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Concave or convex π-dimers: the role of the pancake bond in substituted phenalenyl radical dimers[†]

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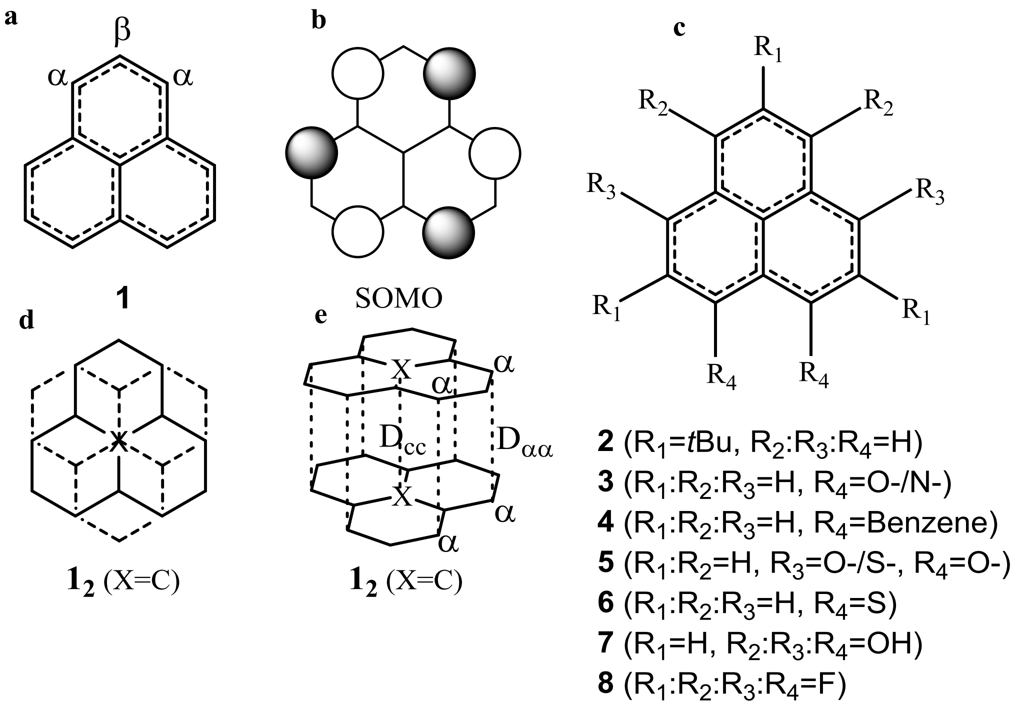
Abstract: π-stacking in dimers of phenalenyl represent the prototypical pancake bonding between radicals. This type π-stacking aggregate formation represents a key structural motif in conducting organic and multifunctional materials. It is driven by the bonding combination of the singly occupied molecular orbitals (SOMOs) of the monomers resulting in π-stacking contacts that are significantly shorter than the sum of the van der Waals (vdW) radii. Analysis of 56 structures from the literature (mostly from the Cambridge Structural Database) coupled with DFT computations shows that the central C···C contact in derivatives of phenalenyl does not contribute directly to the π-stacking pancake bonding in concordance with the fact that the SOMO coefficient is zero at the central carbon. This central C···C contact is typically longer than the contacts between the SOMO bearing α-carbons with a convex dimer shape with one known exception of a complex containing bulky *tert*-butyl groups. This unusual case of a concave shaped dimer with a significantly shorter central C···C contact is due to the steric repulsions at the periphery of the molecule pushing the central atoms closer together relative to the α to α-contacts which provide the attractive driving force for the multicenter pancake bonding. The diradical character of the pancake bonding is revealed by the analysis of the unpaired electron density based on high-level multireference theory.

[†]Electronic supplementary information (ESI) available: This section contains three figures on computational details and structures, four tables on computed parameters and coordinates of optimized geometries.

Keywords: diradical, phenalenyl radical dimer, intermolecular distances, π-stacking, CSD search, multicenter bonding, van der Waals interactions.

Introduction

Phenalenyl (PLY, **1,** Chart 1a), is a prototypical neutral stable radical with an unpaired π-electron delocalized over six of the 13 π-centers as illustrated in Chart 1b.[1]

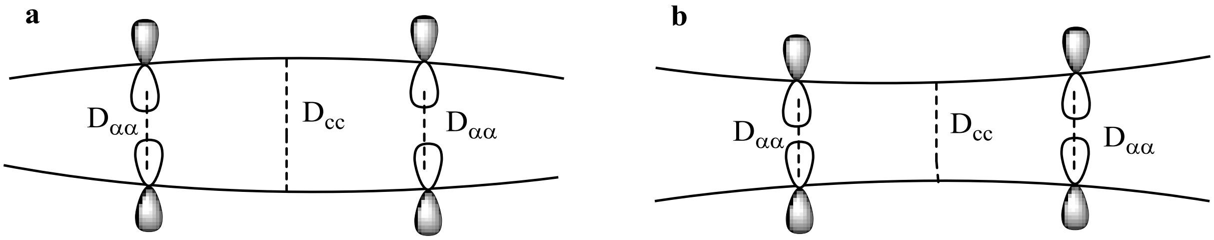


2 (R_1=*t*Bu, R_2:R_3:R_4=H)
3 (R_1:R_2:R_3=H, R_4=O-/N-)
4 (R_1:R_2:R_3=H, R_4=Benzene)
5 (R_1:R_2=H, R_3=O-/S-, R_4=O-)
6 (R_1:R_2:R_3=H, R_4=S)
7 (R_1=H, R_2:R_3:R_4=OH)
8 (R_1:R_2:R_3:R_4=F)

Chart 1. Phenalenyl (PLY) radical (a, **1**) and its singly occupied molecular orbital, SOMO (b). (c) substituted analogues (**2**~**8**), (d) top view of the π-dimers ($\mathbf{1_2}$) of PLY, (e) side view of the π-stacking dimer illustrating the definition of the intermolecular distances, D (D_{cc} for central carbon pair and $D_{\alpha\alpha}$ for α-carbon pairs).

Its *tri*-*tert*-butyl derivative, **2**, and various other derivatives form stable dimers in a π-stacking geometry.[2] By now many phenalenyl radical based systems that show π-stacking geometry have been made, providing a key synthon for highly conducting organic materials and organics showing interesting magnetism.[3] A large number of these systems have been also characterized by single crystal X-ray diffraction (XRD).

This paper aims to discover trends across all 56 dimers in this family of compounds for which XRD data are available. We obtain key characteristics of the chemical bonding in these dimers across the π-stacking space arising from the pairing of these two radical electrons. This pairing is incomplete and the dimers show diradicaloid ground states and intermolecular contacts shorter than the van der Waals (vdW) distance.[2, 4, 5, 6, 7, 8] While in $\mathbf{2_2}$ the contact distance between the two central carbons, D_{cc}, is shorter than the distance between the α-carbons, $D_{\alpha\alpha}$ (as defined in Chart 1 and Scheme 1b), representing a concave shape. The opposite convex shape is found for the overwhelming majority of PLY-derived radical dimers (Scheme 1a). Why should this be so, and what can we learn about intermolecular π-stacking and bonding from the analysis of these contact distances? Multireference wave function approach calculations[8] have been performed recently in order to take the fractional occupation specifically of the HOMO and LUMO properly into account. The occupancy of the HOMO is found to be significantly smaller than two and the occupancy of the LUMO is larger than zero indicating the afore-mentioned diradicaloid character for pancake bonding. One of the most practical multireference methods today is the multireference average quadratic coupled cluster, MR-AQCC, theory[9] which provides the simultaneous treatment of static (multireference) and dynamic (including dispersion) electron correlation. It has been successfully used previously in interpreting the bonding characteristics of pancake bonded systems: the phenalenyl dimer[6] and the $TCNE^-$ anion dimer[7], two prototypical examples of pancake bonding.



Scheme 1. Schematic illustration of the (a) convex and (b) concave shaped substituted phenalenyl dimers. Only two of the six pairs of overlapping π-orbitals at the α-carbons are shown in each dimer configuration.

Several PLY-based radicals have been synthesized and characterized which are of interest for their applications in materials chemistry due to their high electrical conductivity often coupled with unusual magnetism and optical properties resulting from the diradicaloid singlet ground state and low lying singlet-triplet and singlet-singlet excitations.[10] Utilizing the electronic and steric strategies to suppress the σ-dimerization of PLY[4], various PLY-based π-dimer structures have been characterized in the solid state, as well as in solution at low temperatures.[5] Following Mulliken and Person,[11] Suzuki et al.[12] recently revived the term “pancake bonding” to describe this specific category of π-π bonding interactions. Note that the stronger the pancake bonding is, the less in the present context unwanted σ-dimerization can provide an alternative stabilization mechanism for radical-radical interaction. The large π-π overlap that facilitates a conducting pathway between the π-electrons dominates the interaction in pancake bonding as illustrated in a simple MO picture shown in Chart 2a [13, 14, 15, 16, 17, 18] showing another characteristics of pancake bonding favoring maximum overlapping π-stacking geometry. A natural consequence of this SOMO-SOMO bonding contribution would be that the contact distances between the α-carbons across the inter-radical space, $D_{\alpha\alpha}$, should be smaller than D_{cc}, the contact distance between the two central carbons. However, is it true in general that $D_{\alpha\alpha} < D_{cc}$, i.e. that the convex shape is preferred to the concave one?

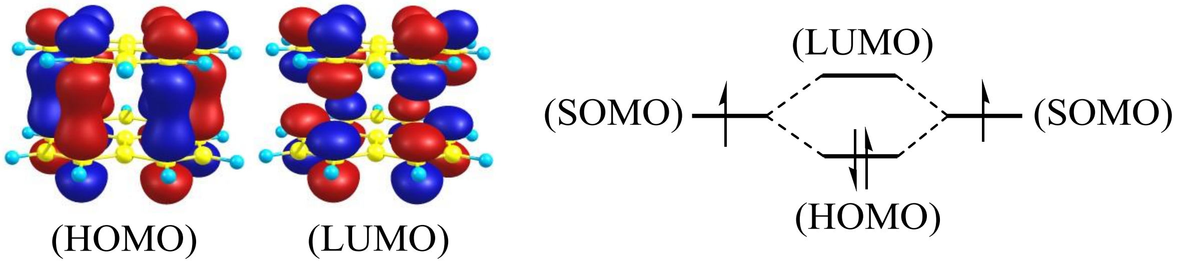


Chart 2. (a) Illustration of the bonding and antibonding combinations of the two SOMOs in PLY as obtained by Hartree-Fock (HF/6-31G(d)) calculation; isodensity value is 0.03 a.u. (b) Idealized energy level diagram.

The high stability of PLYs originates from the π-electron delocalization of the singly occupied molecular orbital (SOMO). Due to symmetry, in PLY the SOMO is exactly localized on six α-position carbons on the periphery of the molecule as illustrated in Chart 1.[3] For the π-dimers listed in Chart 1 and 3 ($\mathbf{1_2}$~$\mathbf{8_2}$), the SOMO-SOMO inter-radical bonding interaction serves as the stabilizing driving force although some of the substitutions lower the symmetry as for **3**, **4**, **5**, and **6** shown in Chart 3. These bonding interactions pull the two PLY radical closer together as compared to the vdW distance.[2, 6, 7, 16, 17] This unique intermolecular interaction associated with the π-stacking has been recognized as a new class of two electron/multicenter (2e/mc) π-π bonding.[5, 6, 7, 12, 16, 17] For example, PLY-based dimers have two electron 12 center (2e/12c) bonding counting the six pairs of spin-bearing carbons that participate in the SOMO-SOMO overlap interaction. Generally, a maximum overlap principle of the SOMO orbitals [19] qualitatively describes the structural preferences of the overlapping π-radicals. [6] This principle is in general agreement with experimental configurations with respect to the relative orientations of the monomers in the dimer as opposed to packing dominated by vdW interactions where no such preferences are generally observed. As already mentioned above, from this picture one would expect that the $D_{\alpha\alpha}$ distances are smaller than D_{cc} since there is no SOMO contribution to the central carbon atom. Equivalently, the difference

$$\Delta = D_{cc} - D_{\alpha\alpha}. \tag{1}$$

should be positive. Accordingly, the structure of the dimer of **2** would be an exception. However, based on their AIM (atoms-in-molecules) analysis of the bond critical points of the electron density, Mota et al. argued[17] that the PLY_2 dimer possesses a 2e/14c bonding by including the central carbon pair, rather that 2e/12c bond suggested by SOMO-SOMO interaction picture.

In fact, the X-ray structure[2] of the dimer of **2** with bulky *t*Bu substituents shows a shorter C(central)$\cdots$C(central) inter-radical contact of D_{cc} = 3.201 Å as compared to the longer average C(α)$\cdots$C(α) contact of $D_{\alpha\alpha}$ = 3.306 Å, which seems to support the 2e/14c bonding scheme. It should be noted, however, that both values are significantly shorter than the sum of the vdW radii at 3.40 Å [20] still indicating a two electron multicenter (2e/mc) pancake bonding. The conjugated framework of phenalenyl is rigid, so one expects Δ to be small, but based on the SOMO overlap argument, it should be always *positive*. Two questions arise out of these observations that shed light on the nature of pancake bonding. Why is the observed $\Delta < 0$ in this particular case of the dimer of **2**, and is this typical?

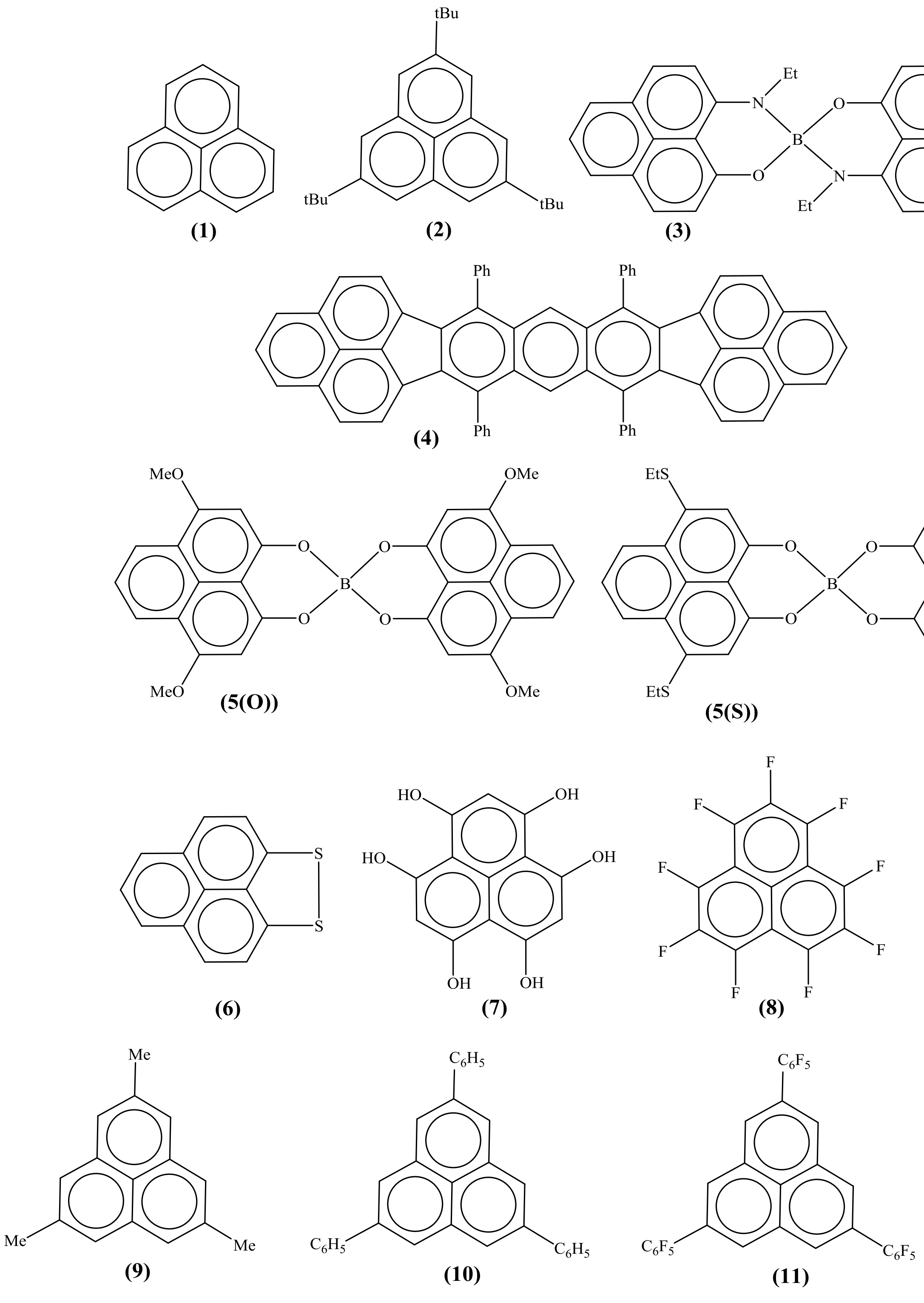


Chart 3. Overview of the phenalenyl based radicals discussed. Note that substitutions are at the α-sites for **1**, **3**, **4**, **5**, **6**, **7**; at the β-sites for **2**, **9**, **10**, **11**, and at both for **8**.

Two complementary approaches are used in this work for the analysis of pancake bonding. We present analysis of the crystallographically characterized structures of PLY-derivatives forming π-stacking dimers with emphasis on the observed Δ values. This is followed by a systematic quantum mechanical analysis of the structures of a selected set of model compounds representing the major categories of these experimentally characterized derivatives combined with the analysis of the unpaired electron density[21] computed at the MR-AQCClevel. It has been shown in several previous investigations[22] that this combination provided a good description of the bi- and polyradical character in conjugated π systems.

Methods

Computational Methods: The molecular equilibrium geometries and harmonic vibrational frequencies of the local minima were obtained at the spin-unrestricted level of theory based on the broken spin-symmetry (BS)[23] approach. Density functional theory (DFT) using the UM05-2X was used.[24] We also applied the UM06-2X method[25] and report the results in the SI section. While UM05-2X and UM06-2X provide similar results, the former agrees better with the experimental structures. The 6-31+G(d,p) basis set has been used in the geometrical and frequency prediction for these π-dimers. The above computations have been performed by the Gaussian 09 program package.[26] Computations with the multireference average quadratic coupled cluster (MR-AQCC)[9] theory were performed using a complete active space CASSCF(2,2) with two electrons and two orbitals to investigate the diradical character of PLY_2 dimer. The CASSCF(2,2) calculations have been performed using the bonding and antibonding orbitals of two SOMOs of **1** as the active orbital space for $\mathbf{1_2}$ (see Chart 2). The total space of configuration state functions (CSFs) was constructed by applying single and double excitations from valence orbitals to all virtual orbitals for all reference CSFs, imposing generalized interacting space restrictions[27] and freezing the 1s core orbitals. The 6-31G(d)[28] basis set has been used for the MR-AQCC computations for which the COLUMBUS program package[29] was applied. The total number of effectively unpaired electrons[30] (N_U) was computed by Head-Gordon's non-linear equation.[30]

Cambridge Structural Database Search: We performed Cambridge Structural Database[31] (CSD version 5.35) searches using the ConQuest program[31] (version 1.16) that contains published structures through November 2013. Two phenalenyl fragments were drawn in the search interface of ConQuest, and one fragment was defined as plane 1 and the other as plane 2. We defined the intermolecular distance of two central carbons from each phenalenyl fragments as DIST1, which was used to specify the search range from 2.95 and 3.50 Å (No examples were found below 3.0 Å). Out of the 360 hits and 567 fragments, about 280 structures are not PLY derivatives but are obtained as a result of the search strategy and had to be eliminated one-by-one. The remaining PLY derivatives are listed and categorized in the SI section. Furthermore, by selecting the relevant phenalenyl bearing dimer (no charges on PLY unit and no significant parallel shift between two PLY units, see details in the SI section), we found 54 structures dominated by SOMO-SOMO interaction rather than vdW interaction and we added two recently synthesized ones with bulky substituents (*tri*-methyl and *tri*-phenyl)[32].

A number of PLY-derivatives were not included in the presented statistical analysis of the intermolecular distances due to the significantly weakened or lack of SOMO-SOMO interaction as it appears from their crystal structures. The SI section discusses these molecules which we organized in five groups depending on their electronic structures. These include lack of pancake bonding due to formation of σ-bonded dimers, charged PLY systems without an unpaired electron, and substituted PLY derivatives also without an unpaired electron.

Results and Discussions

D_{cc} and $D_{\alpha\alpha}$ analysis: Figure 1 shows the distribution of the observed $\Delta = D_{cc} - D_{\alpha\alpha}$ values as a function of $D_{\alpha\alpha}$, There is only one structure (**2**$_2$) with a significant negative value of $\Delta = -0.105$ Å; there are six structures with small $|\Delta|$ values ranging from -0.008 to +0.012 Å, while the rest has significant positive Δ values with a typical value of around 0.05 Å and larger. Moreover, almost all structures have shorter intermolecular distances than the vdW contact (3.40 Å), indicating pancake bonding.

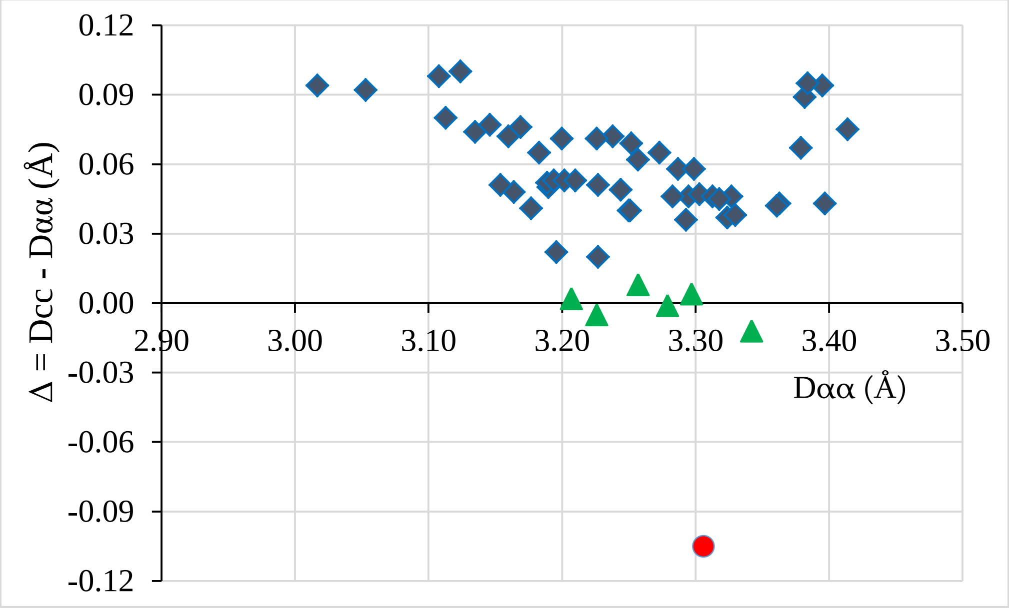


Figure 1. The 56 data pairs from the CSD showing bond distance distribution. $\Delta = D_{cc} - D_{\alpha\alpha}$ as a function of $D_{\alpha\alpha}$. Triangles and the circle refer to small $|\Delta|$ values and a significantly negative Δ value, respectively.

Furthermore, the correlation between the D_{cc} and $D_{\alpha\alpha}$ values is plotted in Figure 2. The figure shows that D_{cc} values correlate very well with $D_{\alpha\alpha}$ except again for the **2_2** case. There are six structures close to the dashed line at 45°, indicating that the difference between D_{cc} and $D_{\alpha\alpha}$ is very small. The root mean square (RMS) linear trend line provides a good fit to all data except **2_2** and has a slope value of less than 1 indicating that the trend of the $D_{cc} > D_{\alpha\alpha}$ gradually decreases along with the increasing intermolecular distance. The analysis of a subset of these systems, derivatives of **3_2**, from Haddon et al. shows an even better correlation between the D_{cc} and $D_{\alpha\alpha}$ values (see Figure S1), where the slope of the trend line is nearly one, indicating that the Δ value is nearly constant (about 0.04 Å) and independent of $D_{\alpha\alpha}$ in a broad range of π-stacking interactions. According to the RMS linear trend line, with $D_{\alpha\alpha}$ ~ 3.30 Å, structure **2_2** should have a D_{CC} value of ~3.35 Å in comparison to the actual value of 3.20 Å, or conversely, for D_{CC} = 3.20 Å, $D_{\alpha\alpha}$ should be around 3.15 Å. Thus the deviations from the fitted line by ~0.15 Å is significant and must have special reasons. Thus, we conclude that **2_2** is an outlier that is not typical as far as Δ is concerned. It still displays the other properties of pancake bonding, such as short contacts, low lying triplet, diradicaloid character and SOMO directed configuration.

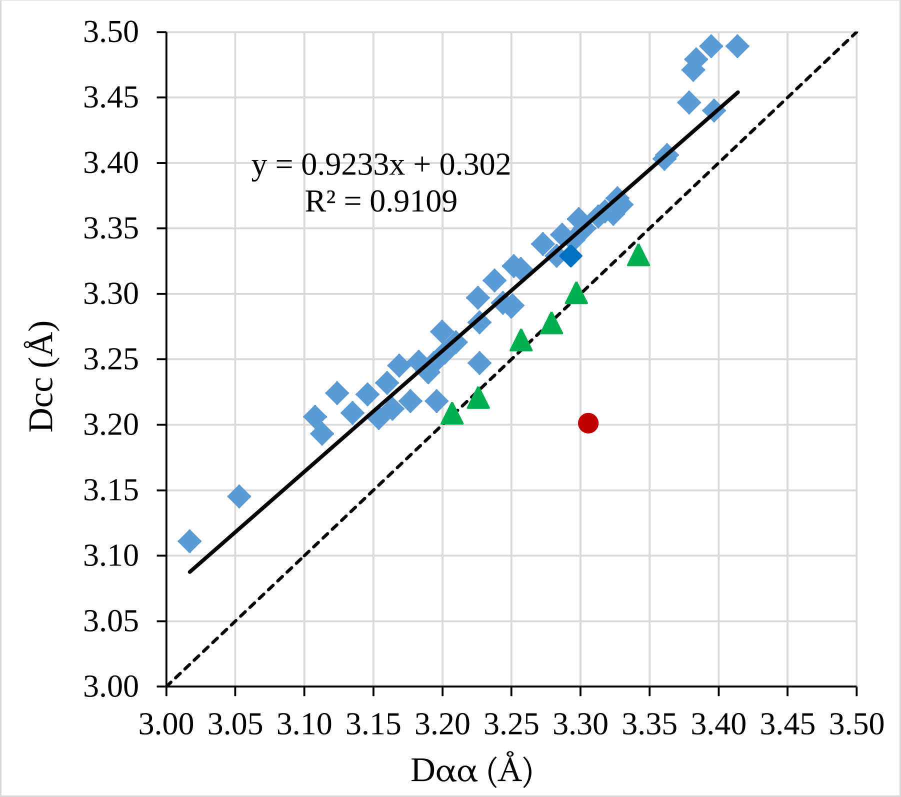


Figure 2. D_{cc} as a function of $D_{\alpha\alpha}$ from the data shown in Figure 1. All data except for the red circle for **2**$_2$ are included in the straight trend line. Green triangles and the red circle refer to small $|\Delta|$ values (<0.012 Å) and a significantly negative Δ value, respectively. The dashed line corresponds to $D_{cc} = D_{\alpha\alpha}$.

Comparison between experimental and theoretical data: We applied the M05-2X Minnesota type model in its spin-unrestricted UM05-2X/6-31+G(d,p) form, due to the fact that the dimer retains a significant degree of diradicaloid character and describes well the important case of **2**$_2$.[13g]

Three basic π dimers (**1**$_2$, **7**$_2$ and **8**$_2$) and six typical dimers with well described crystal structures (**2**$_2$, **3**$_2$, **4**$_2$, **5**$_2$, and **6**$_2$**)** were investigated at the UM05-2X/6-31+G(d,p) level. The experimental and computed Δ values are listed in Table 1 and their correlation is displayed in

Figure 3. Calculations for $\mathbf{3_2}$, $\mathbf{4_2}$, and $\mathbf{5_2}$, were performed on simplified model dimers as listed in Chart S1 in the Supporting Information. The monomers of **3**, **4**, and **5** contain two phenalenyl units, which through pancake bonding generate infinite chains rather than dimers. In the modeling we retained one phenalenyl with its environment and substituted atoms and terminated them with conjugated hydrocarbon units while retaining the local hybridization. In the same vein we also simplified the side groups to make the computations feasible. The simplified computational models still provide good agreement with the XRD data. The good correlation between the experimental and computed Δ values (Figure 3) indicates that our model approach is well suited and further confirming that the significant positive Δ values result from the SOMO-SOMO interaction rather than from the crystal packing effects

Table 1. The experimental and theoretical intermolecular distances and Δ values of π dimers. A geometry with $\Delta<0$ represent a convex overall shape, dimers with $\Delta>0$ are concave.

Species	CSD Refcode	Experimental[a]			UM05-2X/6-31+G(d,p)				Models
		D_{cc} (Å)	$D_{\alpha\alpha}$ (Å)	Δ (Å)	D_{cc} (Å)	$D_{\alpha\alpha}$ (Å)	Δ (Å)	Point Group	
$\mathbf{1_2}$					3.161	3.124	0.037	D_{3d}	
$\mathbf{2_2}$	CORFIY[2]	3.201	3.306	-0.105	3.239	3.334	-0.095	C_i	
$\mathbf{3_2}$	UBUQIR[33]	3.212	3.164	0.048	3.205	3.160	0.045	C_i	[b]
$\mathbf{4_2}$	RAYBEA[34]	3.206	3.108	0.098	3.250	3.126	0.124	C_{2h}	[b]
$\mathbf{5_2}$ **(O)**	FUTHEI[35]	3.247	3.227	0.020	3.179	3.155	0.024	C_i	[b, d]
$\mathbf{5_2}$ **(S)**	QAMVUX[36]	3.265	3.257	0.008	3.205	3.187	0.018	C_i	[b]
$\mathbf{6_2}$	DIBTEO[37]	3.218	3.177	0.041	3.246	3.238	0.008	C_{2h}[c]	
$\mathbf{7_2}$					3.116	3.022	0.094	D_{3d}[c]	[d]
$\mathbf{8_2}$					3.160	3.090	0.070	D_{3d}[c]	
$\mathbf{9_2}$	[32]	3.145	3.053	0.092	3.061	2.950	0.111	D_{3d}	
$\mathbf{10_2}$	[32]	3.111	3.017	0.094	3.066	2.936	0.130	S_6	
$\mathbf{11_2}$	[32]				3.141	3.100	0.041	S_6	

[a]Average values. [b]Calculations were done on simplified model dimers as listed in Chart S1 of the Supporting Information. [c]Close to symmetry. [d]Imaginary frequency.

While the correlation between the computed and experimental Δ values is good, note that the only data point in the 3rd quadrant refers to the anomalous structure of dimer $\mathbf{2_2}$. It appears that the large negative Δ value for $\mathbf{2_2}$ (CORFIY) in Figure 3, both experimentally and computationally arises from the steric repulsions and packing effect due to the bulky *tert*-butyl groups at all β-carbons (see also the next sub-section). The three hypothetical systems with substitutions by H (**1**), OH (**7**) and F (**8**) at the α-carbons present also shorter intermolecular distance than the vdW distance, and they also have significant positive Δ values of 0.037, 0.070 and 0.094 Å, respectively.

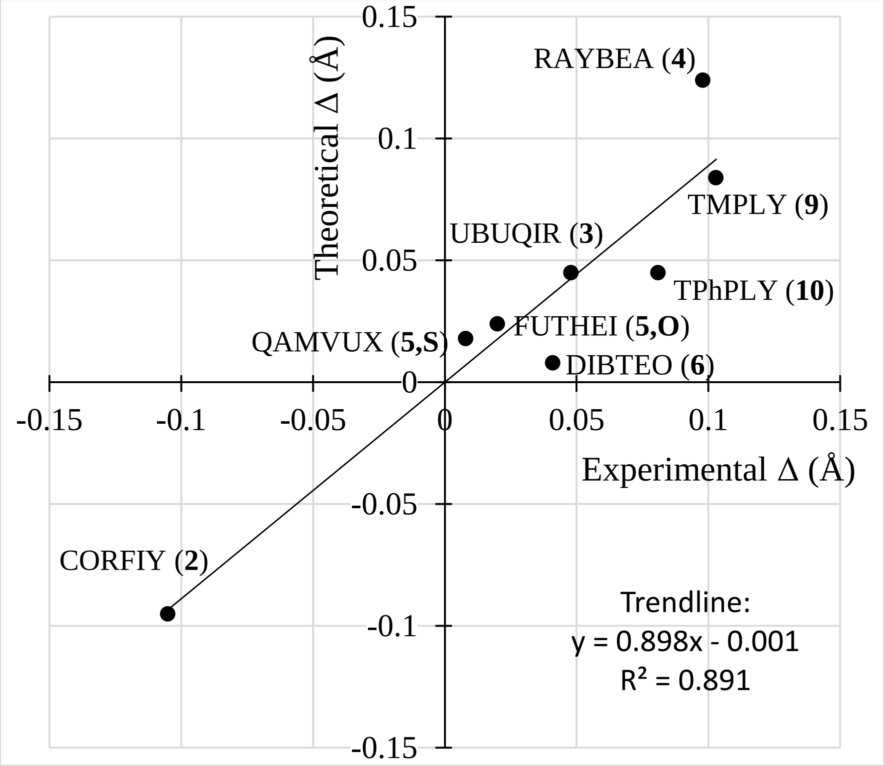
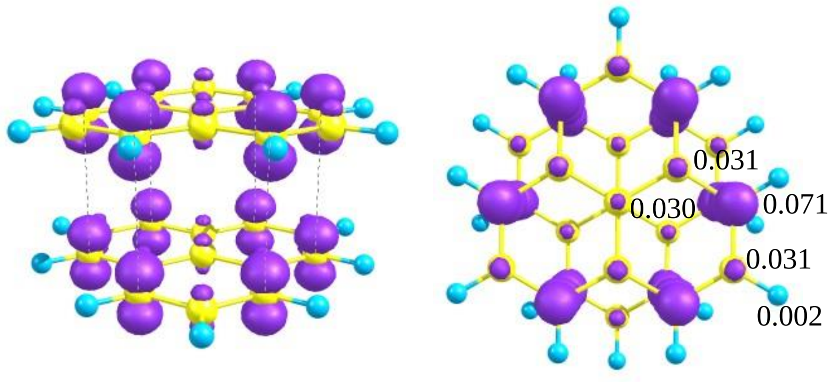


Figure 3. The correlation between experimental and theoretical Δ values (UM05-2X/6-31+G(d,p)). The CSD Refcodes of the experimental crystal structures were provided. TMPLY and TPhPLY indicate **9** and **10**, respectively. The linear trend line used all eight data points. Δ<0 represent a concave overall shape, dimers with Δ>0 are convex.

The unpaired electron density: Further evidence for the difference between roles of the central and α-carbons in pancake bonding of PLY derivatives comes from the analysis of the unpaired electron density computed at a highly correlated level. Plots are shown in Figure 4. Individual atomic values are based on a Mulliken analysis[38] of the unpaired density of the PLY_2 dimer and are also given in Figure 4. This density is largely localized on the twelve α-carbons (0.07 e) as expected for a 2e/12c bond. Note that the unpaired electron density is not zero at the two central carbons nor on the β-carbons and hydrogens. Their relative values to those of the α-carbons clearly indicate the dominant contribution to the bonding from the α–carbons on which the SOMO orbitals of the monomer are localized. The diradical character can be also described by the α-carbon spin densities computed at the UDFT level. These values are provided in Table S4 and Figure S3 at the equilibrium geometries indicating very similar diradicaloid character as measured by these α-carbon spin densities. The significant spin density values on the α-positions for all studied cases indicate that these pancake bonded π dimers possess strong diradical character with values very similar to that of the prototypical $\mathbf{1_2}$ case.



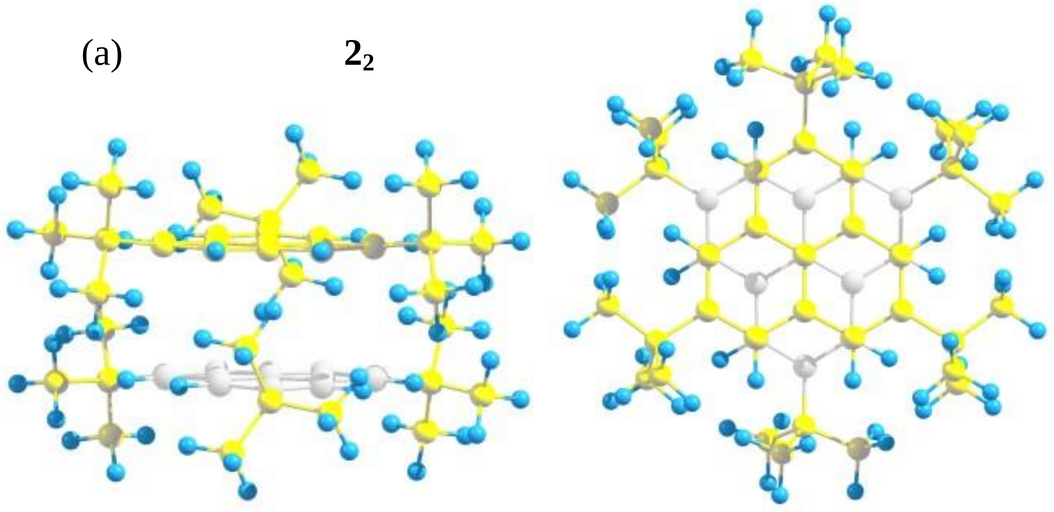
(side view) (top view)

Figure 4. Unpaired electron density (isovalue 0.003 a.u.) for $\mathbf{1_2}$ computed at the MR-AQCC(2,2)/ 6-31G(d) level. Individual values attributed to the atoms based on a Mulliken analysis for the unpaired density are also given. (N_U=1.326 e.)

The role of steric repulsions: There is a delicate balance between pancake bonding and steric repulsions in some substituted phenalenyls. The structure of the perchloro-phenalenyl (Cl analogue of **8**) deserves attention because of the large vdW radius of Cl: 1.75 Å. As analyzed in detail by Koutenis et al.[39] due to steric repulsions arising from this large size of Cl the phenalenyl part of the radical is strongly distorted from planarity yielding a ruffled edge which prevents the proximity of the α-carbons necessary for pancake bonding. Here the shortest contact distances between carbons are 3.78 Å[39] to be compared with the UM05-2X/6-31G(d,p) modeling that provided optimized dimer geometries with the shortest CC contacts in the 3.62 – 3.71 Å range with a low symmetry slipped structure. The lack of pancake bonding is evident and due to the steric repulsions of the chlorines.

Another pair of examples worthy to consider in the context of the role of steric repulsions are the *tri*-methyl (**9**) and *tri*-phenyl (**10**) derivatives which were synthesized and their pancake dimers were also characterized recently.[32] These two molecules exhibit substituents at all three β sites with a certain degree of steric requirements similar to the *tri*-*tert*-butyl case (**2**). However, only the dimer of **2** has the anomalously large negative $\Delta = -0.105$ Å. The *tri*-methyl case with its large positive $\Delta = 0.092$ Å [32] indicates that a smaller steric requirement represented by the methyl compared to the *tert*-butyl is not sufficient to suppress the primacy of the α–α contacts and their relative shortness compared to the central carbons. The *tri*-phenyl case appears more relevant, since it has a much larger overall size and steric bulk. However, the experimental π–stacking dimer structure has the “antiblade” configuration[32] and thus instead of steric crowding suppressing or preventing pancake bonding, rather, the CH…(π) phenyl interactions allow the dimer to develop full pancake bonding with a substantial and positive $\Delta = 0.094$ Å. The “antiblade” configuration refers to the observed arrangements of the six phenyl groups (the "blades") around the two phenalenyl molecules in the dimer in an arrangement that resembles two propellers put together with the blades having opposite chirality thereby providing maximum steric avoidance as illustrated in Figure 5. Such an arrangement is not possible for $\mathbf{2_2}$ with *tert*-butyls, which explains its relatively high steric crowding and the resulting anomalous behavior among the dimers of phenalenyl derivatives.

(a) $\mathbf{2_2}$



(b) $\mathbf{10_2}$

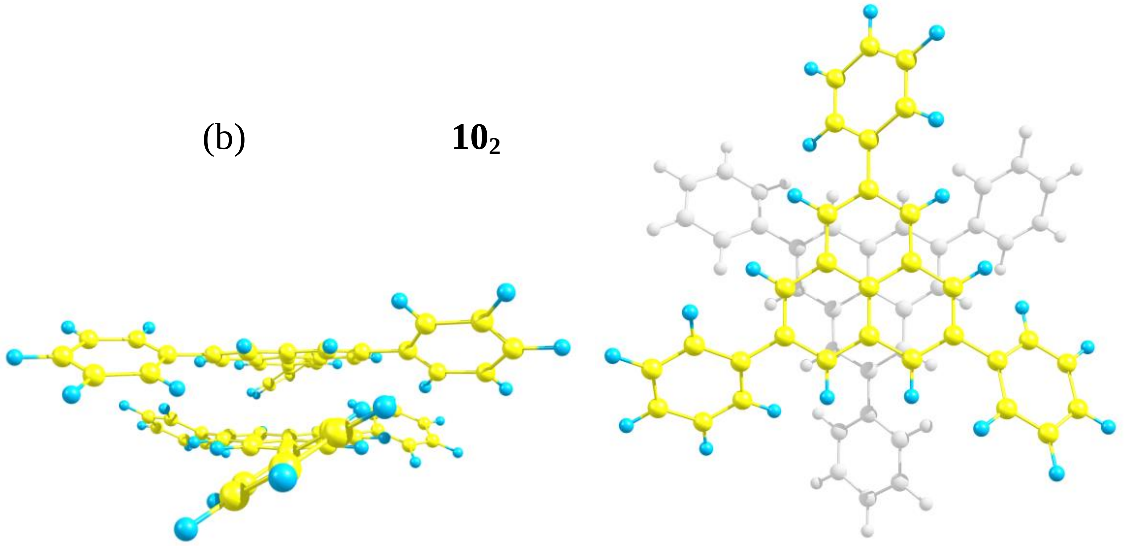


Figure 5. (a) Side and top view of the orientation of the *tert*-butyl groups in the pancake bonded dimer of $\mathbf{2_2}$ with C_i symmetry.[2] (b) Side and top view of the orientation of the phenyl "blades" in the pancake bonded dimer of **10** with S_6 symmetry.[32]

Conclusion

Chemical bonding is often inferred from structural data, especially bond distance information. For pancake bonding with two-electron multicenter bonding between π-stacking radicals two effects are essential: the characteristics of the delocalization of the two unpaired electrons from the SOMOs of the constituent radicals, and vdW interactions. Previous analysis indicates that at the short contact distances that are typical for pancake bonding the vdW term is repulsive.[6] Therefore, one generally expects that the SOMO-bearing atoms should be the closest across the π-stacking gap. An ideal system to address this question should be one that is neutral (so that the Coulomb part of the vdW interaction is small) and has a SOMO that is well localized over specific sites. PLY satisfies these criteria. It turns out, however, that one of its most studied derivatives, *tert*-butyl-PLY (**2**) has a crystal structure that indicates that the SOMO-bearing atoms are slightly farther across the π-stacking space as compared to the central CC contact where the SOMO coefficients are zero by symmetry.

The paper provides statistical evidence based on computed and XRD structures that this is an anomaly: The overwhelming majority of the PLY-derivatives that form pancake bonds have the SOMO-bearing atoms closer across the π-stacking gap as compared to the central CC contact. Computational evidence supports this finding and shows that the central atoms have an unpaired electron density much smaller than that of the SOMO-bearing α-carbons. While an earlier atoms-in-molecules (AIM) analysis based on the CASSCF(2,2)/3-21G(d) computed density indicated the presence of a bond critical point between the central CC contacts similar to those between the α-carbons across the π-stacking gap,[17] there is no evidence found in this work indicating the presence of significant electron sharing bonds involving electron density located at the central C atoms . The attractive interactions provided by the overlap of the SOMO electrons is the primary driving force for pancake bonding, and this insight should help better understand and design new pancake bonded π-stacking systems.

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