organic compounds

1-[2-(2,4-Dichlorophenyl)pentyl]-1H-1,2,4-triazole

Corrado Rizzoli,[a]* Elda Marku[b] and Lucedio Greci[c]

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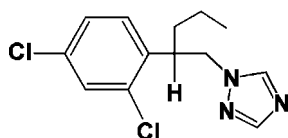Correspondence e-mail: corrado.rizzoli@unipr.it

The title compound, $C_{13}H_{15}Cl_2N_3$, also known as penconazole, crystallizes as a racemate. The dihedral angle between the benzene and triazole rings is 24.96 (13)°. In the crystal structure, molecules are linked into chains running parallel to the c axis by intermolecular C—H···N hydrogen-bonding interactions.

Related literature

For the synthesis and toxicity of the title compound, see: Maier *et al.* (1987); Worthing (1987); Tao *et al.* (2003). For the crystal structure of a related compound, see: Peeters *et al.* (1993).

Experimental

Crystal data

$C_{13}H_{15}Cl_2N_3$
$M_r = 284.18$
Monoclinic, $C2/c$
$a = 25.083$ (8) Å
$b = 10.763$ (2) Å
$c = 11.206$ (3) Å
$\beta = 105.654$ (3)°

$V = 2913.1$ (13) Å^3
$Z = 8$
Cu $K\alpha$ radiation
$\mu = 3.89$ mm^{-1}
$T = 297$ K
$0.23 \times 0.20 \times 0.16$ mm

Data collection

Siemens AED diffractometer
Absorption correction: empirical (refined from ΔF) (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.432$, $T_{max} = 0.538$
2737 measured reflections

2611 independent reflections
1183 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$
3 standard reflections every 100 reflections intensity decay: 0.01%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.127$
$S = 0.99$
2611 reflections

163 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···N3^i	0.97	2.52	3.489 (4)	174

Symmetry code: (i) $x, -y + 1, z + \frac{1}{2}$.

Data collection: *AED* (Belletti *et al.*, 1993); cell refinement: *AED*; data reduction: *AED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *SCHAKAL* (Keller, 1997); software used to prepare material for publication: *SHELXL97* and *PARST95* (Nardelli, 1995).

References

Belletti, D., Cantoni, A. & Pasquinelli, G. (1993). *AED*. Internal Report 1/93. Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Keller, E. (1997). *SCHAKAL97*. University of Freiburg, Germany.
Maier, L., Kunz, W. & Rist, G. (1987). *Phosphorus Sulfur Silicon*, **33**, 41–52.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Peeters, O. M., Schuerman, G. S., Blaton, N. M. & De Ranter, C. J. (1993). *Acta Cryst.* C**49**, 1958–1961.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tao, C., Yang, F. & Chen, N. (2003). CN Patent No. 1451646.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.
Worthing, C. R. (1987). *The Pesticide Manual, a World Compendium*, 8th ed. Farnham, Surrey, England: British Crop Protection Council.

1-[2-(2,4-Dichlorophenyl)pentyl]-1*H*-1,2,4-triazole

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S1. Comment

The synthesis of the title compound, **I**, commonly known as penconazole, was described years ago (Maier *et al.*, 1987). Due to its ability to inhibit the development of fungi by interfering with sterol biosynthesis of their cell membranes, this product was introduced as an agriculture systemic fungicide affecting cucurbits, grapes, pome fruits and vegetables. The advantages of this compound is its low toxicity: acute oral dose (LD50) of 2125 mg/kg for rats (Worthing, 1987). More recently, penconazole was prepared by condensation of 2-(2,4-dichlorophenyl)-1-pentanole with 1,2,4-triazole (Tao *et al.*, 2003), but this method also leads to the formation of 1-(1*H*-1,3,4-triazol-1-yl)-2-(2,4-dichlorophenyl)-pentane (**II**) as a by-product. In repeating this reaction, our purpose was the determination of the crystal structure of the desired compound **I** and the evaluation of the percentage of the by-product **II**.

The title compound (Fig. 1) crystallizes as a racemate. The triazole ring is substantially planar (maximum deviation from planarity 0.006 (3) Å for atom C2) and forms a dihedral angle of 24.96 (13)° with the benzene ring. The N—N (1.351 (3) Å) and C—N (mean value 1.328 (4) Å) bond lengths within the triazole ring are comparable with those observed in 6-[(4-chlorophenyl)(1*H*-1,2,4-triazol-1-yl)methyl]-1-methyl-1*H*-benzotriazole (vorozole; Peeters *et al.*, 1993) and suggest electron delocalization over the ring. In the crystal structure, an intermolecular C—H···N hydrogen bonding interaction (Table 1) link the molecules into chains running parallel to the *c* axis (Fig. 2).

S2. Experimental

The title compound was prepared according to the literature reports (Tao *et al.*, 2003). This method afforded compounds **I** and **II** in a 93:3 ratio. The two compounds were separated by chromatography on SiO_2 column eluting with cyclohexane/ethyl acetate (9:1 *v/v*). Crystals of the title compound suitable for X-ray analysis were obtained on slow evaporation of an *n*-pentane solution (m. p. 60–61°C). IR data, *v*, cm^{-1}: 3060, 1597, 1448, 760, 746, 700. ^{1}H-NMR, *δ* in CDC*L*$_3$: 0.87 (t, 3H, –CH2*CH3*), 1.23 (sextet, 2H, -*CH2*CH3), 2.6–2.8 (m,2*H*, –CH*CH2*CH2CH3), 3.78 (1*H*, quintet, –CH2*CH*CH2-), 4.34 (d, -*CH2*CH<), 7.23 (1*H*, speudo-q, H-5, J=8.3 Hz, J=2.2 Hz), 7.38 (1*H*, d, H-3, J=2.2 Hz), 7.71 (s, 1H, triazolyl-H-3), 7.89 (s,1*H*, triazolyl-H-5). MS, Calcd for $C_{13}H_{15}Cl_2N_3$, 284.2; Found. *M* (%): 250 (12.72), 248 (36.93), 161 (63.69), 159 (100); no molecular ion peak was observed; the highest peaks are those corresponding to the loss of a chlorine atom. The ^{1}H-NMR spectrum of compound **II** shows a singlet at *δ* = 7.89 corresponding to the two equivalent H atoms of the 1,3,4-triazol-1-yl ring, the other part of the spectrum is strictly similar to that of compound **I**. Melting points were determined by an electrochemical apparatus and were uncorrected. ^{1}H-NMR spectra were recorded on a Varian Gemini 200 MHz. IR spectra were recorded in the solid state with a Perkin-Elmer MGX1 spectrophotometer equipped with Spectra Tech. Mass spectra were recorded with a Carlo Erba QMD 1000 mass spectrometer in positive EI mode.

S3. Refinement

All H atoms were positioned geometrically with C—H = 0.93–0.98 Å, and refined using a riding model approximation with $U_{iso}(H) = 1.2\ U_{eq}(C)$ or $1.5\ U_{eq}(C)$ for methyl H atoms.
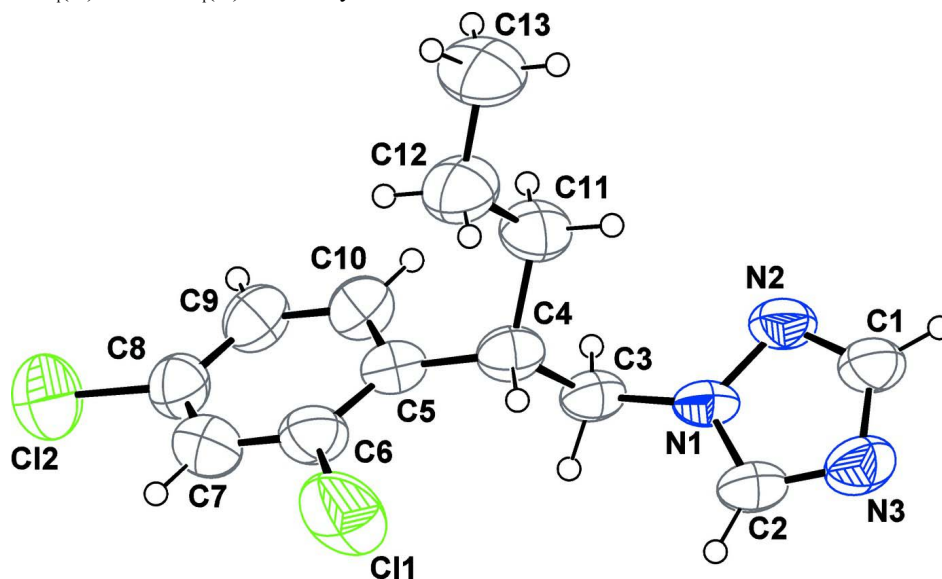

Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.
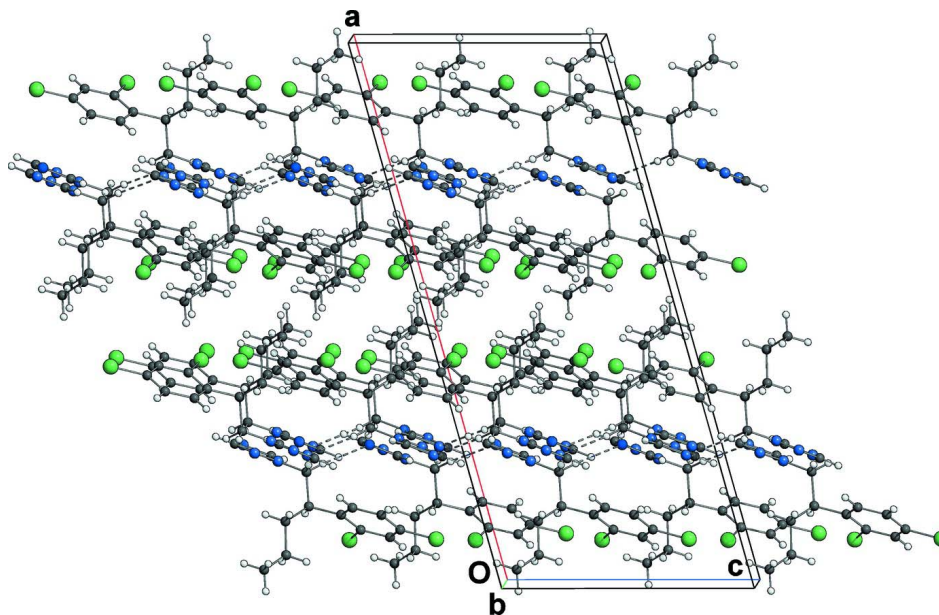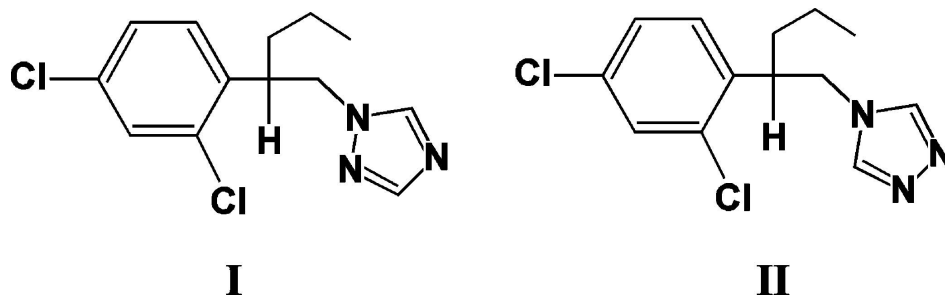

Figure 2

Crystal packing of the title compound viewed approximately along the *b* axis. Intermolecular C—H···N hydrogen bonds are shown as dashed lines.

Figure 3

The structures of (I) and (II).

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$\beta = 105.654\ (3)°$
$V = 2913.1\ (13)$ Å^3
$Z = 8$

$F(000) = 1184$
$D_x = 1.296$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 48 reflections
$\theta = 18.4–42.5°$
$\mu = 3.89$ mm^{-1}
$T = 297$ K
Block, colourless
$0.23 \times 0.20 \times 0.16$ mm

Data collection

Siemens AED
  diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\theta/2\theta$ scans
Absorption correction: empirical (using
  intensity measurements)
  (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.432$, $T_{max} = 0.538$
2737 measured reflections

2611 independent reflections
1183 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$
$\theta_{max} = 67.9°$, $\theta_{min} = 3.7°$
$h = -29 \rightarrow 28$
$k = -2 \rightarrow 12$
$l = -5 \rightarrow 13$
3 standard reflections every 100 reflections
intensity decay: 0.01%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.127$
$S = 0.99$
2611 reflections
163 parameters
0 restraints
Primary atom site location: structure-invariant
  direct methods

Secondary atom site location: difference Fourier
  map
Hydrogen site location: inferred from
  neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Special details

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Cl1	0.08070 (6)	0.51687 (9)	0.93474 (12)	0.1422 (6)
Cl2	0.08744 (5)	0.18168 (11)	1.28987 (10)	0.1305 (5)
N1	0.22774 (10)	0.3780 (2)	0.7443 (2)	0.0595 (7)
N2	0.24356 (12)	0.3032 (2)	0.6633 (2)	0.0757 (8)
N3	0.25582 (12)	0.5043 (2)	0.6210 (3)	0.0815 (9)
C1	0.25951 (15)	0.3839 (3)	0.5932 (3)	0.0808 (10)
H1	0.2728	0.3591	0.5270	0.097*
C2	0.23549 (13)	0.4960 (3)	0.7196 (3)	0.0714 (9)
H2	0.2279	0.5634	0.7644	0.086*
C3	0.20829 (13)	0.3285 (3)	0.8460 (3)	0.0638 (8)
H3A	0.2230	0.3790	0.9192	0.077*
H3B	0.2226	0.2449	0.8646	0.077*
C4	0.14554 (13)	0.3253 (3)	0.8180 (3)	0.0666 (8)
H4	0.1313	0.4086	0.7921	0.080*
C5	0.13060 (12)	0.2927 (3)	0.9380 (3)	0.0648 (8)
C6	0.10164 (15)	0.3713 (3)	0.9946 (3)	0.0807 (10)
C7	0.08852 (16)	0.3387 (3)	1.1047 (4)	0.0927 (11)
H7	0.0695	0.3937	1.1424	0.111*
C8	0.10441 (15)	0.2235 (4)	1.1558 (3)	0.0790 (10)
C9	0.13257 (14)	0.1450 (3)	1.1013 (3)	0.0787 (10)
H9	0.1435	0.0680	1.1372	0.094*
C10	0.14543 (13)	0.1774 (3)	0.9930 (3)	0.0724 (9)
H10	0.1643	0.1211	0.9562	0.087*
C11	0.11930 (14)	0.2323 (3)	0.7113 (3)	0.0830 (10)
H11A	0.1315	0.2537	0.6389	0.100*
H11B	0.1326	0.1492	0.7368	0.100*
C12	0.05814 (16)	0.2321 (4)	0.6773 (3)	0.1057 (13)
H12A	0.0450	0.3152	0.6514	0.127*
H12B	0.0460	0.2115	0.7501	0.127*
C13	0.03234 (16)	0.1433 (4)	0.5764 (4)	0.1191 (15)
H131	−0.0072	0.1482	0.5589	0.179*
H132	0.0442	0.0604	0.6020	0.179*
H133	0.0434	0.1640	0.5032	0.179*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.2339 (15)	0.0687 (6)	0.1461 (10)	0.0447 (8)	0.0895 (10)	0.0118 (7)
Cl2	0.1620 (11)	0.1516 (11)	0.0905 (7)	−0.0169 (8)	0.0558 (7)	0.0066 (7)

N1	0.0728 (18)	0.0384 (12)	0.0602 (15)	−0.0030 (12)	0.0061 (13)	−0.0050 (12)
N2	0.103 (2)	0.0486 (14)	0.0760 (18)	−0.0110 (15)	0.0248 (16)	−0.0087 (14)
N3	0.101 (2)	0.0588 (17)	0.081 (2)	−0.0131 (15)	0.0183 (18)	0.0088 (15)
C1	0.111 (3)	0.0566 (19)	0.075 (2)	−0.016 (2)	0.026 (2)	−0.0020 (18)
C2	0.084 (3)	0.0447 (17)	0.079 (2)	−0.0054 (16)	0.0105 (19)	−0.0048 (17)
C3	0.076 (2)	0.0485 (16)	0.0612 (19)	−0.0073 (15)	0.0083 (16)	0.0029 (15)
C4	0.072 (2)	0.0545 (18)	0.067 (2)	0.0001 (16)	0.0072 (17)	0.0065 (16)
C5	0.064 (2)	0.0564 (18)	0.066 (2)	−0.0038 (16)	0.0049 (16)	−0.0013 (16)
C6	0.105 (3)	0.057 (2)	0.082 (2)	−0.003 (2)	0.027 (2)	−0.0030 (19)
C7	0.109 (3)	0.079 (3)	0.094 (3)	−0.006 (2)	0.035 (2)	−0.019 (2)
C8	0.086 (3)	0.089 (3)	0.064 (2)	−0.015 (2)	0.0244 (19)	0.002 (2)
C9	0.079 (2)	0.074 (2)	0.079 (2)	−0.0020 (19)	0.014 (2)	0.019 (2)
C10	0.073 (2)	0.066 (2)	0.076 (2)	0.0035 (17)	0.0154 (18)	0.0082 (18)
C11	0.084 (3)	0.094 (3)	0.060 (2)	−0.011 (2)	0.0009 (18)	−0.0074 (19)
C12	0.096 (3)	0.121 (3)	0.091 (3)	−0.026 (3)	0.011 (2)	−0.011 (3)
C13	0.095 (3)	0.140 (4)	0.100 (3)	−0.016 (3)	−0.013 (2)	−0.030 (3)

Geometric parameters (Å, º)

Cl1—C6	1.729 (3)	C5—C10	1.391 (4)
Cl2—C8	1.728 (3)	C6—C7	1.404 (5)
N1—C2	1.326 (3)	C7—C8	1.379 (4)
N1—N2	1.351 (3)	C7—H7	0.9300
N1—C3	1.457 (3)	C8—C9	1.348 (4)
N2—C1	1.304 (4)	C9—C10	1.382 (4)
N3—C2	1.339 (4)	C9—H9	0.9300
N3—C1	1.342 (4)	C10—H10	0.9300
C1—H1	0.9300	C11—C12	1.478 (4)
C2—H2	0.9300	C11—H11A	0.9700
C3—C4	1.520 (4)	C11—H11B	0.9700
C3—H3A	0.9700	C12—C13	1.488 (5)
C3—H3B	0.9700	C12—H12A	0.9700
C4—C5	1.530 (4)	C12—H12B	0.9700
C4—C11	1.562 (4)	C13—H131	0.9600
C4—H4	0.9800	C13—H132	0.9600
C5—C6	1.377 (4)	C13—H133	0.9600
C2—N1—N2	110.2 (3)	C8—C7—H7	120.7
C2—N1—C3	127.8 (3)	C6—C7—H7	120.7
N2—N1—C3	122.0 (2)	C9—C8—C7	120.2 (3)
C1—N2—N1	101.6 (2)	C9—C8—Cl2	120.9 (3)
C2—N3—C1	101.1 (3)	C7—C8—Cl2	118.9 (3)
N2—C1—N3	116.8 (3)	C8—C9—C10	121.0 (3)
N2—C1—H1	121.6	C8—C9—H9	119.5
N3—C1—H1	121.6	C10—C9—H9	119.5
N1—C2—N3	110.2 (3)	C9—C10—C5	121.1 (3)
N1—C2—H2	124.9	C9—C10—H10	119.5
N3—C2—H2	124.9	C5—C10—H10	119.5

N1—C3—C4	113.2 (2)	C12—C11—C4	113.1 (3)
N1—C3—H3A	108.9	C12—C11—H11A	109.0
C4—C3—H3A	108.9	C4—C11—H11A	109.0
N1—C3—H3B	108.9	C12—C11—H11B	109.0
C4—C3—H3B	108.9	C4—C11—H11B	109.0
H3A—C3—H3B	107.8	H11A—C11—H11B	107.8
C3—C4—C5	108.0 (2)	C11—C12—C13	113.9 (3)
C3—C4—C11	111.8 (3)	C11—C12—H12A	108.8
C5—C4—C11	111.9 (2)	C13—C12—H12A	108.8
C3—C4—H4	108.3	C11—C12—H12B	108.8
C5—C4—H4	108.3	C13—C12—H12B	108.8
C11—C4—H4	108.3	H12A—C12—H12B	107.7
C6—C5—C10	117.1 (3)	C12—C13—H131	109.5
C6—C5—C4	123.3 (3)	C12—C13—H132	109.5
C10—C5—C4	119.6 (3)	H131—C13—H132	109.5
C5—C6—C7	122.0 (3)	C12—C13—H133	109.5
C5—C6—Cl1	121.4 (3)	H131—C13—H133	109.5
C7—C6—Cl1	116.7 (3)	H132—C13—H133	109.5
C8—C7—C6	118.7 (3)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···N3[i]	0.97	2.52	3.489 (4)	174

Symmetry code: (i) x, −y+1, z+1/2.