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N-(2-Cyanopropan-2-yl)isobutyramide

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.007 Å
R factor = 0.052
wR factor = 0.152
Data-to-parameter ratio = 8.3

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

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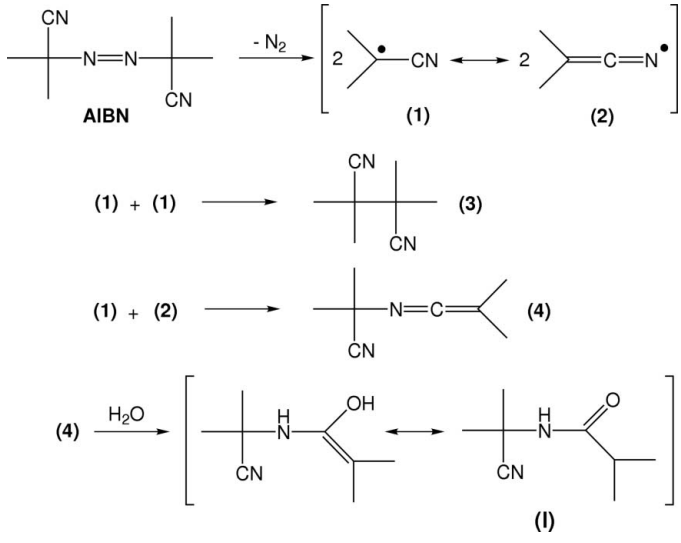
The title compound, $C_8H_{14}N_2O$, is stabilized in the solid state as a keto tautomer. The asymmetric unit contains two molecules with different conformations. In the crystal structure, intermolecular N—H···O hydrogen bonds of moderate strength link the molecules into chains along the *c* axis.

Comment

AIBN (2,2′-azobisisobutyronitrile) is probably the most used initiator for free-radical chain reactions (Motherwell & Crich, 1992). The efficiency of AIBN in such reactions has been explained through thermal decomposition studies, the homolytic fragmentation of AIBN with N_2 release being the key step (Weiner & Hammond, 1968). Generally, in thermal decomposition, two side products are observed, namely tetramethylsuccinonitrile, (3), and dimethyl-*N*-(2-cyano-2-propyl)ketenimine, (4). Since catalytic amounts of AIBN are required when chain reactions are carried out, compounds (3) and (4) are almost always neither detected nor isolated. However, they have been prepared by formal synthetic methods (Smith *et al.*, 1962).



When working on the synthesis of optically pure γ-aminobutyric acid derivatives (Rodríguez *et al.*, 2004), we noted a poor efficiency of AIBN during the radical cyclization key step. Sometimes, non-catalytic amounts of AIBN were necessary in order to obtain reasonable yields for the expected product, and we observed a significant production of the title compound, (I). The present X-ray characterization of (I), together with a careful examination of the experimental

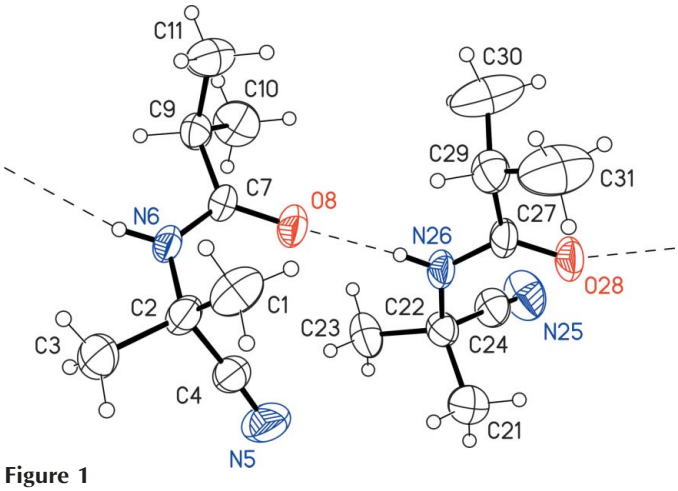


Figure 1
The asymmetric unit of (I), with displacement ellipsoids at the 30% probability level. Intermolecular hydrogen bonds are shown as dashed lines.

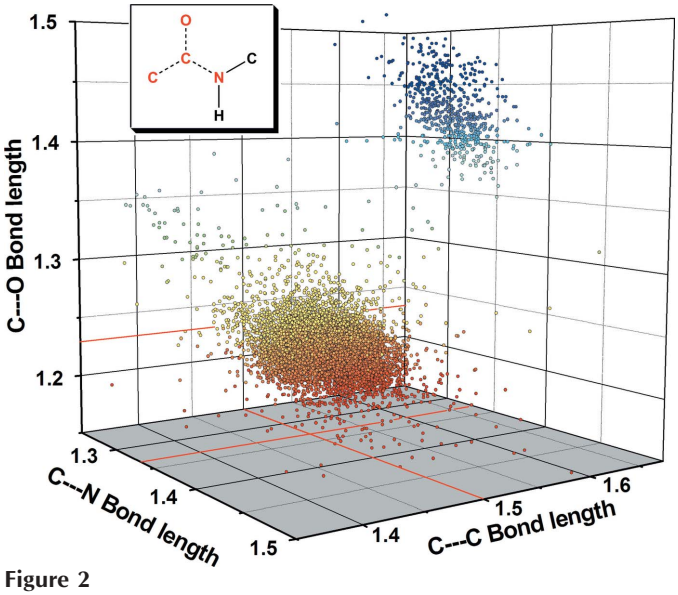


Figure 2
Correlation diagram for bond lengths around C atom of *N*-substituted amides. A search of the Cambridge Structural Database (CSD; Version 5.26, update of May 2005; Allen, 2002) was carried out for organics including the fragment displayed as inset, with bond types set as 'any' for dashed bonds and 'single' for solid bonds. 6586 refcodes including three-dimensional coordinates were recovered, omitting disordered and ion-containing structures. 12133 triplets (C—C, C—N, C—O) are plotted using a colour map following the C—O bond length (red: 1.15 Å; blue: 1.55 Å). Two well separated clusters are observed, corresponding to keto (red cluster) and enol (blue cluster) tautomers. Dimensions for (I) are indicated with red lines, showing that the keto tautomer is stabilized in the solid state for this compound.

workup, allowed us to determine that this side product resulted from a hydrolysis of ketenimine (4). This non-chain radical reaction no longer occurred when using a fresh batch of dry AIBN and avoiding moisture during the synthesis. This unwanted behaviour of AIBN has been commented on in some previous reports (*e.g.* Russell Bowman *et al.*, 2000) although apparently never fully probed. We eventually synthesized (I) using only AIBN and water as starting materials (see *Experimental*) and determined its crystal structure.

There are two molecules in the asymmetric unit (Fig. 1). The two molecules have similar dimensions but different conformations for the isobutyramide group (Table 1): the molecule has a degree of free rotation around the formal σ bonds C7—C9 and C27—C29 and the two conformations stabilized in the solid state differ by *ca* 52° for torsion angles N—C—C—CH_3 and O═C—C—CH_3 (Table 1). Observed conformations for these groups are very different from those observed in isobutyramide (Cohen-Addad & Cohen-Addad, 1978) and *N*-(1-phenylethyl)isobutyramide (Aubry *et al.*, 1980), in which the O═C—C—CH_3 angles are (±)synclinal [(±)*gauche*)] and the N—C—C—CH_3 angles are (±)anticlinal. However, a conformation close to that of (I) is stabilized for *N*-(2,6-dichlorophenyl)isobutyramide (Gowda *et al.*, 2000).

The geometry of the amide groups (Table 1 and Fig. 2) clearly demonstrates that the keto tautomer is stabilized in (I), a feature favouring the formation of intermolecular hydrogen bonds (Table 2). The crystal structure is thus built up of chains of molecules, arranged along [001]. The strength of hydrogen bonds in (I) is of the same magnitude as those observed in the above cited isobutyramide derivatives. The steric demand of substituent groups functionalizing the amide core probably prevents the formation of stronger hydrogen bonds.

Experimental

Compound (I) was obtained in 8–10% yield by refluxing hydrated AIBN in benzene. Single crystals were obtained from a solution in AcOEt–MeOH (10:1, *v*/*v*).

Crystal data

$C_8H_{14}N_2O$
M_r = 154.21
Orthorhombic, $Pna2_1$
a = 11.452 (3) Å
b = 8.859 (2) Å
c = 19.352 (8) Å
V = 1963.3 (10) Å^3
Z = 8
D_x = 1.043 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 60 reflections
θ = 4.7–11.4°
μ = 0.07 mm^{-1}
T = 296 (1) K
Plate, colourless
0.60 × 0.44 × 0.14 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: none
2383 measured reflections
1785 independent reflections
1157 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 25.0°
$h = -1 \rightarrow 13$
$k = -10 \rightarrow 2$
$l = -1 \rightarrow 22$
3 standard reflections
every 97 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.152
S = 1.01
1785 reflections
216 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0855P)^2 + 0.0673P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Extinction correction: *SHELXTL-Plus*
Extinction coefficient: 0.0054 (18)

Table 1
Selected geometric parameters (Å, °).

C2—N6	1.453 (6)	C22—N26	1.460 (6)
C4—N5	1.156 (6)	C24—N25	1.131 (6)
N6—C7	1.336 (6)	N26—C27	1.337 (6)
C7—O8	1.241 (5)	C27—O28	1.232 (5)
C7—C9	1.492 (6)	C27—C29	1.511 (7)
N5—C4—C2	175.4 (5)	N25—C24—C22	174.0 (6)
C7—N6—C2	125.0 (4)	C27—N26—C22	125.3 (4)
N6—C7—C9—C10	−144.7 (4)	N26—C27—C29—C30	−89.3 (7)
N6—C7—C9—C11	93.5 (5)	N26—C27—C29—C31	146.0 (6)
O8—C7—C9—C10	36.6 (6)	O28—C27—C29—C30	89.1 (8)
O8—C7—C9—C11	−85.2 (6)	O28—C27—C29—C31	−35.6 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6···O28^{i}	0.82 (6)	2.10 (6)	2.911 (5)	168 (5)
N26—H26···O8	0.80 (7)	2.06 (7)	2.857 (5)	173 (6)

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

H atoms bonded to N6 and N26 were found in a difference Fourier map and refined isotropically. C-bound H atoms were placed in idealized positions and refined as riding on their parent atoms, with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl groups, and C—H = 0.98 Å and U_{iso}(H) = 1.2U_{eq}(C) for methine groups. Terminal atoms C30 and C31 have large displacement parameters compared with the neighbouring atoms. Attempts to model these sites as disordered were unsuccessful, probably because of the unfavourable data-to-parameter ratio. In the absence of significant anomalous scatterers, Friedel pairs were merged.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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