Supporting information

Charge Density Study of the π-Delocalization and Intermolecular Interactions

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Supplementary Materials

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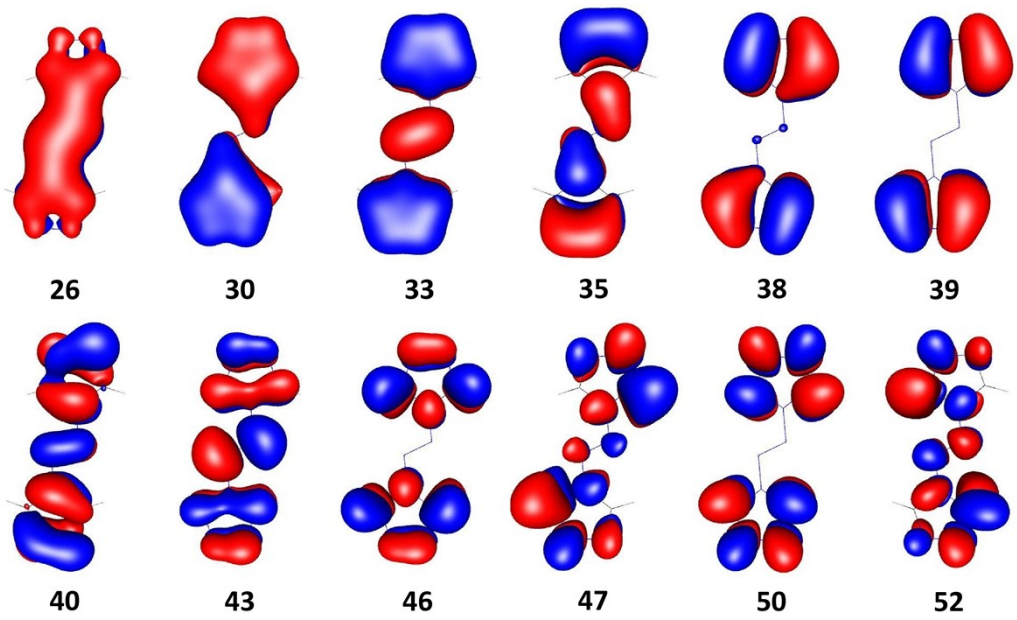

Figure S1. Twelve p_{π}-molecular orbitals of **atrz**

Table S1. Crystal data and structure refinement for **atrz**.

Empirical formula	$C_4H_4N_8$
Formula weight	164.15
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 4.9579(10) Å
	b = 6.4613(13) Å
	c = 10.181(2) Å
	β = 92.28(3)°
Volume	325.87(11) $Å^3$
Z	2
Density (calculated)	1.673 Mg/m^3
Absorption coefficient	0.126 mm^{-1}
F(000)	168
Crystal size	0.24 x 0.20 x 0.20 mm^3
Theta range for data collection	3.74 to 58.52°
Index ranges	-11<=h<=11, -15<=k<=15, -24<=l<=24
Reflections collected	60794
Independent reflections	4718 [R(int) = 0.0315]
Completeness to theta = 58.52°	100.0 %
Max. and min. transmission	0.9752 and 0.9704
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4181 / 0 / 63
Goodness-of-fit on F^2	1.083
Final R indices [I>2σ(I)]	R1 = 0.0283, wR2 = 0.0891
R indices (all data)	R1 = 0.0333, wR2 = 0.0941
Largest diff. peak and hole	0.677 and -0.317 $e.Å^{-3}$

[a] $R_{int}=\sum|F_o^2-F_o^2{}_{(mean)}|/\sum|F_o^2|$; $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2=\{\Sigma|w(F_o^2-F_c^2)^2|/\Sigma|w(F_o^2)^2|]\}^{1/2}$;
[c] $GOF=[\Sigma w|F_o-F_c|^2/(N_{ref}-N_v)]^{1/2}$;

Table S2. Agreement Indices of Various LS-Refinements for **atrz**.

N_{ref}[a]: 4086	N_v[b]	N_{ref}/N_v	R_1[c]	R_{1w}[d]	R_2[e]	R_{2w}[f]	GOF[g]
Conventional	54	75.67	0.031	0.044	0.057	0.088	5.318
Monopole	64	64.86	0.032	0.047	0.063	0.093	5.637
Dipole	88	46.97	0.029	0.042	0.060	0.083	5.083
Quadrupole	118	34.92	0.025	0.036	0.054	0.072	4.422
Octupole	180	25.70	0.016	0.016	0.030	0.033	2.001

[a] $N_{ref.}$ number of reflections. [b] N_v: number of variables. [c] $R_1=[\sum|F_o-F_c|/\sum|F_o|]^{1/2}$. [d] $R_1=\Sigma|F_o-F_c|/\Sigma|F_o|$; $R_{1w}=(\Sigma|w|F_o-F_c|^2|/\Sigma|wF_o^2|)^{1/2}$; $R_2=[\Sigma|F_o^2-F_c^2|/\Sigma\,(F_o^2)]$; $R_{2w}=\{\Sigma|w(F_o^2-F_c^2)^2|/\Sigma|w(F_o^2)^2|]\}^{1/2}$; GOF=$[\Sigma w|F_o-F_c|^2/(N_{ref}-N_v)]^{1/2}$, $w = 1/[\sigma(F_o^2)]$

Table S3 Atomic Thermal parameters (U_{ij}) and multipole populations (P_{lm}) of **atrz**.

N(1)	U_{ij}	0.012025 0.010482 0.014981 -0.003082 0.001462 -0.002119
	P_{lm}	4.9678 0.0000 0.0197 -0.0515 -0.0273 0.0669 -0.0067 0.0969 -0.0651 -0.0163
		0.1170 -0.0015 -0.0304 0.0470 0.0018 -0.0003 -0.0462 0.0000 0.0000 0.0000
		0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
N(2)	U_{ij}	0.013111 0.010509 0.013515 -0.001007 0.001523 -0.003244
	P_{lm}	4.9990 0.0000 -0.0061 -0.0648 -0.0290 0.0622 0.0055 0.0908 -0.0598 -0.0073
		0.0988 0.0059 -0.0269 0.0668 -0.0030 -0.0013 -0.0470 0.0000 0.0000 0.0000
		0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
N(3)	U_{ij}	0.009537 0.008225 0.009763 -0.001171 0.001078 -0.000816
	P_{lm}	5.0386 0.0000 0.0214 -0.0003 -0.0177 0.0119 -0.0055 0.0005 0.0042 0.0213
		0.1553 -0.0107 0.0785 0.1201 0.0052 -0.0011 0.0064 0.0000 0.0000 0.0000
		0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
N(4)	U_{ij}	0.010567 0.008828 0.010642 -0.001645 0.001835 -0.001220
	P_{lm}	4.9735 0.0000 -0.0099 0.0477 -0.0541 -0.0281 -0.0120 -0.0328 -0.1395 0.0005
		0.1356 -0.0066 0.0279 0.0473 -0.0018 -0.0198 0.0262 0.0000 0.0000 0.0000
		0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
C(1)	U_{ij}	0.010302 0.010450 0.012192 -0.001931 0.002053 -0.001202
	P_{lm}	4.4996 0.0000 0.0008 0.0500 0.0689 0.1549 -0.0037 -0.0493 -0.1106 -0.0095
		0.2496 0.0013 0.0187 0.1893 0.0117 -0.0062 0.0312 0.0000 0.0000 0.0000
		0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
C(2)	U_{ij}	0.010967 0.010225 0.011015 -0.000888 0.002071 -0.001233
	P_{lm}	4.5099 0.0000 -0.0036 0.0764 0.0525 0.1802 0.0030 -0.0554 -0.1121 0.0157
		0.2661 0.0004 0.0117 0.1952 0.0000 0.0173 0.0360 0.0000 0.0000 0.0000
		0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
H(1)	U_{ij}	0.013112 0.000000 0.000000 0.000000 0.000000 0.000000
	P_{lm}	0.5071 0.0000 0.0199 0.0007 -0.1027 0.0000 0.0000 0.0000 0.0000 0.0000
		0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
		0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
H(2)	U_{ij}	0.012820 0.000000 0.000000 0.000000 0.000000 0.000000
	P_{lm}	0.5046 0.0000 -0.0048 -0.0373 -0.0906 0.0000 0.0000 0.0000 0.0000 0.0000
		0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
		0.0000 0.0000 0.0000 0.0000 0.0000 0.0000

Table S4. π–π interactions of **atrz** in crystal.[a]

Ring(i) → Ring(j)	Slip angle[b] (i,j)/°	Interplanar (i,j) distance[c]/Å	Horizontal shift between the (i,j) ring centroids[d]/Å	Distance between the (i,j) ring centroids/Å
R(1) → $R(1)_i$	17.8	3.17	1.02	3.33

[a] Symmetry code: i = -x, 1-y, -z, Ring(i)/Ring(j) denotes the centroids of i-th/j-th of triazole/triazole rings; R(1) = N(1)–N(2)–C(2)–N(3)–C(1). [b] Slip angle: the angle formed between the ring-centroid vector (CC) and the ring normal to one of the triazole planers. [c] Interplanar distance: the perpendicular distance between two parallel triazole rings. [d] Horizontal shift between the ring centroids: a shift from the face-to-face alignment.

Table S 5. H-bonds of **atrz**.[a]

D–H···A	H···A (Å)	D···A (Å)	∠ D–H···A (°)
C1–H1···$N1_i$	2.45	3.252(4)	130
C2–H2···$N2_{ii}$	2.39	3.343(2)	146

[a] Symmetry operations: *i* = 1-x, 1-y, -z ; *ii* = -0.5-x, -0.5+y, 0.5-z.