Functionalization and coordination effects on the structural chemistry of pendant arm derivatives of 1-aza-3,7,10-trithiacyclo dodecane ([12]aneNS$_3$)

Claudia Caltagirone [1], Alexander J. Blake [2,*], Francesco Demartin [3], Alessandra Garau [1], Enrico Podda [4], Alexandra Pop [5], Vito Lippolis [1,*] and Cristian Silvestru [5]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, S.S. 554 Bivio per Sestu, Monserrato (CA), 09042, Italy.
[2] School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK
[3] Dipartimento di Chimica, Università degli Studi di Milano, Milano, 20133, Italy.
[4] Centro Servizi di Ateneo per la Ricerca-CeSAR, Università degli Studi di Cagliari, S.S. 554 Bivio per Sestu, Monserrato (CA), 09042, Italy.
[5] Supramolecular Organic and Organometallic Chemistry Centre, Department of Chemistry, Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Str. Arany Janos 11, Cluj-Napoca, 400028, Romania.

* Correspondence: lippolis@unica.it (V.L.); alexanderjohnblake@outlook.com (A.J.B.)

SUPPORTING INFORMATION

Table of contents

Table S1 Crystallographic data and structure refinement parameters for **L12**, **L20**, and **L21**·$CHCl_3$.

Compound	**L12**	**L20**	**L21**·$CHCl_3$
Empirical formula	$C_{18}H_{23}ClN_2OS_3$	$C_{15}H_{22}BrNS_3$	$C_{16}H_{23}Cl_3N_2O_3S_3$
Formula weight	415.01	392.42	493.89
Temperature/K	150(2)	293(2)	293(2)
Crystal system	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1
a/Å	8.4811(6)	8.0769(6)	8.5163(9)
b/Å	9.8093(7)	8.5225(6)	9.5058(10)
c/Å	11.8739(9)	12.5476(9)	14.5582(15)
α/°	99.469(2)	99.941(6)	73.290(10)
β/°	99.016(2)	96.608(6)	89.590(10)
γ/°	93.623(2)	93.121(6)	85.960(10)
Volume/$Å^3$	958.31(12)	842.65(11)	1125.9(2)
Z	2	2	2
$\rho_{calc}g/cm^3$	1.438	1.547	1.457
μ/mm^{-1}	0.536	2.801	0.704
F(000)	436.0	404.0	512.0
Crystal size/mm^3	0.98 × 0.9 × 0.59	0.53 × 0.41 × 0.07	0.21 × 0.09 × 0.07
Radiation	Mo *K*α (λ = 0.71073)	Mo *K*α (λ = 0.71073)	Mo *K*α (λ = 0.71073)
2Θ range for data collection/°	4.228 to 54.948	6.37 to 53.752	4.486 to 56.084
Index ranges	$-10 \le h \le 10$, $-12 \le k \le 12$, $-15 \le l \le 15$	$-9 \le h \le 9$, $-8 \le k \le 10$, $-15 \le l \le 14$	$-11 \le h \le 10$, $-12 \le k \le 12$, $-19 \le l \le 19$
Reflections collected	8758	4265	10525
Independent reflections	4271 [R_{int} = 0.036, R_{sigma} = 0.021]	3181 [R_{int} = 0.0182, R_{sigma} = 0.0432]	4989 [R_{int} = 0.0275, R_{sigma} = 0.0412]
Data/restraints/parameters	4271/0/228	3181/0/181	4989/3/273
Goodness-of-fit on F^2	1.066	1.047	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0295, wR_2 = 0.0775	R_1 = 0.0352, wR_2 = 0.0687	R_1 = 0.0489, wR_2 = 0.1326
Final R indexes [all data]	R_1 = 0.0338, wR_2 = 0.0793	R_1 = 0.0470, wR_2 = 0.0753	R_1 = 0.0751, wR_2 = 0.1428
Largest diff. peak/hole / e $Å^{-3}$	0.38/−0.24	0.34/−0.61	0.31/−0.38

Table S2. Selected bond lengths (Å) and angles (°) for **L12**.

N1−C2	1.4717(18)	C5−C6	1.521(2)
N1−C12	1.4719(17)	C8−C9	1.518(2)
N1−C13	1.4697(18)	C11−C12	1.536(2)
N23−C18	1.3676(18)	C13−C14	1.5085(19)
N23−C22	1.3190(19)	C14−C15	1.4175(19)
O24−C19	1.3592(16)	C14−C19	1.3787(19)
S4−C3	1.8137(16)	C15−C16	1.361(2)
S4−C5	1.8089(16)	C16−C17	1.4177(19)
S7−C6	1.8156(16)	C17−C18	1.4217(18)
S7−C8	1.8125(16)	C17−C20	1.4082(19)
S10−C9	1.8166(16)	C18−C19	1.4206(19)
S10−C11	1.8132(15)	C20−C21	1.366(2)
Cl25−C16	1.7460(14)	C21−C22	1.408(2)
C2−C3	1.522(2)	C19−C14−C13	120.93(12)
C12−N1−C2	113.65(11)	C19−C14−C15	118.84(12)
C13−N1−C2	111.20(11)	C16−C15−C14	120.90(13)
C13−N1−C12	110.18(11)	C15−C16−Cl25	119.49(11)
C22−N23−C18	117.59(12)	C15−C16−C17	121.89(12)
C5−S4−C3	101.03(7)	C17−C16−Cl25	118.62(10)
C8−S7−C6	100.60(7)	C16−C17−C18	117.52(12)
C11−S10−C9	101.05(7)	C20−C17−C16	125.28(12)
N1−C2−C3	112.52(12)	C20−C17−C18	117.20(12)
C2−C3−S4	112.68(11)	N23−C18−C17	122.55(12)
C6−C5−S4	112.75(11)	N23−C18−C19	117.69(12)
C5−C6−S7	113.71(11)	C19−C18−C17	119.75(12)
C9−C8−S7	114.27(11)	O24−C19−C14	119.20(12)
C8−C9−S10	113.18(11)	O24−C19−C18	119.74(12)
C12−C11−S10	113.57(10)	C14−C19−C18	121.05(12)
N1−C12−C11	116.02(12)	C21−C20−C17	119.94(13)
N1−C13−C14	112.71(11)	C20−C21−C22	118.65(14)
C15−C14−C13	120.20(12)	N23−C22−C21	124.05(14)

Table S3. Selected bond lengths (Å) and angles (°) for **L20**.

Br20−C19	1.895(3)	N1−C2	1.462(3)
S4−C5	1.803(3)	N1−C13	1.471(3)
S4−C3	1.811(3)	C2−C3	1.517(3)
C5−C6	1.516(4)	C13−C14	1.499(3)
C6−C7	1.810(3)	C14−C15	1.387(4)
S7−C8	1.813(3)	C14−C19	1.400(4)
C8−C9	1.506(4)	C15−C16	1.375(4)
C9−S10	1.805(3)	C16−C17	1.370(4)
S10−C11	1.810(3)	C17−C18	1.371(4)
C11−C12	1.516(4)	C18−C19	1.375(4)
C12−N1	1.468(3)	N1−C2−C3	111.5(2)
C5−S4−C3	101.04(13)	C2−C3−S4	114.86(18)
C6−C5−S4	114.28(19)	N1−C13−C14	113.4(2)
C5−C6−S7	114.11(19)	C15−C14−C13	120.5(2)
C6−S7−C8	101.20(13)	C15−C14−C19	116.5(3)
C9−C8−S7	115.64(19)	C19−C14−C13	123.0(2)
C8−C9−S10	113.31(19)	C16−C15−C14	122.1(3)
C9−S10−C11	102.40(13)	C17−C16−C15	119.8(3)
C12−C11−S10	114.8(2)	C16−C17−C18	120.0(3)
N1−C12−C12	114.4(2)	C17−C18−C19	120.1(3)
C12−N1−C13	111.1(2)	C14−C19−Br20	120.2(2)
C2−N1−C12	111.5(2)	C18−C19−Br20	118.3(2)
C2−N1−C13	110.7(2)	C18−C19−C14	121.5(3)

Table S4. Selected bond lengths (Å) and angles (°) for **L21**·$CHCl_3$.

C2−C3	1.510(3)	C13−C14	1.514(3)
C2−N1	1.478(3)	C13−N1	1.479(3)
C3−S4	1.813(3)	C14−C15	1.403(3)
C5−C6	1.510(3)	C14−C19	1.377(3)
C5−S4	1.811(2)	C15−C16	1.390(3)
C6−S7	1.810(2)	C15−O20	1.344(3)
C8−C9	1.522(4)	C16−C17	1.369(4)
C8−S7	1.808(3)	C17−C18	1.375(4)
C9−S10	1.816(3)	C18−C19	1.385(3)
C11−C12	1.527(3)	C18−N21	1.466(3)
C11−S10	1.808(3)	N21−O22	1.215(3)
C12−N1	1.479(3)	N21−O23	1.211(3)
N1−C2−C3	112.39(19)	C17−C16−C15	120.8(2)
C2−C3−S4	112.82(17)	C16−C17−C18	118.4(2)
C6−C5−S4	113.07(18)	C17−C18−C19	122.0(2)
C5−C6−S7	114.25(18)	C17−C18−N21	119.2(2)
C9−C8−S7	114.3(2)	C19−C18−N21	118.8(2)
C8−C9−S10	113.0(2)	C14−C19−C18	119.9(2)
C12−C11−S10	112.81(19)	C2−N1−C12	114.18(17)
N1−C12−C11	116.1(2)	C2−N1−C13	110.35(18)
N1−C13−C14	111.30(18)	C12−N1−C13	112.18(18)
C15−C14−C13	120.4(2)	O22−N21−C18	118.7(3)
C19−C14−C13	121.1(2)	O23−N21−C18	118.4(3)
C19−C14−C15	118.4(2)	O23−N21−O22	122.9(3)
C16−C15−C14	120.3(2)	C5−S4−C3	99.95(11)
O20−C15−C14	120.7(2)	C8−S7−C6	102.18(12)
O20−C15−C16	119.0(2)	C11−S10−C9	101.14(12)

Table S5. Conformational study with data retrieved from the [12]aneNS$_3$ derivatives reported in the Cambridge Structural Database (CSD). Consecutive dark green regions identify corners according to the Dale convention (see Figures S2 and 6 in the main text).

Refcode	Fragment	**N1**-C2-C3-**S4**	C2-C3-**S4**-C5	C3-**S4**-C5-C6	**S4**-C5-C6-**S7**	C5-C6-**S7**-C8	C6-**S7**-C8-C9	**S7**-C8-C9-**S10**	C8-C9-**S10**-C11	C9-**S10**-C11-C12	**S10**-C11-C12-**N1**	C11-C12-**N1**-C2	C12-**N1**-C2-C3	Dale's notation
BEYFUH	1	**-52,7**	**-61,6**	**92,3**	**52,1**	-169,1	**64,1**	**58,3**	-144,7	**64,3**	**59,5**	-177,1	160,9	**[11334]**
	2	**-55,4**	**-62,5**	**87,3**	**58,2**	-173,0	**66,6**	**57,4**	-145,3	**61,2**	**59,6**	-172,7	165,4	**[11334]**
	3	**62,2**	-142,4	**61,7**	**63,6**	-154,5	155,0	**-63,3**	**-62,9**	**88,1**	**53,1**	171,7	**75,5**	**[34113]**
DAVHEO	1	**-51,8**	**-77,5**	151,9	**-60,4**	**-71,0**	157,0	**-52,8**	**-81,8**	145,5	**-65,1**	**-75,2**	169,5	**[3333]**
	2	**71,4**	-150,0	**70,0**	**62,7**	-165,8	**67,0**	**66,5**	-153,2	**75,0**	**55,2**	-173,8	**72,9**	**[3333]**
DEDXIU	1	**48,0**	**75,1**	-113,7	79,3	-158,9	130,6	-68,1	126,5	**-72,6**	**-54,0**	167,6	-174,7	**[84]**
DEGREP	1	**62,3**	**71,7**	-150,2	**60,7**	**65,5**	-171,7	**69,2**	**69,4**	-144,1	**67,9**	**74,0**	178,4	**[3333]**
DEGREP01	1	**62,1**	**71,5**	-149,7	**60,2**	**66,9**	-171,2	**67,0**	**71,5**	-144,0	**66,8**	**75,4**	179,1	**[3333]**
DEGROZ	1	**61,4**	**73,4**	-148,1	**63,2**	**62,7**	-172,9	**67,8**	**71,5**	-143,1	**66,6**	**71,7**	175,8	**[3333]**
GADMON	1	-163,0	**91,8**	**-84,1**	171,6	**-75,5**	**-76,1**	163,6	**-74,1**	**-73,3**	165,4	**-89,6**	**100,6**	**[3333]**
	2	-168,7	**64,7**	**68,3**	-168,8	**72,7**	**74,4**	-175,7	**69,0**	**65,1**	-165,5	**78,3**	**77,7**	**[3333]**
GIHKOZ	1	**74,2**	-139,1	**72,6**	**60,2**	-175,3	**57,5**	**68,6**	-143,7	**79,6**	**48,2**	-176,6	**69,1**	**[3333]**
MAPYOV	1	168,5	**-76,4**	**-78,5**	172,7	**-64,2**	**-64,2**	173,3	**-77,1**	**-74,4**	166,5	**-66,3**	**-69,1**	**[3333]**
MAPZAI	1	**58,8**	**70,2**	-168,5	**65,2**	**69,1**	-152,4	**64,8**	**68,4**	-162,4	**69,1**	**75,5**	-164,1	**[3333]**
	2	**66,8**	-161,9	**65,3**	**67,7**	-154,4	**70,0**	**64,3**	-166,1	**68,2**	**58,0**	-165,4	**81,0**	**[3333]**
MAPZIQ	1	**-52,7**	**-79,5**	152,1	**-65,3**	**-62,6**	167,3	**-62,0**	**-74,5**	149,6	**-65,9**	**-76,3**	174,1	**[3333]**
	2	**61,3**	-142,2	**66,0**	**61,9**	-158,5	149,9	**-62,2**	**-59,4**	**99,7**	**45,0**	177,8	**68,1**	**[34113]**
MEXBOG	1	**-53,7**	**-78,1**	127,7	-73,6	153,6	-149,2	67,0	-123,0	**79,2**	**52,4**	-168,0	169,0	**[84]**
	2	**-57,4**	**-77,7**	117,1	-62,6	148,6	-152,0	71,0	-123,4	**76,3**	**54,7**	-168,5	168,0	**[84]**
MEXCAT	1	**-72,3**	159,2	**-76,5**	**-62,8**	151,3	**-63,4**	**-68,2**	162,7	**-75,3**	**-56,2**	164,7	**-73,3**	**[3333]**
NEGBIL	1	163,0	**-70,3**	**-78,2**	170,7	**-102,8**	**90,3**	-165,1	**84,1**	**81,1**	-158,3	**91,6**	**-102,5**	**[3333]**
ODOFAQ	1	**-57,4**	**-71,6**	175,7	**-62,1**	**-67,6**	145,6	**-64,5**	**-72,7**	170,9	**-63,0**	**-79,2**	158,8	**[3333]**
ODOFEU	1	**-56,8**	**-65,1**	149,8	**-54,4**	**-71,8**	170,2	**-53,8**	**-90,0**	**70,4**	**56,0**	-166,2	163,4	**[33114]**
PIYPAP	1	**52,9**	**71,5**	-165,1	**66,0**	**68,9**	-158,3	**64,7**	**67,4**	-158,8	**70,2**	**80,6**	-166,7	**[3333]**
PIYPET	1	**-69,9**	159,6	**-66,5**	**-64,7**	156,2	**-71,0**	**-64,7**	163,6	**-69,7**	**-53,9**	164,4	**-81,4**	**[3333]**
PIYPIX	1	**-53,2**	**-70,0**	164,2	**-64,8**	**-72,6**	154,2	**-63,6**	**-67,2**	158,3	**-67,3**	**-83,2**	163,4	**[3333]**
	2	**69,3**	-160,0	**68,2**	**63,7**	-155,5	**71,7**	**63,5**	-162,7	**70,0**	**55,0**	-164,1	**80,4**	**[3333]**
PIYPOD	1	**-65,9**	164,6	**-71,3**	**-69,4**	151,6	**-69,7**	**-64,0**	170,2	**-68,7**	**-56,3**	162,3	**-75,0**	**[3333]**
PIYPUJ	1	**57,5**	**70,0**	-164,1	**64,1**	**71,7**	-155,1	**62,6**	**68,7**	-160,9	**69,3**	**77,7**	-166,4	**[3333]**
	2	**-69,4**	163,8	**-62,2**	**-65,2**	156,4	**-75,9**	**-61,9**	165,6	**-67,6**	**-59,1**	163,9	**-79,3**	**[3333]**
	3	**-68,4**	157,7	**-68,0**	**-64,5**	161,0	**-71,4**	**-63,4**	161,3	**-70,7**	**-58,0**	168,5	**-77,9**	**[3333]**
PIYQAQ	1	**67,4**	-153,8	**72,5**	**57,9**	-152,7	**72,0**	**66,7**	-163,2	**70,8**	**57,6**	-166,3	**78,1**	**[3333]**
TECYUW	1	**60,5**	**74,9**	-162,0	**65,9**	**64,5**	-157,8	**65,5**	**70,6**	-157,9	**70,5**	**69,0**	-166,5	**[3333]**
TECZEH	1	**65,2**	-158,1	**68,7**	**68,5**	-157,4	**64,8**	**65,0**	-162,7	**71,7**	**63,9**	-167,8	**74,0**	**[3333]**
WERSOC	1	-168,0	**64,5**	**65,2**	-172,6	**73,9**	**72,2**	-173,0	**72,4**	**66,1**	-163,8	**71,6**	**82,8**	**[3333]**
	2	166,9	**-63,7**	**-68,0**	172,7	**-77,0**	**-73,0**	170,1	**-64,5**	**-72,1**	167,3	**-70,6**	**-79,1**	**[3333]**
WERSUI	1	-169,4	**71,8**	**67,9**	-170,6	**72,3**	**73,2**	-173,1	**66,5**	**68,3**	-165,9	**79,8**	**67,7**	**[3333]**
WERTOD	1	**70,1**	-154,4	**65,7**	**65,1**	-161,1	**71,8**	**59,9**	-158,3	**75,2**	**56,5**	-173,3	**77,1**	**[3333]**
ZEZSII	1	**-48,6**	**-94,0**	**85,2**	**-81,6**	159,5	-155,9	**51,1**	**47,4**	-165,0	**100,9**	**-64,1**	164,9	**[11433]**
ZINHUC	1	**69,3**	-152,5	**67,0**	**67,2**	-162,3	**68,5**	**64,9**	-155,1	**67,0**	**58,9**	-174,9	**79,5**	**[3333]**
ZINJAK	1	**-48,2**	**-74,8**	152,1	**-67,5**	**-66,3**	169,3	**-61,7**	**-67,7**	146,0	**-74,1**	**-77,8**	173,1	**[3333]**
ZINJEO	1	**-51,4**	**-74,6**	155,6	**-66,4**	**-66,5**	166,1	**-61,7**	**-70,9**	148,6	**-73,6**	**-75,4**	171,2	**[3333]**
	2	**-51,7**	**-64,3**	164,6	**-64,8**	**-87,5**	**88,6**	**42,4**	-130,6	143,7	**-69,9**	**-77,3**	168,9	**[31143]**

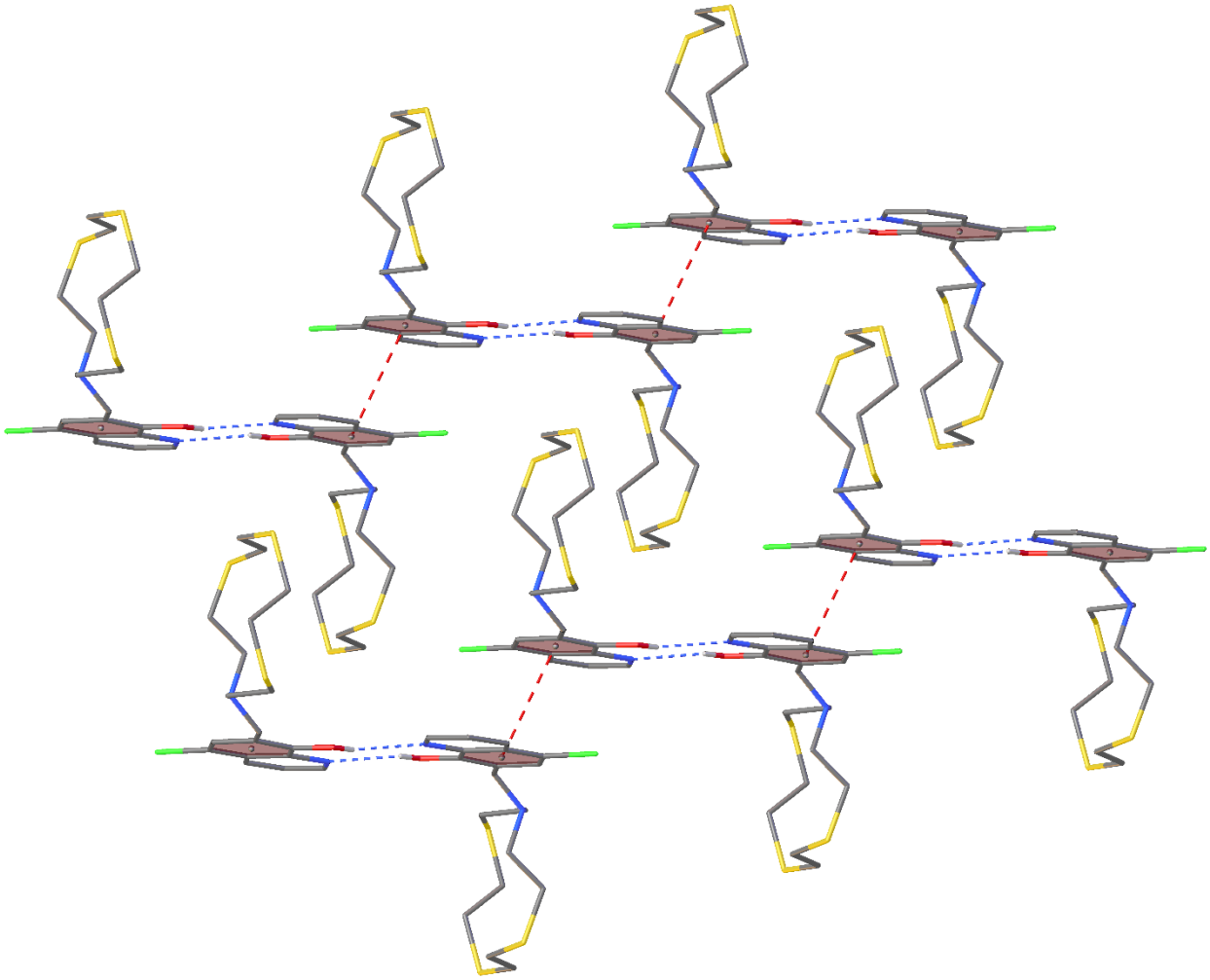

Figure S1. Partial view along the (100) direction of the crystal packing in **L12** showing the slipped π-π stacking interactions of adjacent dimers: centroid-centroid distance = 3.77 Å, shift distance = 1.42 Å.

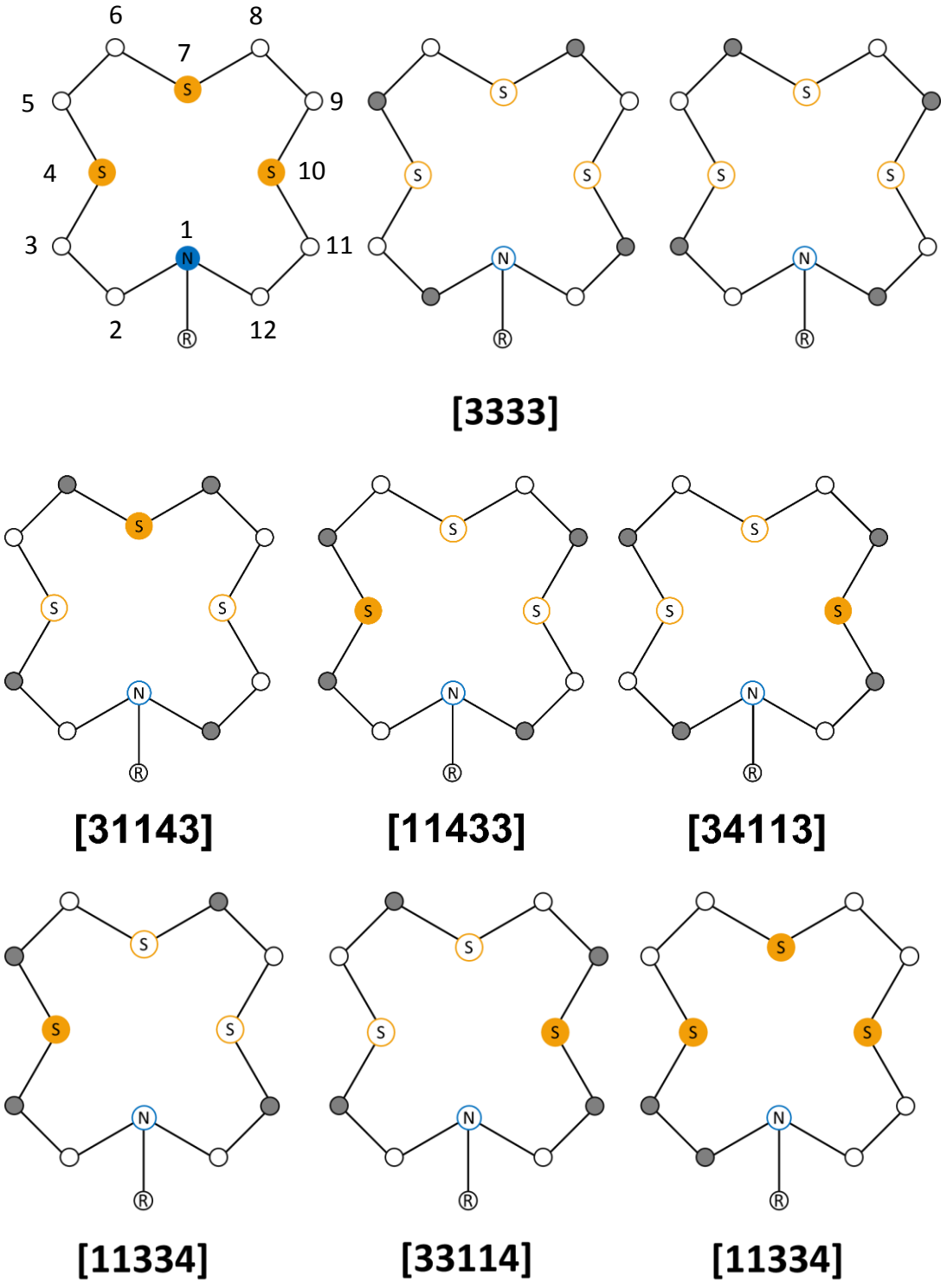

Figure S2. Pictorial representation of the conformations assumed by the [12]aneNS$_3$ moieties in crystallographycally-characterized derivatives of the macrocycle with corners depicted as full circles and numbering scheme adopted. The reported Dale notation has been assigned by counting the number of bonds between each pair of corners starting from the first corner to the left of the N atom as shown in the Figure and proceeding clockwise. For the two couples of conformations [11433]/[34113] and [11334]/[33114] the same Dale notations, [11433] and [11334], respectively, would be obtained if the count of bonds between each pair of corners starts from the first corner to the right of the N atom and proceeds anti-clockwise.