Electronic Supplementary Material (ESI) for CrystEngComm

Supplementary Information

The unexpected but predictable tetrazole packing in flexible 1-benzyl-1H-tetrazole

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1. Further Crystallographic Data

Table S1: Crystal data and structure refinement for 1-benzyl-*1H*-tetrazole (2008src0576).

Identification code	2008src0576	
Empirical formula	C_8 H_8 N_4	
Formula weight	160.18	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P2₁*	
Unit cell dimensions	a = 7.6843(5) Å	α = 90°
	b = 5.5794(4) Å	β = 100.949(4)°
	c = 9.4459(7) Å	γ = 90°
Volume	397.61(5) $Å^3$	
Z	2	
Density (calculated)	1.338 gcm^{-3}	
Absorption coefficient	0.088 mm^{-1}	
F(000)	168	
Crystal size	0.09 x 0.03 x 0.02 mm^3	
Theta range for data collection	3.14 to 27.45°.	
Index ranges	$-8 \le h \le 9$, $-7 \le k \le 7$, $-12 \le l \le 12$	
Reflections collected	5629	
Independent reflections	977 [R(int) = 0.0625]	
Completeness to theta = 27.45°	97.0 %	
Max. and min. transmission	0.9982 and 0.9921	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	977 / 1 / 113	
Goodness-of-fit on F^2	1.259	
Final R indices [I>2σ(I)]	R_1 = 0.0426, wR_2 = 0.0753	
R indices (all data)	R_1 = 0.0636, wR_2 = 0.0827	
Largest diff. peak and hole	0.186 and -0.207 $e.Å^{-3}$	

Table S2: *1H*-Tetrazole ring angles and bond lengths in1-benzyl-*1H*-tetrazole.

Angles	X-ray/ °	*ab initio*/ °
N(1)-N(2)-N(3)	106.9(2)	106.59
N(2)-N(3)-N(4)	110.2(2)	111.19
N(3)-N(4)-C(5)	105.2(2)	105.56
N(4)-C(5)-N(1)	109.6(2)	108.77
C(5)-N(1)-N(2)	108.0 (2)	107.88
C(5)-N(1)-C(6)	130.5(2)	131.14
N(2)-C(1)-C(6)	121.5(2)	120.91

bond lengths	X-ray / Å	*ab initio*/ Å
N(1)-N(2)	1.343(2)	1.34
N(2)-N(3)	1.301(2)	1.288
N(3)-N(4)	1.368(2)	1.349
N(4)-C(5)	1.314(2)	1.314
C(5)-N(1)	1.336(2)	1.341
N(1)-C(6)	1.472(2)	1.455

The phenyl ring has normal geometry, with average C – C bond length 1.386(4) Å, average bond angle 120.0(7)° and ring planarity rms deviation of 0.0057Å including the link atom C(7). Bond angles in the tetrazole ring average 108.0(1.7) ° which is consistent with the planarity of the ring having an rms deviation of 0.012 Å, including the link C atom and H(5) on C(5).

Table S3: Hydrogen bonds for 1-benzyl-*1H*-tetrazole. In additional there is a CH---π intermolecular interaction: C(8)-H(8)---Benzyl Centroid #1 = 2.859 Å

D-H···A	d(D-H)/ Å	d(H···A)/ Å	d(D···A)/ Å	<(DHA)/ °
(1) C(8)-H(8)...C(8)#1	0.95	2.93	3.743(3)	144.3
(2) C(9)-H(9)...C(6)#1	0.95	2.93	3.668(4)	135.4
(3) C(10)-H(10)...N(3)#2	0.95	2.91	3.723(3)	143.9
(4) C(10)-H(10)...N(4)#2	0.95	2.78	3.674(4)	157.2
(5) C(12)-H(12)...N(2)#3	0.95	2.78	3.617(4)	148.1
(6) C(6)-H(6B)...N(2)#3	0.99	2.65	3.598(4)	159.7
(7) C(6)-H(6B)...N(3)#3	0.99	2.93	3.766(4)	142.4
(8) C(5)-H(5)...N(3)#3	0.90(3)	2.70(3)	3.490(4)	146(2)
(9) C(6)-H(6A)...N(3)#4	0.99	2.75	3.245(3)	111.5
(10) C(5)-H(5)...N(4)#5	0.90(3)	2.64(3)	3.292(4)	130(2)
(11) C(12)-H(12)...N(3)#3	0.95	3.14	3.991(3)	150.5
(12) C(6)-H(6B)...N(3)#3	0.99	2.93	3.766(4)	142.4
(13) C(9)-H(9)...N(4)#6	0.95	3	3.664(3)	127.8
(14) C(10)-H(10)...N(4)#6	0.95	3.04	3.679(4)	126.4
(15) C(10)-H(10)...C(5)#6	0.95	3.15	3.882(4)	135

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y-1/2,-z+2**;** #2 -x+2,y+1/2,-z+2**;** #3 x,y+1,z**;** #4 -x+1,y+1/2,-z+1**;**

#5 -x+2,y+1/2,-z+1**;** #6 x,y,z+1

2. Conformational energy grid

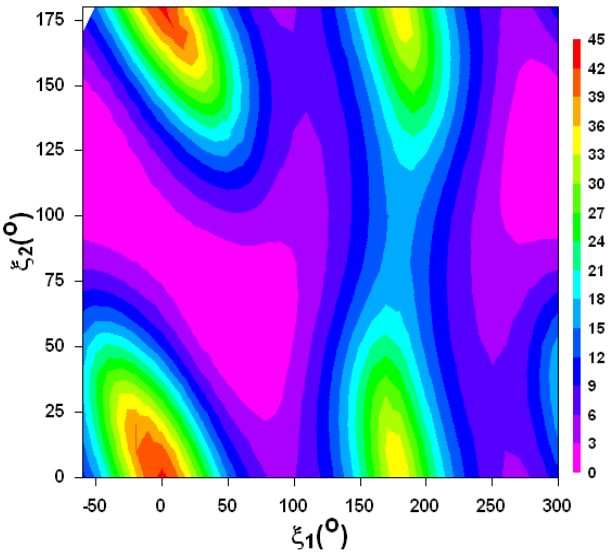

Fig. S1: The conformational energy grid used in the search. Relative intramolecular energies, ΔE_{intra} (kJmol^{-1}) for isolated molecule calculations at MP2 6-31G(d,p) level.

3. Crystal Energy landscape with approximate energy model

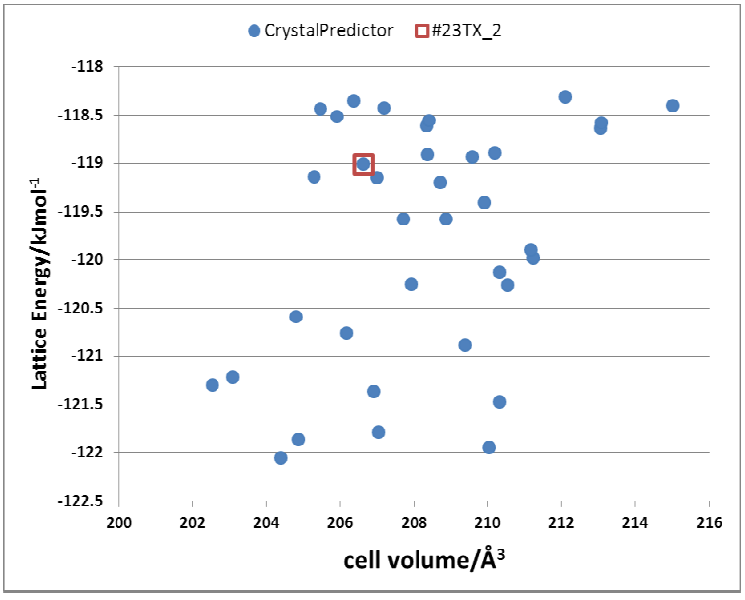

Fig. S2: The crystal energy landscape of 1-benzyl-*1H*-tetrazole after CrystalPredictor search. The lattice energy was estimated using interpolated atomic charges and intramolecular energies (Fig. S1). The closest match to the experimental structure is picked out in red.

4. Structures on crystal energy landscape

Table S4: Summary of experimental structure (highlighted in blue) and the crystal structures on the crystal energy landscape (Fig. 7), where the structure has been refined using CrystalOptimizer and the polarizable continuum model. The first integer in the structure label is the energy order of the final lattice energies (Fig. 7), whereas the final integer is that after the CrystalPredictor stage, (i.e. using an atomic point charge model, Fig. S2). The computed structure that corresponds to the X-ray structure is highlighted in bold. All structures can be obtained in shelx (.res) format from the UCL authors.

Label	SG	*a* Å	*b* Å	*c* Å	β °	ρ gcm^{-3}	U_{inter} $kJmol^{-1}$	ΔE_{intra} $kJmol^{-1}$	E_{latt} $kJmol^{-1}$
#1BT_120	$P2_1/c$	9.99	8.17	11.04	117.50	1.33	-121.76	2.25	-119.52
#2BT_23	***P2₁***	**7.93**	**5.55**	**9.44**	**101.32**	**1.31**	**-121.52**	**2.08**	**-119.44**
Experiment	$P2_1$	*7.68*	*5.58*	*9.45*	*100.95*	*1.34*	-	-	-
#3BT_165	$P2_1/c$	10.86	5.54	15.97	121.41	1.30	-121.09	2.70	-118.39
#4BT_335	$P2_12_12_1$	9.38	15.81	5.56	90.00	1.29	-120.32	2.00	-118.33
#5BT_767	$P2_1/c$	9.41	5.53	15.80	102.34	1.32	-120.44	2.14	-118.30
#6BT_167	$P2_1$	5.68	8.39	8.81	103.22	1.30	-122.89	5.04	-117.85
#7BT_912	$P2_1$	5.57	8.69	8.61	103.65	1.32	-118.82	1.43	-117.39
#8BT_34	$P2_1/c$	8.09	5.53	18.59	101.66	1.31	-119.19	2.19	-117.00
#9BT_491	$Pna2_1$	16.66	5.66	8.58	90.00	1.31	-122.99	6.26	-116.73
#10BT_250	$P2_12_12_1$	19.04	5.57	7.78	90.00	1.29	-119.16	3.25	-115.91
#11BT_55	$P2_1/c$	10.80	5.56	15.82	122.32	1.32	-119.79	3.96	-115.83
#12BT_490	$P2_1/c$	6.53	8.66	13.94	94.28	1.35	-120.98	5.21	-115.77
#13BT_178	$P2_12_12_1$	8.33	5.61	17.64	90.00	1.29	-117.89	2.32	-115.57

The generation of the crystal energy landscape took about 2 months computer time using between 10 and 20 cores of a research cluster depending on the stage.

5. Comparison with other 1-substituted 1H-tetrazole crystal structures

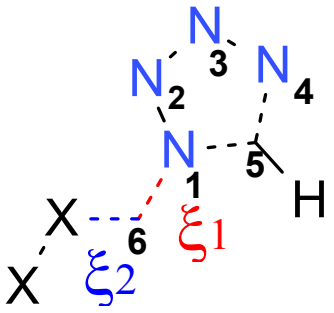

Fig. S3: Query used in Conquest to search the CSD for similar fragment.

The CSD version 5.33 March 2012 was searched for the fragment defined above, yielding 34 structures, including 2 redeterminations. The statistical and packing analysis was carried out on the 32 structures (refcodes: ACIROU, ACIRUA, BEGRIP, CAZWIK, DOKQEA, DOKQIE, EKAJOQ, HISYEO, IQUJEK, ABMIL, LUVPIC, MEVWOZ, MUKMAG, PHTETZ01, PUGLUZ, QALNOH, QALNUN, QALPAV, QALPID, QALPOJ, QALPUP, QALQAW, QALQEA01, QALQIE, QEBPUI01, REVMOV, REZNUG, RIZXEE, SOLHAD, TIJLIH, VUNNUO and OBAREQ).

There is little variation of angles within the tetrazole groups, consistent with the variation in bondlengths in this 5 membered ring (Fig. 5). The distribution of torsion angles is wide, with the distribution for ξ_1= X-C6-N1-C5 being very similar to that for X-C6-N1-C5 because of the near planarity of the tetrazole unit, with some structures being very close to the bin boundaries in Fig. S**3**. The distributions are compatible with Fig. S**1**, with more structures being seen in the low energy regions.

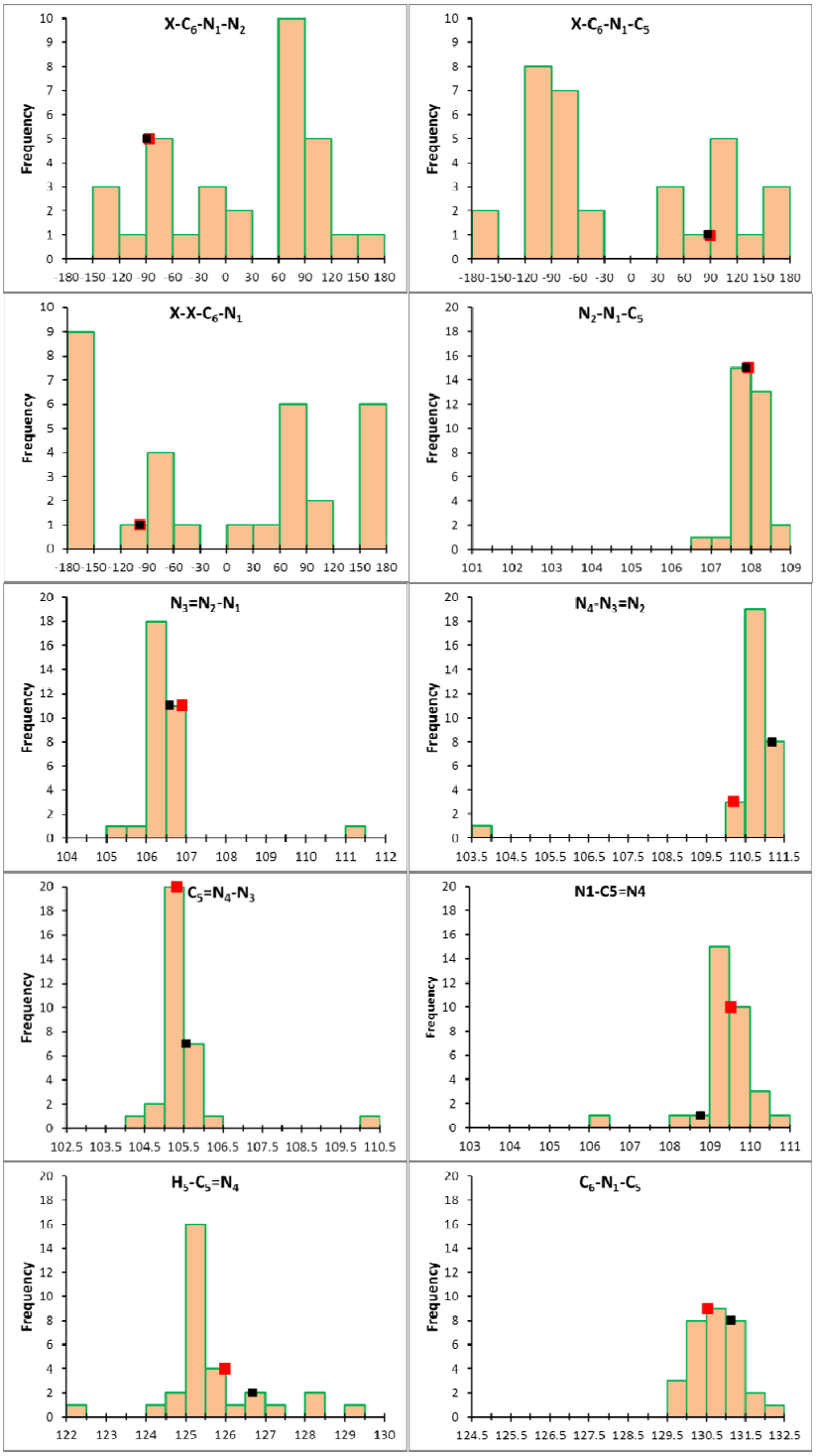

Fig. S4: Histograms showing the distributions of the torsions and angles of the 32 tetrazole rings found during the CSD survey. The experimental bondlength in1-benzyl-*1H*-tetrazole is denoted by the red square, while the *ab initio* bondlength in the corresponding calculated structure #2BT_23 is denoted by the black square.