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(*E*)-3-Dimethylamino-2-(1*H*-indol-3-ylcarbonyl)acrylonitrile: a chain of edge-fused rings built from a three-centre N—H···(N,O) hydrogen bond

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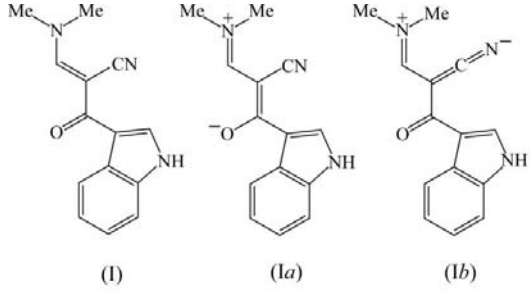
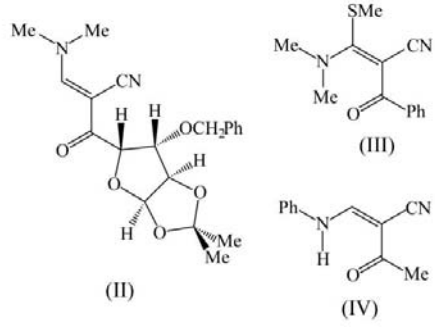
In the title compound, $C_{14}H_{13}N_3O$, the intramolecular distances provide evidence for polarization of the molecular–electronic structure. A single three-centre N—H···(N,O) hydrogen bond links the molecules into chains of edge-fused $R_2^2(16)$ and $R_2^4(12)$ rings. Comparison with a number of related structures identifies factors of significance controlling the pattern of supramolecular aggregation.

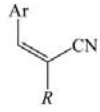
Comment

Indolylpyrimidines, which are analogues of the marine natural product meridianin D (Radwan & El-Sherbiny, 2007), are promising bioactive compounds (Jiang *et al.*, 2001). In order to introduce this interesting naturally occurring indole group as a substituent in other heterocyclic frameworks, with the aim of testing its biological influence, we have prepared the title α,β-unsaturated 1-indolyl ketone (I) as a useful synthetic intermediate, using a condensation reaction between 3-(1*H*-indol-3-yl)-3-oxopropionitrile and dimethylformamide dimethyl acetal. We report here the structure of (I) for comparison with three closely-related amino-substituted derivatives, *viz.* (II) [Cambridge Structural Database (Allen, 2002) refcode LEMSUS (Hashmi *et al.*, 2006)], (III) (AMIMZF10; Adhikesavalu & Venkatesan, 1981) and (IV) (PELZUC; Langer *et al.*, 2006), as well as with the thienyl analogues (V)–(IX) (Cobo *et al.*, 2005; Cobo, Quiroga *et al.*, 2006; Cobo, Cobo *et al.*, 2006).

The molecule of (I) (Fig. 1) is very nearly planar, as indicated by the torsion angles defining the conformation of the open-chain portion (Table 1). For the atoms forming the spine of this portion, the deviations from the mean plane of the five-membered ring range from 0.207 (2) Å for atom C32 to 0.006 (2) Å for atom C33. The bond distances within the exocyclic portion of the molecule provide evidence for polarization of the molecular–electronic structure. While the C3—C31 bond length is entirely typical of its type (mean value 1.464 Å; Allen *et al.*, 1987), the C32—C33 bond is long for its type, while C33—N33 is short (mean values 1.340 and 1.355 Å, respectively); in addition, the C31—O31 bond is long for an amide carbonyl group (mean value 1.231 Å). These observations point to the importance of the polarized form (I*a*) as a contributor to the overall molecular–electronic structure. Furthermore, the C32—C321 bond is rather shorter than the corresponding bonds in (V)–(IX), where the distances range from 1.443 (2) Å in (VI) to 1.448 (3) Å in (V), while the C321—N322 bond is rather longer than the corresponding bonds in (V)–(IX), which range from 1.143 (4) Å in (VI) to 1.1499 (18) Å in (IX), supporting a contribution to the overall molecular–electronic structure of (I) from the polarized form (I*b*). Forms analogous to (I*b*) are not possible for (V)–(IX), but they are possible for (II)–(IV), which do, in fact, all show values for the corresponding bond lengths that are very similar to those in (I).







(V) Ar = 4-ClC_6H_4, *R* = 2-thienyl
(VI) Ar = 4-BrC_6H_4, *R* = 2-thienyl
(VII) Ar = 3,4,5-$(MeO)_3C_6H_2$, *R* = 2-thienyl
(VIII) Ar = C_6H_5, *R* = 3-thienyl
(IX) Ar = 4-MeC_6H_4, *R* = 3-thienyl

A single three-centre N—H···(N,O) hydrogen bond (Table 2) links the molecules of (I) into a chain of edge-fused rings. The N—H···N component of this system links pairs of molecules into centrosymmetric $R_2^2(16)$ (Bernstein *et al.*, 1995) rings, while the N—H···O component links molecules related by the *C*-centring translation into *C*(6) chains running parallel to the [110] direction. In combination, these two interactions generate a chain of centrosymmetric rings along [110] in which

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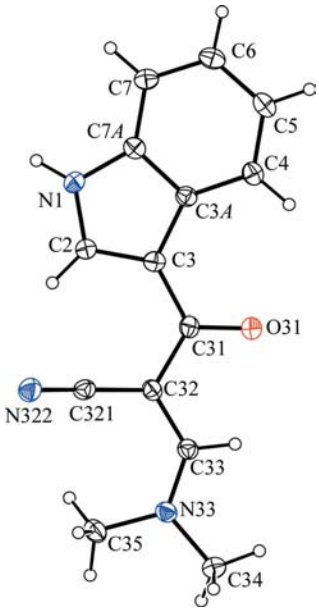

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

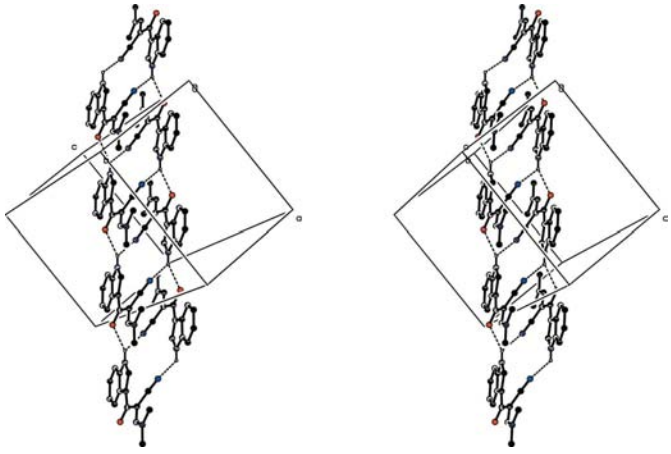

Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain of edge-fused rings along [110]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

$R_2^2(16)$ rings centred at ($\frac{1}{2}n + \frac{1}{4}, \frac{1}{2}n + \frac{1}{4}, \frac{1}{2}$), where n represents zero or an integer, alternate with $R_2^4(12)$ rings centred at ($\frac{1}{2}n$, $\frac{1}{2}n$, $\frac{1}{2}$), where n represents zero or an integer (Fig. 2). Two chains of this type, related to one another by the action of the twofold rotation axes, pass through each unit cell, but there are no direction-specific interactions between the chains; in particular, there are no C—H$\cdots\pi$(arene) hydrogen bonds and no aromatic π–π stacking interactions.

In the crystal structures of (II) (Hashmi *et al.*, 2006) and (III) (Adhikesavalu & Venkatesan, 1981), both close related to (I), there are no significant direction-specific intermolecular interactions of any kind, and neither the carbonyl O atoms nor the nitrile N atoms act as hydrogen-bond acceptors. In (IV)

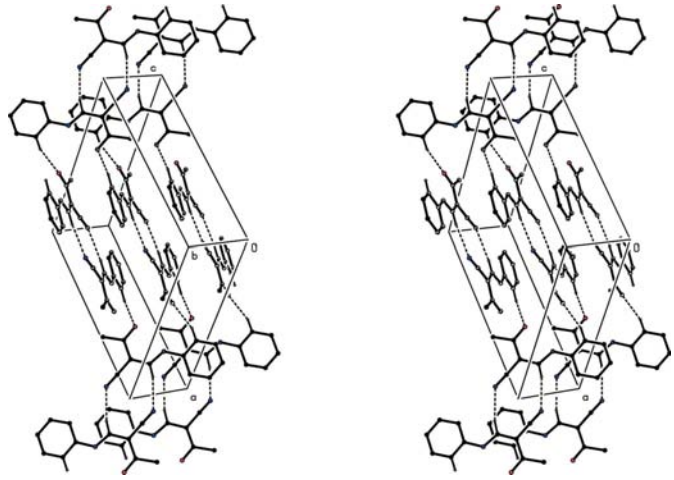

Figure 3
A stereoview of part of the crystal structure of (IV), showing the formation of a hydrogen-bonded sheet parallel to (101). The original atomic coordinates (Langer *et al.*, 2006) have been used and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

(Langer *et al.*, 2006), there is an intermolecular N—H$\cdots$O hydrogen bond; while the original report of this compound listed intermolecular C—H$\cdots$O and C—H$\cdots$N hydrogen bonds, no analysis or discussion of the resulting supramolecular aggregation was provided. Analysis of this structure using the published atomic coordinates shows that the molecules are linked into sheets lying parallel to (101) and built from alternating centrosymmetric $R_2^2(10)$ and $R_6^6(38)$ rings (Fig. 3).

The marked difference in the pattern of supramolecular aggregation in (I) as compared with those in (II)–(IV) may be traced to two significant factors. First, neither of compounds (II) and (III) contains an N—H bond, which acts as the sole hydrogen-bond donor in (I), while the N—H bond in (IV) is effectively masked by the formation of the intramolecular hydrogen bond. Secondly, the configuration about the C=C double bond places the amino substituent remote from the carbonyl group in each of (I) and (II), but close to it in each of (III) and (IV). Intermolecular hydrogen bonding with the carbonyl O atom as acceptor may be prevented in (III) by the steric effects of the adjacent methyl group. However, it is unclear why there are no intermolecular C—H$\cdots$O hydrogen bonds formed in (II) between the C—H bonds of the aryl ring and either the carbonyl O atom or the nitrile N atom.

Experimental

A solution of 3-(1*H*-indol-3-yl)-3-oxopropionitrile (3.2 mmol) in dry toluene (6 ml) was added to dimethylformamide dimethyl acetal (5 mmol) and the mixture was heated under reflux for 30 min. After cooling the mixture to ambient temperature, the product (I) was collected by filtration, washed with ethanol, dried and recrystallized from ethanol to afford crystals suitable for single-crystal X-ray diffraction (light-yellow plates, yield 68%, m.p. 474–476 K). MS *m*/*z* (relative abundance, %): 239 (M^+, 40), 238 (100), 222 (16), 144 (93), 116 (46), 89 (46), 42 (19).

Crystal data

$C_{14}H_{13}N_3O$
$M_r = 239.27$
Monoclinic, $C2/c$
$a = 11.5945$ (5) Å
$b = 8.6412$ (6) Å
$c = 23.1522$ (18) Å
$\beta = 92.325$ (7)°
$V = 2317.7$ (3) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 120$ (2) K
0.44 × 0.43 × 0.12 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.965$, $T_{max} = 0.989$
15301 measured reflections
2660 independent reflections
1543 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.225$
$S = 1.06$
2660 reflections
165 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.352 (4)	N33—C34	1.460 (4)
N1—C7*A*	1.385 (3)	N33—C35	1.463 (3)
C3—C31	1.467 (4)	O31—C31	1.249 (3)
C31—C32	1.471 (4)	C32—C321	1.420 (4)
C32—C33	1.385 (4)	C321—N322	1.158 (4)
C33—N33	1.323 (3)		
C2—C3—C31—C32	−15.7 (4)	C2—C3—C31—O31	163.5 (3)
C3—C31—C32—C33	173.5 (2)	C3—C31—C32—C321	−12.9 (4)
C31—C32—C33—N33	−172.9 (3)	C32—C33—N33—C35	7.6 (5)
C32—C33—N33—C34	−171.2 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O31^{i}	0.88	2.20	2.985 (3)	148
N1—H1···N322^{ii}	0.88	2.50	3.099 (4)	126

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

The systematic absences permitted $C2/c$ and Cc as possible space groups. $C2/c$ was selected and confirmed by the subsequent structure refinement. All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H distances of 0.95 (ring or alkene H) or 0.98 Å (methyl) and N—H distances of 0.88 Å, and with $U_{iso}(H) = kU_{eq}$(carrier), where $k = 1.5$ for the methyl groups and $k = 1.2$ for all other H atoms.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3169). Services for accessing these data are described at the back of the journal.

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