

## 2C1a

### Conformations of 4,4-Bisphenylsulfonyl-*N,N*-dimethylbutylamine: Interplay of Intramolecular C–H···N, C–H···O and $\pi$ ··· $\pi$ Interactions

Jiong Ran, and Ming Wah Wong

#### Computational Methods

Conformational search at HF/3-21G level was carried out using the SPARTAN program. The unique conformers were fully optimized at B3LYP/6-31+G\* level. Higher-level relative energies were obtained at the MP2/6-311+G\*\* level. The solvent effect of was examined by SCRF theory. In addition, a series of intermolecular AH···NH<sub>3</sub> (AH = proton donor) complexes which involve a C–H···N hydrogen bond were studied at the B3LYP/6-31+G\* level. The binding energies were corrected by BSSE. Charge density analysis was based on Bader's theory of atoms in molecules (AIM).

#### Results and Discussion

All 17 unique conformers of BPSDMBA are stabilized by the non-conventional C–H···X (X = N or O) type of internal hydrogen bonding interactions. The 4 most stable conformers (**Figure 1**) exhibit an intramolecular C–H···N hydrogen bond. The calculated structure is in excellent agreement with the X-ray structure of the methyl analogue (BPSTMBA) [2], Solvent effect has small effect on the calculated geometries. Most importantly, the weak intramolecular C–H···N, C–H···O and  $\pi$ - $\pi$  interactions are found to prevail in solution.

The computed <sup>1</sup>H chemical shift (6.2 ppm) of the disulfone methine proton agrees well the experimental value (6.6 ppm) [3].

The electron density ( $\rho$ ) correlates very well with the interaction energy ( $E_{\text{int}}$ ) for the various intermolecular AH···NH<sub>3</sub> complexes investigated here. The almost perfect linear fit ( $R^2 = -0.999$ , **Figure 2**) provides a simple equation to estimate C–H···N hydrogen bond strength based on calculated  $\rho$  value.

$$E_{\text{int}} = -1418.33 \rho + 9.0199$$

Using above equation, we can estimate the strength of intramolecular C–H···N interaction in BPSDMBA. These  $\rho$  values yield interaction energies of 13.5 and 15.2 kJ mol<sup>-1</sup> in the gas phase and in solution, respectively, for the intramolecular C–H···N hydrogen bond in BPSDMBA. Thus, the strength of the intramolecular C–H···N hydrogen bond in BPSDMBA is slightly increased in a dielectric solvent medium. Our calculated result is consistent with the experimental observation that the C–H···N hydrogen bond in BPSDMBA is prevailed in solution [1].

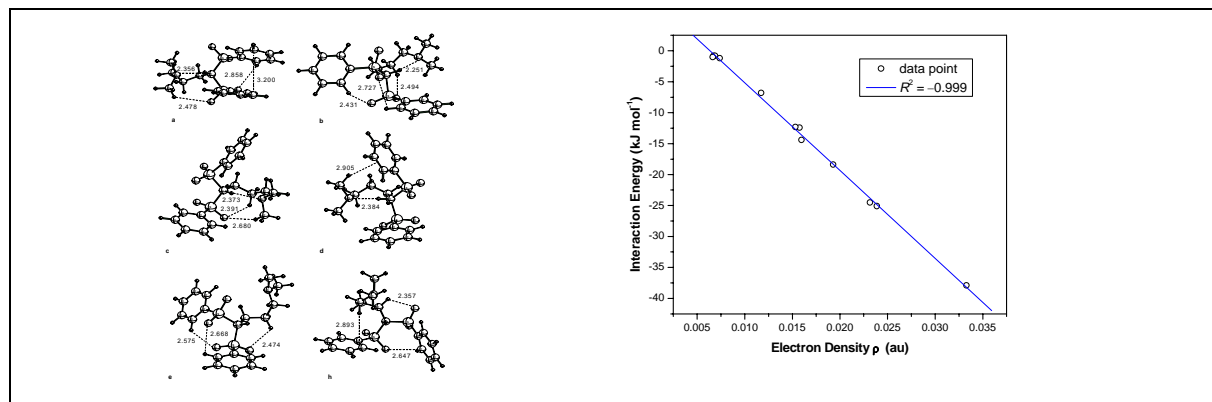


Figure1

Figure 2

#### References

- [1] Arunima, N.D. Kurur, Chem. Phys. Lett. 401 (2005) 470.
- [2] R.L. Harlow, C. Li, M.P. Sammes, J. Chem. Soc., Chem. Commun. (1984) 818.
- [3] C. Li, M.P. Sammes, J. Chem. Soc, Perkin Trans. I (1983) 2193.