Rotational Barrier in Phenalenyl Neutral Radical Dimer: Separating Pancake and van der Waals Interactions

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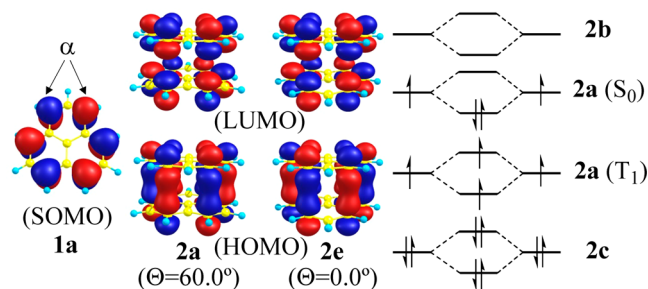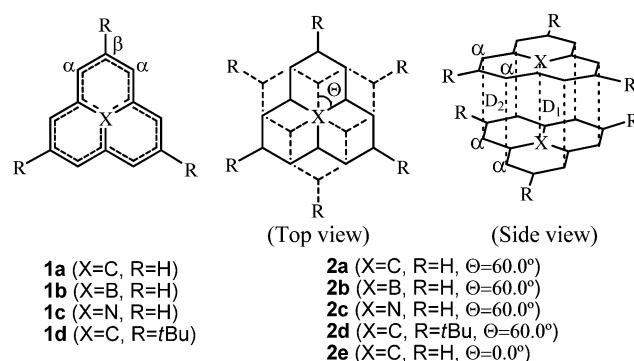
ⓢ *Supporting Information*

ABSTRACT: Pancake π-stacking produces shorter contacts than van der Waals bonding but it has strongly preferred configurations. By high-level multireference average quadratic coupled cluster theory for the singlet and triplet, we identify the specific orbital component and the nonspecific vdW contributions in the prototypical pancake-bonded dimer of phenalenyl thereby explaining the configurational preferences.

P ancake interactions[1] occurring in π-stacked radical dimers possess very interesting bonding properties and play also an important role in material design since they lead to intermolecular contact distances significantly shorter than the sum of the vdW radii,[2] resulting in enhanced electron transfer and high electrical conductivity for organic materials[3] as well as varied and interesting magnetism.[4] Pancake bonding is used to describe interradical π–π bonding interaction driven by the overlap of the singly occupied molecular orbitals (SOMOs) and characterized by two electron/multicenter (2e/mc) bonding. High conductivity is due to short radical−radical contacts induced by the π–π stacking that distinguish pancake bonding from ordinary vdW bonding.[5] This work is focused on determining the interaction energy and its components using high-level multireference average quadratic coupled cluster (MR-AQCC) theory[6] including both van der Waals (vdW) and diradicaloid multicenter interactions in a balanced manner.[6] In spite of numerous attempts[7−10] it remains a challenge to separate quantitatively this specific π–π bonding SOMO−SOMO interaction ($E_{SOMO-SOMO}$) in stacking radical dimers from the ubiquitous vdW term[8] including dispersion, Pauli repulsion, $E_{P.rep}$, and electrostatic interactions, E_{ES}):

$$E_{vdW} = E_{disp} + E_{P.rep} + E_{ES} \qquad (1)$$

Phenalenyl $C_{13}H_9$ (PLY, **1a**) is a neutral radical forming the prototypical pancake-bonded dimer, **2a** as shown in Scheme 1. It and its closed-shell hypothetical analogues $BC_{12}H_9$ (**1b**) and $NC_{12}H_9$ (**1c**) consist of three fused six-membered rings, sharing a central carbon, boron, and nitrogen atom, respectively. The dimers **2b** and **2c** can serve as models for vdW-bonded dimers.[11] For the radical dimer, maximum overlap[9,12] of the two SOMOs is predicted based on the MO diagram[13] shown in Figure 1 for **2a**. If the pancake interaction in **2a** was dominated by vdW interactions, then one would not expect the specificity of nearly perfect overlaps of the α-carbons. However, that is exactly what is

Scheme 1

1a (X=C, R=H)
1b (X=B, R=H)
1c (X=N, R=H)
1d (X=C, R=tBu)

(Top view) (Side view)

2a (X=C, R=H, Θ=60.0°)
2b (X=B, R=H, Θ=60.0°)
2c (X=N, R=H, Θ=60.0°)
2d (X=C, R=tBu, Θ=60.0°)
2e (X=C, R=H, Θ=0.0°)

Figure 1. Illustration of the bonding and antibonding combinations of the two SOMOs in the PLY for the staggered (**2a**) and eclipsed (**2e**) configurations of the PLY π-dimer from HF/6-31G(d). The energy level diagrams are on the right. S_0 and T_1 indicates the schematic occupancies for the singlet and triplet, respectively. **2b** (boron) and **2c** (nitrogen) have closed shells and show no pancake bonding, only vdW bonding as does the triplet, **2a**(T_1) of PLY_2.

observed by X-ray diffraction (XRD) for nearly all of over 50 π-stacking arrangements found in neutral radical derivatives of **1a**. Here we provide a simple but generally applicable model that allows an approximate separation of the interaction energy of the singlet pancake-bonded dimer into a vdW component that is always present from the "bare" pancake interaction arising from the SOMO−SOMO bonding term similar to the energy decomposition by Mota et al.,[8] and it is theory-independent and is widely applicable so long as the theory adequately includes both vdW and pancake bonding terms. We use this model at a

high theory level to obtain a sufficiently reliable decomposition. We approximate the total interaction energy as the sum of the bare pancake bonding ($E_{SOMO-SOMO}$) and the vdW term (E_{vdW}) and write for the singlet state:

$$E_{tot}^S = E_{SOMO-SOMO} + E_{vdW} \qquad (2)$$

We then assume following Mota et al.,[8] and subsequently validate, that E_{vdW} can be well approximated by the total interaction energy of the triplet:

$$E_{vdW} \approx E_{tot}^T \qquad (3)$$

It is important that both singlet and triplet energies are evaluated at the same geometry. The validation of this triplet-based model proceeds by comparing it with the closed-shell heteroatomic model systems **2b** and **2c**. Figure 1 shows the MO interaction diagram of these two closed-shell models which lack the SOMO−SOMO bonding term: In **2b** and **2c** the central C is replaced by B and N, respectively. These are compared with the triplet case where the net bonding effect of the SOMO−SOMO overlap is expected to approximately cancel. If the three models provide a similar representation of the E_{vdW} interaction between the two phenalenyls, then the triplet can be used in eq 2 as a tool to obtain an approximation for the bare $E_{SOMO-SOMO}$ component.

Rotational energy scans provide an alternative way to separate $E_{SOMO-SOMO}$ by realizing that large barriers should separate the staggered and eclipsed configurations where the SOMO−SOMO overlap is a maximum. On the top of the barrier the vdW interaction is still present, but the SOMO−SOMO overlap is zero. The electronic nature of the bonding is reflected in low lying singlet and triplet excitations; the latter is a sign of significant diradicaloid character.[7] Since the SOMO is delocalized (for PLY over six α-carbons) the bonding supermolecular MO is considered as the basis of a two-electron multicenter delocalized bonding.[2] The occupancy of the antibonding SOMO−SOMO configuration is significant, and it is a measure of the diradicaloid character[4] necessitating the use of a multireference based theory that also includes dynamical correlation. We have applied the MR-AQCC theory with analytic MR-AQCC energy gradients[14] using a complete active space (CAS) with two electrons and two orbitals and the 6-31G(d) basis set.[15] This theory level is simultaneously capable to describe the multi reference (diradicaloid) nature of the ground state while accounting for the dynamical electron correlation necessary for the dispersion part of the vdW interaction by including explicitly singles and doubles excitations and approximately accounting for higher excitations.[16] The calculations were performed using the COLUMBUS program system.[17]

An alternative insight into the binding energy analysis is obtained by examining the total number of effectively unpaired electrons (N_U) as a function of intradimer **2a**→**2e** rotation for the singlet and triplet. The analysis of the radical character of the complexes was performed by computing the effectively unpaired density, which provides a measure for the splitting of an electron pair into different spatial regions. It was computed in terms of the nonlinear formula in eq 4:

$$N_U = \sum_{i=1}^{N} n_i^2 (2 - n_i)^2 \qquad (4)$$

where n_i is the i-th natural orbital occupancy.[18] The nonlinear formula reduces the relative contributions of the n_i values that are

close to 0 or 2 diminishing the contributions from dynamical correlation and thus highlighting only the truly open-shell contributions of the radical centers. The results for the singlet shown in Figure 2 are puzzling at first sight. The triplet has a high
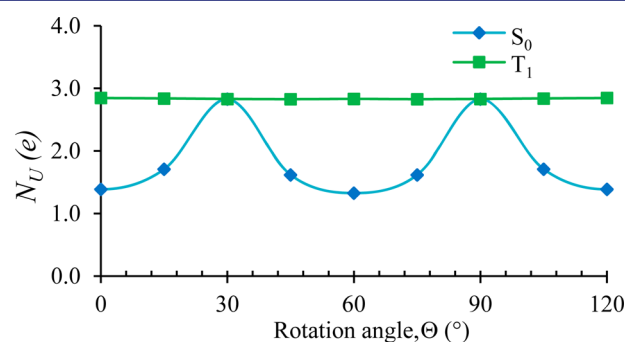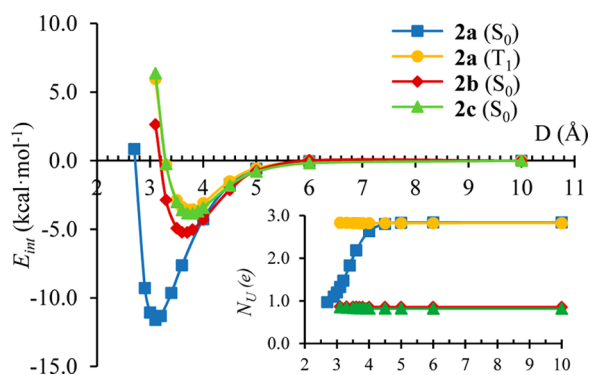

Figure 2. Total number of effectively unpaired electrons (N_U) as a function of the rotational angle Θ for the singlet and triplet **2a**→**2e** scan. The contact distance is $D_1 = 3.104$ Å at the minimum of the singlet. The rigid rotation is performed around D_1.

N_U value due to its two unpaired electrons in the two SOMO-derived orbitals (bonding and antibonding between the dimers). In addition, the numerous very small contributions due to dispersion interactions also add up resulting in a total N_U value of almost 3. For the triplet there is virtually no variation with the rotational angle since no electron pair bonding occurs. The singlet displays an interesting maximum of N_U equal to that of the triplet at a rotation approximately halfway between the two minima at $\Theta = 0°$ (eclipsed) and $\Theta = 60°$ (staggered) both exhibiting maximum SOMO−SOMO overlap. In the middle at $\Theta \approx 30°$ the two SOMO electrons do not show pairing at all, while at $\Theta = 0°$ and $\Theta = 60°$ they do, which is indicative of a reduction of the diradicaloid character and bond formation. If there were only vdW bonding between the two molecules the singlet curve would look very much like the triplet curve. The dramatic change of N_U as a function of rotation is a sensitive indicator of pancake bonding which vanishes at $\Theta \approx 30°$. This observation is the basis of the present work. It suggests that an alternative measure of the bare pancake interaction energy, $E_{SOMO-SOMO}$, can be obtained by analyzing the energy differences of the configuration at $\Theta \approx 30°$ (no pancake bonding) with the most stable pancake-bonded ones at $\Theta = 0°$ or $60°$. Note that E_{ES} is not sensitive to Θ, see Table S1.

We now turn to the analysis of the optimized geometries and energy components. Full geometry optimization has been performed for both the singlet and triplet of the **2a** PLY$_2$ dimer at the MR-AQCC(2,2)/6-31G(d) level. The geometries of the PLY radicals are virtually identical in the dimer and in the isolated radical. The optimized contact distances for the singlet are $D_1 = 3.104$ Å and $D_2 = 3.092$ Å. The fact that $D_1 > D_2$ is significant, because it is yet another feature of pancake bonding in this system. D_2 is smaller because it connects two sites that directly participate in the SOMO−SOMO bonding term by virtue of nonzero SOMO coefficients at those carbons. In contrast, D_2 refers to the central carbons where the SOMO has a node, and thus these two carbons are not directly participating in the bonding interaction. The optimized contact distances for the triplet are $D_1 = 3.676$ Å and $D_2 = 3.719$ Å. Here the order of distances is reversed: the dispersion interactions dominate, and the two central carbons simply have more neighbors across the vdW gap leading to a slightly shorter D_1 contact compared to D_2.

Figure 3 shows the computed dissociation scan for the singlet and triplet **2a** as well as the B- and N-substituted analogue

Figure 3. Rigid potential energy scans of the singlet and triplet **2a** and singlet **2b** and **2c** in the D_{3d} staggered configuration as a function of D_1 (in Å). The inset shows the total number of effectively unpaired electrons, N_U. For numerical values see Table S2.

dimers. The rigid PE scans are based on the equilibrium geometry for the singlet **2a** and use two parallel staggered monomers for the triplet **2a** and singlet **2b** and **2c**. The minimum for the singlet provides a interaction energy of −11.5 kcal/mol by estimating the energy difference between the separation D_1 at the minimum at 3.104 and 15.0 Å, which is in good agreement with recent experimental data (in various solvents) in the −7.5 to −10.0 kcal/mol range in ESR measurements and theoretical values for **2d**.[1b,7] Note that Mota et al. obtained a much higher value of −26.0 kcal/mol using MRMBPT2.[8]

The estimation of the vdW component of the interaction energy is one of the key challenges in the theoretical analysis of pancake bonding. Figure 3 shows a shallow minimum in the interaction energy for **2b** and **2c** and the triplet **2a** at about 3.7 Å with interaction energies of −5.2, −3.8, and −3.3 kcal/mol, respectively. The close energetic proximity of these three terms reveals that their intermolecular interaction arises mostly from similar vdW interactions. The potential curve is somewhat deeper for **2b** than **2c** and triplet **2a**, which is due to the larger static atomic dipole polarizability of B as compared to C and N. Notably, these PE scans showed that at shorter intermolecular distances around 3.1 Å relevant for pancake bonding, vdW terms become repulsive with an overall repulsion of ∼5.7 kcal/mol at D = 3.104 Å.

Based on this validation we use the triplet energy as an approximation for the vdW term with eqs 2 and 3 to extract the bare SOMO−SOMO term similarly to Mota et al.[8] as

$$E_{SOMO-SOMO}(D) \approx E_{tot}^S(D) - E_{tot}^T(D) \qquad (5)$$

The combination of the total computed interaction energy of −11.5 and the vdW interaction of 5.7 leads to a SOMO−SOMO interaction of −17.2 kcal/mol. Thus, the pancake bonding for **2a** not only overcomes a repulsive vdW interaction but also provides further binding. The energies of these three models are quite consistent with each other leading to the conclusion that triplet **2a** is a good candidate to approximate the vdW term. The N_U values in the inset in Figure 3 are consistent with this interpretation: Its value changes only significantly for the pancake-bonded case; the others remain almost constant as a function of intermolecular separation.

A singlet−triplet splitting of ΔE_{ST} = −8.2 kcal/mol is obtained as the difference between the respective equilibrium energies of

the singlet and the triplet states, which is consistent with the −6.64 kcal/mol value obtained by ESR experiments for **2d**.[1b] This also indicates that PLY_2 has a low singlet−triplet splitting similar to other pancake-bonded systems.[13] A low ΔE_{ST} is associated with a high diradicaloid character and properties of weak bonds compared to ordinary covalent bonds.[19]

Next we compare the eclipsed and staggered configurations in Figure 4, the vdW term (triangles in red) is repulsive in the short
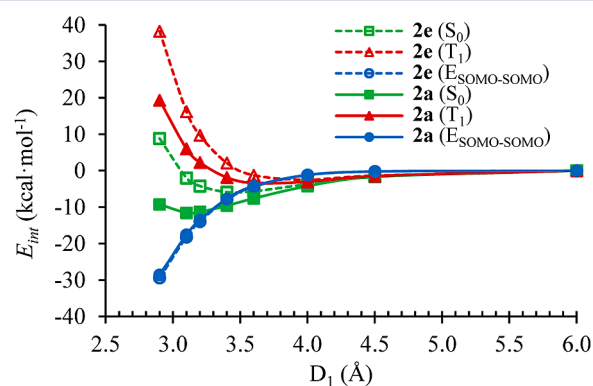
Figure 4. Rigid potential energy scans of the **2a** and **2e**.

D_1 region (2.9–3.5 Å). **2e** possesses shorter interatomic distances compared to **2a**, producing substantial repulsions in **2e** and resulting in a minimum of only −5.9 kcal/mol interaction energy at a longer D_1 = 3.4 Å. It is remarkable that the curves of the bare pancake term ($E_{SOMO-SOMO}$) are so close for **2a** and **2e**. Note that these are the two cases when the SOMOs overlap perfectly. As shown before, the $E_{SOMO-SOMO}$ is −17.2 kcal/mol for **2a** at D = 3.104 Å. Moreover, the $E_{SOMO-SOMO}$ is nearly zero at about 4 Å and beyond. The vdW term, however, is still considerably attractive in this region. The key conclusion of this analysis is that the SOMO−SOMO overlap provides a stabilization that starts at distances typical for vdW interactions and becomes increasingly stabilizing as D_1 is reduced to shorter than vdW contact distances. However, at even shorter distances the repulsive vdW terms increase dramatically as expected and overcome the $E_{SOMO-SOMO}$ interaction energy.

The rotational energy curves in Figure 5 of the triplet vs singlet PLY_2 confirm this interpretation. At the optimized D_1 value for the triplet state (3.676 Å) the triplet rotational scan is very flat, indicating that the interaction of the triplet PLY_2 at 3.676 Å is dominated by dispersion interactions. Yet, the interaction energy
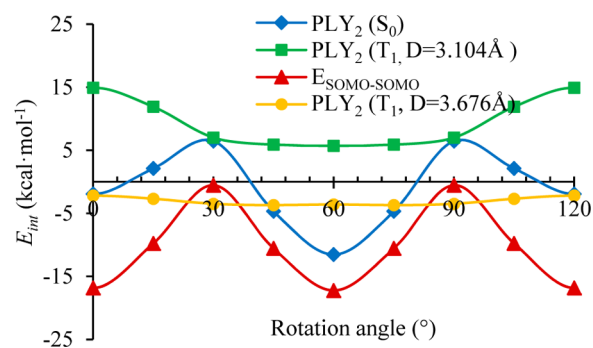
Figure 5. Rigid rotational energy scans of PLY_2 at D_1 = 3.104 Å for the singlet and at D_1 = 3.676 Å for the triplet as a function of Θ.

of triplet PLY_2 dimer at $D_1 = 3.104$ Å, changes by $\sim$9 kcal/mol from $\Theta = 0°$ to $60°$. Key data are summarized in Table 1.

Table 1. Interaction Energies (kcal/mol)

	total	vdW[b]	$E_{SOMO–SOMO}$[c]
2a (staggered)	-11.5[a]	$+5.7$	-17.2
2e (eclipsed)	-1.9	$+14.9$	-16.8
2a–2e[d]	-18.0	-1.3	-16.7

[a]Experiment $-7.5 \sim -10.0$ for *tert*-butyl-substituted **2d**. [b]Based on eq 3. [c]Based on eq 5. [d]Barrier taken from the top at $\Theta = 30°$ to the minimum at $60°$, see Figure 5.

The comparison of the total singlet interaction energy and $E_{SOMO–SOMO}$ indicates that the barrier from $\Theta = 60°$ (**2a**) to $0°$ at $30°$ is mostly due to the reduction in the bare SOMO–SOMO term, which provides an approximate contribution of 16.7 kcal/mol to the barrier. This rotational barrier is largely due to the SOMO–SOMO term. The SOMO–SOMO contribution to the rotational barrier provides another independent estimate of $E_{SOMO–SOMO}$ at -16.7 kcal/mol to be compared with the -17.2 kcal/mol value based on the dissociation process.

The above interpretation is fully consistent with Figure 2 showing two nearly equivalent minima of the N_U at $0°$ and $60°$ corresponding to the maximally paired electrons with maximum overlap. The preference for the staggered configuration is due to the stronger Pauli repulsion at $\Theta = 0°$. On the other hand, the near agreement of the triplet and singlet interaction energy both taken at $D_1 = 3.104$ Å and at $\Theta \approx 30°$ signifies the near disappearance of the SOMO–SOMO energy component where the SOMO–SOMO overlap is nearly zero.

The analysis presented here leads us to conclude that the interaction in the phenalenyl dimer is dominated by the SOMO–SOMO interaction and cannot be interpreted as a pure vdW complex as has been done by Mota et al.[8] Thus, it is justified to classify the bonding as a 2e/12c short inter-radical pancake bond for which the bare SOMO–SOMO term provides an approximately -17.2 kcal/mol contribution to the interaction energy in comparison to the vdW term of $+5.7$ kcal/mol at the energy minimum distance of $D_1 = 3.104$ Å. The latter term is repulsive at this short distance obviously due to Pauli repulsion. Thus, the total interaction energy is reduced to -11.5 kcal/mol in the staggered configuration, being in good agreement with available experimental evidence[1b,7] of -7.5 to -10.0 kcal/mol for the enthalpy of formation for **2d** depending on the solvent. We find that the preferred staggered configuration is in agreement with the maximin principle.[9] We want to stress that estimating the vdW term from the triplet interaction energy is quite general and applicable to other cases of radical–radical interactions as long as the theory level is sufficiently high to account for both the MR nature of the singlet and triplet states and at the same time credibly describes the vdW component of the interaction. The SOMO–SOMO term is substantial and much larger than typical vdW interaction energies. Its understanding paves the way to gaining more control and possibly obtaining stronger and shorter bonding in π-stacking dimers and others aggregates of radicals.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Computational details and complete ref 17. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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