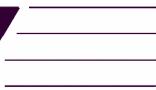


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How Can Rotaxanes Be Modified by Varying Functional Groups at the Axle?----A Combined Theoretical and Experimental Analysis of Thermochemistry and Electronic Effects

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The calculation of the strained interaction energy $\Delta E_{\text{strain}}^{\text{CP}}$ formally leads to an overall cancellation of the BSSE-contribution from the monomers in the original monomer basis according to

$$\begin{aligned}
 \Delta E_{\text{strain}}^{\text{CP}} &= E_{\text{tot}}^{\text{complex}}(\text{complex}) - E_{\text{wheel}}^{\text{relax}}(\text{wheel}) - E_{\text{guest}}^{\text{relax}}(\text{guest}) \\
 &- (E_{\text{wheel}}^{\text{unrelax}}(\text{complex}) - E_{\text{wheel}}^{\text{unrelax}}(\text{wheel})) - (E_{\text{guest}}^{\text{unrelax}}(\text{complex}) - E_{\text{guest}}^{\text{unrelax}}(\text{guest})) \\
 &+ (E_{\text{wheel}}^{\text{relax}}(\text{wheel}) - E_{\text{wheel}}^{\text{unrelax}}(\text{wheel})) + (E_{\text{guest}}^{\text{relax}}(\text{guest}) - E_{\text{guest}}^{\text{unrelax}}(\text{guest})) \\
 &= E_{\text{tot}}^{\text{complex}}(\text{complex}) - E_{\text{wheel}}^{\text{unrelax}}(\text{complex}) - E_{\text{guest}}^{\text{unrelax}}(\text{complex}) .
 \end{aligned} \tag{1}$$

Here the subscript denotes the component referred to, the superscript indicates the geometry (relax = isolated component, unrelax = component in complex geometry), and the term in parentheses refers to the basis applied (full basis of the complex including ghost atoms or basis of the corresponding component).

All starting structures for the geometry optimisation calculations were arranged in such a way as to establish two hydrogen bonds from wheel to axle and one hydrogen bond from axle to wheel, i.e. the oxygen atom of one amide group in the wheel pointed to the inner side of the rotaxane, cf. Fig. 1. The starting geometries of **1-7** and **1-8** contained one single hydrogen bond between a chlorine atom and one of the wheel's amide groups.

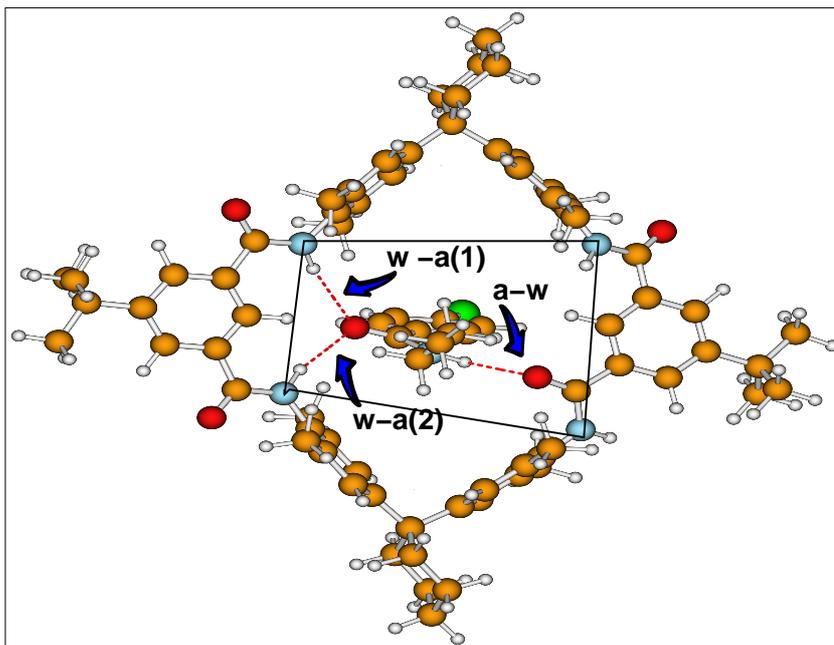


Figure 1: Starting conformation of rotaxane complexes shown exemplarily for complex **1-3**. Hydrogen bonds are marked; abbreviations: a = axle, w = wheel. Colour code: white (H), yellow (C), blue (N), red (O), green (Cl).

For results of the structure optimisations cf. Fig. 2. The guest N-H does not form a twofold hydrogen bond, because the formation of this fourth interaction would stretch all other hydrogen bonds. Furthermore, it requires the macrocycle to adopt a 2-in-2-out conformation, which would suffer from some strain. In case of complexes **1-7** and **1-8**, the starting geometries were selected to contain one $\text{NH} \rightarrow \text{Cl}$ hydrogen bond, which are both lost during the optimisation process. Both systems develop a $\text{CH}_{\text{guest}} \rightarrow \text{OC}_{\text{wheel}}$ bond instead as indicated in Fig. 2, lower right, for the example of **1-7**.

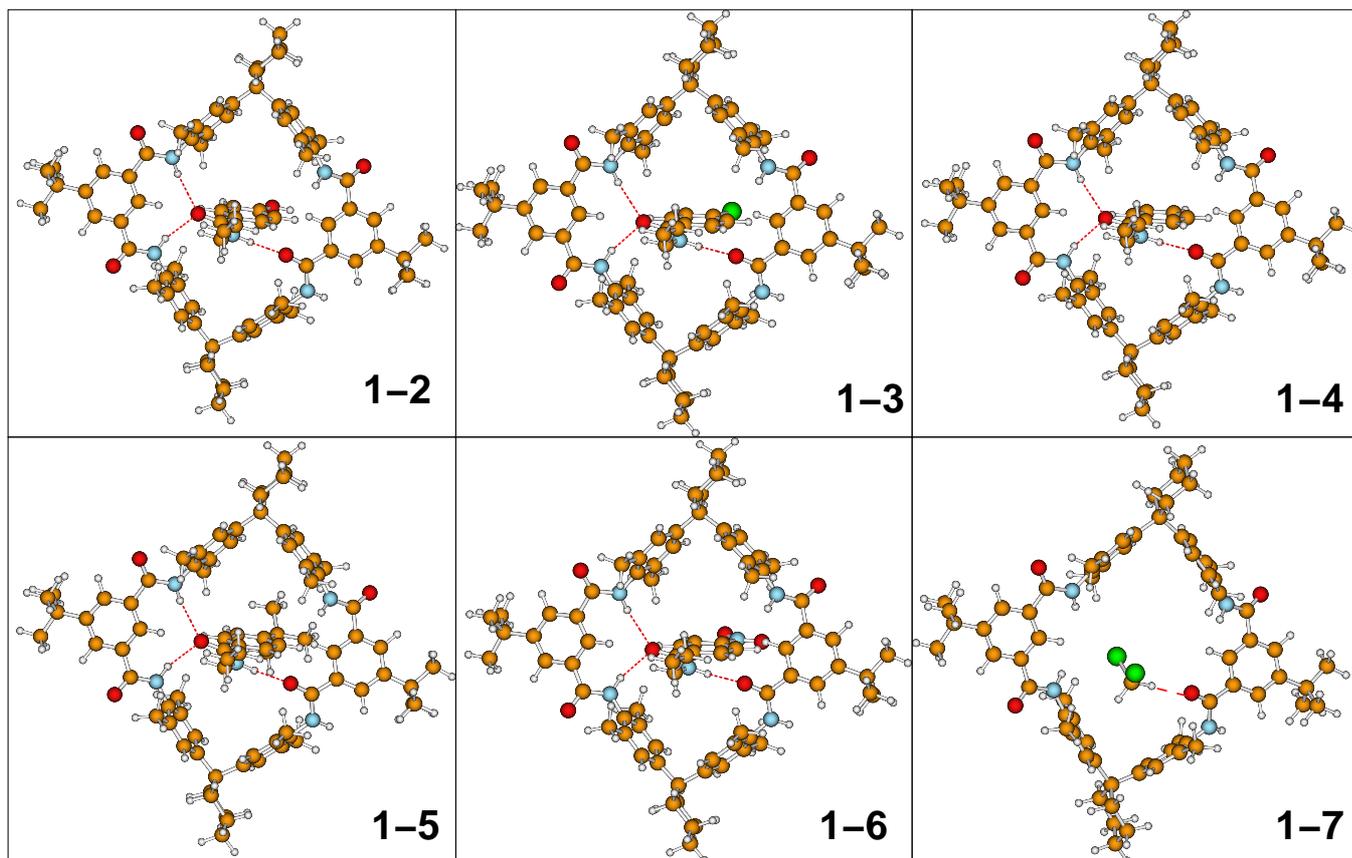


Figure 2: Minimum structures for all investigated pseudorotaxanes and the dichloromethane complex **1-7** (BP86/TZVP). Colour code: white (H), yellow (C), blue (N), red (O), green (Cl).

Table 1: Size of the area defined by the four nitrogen atoms in the wheel for each investigated complex and the free macrocycle (cf. Fig. 1). The adiabatic interaction energy is determined as pointed out in section 3.2 (cf. table 3).

No.	A [pm ²]	$\Delta E_{\text{adia}}^{\text{CP}}$ [kJ/mol]
1-2	470431	-37.9
1-3	471277	-36.6
1-4	471021	-36.5
1-5	470704	-36.0
1-6	472256	-35.7
1-7	473997	-13.9
1-8	476744	-6.8
1-9	466921	-23.2
1-10	475032	-65.2
1-11	476355	-
wheel	477285	0

Table 2: Absolute thermochemical properties of all investigated pseudorotaxanes at $T = 298.15$ K and $p = 101325$ Pa. Values for the enthalpy H and Gibbs free enthalpy G are in [kJ/mol], whereas heat capacities C_V are given in [kJ/(mol K)] and entropies S in [J/(mol K)]. Enthalpy contributions from the electronic energy are not included.

No.	contribution	H	C_V	S	G
1-2		4279.4	1517.1	1993.0	3685.2
	trans	3.7	12.5	197.3	—
	rot	3.7	12.5	178.5	—
	vib	4272.0	1492.1	1617.2	—
1-3		4168.9	1493.8	1968.8	3581.9
	trans	3.7	12.5	197.3	—
	rot	3.7	12.5	178.5	—
	vib	4161.4	1468.8	1593.0	—
1-4		4190.5	1477.3	1937.9	3612.7
	trans	3.7	12.5	197.0	—
	rot	3.7	12.5	178.1	—
	vib	4183.0	1452.4	1562.9	—
1-5		4491.3	1572.0	2044.9	3881.6
	trans	3.7	12.5	197.5	—
	rot	3.7	12.5	178.8	—
	vib	4483.9	1547.1	1668.6	—
1-6		4202.4	1514.6	1997.5	3606.8
	trans	3.7	12.5	197.4	—
	rot	3.7	12.5	178.7	—
	vib	4195.0	1489.7	1621.5	—

Table 3: Absolute thermochemical properties of the investigated solvent complexes at $T = 298.15$ K and $p = 101325$ Pa. Values for the enthalpy H and Gibbs free enthalpy G are in [kJ/mol], whereas heat capacities C_V are given in [kJ/(mol K)] and entropies S in [J/(mol K)]. Enthalpy contributions from the electronic energy are not included.

No.	contribution	H	C_V	S	G
1-7		3700.8	1335.8	1792.4	3166.4
	trans	3.7	12.5	196.1	—
	rot	3.7	12.5	177.7	—
	vib	3693.4	1310.8	1418.6	—
1-8		3677.8	1343.6	1804.6	3139.7
	trans	3.7	12.5	196.5	—
	rot	3.7	12.5	177.8	—
	vib	3670.3	1318.6	1430.4	—
1-9		3679.1	1311.7	1736.3	3161.4
	trans	3.7	12.5	195.3	—
	rot	3.7	12.5	177.5	—
	vib	3671.7	1286.7	1363.5	—
1-10		3894.1	1414.5	1874.7	3335.1
	trans	3.7	12.5	196.0	—
	rot	3.7	12.5	177.7	—
	vib	3886.7	1389.6	1501.1	—

Table 4: Thermochemical reaction data for the exchange reaction at $T=298.15$ K and $p=101325$ Pa employing different solvent complexes as reactants. All reaction enthalpies $\Delta_{\text{R}}H$, reaction entropy contributions $T\Delta_{\text{R}}S$ and Gibbs free enthalpies $\Delta_{\text{R}}G$ in [kJ/mol].

Guest	No.	1-7 CH ₂ Cl ₂			1-9 H ₂ O			1-10 (H ₂ O) ₄		
		$\Delta_{\text{R}}H$	$T\Delta_{\text{R}}S$	$\Delta_{\text{R}}G$	$\Delta_{\text{R}}H$	$T\Delta_{\text{R}}S$	$\Delta_{\text{R}}G$	$\Delta_{\text{R}}H$	$T\Delta_{\text{R}}S$	$\Delta_{\text{R}}G$
MeO-	1-2	-23.6	-7.5	-16.1	-15.4	-15.4	0.0	26.6	3.7	22.9
Cl-	1-3	-22.0	-9.0	-13.0	-13.8	-16.9	3.1	28.2	2.2	26.0
H-	1-4	-22.0	-8.9	-13.1	-13.8	-16.7	2.9	28.1	2.3	25.8
t-Bu-	1-5	-22.1	-8.0	-14.1	-13.9	-15.8	1.9	28.1	3.3	24.8
NO ₂ -	1-6	-20.8	-10.5	-10.3	-12.6	-18.4	5.8	29.4	0.7	28.7