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COMMUNICATIONS

Published on Web 02/03/2006

# Aromaticity on the Pancake-Bonded Dimer of Neutral Phenalenyl Radical as Studied by MS and NMR Spectroscopies and NICS Analysis

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The development of stable organic radicals has created a new class of magnetic[1] and conducting materials.[2] Among them, certain $\pi$-radicals were found to form unusual molecular aggregates in crystals that raised a question on the nature of chemical bonds, as seen in exceptionally long ($\geq$2.9 Å) C−C bonds[3] or *pancake* bonds[4,5] between planar $\pi$-radicals. The phenomenon has also been observed in liquid phase by ESR/UV−vis studies, showing exothermic enthalpy changes of $-6$ to $-10$ kcal mol$^{-1}$ upon $\pi$-dimerization.[3c] Regardless of whether the radicals are ionic or neutral, the attractive force may be dominated by effective $\pi-\pi$ interactions between singly occupied molecular orbitals (SOMOs). However, the structural ambiguity in solution has prevented detailed assessment of the electronic nature of the supramolecular $\pi$-complexes.

Tri-*tert*-butylated phenalenyl (TBPLY) **1**, synthesized and isolated by our hands,[6] has drawn attention as a good model of a pancake-bonded dimer, showing a 12-center-2-electron cofacial association with well-defined $D_{3d}$ symmetry (Figure 1).[7] It is also noted that **1** is a neutral hydrocarbon that is free from charges, counterions, and heteroatoms. These features have facilitated the quantum chemical analyses of such intermediate regions in chemical bond formation.[8] Furthermore, **1** is believed to form the same $\pi$-dimer in solution as that in crystal, as indicated by a spectroscopic study of Kochi's group.[9,10] In this report, we have probed into the molecular and electronic structures of this dimeric $\pi$-complex in solution by direct spectroscopic measurements and theoretical analysis.

The compelling evidence of the dimeric entity of **1** in the equilibrium state in solution was provided by cold-spray ionization mass spectrometry (CSI-MS),[11] where substances can be ionized at much lower temperatures than conventional ESI-MS. The dimer signal of **1** was clearly observed at $m/z = 666.5$ (Figure 2). The accompanying signals are reproduced by isotope pattern calculation. A peak enhancement ratio, $I_{\mathrm{CSI}}/I_{\mathrm{ESI}} = 25$ at the main dimer signal has demonstrated the advantage of CSI-MS for detecting molecular aggregates in solution.

We examined NMR spectroscopy to identify the chemical entity because a significant dimer concentration of **1** was suggested at lower temperatures.[9,10] In $^{1}$H NMR at 270 K (Figure 3), a broad peak at 3.2 ppm is attributed to the *tert*-butyl protons of the monomer **1**, which undergoes a downfield shift due to the unpaired electron density.[6b] With decreasing temperature, this peak shifted upfield, and finally came to the normal region of alkyl protons (1.48 ppm) at 180 K. Also, a new peak emerged in the aromatic region (6.47 ppm). The intensity ratio of these peaks was 27:6, giving a sure proof of a highly symmetric structure of the dimer. Moreover, four $^{13}$C signals appeared at 120−143 ppm, which meets the symmetry requirement of $D_{3d}$. It is noted that thermochromism[12] is observed for **1** as seen in the solution color (Figure 3) and UV−vis spectra,[9,13] which coincided with the NMR spectral change. Thus, the coloring process should be governed by the $\pi$-dimerization. To our knowledge, this is the first solution NMR observation of a pancake-bonded radical dimer.

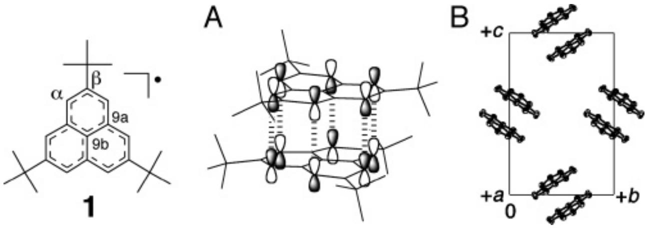

***Figure 1.*** (A) Schematic drawing of $\pi$-dimerization of TBPLY **1**, and (B) crystal packing diagram (*tert*-butyl groups are omitted).

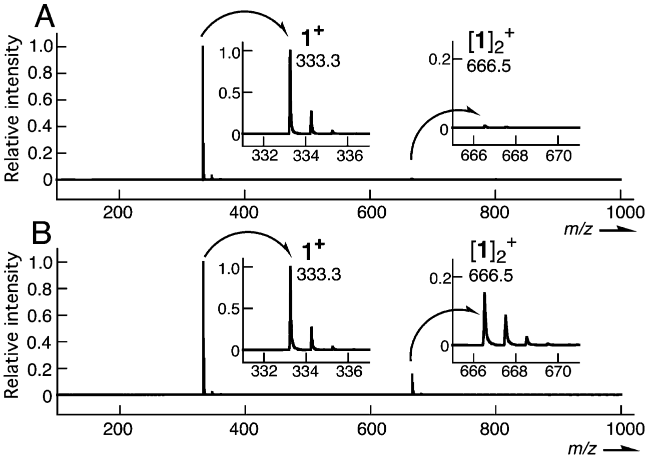

***Figure 2.*** (A) ESI-MS spectra ionized at 523 K and (B) CSI-MS spectra ionized at 273 K of **1** in a 1:1 $CH_3CN$−toluene solution.

The emergence of the NMR signals in the aromatic region has provided a fascinating viewpoint of analysis. To reveal the local environment of the dimer in terms of aromaticity, we first computed NMR chemical shifts based on an optimized structure with $D_{3d}$ symmetry,[14] giving a satisfactory agreement with the experiment; all the $^{1}$H and $^{13}$C peaks at 180 K were well reproduced (Figure 3). Next, we focused on nucleus-independent chemical shift (NICS), a representative measure of aromaticity.[15,16] As shown in Figure 4, the ring center of the $\pi$-dimer became more aromatic ($-7.1$ ppm)

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10.1021/ja058387z CCC: $33.50 © 2006 American Chemical Society

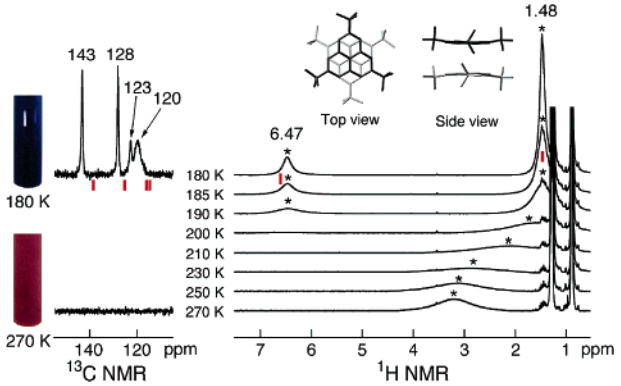

***Figure 3.*** $^1$H and $^{13}$C NMR spectra of **1** in hexane-$d_{14}$ ($3 \times 10^{-2}$ M). Asterisks denote the peak top positions. Red lines show the calculated chemical shifts for an optimized $\pi$-dimer structure (see the inset). The observed thermochromism in solution is also shown.

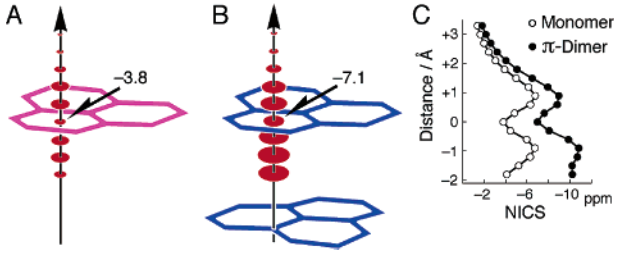

***Figure 4.*** Out-of-plane NICS distributions at the ring center of (A) the monomer **1** and (B) the $\pi$-dimer of **1** at the interval of 0.6 Å. The radius of each red circle corresponds to the magnitude of each negative NICS. (C) Another representation of the distributions; the interval is 0.3 Å.

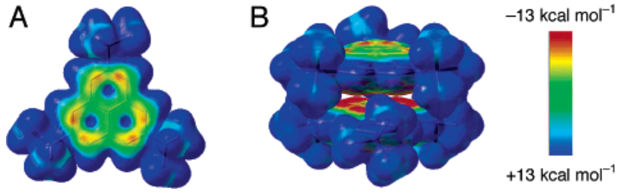

***Figure 5.*** Electrostatic potential surface of (A) the monomer **1** and (B) the $\pi$-dimer of **1**.

than that of the monomer (−3.8 ppm). The trend of the enhancement was more pronounced in the interior of the dimer. For comparison, we calculated benzene $\pi$-dimers[17] and found that the similar effect was seen but was not so large in magnitude as the present case.

The magnetically shielded interior of the dimer of **1** indicates a significant increase in electron density there. Then we moved on to the electrostatic potential surface (Figure 5). Despite the whole neutrality of the dimer, negative electron density was largely populated at the internal region, contrasting with the external environment. The imbalanced electron distribution is totally consistent with the anomalous NICS distribution. The feature seems reasonable for a covalent bonding region, where unpaired electrons are shared by interacting atoms, or interacting molecules in this case.[18]

In conclusion, we have reported the first observation of CSI-MS and NMR spectra in solution of a pancake-bonded radical dimer, using tri-*tert*-butylated phenalenyl **1**. The 12-center-2-electron-long C−C bond[3b] with the $D_{3d}$ structure has been experimentally confirmed and interpreted from the viewpoint of the local magnetic environment. The aromaticity generation in the bonding region can be another factor of gaining stability in $\pi$-dimerization, the generality of which is of interest to be explored using other model systems.[3,19]

**Acknowledgment.** We thank Mr. K. Konuma for CSI-MS measurements. This work was partly supported by PRESTO-JST, Grant-in-Aid for Scientific Research in Priority Areas "Application of Molecular Spins" (Area No. 769) from Ministry of Education, Culture, Sports, Science, and Technology, Japan, and 21COE program "Creation of Integrated EcoChemistry" of Osaka University.

**Supporting Information Available:** All the authors of ref 14b, ESR and UV−vis study on thermodynamic parameters, NICS analysis of benzene dimers, and the coordinate data of the optimized $\pi$-dimer structure of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA058387Z