

## Crystals of isomeric tritollylamines: embrace motifs in crystals, and their thermochemical properties.

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### Calculations of intermolecular potentials

Calculations of intermolecular potentials have been made by two independent methods, density functional and empirical van der Waals/coulombic methods. The density functional calculations were made with the program DMol,<sup>1,2</sup> with care to employ the pwc functional of Perdew and Wang<sup>3</sup> because it behaves correctly at large distances.<sup>4</sup> In addition, basis set superposition errors were avoided by using numerical basis sets<sup>1</sup> calculated to a large 20Å cutoff. This methodology for intermolecular potentials has been tested for benzene pairs (for which there are experimental data and accurate calculations), with the conclusion that the actual intermolecular energy is ca 70% of that calculated.<sup>5</sup> Calculations for the neutral pairs of TTA isomers used symmetry  $C_i$ .

The empirical calculations used the 12-6 potential for van der Waals interactions, and a coulombic potential for electrostatic interactions, within the force-field cvff of the program Discover\_3.<sup>6</sup> The atom parameters ( $r^*$ ,  $\epsilon$ , charge) used had been refined<sup>7</sup> for use with molecules such as these: C, 1.94, 0.093, -0.10; N 1.85, 0.15, -0.21; H 1.62, 0.02, +0.11. The permittivity was set to be numerically equal to interatomic distance.

The results are shown in the Figure. The minima in the density functional calculated potentials for 333TTA and 334TTA occur at distances ca 0.3Å shorter than those observed in the crystals, while the empirical potential wells are ca 0.2Å longer than observed. An isolated molecule pair is expected to be tighter than the same molecule pair in a condensed phase. The differences between the potentials calculated by the two methods are consistent with the expected overbinding of the pwc density functional methodology. The two methods yield similar energies at the crystal intermolecular distances. Notice that the embrace with the smallest N--N separation is not the most stable: the N--N separation reflects instead the canting of the tolyl rings to the molecular plane. This is another example of the principle for intermolecular interactions that 'shorter is not necessarily stronger'.<sup>8</sup>

energy, kJ mol<sup>-1</sup>

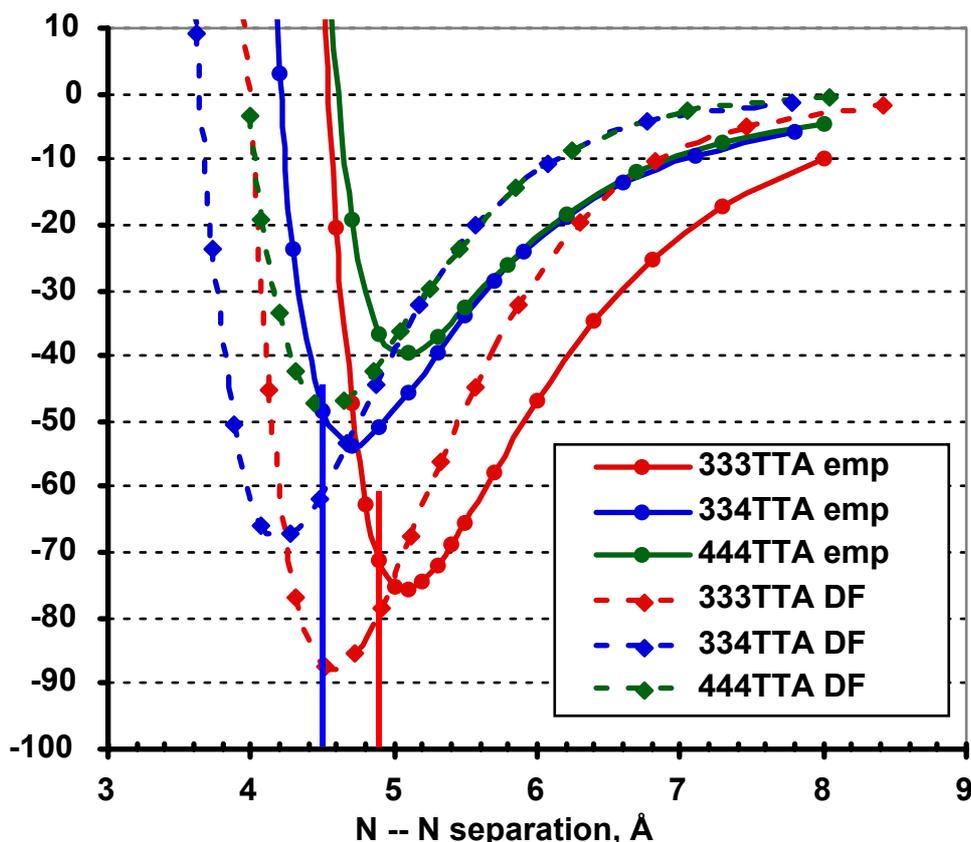


Figure. Calculated intermolecular potentials for the sixfold aryl embraces between pairs of 333TTA (red) and 334TTA (blue) molecules, and for the hypothetical sixfold aryl embrace between two 444TTA molecules (green). The tolyl ring conformations are as they occur in the crystal for 333TTA and 334TTA, and are those of 333TTA for the hypothetical 444TTA embrace. Broken lines are density functional potentials, solid lines empirical potentials. The vertical lines show the crystal separations for 333TTA and 334TTA.

Given the uncertainties in both methods, and noting the correction of ca 70% for the density functional calculation, the dissociation energy of the 6AE in (333TTA)<sub>2</sub> is estimated to be  $65 \pm 10$  kJ mol<sup>-1</sup>, and in (334TTA)<sub>2</sub> about  $50 \pm 10$  kJ mol<sup>-1</sup>. The unobserved 6AE for (444TTA)<sub>2</sub> is estimated to have a dissociation energy of  $35 \pm 10$  kJ mol<sup>-1</sup>. From the participation of the tolyl methyl groups in the EF motifs of these embraces — 6 methyl groups per 6AE in (333TTA)<sub>2</sub>, 2 methyl groups per 6AE in (334TTA)<sub>2</sub>, none in (444TTA)<sub>2</sub> — it could be concluded that each methyl group augments the stabilisation of the underlying embrace by ca 5 kJ mol<sup>-1</sup>.

These results are consistent with the crystal packing. The most stabilised 6AE occurs as such in the crystal, while the least stabilised does not.

## References

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