Angewandte Chemie

π Stacking

Redox-Induced Transformation from an Extended to a π-Stacked Conformer in Acyclic Bis(catecholacetal)s of Acetylacetone**

Rajendra Rathore, Vincent J. Chebny, Erica J. Kopatz, and Ilia A. Guzei*

The design and synthesis of new π-stacked molecular arrays holds potential for the preparation of wirelike materials for applications in the ever-evolving area of molecular electronics and nanotechnology.[1] We have recently demonstrated that polyfluorenes adopt cyclophane-like π-stacked structures when woven at the alternating carbon atoms of the backbone of an acyclic alkane (Figure 1).[2] This π-stacked arrangement of the aromatic moieties in the depicted bifluorene (as well as its higher homologues) arises because of the disk-shaped structure of the fluorene moieties, as well as the *anti* arrangement of all the bonds in the alkane backbone, allow the π-stacked structure to be stabilized both in solution and solid state, as confirmed by NMR spectroscopy and X-ray crystallography.[2]

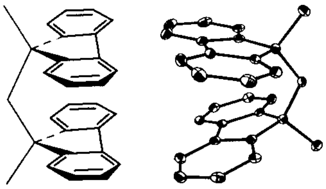


Figure 1. Molecular structure of a π-stacked bifluorene.

Our ongoing interest in such cofacially stacked polybenzenoid structures led us to hypothesize that a π-stacked arrangement should be feasible in the bis(catecholacetal) of acetylacetone (**1a**). This compound is readily available by the reaction of acetylacetone (a 1,3-diketone) with catechol in toluene in the presence of an acid catalyst [Eq. (1)].[3]

The molecular structures of various conformers of **1a**, calculated by density functional theory (DFT) at the B3LYP/6-31G* level, showed that both the π-stacked and extended conformers are accessible. The extended conformer **1aE** is only about 2.1 kcal mol^{-1} lower in energy than the π-stacked

---

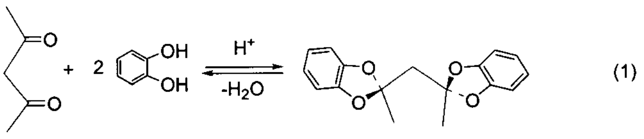
[*] Prof. R. Rathore, V. J. Chebny, E. J. Kopatz
Department of Chemistry
Marquette University
P.O. Box 1881, Milwaukee, WI 53201-1881 (USA)
Fax: (+1) 414-288-7066
E-mail: rajendra.rathore@marquette.edu

Dr. I. A. Guzei
Molecular Structure Laboratory
Department of Chemistry, University of Wisconsin
Madison, WI (USA)

[**] We thank the National Science Foundation (Career Award) and the donors of the Petroleum Research Fund (AC12345), administered by the American Chemical Society, for financial support.

DOI: 10.1002/ange.200463103

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



(1)

1a

conformer **1aS** (Figure 2). Interestingly, the energy optimization of the π-stacked conformer of bis(catecholacetal) of acetonoylacetone **2aS** (a 1,4-diketone) always resulted in the extended conformer **2aE** (Figure 3). This suggests that the stacked conformer is substantially higher in energy and not readily attainable.

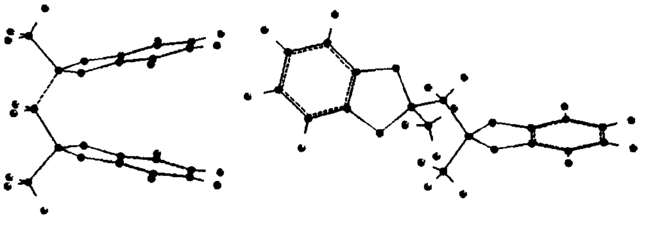


Figure 2. Structures of the π-stacked conformer **1aS** (left) and the extended conformer **1aE** (right).

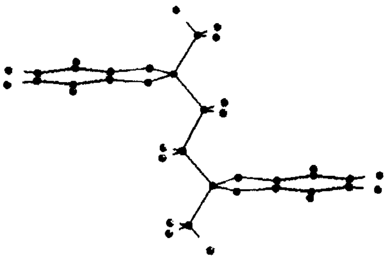
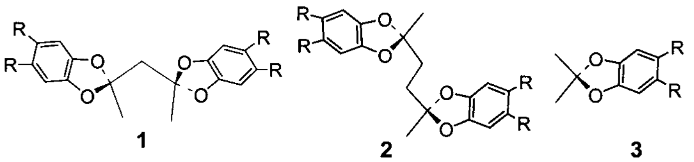


Figure 3. Structure of the extended conformer **2aE**.

Accordingly, herein, we will delineate that the extended conformers of *bis*-catechol acetals of acetylacetone (**1E**) undergo instantaneous folding into cyclphane-like stacked conformers (**1S**) upon one-electron oxidation by using electrochemistry and time resolved laser-flash photolysis as follows.

Various catechol acetals as well as the dimethylcatechol acetals **1**–**3** were readily synthesized by acid-catalyzed con-



1 **2** **3**

a: R = H
b: R = CH_3

densation with the corresponding ketones in refluxing toluene.[3] An X-ray structure analysis confirmed that **1b** in the solid state exists exclusively as the extended conformer (Figure 4),[4] as expected based on DFT calculations

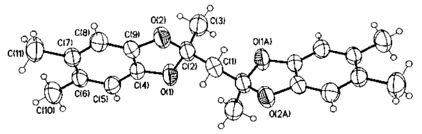


Figure 4. Molecular structure of **1b** in the solid state showing the extended conformer.

To demonstrate whether both the extended and the π-stacked conformers of **1** exist in solution, we examined the electron donor–acceptor (EDA) complexes of **1**–**3** with tetrachloro-*p*-benzoquinone (chloranil as an electron acceptor) by UV/Vis spectroscopy. It has been well established that the redox potentials (or π basicity) of the π-stacked cyclophane-like aromatic donors are significantly lower than that of their extended analogues.[5] The π basicity can be readily gauged by formation of the EDA complexes in solution according to the Mulliken theory.[6]

Interestingly, when colorless solutions of diacetals **1a** and **2a** as well as the monoacetal **3a** were exposed to a pale yellow solution of chloranil in CH_2Cl_2, they all instantaneously produced red solutions. Furthermore, the UV/Vis spectra showed a broad charge-transfer (CT) absorption band centered at $\lambda_{max} = 522 \pm 2$ nm. Similarly, the dimethylcatechol acetals **1b**, **2b**, and **3b** produced green solutions upon exposure to solutions of chloranil, and they each showed a charge-transfer absorption band centered at $\lambda_{max} = 608 \pm 2$ nm.[7] The identical CT transitions for various acetals in a given series suggests that the electron-donor strength is the same, and thus indicates that there is little or no contribution of the π-stacked conformer **1S** in solution. Moreover, the similarity of the chemical shifts for the aromatic and aliphatic protons in **1**–**3** (see the Experimental Section) further supports that **1a** and **1b** exist mostly as the extended conformer in solution. The variable temperature NMR analyses of **1** indicated that the postulated conformers **1E** and **1S** cannot be frozen out, even at −100 °C in CH_2Cl_2.

The cyclic voltammograms of **1a**, **2a**, and **3a** showed irreversible oxidation because of the presence of substitution-labile positions *para* to the oxygen atoms. On the other hand, the electrochemical oxidation of **1b**, **2b**, and **3b** at a platinum electrode in CH_2Cl_2 (containing $n\mathrm{Bu_4NPF_6}$ as the supporting electrolyte) was reversible at a scan rate of 25–400 $\mathrm{mV\,s^{-1}}$; all anodic/cathodic peak current ratios were $I_a/I_c = 1.0$ (theoretical) at room temperature (Figure 5). Furthermore, both monoacetal **3b** and diacetal **2b** showed only a single reversible (CV) wave at a potential of $E_{ox} = 1.23 \pm 0.01$ V versus SCE. A quantitative evaluation of the CV peaks and peak currents with added ferrocene (as an internal standard, $E_{ox} = 0.45$ V vs. SCE) revealed that the reversible oxidations correspond to the production of monocation $\mathbf{3b}^{\cdot+}$ and dication $\mathbf{2b}^{2+}$ by transfer of one and two electrons, respectively. In contrast, dimethylcatechol acetal **1b** showed two reversible one-electron oxidation waves at $E_{ox} = 1.13$ and 1.50 V versus SCE (Figure 5).

The observation of a two-electron oxidation of **2b** at a single potential is consistent with the fact that it exists exclusively in the extended conformer, and thus the two dimethylcatechol rings in **2b** are not in electronic communi-

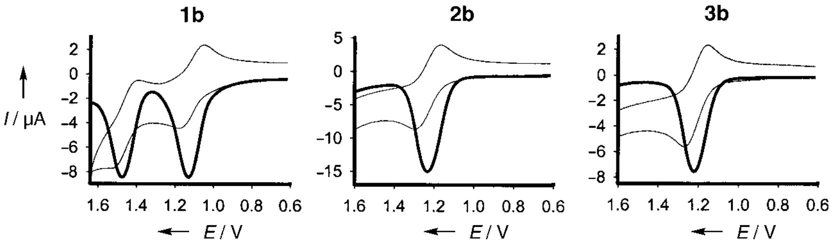
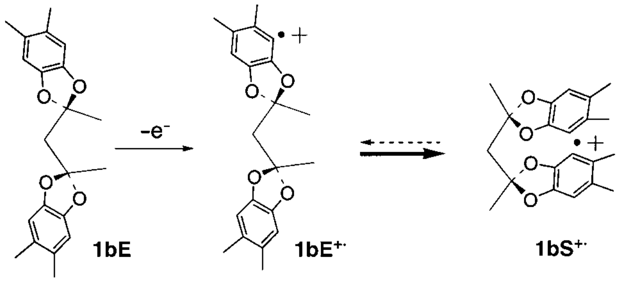


Figure 5. Cyclic voltammograms of **1b**, **2b**, and **3b** (5 mM) in CH_2Cl_2 measured at a scan rate of $\nu = 200\ mV\,s^{-1}$ at 25 °C. The corresponding square wave voltammograms are shown as bold curves. E = electric potential, I = current.

cation. On the other hand, the two well-separated one-electron oxidation waves in **1b** are easily explained by the following: Upon removal of a single electron the extended conformer transforms into the π-stacked conformer by a simple C–C bond rotation. This leads to cyclophane-like stabilization of the cationic charge in **1b**$^{\cdot+}$ and thus renders the oxidation of the second dimethylcatechol ring more difficult (by about 370 mV; Scheme 1).[8]



Scheme 1. Transformation of the extended conformer of **1b** into the π-stacked conformer upon one-electron oxidation.

As such, the effective electronic coupling between cofacially oriented aryl moieties in **1b** is readily judged by the reversible electrochemical oxidation at significantly (namely, 100 mV) lower potential as compared to the model electron donors **2b** and **3b**. Such through-space electronic coupling between cofacially stacked aryl moieties can also be seen in the electronic spectra of their radical cation, where characteristic charge-resonance transitions in the near-IR region are observed.[9] Accordingly, we generated the radical cations of **1**–**3** based on time-resolved absorption measurements upon diffusional electron-transfer quenching of photoexcited chloranil triplet as an oxidant ($E_{red} = 2.2$ V vs. SCE) using laser-flash photolysis.[10]

The transient spectrum obtained 100 ns after laser excitation (10 ns) of chloranil (5 mM) in the presence of **1a** (10 mM) in CH_2Cl_2/CH_3CN (1/1) showed an absorption band at $\lambda_{max} = 450$ nm with a shoulder at 420 nm, characteristic of a chloranil radical anion,[11] together with a broad absorption band centered at $\lambda_{max} = 1400$ nm (Figure 6a). The local absorption band of the catechol ether radical cations only have maxima at about 450 nm,[11] and thus lie within the envelope of the signal for the chloranil radical anion. Similarly, the radical cation **1b**$^{\cdot+}$ showed an intense near-IR transition with a red-shifted absorption maximum at $\lambda_{max} \approx 1600$ nm (Figure 6b). The radical cations **2a**$^{\cdot+}$, **2b**$^{\cdot+}$, **3a**$^{\cdot+}$, and **3b**$^{\cdot+}$, generated similarly, lacked any absorption in the near-IR region. The observation of the charge-resonance transitions in the radical cations **1a**$^{\cdot+}$ and **1b**$^{\cdot+}$ (because of effective through-space electronic coupling) confirms a rapid transformation of the extended conformers into the π-stacked conformers upon one-electron oxidation (Scheme 1).

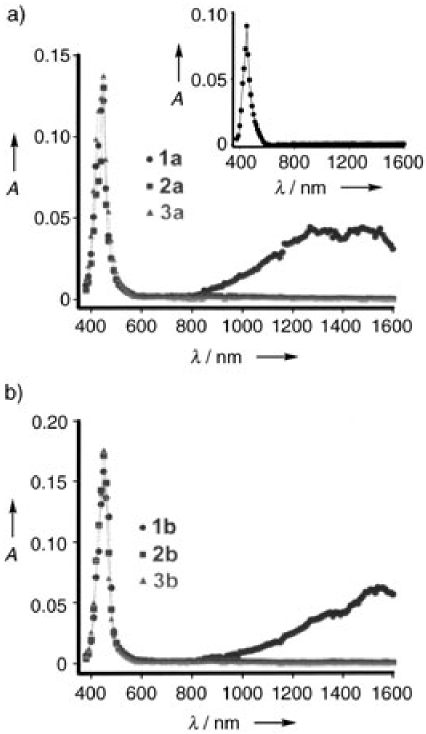


Figure 6. The transient absorption spectra of the radical ions formed from 0.005 M chloranil and 0.01 M **1a**, **2a**, and **3a** (a) or 0.01 M **1b**, **2b**, and **3b** (b) in a CH_2Cl_2/CH_3CN (1:1) following laser excitation at 355 nm for 10 ns. Inset in (a): The absorption spectrum of chloranil radical anion generated under identical conditions using 1,4-diazabicyclo[2.2.2]octane (DABCO) as an electron donor (the radical cation absorbs at $\lambda < 350$ nm).

In summary, we have demonstrated that catechol acetals of acetylacetone (**1**) in the neutral state exist exclusively as the extended conformers. However, the one-electron oxidation readily transforms these extended conformers into the folded π-stacked conformers. We are actively investigating the usefulness of such a redox-controlled molecular motion in readily available catechol acetals **1a** and **1b** as well as the design and synthesis of higher homologues of these electroactive materials.

Experimental Section

Compounds **1**–**3** were synthesized using standard literature procedures.[3] Their molecular structures were calculated with the aid of the

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

"Spartan 02" graphics program. NMR spectra were recorded using a 300-mHz Varian spectrometer.

1a: M.p. 67–68 °C; ^{1}H NMR ($CDCl_3$): $\delta = 1.74$ (s, 6H), 2.60 (s, 2H), 6.75 ppm (sym m, 8H); ^{13}C NMR ($CDCl_3$): $\delta = 25.36$, 46.57, 108.80, 116.48, 121.42, 146.96 ppm; GC–MS: m/z 284 ($[M^+]$ calcd for $C_{17}H_{16}O_4$); elemental analysis (%) calcd for $C_{17}H_{16}O_4$: C 71.82, H 5.67; found: C 71.91, H 5.72.

2a: M.p. 120–121 °C; ^{1}H NMR ($CDCl_3$): $\delta = 1.62$ (s, 6H), 2.15 (s, 4H), 6.77 ppm (m, 8H); ^{13}C NMR ($CDCl_3$): $\delta = 25.00$, 32.98, 108.54, 118.31, 121.21, 147.42 ppm; GC–MS: m/z 298 ($[M^+]$ calcd for $C_{18}H_{18}O_4$); elemental analysis (%) calcd for $C_{18}H_{18}O_4$: C 72.47, H 6.08; found: C 72.57, H 6.10.

3a: Liquid; ^{1}H NMR ($CDCl_3$): $\delta = 1.69$ (s, 6H), 6.78 ppm (sym m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 26.25$, 108.75, 117.62, 121.27, 147.47 ppm; GC–MS: m/z 150 ($[M^+]$ calcd. for $C_9H_{10}O_2$); elemental analysis (%) calcd for $C_9H_{10}O_2$: C 71.98, H 6.71; found: C 72.07, H 6.75.

1b: M.p. 139–140 °C; ^{1}H NMR ($CDCl_3$): $\delta = 1.70$ (s, 6H), 2.15 (s, 12H), 2.54 (s, 2H), 6.54 ppm (s, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 20.02$, 25.28, 46.38, 110.21, 116.47, 128.88, 145.06 ppm; GC–MS: m/z 340 ($[M^+]$ calcd for $C_{21}H_{24}O_4$); elemental analysis (%) calcd for $C_{21}H_{24}O_4$: C 74.09, H 7.11; found: C 74.14, H 7.17

2b: M.p. 181–182 °C; ^{1}H NMR ($CDCl_3$): $\delta = 1.57$ (s, 6H), 2.09 (s, 4H), 2.15 (s, 12H), 6.53 ppm (s, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 19.90$, 24.96, 32.91, 109.81, 118.18, 128.52, 145.43 ppm; GC–MS: m/z 354 ($[M^+]$ calcd for $C_{22}H_{26}O_4$); elemental analysis (%) calcd for $C_{22}H_{26}O_4$: C 74.55, H 7.39; found: C 74.61, H 7.42.

3b: Colorless liquid; ^{1}H NMR ($CDCl_3$): $\delta = 1.66$ (s, 6H), 2.18 (s, 6H), 6.56 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 19.92$, 26.03, 109.95, 117.31, 128.51, 145.28 ppm; GC–MS: m/z 178 ($[M^+]$ calcd for $C_{11}H_{14}O_2$); elemental analysis (%) calcd for $C_{11}H_{14}O_2$: C 74.13, H 7.92; found: C 74.17, H 7.99.

Received: December 30, 2004
Published online: March 30, 2005

Keywords: cyclic voltammetry · cyclophanes · photolysis · pi interactions · radicals

---

[1] a) *Introduction to Molecular Electronics* (Eds.: M. C. Petty, M. R. Bryce, D. Bloor), Oxford University Press, New York, **1995**; b) B. G. Maiya, T. Ramasarma, *Curr. Sci.* **2001**, *70*, 1523–1530; c) F. D. Lewis, R. L. Letsinger, M. R. Wasielewski, *Acc. Chem. Res.* **2001**, *34*, 159–170; d) A. R. Wartini, J. Valenzuela, H. A. Staab, F. A. Neugebauer, *Eur. J. Org. Chem.* **1998**, 139–148; e) W. Grimme, H. T. Kaemmerling, J. Lex, R. Gleiter, J. Heinze, M. Dietrich, *Angew. Chem.* **1991**, *103*, 215–217; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 205–207; f) also, see: J. M. Tour, *Acc. Chem. Res.* **2000**, *33*, 791–804, and references therein.

[2] R. Rathore, S. H. Abdelwhaed, I. A. Guezi, *J. Am. Chem. Soc.* **2003**, *125*, 8712–8713.

[3] a) T.-S. Li, L.-J. Li, B. Lu, F. Yang, *J. Chem. Soc. Perkin Trans. 1* **1998**, 1561–3564; b) E. R. Cole, G. Crank, H. T. H. Minh, *Aust. J. Chem.* **1980**, *33*, 675–680.

[4] A suitable crystal ($0.37 \times 0.25 \times 0.16$ mm^3) of **1b** was obtained from CH_2Cl_2/CH_3OH at 23 °C. Crystal data for **1b**: $C_{21}H_{24}O_4$, $M_r = 340.4$, orthorhombic, space group *Pbcn*, $a = 119.591(4)$, $b = 10.5813(18)$, $c = 9.1146(15)$ Å, $\rho_{calcd} = 1.197$ Mg m^{-3}, $V = 1889.4(6)$ Å^3, $Z = 4$. Of 6523 total reflections measured, 1878 were symmetrically nonequivalent; $R1 = 0.0467$ and $wR2 = 0.1079$ for 1878 reflections with $I > 2\sigma(I)$. CCDC-247657 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[5] a) D. J. Cram, R. H. Bauer, *J. Am. Chem. Soc.* **1959**, *81*, 5971–5977; b) L. A. Singer, D. J. Cram, *J. Am. Chem. Soc.* **1963**, *85*, 1080–1084; c) M. Taniguchi, S. Mataka, T. Thiemann, T. Sawada, K. Mimura, Y. Mitoma, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2661–2668.

[6] R. Rathore, S. V. Lindeman, J. K. Kochi, *J. Am. Chem. Soc.* **1997**, *119*, 9343–9404, and references therein.

[7] Veratrole (1,2-dimethoxybenzene) and 4,5-dimethylveratrole (1,2-dimethoxy-4,5-dimethylbenzene) show similar charge-transfer absorption bands at 518 and 606 nm, respectively, with chloranil as an electron acceptor in CH_2Cl_2.

[8] Compare: S. Mataka, K. Shigaki, T. Sawada, Y. Mitoma, M. Taniguchi, T. Thiemann, K. Ohga, N. Egashira, *Angew. Chem.* **1998**, *110*, 2626–2628; *Angew. Chem. Int. Ed.* **1998**, *37*, 2532–2534.

[9] a) S. F. Nelsen, *Chem. Eur. J.* **2000**, *6*, 581–588; b) B. Badger, B. Brocklehurst, *Trans. Faraday Soc.* **1969**, *65*, 2576–2588; c) B. Badger, B. Brocklehurst, *Nature* **1968**, *219*, 263–264; d) M. A. J. Rodgers, *J. Chem. Soc. Faraday Trans. 1* **1972**, *68*, 1278–1292; e) R. Rathore, C. L. Burns, S. A. Abdelwahed, *Org. Lett.* **2004**, *6*, 1689–1692.

[10] a) R. Rathore, S. M. Hubig, J. K. Kochi, *J. Am. Chem. Soc.* **1997**, *119*, 11 468–11 480; b) S. M. Hübig, R. Rathore, J. K. Kochi, *J. Am. Chem. Soc.* **1999**, *121*, 617–626.

[11] T. Shida, *Electronic Absorption Spectra of Radical Ions*, Elsevier, Amsterdam, **1988**.