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Structure of 1-(4-Chloro-2-fluorophenyl)-4,4-dimethyl-2-(1H-1,2,4-triazol-1-yl)-3-pentanone

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Abstract. $C_{15}H_{17}ClFN_3O$, $M_r = 309 \cdot 8$, orthorhombic, $P2_12_12_1$, $a = 19 \cdot 813$ (8), $b = 13 \cdot 699$ (6), $c = 5 \cdot 777$ (3) Å, $V = 1568 \cdot 0$ Å^3, $Z = 4$, $D_m = 1 \cdot 29$ (2), $D_x = 1 \cdot 31$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 213$ mm^{-1}, $F(000) = 648$, room temperature, final $R = 0 \cdot 053$ for 1003 reflections classed as observed. C atom 1 of the phenyl ring and C atoms 1 to 4 of the pentanone function adopt an extended 'W' conformation with the atoms essentially coplanar. The triazolyl ring, which shows significant delocalization [N—N bond length $1 \cdot 357$ (9) Å; C—N $1 \cdot 324$–$1 \cdot 337$ Å], and the chlorofluorophenyl ring are twisted by 86 (1) and 58 (1)°, respectively, out of this plane. The exocyclic angles of the triazolyl ring are very asymmetric with C—N—C [$130 \cdot 6$ (7)°] significantly larger than C—N—N [$119 \cdot 1$ (6)°]. The F atom is disordered being distributed (80,20% occupancy) between positions 2 and 6 in the phenyl ring. The title compound was recrystallized from a racemic mixture but the absolute configuration [(2S)-enantiomer] of the molecules in the crystal under investigation was established by comparison of wR values for the determined and the inverted structure.

Introduction. The title compound is one of a group of azolylmethane fungicides (Balasubramanyan & Shephard, 1975) which are related to the well established systemic fungicide triadimefon (Martin & Morris, 1979), whose structure has been reported previously (Nowell, Walker & Anderson, 1982). We have determined the structure of the title compound to establish its solid-state conformation as part of a programme investigating the relationship between conformation and biological activity in this class of compounds. A preliminary description of this structure has been published (Anderson, Branch, Loeffler, Mann, Nowell & Walker, 1984).

Experimental. Recrystallization from ethanol:water (2:1); D_m by flotation in benzene/CCl$_4$; crystal, clear colourless needle, approximate dimensions $0 \cdot 38 \times 0 \cdot 24 \times 0 \cdot 16$ mm, mounted about crystallographic c axis; Stoe Stadi-2 two-circle diffractometer, Mo $K\alpha$ radiation; Lorentz, polarization but no absorption corrections applied; one standard reflection monitored for each layer collected, intensity variation $< 4\%$; 1890 reflections up to $\theta = 27 \cdot 5°$; index ranges h 0 to 24, k 0 to 17, l 0 to 6; 1829 independent reflections of which 1003 with $I \geq 2 \cdot 0\sigma(I)$ con-

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sidered observed; structure solved by multisolution direct methods; block-diagonal least-squares refinement of atomic coordinates and anisotropic temperature factors for all non-H atoms except F, and isotropic temperature factors for all H and F atoms, minimizing $\sum w(F_o - F_c)^2$ with $w = 0.9736/[\sigma^2(F_o) + 0.0002(F_o)^2]$; all H atoms included in positions calculated from the geometry of the molecule (C—H 1.08 Å); max. $(\Delta/\sigma) = 0.13$; min. $\Delta\rho = -0.17$, max. $\Delta\rho = 0.26$ e Å^{-3}; no correction for secondary extinction; scattering factors calculated from an analytical approximation (*International Tables for X-ray Crystallography*, 1974); computer programs: *SHELX76* (Sheldrick, 1976), *PLUTO* (Motherwell & Clegg, 1978). During the early stages of refinement, the electron density at H(76) was higher than expected and refinement of a common temperature factor for the phenyl H atoms led to a very low value. Thus, disorder of the F atom between C(72) and C(76) was indicated and subsequent refinement revealed relative populations at each site of 80 (1) and 20 (1)% respectively. A final value of $U = 0.055$ (18) Å^2 was refined for H(5) while common isotropic temperature factors applied to the methyl, methylene and triazolyl H atoms, to H(73) and H(75), and to the disordered F atom at C(72) and C(76) refined to final values of $U = 0.183$ (17), 0.050 (11), 0.116 (21), 0.137 (24) and 0.071 (1) Å^2 respectively. Although the title compound was recrystallized from a racemic mixture, the noncentrosymmetric space group indicates that the crystal examined contains only one of the two possible enantiomeric forms [(2R)- or (2S)-configuration]. Equal refinement of the atomic coordinates representing the R- and S-enantiomers led to final values of $wR = 0.0522$ and 0.0519 respectively. Application of the R-factor-ratio test (Hamilton, 1965) gave $\mathscr{R} = 1.0058$, greater than the value $\mathscr{R}_{1,808,0.005} = 1.0042$ interpolated from the Hamilton tables for the 0.005 significance level for a one-dimensional hypothesis and 808 degrees of freedom. Hence the probability of the R configuration being correct can be rejected with a confidence level of 99.5%. Thus, application of the statistical test indicates the S-enantiomer to be present although we note that the confidence level may be overestimated (Rogers, 1981).

Discussion. The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1;* bond distances and angles in Table 2 and the atomic numbering scheme in Fig. 1. The molecule adopts a conformation such that the carbon chain C(31)—C(4)—C(5)—C(6)—C(71) is extended and the atoms are

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* Lists of structure amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42445 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional positional parameters* $(\times 10^4)$ *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

B_{eq} values have been calculated by reference to Willis & Pryor (1975).

	x	y	z	$B_{eq}(\text{Å}^2)$
Cl	3080 (1)	2926 (1)	5102 (6)	8.3 (1)
N(1)	−52 (2)	3576 (3)	1354 (12)	3.6 (2)
N(2)	−117 (3)	3021 (4)	−580 (11)	4.4 (3)
N(3)	−175 (4)	2088 (4)	2620 (18)	7.1 (4)
O	−350 (2)	5263 (4)	−2431 (12)	6.1 (3)
C(1)	−88 (4)	3021 (6)	3228 (16)	5.4 (4)
C(2)	−181 (4)	2138 (5)	328 (20)	5.5 (4)
C(31)	−1228 (3)	5149 (4)	372 (16)	4.6 (4)
C(32)	−1284 (4)	5217 (12)	2859 (21)	12.5 (9)
C(33)	−1519 (4)	6069 (7)	−824 (24)	9.7 (7)
C(34)	−1616 (3)	4276 (7)	−537 (28)	10.3 (7)
C(4)	−495 (3)	5045 (4)	−493 (16)	3.9 (3)
C(5)	58 (2)	4638 (3)	1110 (13)	3.4 (3)
C(6)	761 (2)	4843 (4)	55 (15)	4.0 (3)
C(71)	1323 (2)	4335 (4)	1384 (15)	4.1 (3)
C(72)	1557 (3)	4679 (4)	3445 (14)	4.4 (3)
C(73)	2095 (3)	4264 (4)	4646 (16)	4.9 (3)
C(74)	2404 (3)	3457 (4)	3650 (18)	5.5 (4)
C(75)	2187 (3)	3080 (5)	1608 (18)	5.7 (4)
C(76)	1646 (3)	3516 (4)	510 (15)	4.7 (3)
F(72)*	1268 (2)	5446 (3)	4446 (10)	
F(76)*	1448 (9)	3140 (13)	−1247 (45)	

* Disordered F atom given common isotropic temperature factor [final value $U = 0.071$ (1) Å^2]; F(72), 80 (1)% occupancy; F(76), 20 (1)% occupancy.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

N(1)—N(2)	1.357 (9)	C(5)—C(6)	1.546 (8)
N(2)—C(2)	1.324 (9)	C(6)—C(71)	1.522 (8)
C(2)—N(3)	1.326 (16)	C(71)—C(72)	1.361 (11)
N(3)—C(1)	1.337 (10)	C(72)—F(72)*	1.330 (8)
C(1)—N(1)	1.324 (11)	C(72)—C(73)	1.393 (9)
N(1)—C(5)	1.478 (6)	C(73)—C(74)	1.388 (9)
C(31)—C(32)	1.444 (15)	C(74)—Cl	1.739 (7)
C(31)—C(33)	1.549 (12)	C(74)—C(75)	1.357 (13)
C(31)—C(34)	1.515 (12)	C(75)—C(76)	1.380 (10)
C(31)—C(4)	1.542 (9)	C(76)—F(76)*	1.204 (25)
C(4)—O	1.194 (11)	C(76)—C(71)	1.386 (8)
C(4)—C(5)	1.540 (9)		
C(1)—N(1)—N(2)	110.3 (5)	C(4)—C(5)—N(1)	108.0 (5)
C(1)—N(1)—C(5)	130.6 (7)	N(1)—C(5)—C(6)	110.5 (4)
N(2)—N(1)—C(5)	119.1 (6)	C(5)—C(6)—C(71)	112.2 (6)
N(1)—N(2)—C(2)	101.2 (7)	C(6)—C(71)—C(72)	122.1 (5)
N(2)—C(2)—N(3)	116.2 (7)	C(6)—C(71)—C(76)	121.6 (7)
C(2)—N(3)—C(1)	102.4 (7)	C(72)—C(71)—C(76)	116.2 (6)
N(3)—C(1)—N(1)	109.9 (8)	C(71)—C(72)—F(72)*	120.5 (6)
C(32)—C(31)—C(33)	111.2 (9)	C(71)—C(72)—C(73)	123.7 (6)
C(32)—C(31)—C(34)	110.9 (9)	F(72)—C(72)—C(73)*	115.8 (7)
C(33)—C(31)—C(34)	107.3 (7)	C(72)—C(73)—C(74)	117.1 (8)
C(32)—C(31)—C(4)	113.7 (6)	C(73)—C(74)—Cl	118.2 (7)
C(33)—C(31)—C(4)	106.3 (6)	C(73)—C(74)—C(75)	121.6 (6)
C(34)—C(31)—C(4)	107.0 (6)	Cl—C(74)—C(75)	120.3 (5)
C(31)—C(4)—O	120.5 (7)	C(74)—C(75)—C(76)	118.7 (6)
C(31)—C(4)—C(5)	120.6 (7)	C(75)—C(76)—F(76)*	117.1 (10)
O—C(4)—C(5)	118.9 (5)	F(76)—C(76)—C(71)*	120.1 (10)
C(4)—C(5)—C(6)	109.8 (6)	C(75)—C(76)—C(71)	122.7 (8)

* Disordered F atom.

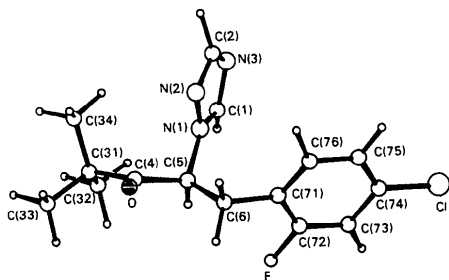Fig. 1. The conformation of the molecule (2S-enantiomer depicted). The F atom is disordered between positions 2 and 6 of the phenyl ring (80,20% occupancy respectively).

essentially coplanar. It is likely that this 'W' conformation minimizes steric interactions between the three most bulky functional groups in the molecule, namely the *tert*-butyl, halophenyl and triazolyl groups. The triazolyl and halophenyl rings are also arranged to minimize intramolecular interactions, being inclined at angles of 85·5 (10) and 57·8 (10)° respectively to the plane containing C atoms C(31), C(4), C(5), C(6) and C(71) and at an angle of 55·3 (10)° to each other. The triazolyl ring is orientated such that C(1) and H(5) are almost eclipsed, the torsion angle C(1)—N(1)—C(5)—H(5) being 8·4 (11)°.

All four C—N distances and the N—N distance in the heterocyclic ring are intermediate between the expected single-bond lengths (1·47 and 1·45 Å respectively) and double-bond lengths (1·265 and 1·2 Å respectively) and the three atoms bonded to N(1) are coplanar with it. These data indicate extensive delocalization in the triazolyl ring. The exocyclic angles at N(1) show

considerable asymmetry, C(5)—N(1)—C(1) being significantly larger than C(5)—N(1)—N(2), and, as previously noted (Branch & Nowell, 1985), this asymmetry appears to be characteristic of the triazolyl ring itself rather than due to the influence of any intra- or intermolecular interactions.

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Structure and Absolute Configuration of a Penam Derivative

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Abstract. *p*-Nitrobenzyl 6-(1-*tert*-butyldimethylsiloxy-ethyl)-3-methylthio-3-nitromethyl-7-oxo-4-thia-1-aza-bicyclo[3.2.0]heptane-2-carboxylate, $C_{23}H_{33}N_3O_8S_2Si$, $M_r = 571·75$, monoclinic, $P2_1$, $a = 8·6734$ (16), $b = 10·420$ (7), $c = 16·785$ (4) Å, $\beta = 93·75$ (2)°, $V = 1513·7$ Å³, $Z = 2$, $D_x = 1·254$ Mg m⁻³, $\lambda(Cu K\alpha) = 1·54178$ Å, $\mu = 2·33$ mm⁻¹, $F(000) = 604$, $T = 293$ K, $R = 0·061$ for 1548 observed reflections. The absolute configuration was established. The main feature of this molecule is the bicyclic system related to that of penicillin. The five-membered ring, in the envelope conformation, shows a strong distortion when compared to carpetimycin or thienamycin. The four-membered ring is not planar and has torsion angles of ±10° as in the other two related compounds.

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