Calculating Harmonic Oscillator Stabilisation Energies (HOSE) from Bond Distance Measurements

Application of HOSE

Single-crystal X-ray crystallography provides a three-dimensional model of the molecular entity comprising the crystal, from which geometric parameters (interatomic distances, bond angles, etc) can be measured. Provided these measurements are precise enough they can be used to inform other properties of the material.

Calculating the Harmonic Oscillator Stabilisation Energy (HOSE) can provide a quantitative measure of the contribution of individual resonance structures to the overall bond length pattern of an aromatic ring. This may be useful for estimating the extent and likely pathways of charge transfer across the molecule.

HOSE Calculation

To calculate HOSE for an aromatic ring, first all feasible resonance forms of that ring must be identified. Using the bond length values from the crystal structure, the energy required to distort the ring into each resonance form can be calculated. The resulting energies can then be used to determine the contribution of each resonance form to the overall observed bond length pattern.

These values are calculated using a program that has been written to accommodate five- and six-membered aromatic rings comprising carbon, nitrogen and oxygen.

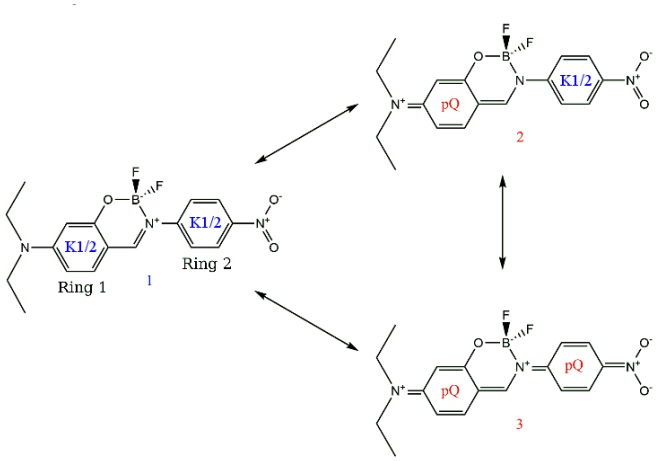

Figure 1: The resonance forms of a boranil molecule

	K1	K2	pQ
Ring 1	72.80	53.30	18.95
Ring 2	60.10	59.88	62.43

Table 1: The values of HOSE for each bond length pattern (kJ/mol)

	K1	K2	pQ
Ring 1	16.11	22.01	61.88
Ring 2	33.71	33.83	32.45

Table 2: The percentage contribution of each bond length pattern (%)

Benefits of HOSE calculations

HOSE can provide insights into the optical and electronic properties of a material. The example shown here can be interpreted to demonstrate that charge transfer from the amine group to the imine nitrogen in this compound is the most stable pathway. In ring 1 the pQ energy is low and the contribution of this motif to the bond length pattern is very high and hence there is a large contribution to the overall structure from the charge separated resonance forms.

The ease of charge transfer across a molecular can influence its absorption and emission properties and hence the measure of how different aspects of the structure can influence this charge transfer, as quantified by HOSE, can inform the derivation of structure-property relationships and aid the design of new materials with bespoke properties.

References

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