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Is There a Lower Limit to the CC Bonding Distances in Neutral Radical π-Dimers? The Case of Phenalenyl Derivatives

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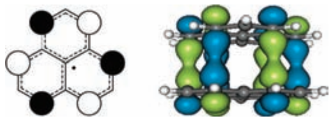
Abstract: Two-electron multicenter (2e/mc) bonding of phenalenyl (PHYL) π-dimers was found to be significantly affected by the electron density on the bonding active sites. The computational analysis shows that, upon appropriate β-substitutions, the newly introduced dimers have the shortest and strongest covalent bonding interactions seen in any neutral π-dimer. The unusual strengthening of the bonding was attributed to the reduced lone pair bond weakening effect, LPBWE, upon substitutions with electron-withdrawing groups.

Chemical bonding is one of the most fundamental concepts in chemistry. For the bonding of two carbon atoms, there is a wide ‘forbidden’ zone extending from approximately 1.77 (as in stretched C−C bonds[1]) to 2.806 Å (as in $[\mathrm{TCNE}]_2^{2-}$)[2]. Can molecules be imagined, and perhaps be made, that show contacts in this hitherto forbidden zone? What interesting properties would such molecules exhibit?

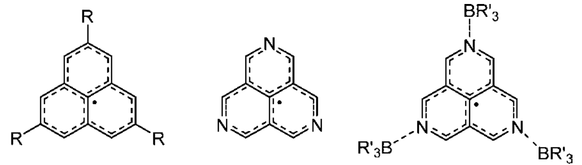
Phenalenyl (PHYL) is a neutral π-radical that has been used recently to construct organic conductors.[3] The neutral PHYL radicals can be stabilized by forming singly occupied molecular orbital based two-electron 12-center (2e/12c) bonding as shown in Scheme 1 and supported by NMR.[4] However, the long bonding distance (3.10−3.30 Å) and small interaction energies[5] weaken the argument to regard the 2e/mc bonding as covalent. The shortest 2e/mc (mc = multicenter) bonding of 2.806 Å occurs in a $[\mathrm{TCNE}]_2^{2-}$ π-dimer,[3] but the electrostatic cation−anion interactions dominate its binding energy.[6] Can a neutral covalent π-dimer be found that pushes the 2e/mc bonding distances toward the shortest possible values and dimer interaction energies toward the largest possible values by means of chemical modifications of the radical π-dimers without becoming a σ-bond?

Scheme 1



Herein, by introducing a series of substituted neutral PHYL π-dimers, we purposed to answer these questions and to explore the factors affecting the interactions. Since the SOMO density is localized on the α-positions, the α-substitutions offer a natural strategy to modify the properties of PHYL π-dimers, and actually most of the PHYL derivatives in the literatures are α-substituted (the α-substitution effects are shown in Table S-1).[7] However, in this study, we found that the β-substitutions (Scheme 2) are more effective to strengthen the 2e/12c bonding.[8]

Scheme 2



1-3 **4** **5-6**

1 R = H; **2** R =CN; **3** R=NO_2 **5** R'=H; **6** R'=Me

The M05-2X density functional method was used for geometry optimization. Interaction energies were calculated by the M05-2X DFT and the MRMP2/CASSCF(2,2) method (see Supporting Information (SI) for computational details). Both methods include dynamic electron correlations and perform well for 2e/12c bonding in π-dimers.[5,9]

The interaction energies (see Table 1) for β-substitutions are significantly enhanced, and bond distances are remarkably reduced compared to the case of $\mathbf{1}_2$(H). Although there are differences in binding energies by using the two methods, the trend is the same. Upon substitutions, the strongest bonding occurs in the dimer $\mathbf{5}_2$(NBH). The interaction energy is as high as 31.57 kcal mol^{-1} by the M05-2X method, and the calculated bond distance of 2.744 Å is the shortest in the PHYL dimer family.[10] Interestingly, the differences between R_1 and R_2 increase with increasing bond strength, which is indicative of stronger attractive forces between the α-carbon pairs than those between central carbon pairs. This is strong evidence for the presence of covalent bonding due to SOMO electron pairing. The binding energies were also evaluated for the dimers composed of the closed shell nitrogen-substituted analogues of **1**−**6** (see Table S-2), ruling out the possibility that the bond strengthening is due to multipole or dispersion forces.

Table 1. Interaction Energies (E_{int}[11] in kcal mol^{-1}) and Contact Distances (R^a in Å) of the β-Trisubstituted PHYL π-Dimers

	UM05-2X				MRMP2[b]
	R_1	R_2	$R_2 - R_1$	E_{int}	E_{int}
$\mathbf{1}_2$(H)	3.124	3.161	0.038	−8.87	−10.53
$\mathbf{2}_2$(CN)	2.967	3.091	0.124	−14.10	−19.38
$\mathbf{3}_2$(NO_2)	2.896	3.048	0.152	−11.22	−18.82
$\mathbf{4}_2$(N)	2.821	2.990	0.169	−18.91	−17.38
$\mathbf{5}_2$(NBH)	2.744	3.029	0.285	−31.57	−31.51
$\mathbf{6}_2$(NBMe)	2.831	2.937	0.112	−25.00	−

[a] R_1 and R_2 are the intradimer distances between the α-carbons and central carbons, respectively. [b] The single-point calculations at the UM05-2X optimized geometries.

Given the wide range of interaction energies obtained in this study we are intrigued by the role of covalent bonding in the newly introduced neutral radical π-dimers. If we treat the π-dimer as a two-electron model analogous to the prototypical H−H bond, within the Heitler−London approximation, the covalent term K can be estimated (see SI for the justification of this model):

$$K = 1/2(E_{\mathrm{GS}} - E_{\mathrm{T}}) \qquad (1)$$

wherein E_{GS} and E_{T} are the ground state and triplet state energies calculated with CASSCF(2,2). A similar approach has been applied to a 2,5,8-tri-*tert*-butyl-phenalenyl π-dimer.[6]

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As shown in Table 2, $|K|$ increases with increasing total interaction energy. For **5_2**(NBH), $|K|$ is almost double that of the parent PHYL dimer **1_2**(H) providing direct evidence that covalent bonding plays a key role in holding the dimer together, although the total interaction is weakened by some repulsive forces. The greatly enhanced covalent bonding indicates that carbon based 2e/12c covalent bonding might be constructed with the bond strength further approaching that of normal C−C bonds.

Table 2. Covalent Interaction Energy Components (K in kcal mol^{-1}) for Neutral Radical Dimers

1_2(H)	**2_2**(CN)	**3_2**(NO$_2$)	**4_2**(N)	**5_2**(NBH)	**6_2**(NBMe)
−10.21	−14.84	−17.14	−19.08	−21.94	−19.34

Next we explored some factors affecting the strength of the interaction. For the PHYL derivatives **1**−**6**, the substituents are only situated at the β-positions, which are at the nodes of the SOMO. Accordingly, the SOMO populations at the bonding sites (i.e., the α-site) are nearly the same for all these dimers (see Figure S-2). This excludes the effect of the SOMO−SOMO overlap populations. Note that all substituents discussed here are electron withdrawing compared to hydrogen. The inductive effect of the CN and NO$_2$ groups is to withdraw electron density through the $C_\beta - C_\alpha$ σ bonds. In addition, the resonance effect withdraws π-electrons from the conjugated PHLY plane. Both of these effects reduce the electron density at the α-carbons. The calculated NPA (natural population analysis) charges are listed in Table 3. Compared to the parent PHYL, there is a significant reduction of the total electron density at the α-carbons. For the hypothetical dimers **5_2**(NBH) and **6_2**(NBMe), a dative bond forms between boron and the sp^2 nitrogen which results in an even stronger effect for **5** and **6** compared to **4**.

Table 3. NPA Atomic Charges (e) on the α-Carbons of the PHYL Derivatives[a]

	NPA	π[b]	σ[c]
1(H)	−0.20 (0.00)[d]	+0.01 (0.00)	−0.21 (0.00)
2(CN)	−0.14 (0.06)	+0.05 (0.04)	−0.19 (0.02)
3(NO$_2$)	−0.17 (0.03)	+0.09 (0.08)	−0.26 (−0.05)
4(N)	+0.07 (0.27)	+0.09 (0.08)	−0.02 (0.19)
5(NBH)	+0.13 (0.33)	+0.13 (0.12)	0.00 (0.21)
6(NBMe)	+0.13 (0.33)	+0.13 (0.12)	0.00 (0.21)

[a] UM05-2X/6-31G(d) method. [b] π contribution. [c] σ contribution. [d] The numbers in parentheses are charges relative to **1**(H).

Based on the data in Tables 1 and 3, it appears that the reduction of electron density at the α-carbons correlates with stronger 2e/12c bonding. This can be qualitatively explained by the lone pair bond weakening effect (LPBWE), which exists in diatomic covalent bonds composed of electron rich elements like F−F and HO−OH.[12] For the parent PHYL radicals, the SOMO can be viewed as the radical orbital of F$^\bullet$ or HO$^\bullet$, and the electrons from the other π-electrons and the electrons from the σ-bonds behave effectively as lone pairs. Accordingly, the LPBWE effect is expected to be strong in the parent PHYL dimers. It accounts for the noncovalent Coulomb repulsions and Pauli repulsions, which weaken the total interaction energies of the dimers. With the introduction of electron withdrawing groups, the electron density on the α-carbons decreases. Consequently, the LPBWE effect between the SOMO electron and the "lone pairs" at the α-carbons is reduced, leading to stronger 2e/12c bonds. This indicates that the 2e/12c bonds might become more similar to normal C−C bonds upon proper substitutions. However, further quantitative investigations are needed to understand the origin of the strong covalent bonding in the substituted PHYL dimers, specifically the charge density fluctuations represented by the "pure" covalent and ionic mixing according to VB description.

Table 4. Coulomb Repulsions (U), SOMO−SOMO Splittings ($2|t|$), and Ratios of $2|t|/U$

	U/eV	$|t|$eV[13]	$2|t|/U$
1_2(H)	1.71	0.58	0.68
2_2(CN)	1.46	0.73	1.00
3_2(NO$_2$)	1.42	0.80	1.3
4_2(N)	1.53	0.88	1.15
5_2(NBH)	1.28	0.86	1.34
6_2(NBMe)	–	0.87	–

The ratio of the SOMO−SOMO splitting ($2|t|$) to the Hubbard on-site Coulomb repulsion (U) is an important parameter determining electron localization and thereby many properties of organic conductors. For the presented series of neutral π-radical dimers the approximate $2|t|/U$ values are shown in Table 4. U was estimated by the equation[13,14]

$$U = S_0 + S_2 - 2T \tag{2}$$

where S_0, S_2, and T are the energies of the ground state, the second excited singlet, and excited triplet state, respectively. Note that the SOMO−SOMO splittings depend considerably on the intermolecular packing. Therefore, the substituted PHYL dimers are predicted to have a much larger $2|t|/U$ than the parent dimer **1_2**(H). This may provide opportunities to control the properties of extended materials composed of these and analogous radicals.

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Supporting Information Available: Computational details and structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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