Dispersia - Balance scale solvent dependent?

C106

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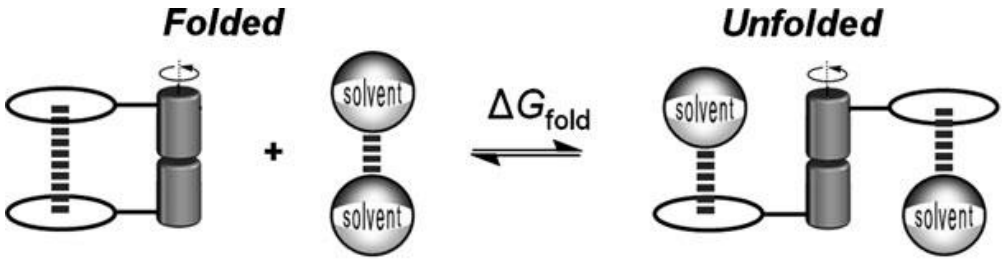
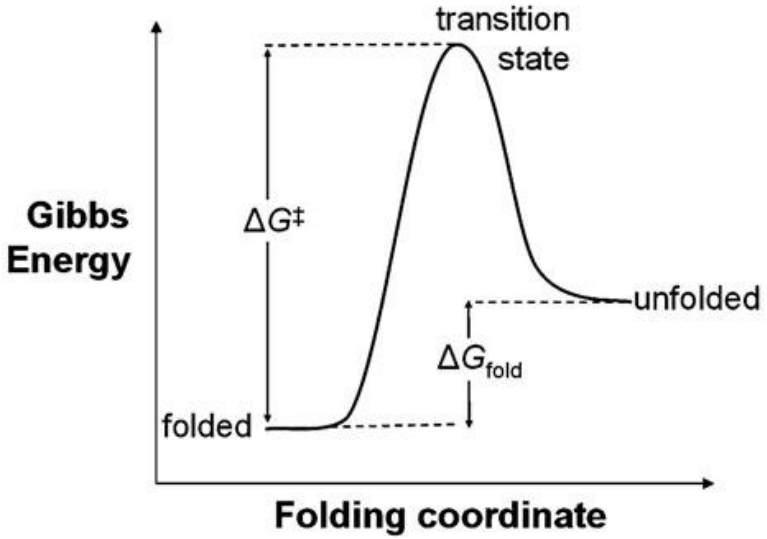
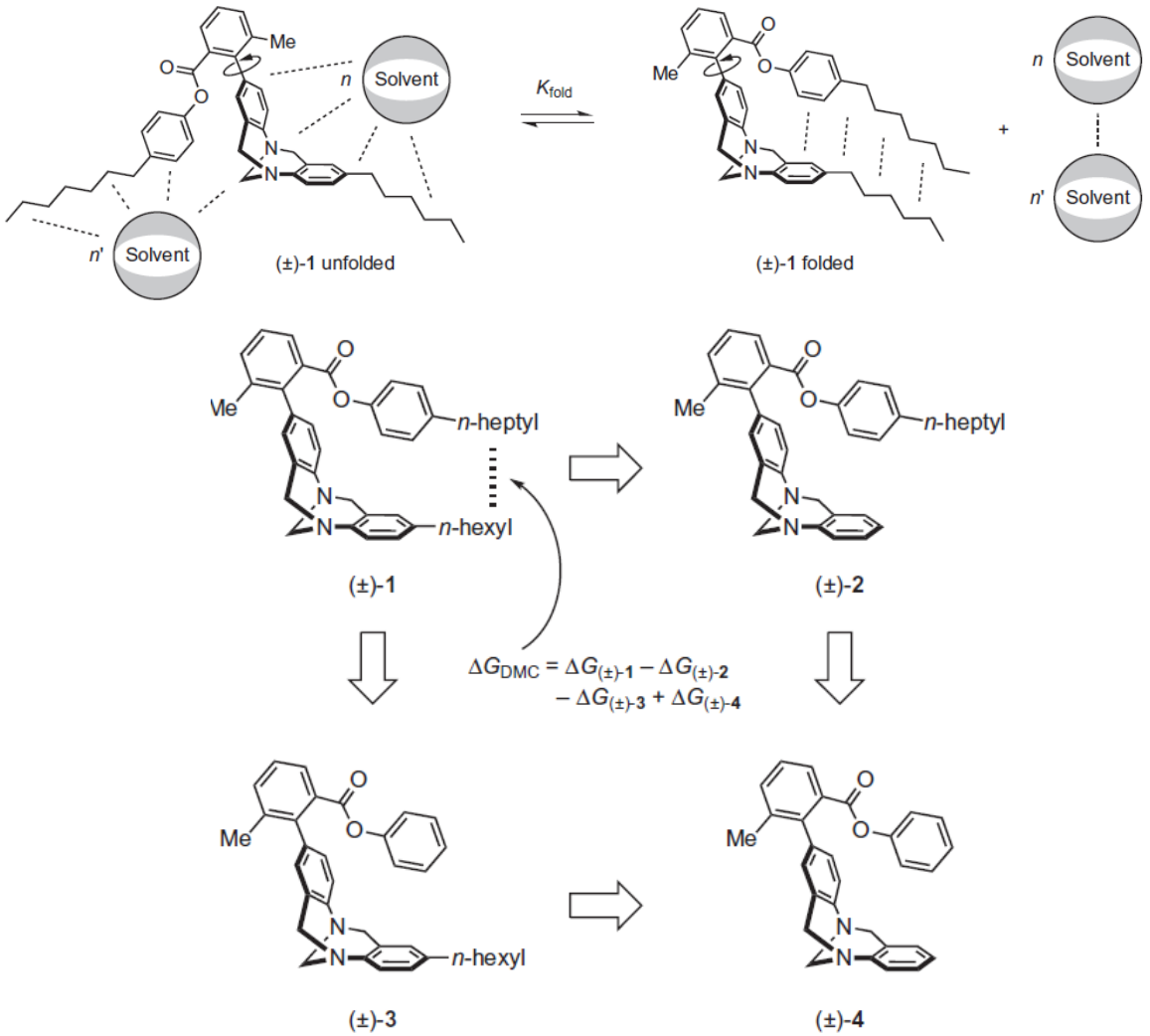
What is a molecular balance?





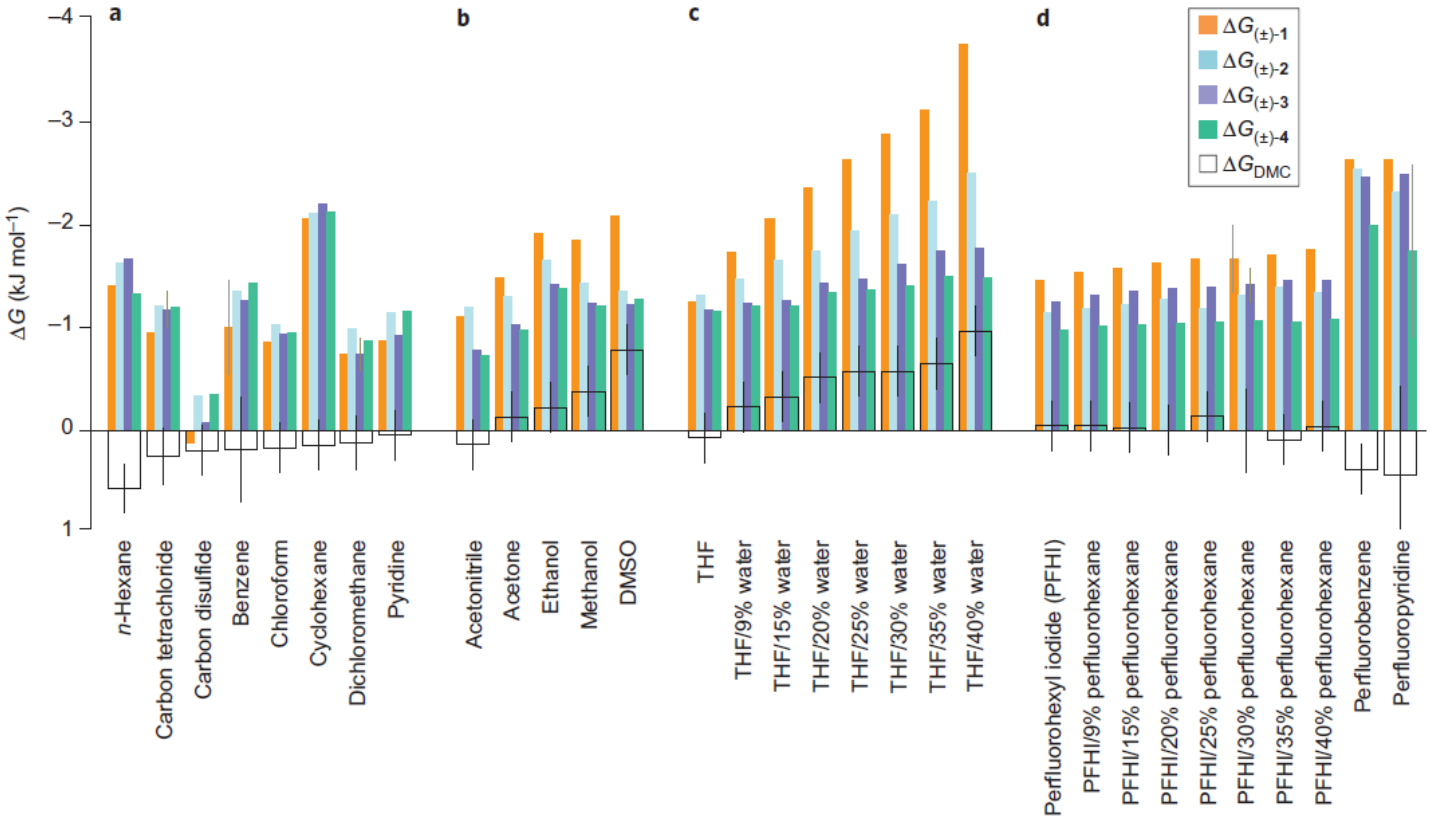
I. K. Mati, S. L. Cockroft, *Chem. Soc. Rev.* **2010**, *39*, 4195-4205.

Examples for torsion balances



L. Yang, C. Adam, G. S. Nichol, S. L. Cockroft, *Nat. Chem.* **2013**, *5*, 1006-1010.

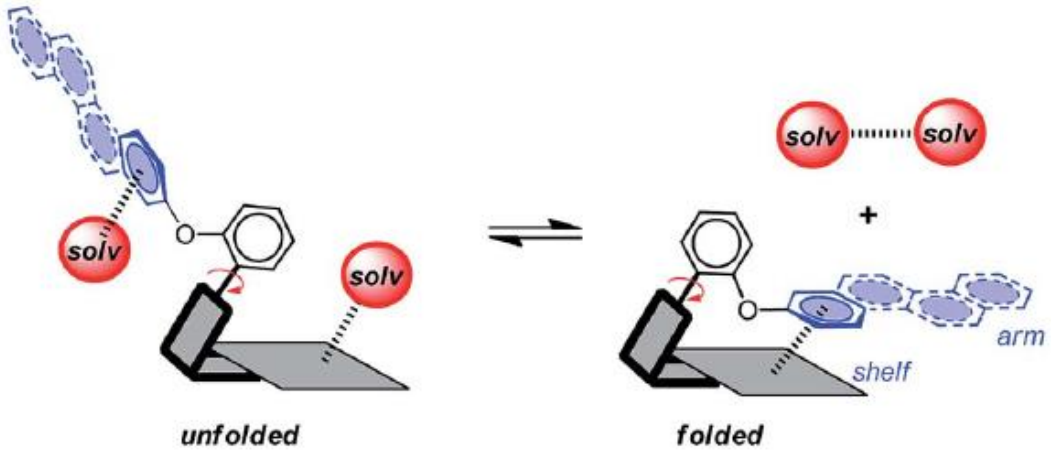
Examples for torsion balances

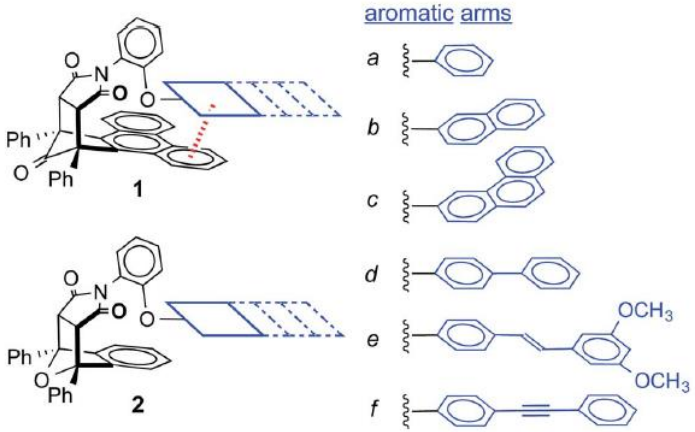


The small magnitude of the dissected alkyl–alkyl interaction energies is particularly notable when compared to the much larger energies associated with experimental enthalpies of vaporization for alkanes and computational estimates of alkyl–alkyl interactions in the gas phase.- Cockroft ***2013***

L. Yang, C. Adam, G. S. Nichol, S. L. Cockroft, *Nat. Chem.* **2013**, *5*, 1006-1010.

Examples for torsion balances (π-π-Interactions)

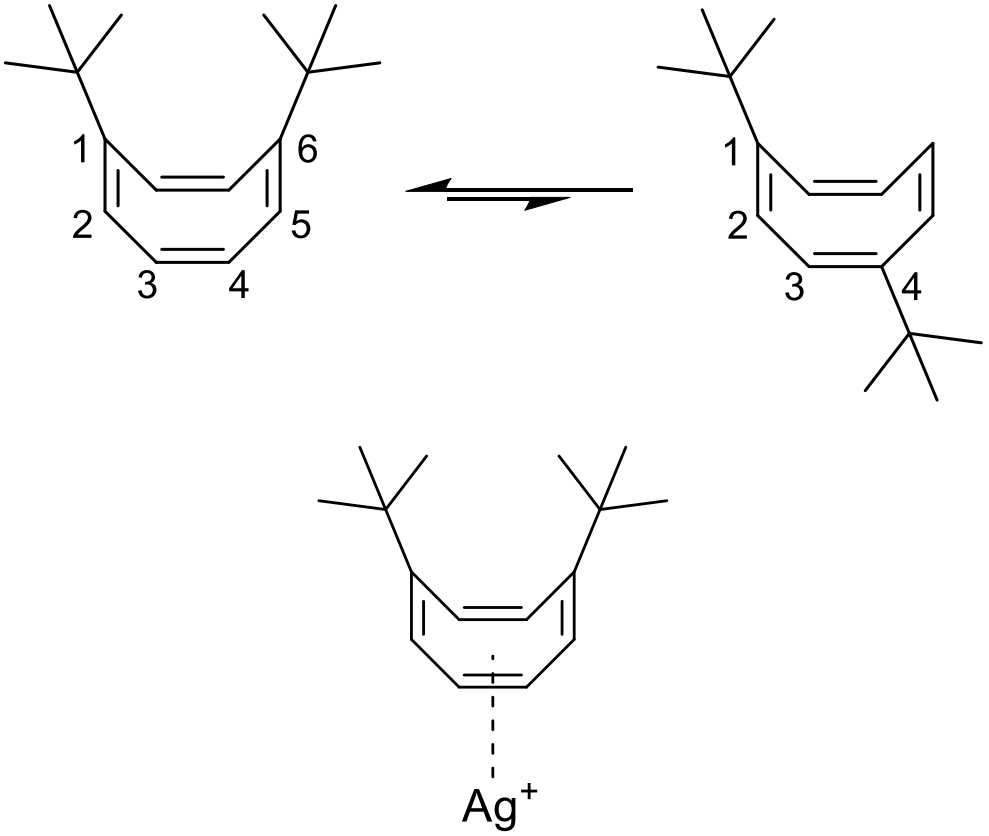




No correlation was observed between the polarizabilities of the aromatic surfaces and the stacking energies. There was relatively little variance in the strengths of the stacking energies despite the wide range in the sizes and conjugation lengths of the aromatic surfaces. These results suggest that the dispersion contributions to the aromatic stacking interaction in solution are relatively minor.

J. Hwang, B. E. Dial, P. Li, M. E. Kozik, M. D. Smith, K. D. Shimizu, *Chem. Sci.* **2015**, *6*, 4358-4364.

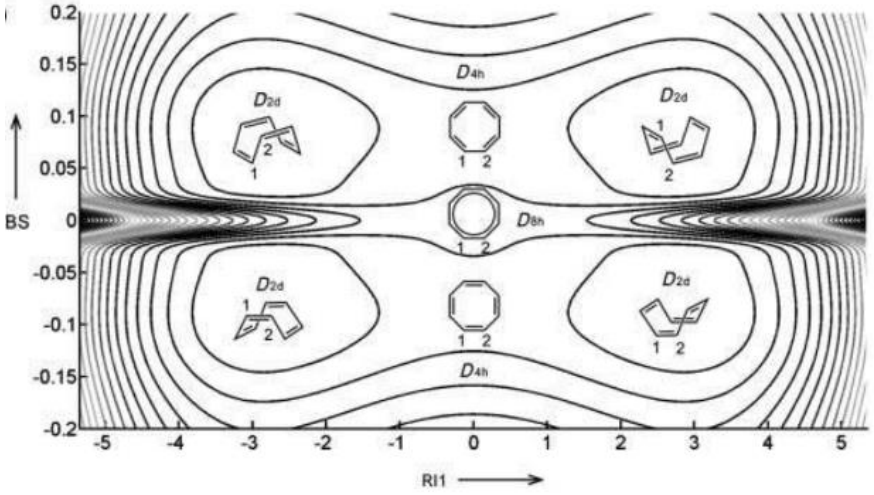
Unexpected conformation of a Uranocenligand

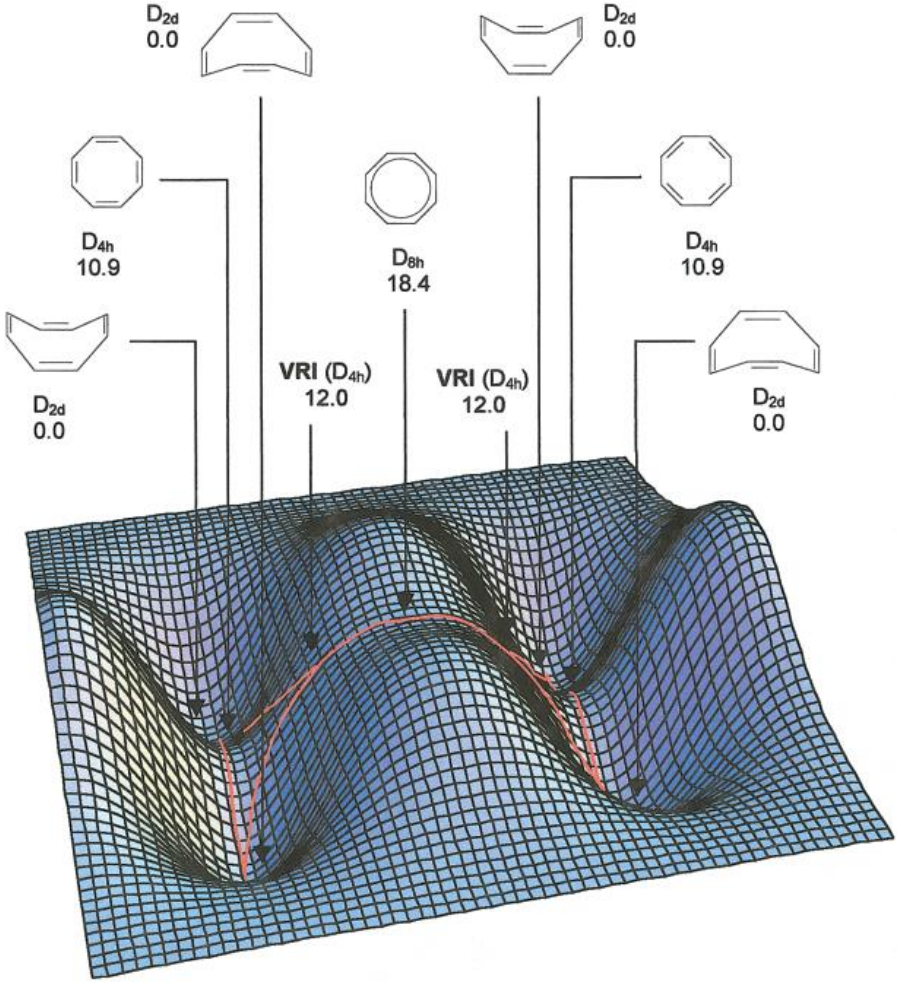


M. H. Lyttle, A. Streitwieser, R. Q. Kluttz, *J. Am. Chem. Soc.* **1981**, *103*, 3232-3233.

L. A. Paquette, G. J. Hefferon, R. Samodral, Y. Hanzawa, *J. Org. Chem.* **1983**, *48*, 1262-1266.

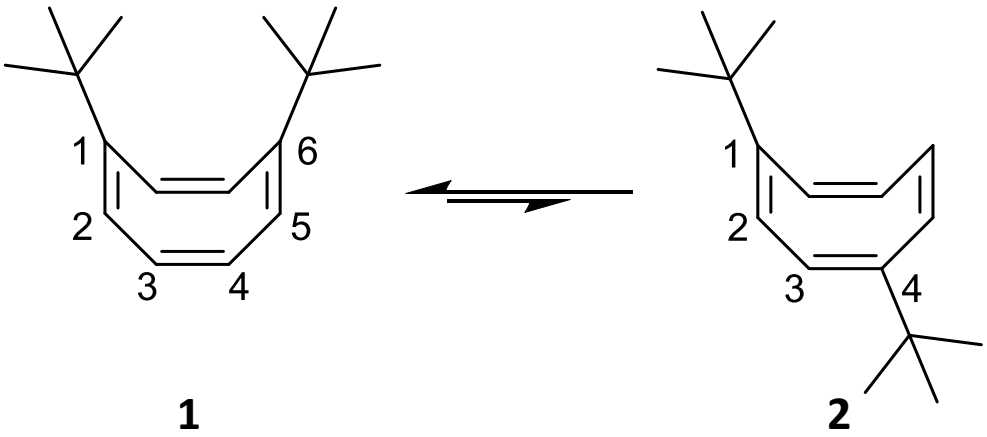
Double bond shift isomerism





D. H. Paik, D.-S. Yang, I. R. Lee, A. H. Zewail, *Angew. Chem. Int. Ed.* **2004**, *43*, 2830-2834.
O. Castaño, R. Palmeiro, L. M. Frutos, J. Luisandrés, *J. Comput. Chem.* **2002**, *23*, 732-736.

First Investigation of the folding



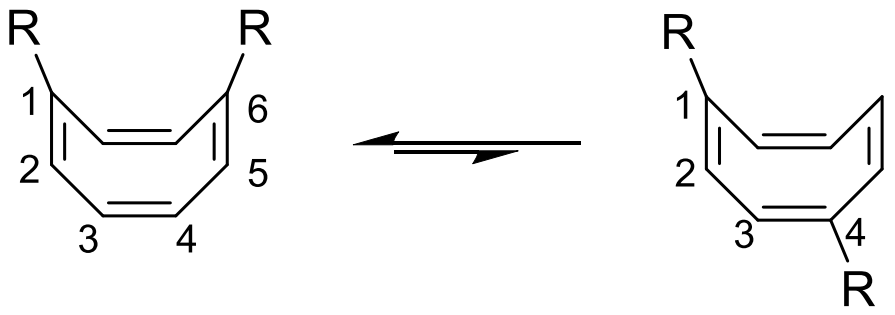
1 **2**

*„Measurement of the equilibrium constant k [2]/[1] by NMR integration at several temperatures … Isomer **1** is more stable by ΔH° = 0.48 kcal/mol, but small entropy change of ΔS° = 0.92 e.u. favors isomer **2**.“ – Streitwieser **1981***

*„…, we proceeded to determine the equilibrium constant,…,at various temperatures in $CDCl_3$ at 300 MHz. ...,k_{eq} was determined to equal 0.48 at 25 °C. … Of a particular note is the finding that a solvent change from $CDCl_3$ to C_6D_6 caused a reversal in the relative intensities of the upfield peaks.“ – Paquette **1983***

M. H. Lyttle, A. Streitwieser, R. Q. Kluttz, *J. Am. Chem. Soc.* **1981**, *103*, 3232-3233.
L. A. Paquette, G. J. Hefferon, R. Samodral, Y. Hanzawa, *J. Org. Chem.* **1983**, *48*, 1262-1266.

Variation of the balance



R = Me, Et, *i*Pr, *t*Bu, Ph
and mixtures

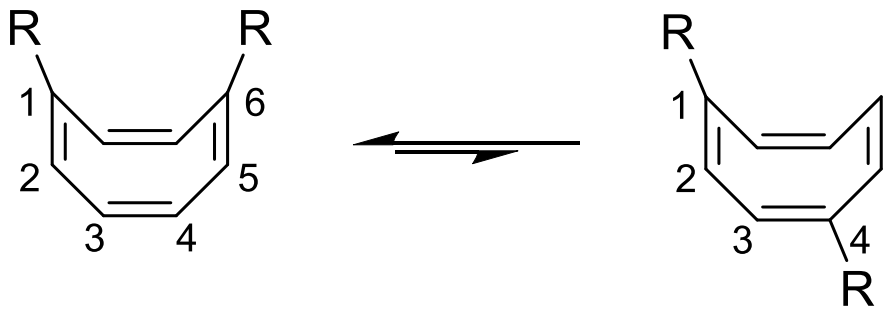
„… Measurements of the equilibrium were carried out at several temperatures for each of the compounds, taking care to allow sufficient time for equilibration at each temperature studied.

...The larger the alkyl group, the more the 1,6-isomer with the alkyl groups close together, is favoured, but the proportion of the 1,4 isomer increases slightly with temperature.“ – Anderson ***1992***

(Measurements with different temperatures only in $CDCl_3$ and in C_6D_6 only at 20 °C)

J. E. Anderson,P. A. Kirsch, *J. Chem. Soc., Perkin Trans. 2* **1992**, 1951-1957.

Variation of the balance



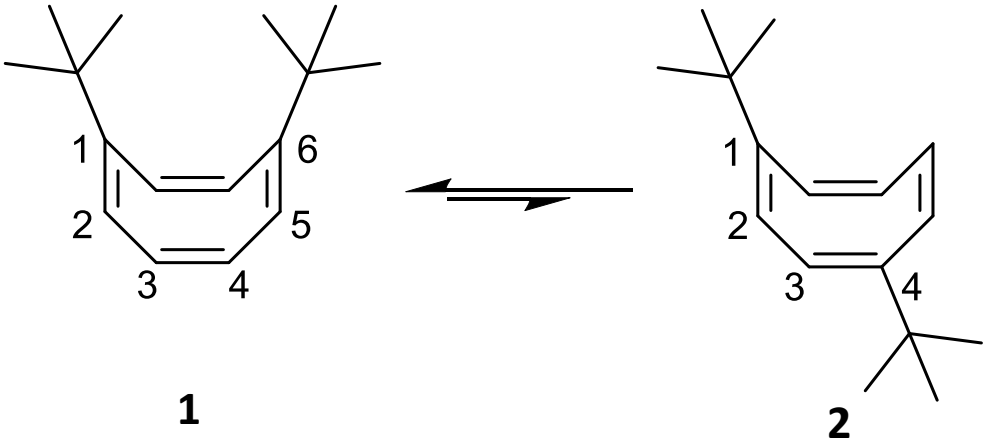
$$\log_{10} k_{\text{eq.}} = -\Delta H_0 (2.3RT)^{-1} + \Delta S_0\ (2.3R)^{-1}$$

Compound and alkyl group R =	$-\Delta H_0$ [kcal mol^{-1}]	$-\Delta S_0$ [cal mol^{-1} K^{-1}]*	Correlation coefficient	$-\Delta G_0^{293\ \text{K}}$ [kcal mol^{-1}]
Methyl	0.05	+0.3	0.064	0.08
Ethyl	0.52	-1.0	0.851	0.24
Isopropyl	0.61	-1.0	0.837	0.36
tert.-Butyl	1.14	-2.5	0.952	0.39*

*At 298 K in $CHCl_3$-d^1 solution whereas other results are for benzene-d^6 solution

J. E. Anderson,P. A. Kirsch, *J. Chem. Soc., Perkin Trans. 2* **1992**, 1951-1957.

Computations



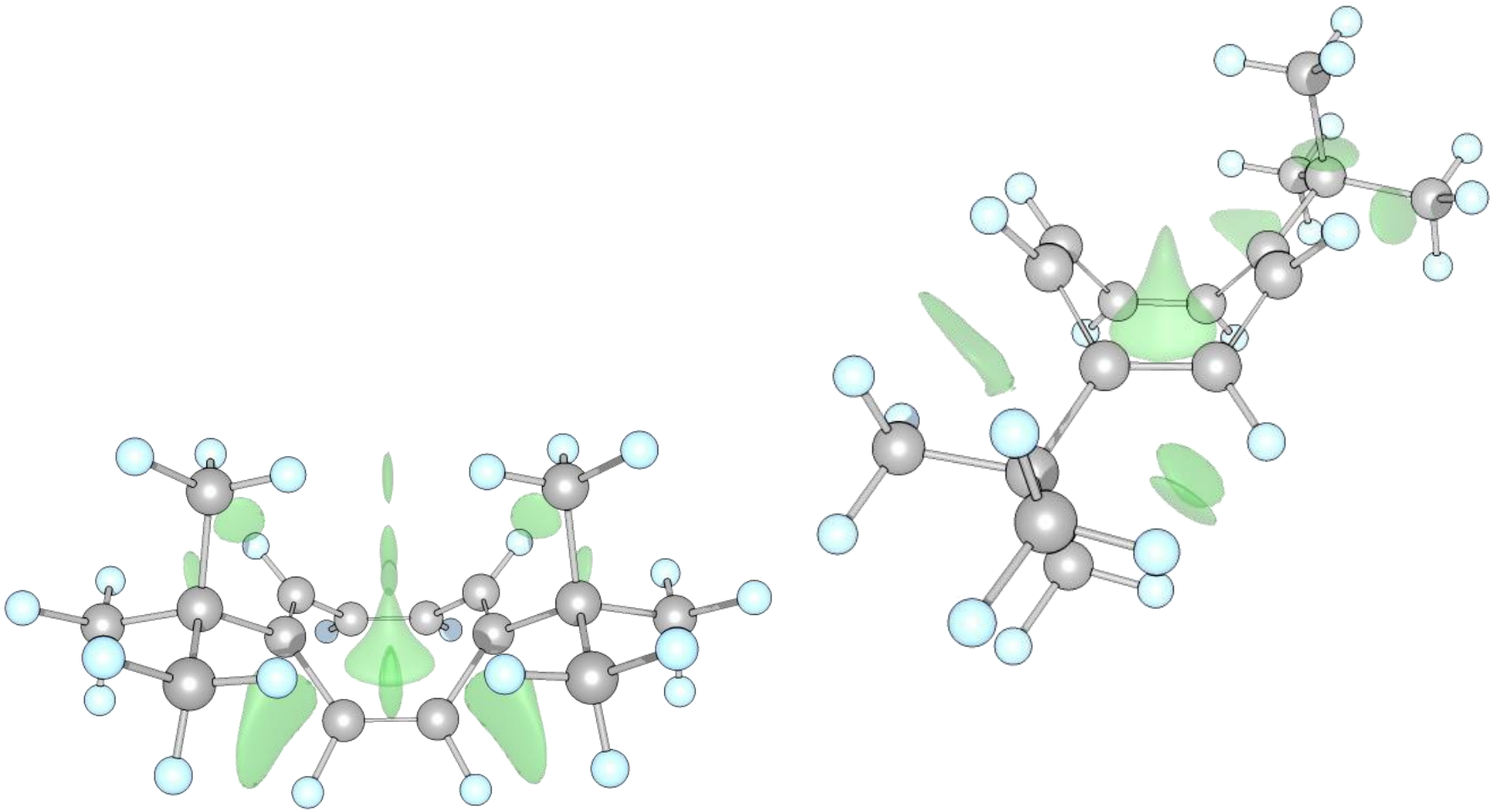
1 **2**

*„… MMP2 force field clearly indicates **1** to be more stable than **2** in the gas phase. …The mesurements by Streitwieser are in solution, and some change in the equilibrium constant may attend a change to the gas phase. … The proposal by Streitwieser that this equilibrium is determind primarily by van der Waals attraction between the tert-butyl groups is borne out by the molecular mechanics calculations.“ – Allinger **1982***

*„Molecular orbital computations give clear indication that the more congested 1,6-dialkylcyclooctatetraene isomers, …, are more stable than the corresponding 1,4 isomers in the gas phase. The ability of PCILO to account for this, coupled to the inhability of ab initio unless a dispersion energy correction is introduced, bears out the attribution of this behavior to van der Waals attraction between the two alkyl groups.“ – Tosi **1983***

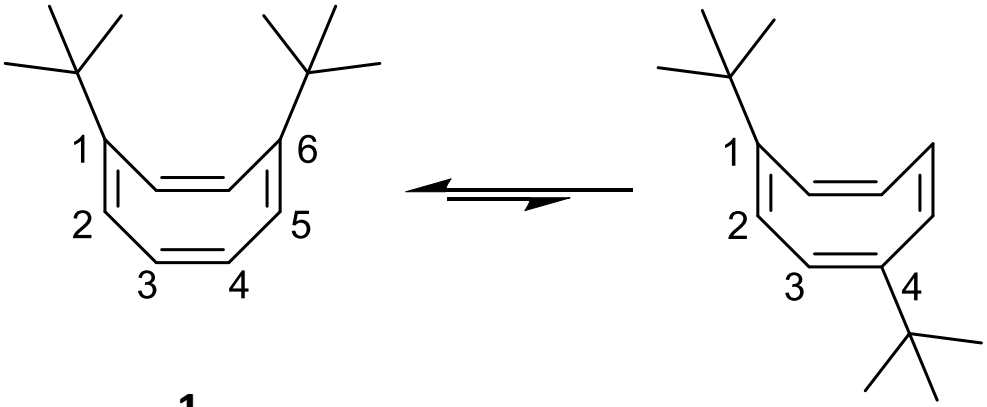
N. L. Allinger, M. Frierson, F. A. Van-Catledge, *J. Am. Chem. Soc.* **1982**, *104*, 4592-4593.
C. Tosi, *J. Comput. Chem.* **1984**, *5*, 248-251.

Visualization of the non covalent interactions (NCI Plots)



J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J.-P. Piquemal, D. N. Beratan, W. Yang, *J. Chem. Theory Comput.* **2011**, *7*, 625-632.

Henry Rzepa: A molecular balance for dispersion energy?



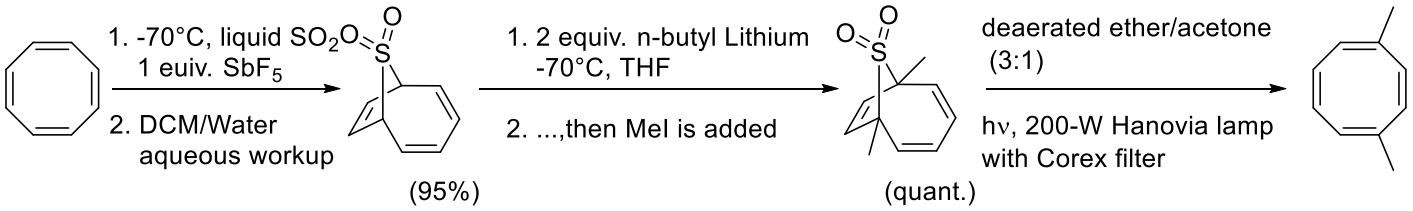
1 **2**

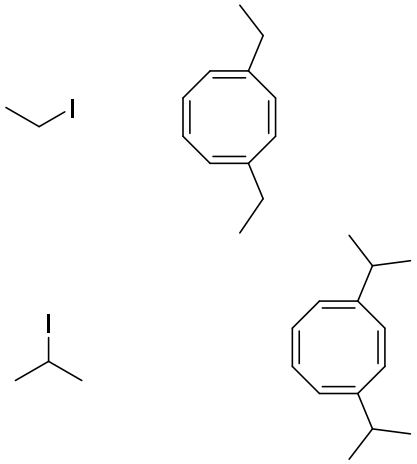
Method	$k_{eq.}$ (298K) [1]/[2]	ΔΔE	$\Delta\Delta H_{298K}$	$\Delta\Delta S_{298K}$	$\Delta\Delta G_{298K}$
Experiment	1.93	-	1.14	-2.5	0.387
B3LYP/Def2-TZVPP/$CDCl_3$ (no dispersion)	1.906*	0.05	0.00	+1.3*	0.382*
B3LYP/Def2-TZVPP/$CDCl_3$ (gd3bj dispersion)	8.36	0.75	0.66	+2.0	1.25

* This contains a contribution of RTLn 2 (= 0.410 kcal/mol = 1.04 in ΔS), where 2 is the symmetry number for a species with C_2 rotational symmetry, to the 1,4-isomer only.

J. E. Anderson,P. A. Kirsch, *J. Chem. Soc., Perkin Trans. 2* **1992**, 1951-1957.
http://www.ch.imperial.ac.uk/rzepa/blog/?p=15671

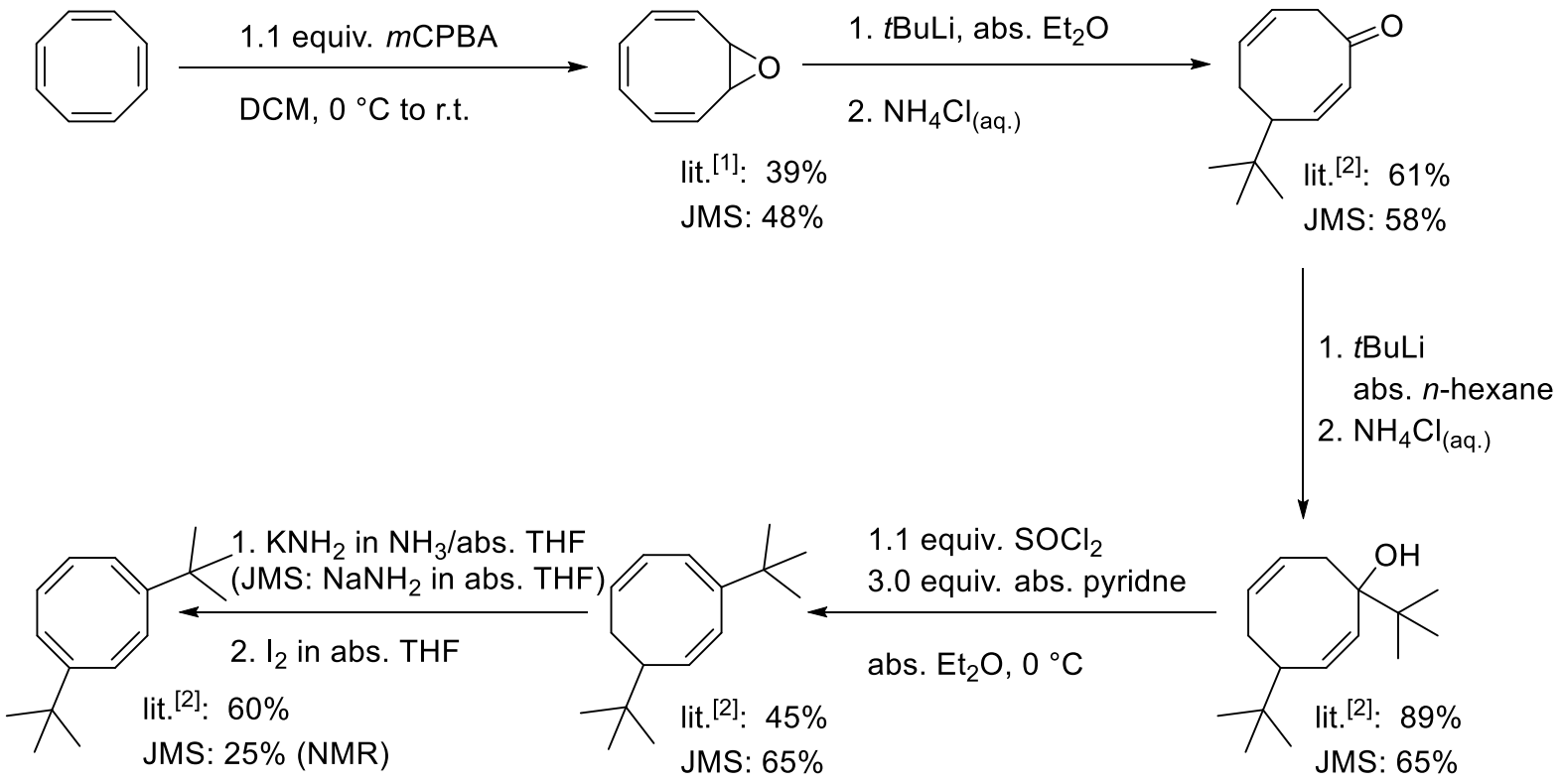
Synthetic routes – Paquette 1974





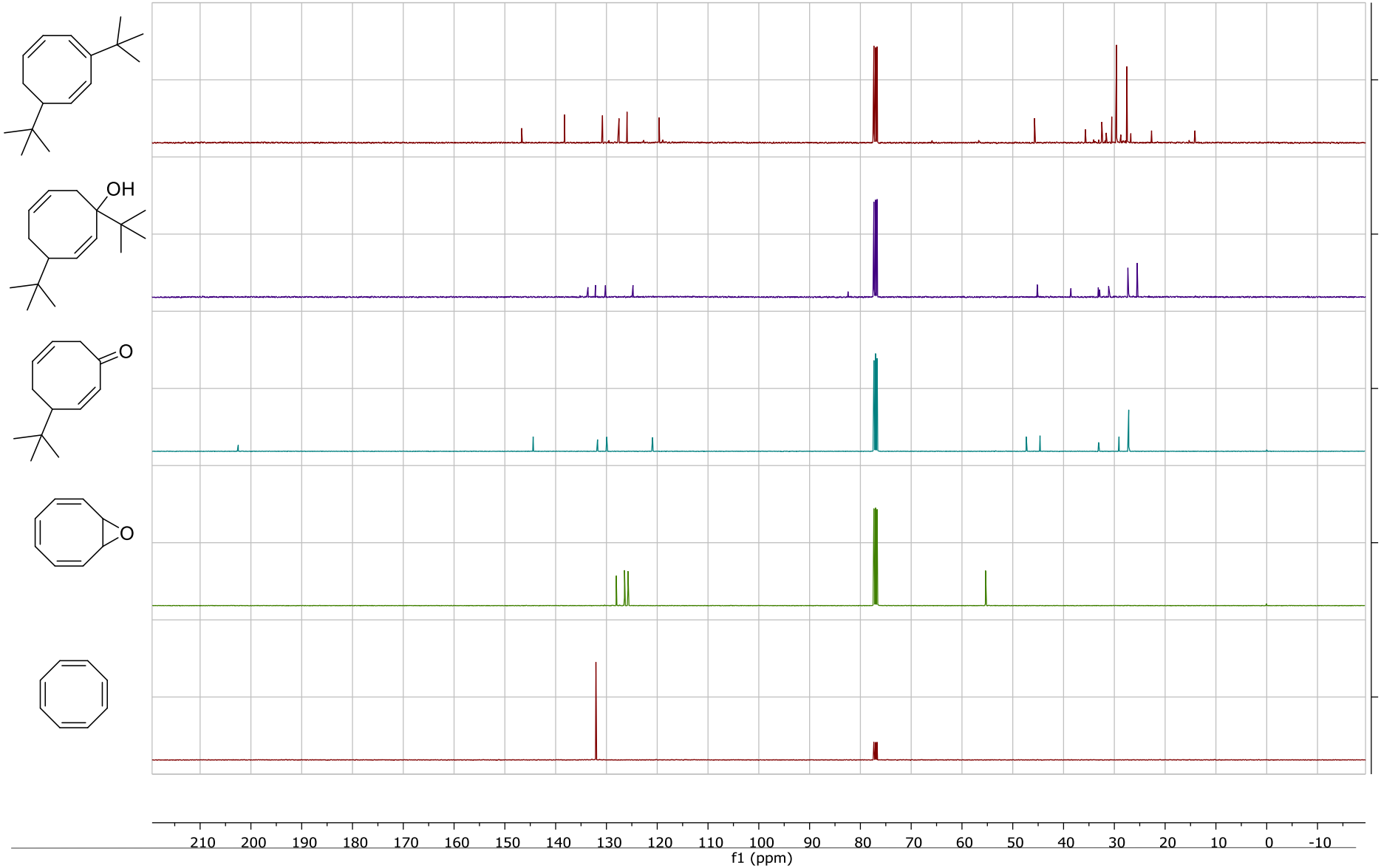
J. Gasteiger, R. Huisgen, *J. Am. Chem. Soc.* **1972**, *94*, 6541-6543.
L. A. Paquette, S. V. Ley, R. H. Meisinger, R. K. Russell, M. Oku, *J. Am. Chem. Soc.* **1974**, *96*, 5806-5815.

Synthetic routes – Streitwieser 1981



[1] A. C. Cope, B. D. Tiffany, *J. Am. Chem. Soc.* **1951**, *73*, 4158-4161.
[2] M. J. Miller, M. H. Lyttle, A. Streitwieser, *J. Org. Chem.* **1981**, *46*, 1977-1984.

Synthetic routes – Streitwieser 1981



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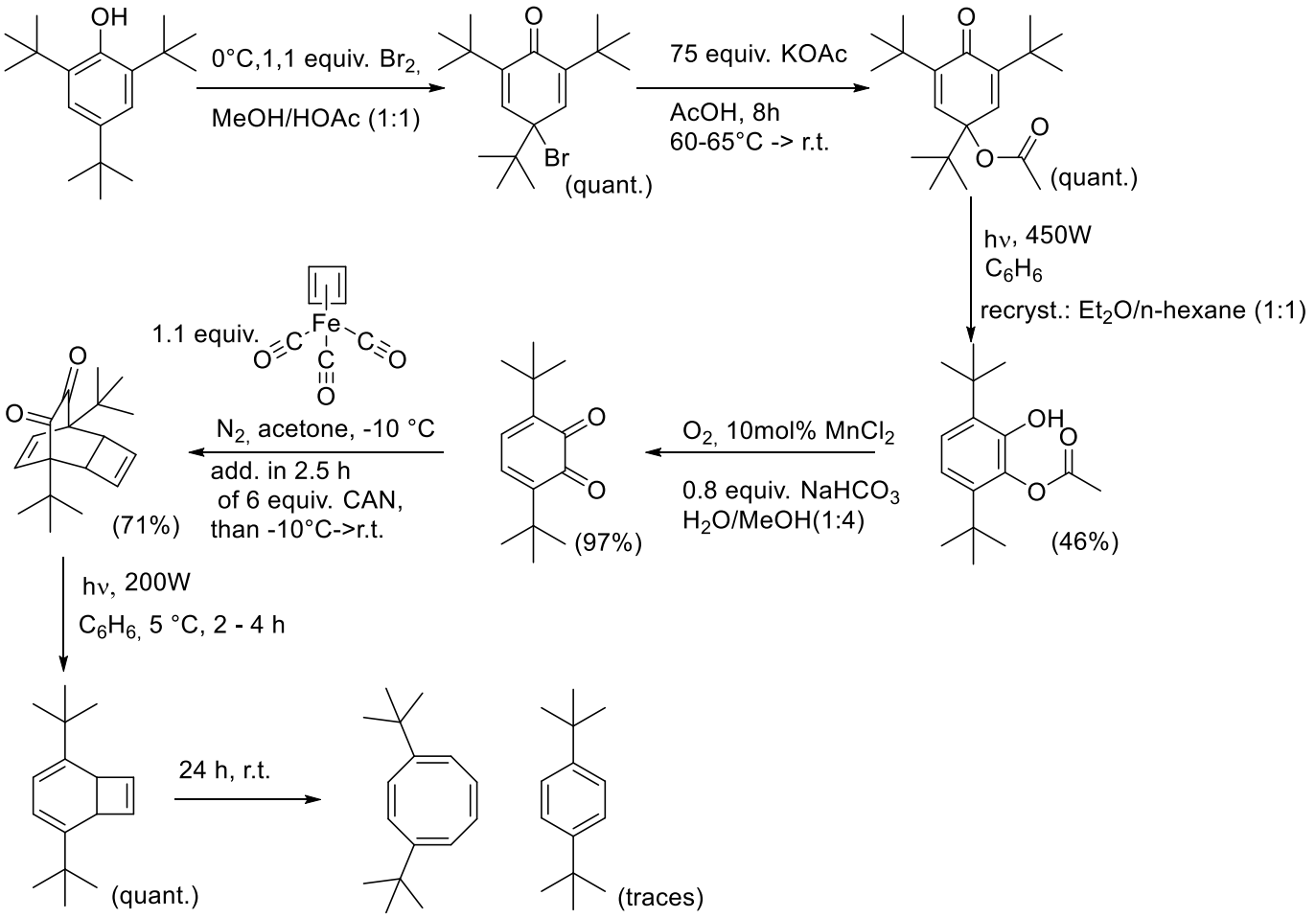
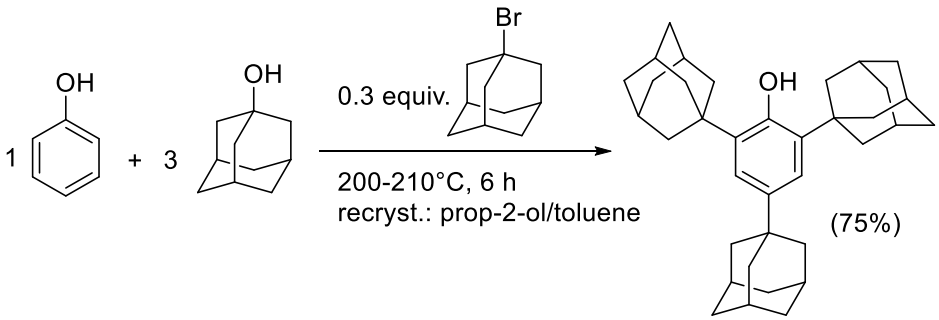
Synthetic routes – Paquette 1983



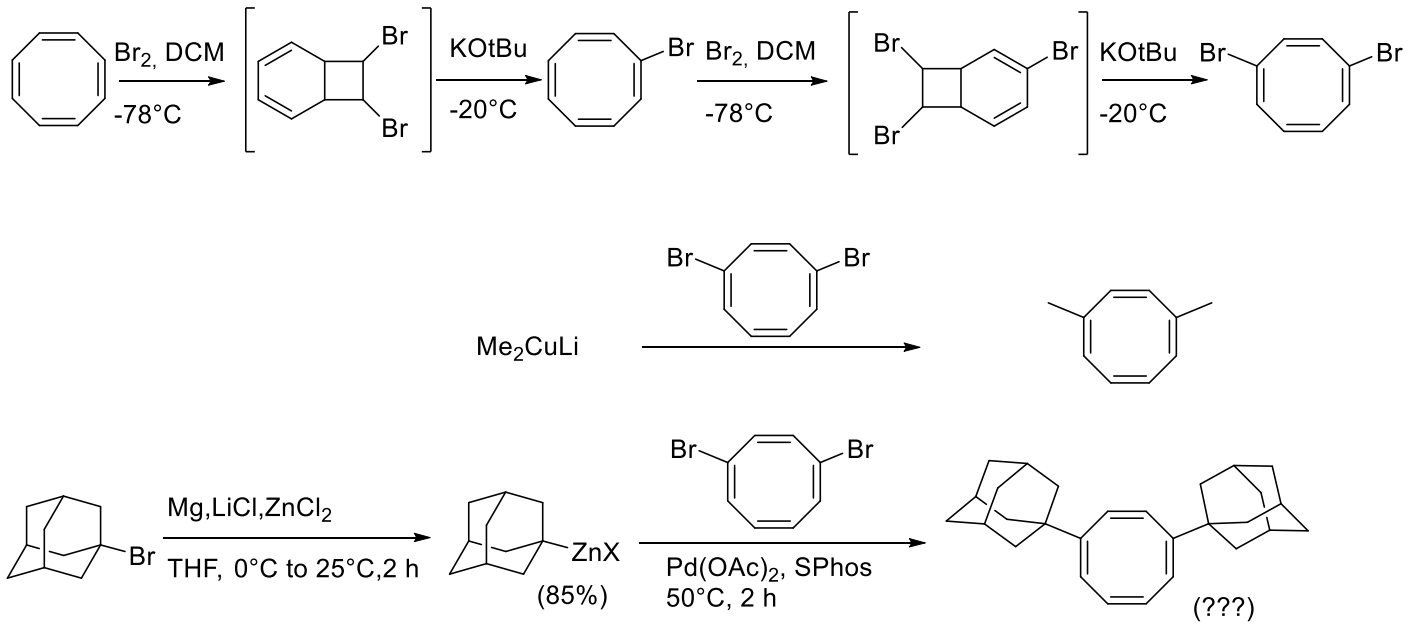
L. A. Paquette, G. J. Hefferon, R. Samodral, Y. Hanzawa, *J. Org. Chem.* **1983**, *48*, 1262-1266.

Synthetic routes – Paquette 1983 with a new substrate?



W. A. Sokolenko, N. M. Svirskaya, A. I. Rubaylo, *Russ. Chem. Bull.* **2014**, *62*, 1293-1296.

Synthetic routes – Krebs 1967 + Sämann 2014



[1] a) Krebs, A. *Angew. Chem.* **1965**, *77*, 966. (b) Krebs, A.; Byrd, D. *Liebigs Ann. Chem.* **1967** ,*707* ,66−74.
[2] C. Sämann, V. Dhayalan, P. R. Schreiner, P. Knochel, *Org. Lett.* **2014**, *16*, 2418-2421.

Thank you for your attention!

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