Aromaticity on the Edge of Chaos: An *Ab initio* study of the bimodal balance between aromatic and non-aromatic structures for 10-π-Dihetero[8]annulenes.

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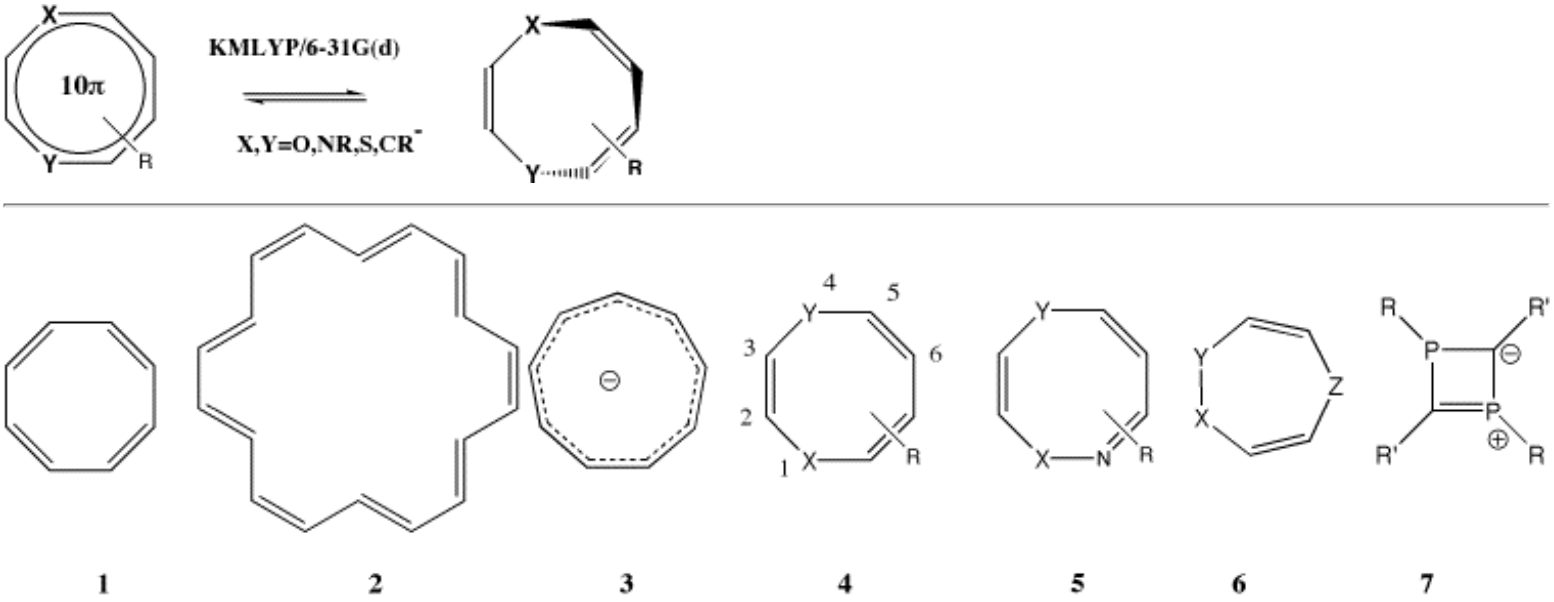
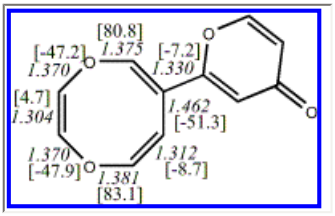
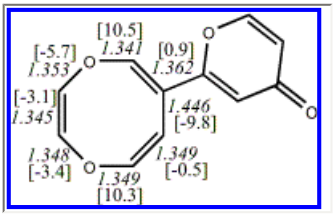
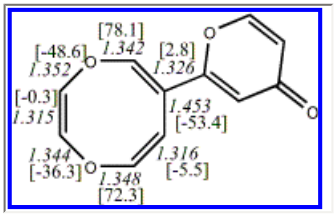
Summary: The computed geometries of a class of 10-π-annulenes containing two heteroatoms, which exhibit an acutely sensitive balance between π and σ influences upon ring planarity, reveal that the recent KMLYP hybridisation of the exchange functional in the DFT method is qualitatively superior to the more commonly used B3LYP hybrid for modelling the aromaticity of such systems.

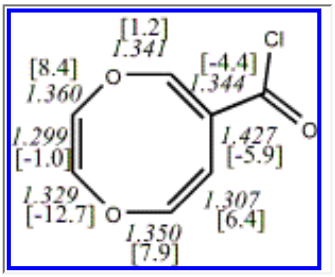
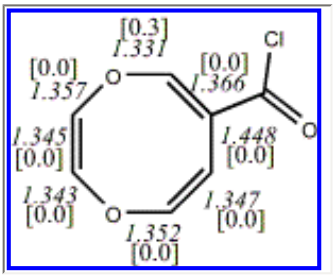
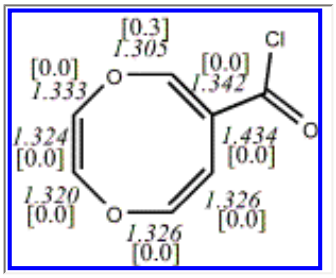
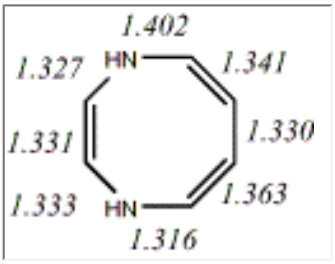
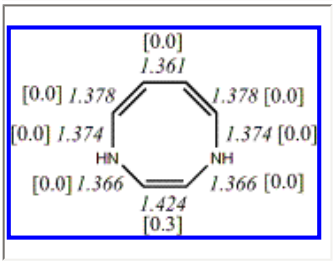
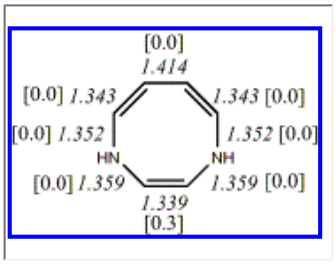
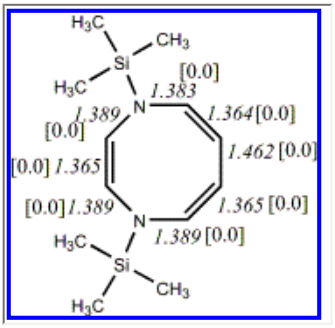
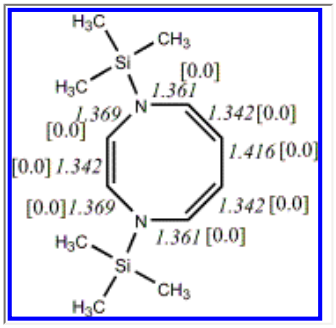
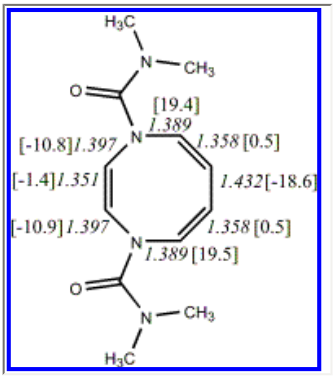
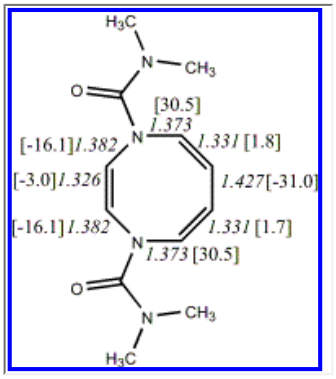
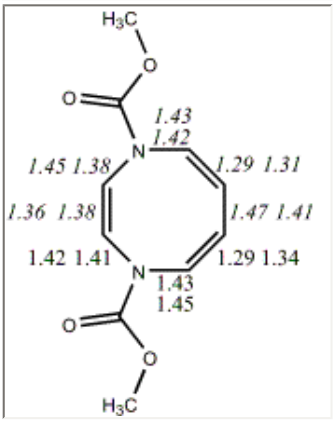
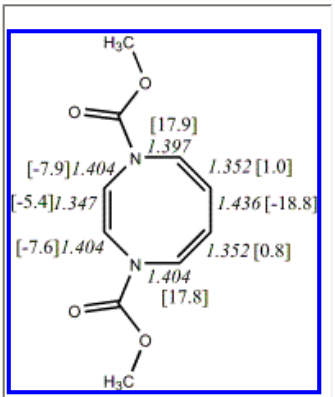
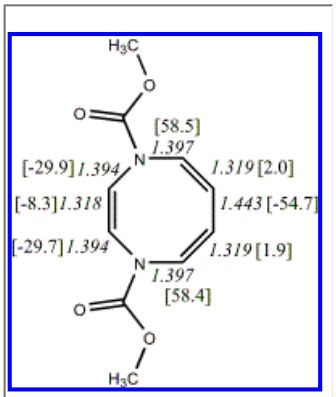
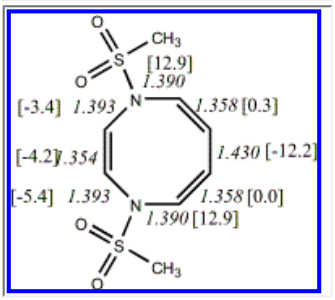
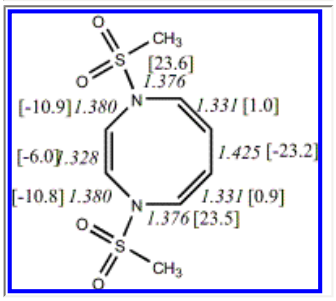


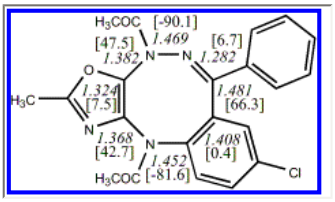
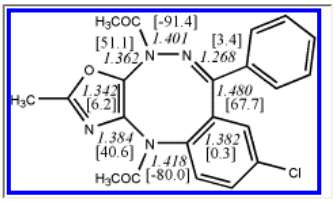
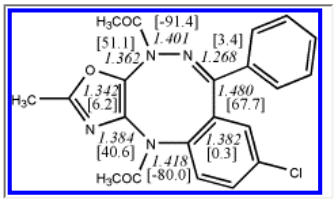
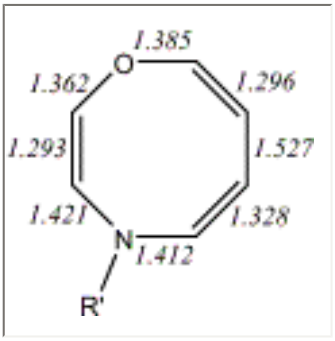
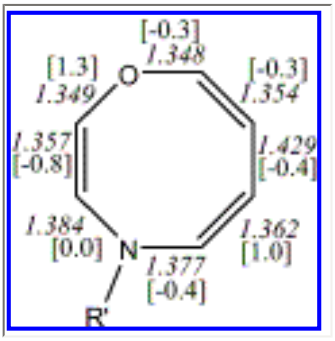
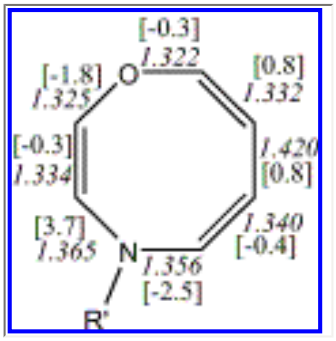
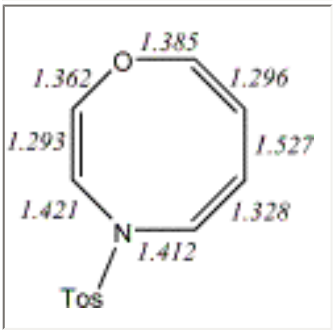
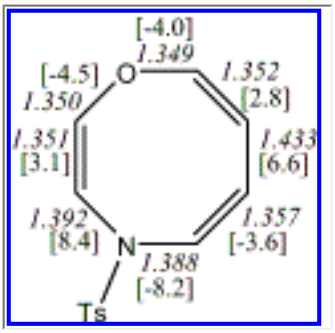
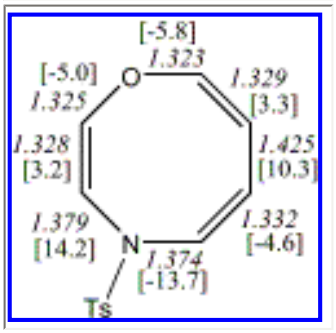
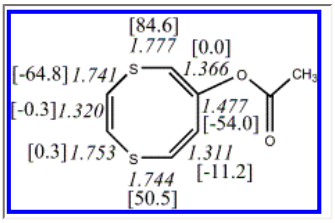
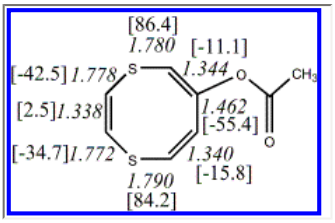
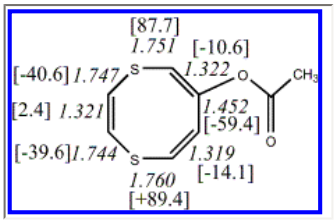
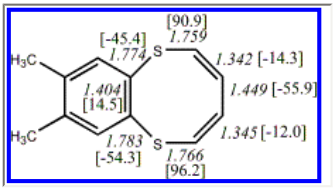
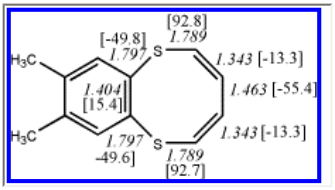
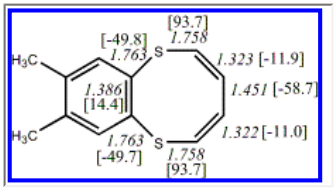
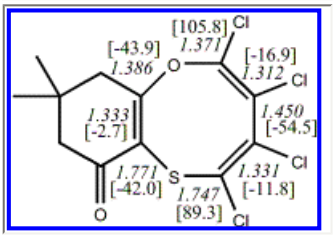
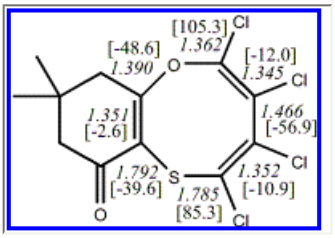
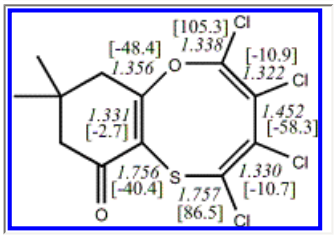
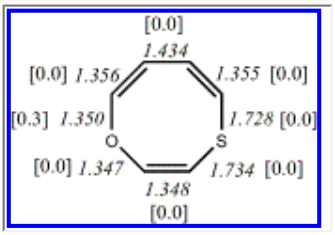
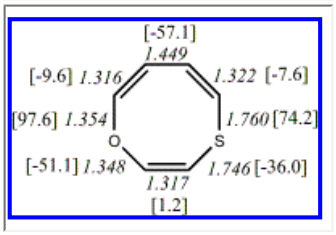
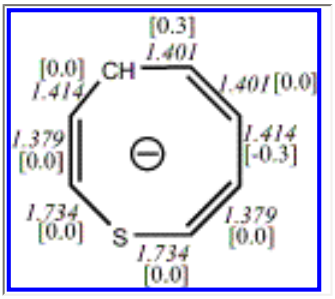
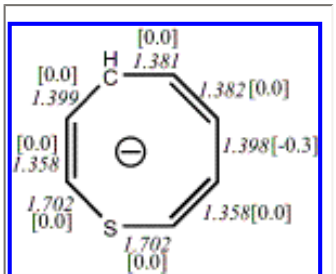
Electronic Supplemental Information

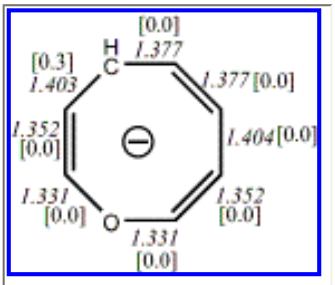
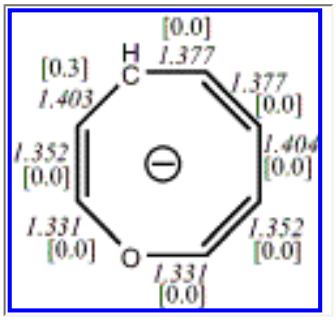
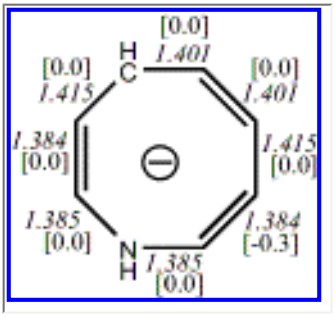
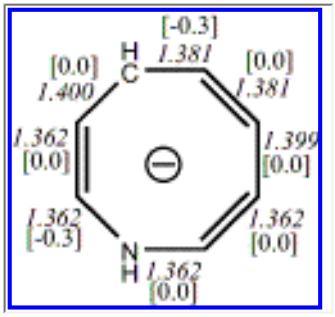
Coordinates are available in the form of Molfiles or PDB files. These can be viewed if the appropriate Browser plugin is installed such as Chime or Chem3D Viewer.

Table 1. Geometries, Energies and NICS values for 4 - 6.

B3LYP/KMLYP 6-31G(d) Energy, Hartree NICS(0), ppm [B3LYP/KMLYP]	Crystal Geometry: length, Å [dihedral, degrees]	Geometry (B3LYP)	Geometry (KMLYP)
4, X=Y=O[17] -724.75782/-723.29019[a,b] [-7.5/0.1]			

4, X=Y=O[17] 955.53210/-954.11459 [-7.7/-7.0]			
4, X=Y=NH[18] -342.89994/-342.21433 [-12.9/-12.5]			
4, X=Y=N-TMS[18] -1160.27700/-1158.59120 [-11.3/-10.8]	Reported as planar		
4, X=Y=N-$CONMe_2$[19] -837.52547/-835.89800 [-8.5/-6.0]	Reported as planar		
4, X=Y=NCO_2Me[19] -798.64839/-797.07613 [-6.0/-1.3]			
4, X=Y=N-SO_2Me[18] -1518.65134/-1516.49681[c,d] [-9.6/-7.4]	Reported as twisted		

5, X=Y=N-Acetyl[24] -1715.32163/-1712.39694 [-0.8/-0.6]			
4, X=O, Y=N, R'=(3,4,5-trimethoxybenzyl)[20] -976.66132/-974.75355 [-10.0/-9.2]			
4, X=O, Y=N-Tosyl[20] -1181.67739/-1179.74661[e,f] [-8.9/-7.6]			
4, X=Y=S[21] -1256.41893/-1254.75146 [-2.5/-2.4]			
4, X=Y=S[22] -1260.83295/-1259.16593 [-2.2/-2.0]			
4, X=S, Y=O[23] -2852.64265/-2849.43451 [-2.17/-2.1]			
4, X=O, X=S -705.57218/-704.57509[g] [-9.2/-1.2]	unknown		
4, X=CH$^-$, X=S -669.09512/-668.17759[-14.1/-14.6]	Diatropic by NMR[25]		

4, X=CH$^-$, X=O -346.1104603/-345.4187586 [-13.5/-13.5]	Diatropic by NMR[18]		
4, X=CH$^-$, X=NH -326.249677/-325.60088 [-15.8/-16.3]	Diatropic by NMR[18]		
6, X=Y=Z=NH -320.79828/-320.16244 [-8.2/-7.4]	Unknown	36.7	12.5

[a]Corrected for ΔG: -723.15206, Total energy (MP2): -722.61300 [b]Planar valence isomer; total energy (KMLYP/MP2) -723.29133/722.61166. Corrected for ΔG(KMLYP): -723.14989, NICS(KMLYP) = -6.1. [c] Total energy (MP2): -1515.42207 [d] Non-planar isomer (MP2); -1515.42046, C3-X4-C5-C6 dihedral = 82.5º. [e] Corrected for ΔG: -1179.53934. Total energy (MP2); -1139.55775. [f]Non-planar isomer; total energy (KMLYP/MP2) -1179.74319/-1139.55812 Corrected for ΔG(KMLYP): -1179.53740. NICS(KMLYP) =-1.2. C3-X4-C5-C6 dihedral (KMLYP) = 82.5º. [g]Valence isomers; total energy (B3LYP/KMLYP) -705.56747/-704.57398 [-1.6/-8.6]. Transition state for interconversion (KMLYP): -704.57242 [-4.1]

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