}}, U_{\text{iso}}$(Å^2)
Form (I)				
Cl(4)	0·75247 (7)	0·05292 (4)	−0·11518 (3)	0·02919 (12)
Cl(5)	0·73791 (6)	0·22367 (4)	0·10314 (3)	0·02449 (11)
O(6)	0·2877 (2)	0·43257 (11)	0·07665 (7)	0·0217 (3)
N(1)	0·1361 (2)	0·37831 (14)	−0·09511 (9)	0·0208 (3)
N(2)	0·1410 (2)	0·31240 (15)	−0·18851 (9)	0·0245 (3)
C(3)	0·3272 (3)	0·2171 (2)	−0·19100 (11)	0·0249 (4)
C(4)	0·5198 (3)	0·1823 (2)	−0·10159 (11)	0·0204 (4)
C(5)	0·5146 (3)	0·2527 (2)	−0·00877 (11)	0·0188 (3)
C(6)	0·3099 (3)	0·36072 (15)	−0·00328 (10)	0·0179 (3)
H(N1)	0·011 (3)	0·435 (2)	−0·0953 (14)	0·023 (4)
H(C3)	0·325 (4)	0·169 (2)	−0·262 (2)	0·037 (5)
Form (II)				
Cl(4′)	0·19343 (5)	0·18564 (2)	0·03907 (4)	0·02625 (10)
Cl(5′)	0·26202 (5)	−0·03412 (2)	0·16228 (4)	0·02558 (10)
O(6′)	0·7242 (2)	−0·05343 (7)	0·39885 (12)	0·0257 (3)
N(1′)	0·8273 (2)	0·10642 (8)	0·39655 (14)	0·0235 (3)
N(2′)	0·7962 (2)	0·19970 (8)	0·35167 (15)	0·0267 (3)
C(3′)	0·6047 (2)	0·22025 (9)	0·2463 (2)	0·0242 (3)
C(4′)	0·4324 (2)	0·14878 (8)	0·18041 (14)	0·0197 (3)
C(5′)	0·4639 (2)	0·05540 (8)	0·23054 (14)	0·0185 (3)
C(6′)	0·6778 (2)	0·02943 (9)	0·34732 (15)	0·0198 (3)
H(N1′)	0·979 (4)	0·093 (2)	0·454 (3)	0·044 (5)
H(C3′)	0·592 (3)	0·2865 (13)	0·220 (2)	0·030 (4)

Discussion. Positional and thermal parameters are listed in Table 1 with the atoms of form (II) labeled with a prime. Bond distances with the atom-labeling scheme are shown in Fig. 1(*a*) while the bond angles are shown in Fig. 1(*b*). Views of the H-bonding network for forms (I) and (II) are shown in Figs. 2 and 3, respectively. There are only very minor differences in the bond distances and angles of the molecules of the two forms and, therefore, they will be discussed together.

The title compound can exist in one of four possible tautomeric forms as represented in Fig. 4. Tautomer (*a*) more closely describes the observed structures. The C—O distances are clearly indicative of a carbonyl group although slightly elongated due to H bonding. O(6) is within H-bonding distance of H(N1) and N(1) [related by $-x$, $1-y$, $-z$ in form (I) and by $2-x$, $-y$,

* Lists of anisotropic thermal parameters, least-squares planes and structure factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42355 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1−z in form (II)] with distances of 2·01 (2) and 2·830 (2) Å, respectively, in form (I), and 1·97 (2) and 2·881 (1) Å, respectively, in form (II). There does appear to be some delocalization of electron density around the ring. The distances between C(5) and C(6) are in the normal range for a C(sp^2)–C(sp^2) single bond while the C(2)–C(4) distances are short for this type of interaction, indicating some partial double-bond character. In addition, N(1) is coplanar with the atoms bound to it, N(2), C(6) and H(N1), implying sp^2 hybridization and thus some delocalization of its lone pair of electrons through the π system of the molecule. The geometry of the rings is quite similar to that of 4,5-dichloro-3,6-pyridazinedione (Ottersen, 1973) which exists as the monolactim tautomer. There are also only minor changes in the ring geometry upon replacement of the Cl atoms with S and O in 4-oxo-3-phenyl-3,4-dihydro-2,3-diazaphenoxathiin (Kimura, 1980) and with S and N in 1-oxo-1,2-dihydro- and 4-oxo-3,4-dihydro-2,3-diazaphenothiazine (Andreetti, Bocelli & Sgarabotto, 1974, 1980).

The pyridazinone rings are planar. The Cl atoms lie on opposite sides of the plane in both forms. The Cl···Cl and the Cl···O intramolecular distances are 3·2248 (8) and 2·980 (1) Å, respectively, in form (I), and 3·2040 (4) and 2·993 (1) Å, respectively, in form (II), which are less than the sum of their van der Waals radii (Bondi, 1964). The staggered arrangement of the Cl atoms and the values of the exocyclic angles at C(4),

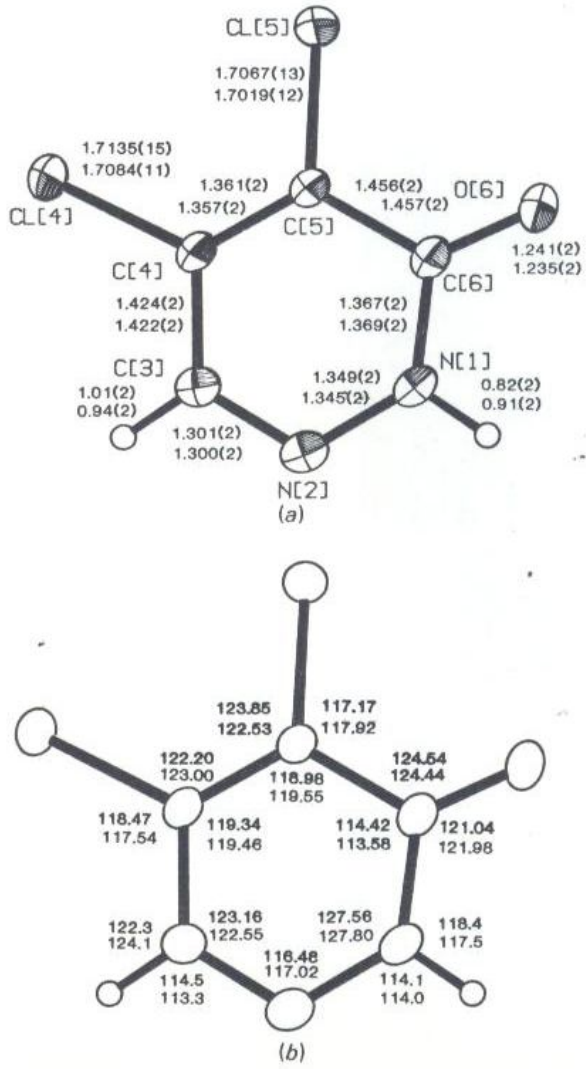

Fig. 1. (*a*) View of molecule of form (I) showing the atom-labeling scheme with bond distances (Å). (*b*) Same view as in (*a*) showing bond angles (°) (e.s.d.'s are in the range 0·09–0·13° for non-H atoms and 1·1–1·3° for angles involving the H atoms). Values for atoms of form (II) are located below those of form (I).

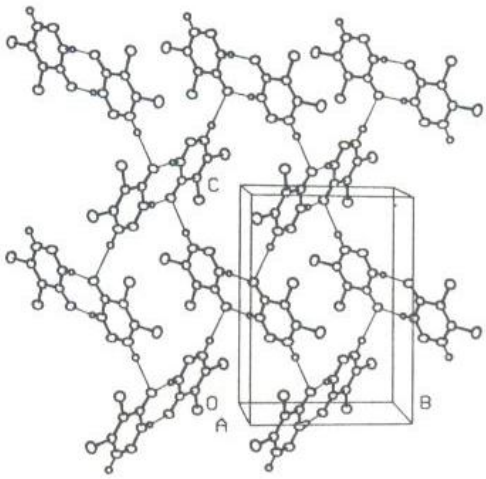

Fig. 2. View of one layer of molecules of form (I) showing the H-bonding network and the orientation in the unit cell.

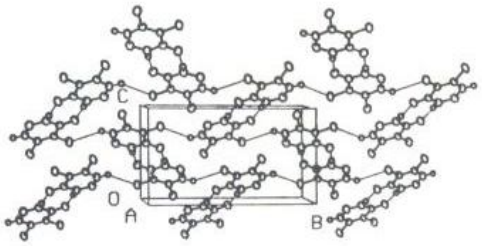

Fig. 3. View of one layer of molecules of form (II) showing the H-bonding network. The orientation of the unit cell is the same as that in Fig. 3.

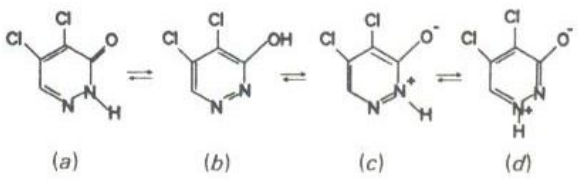

Fig. 4. Representation of the tautomeric equilibria possible for 4,5-dichloro-6(1*H*)-pyridazinone.

C(5) and C(6) are suggestive of unfavorable steric interactions between the Cl atoms and between Cl(5) and O(6). The Cl···Cl distance is within the range of values observed for the S···S distances in thianthrenes.

Although the H-bonded dimers lie around a center of symmetry in both forms, the relative orientation of these dimers is different. This difference in orientation arises from what appear to be C—H(C3)···*X*-type H bonds, where *X* is O(6) in form (I) and Cl(5) in form (II). In form (II), the molecules with short C—H···Cl contacts are nearly parallel with each other, having a dihedral angle of 18·02 (4)° between the ring planes. While in form (I), molecules with short C—H···O contacts are nearly perpendicular to each other, having a dihedral angle of 86·50 (5)° between the ring planes. Such an orientation minimizes Cl···Cl contacts between dimers separated by a translation in **b** (Fig. 2). In form (I), the H(C3)···O(6) and the C(3)···O(6) contacts are 2·25 (2) and 3·076 (2) Å, respectively, while the C—H···O angle is 176 (2)°. In form (II), the H(C3)···Cl(5) and C(3)···Cl(5) contacts are 2·74 (2) and 3·534 (1) Å, respectively, while the C—H···Cl angle is 142 (1)°. The H(C3)···*X* contacts are significantly less than the sum of the van der Waals radii (2·95 Å for Cl···O and 2·7 Å for O···H, Bondi, 1964). The fact that in both forms short H(C3)···*X* contacts are observed is suggestive that these interactions are attractive. It has been observed that molecules with C—H groups adjacent to N atoms frequently have short C—H···*X* contacts where *X* is O, N or Cl (Taylor & Kennard, 1982). The C—H···*X*-type H bonding results in the formation of infinite layers of interconnected dimers parallel to the *bc* plane in form (I) and lying at an angle of 38·07 (1)° to the *ab* plane in form (II).

The authors would like to thank the Robert A. Welch Foundation, grants No. F-017 to SHS and E-792 to GEM, for support of this work.

References

ANDREETTI, G. D., BOCELLI, G. & SGARABOTTO, P. (1974). *Cryst. Struct. Commun.* **3**, 519–522.

ANDREETTI, G. D., BOCELLI, G. & SGARABOTTO, P. (1980). *Acta Cryst.* B**36**, 1839–1846.

BENSON, W. R. & POHLAND, A. E. (1964). *J. Org. Chem.* **29**, 385–391.

BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.

CORDES, A. W. (1983). Personal communication.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

GADOL, S. M. & DAVIS, R. E. (1983). *Organometallics*, **1**, 1607–1613.

HENSLEE, W. H. & DAVIS, R. E. (1975). *Acta Cryst.* B**31**, 1511–1519.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 55. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

KIMURA, M. (1980). Unpublished results.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN*78. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MAKI, Y., SUZUKI, M., TOYOTA, O. & TAKAYA, M. (1973). *Chem. Pharm. Bull.* **21**, 241–247.

MOWRY, D. T. (1953). *J. Am. Chem. Soc.* **75**, 1909–1910.

MUSMAR, M. J., MARTIN, G. E., LYNCH, V. M. & SIMONSEN, S. H. (1985). In preparation.

OTTERSEN, T. (1973). *Acta Chem. Scand.* **27**, 797–813.

RIBEY, P. E. & DAVIS, R. E. (1976). *Acta Cryst.* B**32**, 381–386.

SCAPINI, G., DURO, F. & PAPPALARDO, G. (1968). *Ann. Chim. (Rome)*, **58**, 718–724.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

TRUCE, W. E., KRÊIDER, E. M. & BRAND, W. W. (1970). *Org. React.* **18**, 99–215.

WOMACK, C. H., MARTIN, L. M., MARTIN, G. E. & SMITH, K. (1982). *J. Heterocycl. Chem.* **19**, 1447–1452.

YONEDA, F., OHTAKA, T. & NITTA, Y. (1965). *Chem. Pharm. Bull.* **13**, 580–585.

YONEDA, F., OHTAKA, T. & NITTA, Y. (1966). *Yakugaku Zasshi*, **86**, 887–890.

Acta Cryst. (1985). C**41**, 1810–1814

Structure and Stereochemistry of (±)-Demethoxycarbonyl-3α- and -3β-nauclechine

BY JEFFERY F. SAWYER, AZIM SHARIFF AND STEWART MCLEAN

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

(*Received* 29 *March* 1985; *accepted* 15 *August* 1985)

Abstract. Demethoxycarbonyl-3α-nauclechine (1*a*) as an ethyl acetate solvate, $C_{19}H_{19}N_3O.0{\cdot}5C_4H_8O_2$, M_r = 349·4, monoclinic, $P2_1/c$, a = 11·255 (1), b = 11·515 (2), c = 13·657 (4) Å, β = 91·29 (2)°, U = 1769 Å^3, D_x = 1·31 Mg m^{-3}, Z = 4, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, μ = 0·0801 mm^{-1}, $F(000)$ = 744, T = 298 K, R = 0·072 (wR = 0·091) for 1369 reflections with $I > 2{\cdot}5\sigma(I)$. Demethoxycarbonyl-3β-nauclechine (2*a*) as a monohydrate, $C_{19}H_{19}N_3O.H_2O$, M_r = 323·4, monoclinic, $P2_1/c$, a = 8·253 (4), b = 18·449 (6), c

0108-2701/85/121810-05$01.50

© 1985 International Union of Crystallography