



## Synthesis and electronic properties of nanometer-size symmetrical tetrakis(poly-*p*-phenylene)ethylenes

Vijay S. Vyas, Moloy Banerjee, Rajendra Rathore \*

Department of Chemistry, Marquette University, PO Box 1881, Milwaukee, WI 53233, USA

### ARTICLE INFO

#### Article history:

Received 26 June 2009

Revised 18 August 2009

Accepted 24 August 2009

Available online 27 August 2009

### ABSTRACT

A simple synthesis of soluble tetrakis(poly-*p*-phenylene)ethylenes (TPEs), where poly-*p*-phenylene units contain up to 4 phenylene moieties, is accomplished using an easily available tetrakis(4-bromophenyl)ethylene and phenyl, biphenyl, and *p*-terphenylboronic acids, containing solubilizing *iso*-alkyl groups as the end-capping substituents. Electrochemical oxidation of TPEs (i.e., **T1–T4**) showed that they undergo reversible electrochemical oxidations and form stable cation-radical salts in solution. The evaluation of absorption and emissions characteristics of **T1–T4** in solution indicated that unlike parent tetratolyethylene (**T1**), the higher homologues (i.e., **T2–T4**) show emission centered at 520 nm and the quantum efficiency of emission increases with the increasing number of phenylene moieties in poly-*p*-phenylene units in various TPEs.

© 2009 Elsevier Ltd. All rights reserved.

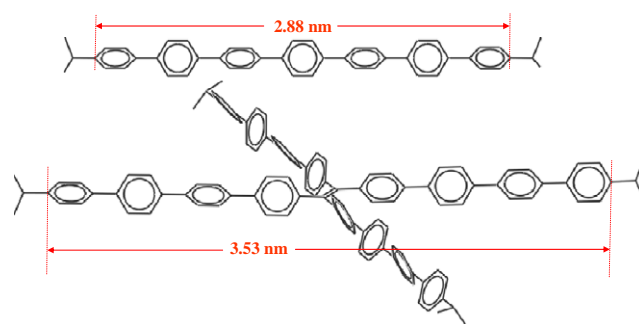
The design and synthesis of new electro-active organic materials based on polyaromatic hydrocarbons continue to attract considerable attention owing to their potential for the practical applications in the emerging areas ranging from molecular electronics and nanotechnology to solar energy storage.<sup>1</sup> Of these, poly-*p*-phenylenes (**PPn**) are especially important due to their high conductivity and high thermal and oxidative stability.<sup>2</sup> We recently carried out a careful study of the optical and electronic properties of a series of well-defined oligomers of the poly-*p*-phenylenes containing up to 7 phenylene moieties; and demonstrated that all the optical and electrochemical properties followed an inverse relationship with the number of phenylene moieties.<sup>3</sup> Longer poly-*p*-phenylenes could not be obtained owing to limitation posed by solubility despite having long alkyl chains at the apical positions (see Fig. 1).<sup>3</sup>

A need for conducting molecules with increased effective conjugation lengths<sup>4</sup> led us to conjecture that if the smaller poly-*p*-phenylenes are incorporated at the vertices of tetraphenylethylene core, nanometer-size electro-active molecules should become readily accessible. For example, an incorporation of a modest length *p*-terphenyl unit onto the vertices of tetraphenylethylene alone would lead to a conducting single molecule which is longer than the largest known (soluble) poly-*p*-phenylene,<sup>3</sup> that is, Figure 1.

Accordingly, herein we describe an efficient synthesis of a well-defined series of tetrakis(poly-*p*-phenylene)ethylenes (TPEs), where poly-*p*-phenylene units contain 2, 3, and 4 phenylene moi-

eties, respectively. The availability of a homologous series of TPEs allows us to evaluate their optical and electrochemical properties as well as the optical characteristics of their cation radicals with increasing number of phenylene units in TPEs. The details of these preliminary findings are presented herein.

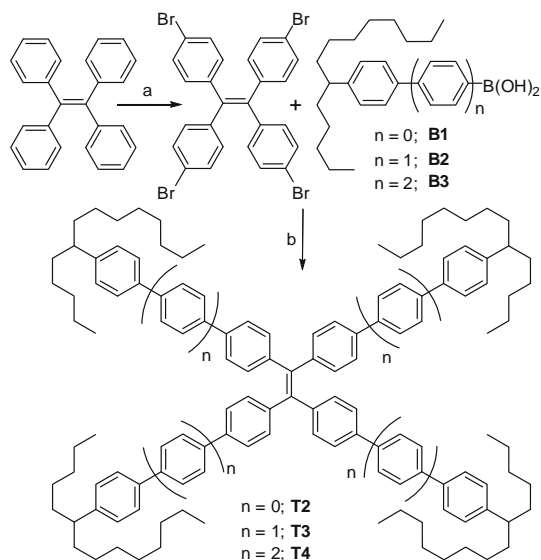
Various soluble tetrakis(poly-*p*-phenylene)ethylenes (**T2–T4**) were synthesized in excellent yields by Suzuki reaction<sup>5</sup> between phenyl, biphenyl, and *p*-terphenylboronic acids (**B1–B3**), containing solubilizing *iso*-alkyl groups as the end-capping substituents, and tetrakis(4-bromophenyl)ethylene (Scheme 1). The desired tetrakis(*p*-bromophenyl)ethylene<sup>6</sup> was easily prepared from tetraphenylethylene via a solid-phase reaction with gaseous bromine while the synthesis of boronic acids **B1–B3** has been described earlier.<sup>3</sup> A model tetratolyethylene (**T1**) was also obtained by a simple



**Figure 1.** Comparison of the size of representative poly-*p*-phenylene and tetrakis(poly-*p*-phenylene)ethylene.

\* Corresponding author. Tel.: +1 414 288 2076; fax: +1 414 288 7066.

E-mail addresses: [Rajendra.Rathore@mu.edu](mailto:Rajendra.Rathore@mu.edu), [Rajendra.Rathore@marquette.edu](mailto:Rajendra.Rathore@marquette.edu) (R. Rathore).

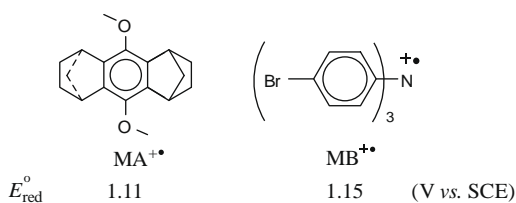


**Scheme 1.** Synthesis of various tetrakis(poly-*p*-phenylene)ethylenes. Reagents: (a) Bromine vapors; (b) Pd(PPh<sub>3</sub>)<sub>4</sub> (2 mol %), dioxane–H<sub>2</sub>O (2:1), Na<sub>2</sub>CO<sub>3</sub>, reflux.

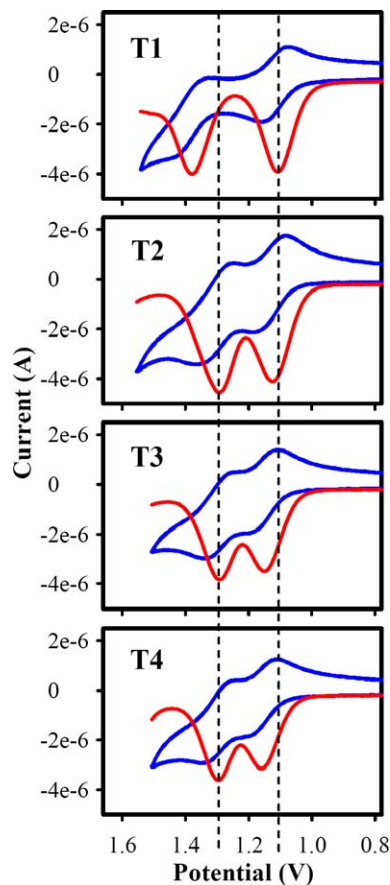
McMurry coupling of 4,4-dimethylbenzophenone.<sup>7</sup> The structures of **T2–T4** were easily established by <sup>1</sup>H/<sup>13</sup>C NMR spectroscopy and were further confirmed by MALDI mass spectrometry (see [Supplementary data](#) section for the experimental details).

The redox properties of **T1–T4** were evaluated by electrochemical oxidation at a platinum electrode as a  $1 \times 10^{-3}$  M solution in dichloromethane containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>) as the supporting electrolyte. The common unifying feature in the cyclic voltammograms of **T1–T4** (Fig. 2) is the presence of two 1-electron oxidation waves with the first wave being completely reversible while the second wave was found to be somewhat quasi reversible.<sup>8a</sup> The oxidation potentials of **T1–T4** corresponding to the first and second oxidations (i.e., loss of one and two electrons, respectively) were referenced to added ferrocene, as an internal standard ( $E_{\text{ox}} = 0.45$  V vs SCE),<sup>8b</sup> and the  $E_{\text{ox}}$  values are compiled in [Table 1](#). With the increasing number of phenylene moieties in **T1** to **T4**, there is a modest increase in their first oxidation potential ( $\sim 50$  mV), while the second oxidation potential largely remain unchanged ([Table 1](#)). The modest increase in the oxidation potentials going from **T1** to **T4** is understandable from the fact that HOMO largely resides on the tetraphenylethylene core (vide infra), and the substitution of electron-releasing alkyl groups in **T1** by electron-withdrawing phenyl, biphenyl, and terphenyl in **T2**, **T3**, and **T4**, respectively, contribute to the progressive increase in the first oxidation potentials of **T2–T4**.

The reversibility of 1-electron oxidation by cyclic voltammetry of various TPE's prompted us to evaluate the stability of their cation radical salts using stable triarylamine (**MB**)<sup>9</sup> and/or a hydroquinone ether (**MA**)<sup>10</sup> cation-radical salt as robust 1-electron oxidants.



Thus, [Figure 3](#) shows the spectral changes attendant upon the reduction of **MB**<sup>+</sup> SbCl<sub>6</sub><sup>-</sup> [ $\lambda_{\text{max}}(\log \epsilon) = 728$  nm (4.45)] by an incremental addition of **T2** to its cation radical **T2**<sup>+</sup> in dichloromethane at 22 °C. The presence of well-defined isosbestic points at



**Figure 2.** Cyclic voltammograms (blue) and the corresponding square-wave voltammogram (red) of  $1 \times 10^{-3}$  M **T1–T4** in CH<sub>2</sub>Cl<sub>2</sub> containing 0.2 M (*n*-Bu)<sub>4</sub>NPF<sub>6</sub> at 22 °C at scan rate of 200 mV s<sup>-1</sup>.

$\lambda_{\text{max}} = 678$  and 766 nm in [Figure 3A](#) established the uncluttered character of the electron transfer.

Furthermore, a plot of the depletion of **MB**<sup>+</sup> and formation of **T2**<sup>+</sup> against the increments of added neutral **T2** ([Fig. 3B](#)) established that **MB**<sup>+</sup> was completely consumed after the addition of 1 equiv of **T2**; the resulting absorption spectrum of **T2**<sup>+</sup> remained unchanged upon further addition of neutral **T2** (i.e., Eq. 1).

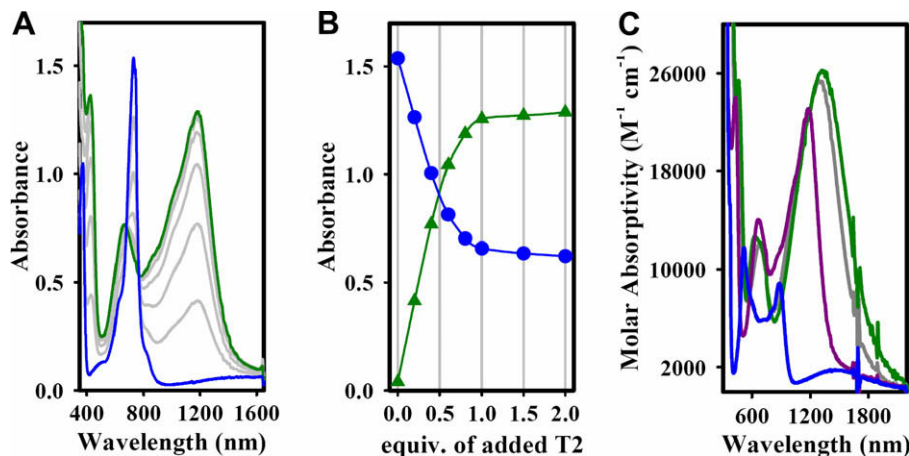


The radical-cation absorption spectra of **T2**<sup>+</sup> [ $\lambda_{\text{max}}(\log \epsilon) = 660, 1160$  (4.38)], **T3**<sup>+</sup> [ $\lambda_{\text{max}}(\log \epsilon) = 454, 670, 1292$  (4.39)], and **T4**<sup>+</sup> [ $\lambda_{\text{max}}(\log \epsilon) = 458, 622, 1300$  (4.40)] contained a pair of absorption bands characteristic of the parent tetratolyethylene cation radical **T1**<sup>+</sup> [ $\lambda_{\text{max}}(\log \epsilon) = 522, 882$  (3.95)];<sup>11</sup> and the twin absorption bands of the purple-colored **T1**<sup>+</sup> not only considerably red shifted in the green-colored **T2**<sup>+</sup>, but there was also a considerable increase in its molar absorptivity (vide infra). However, the absorption spectra of **T3**<sup>+</sup> and **T4**<sup>+</sup> were rather similar and were only slightly red shifted ( $\sim 150$  nm) when compared to **T2**<sup>+</sup>. Furthermore, the molar absorptivities of **T2–T4** cation radical were similar but considerably higher as compared to parent **T1** cation radical ([Fig. 3C](#) and [Table 1](#)).

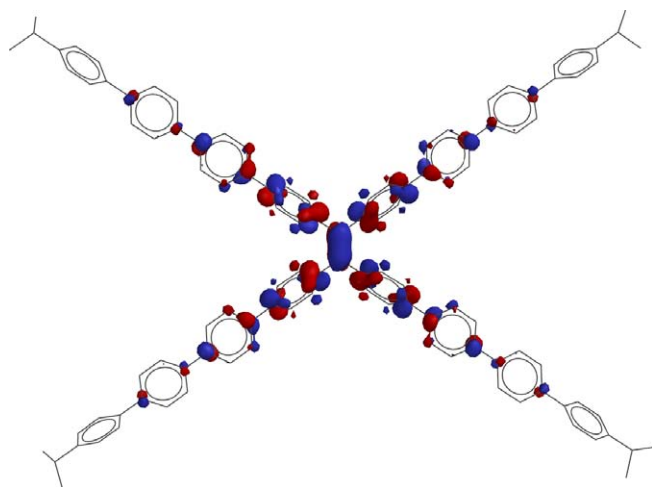
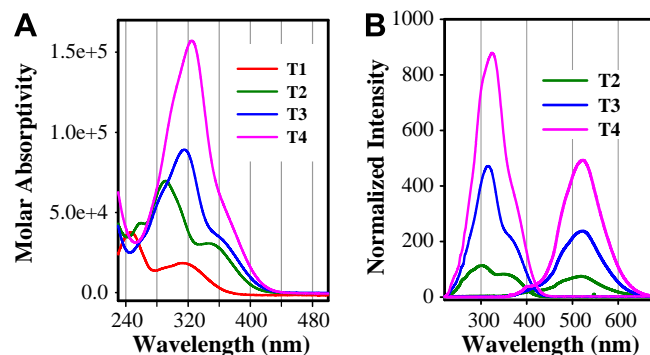
As such, the observed saturation of the low-energy transition as well as molar absorptivity beyond **T3**<sup>+</sup> suggests that conjugation length for the stabilization of the cationic charge in TPEs is limited to only 2–3 phenylene moieties on each poly-*p*-phenylene arm connected to ethylenic core. Furthermore, this observation is also consistent with the localization of HOMO in **T4** which extends only up to 3 phenylene moieties of quarter-*p*-phenylene arms of **T4**, see [Figure 4](#).

**Table 1**  
Optical and electrochemical data of **T1–T4**

Properties		<b>T1</b>	<b>T2</b>	<b>T3</b>	<b>T4</b>
$E_{ox1}$	V vs SCE	1.11	1.12	1.15	1.16
$E_{ox2}$	V vs SCE	1.38	1.29	1.29	1.29
UV-vis $\lambda_{max}$ ( $\epsilon_{max}$ )	nm ( $M^{-1} cm^{-1}$ )	246 (29,227) 313 (16,451)	291 (69,650) ~346 (30,734)	315 (89,172) ~352 (37,854)	326 (157,062) (~356) 68,378
$\lambda_{max}$ (emission)	nm	—	520	520	520
Quantum yield	$\Phi_F$	—	0.01	0.02	0.04
Normalized intensity		—	71	237	492
TPE <sup>+</sup> $\lambda_{max}$ ( $\epsilon_{max}$ )	nm ( $M^{-1} cm^{-1}$ )	522 (11,763) 880 (8838)	428 (22,969) 660 (14,023) 1160 (24,045)	454 (25,295) 670 (12,063) 1292 (24,307)	458 (26,218) 622 (12,640) 1300 (25,391)

**Figure 3.** (A) Spectral changes upon the reduction of  $5.5 \times 10^{-5}$  M **MB<sup>+</sup>** (blue line) by incremental addition of  $2.0 \times 10^{-3}$  M **T2** to its radical cation (green line) in  $CH_2Cl_2$  at 22 °C. (B) A plot of depletion of absorbance of **MB<sup>+</sup>** (blue circles, at 728 nm) and an increase of the absorbance of **T2<sup>+</sup>** (green triangles, at 1158 nm) against the equivalent of added neutral **T2**. (C) Comparison of the absorption spectra and molar absorptivity of **T1<sup>+</sup>** (blue line), **T2<sup>+</sup>** (purple line), **T3<sup>+</sup>** (gray line), and **T4<sup>+</sup>** (green line).

The optical properties of neutral TPEs were evaluated with the aid of UV–vis and emission spectroscopy as follows. The electronic absorption spectra of **T1–T4**, in dichloromethane, were recorded under identical concentration and temperature (22 °C) and are compiled in Figure 5. All TPEs showed a characteristic twin absorption band that shifted bathochromically with the increasing number of phenylene moieties in **T1–T4**. Although, the molar extinction coefficients exhibited almost a linear increase with the increasing

**Figure 4.** Showing the HOMO of **T4** with quarter-*p*-phenylene arms, calculated using Density Functional Theory (DFT) at B3LYP/6-31G\* level, extends only up to 3 phenylene moieties in each arm.**Figure 5.** (A) Comparison of the UV–vis absorption spectra and molar absorptivity of **T1–T4** as dilute solutions in  $CH_2Cl_2$  at 22 °C. (B) Comparison of the excitation (left) and emission spectra (right) of **T2–T4** as  $6.7 \times 10^{-6}$  M solutions in  $CH_2Cl_2$  at 22 °C upon excitation at the low-energy absorption bands (see Table 1).

number of phenylene units in **T1–T4** (Table 1, vide supra), the absorption maxima did not show a similar linear red shift but exhibited a saturation behavior akin to that observed above for the electronic transitions in their cation radical spectra (compare Figs. 3C and 5A).

The emission spectra of **T1–T4** were recorded under conditions of constant concentration ( $6.7 \times 10^{-6}$  M solution in dichloromethane) and temperature (22 °C) and are compared along with their excitation spectra in Figure 5. Expectedly, the parent tetratolyethylene (**T1**) did not show an observable emission owing to the fact that the excited state in terarylethenes and stilbenes undergoes a facile radiation less deactivation owing to a twisting motion

around the C=C bond.<sup>12</sup> Interestingly, however, **T2–T4** showed an (invariant) emission band centered at 520 nm, and the emission intensity linearly increased with the increasing number of phenylene moieties from **T2** to **T4** (see Fig. 5B). The fluorescence quantum yields for **T2–T4** were also determined using 9,10-diphenylanthracene ( $\Phi = 0.91$ )<sup>13</sup> as a standard (see the Supplementary data for the experimental details) and the values are compiled in Table 1. The quantum yield data in Table 1 show that there is a modest increase in the fluorescence quantum yield from **T2** ( $\Phi = 0.01$ ) to **T3** ( $\Phi = 0.02$ ) to **T4** ( $\Phi = 0.04$ ).

As such, the observation of relatively weak emission from **T2–T4** suggests that the emission largely arises from a reorganization of the ethylenic-centered exciton to the poly-*p*-phenylene groups of the **T2–T4**.<sup>14</sup> Indeed, a comparison of the emission spectra of poly-*p*-phenylenes<sup>3</sup> with that of **T2–T4** show a reasonable spectral similarity, however, at this juncture, we are unable to reconcile the invariance of the emission bands of **T2–T4**. Further studies using time-resolved spectroscopy as well as theoretical calculations will be required to pinpoint the origin of the observed emission of **T2–T4**.

In summary, we have developed an efficient synthesis of soluble tetrakis(poly-*p*-phenylene)ethylenes (TPEs), where poly-*p*-phenylene units contain up to 4 phenylene moieties, from easily available precursors. Various TPEs undergo reversible electrochemical oxidations and form stable cation-radical salts in solution which are stabilized by charge delocalization onto the poly-*p*-phenylene arms. The evaluation of absorption/emission properties of various TPEs showed that the intramolecular reorganization of exciton energy from the non-emissive tetraphenylethylene core to the poly-*p*-phenylene arms allows them to emit. Efforts are underway to develop more effective emitters based on tetrakis(poly-*p*-phenylene) derivatives in which C=C bond rotations, responsible for the radiation-less deactivation of the excited state, are hampered.

## Acknowledgment

We thank the National Science Foundation for the financial support.

## Supplementary data

Synthetic details, spectral data, and NMR spectra/mass spectra of various compounds in Scheme 1 are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.08.077.

## References and notes

- (a) *Introduction to Molecular Electronics*; Petty, M. C., Bryce, M. R., Bloor, D., Eds.; Oxford University Press: New York, 1995; (b) *Organic Electronics*; Klauk, H., Ed.; Wiley-VCH: Weinheim, 2006; (c) Gross, M.; Muller, D. C.; Nothofer, H. -G.; Scherf, U.; Neher, D.; Brauchle, C.; Meerholz, K. *Nature* **2000**, *405*, 661.
- (a) Gale, D. M. *J. Appl. Polym. Sci.* **1978**, *22*, 1971; (b) Irvine, P. A.; Wu, D. C.; Flory, P. J. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1795; (c) Baker, K. N.; Fratini, A. V.; Resch, T.; Knachel, H. C.; Adams, W. W.; Succi, E. P.; Farmer, B. L. *Polymer* **1993**, *34*, 1571.
- Banerjee, M.; Shukla, R.; Rathore, R. *J. Am. Chem. Soc.* **2009**, *131*, 1780.
- (a) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350 and references cited therein; (b) Zade, S. S.; Bendikov, M. *Org. Lett.* **2006**, *8*, 5243.
- (a) Suzuki, A. *Chem. Commun.* **2005**, 4759; (b) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359.
- Buckles, R. E.; Hausman, E. A.; Wheeler, N. G. *J. Am. Chem. Soc.* **1950**, *72*, 2494.
- McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405. and references therein.
- (a) The first oxidation wave of TPEs (i.e., TPE→TPE<sup>+</sup>) is completely reversible if the scanning is terminated before the start of second oxidation event as judged by the almost unity anodic/cathodic peak current ratios,  $I_a/I_c = 1.0$  (theoretical), at room temperature.; (b) Bashkin, J. K.; Kinlen, P. *J. Inorg. Chem.* **1990**, *29*, 4507 and references cited therein.
- (a) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, *13*, 2719; (b) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Org. Chem.* **1976**, *13*, 155.
- Rathore, R.; Burns, C. L.; Deselnicu, M. I. *Org. Synth.* **2005**, *82*, 1.
- Rathore, R.; Lindeman, S. V.; Kumar, A. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6931.
- (a) Shaarafy, S.; Muszkat, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 4119; (b) Shultz, D. A.; Fox, M. A. *J. Am. Chem. Soc.* **1989**, *111*, 6311; (c) Ma, J.; Zimmt, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 9723.
- Momicchioli, F.; Bruni, M. C.; Baraldi, I. *J. Phys. Chem.* **1972**, *76*, 3983.
- Compare: (a) Banerjee, M.; Emond, S. J.; Lindeman, S. V.; Rathore, R. *J. Org. Chem.* **2007**, *72*, 8054; (b) Debroy, P.; Lindeman, S. V.; Rathore, R. *J. Org. Chem.* **2009**, *74*, 2080; (c) Gano, J. E.; Osborn, D. J., III; Kodali, N.; Sekher, P.; Liu, M.; Luzik, E. D. Jr. *J. Org. Chem.* **2003**, *68*, 3710.