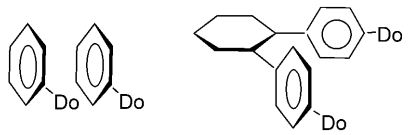
Conjugation

DOI: 10.1002/ange.200501005

Through-Space (Cofacial) π-Delocalization among Multiple Aromatic Centers: Toroidal Conjugation in Hexaphenylbenzene-like Radical Cations**

*Duoli Sun, Sergiy V. Rosokha, and Jay K. Kochi**

Strong (nonbonded) π-to-π interactions were first recognized by the appearance of characteristic near-IR absorption bands and doubled hyperfine lines in the electronic and ESR spectra of various intermolecular dimer cations formed upon electron ejection from stacked aromatic donors, as in $\mathbf{I} \rightarrow \mathbf{I}^{+\cdot} + e^-$.[1,2] Equivalent spectral changes are also observed in the corresponding intramolecular assembly derived from tethering the same aromatic dyad, as in **II** (Do = electron donating functional group).[3,4] Indeed, such a spectral (NIR, ESR) equivalence relates to the common π-electronic transition from the filled HOMO to the singly occupied LUMO that are



I **II**

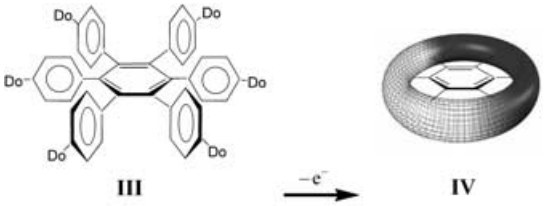
[*] Dr. D. Sun, Dr. S. V. Rosokha, Prof. Dr. J. K. Kochi
Chemistry Department
University of Houston
Houston, TX 77204 (USA)
Fax: (+1) 713-743-2709
E-mail: jkochi@uh.edu

[**] We thank I. S. Neretin for computational assistance and the R. A. Welch Foundation for financial support.

Supporting information for this article (synthesis, characterization, and X-ray data for the hexaarylbenzene donors **1**–**3**, spectral (Vis-NIR) characterization of their radical cations, and Mulliken–Hush (six-state) analysis of the radical cation of **1**) is available on the WWW under http://www.angewandte.org or from the author.

more or less equally disposed in **I** and **II**. This HOMO–LUMO or charge-transfer (intervalence) transition is well accommodated by Mulliken–Hush theory to provide the important connection between the experimental NIR spectrum and the electronic coupling energy (H_{DA}) that binds such cofacial moieties.[5]

In broader context, the further applicability of Mulliken–Hush theory to extended aromatic (stacking) arrays that are inherent to molecular conductors and wires for organic materials science,[6] depends first on the stepwise extension of the dyad structure **II** to the closed-loop hexad structure **III**,[7] in which extensive π-electron delocalization would result in complete toroidal conjugation **IV** in the limit of



strong interactions among the six (Do-phenyl) centers.[8] To this end, we now report the synthesis and structural characterization of the hexadonor **1** (see the Supporting Information for structure) which is an analogue of **III** containing six electron-rich anilinyl groups with the six donor groups Do being *N*,*N*-diethylamino or *N*-methyl-*N*-ethylamino. Compound **1** has highly unusual redox properties in two important ways: First, the linear-sweep voltammogram of the hexaanilinylbenzene **1** (Figure 1 A) shows a reversible one-electron-

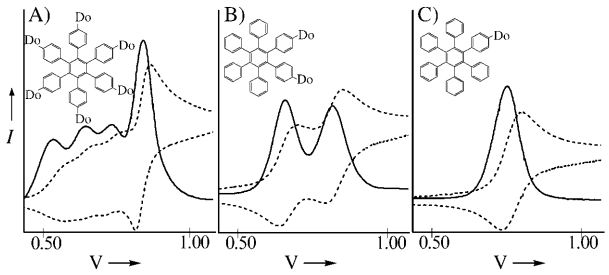


Figure 1. CV (dotted line) and Osteryoung square-wave voltammetry (OSWV; solid line) in V versus SCE of A) hexadonor **1**, B) bidonor **2**, and C) monodonor **3**.

oxidation wave at $E_{1/2} = 0.51$ V (versus saturated calomel electrode (SCE)) which is strongly (negative) shifted relative to those of the bis and monoanilinyl analogues **2** and **3** (Figure 1 B and C). Indeed, the voltammetry of **1** shows four separate anodic waves at 0.51, 0.64, 0.74, and 0.86 V; and controlled-potential coulommetry reveals each of the first three waves to correspond to reversible one-electron changes and the fourth a composite three-electron process.

The wide separation of the potentials of the redox events in **1** allow the radical cation (**1**$^{\bullet+}$) to be quantitatively prepared either by controlled-potential anodic oxidation or by chemical oxidation with dodecamethylcarboranyl (B$^{\bullet}$).[3b] In the latter case, the blue polycrystalline solid is isolated in excellent yields and quantitatively analyzed as **1**$^{\bullet+}$B$^-$.

The second unusual redox property of **1** is detected in the electronic spectrum of **1**$^{\bullet+}$, generated by either method. This spectrum shows the highly distinctive low-energy absorption (Figure 2) that stretches continuously from the visible (red)

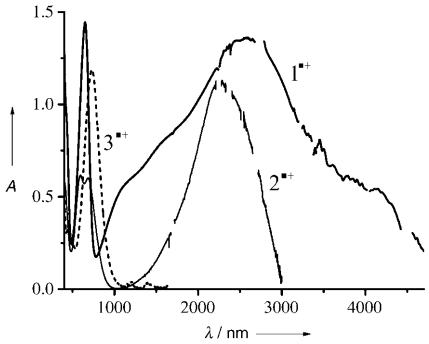
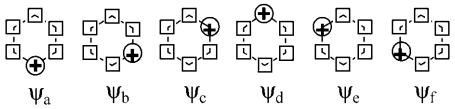


Figure 2. Electronic spectrum of hexadonor radical cation **1**$^{\bullet+}$ in comparison with its bidonor **2**$^{\bullet+}$ and monodonor **3**$^{\bullet+}$ models.

region all the way to the infrared region beyond 4000 nm (with $\lambda_{max} = 2570$ nm, $\varepsilon = 3300\ M^{-1}cm^{-1}$). By comparison, the bidonor analogue **2**$^{\bullet+}$ merely exhibits a single near-Gaussian[9] band in the NIR region with $\lambda_{max} = 2300$ nm ($\varepsilon = 2800\ M^{-1}cm^{-1}$); and the monodonor **3**$^{\bullet+}$ is completely transparent in the region beyond 1000 nm. Indeed, such characteristic low-energy optical behaviors in **1**$^{\bullet+}$ and **2**$^{\bullet+}$ are diagnostic of intervalence transitions as observed in both organic and inorganic mixed-valence systems.[3,5,10]

To account for the spectral and electrochemical properties of the radical cation **1**$^{\bullet+}$, we extend the Mulliken–Hush (two-state) model to the redox system with six equivalent (anilinyl) centers. The diabatic (non-interacting) states $\psi_a - \psi_f$ with the hole localized on different centers in the hexagonal array are presented pictorially in Scheme 1 (hole = ⊕) and the adiabatic wave functions ($\Psi_1 - \Psi_6$) of **1**$^{\bullet+}$ are given in Equation (1).

$$\Psi_i = a_i\,\psi_a + b_i\,\psi_a + c_i\,\psi_c + d_i\,\psi_d + e_i\,\psi_e + f_i\,\psi_f \qquad (1)$$

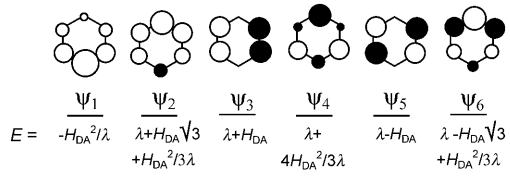


Scheme 1.

To evaluate the adiabatic states, we follow Lambert–Noll[7b] and take into account only equivalent interactions (H_{DA}) between neighboring groups (neglecting other interactions), and set the diabatic state ψ_a with relaxed nuclear geometry of all six centers as the zero point of reaction coordinate (i.e., $H_{aa} = 0$ at $X = 0$). As such, the energy of the other diabatic states at the same point on the nuclear reaction coordinate (Franck–Condon excitation) are equal to the reorganization energy λ; and the secular determinant is expressed as Equation (2).

$$\begin{vmatrix} -E & H_{DA} & 0 & 0 & 0 & H_{DA} \\ H_{DA} & \lambda-E & H_{DA} & 0 & 0 & 0 \\ 0 & H_{DA} & \lambda-E & H_{DA} & 0 & 0 \\ 0 & 0 & H_{DA} & \lambda-E & H_{DA} & 0 \\ 0 & 0 & 0 & H_{DA} & \lambda-E & H_{DA} \\ H_{DA} & 0 & 0 & 0 & H_{DA} & \lambda-E \end{vmatrix} = 0 \quad (2)$$

The resulting energy levels of the adiabatic states (truncated to the second order) and their pictorial representations are shown in Scheme 2 (exact eigenvalues and



Scheme 2.

coefficients a_i–f_i in terms of H_{DA} and λ are given in the Supporting Information). In contrast to bidonor **2**$^{\bullet+}$ with one intervalence transition (i.e., $\nu_{IV}=\lambda$), the absorption band of **1**$^{\bullet+}$ contains five optical transitions with energies determined as differences between ground state Ψ_1 and excited states Ψ_2 to Ψ_6. The intensities of the transitions are related to the corresponding transition moments which can be expressed (according to Mulliken–Hush theory[5]) as Equation (3), in which $i=2$ to 6, and μ_a to μ_f are moments of diabatic states a to f within the arbitrarily chosen coordinate system.

$$\mu_{oi} = \int \Psi_1 \mu \Psi_i = \int (a_1\psi_a + \ldots + f_1\psi_f)\mu(a_i\psi_a + \ldots + f_i\psi_f) \approx (a_1 a_i \mu_a + \ldots + f_1 f_i \mu_f) \quad (3)$$

When the coupling element is small ($H_{DA}\approx 0$), all optical transitions ($\Psi_1 \rightarrow \Psi_i$, $i=2$–6) are essentially degenerate (i.e., $\nu_{IV}\approx\lambda$), however significant electronic coupling between the redox sites leads to broadening of the intervalence absorption and splitting into individual components with the energy difference between the highest and lowest transition given by $\nu_5-\nu_1 = 2H_{DA}\sqrt{3}$. Indeed, the broad intervalence NIR absorption of **1**$^{\bullet+}$ in Figure 2 (with several partially resolved components) points to a significant value of H_{DA}, and digital deconvolution into Gaussian bands (see Supporting Information Figure S2) leads to $\lambda = 5400\pm600\ cm^{-1}$ and $H_{DA} = 1600\pm400\ cm^{-1}$ (see Supporting Information for details). The coefficients (a_1 to f_6) and transition moments are calculated from λ and H_{DA} (see Supporting Information Table S2), and the results in Table 1 demonstrate how the energies and intensities of the optical transitions based on the Mulliken–Hush (six-state) model agree with those obtained by deconvolution of the experimental (intervalence transfer) spectrum.

In conclusion, the compounds **1**–**3**, which are closely related to **III**, have been prepared and studied. The Mulliken–Hush (MH) quantification of λ and H_{DA} confirms for the first time the substantial stabilization allowed in the one-electron oxidized hexadonor system **III** since the resonance energy of $\Delta G_r = -2H_{DA}^2/\lambda \approx -3.5\ kcal\,mol^{-1}$ shows the extensive intra-annular (electron) delocalization in **1**$^{\bullet+}$ relative to the localized **3**$^{\bullet+}$. Furthermore, the MH treatment of the experimental spectral behavior correctly predicts the potential shift of $\Delta E_{ox} = 0.21$ V (for the first anodic wave of **1** relative to **3**) which is close to the experimental value of $\Delta E_{ox} = 0.23$ V when the entropy contribution is taken into account. Finally, the attractive interaction in **1**$^{\bullet+}$ with $H_{DA} = 5.3\ kcal\,mol^{-1}$ is almost sufficient to offset the reorganization penalty of $\lambda/2 = 8.0\ kcal\,mol^{-1}$ and predicts a low barrier for hole (electron) hopping between six (contiguous) anilinyl sites (Scheme 1). Indeed, the value of $\Delta G^{\ddagger} = 0.5\ kcal\,mol^{-1}$ evaluated from H_{DA} and λ[11] is at the threshold of the thermal barrier, and implies that **1**$^{\bullet+}$ has borderline Robin–Day Class II/III behavior.[9,10] As such, we hope that our search for other redox systems will reveal complete toroidal delocalization (i.e., Robin–Day Class III behavior) as in **IV**—of practical interest for the new design of molecular "motors."

Experimental Section

Solvents and chemicals were prepared and handled as described earlier.[3] Hexaanilinylbenzene donors (**1**) were obtained by trimerization of bis(*N*,*N*-diethyl or methylethylanilinyl)acetylene with dicobalt octacarbonyl catalyst.[7b,12a] Bidonor (**2**) and monodonor (**3**) models were synthesized by Diels–Alder addition of tetraphenylcyclopentadienone to the appropriate anilinylacetylene and subsequent decarbonylation.[12b] Electronic spectra were measured on Varian Cary 5 spectrometer, IR spectra measured with a Nexus 470 FT-IR (Thermo Nicolet), and structural studies were carried out with Siemens SMART APEX diffractometer. Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) were performed on BAS 100A Electrochemical Analyzer, as described previously.[3] For full experimental and analytical details see the Supporting Information.

Received: March 18, 2005
Published online: July 12, 2005

Keywords: arenes · charge transfer · conjugation · Mulliken–Hush theory · radical ions

Table 1: Energies[a] and relative intensities[b] of intervalence optical transitions in radical cation **1**$^{\bullet+}$.

	$\Psi_1\rightarrow\Psi_2$	$\Psi_1\rightarrow\Psi_3$	$\Psi_1\rightarrow\Psi_4$	$\Psi_1\rightarrow\Psi_5$	$\Psi_1\rightarrow\Psi_6$
Theoretical (MH)[c]	3.7(0.30)	4.8(0.50)	7.5(0.07)	8.6(0.12)	10.2(≈0)
Spectral[d]	3.7(0.25)	4.8(0.52)	7.4(0.10)	8.6(0.13)	10.1(0.01)

[a] In $10^3\ cm^{-1}$. [b] In parenthesis, normalized intensities. [c] MH = Mulliken–Hush model. Calculated according to MH with $\lambda = 5500\ cm^{-1}$ and $H_{DA} = 1900\ cm^{-1}$. [d] From Gaussian deconvolution of the intervalence absorption.

[1] a) B. Badger, B. Brocklehurst, *Nature* **1968**, *219*, 263; b) B. Badger, B. Brocklehurst, *Trans. Faraday Soc.* **1969**, *65*, 2582; B. Badger, B. Brocklehurst, *Trans. Faraday Soc.* **1970**, *66*, 2939; c) I. C. Lewis, L. S. Singer, *Chem. Phys.* **1965**, *43*, 2712; d) O. W. Howarth, G. K. Fraenkel, *J. Am. Chem. Soc.* **1966**, *88*, 4514.

[2] See also: a) C. Kröhnke, V. Enkelmann, G. Wegner, *Angew. Chem.* **1980**, *92*, 941; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 912; b) J. D.

Stenger-Smith, R. W. Lenz, V. Enkelmann, G. Wegner, *Makromol. Chem.* **1992**, *193*, 575; c) W. Lau, J. K. Kochi, *J. Org. Chem.* **1986**, *51*, 326; d) J. K. Kochi, R. Rathore, P. LeMagueres, *J. Org. Chem.* **2000**, *65*, 6826; Compare also: e) D. Small, V. Zaitsev, Y. Jung, S. V. Rosokha, M. Head-Gordon, J. K. Kochi, *J. Am. Chem. Soc.* **2004**, *126*, 13850.

[3] a) D. Sun, S. V. Rosokha, S. V. Lindeman, J. K Kochi, *J. Am. Chem. Soc.* **2003**, *125*, 15950; b) D. Sun, S. V. Rosokha, J. K. Kochi, *J. Am. Chem. Soc.* **2004**, *126*, 1388.

[4] a) For a few examples of multiple aromatic π-stacking with some evidence of delocalized radical cations, see b) P. LeMagueres, S. V. Lindeman, J. K. Kochi, *Org. Lett.* **2000**, *2*, 3562; c) R. Rathore, S. H. Albelwahed, I. A. Guzei, *J. Am. Chem. Soc.* **2003**, *125*, 9712.

[5] a) R. S. Mulliken, W. B. Person, *Molecular Complexes*, Wiley, New York, **1969**; b) N. S. Hush, *Prog. Inorg. Chem.* **1967**, *8*, 391; c) For recent review, see: M. D. Newton, *Electron Transfer in Chemistry*, *Vol. 1* (Ed.: V. Balzani), Wiley-VCH, New York, **2001**, p. 3.

[6] a) J. M. Williams, *Organic Superconductors: Synthesis, Structure, Properties and Theory*, Prentice Hall, Englewood Cliffs, **1992**; b) *Organic Conductors: Fundamentals and Applications* (Ed.: J.-P. Farges), Marcel Dekker, New York, **1994**; c) *Magnetism: Molecules to Materials* (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2001**; d) See also: Thematic Issue Ed.: P., Batai, *Chem. Rev.* **2004**, *104*, 4887.

[7] For some previous studies of hexaarylbenzenes, see: a) C. Lambert, G. Nöll, *Angew. Chem.* **1998**, *110*, 2239; *Angew. Chem. Int. Ed.* **1998**, *37*, 2107; b) C. Lambert, G. Nöll, *Chem. Eur. J.* **2002**, *8*, 3467; c) R. E. Bauer, V. Enkelmann, U. M. Wiesler, A. J. Berresheim, K. Müllen, *Chem. Eur. J.* **2002**, *8*, 3858; d) H. P. Dijkstra, P. Steenwinkel, D. M. Grove, M. Lutz, A. L. Spek, G. van Koten, *Angew. Chem.* **1999**, *111*, 2321; *Angew. Chem. Int. Ed.* **1999**, *38*, 2186; e) K. Kobayashi, T. Shirasaka, A. Sato, E. Horn, N. Furukawa, *Angew. Chem.* **1999**, *111*, 3692; *Angew. Chem. Int. Ed.* **1999**, *38*, 3483; f) K. Kobayashi, A. Sato, S. Sakamoto, K. Yamaguchi, *J. Am. Chem. Soc.* **2003**, *125*, 3035; g) B. Traber, J. J. Wolff, F. Rominger, T. Oeser, R. Gleiter, M. Goebel, R. Wortmann, *Chem. Eur. J.* **2004**, *10*, 1227; h) X. Shen, D. M. Ho, R. A. Pascal, Jr., *J. Am. Chem. Soc.* **2004**, *126*, 5798; i) R. Rathore, C. L. Burns, M. I. Deselnicu, *Org. Lett.* **2001**, *3*, 2887; j) G. Bottari, T. Torres, *Chem. Commun.* **2004**, 2668.

[8] a) Toroidal conjugation occurring through π-faces is to be distinguished from the usual planar conjugation occurring at π-edges of aromatic moieties; b) A reviewer has kindly pointed out an earlier study[8c] of hexaiodobenzene dication as a stable σ-delocalized or (Hückel) σ-aromatic species. Such extensive conjugation is essentially circular since it occurs among six iodo atoms in a single plane. This contrasts with electron delocalization among six anilinyl faces (each involving multiple π-centers), which is thus enveloped by a toroid-shaped surface. As such, the concept of toroidal conjugation also extends to enlarged systems including perarylnaphthalenes, anthracenes, and to various other polyacenes (in general), as well as to more flexible perarylated polyacetylenes; c) D. J. Sagl, J. C. Martin, *J. Am. Chem. Soc.* **1988**, *110*, 5820.

[9] For analogous distortions of intervalence absorption bands in mixed-valence radical cations, see: a) C. Lambert, G. Nöll, *J. Am. Chem. Soc.* **1999**, *121*, 8434; b) S. F. Nelsen, *Chem. Eur. J.* **2000**, *6*, 581.

[10] a) C. Creutz, *Prog. Inorg. Chem.* **1983**, *30*, 1; b) K. D. Demadis, C. M. Hartshorn, T. J. Meyer, *Chem. Rev.* **2001**, *101*, 2655; c) T. Nishiumi, Y. Nomura, Y. Chimoto, M. Higuchi, K. Yamamoto, *J. Phys. Chem.* **2004**, *108*, 7992.

[11] a) Calculated as $\Delta G^{+} = (\lambda - 2H_{DA})^2/(4\lambda)$ based on two-state model.[11b] Preliminary results indicate that the six-state model predicts even lower energies; b) B. S. Brunschwig, N. Sutin, *Coord. Chem. Rev.* **1999**, 187, 233.

[12] a) K. P. C. Vollhardt, *Acc. Chem. Res.* **1977**, *10*, 1; b) N. Tugcu, S. K. Park, J. A. Moore, S. M. Cramer, *Ind. Eng. Chem. Res.* **2002**, *41*, 6482.

