218 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2 + 0.1227P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
Extinction coefficient: 0.011 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.0 (2)

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

S1—O4	1.479 (5)	N1—C5	1.462 (7)
S1—C13	1.789 (6)	C2—C11	1.512 (8)
S1—C12	1.802 (6)	C2—C3	1.544 (7)
O1—C6	1.342 (6)	C3—C4	1.489 (8)
O1—C7	1.463 (6)	C4—C5	1.517 (8)
O2—C6	1.212 (6)	C7—C10	1.457 (9)
O3—C11	1.196 (7)	C7—C9	1.477 (9)
N1—C6	1.342 (7)	C7—C8	1.517 (8)
N1—C2	1.449 (7)	C11—C12	1.521 (8)
O4—S1—C13	107.5 (3)	O1—C6—N1	111.6 (4)
O4—S1—C12	106.5 (3)	C10—C7—O1	110.7 (5)
C13—S1—C12	95.5 (3)	C10—C7—C9	112.9 (7)
C6—O1—C7	121.3 (4)	O1—C7—C9	110.3 (5)
C6—N1—C2	124.8 (4)	C10—C7—C8	111.0 (7)
C6—N1—C5	121.6 (4)	O1—C7—C8	102.1 (4)
C2—N1—C5	113.6 (4)	C9—C7—C8	109.3 (5)
N1—C2—C11	112.5 (5)	O3—C11—C2	123.3 (5)
N1—C2—C3	102.2 (4)	O3—C11—C12	121.9 (6)
C11—C2—C3	111.1 (5)	C2—C11—C12	114.7 (5)
C4—C3—C2	103.7 (5)	C11—C12—S1	110.5 (4)
C3—C4—C5	105.5 (5)	C18—C13—C14	119.2 (6)
N1—C5—C4	102.7 (4)	C18—C13—S1	119.9 (5)
O2—C6—O1	125.7 (5)	C14—C13—S1	120.9 (5)
O2—C6—N1	122.7 (5)		

The proper enantiomer was chosen on the basis of the known configuration of the substrates and the method described by Flack (1983) was used to confirm the absolute configuration.

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*97.

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Acta Cryst. (1999). C**55**, 1607–1610

Intermolecular N—H···N and C—H···O interactions form one-dimensional chains comprising the two independent molecules of *N*,*N*′-dicyclohexyl-*N*-nicotinoylurea

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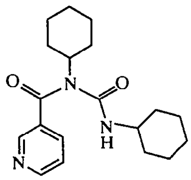
Abstract

The title compound, $C_{19}H_{27}N_3O_2$, crystallizes in space group $P\bar{1}$ with two molecules in the asymmetric unit which differ slightly in conformation. Intermolecular N—H···N and C—H···O interactions generate a hydrogen-bonded ring system between the alternating molecules, graph set $R_2^2(16)$, with N···N distances of 3.021 (3) and 3.041 (3) Å, and C···O distances of 3.219 (3) and 3.296 (3) Å along the hydrogen-bonded chains.

Comment

The general principles underlying molecular recognition processes are reasonably well understood and hydrogen bonding in crystal structures can usually be rationalized in preferred combinations of hydrogen-bond donors and acceptors (Etter *et al.*, 1990). This allows comparison studies to be undertaken between classes of compounds containing analogous functional groups with a view to crystal engineering. However, compounds which are geometrically similar at the molecular level may differ at the supramolecular level, *e.g.* 2,2′-dipyridyl ketone and 2,2′-dipyridyl thioketone (Norsten *et al.*, 1999). Thus, in molecules where several different potential hydrogen-bond donors and acceptors are present (with cooperativity and/or competition among these interactions), the ability to deduce in advance the molecular packing arrangements in the crystal structure largely remains an unrealized vision (Wolff, 1996). The title compound, (I), a nicotinic acid derivative, forms part of a study of hydrogen-bonding interactions in a series of anion receptors (Gallagher & Fitzsimons, 1999; Gallagher *et al.*, 1999*a*,*b*).



(I)

Compound (I) crystallizes in space group $P\bar{1}$ with two independent molecules, *A* and *B*, in the asymmetric unit which differ slightly in conformation; views of the two molecules are depicted in Fig. 1. The r.m.s. deviation for the superposition of the non-H atoms in both molecules is 0.18 Å (Spek, 1998). Torsion-angle differences are evident for the C2—N1—C21—C22 angles, which are 87.0 (3) and 80.1 (3)° in molecules *A* and *B*, respectively (Table 2). Bond lengths and angles are unexceptional and in accord with anticipated values (Orpen *et al.*, 1994), and selected dimensions are given in Table 1. The (sp^2) C1—C11 bond lengths of 1.498 (3) and 1.504 (3) Å are comparable with those in related structures (Orpen *et al.*, 1994). The angles between the pyridinyl ring and the N1/C1/C2/C11 plane are 63.99 (12) and 58.62 (13)°; the angles between the four-carbon plane of the two cyclohexyl rings are 53.11 (12) and 65.71 (12)° in *A* and *B*, respectively.

Molecules *A* and *B* associate through intermolecular (amide)N—H···N(py) and (py)C—H···O═C(amide) interactions, generating hydrogen-bonded ring systems with graph set $R_2^2(16)$ between each pair (Table 2). Each molecule participates in hydrogen bonding both with N—H/C—H donors and (py)N/(amide)C═O acceptors, as depicted in the stereoview in Fig. 2. Chains are formed comprising alternating *A* and *B* molecules, along the *a* axis. Weak C—H···O═C intramolecular interactions are present involving cyclohexyl-ring-H atoms and the carbonyl-O atoms. The structure contains small voids in the crystal lattice of 7 Å^3 (× 2), which are too small to accommodate a solvent molecule (*PLATON*; Spek, 1998).

Crystal structures with more than one molecule present in the asymmetric unit are not uncommon (Gallagher *et al.*, 1998) and we have reported previously structures with more than one molecule in the asymmetric unit in space groups $R\bar{3}$ (Ferguson *et al.*, 1992) and $P\bar{1}$ (Butler *et al.*, 1998). The rationalization of packing interactions in crystals with several independent molecules is difficult (Karthe *et al.*, 1993). These may arise due to the existence of dimers or oligomers in solution (with energetically similar conformations arising from intramolecular hydrogen bonding, solute/solvent interactions *etc.*) and crystallizing to yield multiple formula units in the asymmetric unit (Desiraju, 1989). In (I), molecules *A* and *B* differ slightly in conformation and the overall crystal structure may be facilitated through hydrogen-bonded units crystallizing from solution to produce (I).

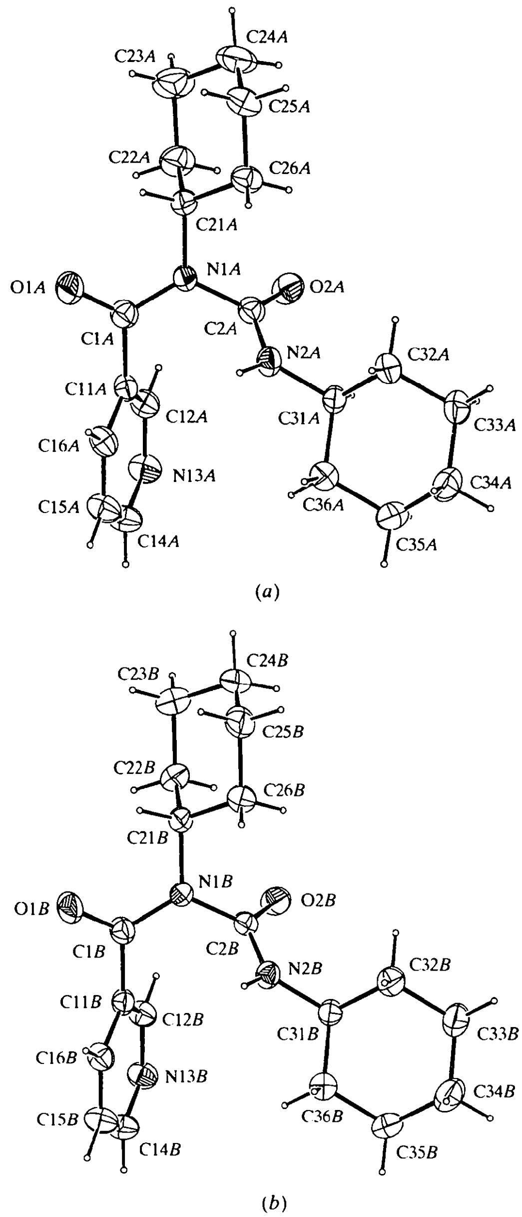


Fig. 1. A view of (*a*) molecule *A* and (*b*) molecule *B* in (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The crystal structure of *N*,*N'*-dicyclohexylurea has been reported (Govindasamy & Subramanian, 1997). A search of the Cambridge Structural Database (Allen & Kennard, 1993) for structures containing the 1,3-dicyclohexylurea moiety reveals several related compounds (Ball *et al.*, 1990; Toniolo *et al.*, 1990; Doucet *et al.*, 1997).

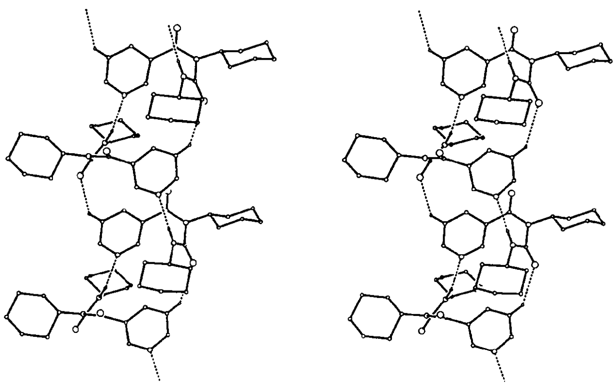


Fig. 2. A stereoview of the intermolecular interactions along the $B\cdots A\cdots B\cdots A_{bottom}$ hydrogen-bonded chain; only the N—H and C—H H atoms participating in hydrogen bonding are included.

Experimental

The title compound was prepared by dissolving L-phenylalanine-L-leucine ethyl ester (1.63 g, 5 mmol) and nicotinic acid (0.62 g, 5 mmol) with 1-hydroxybenzotriazole (0.66 g, 5 mmol) in CH_2Cl_2 (50 ml). The mixture was cooled to 273 K and 1,3-dicyclohexylcarbodiimide (1.03 g, 5 mmol) was added. The reaction temperature was raised to room temperature after 30 min and stirred for 6 h. The title compound, (I), was isolated as the major product of the reaction by initial filtration of the reaction mixture and recrystallized from ethyl acetate/petroleum ether (313–333 K), yielding colourless crystals of (I).

Crystal data

$C_{19}H_{27}N_3O_2$
M_r = 329.44
Triclinic
$P\bar{1}$
a = 9.6855 (11) Å
b = 12.775 (3) Å
c = 16.053 (6) Å
α = 67.29 (3)°
β = 87.640 (17)°
γ = 85.750 (17)°
V = 1827.0 (8) Å^3
Z = 4
D_x = 1.198 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 5.44–19.44°
μ = 0.079 mm^{-1}
T = 290 (1) K
Plate
0.44 × 0.28 × 0.14 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
6786 measured reflections
6786 independent reflections
2796 reflections with $I > 2\sigma(I)$
θ_{max} = 25.4°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 15$
$l = -17 \rightarrow 19$
3 standard reflections
frequency: 240 min
intensity variation: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.111
S = 0.871
6786 reflections
434 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.173 e Å^{-3}
$\Delta\rho_{min}$ = −0.143 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0181 (11)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1*A*—C1*A*	1.216 (3)	O1*B*—C1*B*	1.216 (3)
O2*A*—C2*A*	1.218 (3)	O2*B*—C2*B*	1.209 (3)
N1*A*—C1*A*	1.365 (3)	N1*B*—C1*B*	1.362 (3)
N1*A*—C2*A*	1.445 (3)	N1*B*—C2*B*	1.444 (3)
N1*A*—C21*A*	1.480 (3)	N1*B*—C21*B*	1.483 (3)
N2*A*—C2*A*	1.323 (3)	N2*B*—C2*B*	1.333 (3)
N2*A*—C31*A*	1.461 (3)	N2*B*—C31*B*	1.453 (3)
C1*A*—C11*A*	1.498 (3)	C1*B*—C11*B*	1.504 (3)
C2*A*—N1*A*—C21*A*	117.5 (2)	C2*B*—N1*B*—C21*B*	116.8 (2)
C2*A*—N2*A*—C31*A*	123.2 (2)	C2*B*—N2*B*—C31*B*	121.6 (2)
O1*A*—C1*A*—N1*A*	122.3 (2)	O1*B*—C1*B*—N1*B*	122.8 (2)
O1*A*—C1*A*—C11*A*	120.4 (2)	O1*B*—C1*B*—C11*B*	120.2 (2)
N1*A*—C1*A*—C11*A*	117.3 (2)	N1*B*—C1*B*—C11*B*	117.0 (2)
O2*A*—C2*A*—N1*A*	120.6 (2)	O2*B*—C2*B*—N1*B*	121.4 (2)
O2*A*—C2*A*—N2*A*	125.2 (2)	O2*B*—C2*B*—N2*B*	125.0 (2)
N1*A*—C2*A*—N2*A*	114.2 (2)	N2*B*—C2*B*—N1*B*	113.6 (2)
C1*A*—N1*A*—C2*A*—O2*A*	122.5 (3)		
O1*A*—C1*A*—C11*A*—C12*A*	117.4 (3)		
O1*A*—C1*A*—C11*A*—C16*A*	−58.8 (4)		
C2*A*—N1*A*—C21*A*—C22*A*	87.0 (3)		
C2*A*—N1*A*—C21*A*—C26*A*	−38.6 (3)		
C1*B*—N1*B*—C2*B*—O2*B*	119.2 (3)		
O1*B*—C1*B*—C11*B*—C12*B*	123.3 (3)		
O1*B*—C1*B*—C11*B*—C16*B*	−53.3 (4)		
C2*B*—N1*B*—C21*B*—C22*B*	80.1 (3)		
C2*B*—N1*B*—C21*B*—C26*B*	−45.2 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2*A*—H2*A*···N13*B*	0.86	2.21	3.041 (3)	163
C15*A*—H15*A*···O2*B*	0.93	2.50	3.296 (3)	143
N2*B*—H2*B*···N13*A*'	0.86	2.17	3.021 (3)	172
C15*B*—H15*B*···O2*A*'	0.93	2.46	3.219 (3)	139

Symmetry code: (i) 1 + *x*, *y*, *z*.

Molecule (I) crystallized in the triclinic system, space group $P1$ or $P\bar{1}$; $P\bar{1}$ was assumed and confirmed by the analysis. H atoms were treated as riding atoms (C—H 0.93–0.98 and N—H 0.86 Å).

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET4* and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD2* in *NRCVAX96* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*b*). Program(s) used to refine structure: *NRCVAX96* and *SHELXL97* (Sheldrick, 1997*a*). Molecular graphics: *NRCVAX96*, *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *PREP8* (Ferguson, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1039). Services for accessing these data are described at the back of the journal.

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