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Electronic Supplementary Information

Bonds or Not Bonds ?

Pancake Bonding in 1,2,3,5-dithiadiazolyl and 1,2,3,5-diselenadiazolyl Radical Dimers and their Derivatives†

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Electronic Supplementary Information

¹⁰ This section contains four figures on computational details and structures and two tables on computed parameters.

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Effect of HOMO-LUMO mixing

In all our DFT-based calculations we used the unrestricted wave function method which is found to give the right dissociation limit and also give the lowest energy equilibrium dimer structure.

5 We found it essential to allow HOMO-LUMO mixing at each point of an optimization by setting the Gaussian keyword GUESS=(mix, always) in order to converge to the spin-unrestricted orbitals whenever such a solution exists.¹

Comparison of energy scans for experimental dimer structure of
10 HCNSSN[•] using different methods with and without GUESS=(mix, always) is given in Figure S1. The study clearly demonstrates the significance of using unrestricted wave function and mixing of HOMO-LUMO for studying the structural properties of a dimer formed from neutral radical monomers.

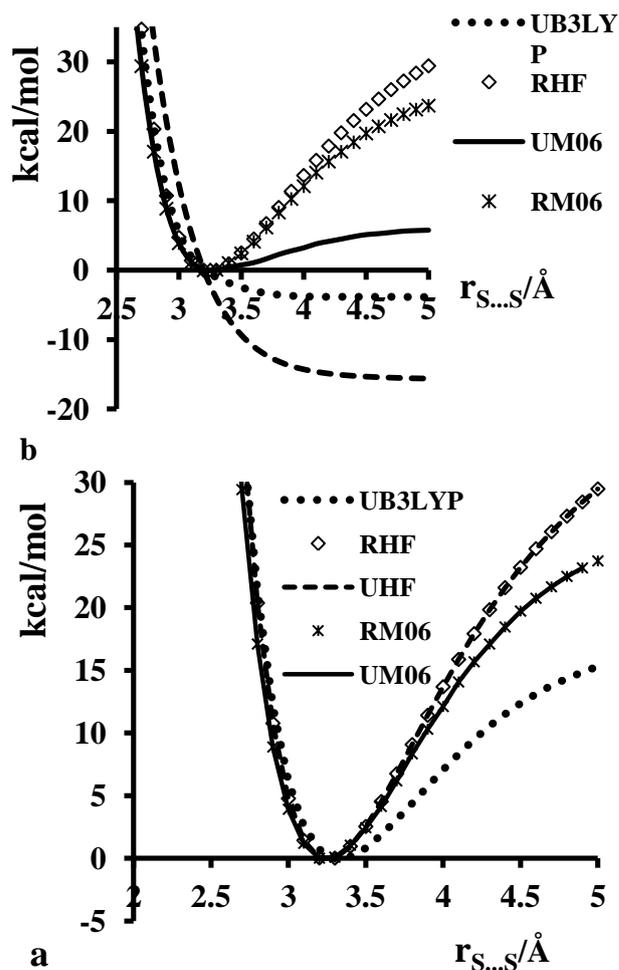


Fig. S1: Comparison of rigid potential energy scan (PES) for the
25 experimental cis-cofacial dimer structure of HCNSSN[•] as a function of intradimer separation $r(S...S)$ while keeping the monomer structures fixed.

- a) Scan computed without the Gaussian key word GUESS=(mix, always). Energy is referenced to the corresponding method minimum value.
- 30 b) Scan computed with the Gaussian key word GUESS=(mix, always). Energy is referenced to the corresponding method values at $r_{S...S} = 3.2$ Å. By contrast, the PES for UHF and UB3LYP do not show an energy minimum. However UM06
35 predicted a stable dimer with an energy minimum relative to the non-interacting dimer.

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Packing of H-DTDA in the Crystal

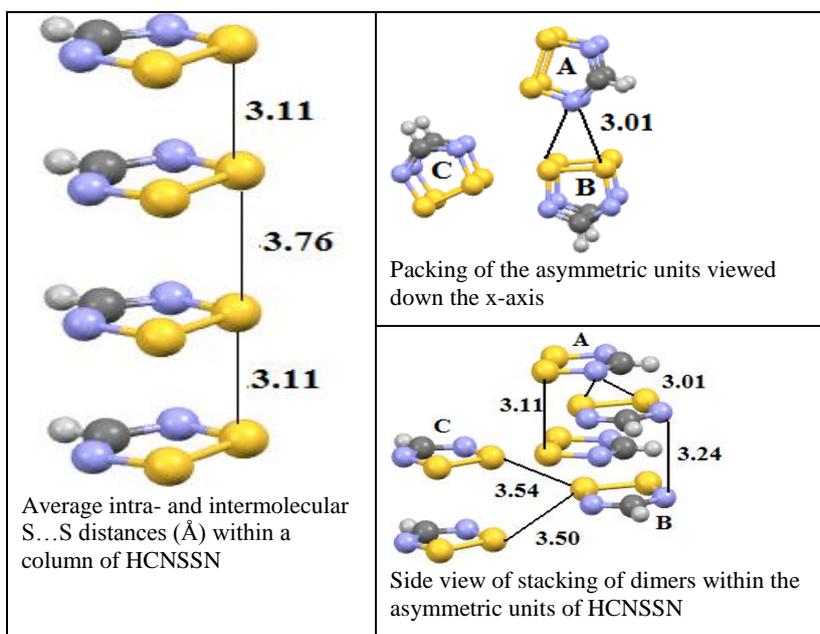
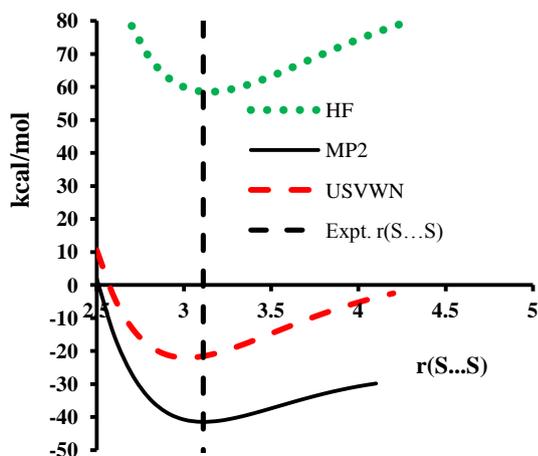


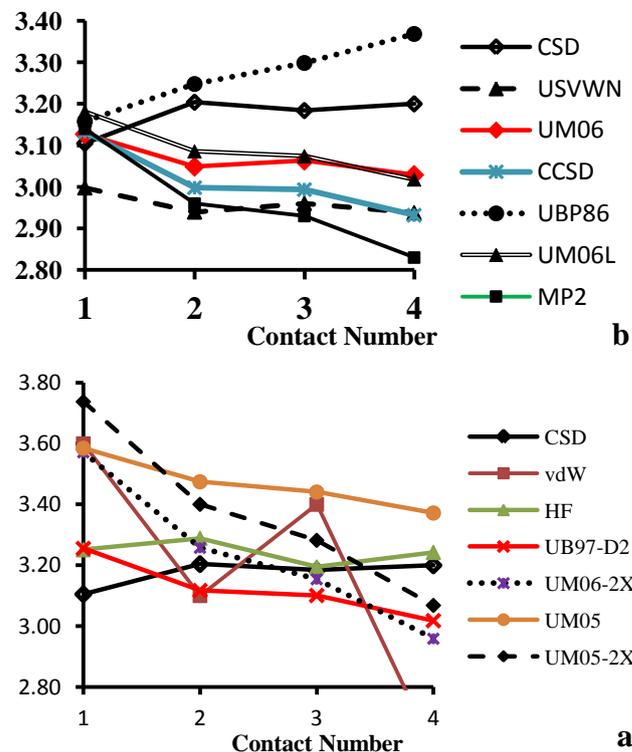
Fig. S2: Packing of HCNSSN· dimers in the crystal structure.²

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Potential energy surface (PES)



10 **Figure S3.** Potential energy surface (PES) rigid scan as a function of intradimer separation for the cis-HDTDA dimer structure using 6-31G(d) basis set. The potential energy for a given intradimer separation, $r(S...S)$, is given relative to the corresponding energy of the non-interacting dimer. We used the
 15 experimental dimer structure for the PES scan.



25 **Figure S4:** Intra-dimer separations in HCNSSN· as a function of contact number for selected WFT and DFT methods. The contact numbers are defined as: 1(S...S), 2(N...N), 3(C...C) and 4(H...H). The experimental (CSD) and vdW contact data are included for comparison. Lines are provided the guide the eye

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Predictions of DFT and WFT methods on D_e and Equilibrium Structure of H-DTDA

We tested the various computational methods by comparing the corresponding optimized geometry intradimer separation and dissociation energy against those from UM06 and experiment. Geometry is optimized using 6-31G(d) basis set and energy is calculated using 6-311++G(d,p) basis set for all methods. $D_e = 2E_{\text{monomer}} - E_{\text{dimer}}$. We chose to compare the different methods based on D_e (without zero point energy correction) to reduce errors introduced in calculating vibrational energy using the different methods. In Table S1 we summarized the predictions of selected DFT and WFT methods on the intradimer separations and dissociation energies of the cis-cofacial, twisted and trans-cofacial dimer structures of the prototype 1,2,3,5-dithiadiazolyl. RHF, MPW1PW91 and UB3LYP are known to give good results on covalent bonding. However, they completely failed in

predicting any SOMO-SOMO interaction stabilized dimer. MP2 which includes dynamic correlation gave a structure with S...S contact comparable to that of UM06 but its predictions on the dissociation energy is too large: $D_e = 45.30$ kcal/mol (cis-cofacial) and 47.61 kcal/mol (twist). UM05, UM05-2X and UM06-2X gave vdW like structures with S...S contact distance greater than 3.57 Å and low corresponding dissociation energies (2.5, 2.4 and 4.0 kcal/mol respectively). UM06-HF gave vdW like but slightly twisted structure. UM06-L and UB97-D2 gave higher dissociation energy (10.7 and 7.8 respectively) and yet the intradimer separations are larger than that obtained from experiment and UM06 (3.18, and 3.26 respectively). Based on the three WFT and a dozen DFT methods we studied in this work we conclude that M06 is superior in predicting the structures and dissociation energies of DTDA containing dimers.

Table S1: Comparison of intra dimer separations and dissociation energies (kcal/mol) for $(\text{HCNSSN}^{\cdot})_2$ computed by the selected methods and with experiment. Geometry is optimized using 6-31G(d) basis set and energy is calculated using 6-311++G(d,p) basis set for all methods. $D_e = 2E_{\text{monomer}} - E_{\text{dimer}}$. The numbering of atoms is given in Figure 2.

Method	D_e	Dimer Structure	Intra-dimer Contact/ Å	% HF Exchange	Method
CSD Exp.		cis-cofacial	S2...S7 = 3.11 N3...N9=3.20		Expt. ²
HF	-57.9	cis-cofacial	S2...S7 = 3.09	100	WFT
CCSD CCSD(T) ^a	-12.9 2.8	cis-cofacial	N3...N9 = 3.00 S2...S7 = 3.13	100	WFT
MP2	45.3	cis-cofacial	S2...S7 = 3.12	100	WFT
MP2	47.6	twist ($\phi = 90^\circ$)	S2...S7 = 3.11	100	WFT
UM06-HF	7.3	small twist	N10...H6=2.91 S2...S7 = 3.61	100	HM-GGA ^c
UM05-2X	2.4	cis-cofacial	S2...S7 = 3.74	56	HM-GGA
UM06-2X	4.0	cis-cofacial	S2...S7 = 3.57	54	HM-GGA
UBMK	1.8	N3...H12=3.4 small twist	S2...S8 = 3.91 N3...N10= 3.20	42	HM-GGA
UM05	2.5	cis-cofacial	S2...S7 = 3.59	28	HM-GGA
UM06 CCSD(T) ^b	5.7 2.9	cis-cofacial	N3...N9 = 3.05 S2...S7 = 3.13	27	HM-GGA
UM06	7.6	twist($\phi = 90^\circ$)	S2...S8= 3.18	27	HM-GGA
UM06	6.5	trans-cofacial	S2...N9=3.17	27	HM-GGA
UB-P86	5.0	cis-cofacial	S2...S7=3.16	20	GGA
UB3LYP	-0.3 ^d	cis-cofacial	S2...S7 >5	20	H-GAG
UM06L	10.7	cis-cofacial	S2...S7 = 3.18	0	M-GGA
UB97D2	7.8	cis-cofacial	S2...S7=3.26	0	GGA-D2
US-VWN	20.8	cis-cofacial	S2...S7 = 3.00	0	LSDA

^a CCSD(T)/ 6-311++G(d,p) energy is calculated on CCSD/6-31G(d) optimized geometry.

^b CCSD(T)/ 6-311++G(d,p) energy is calculated on UM06/6-31G(d) optimized geometry.

^c H(hybrid), M(meta), GGA(generalized gradient approximation), and -D2 (empirical dispersion correction).

^dNo minimum reached, D_e given at 4.34 Å.

Table S2a: Mulliken atomic charges of H-CNSSN obtained from UM06/6-31G(d) used to calculate Coulomb energy via eq 2. The monomer structure for H-DTDA is given in Figure 1a.

Atom	Charge(q)/atomic unit
S	0.279
N	-0.466
C	0.159
H	0.214

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Table S2b: The vdW parameters taken from ref. 3 and used in eq 3 to calculate dispersion energy $E_{\text{disp},c}$. C_6 is the sixth order dispersion coefficient and R_0 is the atomic van der Waals radii. The monomer structure for HCNSSN is given in Figure 1a.

Atom	$C_6/(\text{J nm}^6 \text{ mol}^{-1})$	$R_0/\text{Å}$
S	10.3	1.87
N	1.11	1.55
C	1.65	1.61
H	0.16	1.11

10 $\alpha = 23.0$, $S_6 = 1.4$

Table S2c: Parameters obtained from ref. 4 and used in calculating Lennard-Jones energy, E_{LJ} , using eq 5. R_0 is the van der Waals bond length and D_0 is the van der Waals well depth.

15 The monomer structure for H-CNSSN is given in Figure 1a.

Atom	$R_0/\text{Å}$	$D_0/(\text{kcal/mol})$
H	3.195	0.0152
C	3.8983	0.0951
N	3.6621	0.0774
S	4.0300	0.3440

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