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3-(Benzoylamino)propanoic Acid and 6-[(4-Nitrobenzoyl)amino]hexanoic Acid

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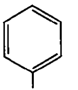
Abstract

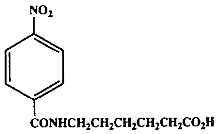
For both structures, $C_{10}H_{11}NO_3$ (I) and $C_{13}H_{16}N_2O_5$ (II), there is one molecule in the asymmetric unit. The hydrogen bonding differs from other carboxylic acid amides studied by us in that the acid dimer motif is not observed and, instead, acid–amide hydrogen bonds are formed.

Comment

As part of a general study of the stability of organic peracids and peracid salts (Kariuki & Jones, 1992), and in particular of the role of hydrogen bonding in controlling the crystal structure of peracid and acid amides (Feeder & Jones, 1992), we report here the structures of two aliphatic (*N*-benzoyl) carboxylic acids, (I) and (II).



(I)



(II)

The bond angles and distances found for both structures are similar to those reported for hippuric acid (Ringertz, 1971), *N*-acetylglycine (Mackay, 1975) and *N*-methylbenzamide (Leiserowitz & Tuval, 1978). There are, however, subtle differences in molecular conformation between the two structures. Molecules in (I) may be divided into three groups: the benzene ring *A*(I), the amide group [C(6)C(7)O(7)N(1)C(8)] *B*(I) and the aliphatic acid group [C(9)C(10)O(101)O(102)H(102)] *C*(I). These groups are each planar to within 0.007, 0.007 and 0.025 Å, respectively. N(1)—C(8)—C(9)—C(10) has a torsion angle of 61.5°; dihedral angles are *A*(I)*B*(I) 3.4, *B*(I)*C*(I) 95.7 and *A*(I)*C*(I) 82.6°.

In (II), the carboxyl group and the alkyl chain are not coplanar, and hence are described as two separate groups, *D*(II) and *E*(II), respectively. The benzene ring and nitro group are almost coplanar such that the angle between them is 2.5° – slightly less than the 7.5° found for *p*-nitrobenzamide (Di Rienzo, Domenicano & Serantoni, 1977) – hence the group as a whole, *A*(II), is planar to within 0.036 Å. The amido group [C(6)C(7)O(7)N(1)C(8)] *B*(II) and alkyl chain [C(8)C(9)C(10)C(11)C(12)] *E*(II) are planar to within 0.014 and 0.039 Å, respectively. The dihedral angles are *A*(II)*B*(II) 9.0, *B*(II)*E*(II) 12.4 and *A*(II)*E*(II) 21.2°. The carboxyl group [C(13)O(131)-O(132)] *D*(II) makes angles of 13.6, 7.5 and 9.9° with *A*(II), *B*(II) and *E*(II), respectively.

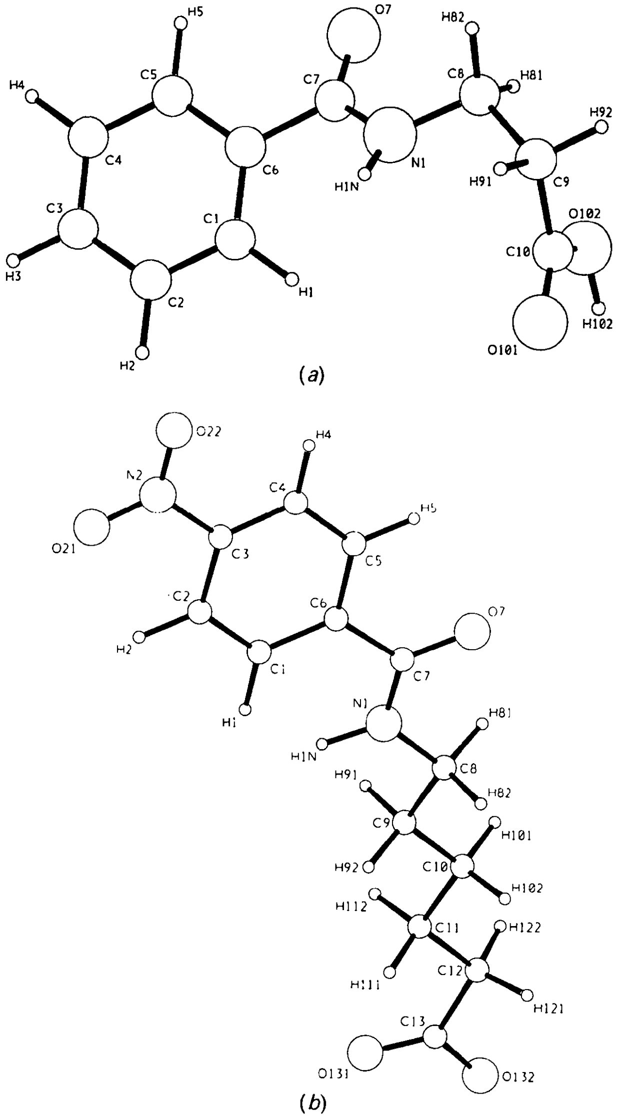


Fig. 1. Atom-numbering scheme for (*a*) (I) and (*b*) (II).

Structures (I) and (II) exhibit similar hydrogen-bond networks. In neither case is the (carboxylic acid) dimer motif observed. This is in contrast to other comparable 'acid amides' previously studied by us (Feeder & Jones, 1993), where additional hydrogen bonding through amide–amide contacts extends the network to form ribbons or sheets. For (I) and (II), however, an arrangement similar to that of *N*-acetylglycine (Mackay, 1975) is seen, involving acid–amide and amide–acid hydrogen bonds.

Fig. 2(*a*) is a *PLUTO* (Motherwell & Clegg, 1978) plot of (I), depicting the intermolecular hydrogen-bonding pattern. Molecules related by a *b* glide are hydrogen bonded through the carboxyl proton to the amido carbonyl group (O—H···O=C 1.679, O···O=C 2.619 Å) yielding a chain-like arrangement. These chains are then involved in additional hydrogen bonding through amido proton to carboxyl carbonyl interactions, forming a 12-membered centrosymmetric ring dimer (*N*—H···O=C 2.070, N···O=C 2.960 Å). Fig. 2(*b*) shows that, as a result of hydrogen bonding, 'blocks' are formed, which are stacked along the *a* axis and held together by π–π interactions between the benzene rings.

Fig. 3 is a *PLUTO* plot of (II), showing a similar intermolecular hyrogen-bonding pattern to that seen for (I). Acid proton to amido-carbonyl group hydrogen bonds result in chains of molecules related by a twofold screw axis (O···O=C 2.593 Å). Again chains related by a centre of symmetry are hydrogen bonded through amido proton to carboxyl carbonyl interactions forming an 18-membered ring dimer (N—H···O=C 1.945, N···O=C 2.997 Å). The result of hydrogen bonding is therefore to generate blocks of molecules as in (I).

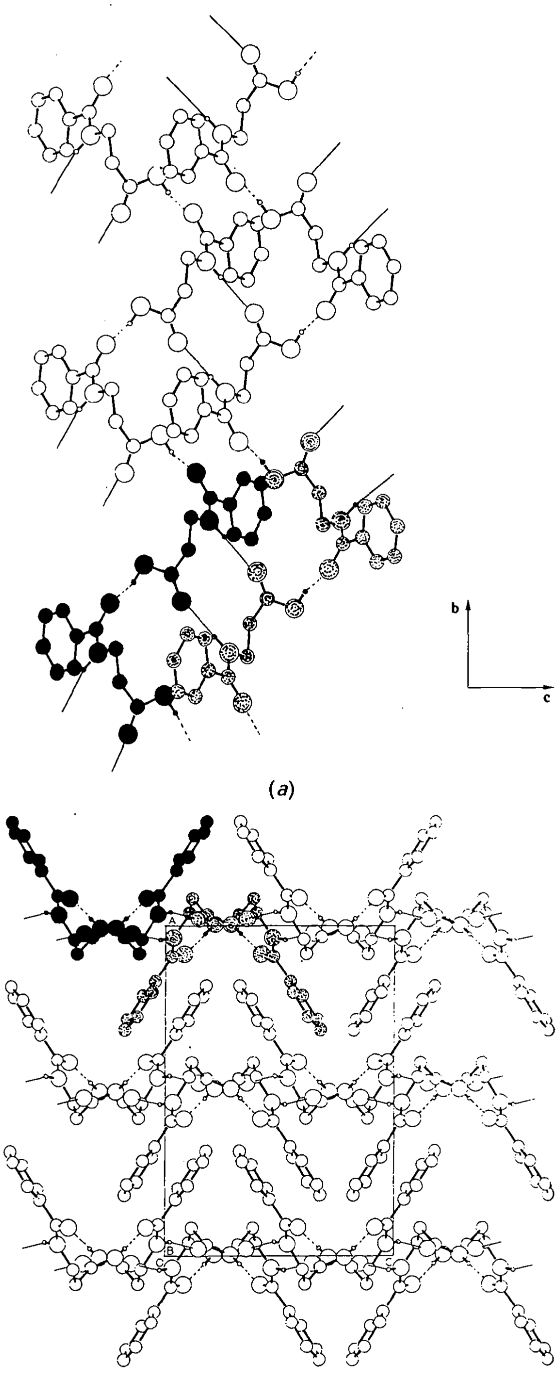


Fig. 2. (*a*) The hydrogen-bond network for the structure of (I), viewed down the *a* axis. The shaded atoms represent one chain. (*b*) Packing of the blocks produced by hydrogen bonding in the structure of (I), viewed down the b axis.

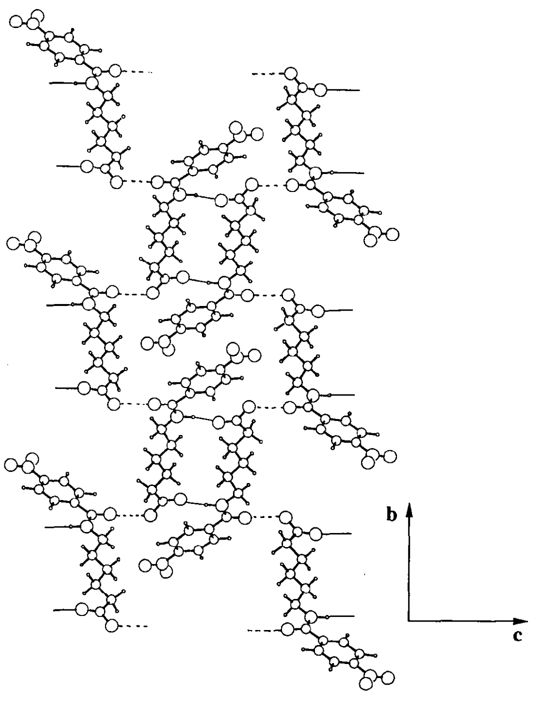


Fig. 3. The hydrogen-bond network for the structure of (II), viewed down the *a* axis.

Packing restrictions determine, in both structures, the conformation of the alkyl chain. In (I), the N(1)—C(8)—C(9)—C(10) and C(8)—C(9)—C(10)—O(102) torsion angles are very much less than 180°, which probably helps to stabilize the hydrogen-bonded dimer. In (II), the hydrogen-bonded chains can only form *via* the twofold screw operation if the carboxyl group adopts the uncommon *anti*-planar conformation (Leiserowitz, 1976).

Experimental

Crystals of (I) were obtained during the attempted recrystallization of the corresponding peracid from glacial acetic acid; crystals of (II) were obtained from a glacial acetic acid solution.

Compound (I)

Crystal data

$C_{10}H_{11}NO_3$
$M_r = 193.20$
Orthorhombic
Pcab
$a = 15.930\ (1)$ Å
$b = 10.860\ (2)$ Å
$c = 11.135\ (4)$ Å
$V = 1926$ Å^3
$Z = 8$
$D_x = 1.33$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10\text{–}15°$
$\mu = 0.09$ mm^{-1}
$T = 295$ K
Cuboid
0.3 × 0.3 × 0.3 mm
White, transparent

Data collection

Enraf-Nonius CAD-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3186 measured reflections
2807 independent reflections
1790 observed reflections $[F > 3\sigma(F)]$

$\theta_{max} = 30°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 15$
2 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
$R = 0.050$
$wR = 0.050$
$S = 1.001$
1790 reflections
142 parameters
Unit weights applied
$(\Delta/\sigma)_{max} = 0.114$

$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (II)

Crystal data

$C_{13}H_{16}N_2O_5$
$M_r = 280.13$
Monoclinic
$P2_1/n$
$a = 5.768\ (2)$ Å
$b = 13.885\ (4)$ Å
$c = 17.136\ (6)$ Å
$\beta = 90.34\ (3)°$
$V = 1372$ Å^3
$Z = 4$
$D_x = 1.37$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8\text{–}12°$
$\mu = 0.10$ mm^{-1}
$T = 295$ K
Needle-like
0.4 × 0.1 × 0.1 mm
White, transparent

Data collection

Enraf-Nonius CAD-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2605 measured reflections
2407 independent reflections
1104 observed reflections $[F > 3\sigma(F)]$

$R_{int} = 0.037$
$\theta_{max} = 25°$
$h = -6 \rightarrow 6$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 20$
2 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
$R = 0.083$
$wR = 0.083$
$S = 1.262$
1104 reflections
188 parameters
Unit weights applied
$(\Delta/\sigma)_{max} = 0.084$

$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
(I)				
N(1)	0.4629 (1)	0.2535 (2)	0.4658 (2)	0.038
O(7)	0.4131 (1)	0.4415 (1)	0.4179 (1)	0.045
O(101)	0.5222 (1)	−0.0537 (2)	0.3546 (2)	0.065
O(102)	0.5046 (1)	0.0884 (2)	0.2152 (2)	0.051
C(1)	0.2971 (2)	0.1996 (2)	0.5574 (2)	0.051
C(2)	0.2241 (2)	0.1807 (3)	0.6237 (3)	0.063
C(3)	0.1839 (2)	0.2783 (3)	0.6770 (2)	0.061
C(4)	0.2153 (2)	0.3954 (3)	0.6647 (2)	0.056
C(5)	0.2876 (1)	0.4155 (2)	0.5979 (2)	0.045
C(6)	0.3291 (1)	0.3177 (2)	0.5453 (2)	0.036
C(7)	0.4057 (1)	0.3428 (2)	0.4712 (2)	0.034
C(8)	0.5409 (1)	0.2678 (2)	0.3969 (2)	0.041
C(9)	0.5849 (1)	0.1437 (2)	0.3845 (2)	0.044
C(10)	0.5344 (1)	0.0491 (2)	0.3188 (2)	0.038
(II)				
N(1)	−0.4096 (14)	0.2000 (6)	0.5848 (4)	0.050
N(2)	0.2342 (15)	0.4662 (6)	0.3654 (5)	0.051
O(7)	−0.1416 (12)	0.2561 (6)	0.6697 (3)	0.060
O(21)	0.1398 (14)	0.4749 (6)	0.3018 (4)	0.084
O(22)	0.4194 (13)	0.5018 (6)	0.3810 (4)	0.073
O(131)	−1.3496 (12)	−0.1742 (6)	0.5693 (3)	0.065
O(132)	−1.4112 (12)	−0.2470 (6)	0.6801 (3)	0.065
C(1)	−0.2100 (16)	0.3152 (7)	0.4634 (5)	0.043
C(2)	−0.0969 (17)	0.3672 (7)	0.4061 (5)	0.050
C(3)	0.1144 (17)	0.4101 (7)	0.4259 (5)	0.044
C(4)	0.2138 (17)	0.4033 (7)	0.4982 (5)	0.048
C(5)	0.0982 (16)	0.3521 (7)	0.5549 (5)	0.043
C(6)	−0.1132 (16)	0.3058 (7)	0.5381 (5)	0.040
C(7)	−0.2272 (16)	0.2527 (7)	0.6024 (5)	0.039
C(8)	−0.5332 (18)	0.1434 (8)	0.6434 (6)	0.059
C(9)	−0.6898 (17)	0.0706 (7)	0.6054 (5)	0.052
C(10)	−0.8134 (17)	0.070 (8)	0.6614 (5)	0.051
C(11)	−0.9871 (18)	−0.0604 (7)	0.6208 (5)	0.055
C(12)	−1.1087 (17)	−0.1306 (7)	0.6765 (5)	0.046
C(13)	−1.2998 (17)	−0.1834 (7)	0.6363 (5)	0.044

Table 2. *Selected geometric parameters* (Å, °)

	(I)	(II)
C(1)—C(2)	1.392 (5)	1.385 (14)
C(2)—C(3)	1.373 (6)	1.396 (14)
C(3)—C(4)	1.373 (6)	1.366 (14)
C(4)—C(5)	1.388 (5)	1.379 (14)
C(5)—C(6)	1.382 (5)	1.407 (14)
C(6)—C(1)	1.387 (5)	1.399 (13)
C(7)—C(6)	1.497 (5)	1.482 (14)
C(7)—N(1)	1.332 (5)	1.315 (13)
C(7)—O(7)	1.232 (4)	1.244 (11)
C(8)—N(1)	1.468 (5)	1.465 (13)
C(8)—C(9)	1.525 (5)	1.501 (14)
C(9)—C(10)	1.496 (5)	1.490 (14)
C(10)—C(11)	-	1.535 (14)
C(11)—C(12)	-	1.537 (14)
C(12)—C(13)	-	1.490 (14)
C(10)—O(101)	1.201 (5)	-
C(10)—O(102)	1.319 (4)	-
C(13)—O(131)	-	1.189 (12)
C(13)—O(132)	-	1.327 (13)
N(2)—C(3)	-	1.473 (13)
N(2)—O(21)	-	1.221 (11)
N(2)—O(22)	-	1.206 (12)
C(8)—N(1)—C(7)	121.7 (3)	122.2 (9)
C(7)—C(6)—C(1)	121.4 (3)	123.3 (10)
C(6)—C(1)—C(2)	119.6 (3)	120.6 (10)
C(5)—C(6)—C(7)	118.9 (3)	117.6 (9)
C(3)—C(2)—C(1)	119.7 (3)	117.7 (9)
C(2)—C(3)—C(4)	120.3 (3)	123.5 (10)
C(3)—C(4)—C(5)	120.1 (3)	118.2 (10)
C(6)—C(5)—C(4)	120.1 (4)	120.9 (9)
C(5)—C(6)—C(1)	120.2 (3)	119.0 (9)
O(7)—C(7)—C(6)	120.2 (3)	120.3 (10)
N(1)—C(7)—C(6)	116.8 (3)	117.7 (9)
N(1)—C(7)—O(7)	123.1 (3)	122.0 (10)
C(9)—C(8)—N(1)	110.1 (3)	110.9 (9)
C(10)—C(9)—C(8)	113.8 (3)	114.0 (9)
C(9)—C(10)—C(11)	-	112.5 (9)
C(10)—C(11)—C(12)	-	113.8 (9)
C(11)—C(12)—C(13)	-	111.4 (8)
O(102)—C(10)—C(9)	113.5 (3)	-
O(101)—C(10)—C(9)	124.3 (3)	-
O(101)—C(10)—O(102)	122.2 (3)	-
O(131)—C(13)—O(132)	-	120.2 (10)
C(12)—C(13)—O(132)	-	115.2 (9)
C(12)—C(13)—O(131)	-	124.5 (10)
C(4)—C(3)—N(2)	-	118.6 (10)
C(2)—C(3)—N(2)	-	117.8 (9)
O(21)—N(2)—C(3)	-	118.2 (9)
O(22)—N(2)—C(3)	-	118.6 (9)
O(22)—N(2)—O(21)	-	123.2 (10)

Standard reflections were recentred every 100 reflections and scanned every hour to check for crystal movement and stability. The structures were solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least-squares analysis using *SHELX*76 (Sheldrick, 1976). For (I), the amino and carboxylic H-atom coordinates were located from a difference Fourier synthesis and refined with isotropic displacement parameters; ring and alkyl H atoms were fixed geometrically and refined with isotropic displacement parameters. For (II), the ring, alkyl and amino H atoms were fixed geometrically and refined with isotropic displacement parameters. The carboxylic H atom could not be located. All non-H atoms were refined with anisotropic displacement parameters. For (II), only very thin needles were obtained. As a result the data set was weak with an associated high *R* factor for the final solution.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71730 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1017]

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6-Oxo-6-(phenylamino)hexanoic Acid [Two Polymorphic Forms, (I) and (II)] and 4-Oxo-4-(*N*-methylphenylamino)-butanoic Acid (III)

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Abstract

Two polymorphs of 6-oxo-6-(phenylamino)hexanoic acid, $C_{12}H_{15}NO_3$, have been observed. In the first, (I), intermolecular hydrogen bonds form ribbons of molecules, while in the second, (II), a more planar molecular conformation allows the hydrogen bonding to extend to form sheets. The structure of (III), $C_{11}H_{13}NO_3$, is also presented and, as a result of the *N*-methyl substitution, hydrogen bonding is restricted to the formation of carboxylic acid dimers.

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