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***A DFT and TDDFT Study of Alkylated
Trimethylene-Bridged Bis(p-Phenylenediamines)***

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A DFT and TDDFT Study of Alkylated Trimethylene-Bridged Bis(*p*-Phenylenediamines)

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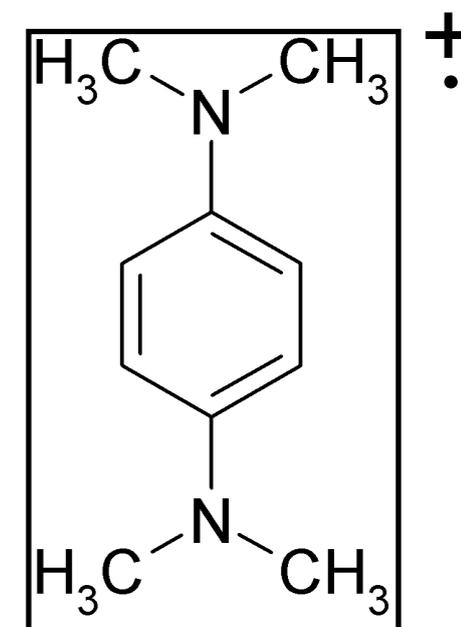
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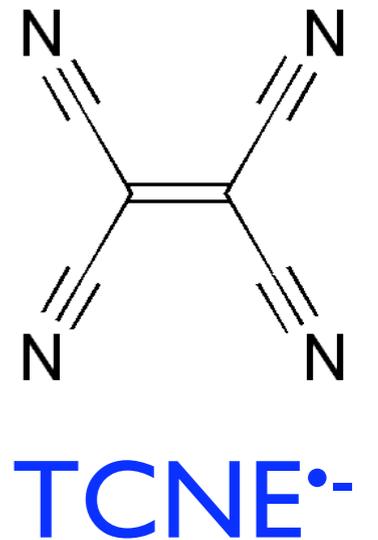
Background

- There has been great interest in the π -dimers formed between organic radicals ever since early studies of the Wurster blue.
- These dimers are diamagnetic, absorb light in the near IR region, and have bond lengths at typically $\sim 3 \text{ \AA}$, which are much longer than conventional covalent bonds but shorter than sum of van der Waals radii.



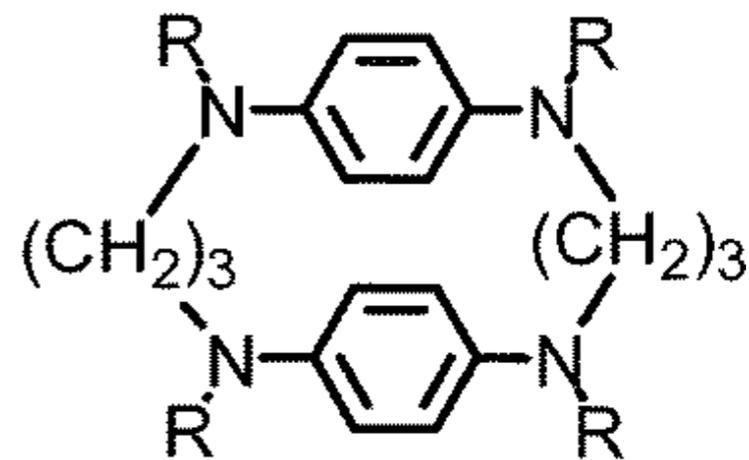
TMPD \cdot^+

- Such long bonds present unique challenges for theoretical studies. Though simple arguments point to the importance of spin pairing in these dimers, there is disagreement over whether the dispersion forces or the counter ions contribute more to stabilize a dimer of radical ions.
- While high-level methods are required to find out the bonding nature, they are computationally too expensive for large dimers. Thus at a practical level, it will be interesting to see how DFT methods perform.



Our systems -- bridged dimers

Reference: S. F. Nelsen, G. Li, K. P. Schultz, H. Q. Tran, I. A. Guzei, and D. H. Evans; **J. Am. Chem. Soc.** 2008, *130*, 11620-11622



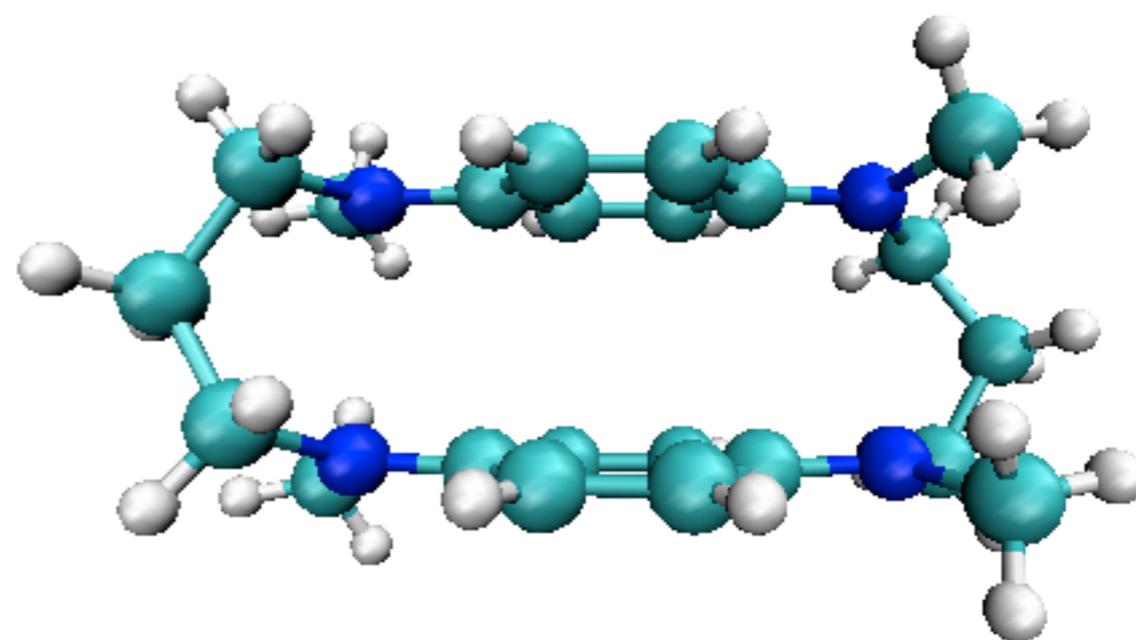
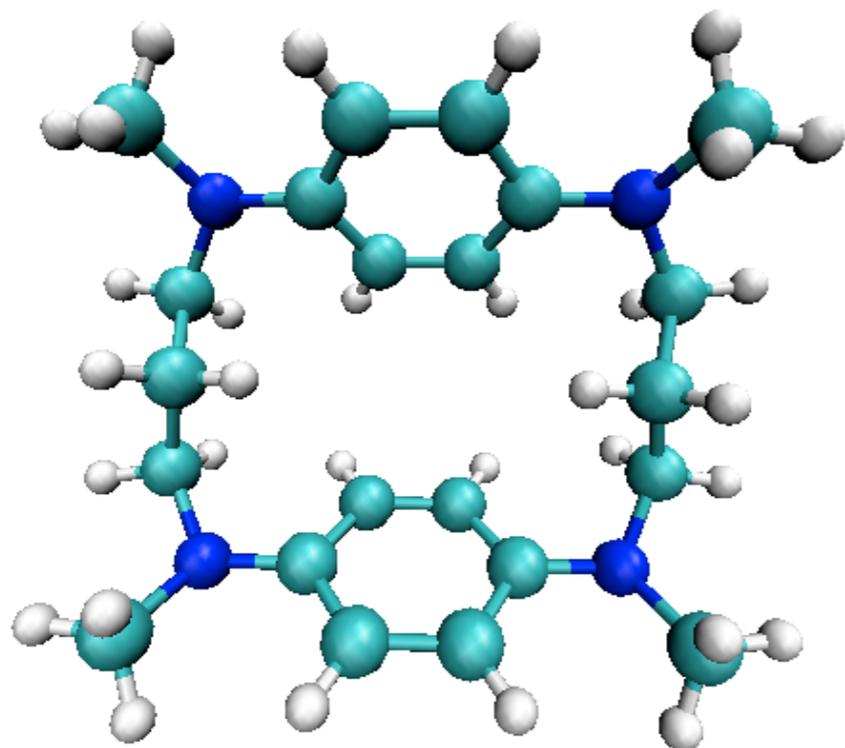
RC₃

X-ray structures of

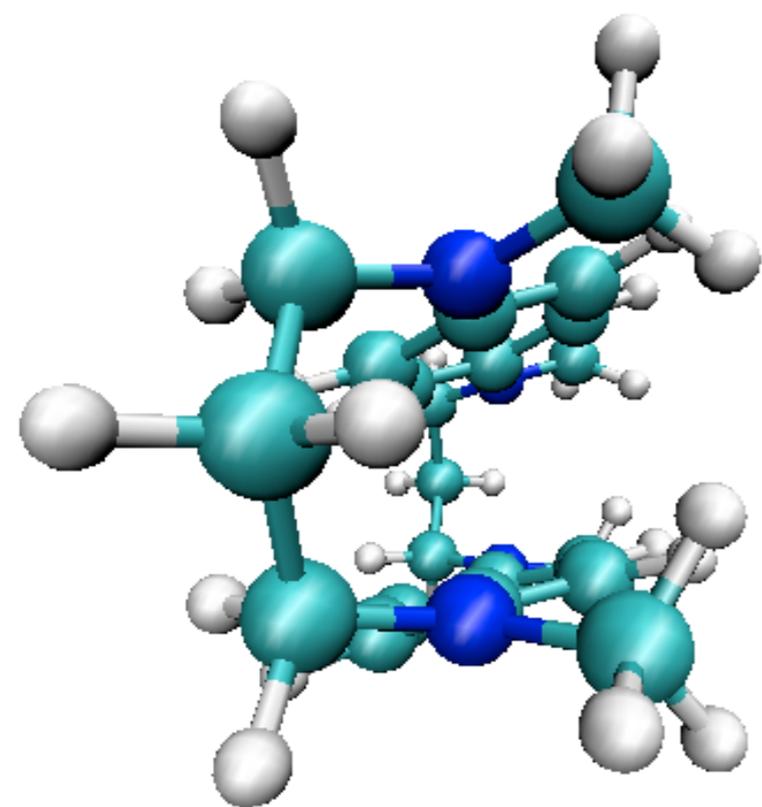
MeC₃ (W-shape)

&

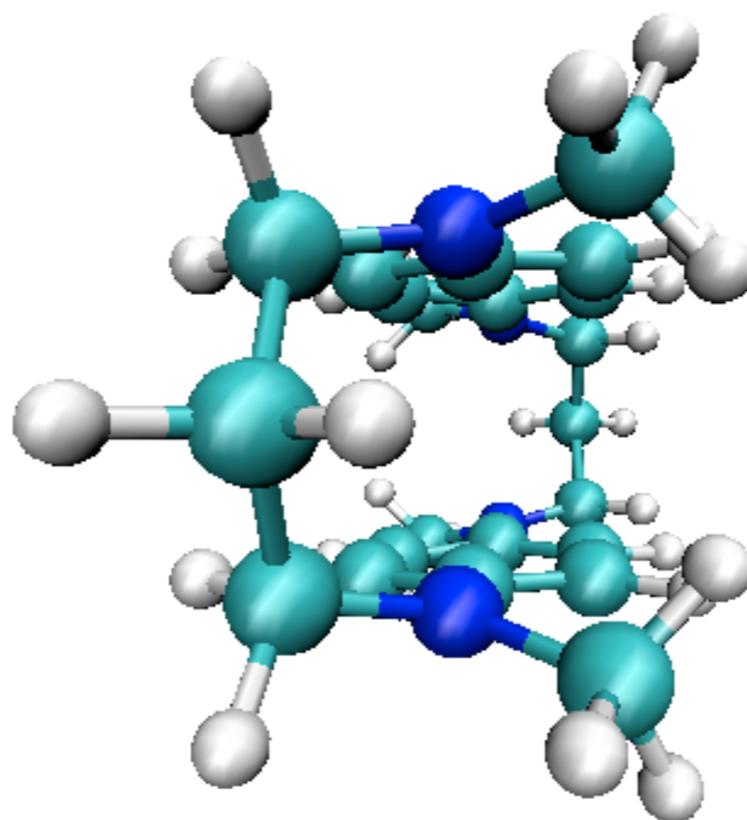
MeC₃²⁺ (coplanar)



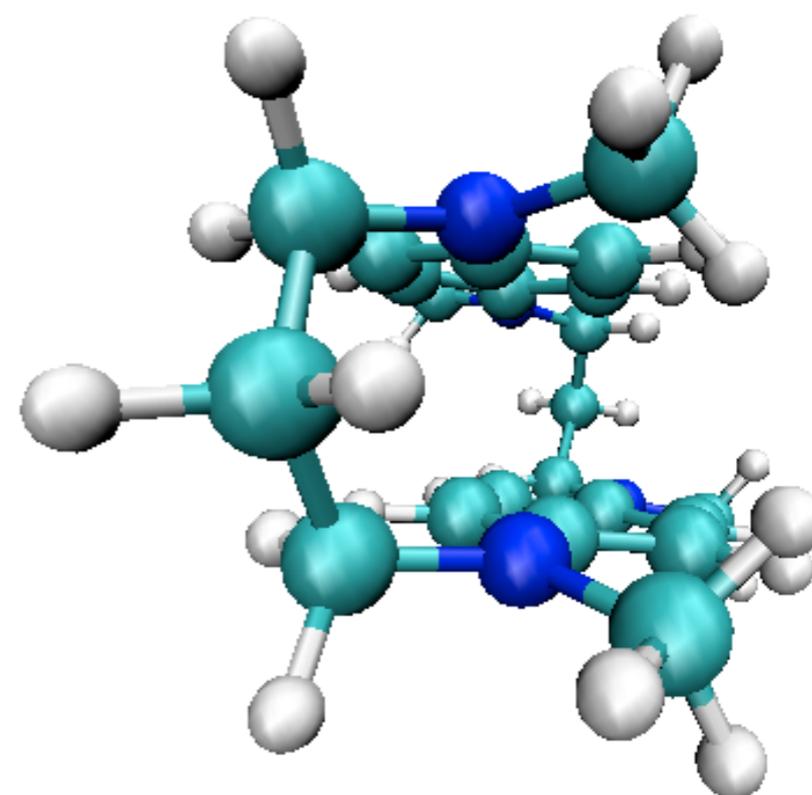
Dominant conformations of MeC_3^{2+}



syn



anti



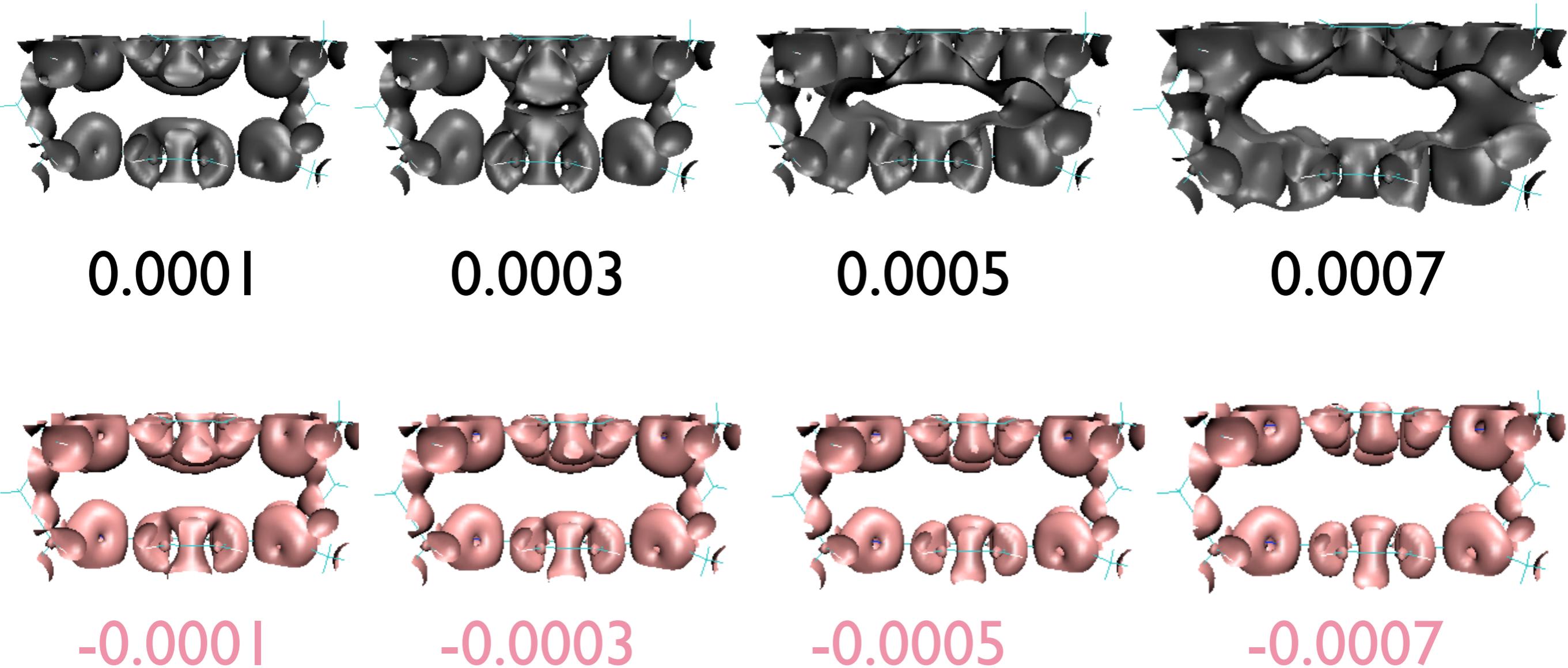
unsymmetrical

*There are two other high energy conformations.

Geometric parameters comparison of the *anti* conformation of MeC_3^{2+}

	X-ray	LDA	B3LYP	M06-2X
N,N distance, Å	2.94	2.90	3.14	2.93
C _q ,C _q distance, Å	3.08	3.00	3.25	3.02
closer CH,CH distances, Å	3.16 3.18	3.06 3.12	3.32 3.38	3.09 3.15
C ₆ mean plane distances, Å	3.07	2.92	3.32	2.95
NCCC twist angles	-67.2, 65.2 -65.2, 67.2	-65.8, 65.5 -65.5, 65.8	-70.0, 70.0 -70.0, 70.0	-66.8, 65.4 -65.4, 66.8
CN twist angles	1.7 18.0	3.5 22.5	13.6 11.5	3.2 23.5

Isosurface of $\rho(\text{LDA}) - \rho(\text{B3LYP})$

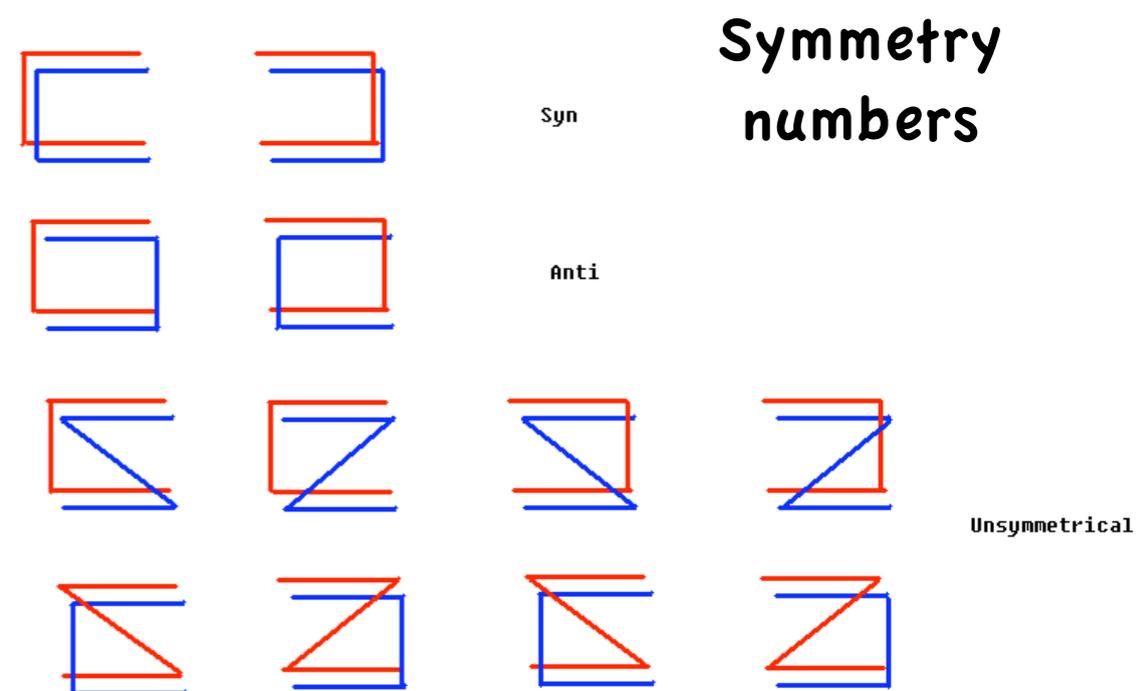


LDA has more electrons between the monomers.

*Calculations are both for the X-ray structure.

Conformational weights

Experimentally, the proton NMR of MeC_3^{2+} sharpens as the temperature is lowered because less triplet is present, and by $-58\text{ }^\circ\text{C}$ (215 K) in 2:1 $\text{CD}_3\text{OD}/\text{CD}_3\text{CN}$ the three conformations interconvert slowly on the NMR time scale. Integration of the partially overlapping signals gave relative weights of approximately *syn*: 0.54, *anti*: 0.17, *uns*: 0.29.



	% (Expt)	Symm. #	E^* (LDA)	% (LDA)	E (B3LYP)	% (B3LYP)	E (M06-2X)	% (M06-2X)
<i>syn</i>	54	2	0.00	61	0.00	41	0.00	65
<i>anti</i>	17	2	0.54	17	0.62	10	0.47	22
<i>uns</i>	29	8	1.02	22	0.52	49	1.28	13

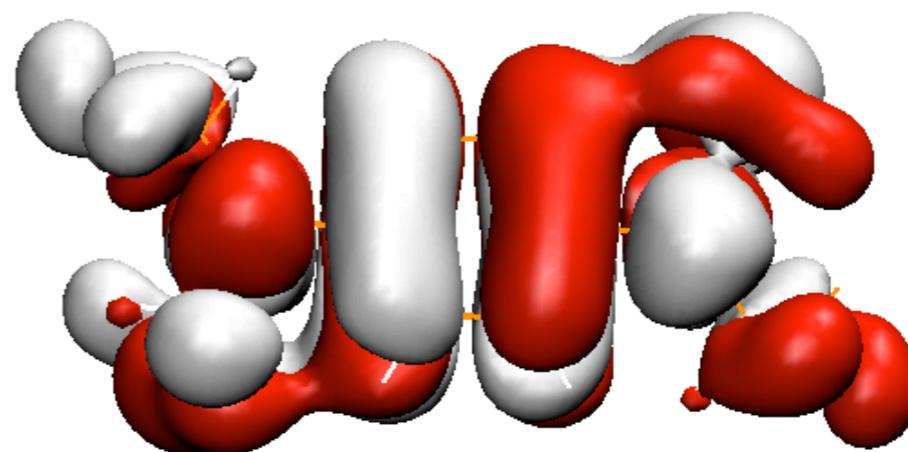
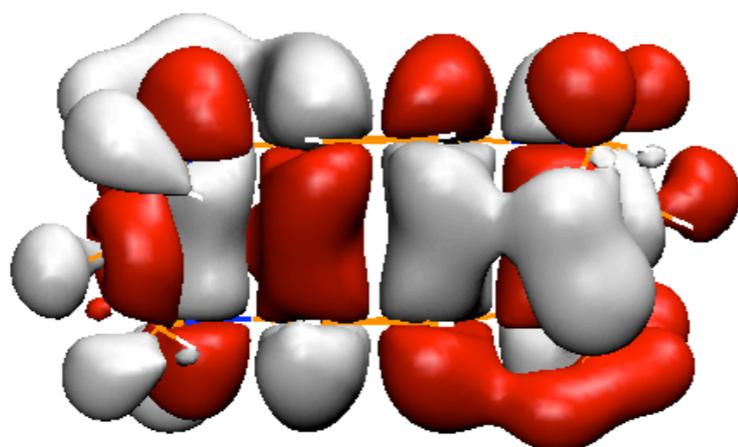
*energies in kcal/mol

MeC₃²⁺ frontier orbitals

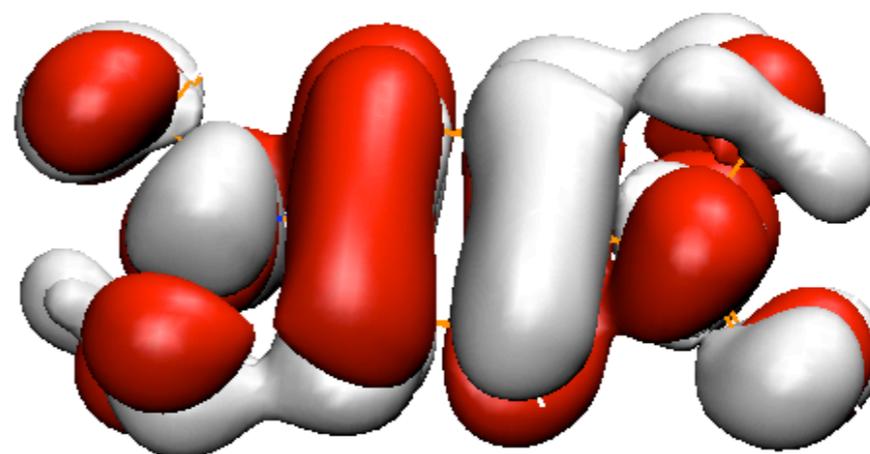
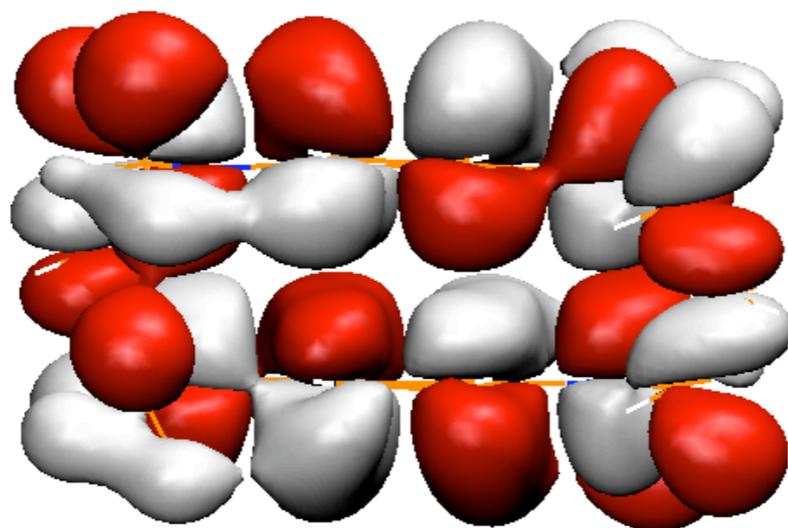
Side view

Top view

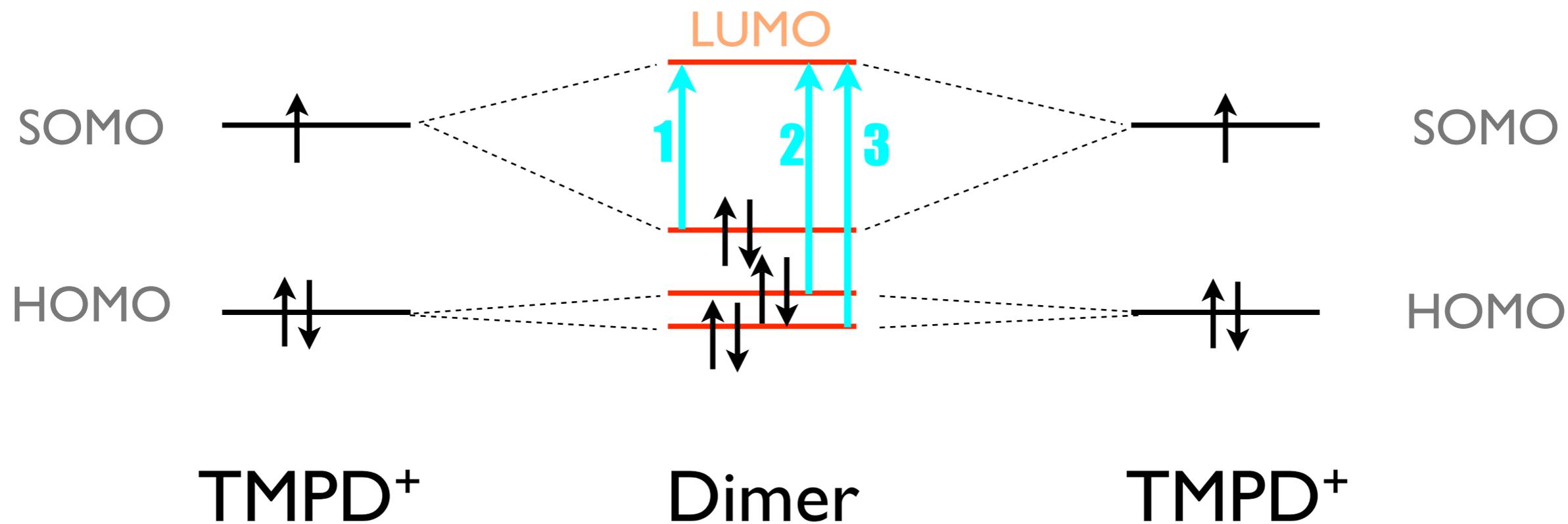
HOMO



LUMO



Orbital interaction diagram



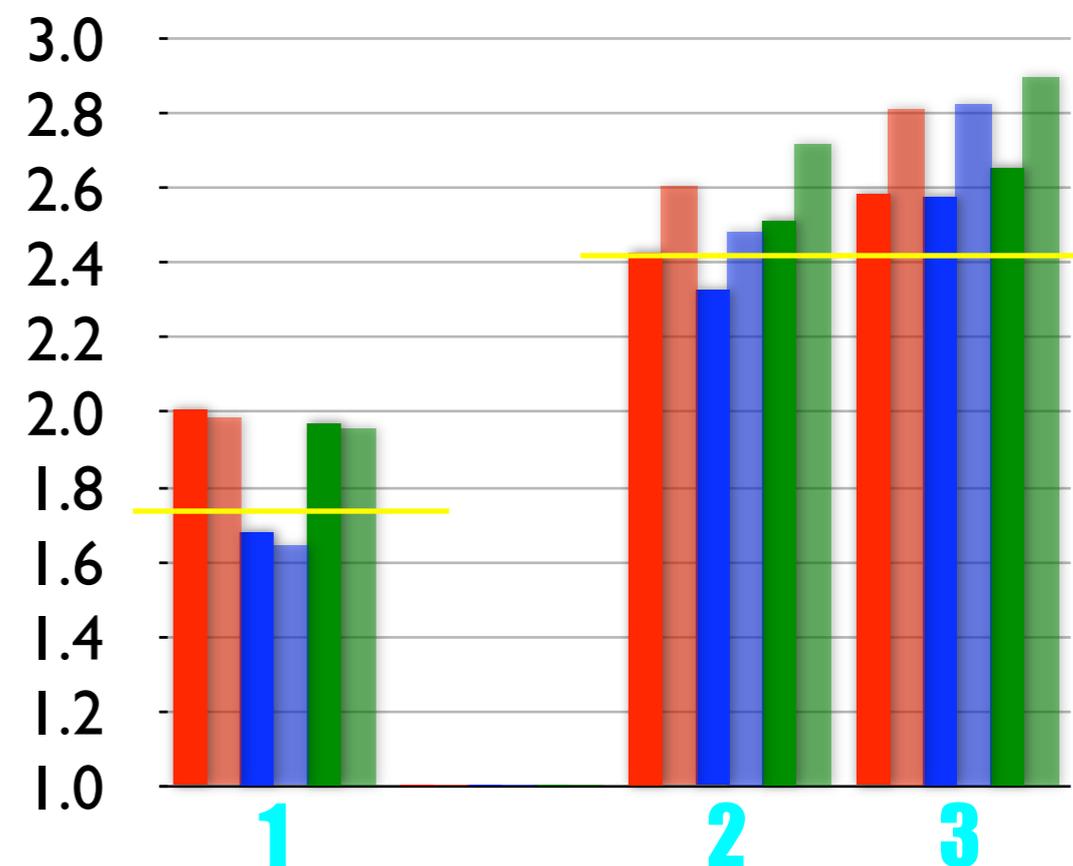
1 2 3 are the dominant orbital contributions to the low lying excitations.

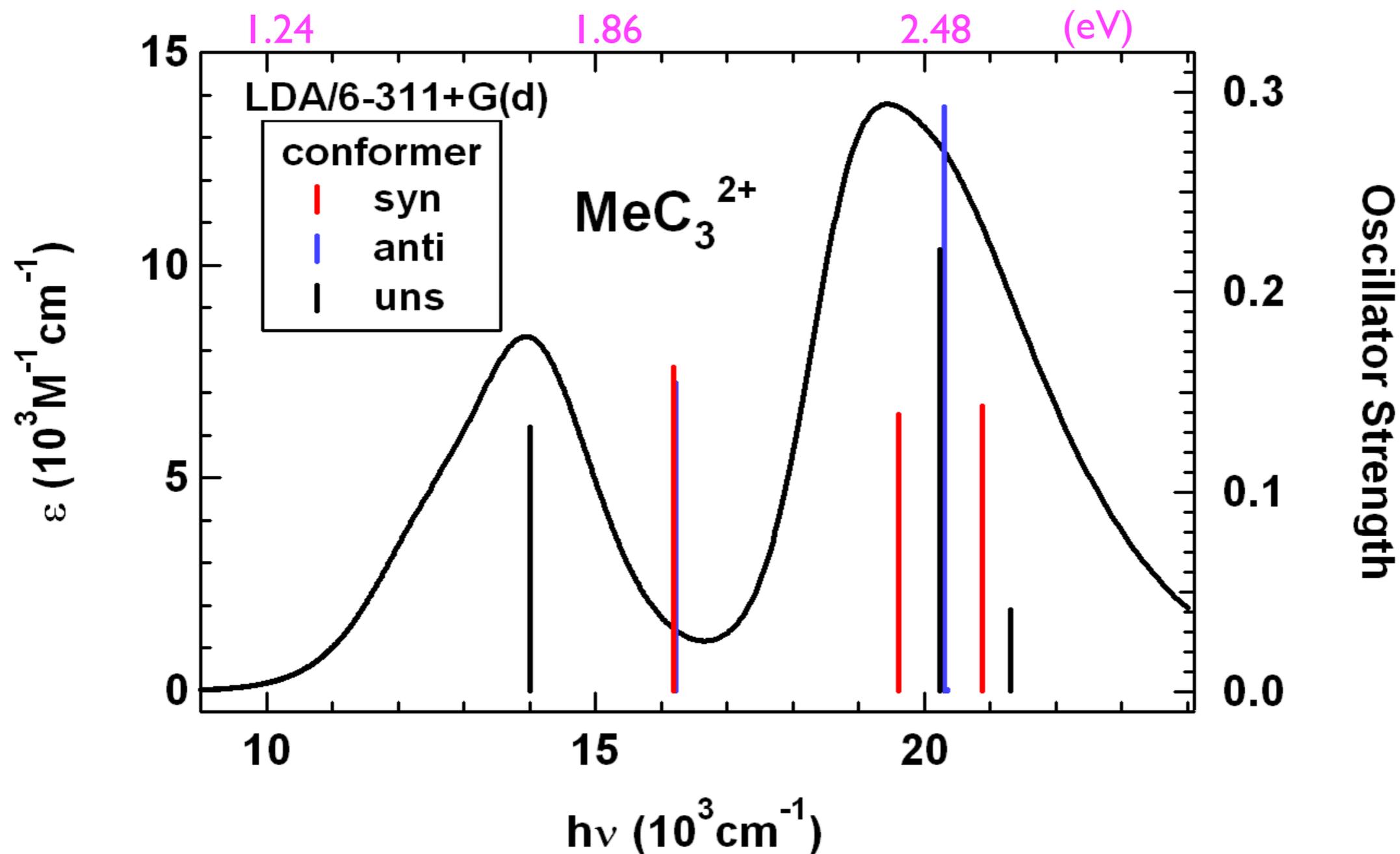
TDDFT results for the *syn* conformation of MeC_3^{2+} at several optimized geometries

Geo.	TD-LDA	TD-B3LYP
LDA	2.01 (0.1622)	1.99 (0.1876)
	2.43 (0.1387)	2.61 (0.0817)
	2.59 (0.1431)	2.81 (0.2760)
B3LYP	1.68 (0.1516)	1.65 (0.1726)
	2.33 (0.0472)	2.49 (0.0337)
	2.58 (0.1995)	2.83 (0.2923)
M06-2X	1.97 (0.1599)	1.96 (0.1859)
	2.52 (0.1329)	2.72 (0.0697)
	2.66 (0.1168)	2.90 (0.2923)

Excitation energy in eV (*Oscillator strength*)

Exp. Peaks are
1.74 & 2.42 eV





Comparison of the observed absorption spectrum of MeC_3^{2+} in CH_2Cl_2 with the TD-LDA/LDA/6-311+G(d) calculation.

More comparisons between B3LYP and LDA

	B3LYP	LDA
restricted KS	interplanar distance too large	slightly short
unrestricted KS	lower in energy and has planes further apart	same as restricted
triplet	more stable than singlet	less stable
most stable structure	W-shape	coplanar

LDA agrees better with experiments in all aspects.

Conclusions

- LDA predicts fairly well the structures of π -dimers. This has been reported before. Here we show that even the small difference between conformers can be described by LDA. Electron densities suggest a stronger bond is formed in LDA than B3LYP.
- Though its good performance is possibly due to error cancelations, LDA may be used as a practical tool for large π -dimer systems.
- TDDFT once again does a good job for the optical transitions. The near-IR band shows a weak dependence on the functional, but a stronger one on the interplanar distance.

Computational methods:

- All calculations are done with **Q-Chem 3.2** using the 6-311+G* basis set and an integration quadrature of 75 radial points (Euler-Maclaurin) and 302 angular points (Lebedev).
- LDA is the Slater exchange and Vosko-Wilk-Nusair correlation. B3LYP is a hybrid functional using Becke exchange and Lee-Yang-Parr correlation. M06-2X is a hybrid meta functional developed by the Truhlar group that shows better performance for π - π stacking.
- All computations are carried out at the computer facility at the **Center for Functional Nanomaterials**.

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