

(5-Bromopyrrol-3-yl)cyclohexylmethanone

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Key indicators

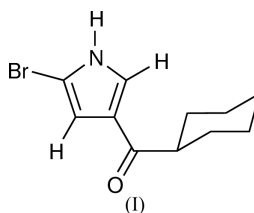
Single-crystal X-ray study
T = 100 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.023
wR factor = 0.056
Data-to-parameter ratio = 14.6

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $\text{C}_{11}\text{H}_{14}\text{BrNO}$, contains a single halo- and keto-substituted pyrrole ring. A very short hydrogen bond between the amine H atom of one molecule and the carbonyl O atom of another has an $\text{N}\cdots\text{O}$ distance of $2.765(2) \text{ \AA}$.

Comment

The bromopyrrole moiety of (5-bromopyrrol-3-yl)cyclohexylmethanone, (I), is quite similar to other halopyrroles in the literature (Allen *et al.*, 1983). Notable among these are: oroidin (Walker *et al.*, 1981), pyrrolomycin B (Kaneda *et al.*, 1981), axinohydantoin (Pettit *et al.*, 1990), 2-bromoaldisin (Xu *et al.*, 2001), 2-cyano-4,5-dibromopyrrole (Konig *et al.*, 1998), 5,5'-dibromo-3,3'-diethyl-4,4'-dimethyl-2,2'-pyrromethene (Becker *et al.*, 1978), and ethyl 4,7-ethano-3-iodo-5,6-dihydro-2H-isoindole-1-carboxylate (Uno *et al.*, 2000). The distances and angles of (I) are as expected (Allen *et al.*, 1983), including the relatively long distance of $1.434(1) \text{ \AA}$ for the C—C bond opposite to the N—H group within the pyrrole ring, and the relatively short N—C distances of $1.357(2)$ and $1.368(2) \text{ \AA}$. The latter N—C distances compare well with those of the substituted pyrroles in 2-bromoaldisin, axinohydantoin, pyrrolomycin B, and ethyl 4,7-ethano-3-iodo-5,6-dihydro-2H-isoindole-1-carboxylate. On the other hand, for the dibromo- and bromo-ethyl-methyl-substituted pyrroles of 2-cyano-4,5-dibromopyrrole and 5,5'-dibromo-3,3'-diethyl-4,4'-dimethyl-2,2'-pyrromethene, respectively, the N—C bond of the H—N—C—Br moiety is the shortest in the ring by about 0.03 \AA . These inequalities demonstrate that the magnitude and symmetrical disposition of bonds in the pyrrole ring are expected to be quite sensitive to the electronic and chemical properties of substituents on the ring.



Although no intramolecular hydrogen bond (to Br) exists, the Br atom of the H—N—C—Br moiety is closer to the N—H group than the adjacent C—H group. For (I), the Br—C—N angle is $120.8(1)^\circ$, which compares well with the average value of $121.2(5)^\circ$ for the seven compounds referenced above. This is significantly smaller than the angle of 125° expected for a symmetrically placed pyrrole-ring substituent.

In (I), there is one H atom that engages in hydrogen bonding; this appears to be the dominant non-dispersive

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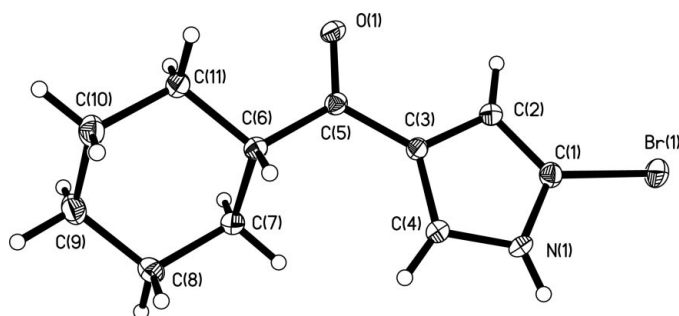


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

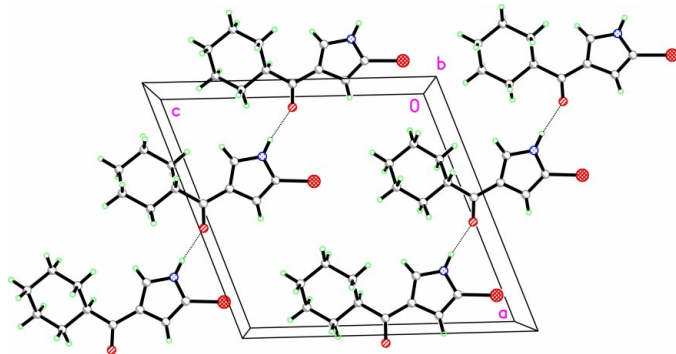


Figure 2
Projection view of the crystal packing of (I), approximately along the *b* axis. Hydrogen bonds are indicated by dotted lines

intermolecular interaction. This hydrogen bond may be expected, since it involves the sole hydrogen-bond donor, namely N—H, and the most likely hydrogen-bond acceptor, the carbonyl O atom. The N—H bond vector is directed nearly along the N···O vector, such that the H···O distance may be regarded as approximately $(2.80 - D)$ Å, where *D* is the N—H distance. This is useful in considering the hydrogen-bond geometry based upon the X-ray derived value for N—H [here, 0.82 (2) Å] versus the more accurate internuclear value (e.g. *D* = 1.03 Å) from neutron-diffraction studies. Although it is approximately planar and contains *sp*² pyrrole ring atoms, the title compound does not engage in significant π – π intermolecular interactions. This characteristic of the crystal packing is probably due to the pyrrole ring being only a small part of the entire molecule and the cyclohexyl substituent being quite bulky.

Experimental

Crystals of (5-bromo-pyrrol-3-yl)cyclohexylmethanone (m.p. 418–419 K) were obtained from a solution in hexanes–ethyl acetate (9:1). Bromination of pyrroles is sometimes difficult to control, both in terms of position selectivity and the extent of bromination (Gilow & Burton, 1981). The initial products may also isomerize under certain reaction conditions (Dvornikova & Kamienska-Trela, 2002). In the course of an alkaloid total synthesis, we had occasion to study the bromination of cyclohexyl(pyrrol-3-yl)methanone. Although bromination with *N*-bromosuccinimide was non-selective, the use of tetrahydrofuran dibromide/sodium acetate as the bromination

reagent (Anderson & Huang, 1967) led smoothly to a single product when the reaction was taken to 40% completion. Analysis of ¹H NMR chemical shifts and coupling constants indicated this to be (5-bromo-pyrrol-3-yl)cyclohexylmethanone [(I); 77% yield], by comparison with (5-bromopyrrol-3-yl)ethanone (Anderson & Huang, 1967). Because the earlier assignment had been based on analogy with non-brominated models, and because the coupling constants are of similar magnitude ($J_{2,4} = 1.8$ Hz, $J_{1,2} = 3.0$ Hz and $J_{1,4} = 2.6$ Hz), we undertook the crystallographic study to confirm the site selectivity of bromination.

Crystal data

$C_{11}H_{14}BrNO$
M_r = 256.14
Monoclinic, $P2_1/n$
a = 12.0951 (6) Å
b = 7.3006 (3) Å
c = 13.0038 (6) Å
 β = 110.280 (1)°
V = 1077.07 (9) Å³
Z = 4

$D_x = 1.580$ Mg m^{−3}
Mo *K*α radiation
Cell parameters from 6056 reflections
 $\theta = 2.8$ – 30.5°
 $\mu = 3.78$ mm^{−1}
T = 100 (2) K
Lath, colourless
0.27 × 0.15 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.685$, $T_{\max} = 0.611$
12893 measured reflections

2677 independent reflections
2380 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\max} = 28.3^\circ$
h = −16 → 16
k = −9 → 9
l = −17 → 17

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.056$
S = 1.01
2677 reflections
183 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.023P)^2 + 0.6P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.38$ e Å^{−3}
 $\Delta\rho_{\min} = -0.30$ e Å^{−3}

Table 1

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1N···O1 ⁱ	0.82 (2)	1.97 (2)	2.765 (2)	163 (2)

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

The hydrogen-bond geometry corresponding to the expected 1.03 Å internuclear distance for N—H in this structure is: N1—H1N 1.03 (2), H1N···O1ⁱ 1.72 (2), N1···O1ⁱ 2.765 (2) Å, N1—H1N···O1ⁱ 161 (2)° [symmetry code: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$]. All H-atom positions were observed in a difference Fourier map and were refined with isotropic displacement parameters. The C—H bond lengths are in the range 0.92–1.02 (2) Å, and the N—H bond length is 0.82 (2) Å.

Data collection: SMART (Bruker, 2000); cell refinement: SMART; data reduction: SAINT-Plus (Bruker, 2000); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2000); software used to prepare material for publication: SHELXTL.

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