Supplementary Information for

A critical approach toward resonance-assistance in the intramolecular hydrogen bond interaction of 3,5-diiodosalicylic acid: A spectroscopic and computational investigation

Bijan K. Paul,[*] Narayani Ghosh, Ramakanta Mondal, and Saptarshi Mukherjee[*]

Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Indore

By-Pass Road, Bhauri, Bhopal 462 066, Madhya Pradesh, India

*To whom correspondence should be addressed: bpaul@iiserb.ac.in (BKP) and saptarshi@iiserb.ac.in (SM).

Computational section

Geometry optimization

GAUSSIAN 09 suite of programs has been employed for the structural and potential energy surface (PES) calculations.[S1] The geometry optimization for different possible ground-state conformations of **3,5DISA** were carried out at the Density Functional Theory (DFT) level using B3LYP hybrid functional (which is comprised of Becke's three-parameter hybrid exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (LYP)), and Lanl2dz basis for iodine and 6-311++G(d,p) basis for C, H, and O (6-311++G(d,p) is a triple-ζ quality basis set[S1,S2] for valence electrons with diffuse functions and hence extensively used in calculations for molecular geometries with lone pair of electrons/anionic structures[S3,S4]). With a view to the key role of the IMHB interaction in governing the overall photophysics of **3,5DISA** the 6-311++G(d, p) basis set has been applied for calculation given the necessity of diffuse functions for full characterization of the IMHB interaction.[S1-S9] No geometrical constraints were imposed during optimizations of equilibrium geometries. The lack of imaginary frequency in the matrices of energy second derivatives (Hessian) was also tested for establishing the characteristic of local minimum.[S1,S2,S10]

Potential energy surface (PES) calculation

The ground-state potential energy surface (PES) for the proton transfer process in **3,5DISA** has been constructed from a relaxed scan performed at the level of calculation as stated earlier. The excited-state PES has been evaluated from TD-DFT optimization method. All the necessary calculations have been performed on GAUSSIAN 09 suite of programs.[S1]

Calculation of aromaticity indices

The Harmonic Oscillator Model of Aromaticity (HOMA)[S11,S12] index has been exploited as a geometrical criterion for estimating the local aromaticity of the benzene nucleus of

3,5DISA. According to the description by Kruszewski and Krygowski[S11,S12] the HOMA index has been calculated using the following relationship:

$$HOMA = 1 - \frac{1}{n}\sum_{j=1}^{n} \alpha_i (R_{opt,i} - R_j)^2$$

(S1)

where, n corresponds to the number of bonds within the ring under investigation ($n = 6$ in **3,5DISA**). The term α designates a constant such that an ideally aromatic system will return a value of HOMA = 1 and all the bond lengths (R_j) will be equal to the optimal value, R_{opt}. On the other hand, a nonaromatic system will be characterized by HOMA = 0. For CC bonds: $\alpha = 257.7$ and $R_{opt} = 1.388$ Å.[S8-S13]

The Nucleus Independent Chemical Shift (NICS) index has been studied as a magnetic indicator of local aromaticity. Following the definition put forward by Schleyer et al.,[S12] the negative value of the absolute shielding at the ring center as calculated by the non-weighted average of the coordinates of the heavy atoms in the ring is designated as NICS(0). The measure of aromaticity of the concerned ring is then given as the negative value of NICS(0), that is, a greater degree of aromaticity will be characterized by a larger negative value of NICS(0). However, NICS(0) is not unequivocally accepted as a genuine descriptor of aromaticity. The in-plane tensor components (which are not related to aromaticity) have been argued by Lazzeretti and Aihara[S13,S14] to introduce non-negligible spurious contributions to the results. Thus, the calculation of the absolute shielding has been proposed at 1 Å above the ring center and the negative value of the resultant magnitude, that is, NICS(1) is used to complement the overall NICS study. It is generally argued that NICS(1) is a better descriptor of aromaticity than NICS(0) because the contributions originating from the π-electron ring current substantially predominate over the local σ-bonding effects at 1 Å above the ring center.

Table S1: Summary of the spectroscopic properties of SA in various solvents

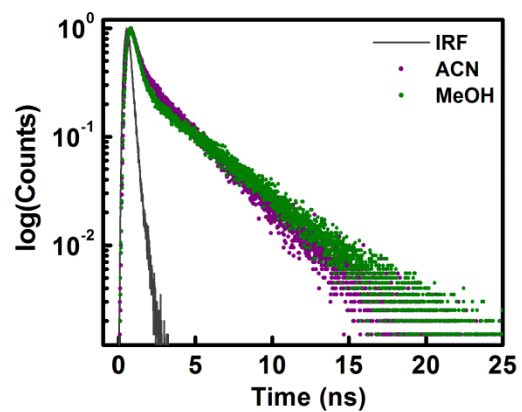| Solvent	Absorbance	Emission	
	λ_{abs} (nm)	λ_1 (nm)	λ_2 (nm)
MCH	310	356	456
ACN	306	337	390
BuOH	302	333	405
^{i}PrOH	304	333	404
MeOH	300	355	440
Water	295	333	425

Figure S1: Time-resolved fluorescence decay of SA in various solvents as specified in the figure legend. The sharp gray profile on the extreme left represents instrument response function (IRF).
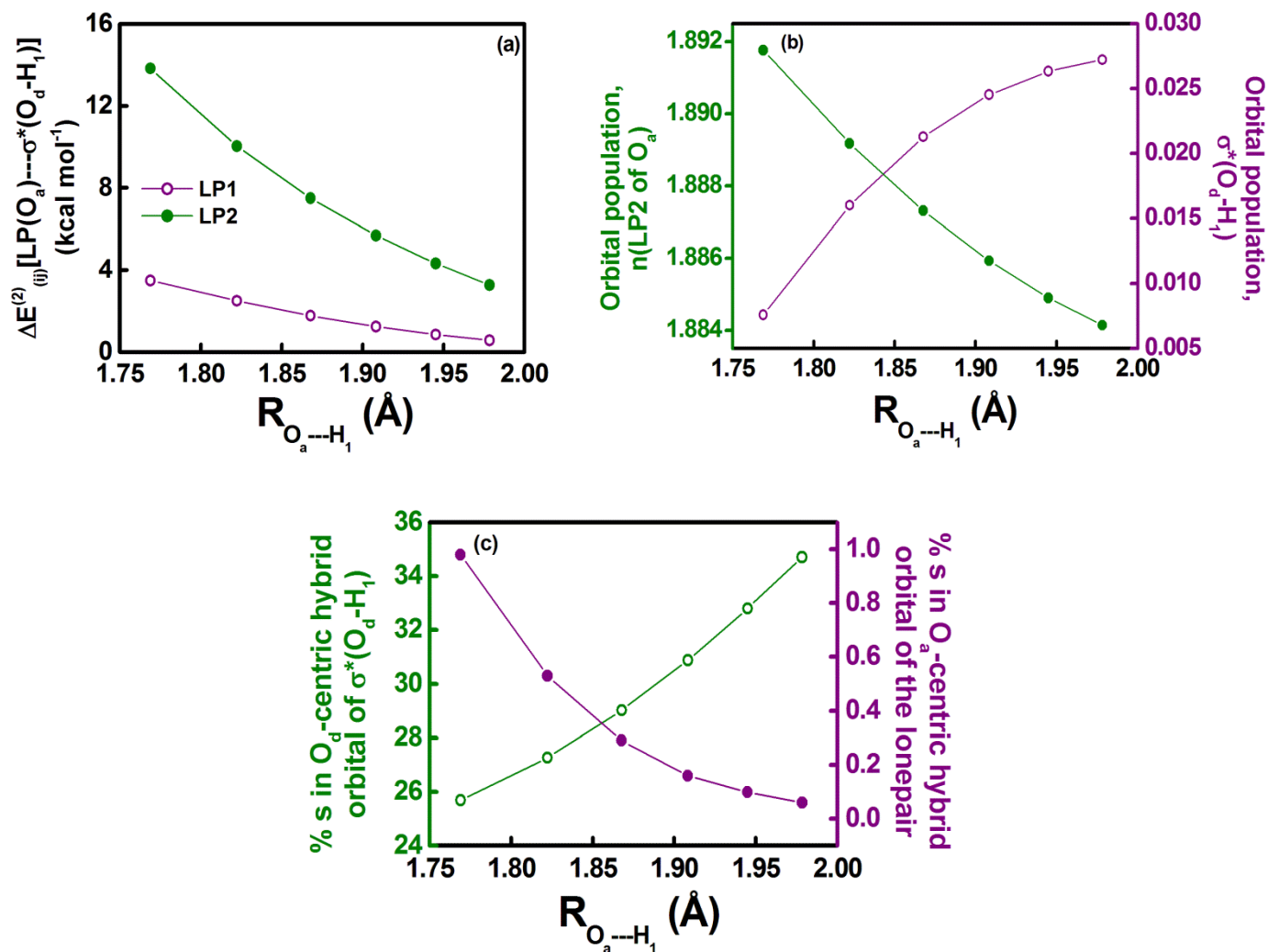
Figure S2: (a) Plot of variation of LP1/LP2 $O_a \rightarrow \sigma^*(O_d–H_1)$) hyperconjugative charge transfer stabilization energy as a function of the $O_a \bullet\bullet\bullet H_1$ IMHB distance in the E-form of **3,5DISA** as obtained from NBO analysis. (b) Plot of variation of orbital population in $\sigma^*(O_d–H_1)$ (–○–) and n(LP2) (–●–) as a function of the $O_a \bullet\bullet\bullet H_1$ IMHB distance in **3,5DISA**. (c) Plot of variation of the percentage s-character in the O_d-centric hybrid orbital of the $\sigma^*(O_d–H_1)$ bond (–○–) and O_a-centric hybrid orbital of the lonepair (–●–) in **3,5DISA** as a function of the $O_a \bullet\bullet\bullet H_1$ IMHB distance. Calculations are performed at MP2/6-311++G(d,p).

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