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Low-temperature study of 3-acetylindole at 110 K

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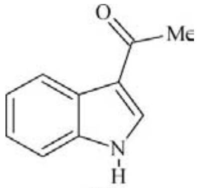
The title compound, $C_{10}H_9NO$, contains an acetyl group that is nearly coplanar with the indole ring system, with an angle between the planes of the heterocyclic ring and the acetyl group of 1.75 (17)°. The planes of the benzene and pyrrole rings in the indole system make a dihedral angle of 2.05 (11)°. Each molecule in the unit cell is linked through $\mathrm{N-H\cdots O}$ hydrogen bonds to two other molecules, forming hydrogen-bonded chains in the [101] direction with graph set *C*(6). The significance of this study lies in the analysis of the interactions occurring *via* hydrogen bonds in this structure, as well as in the comparison drawn between the molecular structure of the title compound and those of several other indole derivatives possessing a 3-carbonyl group. The correlation between the IR spectrum of this compound and the structural data is also discussed.

Comment

The indole ring system is the structural element of many natural and/or synthetic organic compounds exhibiting biological and pharmacological activities, such as anti-allergic (Shigenaga *et al.*, 1993), antimicrobial (Oh *et al.*, 2006), antifungal and antibacterial properties (Quetin-Leclercq *et al.*, 1995; Singh *et al.*., 2000; Ablordeppey *et al.*, 2002), as well as anticancer properties (Dashwood *et al.*, 1994; Andreani *et al.*, 2001; Gul & Hamann, 2005; Gupta *et al.*, 2007). The most well known indole compounds are the tryptophan-derived tryptamine alkaloids, *e.g.* the neurotransmitter serotonin (Simonenkov & Fedorov, 2002; Nichols & Nichols, 2008), the hormone melatonin (Cardinali *et al.*, 2004; Karasek, 2004), the hallucinogens psilocybin (Passie *et al.*, 2002) and *N*,*N*-dimethyltryptamine (DMT) (Strassman, 1996), 2-(5-methoxy-1*H*-indol-3-yl)-*N*,*N*-dimethylethanamine (5-MeO-DMT) (Gouzoulis-Mayfrank *et al.*, 2005), or the ergolines such as lysergic acid diethylamide (LSD) (Appel *et al.*, 2004). The indole derivatives, including the plant hormone auxin (indole-3-acetic acid, IAA) (Chandrasekhar & Raghunathan, 1982; Nigović *et al.*, 2000), the anti-inflammatory drug indomethacin (Chen *et al.*, 2002; Cox & Manson, 2003) and the beta blocker pindolol (Nair *et al.*, 2004), should also be mentioned. In recent years, the synthesis of indole derivatives, especially the triptans, has been a subject of fundamental interest to organic and medicinal chemists. Triptans are selective serotonin (5-$HT_{1B/D}$) agonists developed for the relief of migraine symptoms by targeting the disease pathology (Perry & Markham, 1998; de Vries *et al.*, 1999; Ferrari *et al.*, 2002; Pascual *et al.*, 2007). So far, seven triptans have become available in the USA, *viz.* sumatriptan (Ravikumar *et al.*, 2006), zolmitriptan (Ravikumar *et al.*, 2007*a*), naratriptan (Massiou, 2001), rizatriptan (Ravikumar *et al.*, 2007*b*), frovatriptan (Balbisi, 2006), eletriptan (Goadsby *et al.*, 2000) and almotriptan (Ravikumar *et al.*, 2008). Indole derivatives are also of great importance for the synthesis of pyrroloindoles and carbazoles *via* Diels–Adler cycloaddition or Suzuki–Miyaura reactions (Wenkert *et al.*, 1988; Gribble, 2003; Pathak *et al.*, 2006) or for nucleophilic addition reactions (Agbalyan *et al.*, 1974; Ottoni *et al.*, 1998; Pelkey *et al.*, 1999).



(I)

3-Acetylindole, (I), and indole-3-carbaldehyde have been the subject of a study by us of the generation mechanism of the IR spectra of hydrogen-bonded molecular crystals (Flakus & Hachuła, 2008; Hachuła *et al.*, 2008). Measurement of the IR spectra of polycrystalline and monocrystalline samples of the indole derivatives and theoretical analysis of the results were mainly focused on spectroscopic effects corresponding to the intensity distribution, the influence of temperature, linear dichroism, and the isotopic substitution of deuterium in the above-mentioned molecules measured in the frequency range of the proton and the deuterium stretching vibration bands, *viz.* $\nu_{\mathrm{N-H}}$ and $\nu_{\mathrm{N-D}}$, respectively. These spectroscopic studies were preceded by an analysis of the X-ray crystal structures of the compounds. The crystal structure of indole-3-carbalde-

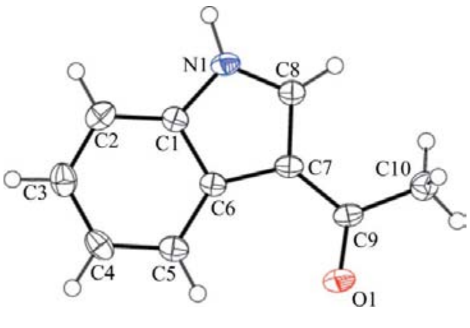


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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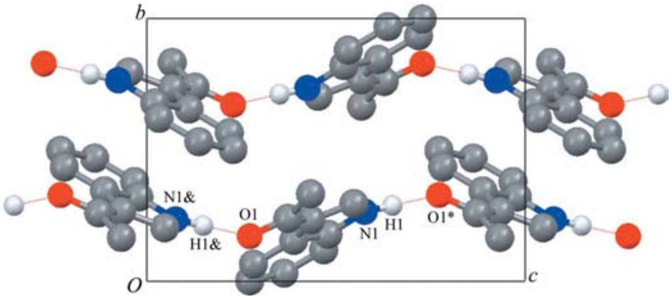

Figure 2
Part of the molecular framework of (I), viewed along the *a* axis, showing the *C*(6) chains. Atoms marked with an asterisk (*) or an ampersand (&) are at the symmetry positions ($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$) and ($x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$), respectively. Dashed lines indicate hydrogen-bonding interactions. For the sake of clarity, all H atoms bonded to C atoms have been omitted.

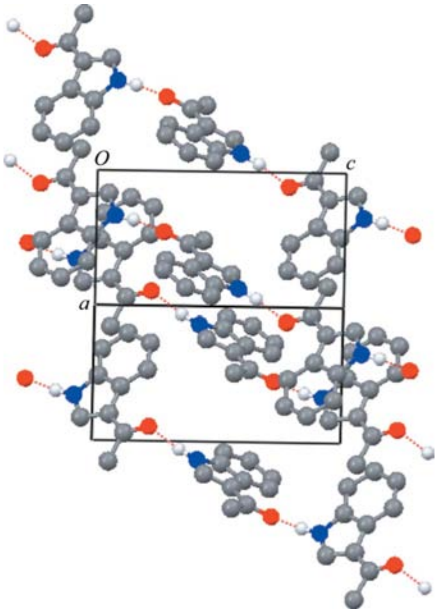

Figure 3
Part of the crystal structure of (I), showing the formation of sheets *via* *C*(6) chains. All H atoms not involved in hydrogen bonding have been omitted for clarity.

hyde has been described previously (Ng, 2007). The molecules of this compound are linked into helical chains along the crystallographic *c* axis by intermolecular N—H···O hydrogen bonds. The structure of (I) has not been reported until now.

Compound (I) crystallizes with one molecule in the asymmetric unit (Fig. 1). The five- and six-membered rings are essentially planar, with r.m.s. deviations from the mean plane of 0.0178 Å. The largest deviations from the least-squares indole plane are observed for atoms C4 [−0.0304 (15) Å] and C6 [0.0225 (16) Å]; atom N1 is out of the indole plane by −0.0185 (13) Å. The dihedral angle between the planes of the pyrrole and benzene rings is 2.05 (11)°. By comparison, this angle is 4.22° in indole-3-carbaldehyde (Ng, 2007) and 0.29° in indole-3-carboxylic acid (Smith *et al.*, 2003). The N1—C1 and N1—C8 bond lengths [1.392 (3) and 1.342 (3) Å, respectively] differ from the corresponding mean values of 1.372 (7) and 1.370 (12) Å, respectively, reported for the indole ring system by Allen *et al.* (1987). This significant asymmetry of the two endocyclic N—C bonds of the heterocyclic ring of (I) may be a result of the electron-withdrawing character of the acetyl group and the preferential conjugation of the C9═O1 bond with C7═C8. Moreover, the N1—C8 bond in (I) is shortened, whereas C7═C8 is elongated (Table 1). The C—C bond opposite the heteroatom is considerably longer than the others. An almost identical shortening of N1—C8 and lengthening of the C7═C8 double bond are found in similar structures, *e.g.* indole-3-carbaldehyde (Ng, 2007), 3-acetyl-1-methoxyindole (Acheson *et al.*, 1980), indole-3-carboxylic acid (Smith *et al.*, 2003) and indole-3-acetic acid (Karle *et al.*, 1964), or in other indole derivatives possessing a 3-carbonyl group but which are unsubstituted at the ring N atom (Damak & Riche, 1977; Hu *et al.*, 2005). This fact is consistent with electron delocalization from the N atom into the acetyl group. Thus, the substitution of an electronegative O atom on the pyrrole ring makes little difference to the π-donor ability of the N atom (Acheson *et al.*, 1980). The sum of the angles around the indole N atom is 359.88°, which indicates that the geometry around this atom is normal sp^2 coordination, as expected for π-conjugation of the indole ring (Huang *et al.*, 2004). The endocyclic C—C bond distances and the angles in (I) are in the normal ranges and are comparable with those of other indole derivatives (Allen *et al.*, 1987).

The acetyl group is almost coplanar with the heterocyclic ring [C8—C7—C9—O1 = −176.80 (18)° and C6—C7—C9—C10 = −177.63 (17)°]. The dihedral angle between the plane of the indole ring system and the plane of the acetyl group (O1/C9/C10) is 1.75 (17)°. The C═O bond distance and O—C—C angle are similar to those in indole-3-carbaldehyde and 3-acetyl-1-methoxyindole [C9—O1 = 1.228 (2) Å and O1—C9—C7 = 124.71 (18)°, and C9—O1 = 1.224 (2) Å and O1—C9—C7 = 120.9 (5)°, respectively]. The geometry of the acetyl group is governed by the repulsive interaction between the carbonyl group and the heterocyclic ring, leading to an enlargement of the O1—C9—C7 and C9—C7—C6 angles and a diminution of O1—C9—C10 and C7—C9—C10 (Table 1). A similar repulsive interaction between the lone pairs on atom O1 and the neighbouring atoms of the indole ring system is observed in indole-3-carbaldehyde (Ng, 2007). The crystal structure similarity between indole-3-carbaldehyde and (I) leads to the conclusion that the replacement of the H atom in the aldehyde group of indole-3-carbaldehyde by a methyl group does not significantly influence the crystal lattice parameters.

There are four molecules in the unit cell at the symmetry positions (x, y, z), ($\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$), ($1 - x, 1 - y, 1 - z$) and ($x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$). Each of these molecules is linked by a single N—H···O hydrogen bond to the other two, forming zigzag chains. Atom N1 of the pyrrole NH group in the molecule at (x, y, z) acts as a hydrogen-bond donor *via* atom H1 to carbonyl atom O1 belonging to the molecule at ($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$) (Fig. 2). The result of this interaction is the formation of hydrogen-bonded chain with a graph-set motif of *C*(6) (Etter

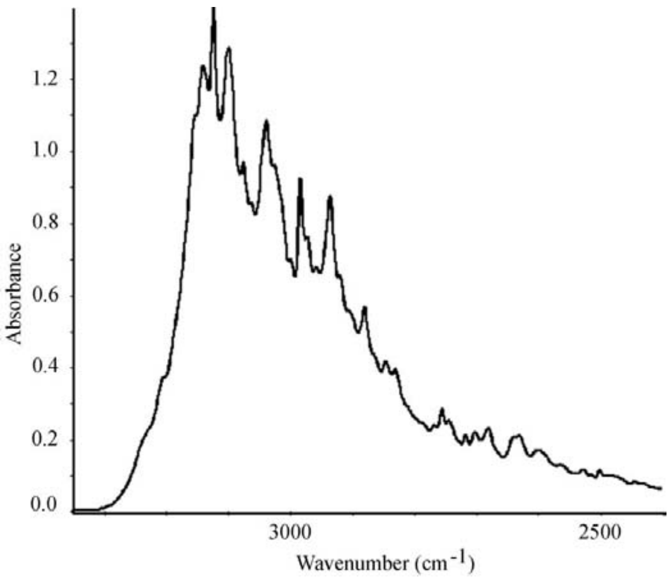

Figure 4
IR spectrum of a sample of 3-acetylindole dispersed in a KBr pellet.

et al., 1990; Bernstein *et al.*, 1995) running along the [101] direction. In the crystal structure of (I), two such chains, related to one another by an inversion centre symmetry operation, pass through each unit cell (Fig. 3). The same graph-set motif of $C(6)$ is observed in indole-3-carbaldehyde (Ng, 2007) and methyl indole-3-carboxylate (Hu *et al.*, 2005). Similar molecular packing can be found in 3-acetoxyindole (Chakraborty *et al.*, 1991), in which the molecules are connected through N—H$\cdots$O hydrogen bonds to form $C(7)$ chains. Judging from the bond distances, the N—H$\cdots$O hydrogen bond between two 3-acetylindole molecules appears to be slightly stronger [N1—H1$\cdots$O1 = 2.788 (2) Å] than that involving two indole-3-carbaldehyde molecules [N1—H1$\cdots$O1 = 2.826 (2) Å]. The hydrogen-bonding interactions are shown in Figs. 2 and 3, and details are given in Table 2.

The polycrystalline spectrum of (I) is shown in Fig. 4. The values of the H—N and N$\cdots$O distances, as well as the N—H$\cdots$O angle (Table 2), characterize this bond as a medium-strength hydrogen bond (Desiraju & Steiner, 1999; Steiner, 2002). The strength of the hydrogen bond in (I) is supported by spectroscopic measurements. The $\nu_{\rm N-H}$ proton stretching vibration band of (I) extends over the frequency range 3300–2400 cm^{-1}. The polycrystalline N—H band is shifted towards the lower frequencies by *ca* 280 cm^{-1} compared with the unperturbed value of 3400 cm^{-1}. This shift in the N—H stretching frequency proves that this N—H$\cdots$ O hydrogen bond is of medium strength. A familiar correlation between the hydrogen-bond energy and the frequency shift of the proton (or deuteron) stretching vibration band is used to justify this statement (Schuster *et al.*, 1976; Schuster & Mikenda, 1999). The N—H$\cdots$O bond length [N1$\cdots$O1 = 2.788 (2) Å] in (I) appears to be slightly shorter than those in other compounds, *e.g.* the *N*-methylamide derivatives [mean N$\cdots$O distance = 2.85 Å; Leiserowitz & Tuval, 1978]. Consequently, the stronger N—H$\cdots$O hydrogen bonds correspond to a larger frequency shift.

Experimental

3-Acetylindole (98% pure), purchased from Sigma–Aldrich, was dissolved in a mixture of acetone and water (1:1 *v*/*v*). After a few weeks, small single crystals of (I) suitable for X-ray diffraction were grown from the solution by slow evaporation at 293 K. The IR spectrum of a polycrystalline sample of (I) dispersed in KBr was measured at the temperature of liquid nitrogen using an FT–IR Nicolet Magna 560 spectrometer operating at a resolution of 2 cm^{-1}. The IR spectrum was recorded in the range 1000–4000 cm^{-1} using an Ever-Glo source, a KBr beamsplitter and a DTGS detector.

Crystal data

$C_{10}H_9NO$
M_r = 159.18
Monoclinic, $P2_1/n$
a = 9.5665 (19) Å
b = 7.6553 (15) Å
c = 11.031 (2) Å
β = 90.77 (3)°
V = 807.8 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 110 (1) K
0.54 × 0.32 × 0.03 mm

Data collection

Oxford Diffraction KM-4-CCD diffractometer with a Sapphire3 detector
4759 measured reflections
1405 independent reflections
974 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.069

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.117
S = 1.00
1405 reflections
114 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.23 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C9	1.238 (2)	C7—C8	1.378 (3)
C1—N1	1.392 (3)	C8—N1	1.342 (3)
C9—C7—C6	126.95 (17)	O1—C9—C10	119.16 (18)
O1—C9—C7	121.66 (19)	C7—C9—C10	119.17 (17)
C8—C7—C9—O1	−176.80 (18)	C6—C7—C9—C10	−177.63 (17)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1$^{\rm i}$	0.97 (2)	1.83 (2)	2.788 (2)	171 (2)

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

Aromatic H atoms were treated as riding on their parent C atoms, with C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). Methyl H atoms were also treated as riding on their parent C atoms, with C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C). Atom H1, which takes part in hydrogen bonding, was located in a difference Fourier map (ΔF) and refined freely with isotropic displacement parameters.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97*

(Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2008).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3245). Services for accessing these data are described at the back of the journal.

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