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2-Amino-4-(4-chlorophenyl)-5,6-dihydrobenzo[*h*]quinoline-3-carbonitrile, a Strongly Fluorescent Phenanthridine Analogue

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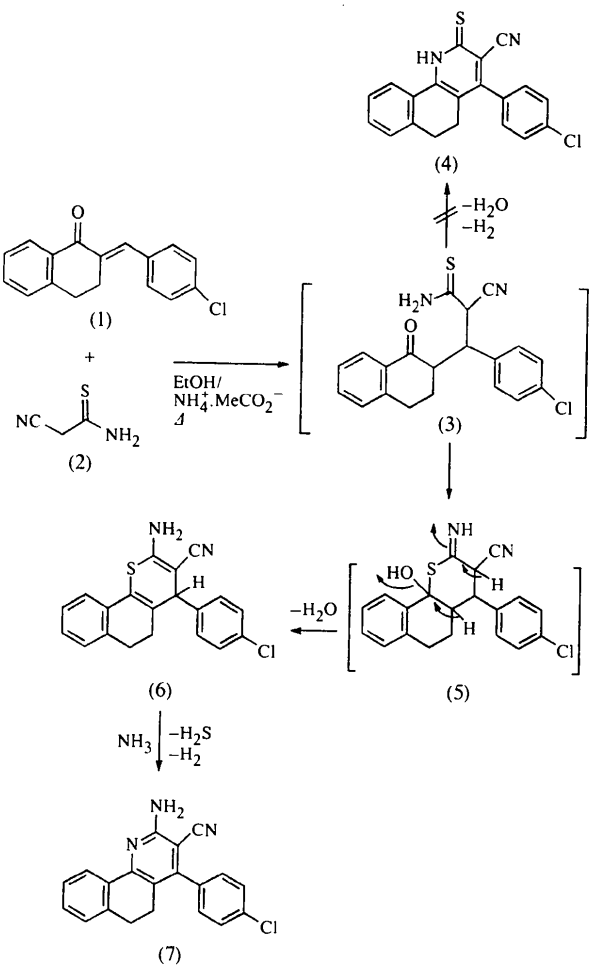
Abstract

The title compound, $C_{20}H_{14}ClN_3$, crystallizes with two independent molecules, differing mainly in the orientation of the chlorophenyl group. The outermost rings of the tricyclic ring system subtend an interplanar angle of 18.10 (9)° in one molecule and 22.51 (6)° in the other. Hydrogen bonding of the form N—H···N leads to ribbons of one molecule and dimers of the other; these occupy distinct regions of the cell.

Comment

In the course of our studies aimed at the development of efficient and simple procedures for the synthesis of laser dyes (Elgemeie & Fathy, 1995; Elgemeie *et al.*, 1992, 1996), we have carried out the reaction of 2-(4-chlorophenyl)methylidene-1-tetralone, (1), with cyanothioacetamide, (2), in boiling ethanol containing a catalytic amount of ammonium acetate, leading to the phenanthridine analogue (7) rather than the expected phenanthridine (4) (see Scheme below). The mechanism for the formation of (7) from the reaction of (1) and (2) is assumed to proceed *via* addition of the active methylene group of cyanothioacetamide, (2), to the double bond of (1) to give the intermediate (3). This Michael adduct then cyclizes *via* water elimination to form a 1,4-dihydrothiopyran, (5), which undergoes ring cleavage by ammonia followed by elimination of hydrogen sulfide and oxidation to give (7). The latter shows high fluorescence efficiency (Φ values as high as 0.99 were obtained), suggesting that this derivative and related analogues may be potential candidates for laser dyes, solar harvesting dyes or fluorogenic dyes.



The X-ray structure analysis determines the product unambiguously to be (7). The compound crystallizes with two independent molecules (Fig. 1). Bond lengths and angles are as expected; in particular, the tricyclic ring systems are closely similar (r.m.s. deviation for 14 ring atoms is 0.047 Å). Minor differences are seen in, for example, the C2—N3 bond length [1.346 (3) and 1.361 (3) Å], which may be associated with the different hydrogen-bonding patterns (see below). The main difference between the two molecules is the orientation of the chlorophenyl group, with C4a—C4—C11—C12 torsion angles of 55.2 (3) and −88.9 (3)°.

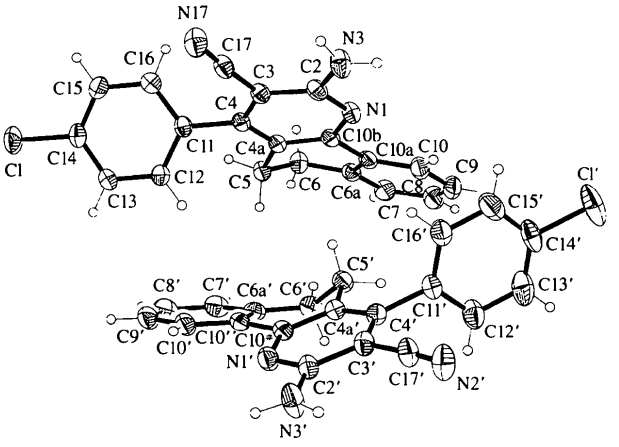


Fig. 1. The molecules of the title compound in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary. The H atom on C9 is obscured by C15′.

The outermost rings of the tricyclic system are each planar, with an interplanar angle of 18.10 (9)° in one molecule and 22.51 (6)° in the other. This twisting is facilitated by the saturation at C5—C6; combined with the absence of steric pressure (there is no H atom at N1), this allows the bay angles at C10a and C10b to adopt normal sp^2 values.

The two independent molecules pack so as to occupy different regions of the cell. The molecules are linked by weak N—H···N hydrogen bonds (Table 2). One type of molecule forms ribbons perpendicular to **b** at $z \simeq \frac{1}{4}$, $\frac{3}{4}$ (Fig. 2), whereas the other forms centrosymmetric dimers in the regions $z \simeq 0$, $\frac{1}{2}$ (not shown). The H02′ atom is not involved in hydrogen bonds.

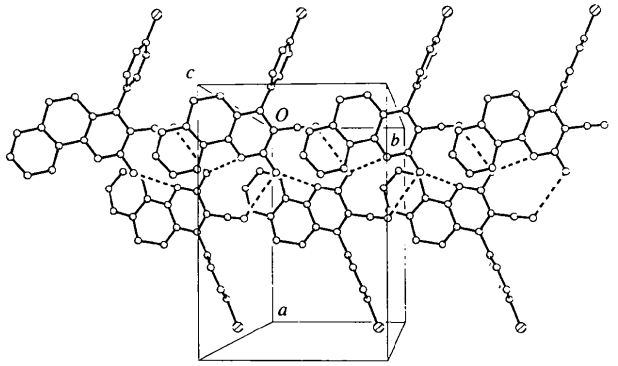


Fig. 2. Packing of one type of molecule to form hydrogen-bonded ribbons. Hydrogen bonds are indicated as dashed lines (H atoms have been omitted for clarity).

Experimental

A solution of 2-(4-chlorophenyl)methylidene-1-tetralone [(1); 2.68 g, 0.01 mol] and cyanothioacetamide [(2); 1.00 g, 0.01 mol] in ethanol (30 ml) and ammonium acetate (1.5 mg, 0.02 mmol) was refluxed for 3 h, cooled, and the precipitate filtered off and crystallized from ethanol in 60% yield (m.p. 483 K).

Crystal data

$C_{20}H_{14}ClN_3$
M_r = 331.79
Monoclinic
$P2_1/n$
a = 11.885 (3) Å
b = 8.004 (2) Å
c = 33.795 (7) Å
β = 90.59 (2)°
V = 3214.6 (13) Å^3
Z = 8
D_x = 1.371 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 60 reflections
θ = 10.0–11.5°
μ = 0.243 mm^{-1}
T = 143 (2) K
Tablet
0.50 × 0.50 × 0.25 mm
Orange

Data collection

Stoe Stadi-4 diffractometer
ω scans
Absorption correction: none
9267 measured reflections
5675 independent reflections
4268 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 25.04°
$h = 0 \rightarrow 14$
$k = -9 \rightarrow 4$
$l = -40 \rightarrow 40$
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.107
S = 1.044
5675 reflections
449 parameters
H-atom treatment: NH_2 free, others riding
$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 1.6551P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.219 e Å^{-3}
$\Delta\rho_{min}$ = −0.317 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C2	1.341 (3)	N1′—C2′	1.337 (3)
N1—C10b	1.341 (3)	N1′—C10#	1.342 (3)
C2—N3	1.346 (3)	C2′—N3′	1.361 (3)
C10—C10a—C10b	120.6 (2)	C10′—C10′′—C10#	120.4 (2)
N1—C10b—C10a	116.14 (18)	N1′—C10#—C10′′	116.3 (2)
C4—C4a—C5—C6	146.4 (2)	C4′—C4a′—C5′—C6′	149.1 (2)
C4a—C5—C6—C6a	49.8 (2)	C4a′—C5′—C6′—C6a′	52.4 (2)
C5—C6—C6a—C7	147.3 (2)	C5′—C6′—C6a′—C7′	146.1 (2)
C4a—C4—C11—C12	55.2 (3)	C4a′—C4′—C11′—C12′	−88.9 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N3—H01···N1′	0.87 (3)	2.27 (3)	3.050 (3)	148 (2)
N3—H02···N17^{ii}	0.85 (3)	2.35 (3)	3.188 (3)	167 (3)
N3′—H01′···N17′^{iii}	0.88 (3)	2.51 (3)	3.324 (3)	155 (2)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $-x, 2 - y, -z$.

Data collection: *DIF*4 (Stoe, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used

to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1235). Services for accessing these data are described at the back of the journal.

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7-(Carboxymethyl)-6-chloropurine Ethyl Ester†

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Abstract

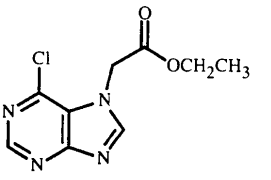
Alkylation of 6-chloropurine using ethyl bromoacetate gives a mixture of regioisomers from which the title compound, $C_9H_9ClN_4O_2$, was isolated in crystalline form. The ethyl acetate fragment attached at N7 avoids steric hindrance by emerging from the ring almost orthogonally. Two ring C atoms donate weak intermolecular hydrogen bonds to the carbonyl O12 and ring N3 atoms.

† Alternative name: ethyl 6-chloropurine-7-acetate.

Comment

Peptidic nucleic acids (PNAs) have important and profound DNA molecular recognition properties (Hyrup & Nielsen, 1996). The achiral uncharged backbone of PNA is composed of covalently linked *N*-(2-aminoethyl)-glycine units to which are attached the heterocyclic bases of DNA through carboxymethyl bridging groups. Since modifications to the PNA bases attract sustained interest in efforts to extend the molecular recognition properties of PNAs, we selected the purine base hypoxanthine as a candidate for incorporation into PNAs. A useful role for hypoxanthine has been as a universal base in polymerase chain reaction (PCR) (Ohtsuka *et al.*, 1985), where the base is attached through the N9 atom to 2′-deoxyribose in oligonucleotide primers. The isomeric α-^{7}H nucleoside, where the N7 of hypoxanthine is connected to α-configured 2′-deoxyribose, displays interesting DNA recognition properties when incorporated into triplex-forming oligonucleotides (Marfurt *et al.*, 1996).

An evaluation of PNAs containing hypoxanthine linked through N9 and N7 necessitates efficient synthesis of protected building blocks of both regioisomers. A general but by no means sole route to PNA building blocks requires attachment of a carboxymethyl substituent, usually as its ethyl ester, to the appropriate heterocyclic base. Direct alkylation of hypoxanthine using ethyl bromoacetate in the presence of potassium carbonate gives peralkylated products with the major component, diethyl 3,7-hypoxanthyldiacetate, isolable in 61% yield (Sood *et al.*, 1998*a*). Direct alkylation of 6-chloropurine can attach substituents at positions N9 or N7 to give a mixture of regioisomers (Dalby *et al.*, 1993). Subsequent hydrolysis or displacement of the chloro group at C6 can then provide hypoxanthine or O6-protected precursors. Reaction of 6-chloropurine with ethyl bromoacetate gave a separable mixture of N9 and N7 regioisomers from which the title compound, (1), was isolated in crystalline form. We undertook the crystal structure determination to establish that the ethyl acetate side chain was indeed attached at N7 in (1).



(1)

Compared with 9-(carboxymethyl)-2,6-dichloropurine ethyl ester, (2) (Chan *et al.*, 1995), the removal of the 2-chloro substituent and the change of regioisomer cause sizeable alternating changes in the internal angles of the six-membered ring: increases of 1.1 (2), 2.4 (2) and 1.5 (2)° at N1, N3 and C5, respectively, and decreases of 1.9 (3), 2.7 (2) and 0.4 (2)° at C2, C4 and C6,