

ω scans	$R_{\text{int}} = 0.046$
Absorption correction:	$\theta_{\text{max}} = 26.02^\circ$
empirical (SADABS;	$h = -8 \rightarrow 9$
Sheldrick, 1996)	$k = -9 \rightarrow 9$
$T_{\text{min}} = 0.534$, $T_{\text{max}} = 0.777$	$l = -10 \rightarrow 10$
3587 measured reflections	76 standard reflections
1386 independent reflections	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.062$	$\Delta\rho_{\text{max}} = 1.415 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.132$	(0.93 \AA from Br1)
$S = 1.080$	$\Delta\rho_{\text{min}} = -1.111 \text{ e } \text{\AA}^{-3}$
1386 reflections	(0.80 \AA from C41)
87 parameters	Extinction correction: none
H atoms: see below	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2$	<i>International Tables for</i>
$+ 2.3936P]$	<i>Crystallography</i> (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

	$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^*$			
	x	y	z	U_{eq}
Br1	0.0527 (2)	0.18021 (17)	1.12747 (18)	0.0430 (3)
N1	0.1897 (13)	0.3823 (12)	0.6779 (12)	0.037 (2)
C2	0.2587 (13)	0.5649 (14)	0.6080 (15)	0.035 (2)
C3	0.3202 (14)	0.6750 (12)	0.4160 (14)	0.032 (2)
C31	0.3942 (18)	0.8784 (15)	0.3438 (19)	0.059 (4)
C4	0.3021 (14)	0.5852 (13)	0.3043 (13)	0.031 (2)
C41	0.3515 (18)	0.6936 (18)	0.0992 (12)	0.059 (3)
C5	0.2296 (14)	0.3954 (13)	0.3833 (14)	0.036 (2)
C6	0.1763 (15)	0.2966 (13)	0.5721 (15)	0.036 (2)

The data collection nominally covered over a sphere of reciprocal space, by a combination of five sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω . The crystal-to-detector distance was 5.95 cm. Coverage of the unique set is over 88% complete to at least 25° in θ . Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. Cell reduction revealed that the cell could be transformed to a monoclinic C -centred one, but R_{int} and R_σ of 0.046 and 0.066, respectively, were significantly better for the triclinic case than for a monoclinic lattice (0.146 and 0.079). Furthermore, the data showed a suspicious value of 0.488 for $\langle E^2 - 1 \rangle$, which is a warning sign for twinning. The structure could be solved in the triclinic space group $P\bar{1}$ with many difficulties. During refinement, large positional shifts led to unreasonable molecular geometry, and additional peaks appeared in the difference map. This behaviour is typical of merohedral twins, which are formed when the metric symmetry of the unit cell is higher than that of its contents. Under these conditions, a distinct symmetry element of the higher symmetry cell can be used as a twin law. Here the mirror plane perpendicular to the b axis of the monoclinic cell was selected and then expressed with respect to the triclinic axes by the matrix $(\bar{1}00/010/\bar{1}01)$. After allowing for twinning, the refinement proceeded normally; the twin scale factor was 0.647 (3). H atoms H1, H2, H31A, H41B and H5 were located by difference Fourier synthesis; the others were placed at calculated positions. While H1 was refined isotropically, the others were refined with fixed individual

displacement parameters [$U(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ or $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] using a riding model with $\text{C}-\text{H}_{\text{methyl}} = 0.98$ or $\text{C}-\text{H}_{\text{aromatic}} = 0.95 \text{ \AA}$.

Data collection: SMART (Siemens, 1995). Cell refinement: SMART. Data reduction: SAINT (Siemens, 1995). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: XP in SHELXTL-Plus (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1209). Services for accessing these data are described at the back of the journal.

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6-Chloro-4-(*o*-chlorobenzyl)-3-methylpyridazine at 173 K

NOUR-EDDINE BENCHAT,^a JAMAL TAOUFIK,^a EL-MOKHTAR ESSASSI,^b ABDELKRIM RAMDANI,^c BRAHIM EL-BALI^d AND MICHAEL BOLTE^e

^aLaboratoire de Chimie Thérapeutique, Faculté de Médecine et de Pharmacie, Rabat, Morocco, ^bLaboratoire de Chimie Organique Hétérocyclique, Faculté des Sciences, Avenue Ibn Batouta, Rabat, Morocco, ^cLaboratoire de Chimie Organique Physique, Faculté des Sciences, Oujda, Morocco, ^dUFR 'Matériaux, Membranes et Environnement', LMPE, Faculté des Sciences, Dhar Mehraz, Fes, Morocco, and ^eInstitut für Organische Chemie, J. W. Goethe-Universität Frankfurt, Marie-Curie-Straße 11, 60439 Frankfurt/Main, Germany.
 E-mail: bolte@chemie.uni-frankfurt.de

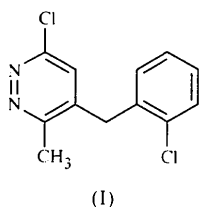
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Abstract

The title compound, C₁₂H₁₀Cl₂N₂, crystallizes with two independent molecules in the asymmetric unit, which differ significantly only in the two central torsion angles. The intermolecular packing is stabilized by short C—H...N contacts.

Comment

Pyridazine derivatives are known particularly for their pharmacological significance. They have attracted notice since the work by Overend & Wiggins (1947) and their chemistry has been described comprehensively by Tišler & Stanovnik (1968). New organic compounds displaying anticonvulsive properties have been reported by Foussard-Blan & Lacroix (1991) and Marion (1991). We have synthesized the title compound, (I), as described by Taoufik (1982), Taoufik *et al.* (1984) and Rubat *et al.* (1990).



Compound (I) crystallizes with two independent molecules in the asymmetric unit, which differ significantly only in the dihedral angles about the pairs of bonds C1—C2 and C1—C11, and C1A—C2A and C1A—C11A (Table 1). The two aromatic rings enclose angles of

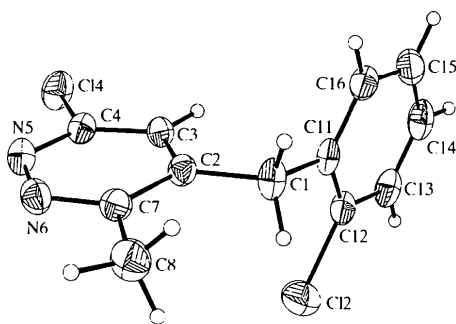


Fig. 1. Perspective view of one of the two independent molecules of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

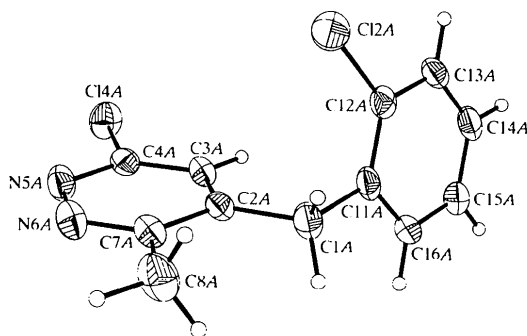


Fig. 2. Perspective view of the second molecule of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

86.38 (5) and 77.56 (5)° for the two molecules in the asymmetric unit. The intermolecular packing is stabilized by short N···H—C contacts: N5···H14ⁱ 2.822 Å and N5···H14ⁱ—C14ⁱ 128.9°; N6···H13ⁱ 2.817 Å and N6···H13ⁱ—C13ⁱ 148.1°; N5A···H14Aⁱⁱ 2.657 Å and N5A···H14Aⁱⁱ—C14Aⁱⁱ 128.1°; N6A···H13Aⁱⁱ 2.562 Å and N6A···H13Aⁱⁱ—C13Aⁱⁱ 148.7° [symmetry codes: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $x, \frac{3}{2} - y, \frac{1}{2} - z$].

Experimental

Condensation of levulinic acid and *o*-chlorobenzaldehyde gives arylmethyllevulinic acid, which is treated with hydrazine in ethanol to give 5-(*o*-chlorobenzylidene)-6-methylpyridazin-3-one. Addition of POCl₃ leads to the title compound. Single crystals were obtained by recrystallization from ether.

Crystal dataC₁₂H₁₀Cl₂N₂ $M_r = 253.12$

Monoclinic

 $P2_1/c$ $a = 12.8011(2) \text{ \AA}$ $b = 9.6258(2) \text{ \AA}$ $c = 19.4453(2) \text{ \AA}$ $\beta = 92.882(1)^\circ$ $V = 2393.04(7) \text{ \AA}^3$ $Z = 8$ $D_x = 1.405 \text{ Mg m}^{-3}$ D_m not measuredMo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 7731 reflections

 $\theta = 1-25^\circ$ $\mu = 0.515 \text{ mm}^{-1}$ $T = 173 \text{ K}$

Block

 $0.70 \times 0.40 \times 0.20 \text{ mm}$

Light yellow

Data collection

Siemens CCD three-circle diffractometer

 ω scans

Absorption correction:

 ψ scan (SADABS;

Sheldrick, 1996)

 $T_{\min} = 0.555, T_{\max} = 0.902$

11 236 measured reflections

3972 independent reflections

3278 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.030$ $\theta_{\max} = 26.23^\circ$ $h = -14 \rightarrow 15$ $k = -9 \rightarrow 10$ $l = -22 \rightarrow 23$ **Refinement**Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.034$ $wR(F^2) = 0.081$ $S = 1.052$

3972 reflections

291 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 0.9979P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.211 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.264 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

C2—C3	1.376 (3)	C2A—C3A	1.373 (3)
C2—C7	1.423 (3)	C2A—C7A	1.420 (3)
C3—C4	1.393 (3)	C3A—C4A	1.393 (3)
C4—N5	1.321 (2)	C4A—N5A	1.322 (2)
C4—C14	1.741 (2)	C4A—C14A	1.742 (2)
N5—N6	1.358 (2)	N5A—N6A	1.360 (2)
N6—C7	1.337 (3)	N6A—C7A	1.334 (3)
C12—C12	1.755 (2)	C12A—C12A	1.753 (2)

C3—C2—C7	116.59 (17)	C3A—C2A—C7A	116.72 (18)
C2—C3—C4	117.34 (17)	C2A—C3A—C4A	117.40 (17)
N5—C4—C3	125.22 (18)	N5A—C4A—C3A	125.11 (19)
N5—C4—C14	114.58 (14)	N5A—C4A—C14A	114.99 (15)
C3—C4—C14	120.19 (15)	C3A—C4A—C14A	119.88 (15)
C4—N5—N6	117.85 (16)	C4A—N5A—N6A	117.65 (17)
C7—N6—N5	120.41 (16)	C7A—N6A—N5A	120.60 (16)
N6—C7—C2	122.54 (18)	N6A—C7A—C2A	122.49 (18)
C11—C1—C2—C3	12.6 (3)		
C11—C1—C2—C7	−168.00 (19)		
C2—C1—C11—C16	−99.7 (2)		
C2—C1—C11—C12	80.4 (2)		
C11A—C1A—C2A—C3A	6.9 (3)		
C11A—C1A—C2A—C7A	−173.37 (18)		
C2A—C1A—C11A—C16A	−105.2 (2)		
C2A—C1A—C11A—C12A	74.9 (2)		

The data collection nominally covered over a sphere of reciprocal space, by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω . The crystal-to-detector distance was 5.95 cm. Coverage of the unique set was over 88% complete to at least 26° in θ . Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters $\{U(\text{H}) = 1.5U_{\text{eq}}[\text{C}(\text{methyl})]\}$ or $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})\}$ using a riding model with C—H(secondary) = 0.99, C—H(methyl) = 0.98 or C—H(aromatic) = 0.95 Å. The methyl groups were allowed to rotate about their local three-fold axis.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1176). Services for accessing these data are described at the back of the journal.

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Phenanthrene-4-carboxylic Acid and 1,2-Dihydrophenanthrene-4-carboxylic Acid

LAWRENCE J. FITZGERALD AND ROGER E. GERKIN

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: gerkin@chemistry.ohio-state.edu

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Abstract

Phenanthrene-4-carboxylic acid, C₁₅H₁₀O₂, crystallized in the centrosymmetric space group *P2₁/n*, while 1,2-dihydrophenanthrene-4-carboxylic acid, C₁₅H₁₂O₂, crystallized in the centrosymmetric space group *Pbca*. In each structure, there is a single type of hydrogen bond: it is of the cyclic dimer type about a center of symmetry. The O_{donor}···O_{acceptor} distances are 2.634 (2) and 2.651 (2) Å, and the O—H···O angles are 176 (3) and 173 (2)°, respectively, for the two structures. In each structure, the carboxy H and O atoms are ordered. The phenanthrene core of the fully aromatic acid is roughly planar; the dihedral angle between the best-fit core plane and the carboxy group plane is 63.7 (1)°. As expected, the hydrogenated ring of the second acid is much less nearly planar; the remaining naphthalenoid core is, however, roughly planar and the dihedral angle between this best-fit plane and the carboxy group plane is 60.4 (1)°.

Comment

This is one of a series of reports on hydrogen bonding in polyaromatic carboxylic acids, and follows a report on phenanthrene-9-carboxylic acid (Fitzgerald & Gerkin, 1997). In phenanthrene-4-carboxylic acid, (1), and in 1,2-dihydrophenanthrene-4-carboxylic acid, (2), the hydrogen bonding is of the cyclic dimer type about a center of symmetry, as shown in Figs. 1(a) and 1(b), which also present the numbering schemes. The geometric parameters of the hydrogen bonds are given in Table 3. In terms of graph-set analysis (Bernstein *et al.*, 1995), for both (1) and (2), the first-level graph set is R₂²(8) and there are no higher-level graphs. As expected for ordered carboxy O atoms, the principal axes of the displacement tensors of O1 and O2 in both structures are almost normal to the carboxy group plane, as evident in Figs. 1(a) and 1(b). The carboxylic H atom, H4, is also ordered in both structures; although in (1), its distance from O1 is greater than customary (Table 3), there is no evidence for a H atom at this or a lesser distance from O2, and refinement is complicated by the occurrence of a small amount of carboxy group disorder as described below.