Double pancake bonds: pushing the limits of strong $\pi-\pi$ stacking interactions

Supplementary Information

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S. I. Computational Methods.
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S. III. Summary of relevant distances.
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S. I. Computational Methods

All CASSCF and MR-AQCC calculations were carried out with the COLUMBUS program package$^1$ with analytic MR-AQCC energy gradients computed using the procedures developed in refs. $^2$ The 6-311++G(2d,2p) basis set$^3$ has been used in the geometrical and potential energy surface (PES) calculations in this work except where indicated otherwise. In addition to single state CASSCF approach, state averaged (SA) CASSCF(4,4) calculations have been performed on the triplet state which was dominated by two main configurations $\Phi_1=|\ldots a_1^2 b_1^1 a_2^1 b_2^0 \rangle$ and $\Phi_2=|\ldots b_1^2 a_1^1 b_2^1 a_2^0 \rangle$. The atomic orbital (AO) integrals and AO gradient integrals have been computed with program modules taken from DALTON.$^4$ Full geometry optimizations were performed within given molecular symmetries in natural internal coordinates using the GDIIS method.$^5$
The unrestricted density functional theory (UDFT) calculations (UB3LYP with GD3BJ\textsuperscript{6} under all circumstances in this work and UM06-2X) based on the broken symmetry (BS)\textsuperscript{7} approach were performed using the Gaussian 09 package.\textsuperscript{8}

**S. II. Validation and convergency of computational modeling**

MR-AQCC theory is not exactly size consistent. We performed a test, accordingly:

$$E(\text{monomer})^2 - E(\text{dimer}, D=10 \text{ Å}) = 0.42 \text{ kcal/mol.}$$

This difference is acceptable for the purposes of this work.

The geometries of the π dimers of 1,3,2,4,6-dithiatriazine (4\textsubscript{2}) and phenyl-substituted dithiatriazine (5\textsubscript{2}) have been fully optimized by UM06-2X and UB3LYP methods using the 6-311++G(2d,2p) basis set. All vibrational frequencies are real at the minimum. As shown in Table S1, the structural predictions of the UM06-2X and UB3LYP levels are in good agreement with the experimental crystal structures for the phenyl-substituted π dimer. The intermolecular distances are slightly shorter in 4\textsubscript{2} relative to 5\textsubscript{2} because the phenyl groups are repelling each other in 5\textsubscript{2}. These geometry differences are minor and validate the use of 4\textsubscript{2} as a reasonable model for the phenyl-dithiatriazine π dimer.
Table S1. Comparison of the structures of 4 and 5 \( \pi \) dimers as obtained at the UB3LYP and UM06-2X level with 6-311++G(2d,2p) basis set and X-ray diffraction. N' represents the terminal N atom in each monomer.

| Methods    | System | Intermolecular Distances (\( \text{Å} \)) | Intramolecular Distances (\( \text{Å} \)) | Dihedral Angle\(^a\) (°) |
|------------|--------|---------------------------------|---------------------------------|-----------------|
|            |        | S-S    | N'-N'   | N-N     | C-C     | N'-S    | S-N     | N-C     | N'-S-S-S-C |
| UM06-2X    | 4\(_2\) | 2.439  | 2.884   | 2.858   | 2.985   | 1.626  | 1.610  | 1.326   | 157.6    |
|            | 5\(_2\) | 2.450  | 2.884   | 2.865   | 2.987   | 1.626  | 1.601  | 1.334   | 158.3    |
| UB3LYP     | 4\(_2\) | 2.539  | 2.915   | 2.876   | 2.977   | 1.643  | 1.622  | 1.330   | 161.6    |
|            | 5\(_2\) | 2.548  | 2.920   | 2.894   | 3.009   | 1.642  | 1.611  | 1.340   | 161.6    |
| Exp.\(^b\) | 5\(_2\) | 2.529  | 2.821   | 2.881   | 2.997   | 1.625  | 1.593  | 1.342   | 164.0    |

\(^a\) Within one ring. All dimers have C\(_{2v}\) symmetry.

Further tests to the effects of basis sets on the binding energy are shown in Table S2. The binding energy increases significantly along with increasing the number of polarization functions. In summary, a double d polarization set is necessary for sulfur in these pancake bonded \( \pi \)-stacking dimers.

Table S2. Computed binding energy values for the dithiatriazine (HCN\(_3\)S\(_2\)) \( \pi \)-dimers with C\(_{2v}\) symmetry. The interaction energy (\( E_{\text{int}} \)) was obtained by equation (S1). All data correspond to optimized geometries at the basis set level given except for those indicated.

| Basis set          | \( E_{\text{int}} \) (kcal/mol) for 4\(_2\) |
|--------------------|---------------------------------|
|                    | UM06-2X | UB3LYP | MR-AQCC(4,4) |
| 6-31++G(d,p)       | -19.0    | -22.6   | -20.4 \(^a\) |
| 6-31++G(2d,2p)     | -28.6    | -31.3   | -31.1 \(^a\) |
| 6-311++G(d,p)      | -19.7    | -23.3   | -19.8       |
| 6-311++G(2d,2p)    | -28.5    | -31.2   | -27.7       |
| 6-311++G(3df,2pd)  | -31.2    | -32.6   | --          |
| aug-cc-pVTZ        | -27.3    | -29.0   | --          |

\(^a\) Optimized geometry at the MR-AQCC(4,4)/6-311++G(2d,2p) level.
S. III. Summary of relevant distances.

Figure S1 compares the crystallographic data for the two experimentally observed derivatives of the double bonded pancake dimer $4_2$.

|          | 5$_2$ (Refcode: DESSID$^9$) |          | 6$_2$ (Refcode: PAFLAJ$^{10}$) |
|----------|-----------------------------|----------|-----------------------------|
|          | Intermolecular (Å)          | Intramolecular (Å) | Intermolecular (Å)          | Intramolecular (Å) |
| S$_1$-S$_3$ | 2.525                       | S$_1$-N$_1$ | 1.622                       |
| S$_2$-S$_4$ | 2.532                       | N$_1$-S$_2$ | 1.623                       |
| N$_3$-N$_6$ | 2.821                       | S$_2$-N$_2$ | 1.599                       |
| N$_1$-N$_3$ | 2.891                       | N$_2$-C$_1$ | 1.351                       |
| N$_2$-N$_4$ | 2.870                       | C$_1$-N$_1$ | 1.338                       |
| C$_1$-C$_8$ | 2.997                       | N$_1$-S$_1$ | 1.589                       |
| C$_2$-C$_9$ | 3.398                       | C$_1$-C$_2$ | 1.470                       |
| S$_3$-N$_3$ | 1.635                       | C$_2$-C$_9$ | 3.347                       |
| N$_2$-S$_4$ | 1.620                       | S$_3$-N$_3$ | 1.635                       |
| S$_4$-N$_4$ | 1.601                       | N$_2$-S$_4$ | 1.644                       |
| N$_4$-C$_3$ | 1.345                       | S$_4$-N$_4$ | 1.590                       |
| C$_8$-N$_3$ | 1.336                       | N$_4$-C$_3$ | 1.343                       |
| N$_3$-S$_3$ | 1.582                       | C$_8$-N$_3$ | 1.340                       |
| C$_8$-C$_9$ | 1.471                       | N$_3$-S$_3$ | 1.593                       |

Figure S1. Two crystal structures of substituted dithia triazine (HCN$_3$S$_2$)$_2$ π dimers indicate close similarity of their structures.

S. IV. Properties of the 1,3,2,4,6-dithia triazine, 4, monomer.

The optimized geometries of the singlet and triplet states of 4 were obtained at the MR-AQCC(2,2)/6-311++G(d,p) level. Key data are summarized in Figure S2 and Table S3.
Both singlet and triplet states have $C_\text{s}$ symmetry with a planar structure for singlet and nonplanar structure for triplet where the mirror plane includes the CH group and the para nitrogen. The system being antiaromatic, the singlet has an unsymmetrical distribution of bond distances. The monomer in the $\pi$ dimer is similar to the triplet aromatic-type geometry as shown in Table S3. The monomer has not been isolated so far. We define the interaction energy based on equation (S1). This equation will overestimate the interaction energy compared to the one based on a relaxed scan. However, this approach permits the decomposition of the interaction into a vdw component and the SOMO-SOMO component by which the different contributions to the binding of the double bonded pancake can be analyzed. Note that the monomer has not yet been isolated. The geometries of monomers in the dimer at the equilibrium geometry of the dimer are quite similar to the geometry of the triplet state of the isolated monomer, rather than that of the singlet of the monomer.

The occupation number of the HONO and LUNO of the JT distorted singlet monomer is 1.83 and 0.17, respectively, and its $N_U = 0.39 \text{ e}$. This monomer has a stronger open shell singlet character than $\text{F}_2$. For comparison, the occupation number of HONO and LUNO of the $\text{F}_2$
molecule is 1.88 and 0.12, respectively using the MR-AQCC(2,2)/aug-cc-pVTZ method. The $N_U$ value is 0.13 e for $F_2$.

Table S3. Comparison of the computational and experimental monomer geometries of $4$. MR-AQCC(4,4)/6-311++G(2d,2p) level of theory was used in the computations.

| Parameters          | Experimental values for the monomer of $4_2$ (averaged from Ref. 11) | Computed values for the monomer at the equilibrium geometry of $4_2$ | Computed values for $4$ (T) | Computed values for $4$ (S) |
|---------------------|-------------------------------------------------------------------------|---------------------------------------------------------------------|---------------------------|---------------------------|
| $S_1$-$N_1$ ($\text{Å}$) | 1.600                                                                  | 1.624                                                               | 1.647                     | 1.571                     |
| $N_1$-$C_1$ ($\text{Å}$) | 1.348                                                                  | 1.327                                                               | 1.335                     | 1.426                     |
| $C_1$-$N_2$ ($\text{Å}$) | 1.337                                                                  | 1.327                                                               | 1.335                     | 1.277                     |
| $N_2$-$S_2$ ($\text{Å}$) | 1.586                                                                  | 1.624                                                               | 1.647                     | 1.751                     |
| $S_2$-$N_3$ ($\text{Å}$) | 1.628                                                                  | 1.633                                                               | 1.662                     | 1.724                     |
| $N_3$-$S_1$ ($\text{Å}$) | 1.622                                                                  | 1.633                                                               | 1.662                     | 1.564                     |
| $\angle C_1X_1N_3$ (°)  | 164.0                                                                  | 162.5                                                               | 155.7                     | 0.0                       |

S. V. Tables of optimized geometries.

$4_2$: MR-AQCC(4,4)/6-311++G(2d,2p), -1995.0169049031 Hartrees

|                  |                  |                  |                  |                  |
|------------------|------------------|------------------|------------------|------------------|
| $S$              | 1.394743000      | 1.285526000      | -0.524605000     |                  |
| $S$              | -1.394743000     | 1.285526000      | -0.524605000     |                  |
| $S$              | 1.394743000      | -1.285526000     | -0.524605000     |                  |
| $S$              | -1.394743000     | -1.285526000     | -0.524605000     |                  |
| $N$              | 1.209509000      | 1.435684000      | 1.081311000      |                  |
| $N$              | -1.209509000     | 1.435684000      | 1.081311000      |                  |
| $N$              | 1.209509000      | -1.435684000     | 1.081311000      |                  |
| $N$              | -1.209509000     | -1.435684000     | 1.081311000      |                  |
| $N$              | 0.000000000      | 1.467290000      | -1.354442000      |                  |
| $N$              | 0.000000000      | -1.467290000     | -1.354442000      |                  |
|   |          |          |          |
|---|----------|----------|----------|
| C | 0.000000000 | 1.477435000 | 1.625547000 |
| C | 0.000000000 | -1.477435000 | 1.625547000 |
| H | 0.000000000 | 1.596134000 | 2.700743000 |
| H | 0.000000000 | -1.596134000 | 2.700743000 |

3\textsubscript{2}: MR-AQCC(2.2)/6-31++G(2d,2p), -1277.5108255441 Hartrees

|   |          |          |          |
|---|----------|----------|----------|
| S | -1.434847000 | 0.000000000 | -1.280478000 |
| S | 1.434847000 | 0.000000000 | -1.280478000 |
| N | -1.550954000 | -1.346197000 | -0.325872000 |
| N | 1.550954000 | -1.346197000 | -0.325872000 |
| N | -1.550954000 | 1.346197000 | -0.325872000 |
| N | 1.550954000 | 1.346197000 | -0.325872000 |
| N | -1.619890000 | 0.000000000 | 1.677001000 |
| N | 1.619890000 | 0.000000000 | 1.677001000 |
| C | -1.613255000 | -1.149627000 | 0.976049000 |
| C | 1.613255000 | -1.149627000 | 0.976049000 |
| C | -1.613255000 | 1.149627000 | 0.976049000 |
| C | 1.613255000 | 1.149627000 | 0.976049000 |
| H | -1.676354000 | -2.054720000 | 1.566559000 |
| H | 1.676354000 | -2.054720000 | 1.566559000 |
| H | -1.676354000 | 2.054720000 | 1.566559000 |
| H | 1.676354000 | 2.054720000 | 1.566559000 |

4\textsubscript{2}: UB3LYP/6-31++G(2d,2p), -1998.7791724 Hartrees

|   |          |          |          |
|---|----------|----------|----------|
| S | 1.397024000 | 1.269369000 | -0.541029000 |
| S | -1.397024000 | 1.269369000 | -0.541029000 |
| S | 1.397024000 | -1.269369000 | -0.541029000 |
| S | -1.397024000 | -1.269369000 | -0.541029000 |
| N | 1.207925000 | 1.438155000 | 1.061093000 |
| N | -1.207925000 | 1.438155000 | 1.061093000 |
| N | 1.207925000 | -1.438155000 | 1.061093000 |
| N | -1.207925000 | -1.438155000 | 1.061093000 |
| N | 0.000000000 | 1.457634000 | -1.384519000 |
| N | 0.000000000 | -1.457634000 | -1.384519000 |
| C | 0.000000000 | 1.488407000 | 1.614458000 |
| C | 0.000000000 | -1.488407000 | 1.614458000 |
| H | 0.000000000 | 1.621307000 | 2.691182000 |
| H | 0.000000000 | -1.621307000 | 2.691182000 |

5\textsubscript{2}: UB3LYP/6-31++G(2d,2p), -2461.0930462 Hartrees

|   |          |          |          |
|---|----------|----------|----------|
| S | 1.391053000 | 1.273883000 | -2.384784000 |
| S | -1.391052000 | 1.273886000 | -2.384792000 |
| S | 1.391051000 | -1.273882000 | -2.384690000 |
| S | -1.391052000 | -1.273878000 | -2.384682000 |
| N | 1.200093000 | 1.447070000 | -0.795039000 |
| N | -1.200100000 | 1.447078000 | -0.795046000 |
|   |   |   |   |
|---|---|---|---|
| N | 1.200100000 | -1.446932000 | -0.794929000 |
| N | -1.200092000 | -1.446924000 | -0.794922000 |
| N | 0.000003000 | 1.460213000 | -3.237373000 |
| N | -0.000003000 | -1.460272000 | -3.237258000 |
| C | -0.000005000 | 1.504406000 | -0.202420000 |
| C | 0.000005000 | -1.504148000 | -0.202291000 |
| C | -0.000011000 | 1.682856000 | 1.264365000 |
| C | -1.206570000 | 1.753692000 | 1.966426000 |
| C | 1.206542000 | 1.753655000 | 1.966440000 |
| C | -1.207750000 | 1.893795000 | 3.345755000 |
| C | 1.203734000 | 1.893757000 | 3.345590000 |
| C | -0.000024000 | 1.961973000 | 4.039614000 |
| H | -2.135146000 | 1.687498000 | 1.421553000 |
| H | 2.135123000 | 1.687432000 | 1.421579000 |
| H | -2.141250000 | 1.940881000 | 3.881485000 |
| H | 2.141240000 | 1.940812000 | 3.881512000 |
| H | -0.000029000 | 2.065007000 | 5.115802000 |
| C | 0.000011000 | -1.682760000 | 1.264472000 |
| C | -1.206542000 | -1.753630000 | 1.966540000 |
| C | 1.206570000 | -1.753667000 | 1.966525000 |
| C | -1.203734000 | -1.893844000 | 3.345678000 |
| C | 1.203775000 | -1.893882000 | 3.345663000 |
| C | 0.0000024000 | -1.962117000 | 4.039696000 |
| H | -2.135123000 | -1.687353000 | 1.421684000 |
| H | 2.135146000 | -1.687420000 | 1.421658000 |
| H | -2.141204000 | -1.940939000 | 3.881596000 |
| H | 2.141250000 | -1.941008000 | 3.881570000 |
| H | 0.0000029000 | -2.065237000 | 5.115875000 |

$7_2$: UB3LYP/6-311++G(2d,2p), -10012.0792667 Hartrees

Se | -1.384824000 | 1.509972000 | -0.314616000 |
Se | -1.384824000 | -1.509972000 | -0.314616000 |
Se | 1.384824000 | 1.509972000 | -0.314616000 |
Se | 1.384824000 | -1.509972000 | -0.314616000 |
N | -1.519723000 | 1.222684000 | 1.445061000 |
N | -1.519723000 | -1.222684000 | 1.445061000 |
N | 1.519723000 | 1.222684000 | 1.445061000 |
N | 1.519723000 | -1.222684000 | 1.445061000 |
N | -1.559339000 | 0.000000000 | -1.283569000 |
N | 1.559339000 | 0.000000000 | -1.283569000 |
C | -1.552256000 | 0.000000000 | 1.957807000 |
C | 1.552256000 | 0.000000000 | 1.957807000 |
H | -1.643470000 | 0.000000000 | 3.043678000 |
H | 1.643470000 | 0.000000000 | 3.043678000 |

$8_2$: UB3LYP/6-311++G(2d,2p), -2717.0028983 Hartrees
### Problem 9

#### UB3LYP/6-311++G(2d,2p), -2717.0029531 Hartrees

|  |          |          |          |
|---|----------|----------|----------|
| N | -1.322498000 | 1.544032000 | 0.176744000 |
| N | -1.327322000 | -0.619090000 | -1.424706000 |
| N | -1.321595000 | -0.925303000 | 1.248940000 |
| S | -1.397580000 | 0.993071000 | -1.340693000 |
| S | -1.394493000 | 0.664618000 | 1.531019000 |
| S | -1.396749000 | -1.658294000 | -0.189440000 |
| N | 1.322293000 | 0.619361000 | 1.425155000 |
| N | 1.323683000 | 0.924944000 | -1.248963000 |
| N | 1.324686000 | -1.543824000 | -0.176920000 |
| S | 1.395167000 | 1.658414000 | 0.189230000 |
| S | 1.395891000 | -0.993202000 | 1.340719000 |
| S | 1.398094000 | -0.664658000 | -1.530945000 |

### Problem 10

#### UB3LYP/6-311+G(d), -1378.8948202 Hartrees

|  |          |          |          |
|---|----------|----------|----------|
| C | 0.000000000 | 1.217107000 | 1.305325000 |
| C | 0.715398000 | -0.984661000 | 1.305325000 |
| C | -0.715398000 | -0.984661000 | 1.305325000 |
| C | -1.157538000 | 0.376107000 | 1.305325000 |
| C | 1.157538000 | 0.376107000 | 1.305325000 |
| C | 0.000000000 | 1.217107000 | -1.305325000 |
| C | 0.715398000 | -0.984661000 | -1.305325000 |
| C | -0.715398000 | -0.984661000 | -1.305325000 |
| C | -1.157538000 | 0.376107000 | -1.305325000 |
| C | 1.157538000 | 0.376107000 | -1.305325000 |
| F | -1.467042000 | -2.019211000 | -1.406024000 |
| F | 1.467042000 | -2.019211000 | -1.406024000 |
| F | -1.467042000 | -2.019211000 | 1.406024000 |
| F | -2.373724000 | 0.771270000 | -1.406024000 |
| F | 0.000000000 | 2.495882000 | -1.406024000 |
| F | 2.373724000 | 0.771270000 | 1.406024000 |
| F | 0.000000000 | 2.495882000 | 1.406024000 |
| F | 2.373724000 | 0.771270000 | 1.406024000 |
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