Communications

Intramolecular π-Stacking Interactions of Bridged Bis-p-Phenylenediamine Radical Cations and Diradical Dications: Charge-Transfer versus Spin-Coupling**

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In memory of Jay Kazuo Kochi

Considerable work has been done on intermolecular π-stacking of radical and radical-ion systems using unlinked examples. Different examples of such systems usually differ so greatly in their $\Delta H°$ and $\Delta S°$ values for association that determining details of the structural factors that change their equilibrium constants for dimerization (where $\Delta S°$ plays a major role)[1a] by comparing different compounds is difficult. The most extensive recent work on formation of neutral compound, π-radical dimers, which are paramagnetic and π-stacked, and dimer radical ions, which are diamagnetic diionic π-stacked pairs, has come from Kochi's group. Characterization of these systems, especially by X-ray crystallography, became the last major project of Jay Kochi's distinguished career (he passed away in August 2008).[1,2]

The work discussed herein concerns the oxidized forms of dimeric PD compounds that are doubly linked by three carbon bridges, making them tetraaza[5,5]paracyclophane derivatives. We previously investigated the oxidation of dimeric doubly polymethylene-bridged p-phenylene diamines (PD derivatives), including **1(R)**, R = Me, Et, and iPr (Scheme 1).[3]

For **1(Me)** and **1(Et)** dicationic forms of dimeric PD compounds in solution there are three conformations in equilibrium (Scheme 2).[4]

1(Me)$^{2+}$ and **1(Et)**$^{2+}$ exist almost exclusively as singlets, and low temperature NMR studies showed that three all *gauche* conformations are present in detectable amounts near −60°C, where N-aryl bond rotation becomes slow enough on the NMR time scale to sharpen up the lines enough to identify the conformations.[4] We were unable to isolate crystals of
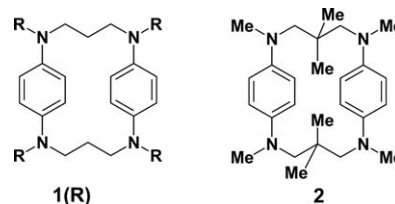
Scheme 1. Dimeric doubly three-carbon-bridged p-phenylene diamines.
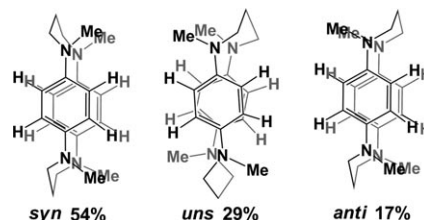
Scheme 2. Three conformations of dimeric diradical dications **1**$^{2+}$.

1(Me)$^+$, even from solutions containing a large excess of neutral **1(Me)**. We still obtained the dication, in an all *gauche* conformation, but one having its PD$^+$ rings displaced from each other instead of being π-stacked. There was intermolecular π-stacking in this crystal, consistent with intermolecular attractive interaction between the PD$^+$ rings when intramolecular stabilization was not available.[4]

The monocation oxidation level is a mixed valence (MV) one for these dimeric compounds, and could be either charge-localized (Robin–Day Class II)[5] or delocalized (Robin–Day Class III). There has been much more study of MV compounds having π-type overlap (p orbitals having nearly parallel axes) than of those having a σ-stacking format (p orbitals having nearly co-linear axes). These two motifs for MV compounds are illustrated in Scheme 3 for the simple cases of MV hydrazine radical cations and diamine dimer radical cations, both of which are Class III MV compounds.

The greater study of the π-bonding than the σ bonding motif has probably occurred both for synthetic reasons (the π-bonded MV pounds are much more stable than the σ-bonded ones) and because the familiar simple Hush theory equations that let us calculate the electronic coupling make the often unstated assumption that there is no direct overlap between the charge-bearing units. The 3 e$^-$ σ-bond/π-stacking motif for bonding clearly causes overlap of charge-bearing units that employ it. In this work we investigate the effect of substituting

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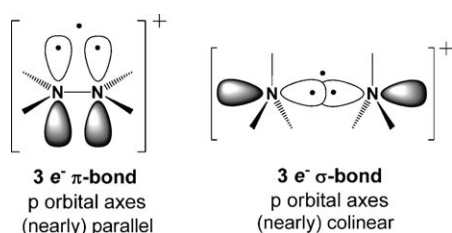
Scheme 3. 3 e⁻ π-bonds in idealized hydrazine radical cations and 3 e⁻ σ-bonds in amine dimer radical cations.

methyl groups at the middle carbons of the trimethylene bridges of **1(Me)** to give the octamethylated compound **2** on its oxidation products. Oxidation of **2** with two equivalents of NO⁺SbF₆⁻ gave the dication. The X-ray structure of **2²⁺**-(SbF₆⁻)₂ shows that it is in a π-stacked, all *gauche* NCCC twist angle conformation that is *uns*, with alkyl groups *syn* at one PD⁺ unit and *anti* at the other (Figure 1).
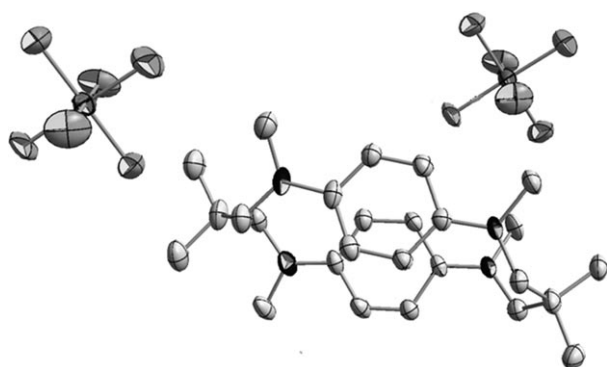

Figure 1. Ellipsoid plot of the asymmetric unit of **2²⁺**(SbF₆⁻)₂·2 CH₃CN·0.5 CH₂Cl₂ (which also contains other solvent that is unresolved), thermal ellipsoids set at 40% probability. Black N atoms.

The monocation **2**⁺B(C₆F₅)₄⁻ was successfully isolated using Ag⁺B(C₆F₅)₄⁻ as oxidant, which as Geiger and Barrière have noted, is a superior counterion for enhancing differences in redox potential for multiple electron-transfer reactions.[6] Electron-transfer disproportionation to the dication occurred with the smaller SbF₆⁻ counterion. **2**⁺B(C₆F₅)₄⁻ also crystallized in the π-stacked all *gauche uns* conformation. Both hexane and methylene chloride appear in the crystal, and an ellipsoid drawing of its structure with solvent omitted appears in Figure 2.

We note that one PD⁺ N,N distance and all six closest CH,CH contacts are at less than van der Waals separation for **2²⁺**. Although the *uns* conformation was observed by NMR spectroscopy in solution for both **1(Me)²⁺** and **1(Et)²⁺**, these are the first available X-ray data for examples having *uns* conformations. The structure of **2**⁺ is the first available X-ray data for any MV + 1 salt in this series, and luckily, both are in the same conformation, making comparison of their geometrical parameters more significant. The most important result for **2**⁺ is that this species, like **2²⁺** is delocalized, demonstrated by having comparable C_ArN distances in both
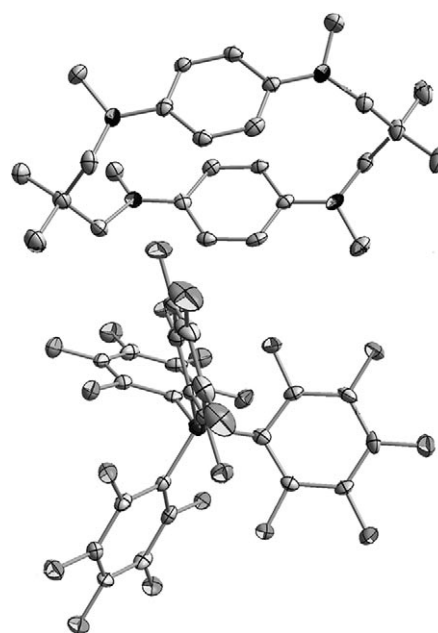

Figure 2. Ellipsoid plot of the ionic units of the X-ray structure of **2**⁺ B(C₆F₅)₄⁻, solvent omitted, thermal ellipsoids set at 50% probability. Black N atoms.

PD units that are as expected, significantly longer than those of **2²⁺**. A π-stacked structure of **2**⁺ makes it obvious that removal of one electron from both PD units also makes them attract each other instead of repel like the neutral compounds do, as expected from the work of Kochi's group on intermolecular examples.[1] The X-ray data are completely unambiguous in demonstrating that both **2**⁺ and **2²⁺** are charge delocalized, and we do not doubt that **1(Me)**⁺ is delocalized as well. The non-bonded heavy atom distances (first three rows of Table 1) are all significantly longer for the monocation than for the dication, showing that the π-stacking interaction is more efficient for the dication singlet than for the monocation doublet, despite the Coulomb repulsion effect for the dication. Such information was not extracted from Kochi's studies of intermolecular examples, which have many more degrees of freedom than these intramolecular cases, and did not have the constraint of three carbon bridges holding the π systems together. Recently Stoddart and co-workers have obtained X-ray structures of both mono- and dications of π-stacked tetrathiafulvalenes in cantenanes that show the same trend, implying that this result is not an isolated phenomenon that only occurs for PD-centered radical ions.[7]

Local density approximation (LDA) calculations like those reported earlier for **1(Me)²⁺** and **1(Et)²⁺**[4] were carried out on the *syn*, *anti*, and *uns* conformations of **2²⁺** and **2**⁺. The relative energies obtained and room temperature populations calculated from them are summarized in Table 2. It will be seen that the *uns* conformation is calculated to dominate the conformational mixture for **2²⁺**, and be almost the only one present for **2**⁺.

It seems conceivable that **2**⁺ might have been delocalized in the solid state, but not in solution. The small effect of solvent changes on its optical absorption spectrum demonstrates that solutions of **2**⁺ are also charge delocalized. Table 3

Table 1: Selected interatomic distances [Å] and angles [°] for the X-ray structures of **2²⁺** and **2⁺** salts, both in *uns* conformations (one PD unit *anti*, the other *syn*).

Parameter	**2²⁺**	**2⁺**
$d(N,N)$	2.935(7), 3.595(8)	3.042(3), 3.591(3)
$d(Cq,Cq)$	3.034(8), 3.320(9)	3.188(4), 3.448(4)
$d(CH,CH)$	3.078(9), 3.184(9)	3.216(4), 3.359(4)
	3.241(9), 3.297(9)	3.397(4), 3.492(4)
$d(C_{Ar}N)$	1.351(8), 1.347(8) (*anti* PD)	1.379(4), 1.374(4)
	1.353(8), 1.359(8) (*syn* PD)	(*trans* PD)
		1.376(4), 1.386(4)
		(*cis* PD)
N lp twist[b]	17.2(4),19.4(4) (*anti* PD)	17.16(12), 18.4(2)
	14.8(5), 21.8(3) (*syn* PD)	(*anti* PD)
		12.08(15), 15.9(2)
		(*syn* PD)
NCCC twist	57.0(8), −67.3(7) (Me's *trans*)	−54.2(4), −56.6(4)
	54.9(9), 58.0(9) (Me's *cis*)	(Me's *trans*)
		−53.8(4), 70.9(3)
		(Me's *cis*)
Mean C₆ plane ∡	2.5(2)°	4.15(9)°
N,N;N,N twist	−10.34(13)°	26.39(8)°

[a] $\mathbf{2^{2+}} = [C_{26}H_{40}N_4]^{2+}[SbF_6]_2 \cdot 2\,MeCN \cdot 0.5\,CH_2Cl_2 \cdot x$ solvent, $\mathbf{2^+} = [C_{26}H_{40}N_4]^+[C_{24}BF_{20}] \cdot 0.36\,C_6H_{14} \cdot 0.27\,CH_2Cl_2$. [b] Calculated as the angle between the mean C_6 plane and the NCH_3CH_2 plane of each nitrogen. Cq = aromatic quaternary carbon atoms.

Table 2: Relative enthalpies [kcal mol⁻¹] and populations (pop.) estimated at 295 K[a] from LDA calculations[b] on the expected solution conformations of **2²⁺**.

Species	Conf.	*syn*	*uns*	*anti*
2²⁺	rel. enthalpy	0.00	0.03	0.48
	295 K pop.	0.19	0.73	0.08
2⁺	rel. enthalpy	1.57	0	2.06
	295 K pop.	0.02	0.97	0.01

[a] Relative population estimates include the symmetry number (2 for *syn* and *anti*, 8 for *uns*, see Supporting Information for details). [b] All calculations used a 6-311 + G(d) basis set and an integration quadrature with 75 radial points (Euler–Maclarin) and 302 angular points (Lebedev).

Table 3: Solvent effect on **2⁺** absorption maxima, unit 10³ cm⁻¹.

Solvent	γ[b]	Low E broad band	High E band
Et₂O	0.316	6.33	15.39
THF	0.375	6.31	15.37
CH₂Cl₂	0.383	6.20	15.31
DMF	0.463	6.37	15.38
PC[a]	0.481	6.39	15.41
Me₂C=O	0.495	6.40	15.43
MeCN	0.528	6.43	15.46
MeOH	0.538	6.40	15.46

[a] Propylene carbonate. [b] γ is the Pekar factor, $n^{-2} - \varepsilon_{static}^{-1}$.

shows the sensitivity to eight solvents of the near IR and visible absorption bands for **2⁺**.

Figure 3 shows the absorption spectrum of **2⁺** in CH₂Cl₂, compared with the TD-LDA (TD = Time dependent) calculation for this compound. As shown in Table 2, **2⁺** is calculated to be almost exclusively (98%) in the *uns* conformation, so only the calculation for the *uns* conformation is shown.
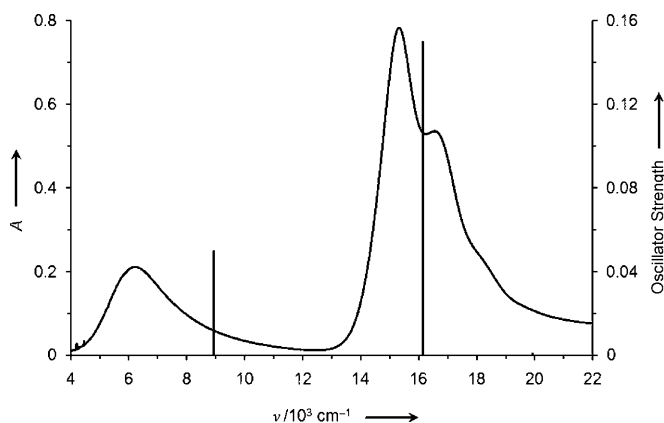

Figure 3. The optical spectrum of **2⁺** in CH₂Cl₂ and the TD-LDA calculated optical spectrum (vertical lines).

The fondly-held assertion that the electronic coupling for a delocalized mixed-valence compound can be obtained simply by dividing its transition energy by two cannot be quantitatively correct, because it assumes that the band being analyzed arises from a single two-state model electronic splitting. Because delocalized mixed-valence compounds are actually symmetrical, the intense and narrow bands that have been assigned as this transition by people using the $H_{ab} = E/2$ relationship would be symmetry forbidden, and vanishingly weak. The energies of these bands are instead determined by at least two electronic couplings and three diabatic energies, as demonstrated in the neighboring orbital model introduced by Zink, Nelsen, and their co-workers.[8]

Figure 4 shows the relative intensities calculated by TD-LDA for the three conformations expected for the dication. Also like the compounds with unmethylated bridges, the *uns* conformation of **2²⁺** is calculated to have its low-energy band significantly lower in energy than the *syn* and *anti* conformations, which are calculated to overlap, and the higher energy band is calculated to lie much closer to the observed value. The higher energy band shows less resolution for **2²⁺** than it does for **2⁺**, and occurs at significantly higher energy, which might be caused by the closer approach of the PD⁺ units in the dication than the half-oxidized PD units in the radical cation.
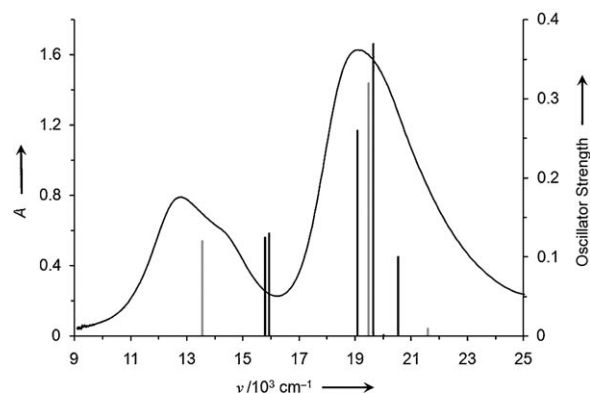

Figure 4. The optical spectrum of **2²⁺** and the TD-LDA calculated spectra of its three expected conformations (vertical lines: light gray *uns*, dark gray *anti*, black *syn* conformations).

The NMR spectrum of our sample of 2^{2+} (SbF_6^-)$_2$ in 3:1 $CD_3OD:CD_3CN$ between about $\delta = 5.3$ and 7.5 ppm (see Supporting Information, Figure S10) shows quite broad signals in the aromatic region near $\delta = 7.2$, 7.04, 6.9, and 5.7 ppm. The aromatic signals of 2^{2+} sharpen as the temperature is lowered and NC rotation becomes slower, revealing doublets assigned to individual hydrogen atoms at $-50\,°C$ at δ values of 7.23 ($J \approx 9.6$ Hz), 7.03 ($J \approx 9.6$ Hz), 6.89 ($J \approx 9.6$ Hz), 6.80 ($J \approx 9.6$ Hz), 6.08 ($J \approx 9.6$ Hz), 6.02 ($J \approx 10$ Hz), 5.55 ($J \approx 9.4$ Hz), and 5.46 ppm ($J \approx 9.5$ Hz), see Figure 5. These
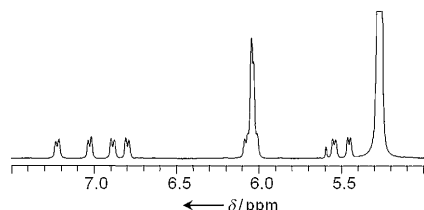

Figure 5. Aromatic region of the 1H NMR spectrum of 2^{2+} at $-50\,°C$ in 3:1 $CD_3OD:CD_3CN$. The intense signal near $\delta = 5.37$ ppm is the methanol OH impurity, which moves upfield as the temperature is lowered, and the small one near $\delta = 5.6$ ppm appears to correspond to the $\delta \approx 5.2$ ppm peak at 20°C (see Supporting information for details).

signals are attributed to the aromatic hydrogen atoms of the *uns* conformation of 2^{2+}. The $\delta = 6.08$ and 6.02 ppm signals partially overlap with a diamagnetic impurity at $\delta = 6.06$ ppm, but the *syn* and *anti* conformation signals are also expected in this region, so we cannot tell how much of these conformations are present.

The EPR and ENDOR spectra of similar molecules with three and five carbon bridges have been published in collaboration with Gescheidt (T.U. Graz), and J values obtained from low temperature EPR intensity changes in collaboration with Teki (Osaka City University).[9]

In Summary, we have shown that changing from two $(CH_2)_3$ bridges to $CH_2CMe_2CH_2$ bridges in "dimeric" three-carbon-bridged PD-containing [5.5]-paracyclophanes significantly increases the population of unsymmetrically substituted conformations for both the $+1$ and $+2$ oxidation states. This result is caused by steric interactions with the methyl groups of the bridge and is predicted by LDA calculations. The $+1$ oxidation state is delocalized both in the solid state, shown by its X-ray crystal structure, and in solution, as shown by the small solvent effect on its band maxima. The distance

between the PD rings of the dication was found to be slightly smaller than that of the monocation in the X-ray structures, as well as in the LDA calculations, so π-stacking is sufficiently more efficient in the spin-paired singlet dication than in the doublet monocation for these intramolecular examples to overcome the Coulomb charge-repulsion effect at significantly less than van der Waals distances. Understanding, at the molecular level, this notion of through-space electron-hopping mechanisms between open-shell radical ions (polarons) and their neutral counterparts, in distinction from competitive dimerization of open-shell radical ions to form diamagnetic closed-shell systems, is crucial to design new organic electronic devices.[10–12]

[1] For the unbridged examples: a) J.-M. Lü, S. V. Rosokha, J. K. Kochi, *J. Am. Chem. Soc.* **2003**, *125*, 12161–12171; b) S. V. Rosokha, J. K. Kochi, *J. Am. Chem. Soc.* **2007**, *129*, 3683–3697; c) S. V. Rosokha, M. D. Newton, A. S. Jalilov, J. K. Kochi, *J. Am. Chem. Soc.* **2008**, *130*, 1944–1952; d) S. V. Rosokha, J. K. Kochi, *Acc. Chem. Res.* **2008**, *41*, 641–653.

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