

ESI

All of the structures were optimised using Jaguar 7.5 (*Jaguar*, version 7.5; Schrodinger LLC: New York, 2005.) the B3LYP functional [(a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789] and the 6-31G** basis set. [Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986]. Normal mode analyses showed that all of the structures are minima on the potential energy surface (except for the ^tBu pentamer, for which attempts to obtain normal mode analysis failed).

Table 2 Absolute Energies of the Cyclic Oligomers [M]_n (in a.u.^a except where stated otherwise)

Oligomer		SCF	U	H	G	ZPE (kcal)*
[M] ₅	Me	-947.23514	-947.134	-947.133	-947.174	58.403
	^t Bu	-1183.1432	-1182.8662	-1182.8653	-1182.9246	163.785
[M] ₄	Me	-1894.612	-1894.41	-1894.4	-1894.47	118.747
	^t Bu	-2366.4126	-2365.8542	-2365.8532	-2365.9472	329.808
[M] ₃	Me	-2841.9106	-2841.6	-2841.6	-2841.69	177.922
	^t Bu	-3549.6151	-3548.7746	-3548.7736	-3548.9048	495.195
[M] ₂	Me	-3789.2283	-3788.81	-3788.81	-3788.93	237.163
	^t Bu	-4732.8451	-4731.7235	-4731.7225	-4731.8864	661.667
[M] ₁	Me	-4736.5324	-4736.01	-4736.01	-4736.14	296.514
	^t Bu	-5916.0314	-	-	-	-

a 1a.u. = 2625.5 kJ mol⁻¹; **b** Zero Point Energy.

Table 3 Relative Thermodynamic Stabilities of Oligomers $[M]_n$. Values are for the t Bu models (where available) are in parenthesis.

Reaction	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)
$4[M]_5 \rightarrow 5[M]_4$	-59.1	-6.6	+0.18
$3[M]_5 \rightarrow 5[M]_3$	-26.3	+26.3	+0.17
$2[M]_5 \rightarrow 5[M]_2$	-91.9	+26.2	+0.22
$3[M]_4 \rightarrow 4[M]_3$	+26.3 (+35.0)	+26.3 (+64.0)	0 (0.10)
$[M]_4 \rightarrow 2[M]_2$	-26.3 (-21.0)	+26.3 (+42.3)	+0.18 (+0.21)
$2[M]_3 \rightarrow 3[M]_2$	-39.4 (-28.0)	0 (-16.3)	+0.13 (+0.08)

- Where the data is available, both sets of calculations show the same trends in ΔG , ΔH and ΔS .
- The first three reactions involving conversion of the pentamer $[M]_5$ into lower oligomers show a marked dependence on ΔS . Only in the case of conversion into the tetramer is ΔH -ve (cf the +ve value in the case of conversion into the dimer $[M]_2$).
- The tetramer $[M]_4$ is thermodynamically stable with respect to the trimer $[M]_3$, largely on the basis of ΔH . However, it is unstable with respect to the dimer $[M]_2$ on the grounds of ΔS . The trimer is unstable with respect to the dimer on the grounds of ΔH and ΔS .

These data suggest that the tetramer represents the most energetically favourable species, but is thermodynamically destabilized with respect to the dimer due to entropy.