

SUPPLEMENTARY DATA

Graph set and packing analysis of H-bonded networks in polyamide structures in the Cambridge Structural Database.

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Abstract

The hydrogen-bond networks and crystal packing of 81 unique secondary di- and polyamides in the Cambridge Structural Database are investigated. Graph set analysis, as implemented in the RPluto program, is used to classify network motifs. These have been rationalised in terms of the relative dispositions of the amide groups. Peptide and retropeptides exhibit significant conformational flexibility which permits alternative H-bonding patterns. In peptides, dihedral angles of $-\psi \sim \phi \sim 105^\circ$ allow an antiparallel ladder arrangement, containing rings of either the same or alternating sizes. For retropeptides, and diamides with an odd number of CH_2 spacers, this conformation leads to a parallel ladder with rings of equal size. If ϕ approaches -60° and ψ 180° , ladders adopt a helical twist, and if the conformation is distorted further, a three-dimensional network is usually adopted. Diamides with aromatic or an even number of CH_2 spacers generally form either antiparallel ladders or sheets, although some exhibit both polymorphs. Symmetry relationships within and between hydrogen-bonded chains, ladders and sheets in the crystal packing have also been analysed. Polyamides form considerably more complex networks, although many of the structural motifs present in the diamides occur as components of these networks.

Supplementary References

- AGLYPR N-Acetyl-glycyl-isopropylamide C₇ H₁₄ N₂ O₂
A.Aubry,M.Marraud,J.Protas,J.Neel, C.R.Acad.Sci.,Ser.C, 278, 163 1974.
- ALEUIP N-Acetyl-L-leucyl-isopropylamide C₁₁ H₂₂ N₂ O₂
A.Aubry,M.Marraud,M.-T.Cung,J.Protas, C.R.Acad.Sci.,Ser.C, 281, 861, 1975.
- ALNMAM DL-Acetyl leucine N-methylamide C₉ H₁₈ N₂ O₂
T.Ichikawa,Y.Iitaka, Acta Cryst., B25, 1824, 1969.
- APALAM N-Acetyl-DL-phenylalanine-N-methylamide C₁₂ H₁₆ N₂ O₂
Y.Harada,Y.Iitaka, Acta Cryst., B30, 726, 1974.
- APHAMA N-Acetyl-L-phenylalanine-N-methylamide C₁₂ H₁₆ N₂ O₂
Y.Harada,Y.Iitaka Acta Cryst., B33, 247, 1977.
- BAFLOJ tris(Formamido)-methane C₄ H₇ N₃ O₃
G.Munninghoff, Cryst.Struct.Comm., 10, 1159, 1981.
- BAGJAU10 N,N'-Hexamethylene-dibenzamide C₂₀ H₂₄ N₂ O₂
C.Pineault,F.Brisse, Acta Cryst., C39, 1434, 1983.
- BIWROO N,N'-Heptamethylene-dibenzamide C₂₁ H₂₆ N₂ O₂
J.Brisson,F.Brisse, Acta Cryst., B38, 2663, 1982.
- BOXFAV N,N'-Diphenylhexanediamide C₁₈ H₂₀ N₂ O₂
S.Harkema,R.J.Gaymans,G.J.van Hummel, Acta Cryst.,C39, 385, 1983.
- BZOPDA10 N,N'-Dibenzoyl-p-phenylenediamine C₂₀ H₁₆ N₂ O₂
W.W.Adams,A.V.Fratini,D.R.Wiff, Acta Cryst.,B34, 954, 1978.
- CAHCIX N,N'-Octamethylene-dibenzamide C₂₂ H₂₈ N₂ O₂
C.Pineault,F.Brisse, Acta Cryst., C39, 1437, 1983.
- CEYLIB Pivaloyl-glycyl-N-isopropylglycinamide C₁₂ H₂₃ N₃ O₃
A.Aubry,C.Lecomte,G.Boussard,M.Marraud, J.Chim.Phys.Phys.-Chim.Biol., 80, 609, 1983.
- CEYLOH Pivaloyl-DL-alanyl-N-isopropylglycinamide C₁₃ H₂₅ N₃ O₃
A.Aubry,C.Lecomte,G.Boussard,M.Marraud, J.Chim.Phys.Phys.-Chim.Biol., 80, 609, 1983.
- DAMEDA NN'-Diacetylhexamethylenediamine C₁₀ H₂₀ N₂ O₂
M.Bailey, Acta Cryst., 8, 575, 1955.

DEBHEX (Z)-N-Acetyl-alpha,beta-dehydrophenylalanine methylamide C₁₂ H₁₄ N₂ O₂
A.Aubry,F.Allier,G.Boussard,M.Marraud, *Biopolymers*, 24, 639, 1985.

DEBHEX01 (Z)-N-Acetyl-alpha,beta-dehydrophenylalanine methylamide C₁₂ H₁₄ N₂ O₂
M.Souhassou,C.Lecomte,N.-E.Ghermani,M.M.Rohmer,R.Wiest,M.Benard,R.H.Blessing,
J.Am.Chem.Soc., 114, 2371, 1992.

DIACHZ Diacetylhydrazine C₄ H₈ N₂ O₂
R.Shintani, *Acta Cryst.*, 13, 609, 1960.

DMOXAM N,N'-Dimethyl-oxalamide C₄ H₈ N₂ O₂
K.-H.Klaska,O.Jarchow,W.Scham,H.Widjaja,J.Voss,H.W.Schmalle, *J.Chem.Res.*, 104, 1643,
1980.

DPTPAM N,N'-Diphenyl-terephthalamide C₂₀ H₁₆ N₂ O₂
S.Harkema,R.J.Gaymans,G.J.van Hummel,D.Zylberlicht, *Acta Cryst.*, B35, 506, 1979.

EDACTM10 Ethylidene-N,N-diacetamide C₆ H₁₂ N₂ O₂
B.Kolakowski, *Acta Cryst.*, B25, 1669, 1969.

ETADAM10 N,N'-Diethyladipamide C₁₀ H₂₀ N₂ O₂
E.Benedetti,M.R.Ciajolo,P.Corradini, *Eur.Polym.J.*, 9, 101, 1973.

ETBZAM N,N'-Ethylene-dibenzamide C₁₆ H₁₆ N₂ O₂
A.Palmer,F.Brisse *Acta Cryst.*, B36, 1447, 1980.

FAPFAD Butadiynylene-bis(m-acetamidobenzene) C₂₀ H₁₆ N₂ O₂
H.Nakanishi,H.Matsuda,M.Kato,C.R.Theocharis,W.Jones, *J.Chem.Soc.,Perkin Trans.2*, 1965,
1986.

FOMHAZ Diformylhydrazine C₂ H₄ N₂ O₂
Y.Tomiie,C.H.Koo,I.Nitta, *Acta Cryst.*, 11, 774, 1958.

FOMHAZ01 Diformylhydrazine C₂ H₄ N₂ O₂
T.Ottersen, *Acta Chem.Scand.Ser.A*, 28, 1145, 1974.

FOMHAZ02 Diformylhydrazine C₂ H₄ N₂ O₂
T.Ottersen, *Acta Chem.Scand.Ser.A*, 28, 1145, 1974.

FOMHAZ04 Diformohydrazide C₂ H₄ N₂ O₂
K.Tanaka, *Acta Cryst.* B34, 2487, 1978.

FOMHAZ05 Diformohydrazide C₂ H₄ N₂ O₂
H.Hope,T.Ottersen, *Acta Cryst.*, B35, 370, 1979.

FOMHAZ13 Diformylhydrazide C₂ H₄ N₂ O₂
H.Hope,T.Ottersen, Acta Cryst., B34, 3623, 1978.

FOMHAZ16 Diformohydrazide C₂ H₄ N₂ O₂
G.A.Jeffrey,J.R.Ruble,R.K.McMullan,D.J.DeFrees,J.A.Pople, Acta Cryst. B38, 1508, 1982.

HEXMPR N,N'-Hexamethylenebispropionamide C₁₂ H₂₄ N₂ O₂
L.H.Jensen, Acta Cryst., 15, 433, 1962.

HEYREI 1,1-bis(Benzamido)-2,2-dimethylpropane C₁₉ H₂₂ N₂ O₂
K.Honda,M.Goto,I.Kojima,I.Shibuya, Anal.Sci., 10, 137, 1994.

HICWOF Poly(hexamethylene adipamide) (C₁₂ H₂₂ N₂ O₂)_n
C.W.Bunn,E.V.Garner, Proc.R.Soc.London,Ser.A, 189, 39, 1947.

HICWUL Poly(hexamethylene sebacamide) (C₁₆ H₃₀ N₂ O₂)_n
C.W.Bunn,E.V.Garner, Proc.R.Soc.London,Ser.A, 189, 39, 1947.

HIDDUT Poly(p-phenylene terephthalamide) (C₁₄ H₁₀ N₂ O₂)_n
M.G.Northolt, Eur.Polym.J., 10, 799, 1974.

JEPHIV 8-Acetamidomethyl-2-naphthoic acid N-isopropylamide C₁₇ H₂₀ N₂ O₂
I.Ernest,J.Kalvoda,G.Rihs,M.Mutter, Tetrahedron Lett., 31, 4011, 1990.

JEPHOB 8-Acetamido-5,6,7,8-tetrahydro-2-naphthoic acid N-isopropylamide C₁₆ H₂₂ N₂ O₂
I.Ernest,J.Kalvoda,G.Rihs,M.Mutter, Tetrahedron Lett., 31, 4011, 1990.

JEYFOI t-Butylcarbonyl-g-alanyl-m-glycine N-isopropylamide retropeptide C₁₃ H₂₅ N₃ O₃
E.J.Gomez,B.Vitoux,M.Marraud,C.Sakarellos,L.El Masdouri,A.Aubry, Int.J.Pept.Protein Res., 34, 480, 1989.

JOFHER N,N'-Dimethylisopropylmalonamide retropeptide C₈ H₁₆ N₂ O₂
L.El-Masdouri,A.Aubry,E.Gomez,B.Vitoux,M.Marraud Acta Cryst., C48, 178, 1992.

JOFHIV N,N'-Methylenediacetamide retropeptide C₅ H₁₀ N₂ O₂
L.El-Masdouri,A.Aubry,E.Gomez,B.Vitoux,M.Marraud, Acta Cryst. C48, 176, 1992.

JOFHOB N-Isobutylidenedipivalamide retropeptide C₁₄ H₂₈ N₂ O₂
L.El-Masdouri,A.Aubry,E.Gomez,B.Vitoux,M.Marraud
Acta Crystallogr.,Sect.C (Cr.Str.Comm.), 48, 175, 1992.

JORKIK Acetyldehydrophenylalanyl-L-valyl-dehydrophenylalanylmethylamine C₂₆ H₃₀ N₄ O₄
M.R.Ciajolo,A.Tuzi,C.R.Pratesi,A.Fissi,O.Pieroni, Int.J.Pept.Protein Res., 38, 539, 1991.

JUDZEN N-Acetyl-dehydroalanine N'-methylamide C₆ H₁₀ N₂ O₂
D.E.Palmer,C.Pattaroni,K.Nunami,R.K.Chadha,M.Goodman,T.Wakamiya,K.Fukase,
S.Horimoto,M.Kitazawa,H.Fukita,A.Kubo,T.Shiba, J.Am.Chem.Soc., 114, 5634, 1992.

JUHJEB rac-Acetyl-glycyl-beta-alanyl-glycyl-beta-alanyl N-(n-propyl)amide C₁₅ H₂₇ N₅ O₅
J.Tormo,J.Puiggali,J.Vives,I.Fita, Biopolymers, 32, 643, 1992.

KUJZOE Pivaloyl-glycyl-glycine-cyclohexylamide C₁₅ H₂₇ N₃ O₃
S.H.Gellman,D.R.Powell,J.M.Desper, Tetrahedron Lett., 33, 1963, 1992.

LAANMA N-Acetyl-L-alanine-N-methylamide C₆ H₁₂ N₂ O₂
Y.Harada,Y.Iitaka, Acta Cryst., B30, 1452, 1974.

LABJED 2,2'-bis(Acetamido)biphenyl C₁₆ H₁₆ N₂ O₂
J.P.Reboul,G.Pepe,D.Siri,Y.Oddon,C.Caranoni,H.Rahal,J.C.Soyfer,J.Barbe, Acta Cryst., C49,
735, 1993.

MEBZAM N,N'-Tetramethylenedibenzamide C₁₈ H₂₀ N₂ O₂
S.Harkema,G.J.van Hummel,R.J.Gaymans Acta Cryst., B36, 3182, 1980.

NAAIBA N-Acetyl-alpha-aminoisobutyric acid methylamide C₇ H₁₄ N₂ O₂
A.Aubry,J.Protas,G.Boussard,M.Marraud,J.Neel, Biopolymers, 17, 1693, 1978.

NAKLOA 1-Acetamido-2,2-dimethyl-3-isopropylaminocarbonyl-cyclobutane C₁₂ H₂₂ N₂ O₂
K.Burgess,Shiming Li,J.Rebenspies, Tetrahedron Lett., 38, 1681, 1997.

NALEUE N-Acetyl-DL-leucyl-ethylamide C₁₀ H₂₀ N₂ O₂
A.Aubry,M.Marraud,J.Protas,J.Neel, C.R.Acad.Sci.,Ser.C, 278, 697, 1974.

NIJCUE Trimethyl 1,3,5-benzenetricarboxamide C₁₂ H₁₅ N₃ O₃
K.Hanabusa,C.Koto,M.Kimura,H.Shirai,A.Takehi, Chem.Lett., , 429, 1997.

NUSDOU N-Benzoyl-L-alanyl-N-phenyl-L-alaninamide C₁₉ H₂₁ N₃ O₃
M.Cirilli, Z.Kristallogr.-New Crystal Structures, 213, 127, 1998.

PABZAM N,N'-(p-Phenylene)-dibenzamide C₂₀ H₁₆ N₂ O₂
S.Harkema,R.J.Gaymans, Acta Cryst., B33, 3609, 1977.

PIVGLY N-Pivalyl-glycyl-isopropylamide C₁₀ H₂₀ N₂ O₂
A.Aubry,M.Marraud,J.Protas,J.Neel, C.R.Acad.Sci.,Ser.C, 276, 1089, 1973.

POLNIN N-Acetyl-2,2-diphenylglycyl-N-methylamide C₁₇ H₁₈ N₂ O₂
C.Toniolo,M.Crisma,N.Fabiano,P.Melchiorri,L.Negri,J.A.Krause,D.S.Eggleston,
Int.J.Pept.Protein Res., 44, 85, 1994.

POLPEL N-Benzoyl-2,2-diphenylglycyl-N'-methylamide C₂₂ H₂₀ N₂ O₂
C.Toniolo,M.Crisma,N.Fabiano,P.Melchiorri,L.Negri,J.A.Krause,D.S.Eggleston,
Int.J.Pept.Protein Res., 44, 85, 1994.

POLPIP N-Acetyl-2,2-diphenylglycyl-N'-benzylamide C₂₃ H₂₂ N₂ O₂
C.Toniolo,M.Crisma,N.Fabiano,P.Melchiorri,L.Negri,J.A.Krause,D.S.Eggleston,
Int.J.Pept.Protein Res., 44, 85, 1994.

PULHUZ N,N'-Diphenylisophthalamide C₂₀ H₁₆ N₂ O₂
J.F.Malone,C.M.Murray,G.M.Dolan,R.Docherty,A.J.Lavery, Chemistry of Materials, 9, 2983,
1997.

PVMGLA N-Pivalyl-N'-methyl-L-glutaminy-methylamide C₁₂ H₂₃ N₃ O₃
A.Aubry,J.Protas,M.Marraud, Acta Cryst., B33, 2534, 1977.

RAPYIQ N,N'-Dimethyl-1,4-phenylenediacetamide C₁₂ H₁₆ N₂ O₂
F.D.Lewis,J.-S.Yang,C.L.Stern, J.Am.Chem.Soc., 118, 12029, 1996.

RAPYOW N,N'-Dimethyl-2,6-naphthalenedicarboxamide
at -120 deg.C C₁₄ H₁₄ N₂ O₂
F.D.Lewis,J.-S.Yang,C.L.Stern, J.Am.Chem.Soc., 118, 12029, 1996.

RAPYUC N,N'-Dimethyl-1,4-naphthalenedicarboxamide C₁₄ H₁₄ N₂ O₂
F.D.Lewis,J.-S.Yang,C.L.Stern, J.Am.Chem.Soc., 118, 12029, 1996.

SAZWEV p,p'-Di-t-butyl-N,N'-tetramethylenedibenzamide
C₂₆ H₃₆ N₂ O₂ J.Brisson,J.Gagne,F.Brisse, Can.J.Chem., 67, 840, 1989.

SUSHOD Poly(iminocarbonyltrimethylene) (C₈ H₁₄ N₂ O₂)_n
R.J.Fredericks,T.H.Doyle,R.S.Sprague, J.Polym.Sci.,Polym.Phys.Ed., 4, 899, 1966.

TERSEO N,N'-bis(4-Methylbenzoyl)-1,4-benzenediamine C₂₂ H₂₀ N₂ O₂
N.Nagel,C.Nather,H.Bock Acta Cryst., C53, 79, 1997.

TIRJIN N-Acetyl-(S)-isovaline methylamide C₈ H₁₆ N₂ O₂
M.Crisma,G.Valle,F.Formaggio,C.Toniolo,J.Kamphuis, Z.Kristallogr., 211, 559, 1996.

TOPPUJ Butanediy di-formamide C₆ H₁₂ N₂ O₂
J.D.Chaney,C.R.Goss,K.Folting,B.D.Santarsiero,M.D.Hollingsworth, J.Am.Chem.Soc., 118,
9432, 1996.

TOPQAQ Hexanediy di-formamide C₈ H₁₆ N₂ O₂
J.D.Chaney,C.R.Goss,K.Folting,B.D.Santarsiero,M.D.Hollingsworth, J.Am.Chem.Soc., 118,
9432, 1996.

TOPQEU Octanediyyl diformamide C₁₀ H₂₀ N₂ O₂

J.D.Chaney,C.R.Goss,K.Folting,B.D.Santarsiero,M.D.Hollingsworth, J.Am.Chem.Soc., 118, 9432, 1996.

VEGXUA N-Methyl-psi-glycyl-glycylmethyamide C₇ H₁₃ N₃ O₃

L.El.Masdouri,A.Aubry,E.J.Gomez,B.Vitoux,M.Marraud, J.Chim.Phys.Phys.-Chim.Biol., 85, 583, 1988.

VEHNUR 1,3-(N,N'-Benzamide)-2-methyl-1-pentene C₂₀ H₂₂ N₂ O₂

G.Bocelli, J.Crystallogr.Spectrosc.Res., 19, 841, 1989.

VISFEI bis(2,2-Dibutyl-N,N'-di(1-naphthyl)malonamide) cyclohexane clathrate

C₃₁ H₃₄ N₂ O₂, 0.5(C₆ H₁₂)

K.Hiratani,M.Goto, Chem.Lett., 89, 1991.

VOKCON t-Butylcarbonyl-D,L-alanyl-alpha,beta-dehydrophenylalanyl ispropylamide C₂₀ H₂₉ N₃ O₃

A.Aubry,G.Pietrzynski,B.Rzeszotarska,G.Boussard,M.Marraud, Int.J.Pept.Protein Res., 37, 39, 1991.

WIMTER Poly(heptamethylene pimelamide) (C₁₄ H₂₆ N₂ O₂)_n

Y.Kinoshita, Makromol.Chem., 33, 21, 1959.

YEKCIA 2R-(Cyclohexylmethyl)-bis(N-1S-phenylethyl)-4S-(2-propenyl)-1,5-pentanedicarboxamide C₃₁ H₄₂ N₂ O₂

N.A.Porter,G.S.Miracle,S.M.Cannizzaro,R.L.Carter,A.T.McPhail,Lin Liu. J.Am.Chem.Soc., 116, 10255, 1994.

ZADHER (R)-2,3-bis(Benzamido)-2-methylpropanoylphenylalanine cyclohexylamide C₃₃ H₃₈ N₄ O₄

D.Obrecht,H.Karajiannis,C.Lehmann,P.Schonholzer,C.Spiegler,K.Muller, Helv.Chim.Acta, 78, 703, 1995.

ZADHOB ((S,S)-(Benzamido)-2-(benzamidomethyl)-4-methylpentanoyl)phenylalanine cyclohexylamide C₃₆ H₄₄ N₄ O₄

D.Obrecht,H.Karajiannis,C.Lehmann,P.Schonholzer,C.Spiegler,K.Muller, Helv.Chim.Acta, 78, 703, 1995.

ZADHUH N-((R)-N-Benzoyl-2-methyl-2-phenylglycyl)-(S)-phenylalanine cyclohexylamide C₃₁ H₃₅ N₃ O₃

D.Obrecht,U.Bohdal,C.Broger,D.Bur,C.Lehmann,R.Ruffieux,P.Schonholzer,C.Spiegler, K.Muller, Helv.Chim.Acta, 78, 563, 1995.

ZADJAP N-((R)-N-Benzoyl-2-methylvalyl)-(S)-phenylalanine cyclohexylamide C₂₈ H₃₇ N₃ O₃

D.Obrecht,U.Bohdal,C.Broger,D.Bur,C.Lehmann,R.Ruffieux,P.Schonholzer,C.Spiegler,
K.Muller, *Helv.Chim.Acta*, 78, 563, 1995.

ZADJET N-((S)-N-Benzoyl-2-methyl-phenylalanyl)-(S)-phenylalanine cyclohexylamide
at 193 deg.K C₃₂ H₃₇ N₃ O₃

D.Obrecht,U.Bohdal,C.Broger,D.Bur,C.Lehmann,R.Ruffieux,P.Schonholzer,C.Spiegler,
K.Muller, *Helv.Chim.Acta*, 78, 563, 1995.

ZALVEN N,N'-Dipropylglutaramide C₁₁ H₂₂ N₂ O₂

E.Navarro,C.Aleman,J.Puiggali, *J.Am.Chem.Soc.*, 117, 7307, 1995.

ZORMEY N-Acetyl-alpha-aminoisobutyryl-alpha-aminoisobutyryl-N\$omega!-benzoyllysyl-
alpha-aminoisobutyryl-alpha-aminoisobutyryl-N\$omega!-benzoyllysyl-alpha-aminoisobutyryl-
alpha-aminoisobutyryl-N-methylamide monohydrate C₅₃ H₈₁ N₁₁ O₁₁,H₂ O₁

C.Toniolo,A.Bianco,F.Formaggio,M.Crisma,G.M.Bonora,E.Benedetti,V.Del Duca,
M.Saviano,B.Di Blasio,C.Pedone,A.Aubry, *Bioorg.Med.Chem.*, 3, 1211, 1995.

ZUKJOE N,N-Dimethyl-4,4'-stilbenedicarboxamide C₁₈ H₁₈ N₂ O₂

F.D.Lewis,Jye-Shane Yang,C.L.Stern, *J.Am.Chem.Soc.*, 118, 2772, 1996.

ZUKJUK N,N'-Dimethyl-4,4'-biphenyldicarboxamide C₁₆ H₁₆ N₂ O₂

F.D.Lewis,Jye-Shane Yang,C.L.Stern, *J.Am.Chem.Soc.*, 118, 2772, 1996.

ZUKKAR N,N'-Dimethyl-4,4'-diphenylacetylenedicarboxamide C₁₈ H₁₆ N₂ O₂

F.D.Lewis,Jye-Shane Yang,C.L.Stern, *J.Am.Chem.Soc.*, 118, 2772, 1996.

Supplementary Figure Captions

- Fig. S1. H-bonded arrangement in JOFHIV, showing chain of rings pattern.
- Fig. S2. Helical ladder structure in ZADJAP, with bifurcated H-bond acceptor, formed around a 6_1 screw axis.
- Fig. S3. Complex sheet arrangement in VOWKON, with 3 independent molecules in the asymmetric unit.
- Fig. S4. Sheet structure in ZADHUH composed of perpendicular H-bond chains (red and green) and additional intramolecular H-bond (blue).
- Fig. S5. Three-dimensional structure of JEYFOI, composed of H-bond ladders (red and green) linked by H-bond chain (blue).
- Fig. S6. Ladder and chain components of the two-dimensional network in JUHJEB.