

Alexander V. Zakharov^a, Yuriy A. Zhabanov^a and Mikhail K. Islyaikin^b

Structures and properties of thiadiazole-containing expanded heteroazaporphyrinoids and their metallocomplexes

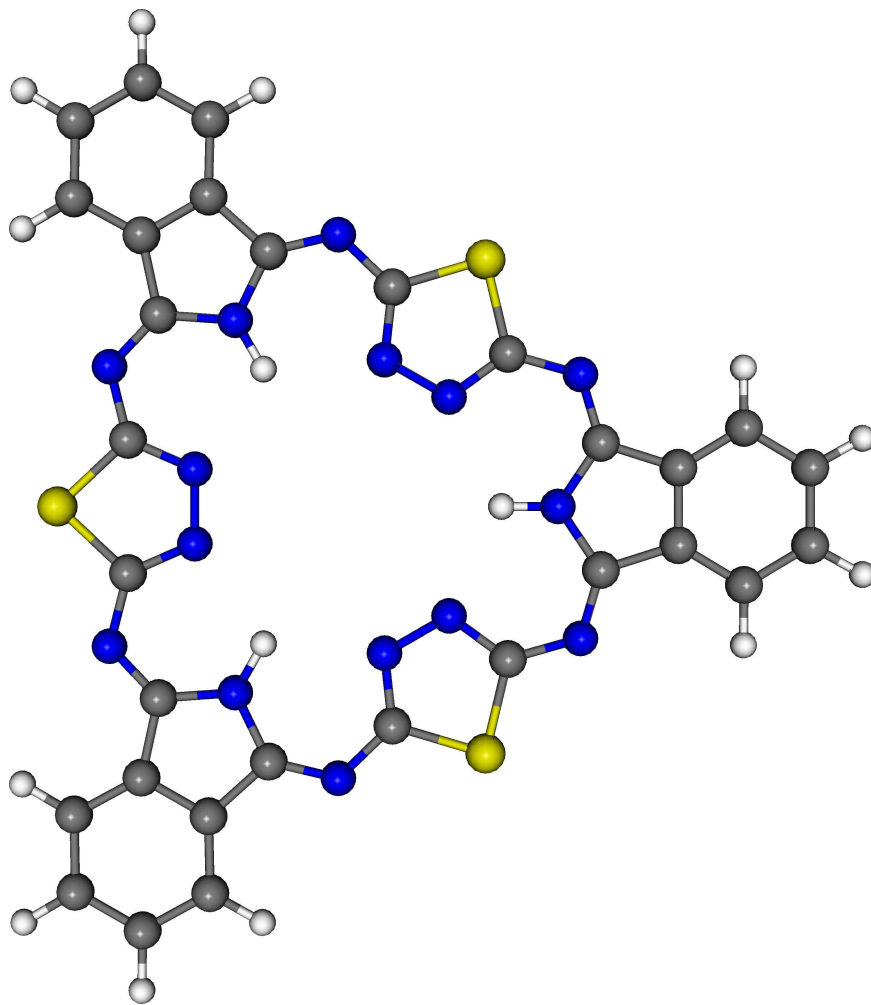


^a Department of Physics

^b Department of Fine organic synthesis

Ivanovo State University of
Chemistry and Technology

1



The unsubstituted thiadiazole-containing expanded heteroazaporphyrinoid
($\text{C}_{30}\text{H}_{15}\text{N}_{15}\text{S}_3$)

History of discovery

First synthesis (no structural characterisation):

V. F. Borodkin and N. A. Kolesnikov, *Khim. Geterotsikl. Soedin.*, 1971, (2), 194; N. A. Kolesnikov and V. F. Borodkin, *Zh. Prikl. Spektrosk.*, 1971, **14**, 1124.

Presented (erroneously) as ABAB-type (“2+2”) macrocycle:

N. A. Kolesnikov and V. F. Borodkin, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1972, **15**, 880.

First synthesis of the *tert*-butylsubstituted macrocycle:

M. K. Islyaikin, V. F. Borodkin, E. A. Danilova, S. P. Kononov, and A. A. Panov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1990, **33**, 18.

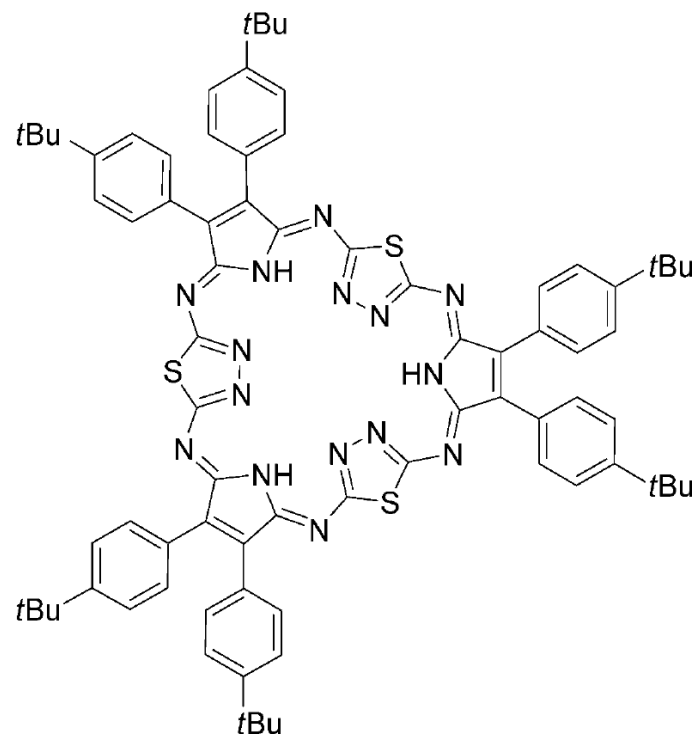
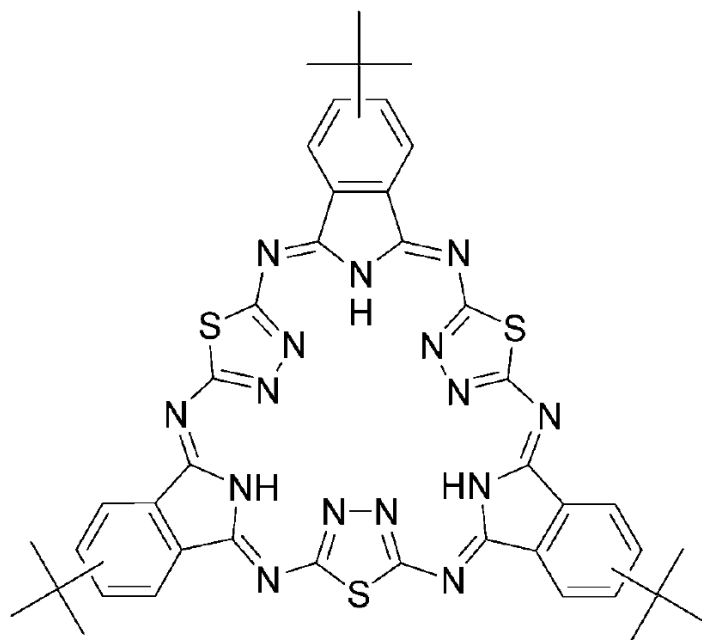
Again, no structural characterisation, supposed to be ABAB-type.

Second-time synthesis, characterisation...

The substituted macrocycle synthesised by two groups:

M. K. Islyaikin, E. A. Danilova, L. D. Yagodarova, M. S. Rodríguez-Morgade, and T. Torres, *Org. Lett.*, 2001, **3**, 2153; N. Kobayashi, S. Inagaki, V. N. Nemykin, and T. Nonomura, *Angew. Chem., Int. Ed.*, 2001, **40**, 2710.

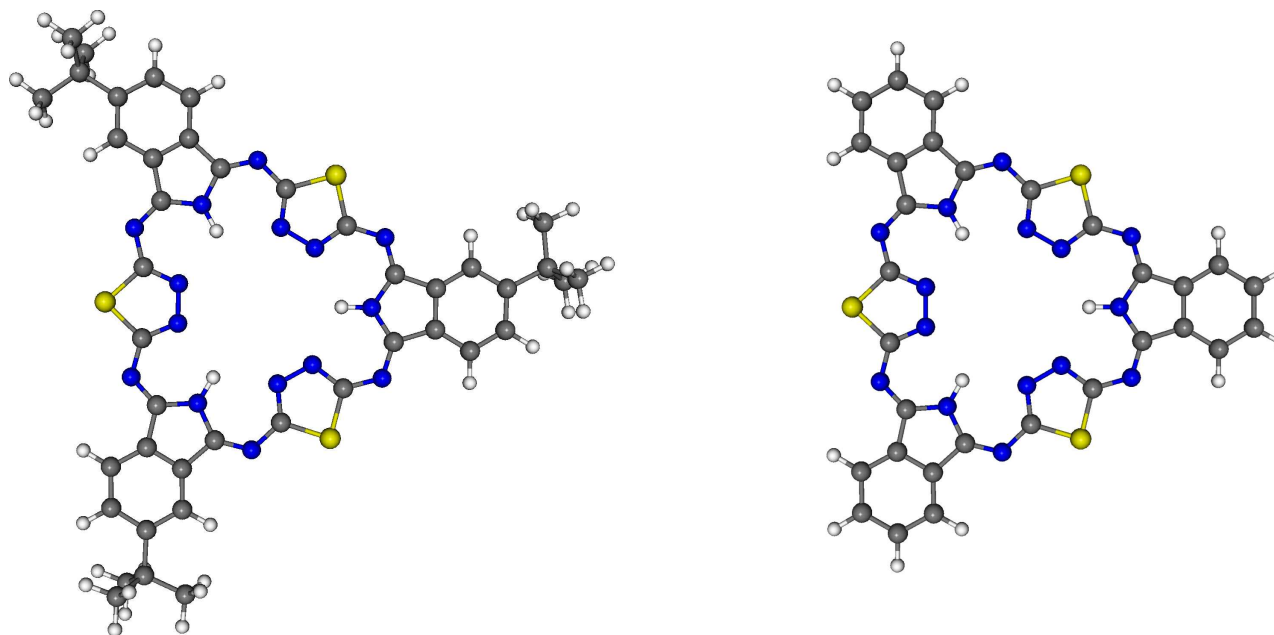
Characterised by mass spectrometry (MALDI, FAB), ^1H and ^{13}C NMR, infrared and UV-vis spectroscopy, and elemental analysis.

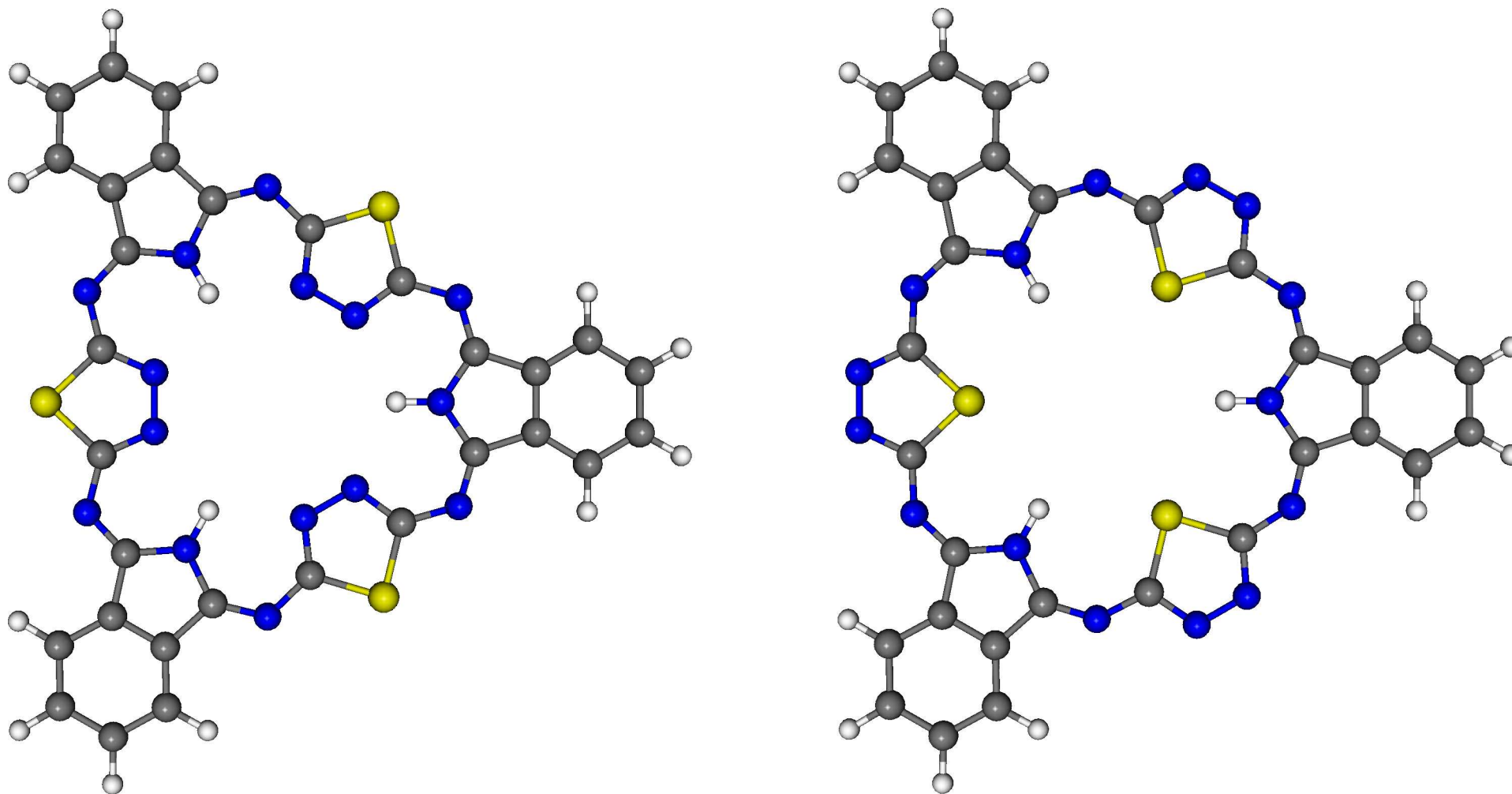


... and direct experimental structural studies (at last)

Gas-phase electron diffraction and computational study:

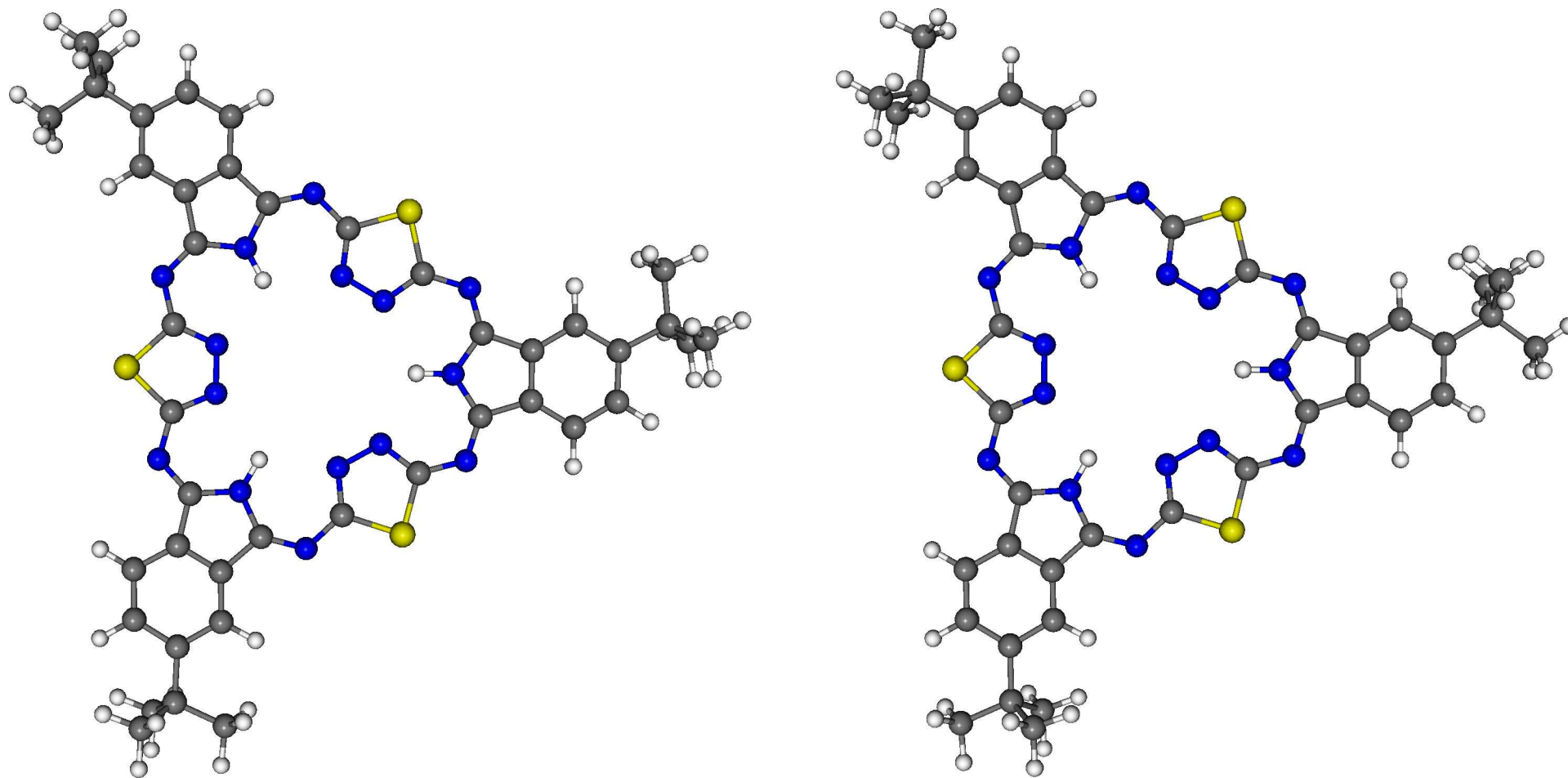
A. V. Zakharov, S. A. Shlykov, N. V. Bumbina, E. A. Danilova, A. V. Krasnov, M. K. Islyaikin, and G. V. Girichev, *Chem. Commun.*, 2008, p. 3573; A. V. Zakharov, S. A. Shlykov, E. A. Danilova, A. V. Krasnov, M. K. Islyaikin, and G. V. Girichev, *Phys. Chem. Chem. Phys.*, 2009, DOI:10.1039/B905436G.



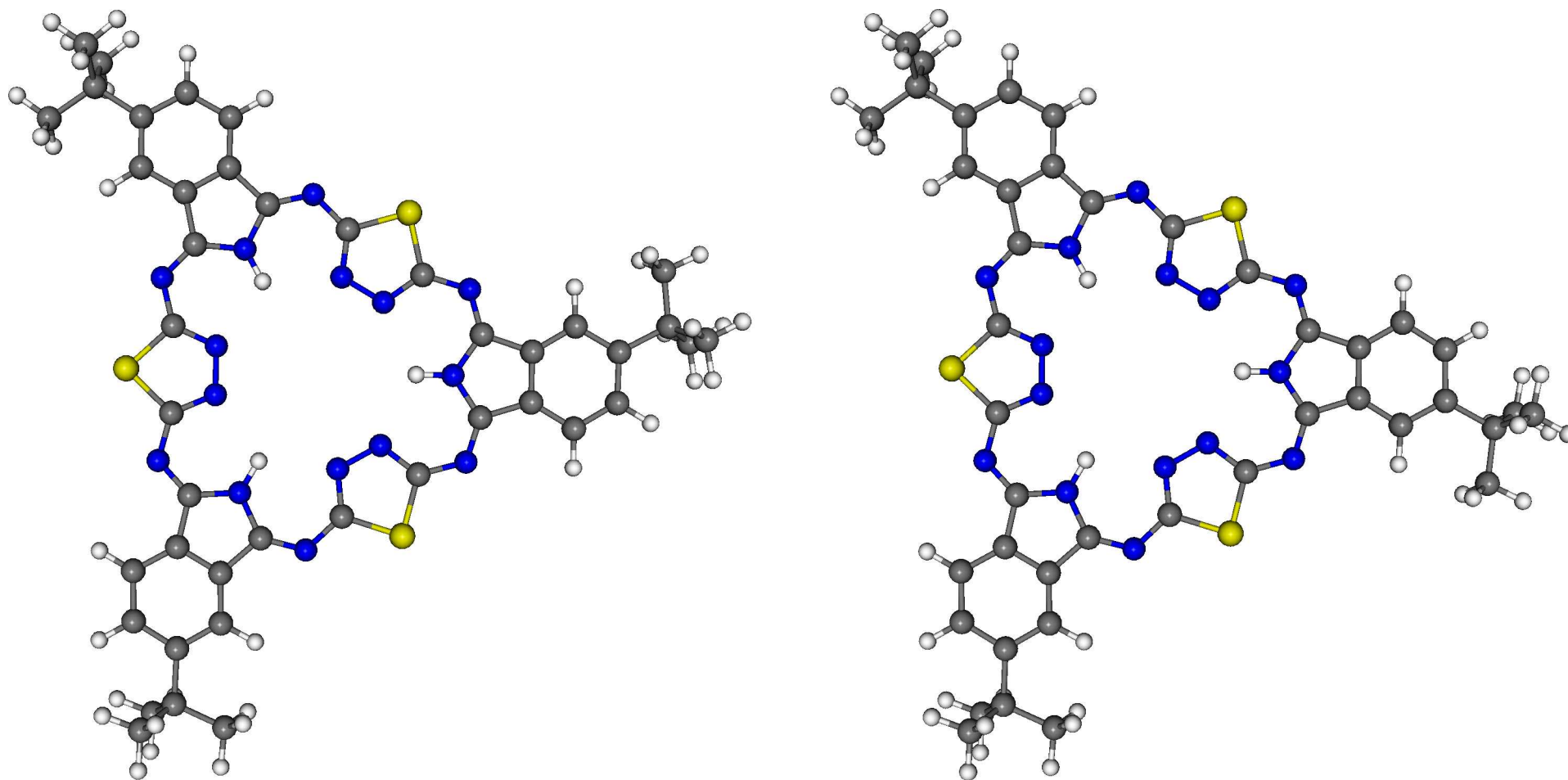


Possible orientations of the thiadiazole rings; the right structure was found to be a saddle point ($\Delta E = 235 \text{ kJ}\cdot\text{mol}^{-1}$)

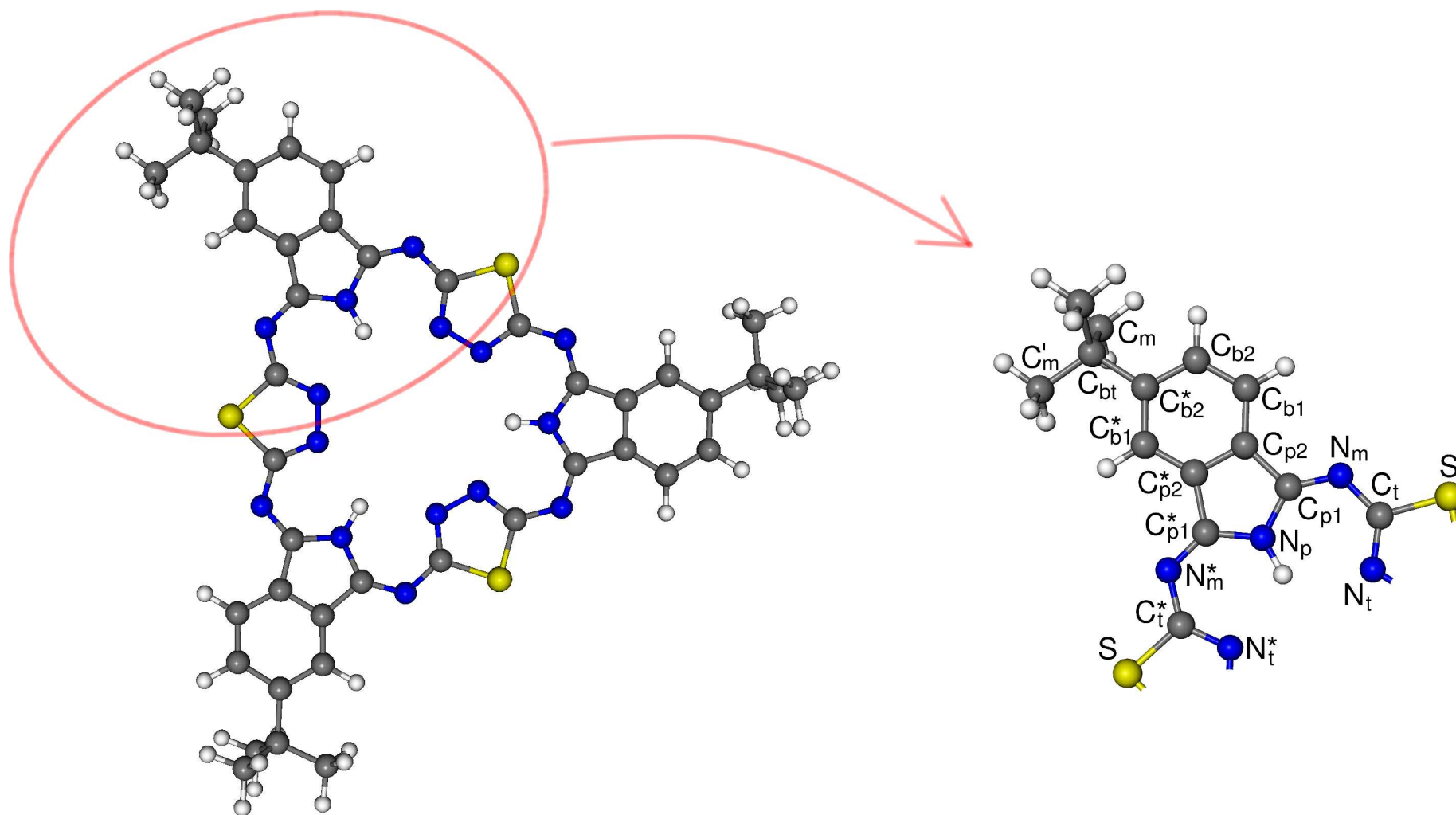
6



Two possible conformers of the *tert*-butylsubstituted macrocycle, $C_{42}H_{39}N_{15}S_3$
($\Delta E = 1.4 \text{ kJ}\cdot\text{mol}^{-1}$)



Two possible regioisomers of the *tert*-butylsubstituted macrocycle
($\Delta E < 0.1 \text{ kJ}\cdot\text{mol}^{-1}$)



Atom designations of the *tert*-butylsubstituted macrocycle

9 Selected structural parameters of C₄₂H₃₉N₁₅S₃ (**1**) and C₃₀H₁₅N₁₅S₃ (**2**)
yielded by B3LYP/cc-pVTZ study

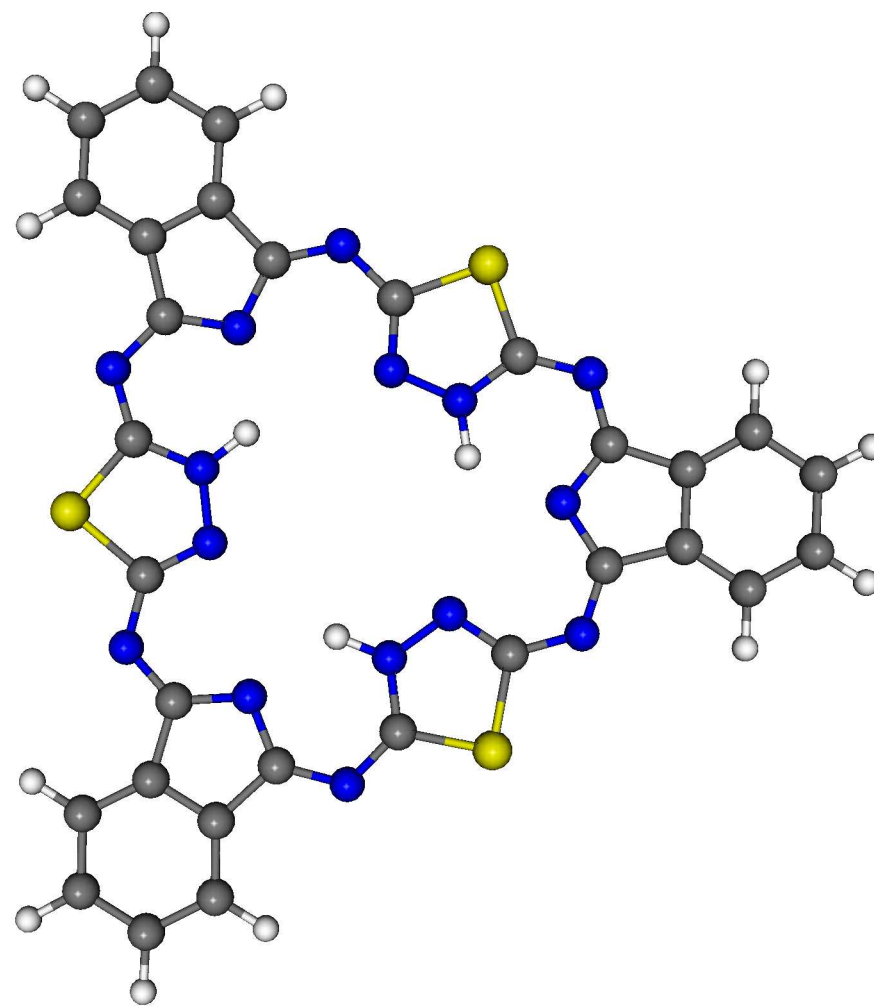
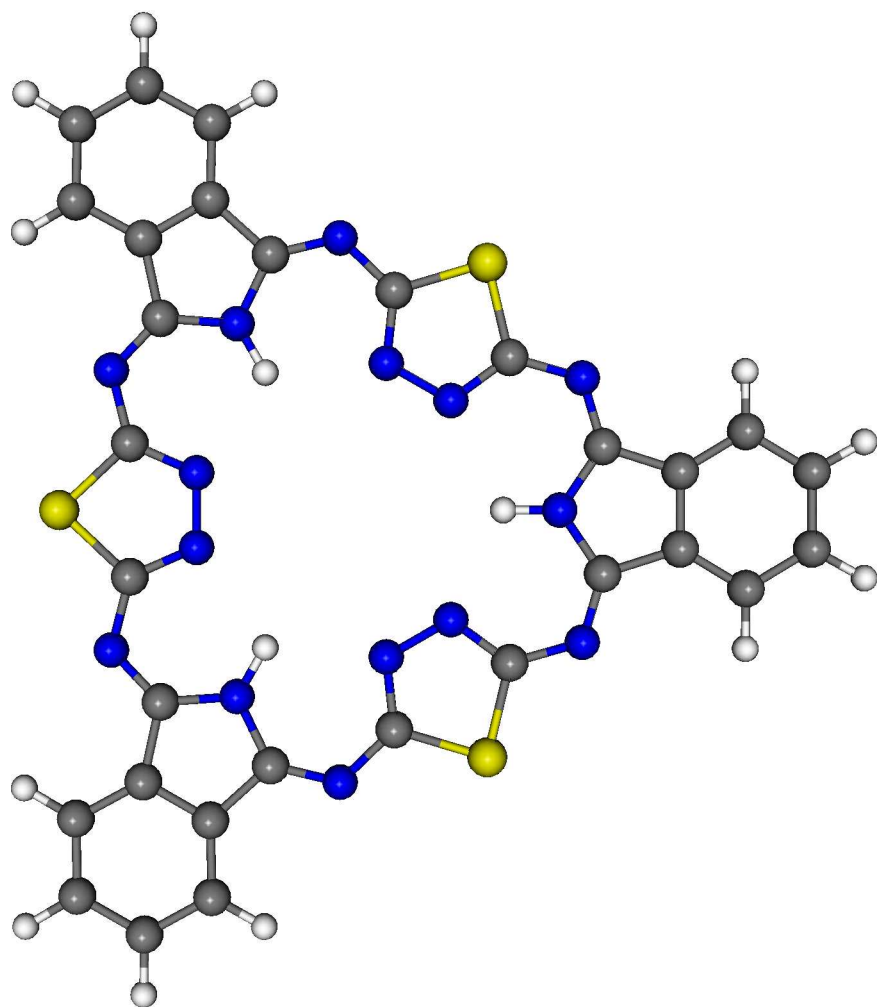
	Distances, Å				Angles, degrees		
	1^a	1^b	2		1^a	1^b	2
$r(\text{N}_p\text{--C}_{p1})$	1.385	1.384	1.384	$\alpha(\text{N}_p\text{--C}_{p1}\text{--N}_m)$	129.3	129.4	129.4
$r(\text{C}_{p1}\text{--N}_m)$	1.290	1.289	1.289	$\alpha(\text{C}_{p1}\text{--N}_m\text{--C}_t)$	122.4	122.4	122.4
$r(\text{N}_m\text{--C}_t)$	1.361	1.361	1.361	$\alpha(\text{N}_m\text{--C}_t\text{--N}_t)$	128.0	127.9	127.9
$r(\text{C}_t\text{--N}_t)$	1.316	1.316	1.316	$\alpha(\text{N}_m\text{--C}_t\text{--S})$	119.2	119.2	119.2
$r(\text{N}_t\text{--N}_t)$	1.346		1.346	$\alpha(\text{N}_t\text{--C}_t\text{--S})$	112.8	112.9	112.9
$r(\text{C}_t\text{--S})$	1.752	1.752	1.751	$\alpha(\text{N}_p\text{--C}_{p1}\text{--C}_{p2})$	106.2	106.3	106.3
$r(\text{C}_{p1}\text{--C}_{p2})$	1.466	1.468	1.468	$\alpha(\text{C}_{p1}\text{--C}_{p2}\text{--C}_{p2})$	108.0	107.8	107.8
$r(\text{C}_{p2}\text{--C}_{p2})$	1.392		1.397	$\alpha(\text{C}_{p1}\text{--C}_{p2}\text{--C}_{b1})$	131.7	130.5	130.9
$r(\text{C}_{p2}\text{--C}_{b1})$	1.386	1.386	1.386	$\alpha(\text{C}_{p2}\text{--C}_{b1}\text{--C}_{b2})$	117.9	119.1	117.6
$r(\text{C}_{b1}\text{--C}_{b2})$	1.388	1.397	1.392	$\alpha(\text{C}_{b1}\text{--C}_{b2}\text{--C}_{b2})$	122.8	118.2	121.1
$r(\text{C}_{b2}\text{--C}_{b2})$	1.409		1.398				
$r(\text{Z}\cdots\text{N}_t)^c$	2.754	2.753	2.753				
$r(\text{Z}\cdots\text{N}_p)^c$	3.880		3.880				
$r(\text{N}_t\cdots\text{N}_t)$	3.951		3.951				
$r(\text{N}_p\cdots\text{N}_p)$	6.720		6.720				

^a Clockwise part of the molecule, atoms labelled without stars.

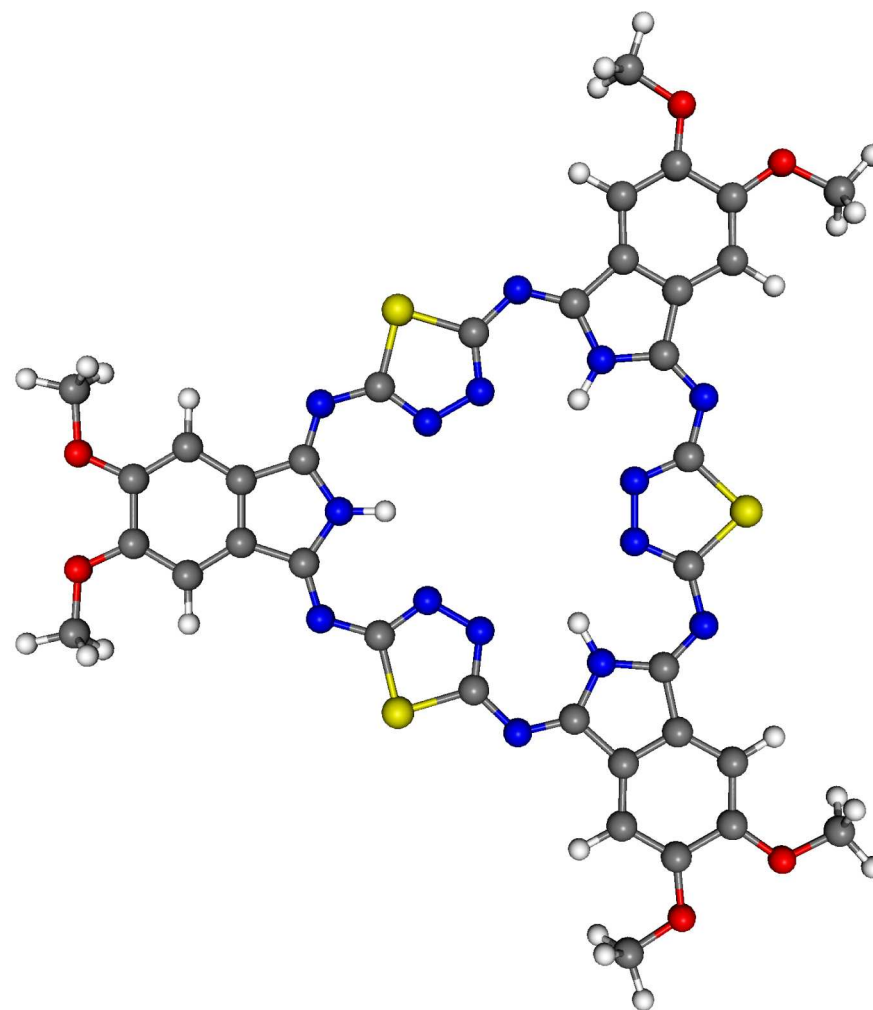
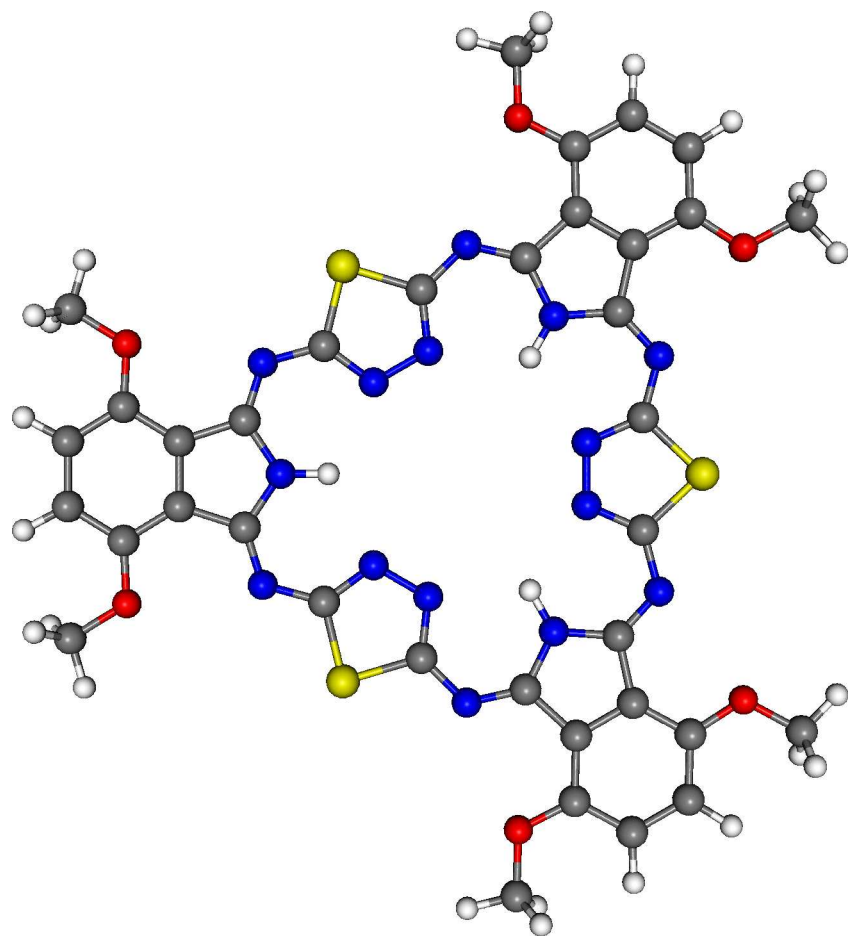
^b Counter-clockwise part, starred atom labels.

^c Distances from the z axis, *i.e.* from the centre of the molecule.

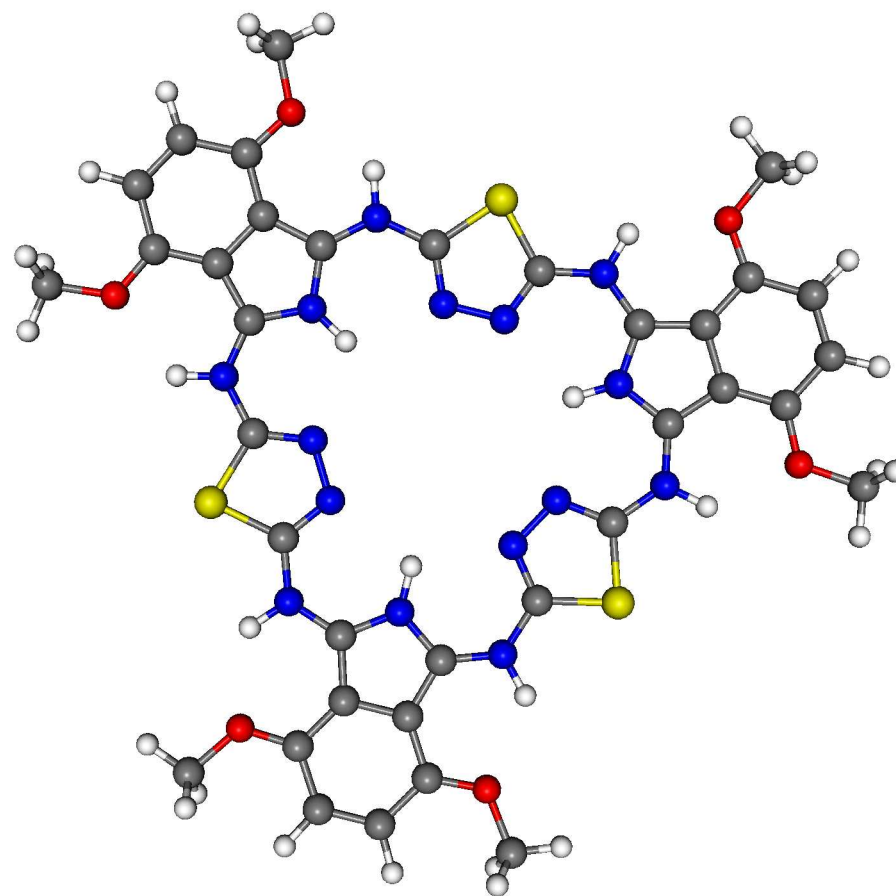
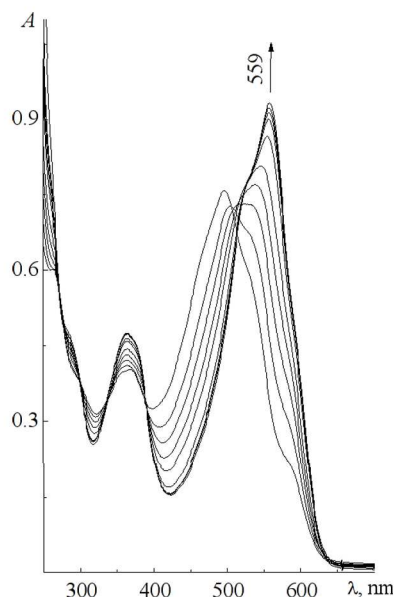
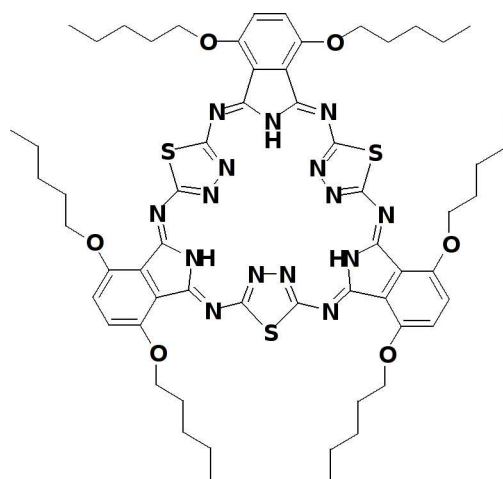
10



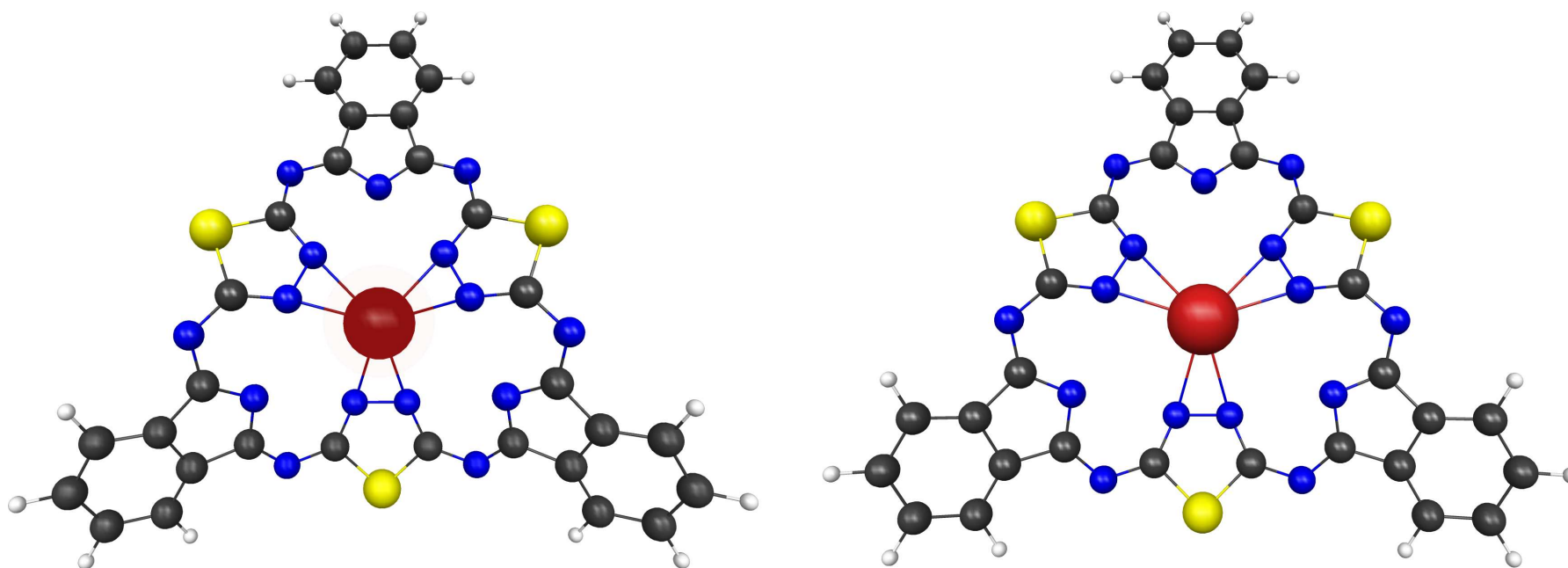
Two possible tautomers of the unsubstituted macrocycle ($\Delta E = 108 \text{ kJ}\cdot\text{mol}^{-1}$)



3,6-methoxy- and 4,5-methoxysubstituted macrocycles



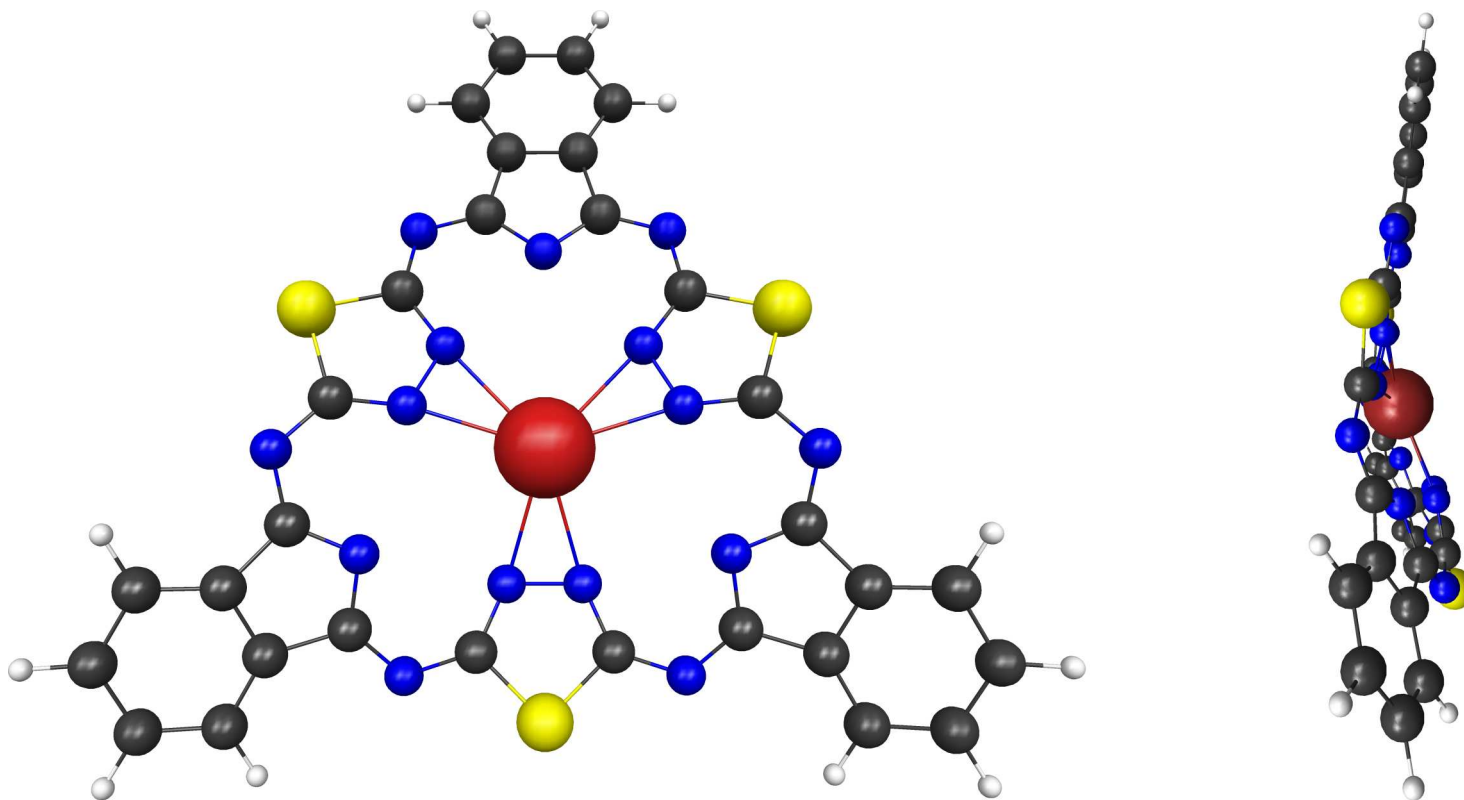
Changes in electronic spectrum of 3,6-alcoxysubstituted macrocycle (left); fully protonated 3,6-methoxysubstituted macrocycle used as a model (right)



Yttrium ($\text{YC}_{30}\text{N}_{15}\text{H}_{12}\text{S}_3$, left) and lanthanum ($\text{LaC}_{30}\text{N}_{15}\text{H}_{12}\text{S}_3$, right) complexes

Synthesis of *tert*-butylsubstituted complexes of La, Tm and Lu:

N. V. Bumbina, E. A. Danilova, M. K. Islyaikin, *Izv. vuzov. Khim. khim. tekhnol.*, 2008, **51**, p. 15; N. V. Bumbina, E. A. Danilova, I. G. Abramov, S. I. Filimonov, V. S. Sharunov, M. K. Islyaikin, *J. Porphyrins and Phthalocyanines*, 2008, **12**, p. 489.



LaC₃₀N₁₅H₁₂S₃ complex, C_s symmetry, front and side views;
 $r(\text{La-N}) = 2.559 - 2.578 \text{ \AA}$, barrier to macrocycle inversion is $6 \text{ kJ}\cdot\text{mol}^{-1}$