Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Material

How focussing on hydrogen bonding interactions in amino acids can miss the bigger picture: a high-pressure neutron powder diffraction study of ε-glycine.

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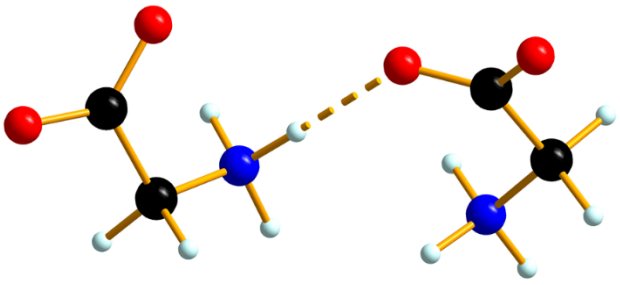
Analysis of intermolecular interactions using purely geometric criteria can be misleading: the crystal structures of γ- and ε-glycine, which can be interconverted using high pressure, exhibit apparently ideal H-bonding geometry for dimers which nevertheless have repulsive interaction energies.



NH…O = 1.95 Å, <NH…O = 179°, Energy = +18.5 kJ/mol

Table S1: Optimised coordinates of γ-glycine at zero pressure and 0 K. The cell dimensions are *a* = 7.080621 and *c* = 5.488664 Å in space group $P3_2$.

Atom	x	y	z
N1	0.245422	0.038095	0.502811
O1	0.241652	0.024566	0.007697
O2	0.542330	-0.006308	-0.013150
C1	0.392577	0.001056	0.102399
C2	0.389470	-0.028960	0.379147
H1	0.253297	0.029003	0.695856
H2	0.298360	0.201514	0.454188
H3	0.084214	-0.061435	0.447867
H4	0.553539	0.065046	0.456801
H5	0.327284	-0.201885	0.419943

Table S2: Optimised coordinates of ε-glycine at zero pressure and 0 K. The cell dimensions are a = 5.103946 b = 6.043677, c = 5.476029 Å, β = 112.742208° with space group *Pn*.

Atom	x	y	z
O1	0.281189	0.785307	1.142781
O2	0.742727	0.692656	1.286547
N1	0.738687	0.679909	0.784643
C1	0.510253	0.753457	1.108456
C2	0.505337	0.796915	0.831600
H1	0.301935	0.745783	0.679954
H2	0.531564	0.975021	0.808707
H3	0.728578	0.705980	0.588045
H4	0.723682	0.509520	0.800165
H5	0.941395	0.730825	0.919408

Table S3: Intermolecular contacts in ε-glycine at 0.55 GPa. All energies are in kJ mol^{-1}.

#	Contact	Operation	H…O/Å	N/C…O/Å	<N/C-H…O/°
Contacts formed within layers					
A	N1H3...O2	*x*,*y*,-1+*z*	1.845(6)	2.816(3)	152.1(8)
	N1H3...O1	*x*,*y*,-1+*z*	2.428(20)	3.256(14)	135.1(7)
	Pixel energies	E_{elec} =-113.3; E_{pol} = -34.5; E_{disp} = -14.8; E_{rep} = 57.5; $\boldsymbol{E_{tot}}$ **= -105.0**			
B	N1H5...O1	1+*x*,*y*,*z*	1.76(3)	2.81(3)	175.2(13)
	Pixel energies	E_{elec} = -36.4; E_{pol} = -38.5; E_{disp} = -14.8; E_{rep} = 58.4; $\boldsymbol{E_{tot}}$ **= -31.3**			
C	C2H1...O2	-1+*x*,*y*,-1+*z*	2.660(12)	3.744(14)	172.5(10)
	Pixel energies	E_{elec} = 19.2; E_{pol} = -4.2; E_{disp} = -3.2; E_{rep} = 2.1; $\boldsymbol{E_{tot}}$ **= 13.9**			
Contacts formed between layers connected by N1-H4					
D	N1H4...O1	½+*x*,1-*y*,-½+*z*	2.17(4)	3.06(4)	141.2(6)
	Pixel energies	E_{elec} = -46.7; E_{pol} = -16.3; E_{disp} = -10.0; E_{rep} = 14.7; $\boldsymbol{E_{tot}}$ **= -58.3**			
E	N1H4...O2	-½+*x*,1-*y*,-½+*z*	2.449(20)	3.191(18)	126.8(13)
	C2H1...O2	-½+*x*,1-*y*,-½+z	2.63(4)	3.08(3)	104.1(6)
	Pixel energies	E_{elec} = 58.0; E_{pol} = -23.6; E_{disp} = -16.5; E_{rep} = 14.9; $\boldsymbol{E_{tot}}$ **= 32.8**			
Contacts formed between layers connected by C2-H2					
F	C2H2...O1	½+*x*,2-*y*,-½+*z*	2.31(4)	3.17(4)	134.7(6)
	Pixel energies	E_{elec} = -28.9; E_{pol} = -12.0; E_{disp} = -8.6; E_{rep} = 13.4; $\boldsymbol{E_{tot}}$ **= -36.1**			
G	C2H2...O2	-½+*x*,2-*y*,-½+*z*	2.42(2)	3.32(3)	138.5(15)
	Pixel energies	E_{elec} = 53.8; E_{pol} = -12.4; E_{disp} = -13.9; E_{rep} = 15.5; $\boldsymbol{E_{tot}}$ **= 43.0**			

Table S4: Intermolecular contacts in ε-glycine optimised by periodic DFT at 0 K and 0 GPa. All energies are in kJ mol^{-1} in the following order: electrostatic, polarisation, dispersion, repulsion and total. Optimised crystallographic parameters are given in Table S2.

#	Contact	Operation	H…O/Å	N/C…O/Å	<N/C-H…O/°
Contacts formed within layers					
A	N1H3...O2	*x*,*y*,-1+*z*	1.68	2.737	168
	N1H3...O1	*x*,*y*,-1+*z*	2.66	2.445	130
	Pixel energies	-131.1	-45.6	-15	88.4 -103.3
	SAPT energies	-133.7	-56.3	-28.4	105.7 -112.6
B	N1H5...O1	1+*x*,*y*,*z*	1.72	2.779	174
	Pixel energies	-46.8	-41.8	-14.2	65.5 -37.3
	SAPT energies	-47.9	-51	-26.6	88.2 -37.4
C	C2H1...O2	-1+*x*,*y*,-1+*z*	2.85	3.934	170
	Pixel energies	23.9	-3.2	-2.3	0.9 19.2
	SAPT energies	23.0	-3.6	-4.1	2.1 17.4
Contacts formed between layers connected by N1-H4					
D	N1H4...O1	½+*x*,1-*y*,-½+*z*	2.05	2.947	143
	Pixel energies	-57.5	-20.9	-11.5	23.2 -66.7
	SAPT energies	-59.9	-23.3	-17.0	36.3 -63.9
E	N1H4...O2	-½+*x*,1-*y*,-½+*z*	2.72	3.391	123
	C2H1...O2	-½+*x*,1-*y*,-½+z	2.76	3.218	84
	Pixel energies	71.1	-19.8	-14.0	8.8 46.1
	SAPT energies	65.0	-18.4	-19.8	21.9 48.7
Contacts formed between layers connected by C2-H2					
F	C2H2...O1	½+*x*,2-*y*,-½+*z*	2.33	3.248	140
	Pixel energies	-23.3	-10.5	-7.5	10.7 -30.7
	SAPT energies	-27.7	-11.5	-12.2	18.3 -33.1
G	C2H2...O2	-½+*x*,2-*y*,-½+*z*	2.47	3.334	135
	Pixel energies	52.8	-10.7	-11.5	10.4 41.0
	SAPT energies	51.0	-11.6	-17.3	20.8 43.0

Table S5: Intermolecular contacts in γ-glycine optimised by periodic DFT at 0 K and 0 GPa. All energies are in kJ mol^{-1} in the following order: electrostatic, polarisation, dispersion, repulsion and total. Optimised crystallographic parameters are given in Table S1. Atom labelling is taken from CSD refcode GLYCIN16.

#	Contact	Operation	H…O/Å	N/C…O/Å	<N/C-H…O/°
1	N1H1…O1	x,y,z+1	1.71	2.773	173
	Pixel energies	-124.6	-41.4	-14.3	76.4	-103.9
	SAPT energies	-126.8	-51.8	-26.6	94.5	-110.6
2	N1H2...O1	-y,x-y,z+2/3	2.64	2.928	95
	Pixel energies	-21.0	-10.5	-6.9	9.0	-29.4
	SAPT energies	-25.3	-11.3	-10.2	16.4	-30.4
3	C2H5...O2	-x+y+1,-x,z+1/3	3.00	3.886	138
	Pixel energies	49.0	-7.7	-9.1	5.4	37.6
	SAPT energies	51.1	-8.6	-13.7	10.1	38.8
4	N1H3...O1	-x+y,-x,z+1/3	1.95	2.992	179
	Pixel energies	28.2	-33.8	-17.0	31.7	9.0
	SAPT energies	24.2	-34.6	-23.1	52.1	18.5
5	C2H5...O2	-y,x-y-1,z+2/3	2.43	3.234	129
	Pixel energies	-36.6	-10.6	-7.8	10.3	-44.8
	SAPT energies	-43.3	-11.9	-12.4	18.3	-49.3
6	N1H2...O2	-x+y+1,-x+1,z+1/3	1.74	2.762	160
	Pixel energies	-37.6	-45.0	-17.4	66.0	-34.0
	SAPT energies	-44.2	-52.8	-31.2	92.9	-35.3
7	C2H4...O1	-y+1,x-y,z+2/3	2.88	3.956	167
	Pixel energies	11.3	-4.3	-3.2	1.1	4.9
	SAPT energies	10.9	-4.2	-5.3	2.8	4.2

Table S6: Comparison of equivalent intermolecular energies ($kJmol^{-1}$) in ε and γ glycine from calculations based on experimental coordinates determined for ε-glycine at 0.55 GPa and RT and γ-glycine at ambient pressure and RT (CSD refcode GLYCIN15). These data can be compared with those in Table 3 in the main text, which were obtained using structures optimised by periodic DFT.

ε-glycine			γ-glycine			Δ(ε→γ)	
Contact	PIXEL	SAPT	Contact	PIXEL	SAPT	PIXEL	SAPT
A	-105	-103.4	1	-104.7	-108.1	0.3	-4.7
B	-31.3	-31.3	2	-30.7	-31.9	0.6	-0.6
C	13.9	12.3	3	37.6	38.9	23.7	26.6
D	-58.3	-56.1	4	10.8	19.3	69.1	75.4
E	32.8	37.4	5	-45.9	-50.1	-78.7	-87.5
F	-36.1	-38.5	6	-32.5	-31.9	3.6	6.6
G	43.0	45.8	7	4.4	3.6	-38.6	-42.2
Totals	-141.0	-133.8		-161.0	-160.2	-20.0	-26.4

Figure S1: Comparison of PIXEL and SAPT total intermolecular interaction energies in ε and γ glycine. Units are kJ mol^{-1}.