ether/hexanes in 150-mL fractions. Fractions 5–7 contained material with >95% purity by capillary GLC analysis. Concentration under reduced pressure and distillation gave 3-methylcyclonon-2-en-1-one (0.68 g, 20%) as a clear oil: bp 103–105 °C at 4.8 Torr; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.00 (s, 1 H), 2.71–2.67 (m, 2 H), 2.61–2.57 (m, 2 H), 1.94 (t, J = 1.3 Hz, 3 H), 1.87–1.77 (m, 2 H), 1.65–1.54 (m, 4 H), 1.46–1.36 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 205.6, 153.4, 130.5, 40.9, 31.0, 28.7, 28.4, 27.2, 26.7, 24.3; IR (neat) 2920, 2860, 1640, 1470, 1440, 1225, 1165 cm^{-1}; HRMS (M^+) 152.1198 (calculated 152.1201).

3-Methylcyclonon-2-en-1-one Tosylhydrazone (14). 3-Methylcyclonon-2-en-1-one (0.50 g, 3.3 mmol) was added to a stirring suspension of tosylhydrazide (0.61 g, 3.3 mmol) in 10 mL of benzene. The mixture was stirred at room temperature for 60 min and cooled to 0 °C, and pentane was added to induce crystallization. The crystals were collected, washed with pentane, and dried to give the desired tosylhydrazone (0.57 g, 1.8 mmol, 55%) as off-white crystals: mp 108–112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2 H), 7.62 (br s, 1 H), 7.29 (d, J = 8.2 Hz, 2 H), 5.35 (d, J = 1.2 Hz, 1 H), 2.42 (s, 3 H), 2.36–2.31 (m, 2 H), 1.77 (d, J = 1.2 Hz, 3 H), 1.81–1.74 (m, 1 H), 1.65–1.55 (m, 3 H), 1.45–1.25 (m, 6 H); IR (KBr) 3195, 2920, 2850, 1645, 1595, 1440, 1380, 1330, 1155, 1035 cm^{-1}. Anal. Calcd for $C_{17}H_{24}N_2O_2S$: C, 63.72; H, 7.55; N, 8.74. Found: C, 63.44; H, 7.71; N, 8.85.

Photolysis of the Sodium Salt of 3-Methylcyclonon-2-en-1-one Tosylhydrazone (14). Reaction of 3-methylcyclonon-2-en-1-one tosylhydrazone (14, 250 mg, 0.78 mmol) as described above gave 87 mg (0.64 mmol, 82%) of hydrocarbon product as a clear oil. Capillary GLC (column B) analysis indicated five components. GC–MS showed all products to be isomeric. These were isolated on a preparative scale and were characterized by the identity of their capillary GLC (column B) retention times and 300-MHz ^{1}H NMR spectra with those of authentic samples, with the exception of *cis,trans*-2-methyl-1,3-cyclononadiene. *cis,trans*-2-Methyl-1,3-cyclononadiene was characterized by its 300-MHz ^{1}H NMR spectrum, and by its facile photoisomerization to *cis,cis*-2-methyl-1,3-cyclononadiene. Products were identified as follows: 8-methylbicyclo[6.1.0]non-1(9)-ene (4, 30%); *cis*-8-methylbicyclo[4.3.0]non-7-ene (5, 9%); *cis*-3-methylbicyclo[4.3.0]non-2-ene (6, 36%); *cis,cis*-1-methyl-1,3-cyclononadiene (10, 19%); *cis,trans*-2-methyl-1,3-cyclononadiene (16, 5%) [^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 (d, J = 16.3 Hz, 1 H), 5.56–5.45 (m, 2 H), 2.40–2.15 (m, 2 H), 2.15–1.90 (m, 2 H), 1.75–1.25 (m, 6 H), 1.78 (s, 3 H)].

Vapor-Phase Benzene-Sensitized Irradiation of 1-Methyl-1,2-cyclononadiene. 1-Methyl-1,2-cyclononadiene (350 mg) and benzene (500 μL) were placed into a 3.7-L Vycor tube, the system was degassed as described previously,[2] and the vapor-phase mixture was irradiated for 5 days in a Rayonet photoreactor fitted with 254-nm lamps. The reaction vessel was then cooled on the bottom to −78 °C and vented to nitrogen, and the product was collected in pentane. The pentane solution was filtered through neutral alumina and was concentrated under reduced pressure at 0 °C to give 294 mg of a clear oil. Capillary GLC (column A) analysis indicated 97% conversion to six major products. These were isolated on a preparative scale (column E at 80 °C), and the major products were identified as follows: 9-methyltricyclo[4.3.0.0^{2,9}]nonane (7, 46%, t_R 3.91 min) [^{1}H NMR (300 MHz, $CDCl_3$) δ 2.50–2.42 (m, 1 H), 2.30–2.15 (m, 1 H), 1.88–1.78 (m, 3 H), 1.62–1.54 (m, 1 H), 1.41–1.20 (m, 6 H), 1.11 (s, 3 H), 0.70–0.64 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 38.2, 33.8, 32.8, 31.3, 28.6, 28.0, 24.5, 23.9, 19.2, 17.2; IR (neat) 3020, 2990, 2940, 2870, 1480, 1450 cm^{-1}; HRMS (M^+) 136.1249 (calculated 136.1252)]; 2-methyltricyclo[4.3.0.0^{2,9}]nonane (8, 41% t_R 4.20 min) [^{1}H NMR (300 MHz, $CDCl_3$) δ 2.46–2.40 (m, 1 H), 2.23–2.08 (m, 1 H), 1.94–1.53 (m, 4 H), 1.47–1.25 (m, 6 H), 1.08 (td, J = 7.4 Hz, J = 2.0 Hz, 1 H), 0.90 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 40.1, 33.8, 33.4, 31.3, 28.8, 28.7, 27.1, 26.9, 21.1, 18.3; IR (neat) 3020, 2940, 2880, 1480, 1450 cm^{-1}; HRMS (M^+) 136.1254 (calculated 136.1252)]. Minor products (five in 2–4% yield each) were incompletely characterized.

In other experiments conducted at lower conversion (18–40%), the ratio of photoproducts remained unchanged.

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Registry No. **2**, 42915-27-5; **4**, 124267-67-0; **5**, 57497-08-2; **6**, 79884-82-5; **7**, 124267-68-1; **8**, 124267-69-2; **9**, 124267-70-5; **10**, 124267-74-9; **11**, 124267-72-7; **13**, 124267-77-2; **14**, 124267-78-3; **16**, 124267-80-7; **20**, 4103-11-1; **21**, 17339-74-1; **22**, 124286-31-3; **23**, 77197-66-1; **24**, 80304-18-3; *cis*-bicyclo[4.3.0]nonan-8-one, 5689-04-3; *cis*-8-methylbicyclo[4.3.0]nonan-8-ol, 124267-71-6; *cis*-bicyclo[4.3.0]nonan-3-one, 4668-91-1; 1-methyl-9,9-dibromobicyclo[6.1.0]nonane, 70239-06-4; bicyclo[4.3.0]nonan-3-ol, 3716-38-9; *cis*-3-methylbicyclo[4.3.0]non-3-ene, 124267-73-8; (*Z,Z*)-2-methyl-1,4-cyclononadiene, 124267-75-0; (*Z,Z*)-1-methyl-1,4-cyclononadiene, 124267-76-1; 2-cyclononen-1-one, 1195-60-4; 1-methylcyclonon-2-en-1-ol, 124267-79-4.

Structural Effects on the Disproportionation Equilibrium of Tethered Tetraphenylethylene Radical Anions

David A. Shultz and Marye Anne Fox*

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

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The electrochemistry of four bis[*n*.1]metacyclophanylidenes has been studied by cyclic and differential pulse voltammetric methods. The potential differences between the first and second reduction steps for these cyclophanes depend on the length of the hydrocarbon tethers and therefore on the magnitude of phenyl ring torsion. This behavior can be correlated with the photophysical properties of these compounds, on the basis that the lowest singlet excited state is isolobal with the dianion. Since the potential difference between the first and second reduction steps is related to the disproportionation equilibrium constant, phenyl ring torsion, rather than olefinic torsion, may play a major role in determining the ion pairing and electrochemical properties of tetraphenylethylenes.

Introduction

Recently we have demonstrated that phenyl ring torsion plays a dominant role in the partitioning among tetraphenylethylene (TPE) singlet excited-state relaxation pathways.[1] For example, a strong increase in fluorescence quantum yield is observed if phenyl ring torsion is restricted by hydrocarbon tethers connecting geminal phenyl

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(1) (a) Shultz, D. A.; Fox, M. A. *Tetrahedron Lett.* **1988**, *29*, 4377. (b) Shultz, D. A.; Fox, M. A. *J. Am. Chem. Soc.* **1989**, *111*, 6311.

0022-3263/90/1955-1047$02.50/0

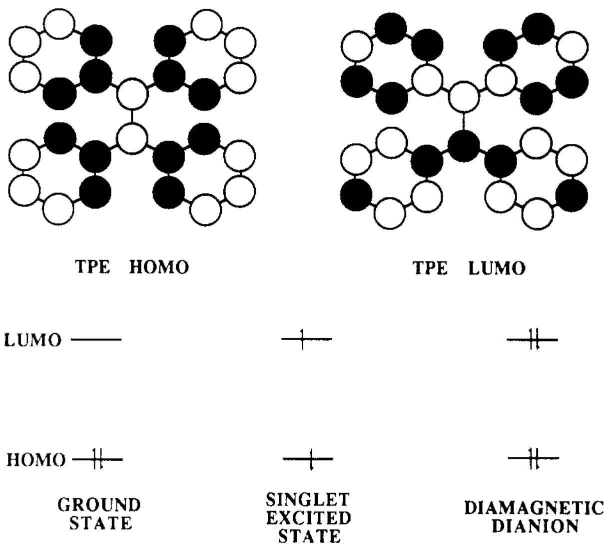


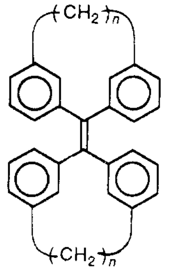
Figure 1. Tetraphenylethylene HOMO and LUMO (top). Orbital occupancies for the tetraphenylethylene singlet excited state (bottom left) and the tetraphenylethylene diamagnetic dianion (bottom right), illustrating the isolobal analogy.

Table I. Cyclic Voltammetric Data[a] for the Bis[*n*.1]metacyclophanylidenes and Tetra-*m*-tolylethylene

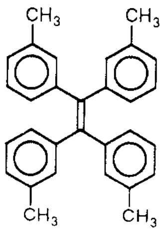
	first reduction		second reduction	
cmpd	$E_{1/2}$ (V ± 5 mV)[b]	$\Delta E_{p,1}$ (V ± 10 mV)[c]	E_p (V ± 5 mV)[d]	$\Delta E_{p,2}$ (V ± 20 mV)[e]
[4.1]MC	-2.30	0.10	-2.63	0.10
[5.1]MC	-2.35	0.10	-2.58	0.10
[6.1]MC	-2.35	0.10	-2.61	0.10

[a] Potentials vs Ag wire quasi-reference electrode, sweep rate = 100 mV/s. [b] Half-wave potential for the first reduction step. [c] Separation between cathodic and anodic peak potentials for the first reduction step. [d] Peak potential for the second reduction step. [e] Separation between cathodic and anodic peak potentials for the second reduction step.

rings. The molecules studied were bis[*n*.1]metacyclophanylidenes ([*n*.1]MCs, where *n* = 4–7) and tetra-*m*-tolylethylene (TTE). Although the magnitude of phenyl ring torsion is controlled by the length of the hydrocarbon tethers in the [*n*.1]MCs, olefinic torsion is unaffected by the aliphatic chains.[1]



[n.1]MCs



TTE

Upon occupation of the TPE LUMO, the olefinic π bond order decreases and the π bond orders between the phenyl rings and the olefinic carbons increase. Since the TPE singlet excited state and the diamagnetic TPE dianion are isolobal[2] (Figure 1), the structural changes involved in singlet excited-state dynamics and those that take place upon dianion formation are expected to be similar.

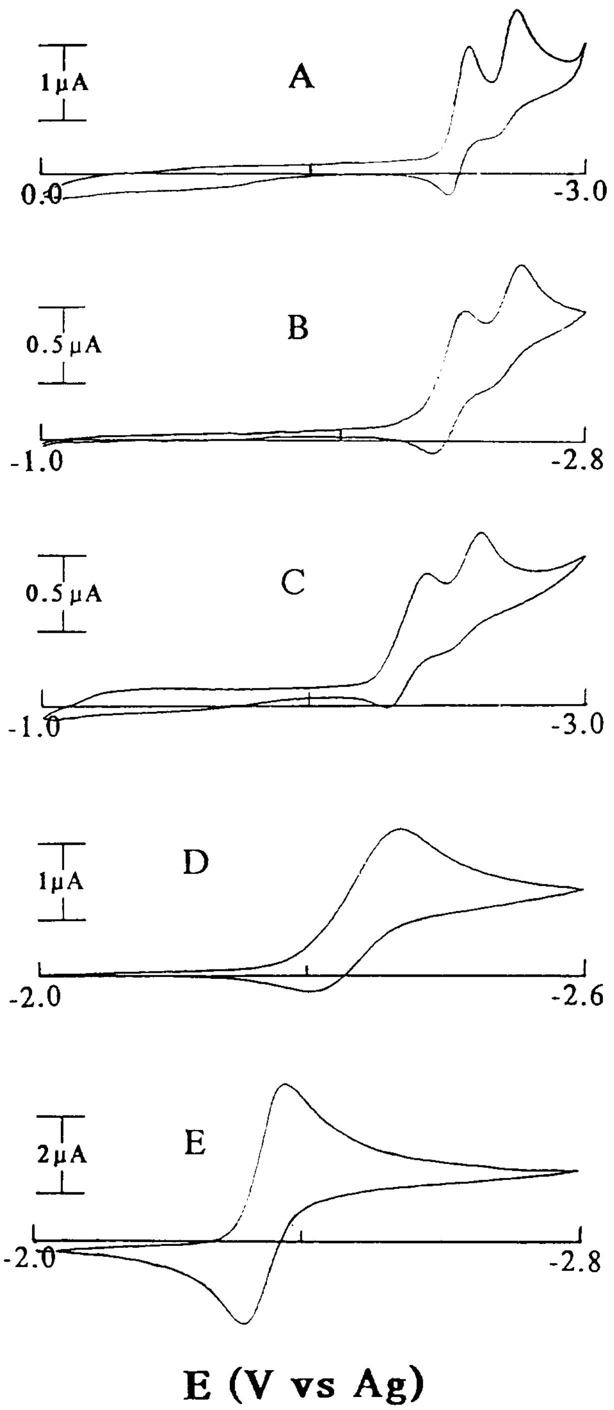


Figure 2. Cyclic voltammograms of the bis[*n*.1]metacyclophanylidenes ([*n*.1]MCs) and tetra-*m*-tolylethylene (TTE) in 0.1 M tetra-*n*-butylammonium perchlorate–tetrahydrofuran at a Pt disk electrode. Concentration of substrates was ca. 1 to 3 mM. A: [4.1]MC; B: [5.1]MC; C: [6.1]MC; D: [7.1]MC; E: TTE. Scan rate = 200 mV/s. Potentials vs Ag wire quasi-reference electrode.

This hypothesis may be tested by examining the disproportionation equilibrium of TPE radical anions as a function of phenyl ring torsion. We have examined the electrochemistry of the [*n*.1]MC (*n* = 4–7) series and a model compound, TTE, in tetrahydrofuran/tetra-*n*-butylammonium perchlorate via cyclic voltammetry and differential pulse voltammetry. This series was chosen in order to probe structural effects with minimal electronic perturbations. Our goal is to test whether phenyl ring

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[2] (a) Hoffmann, R. *Science* **1981**, *21*, 995. (b) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711. (c) Pinhas, A. R.; Albright, T. A.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta* **1980**, *63*, 29. Two systems are isolobal if "the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar–not identical, but similar."

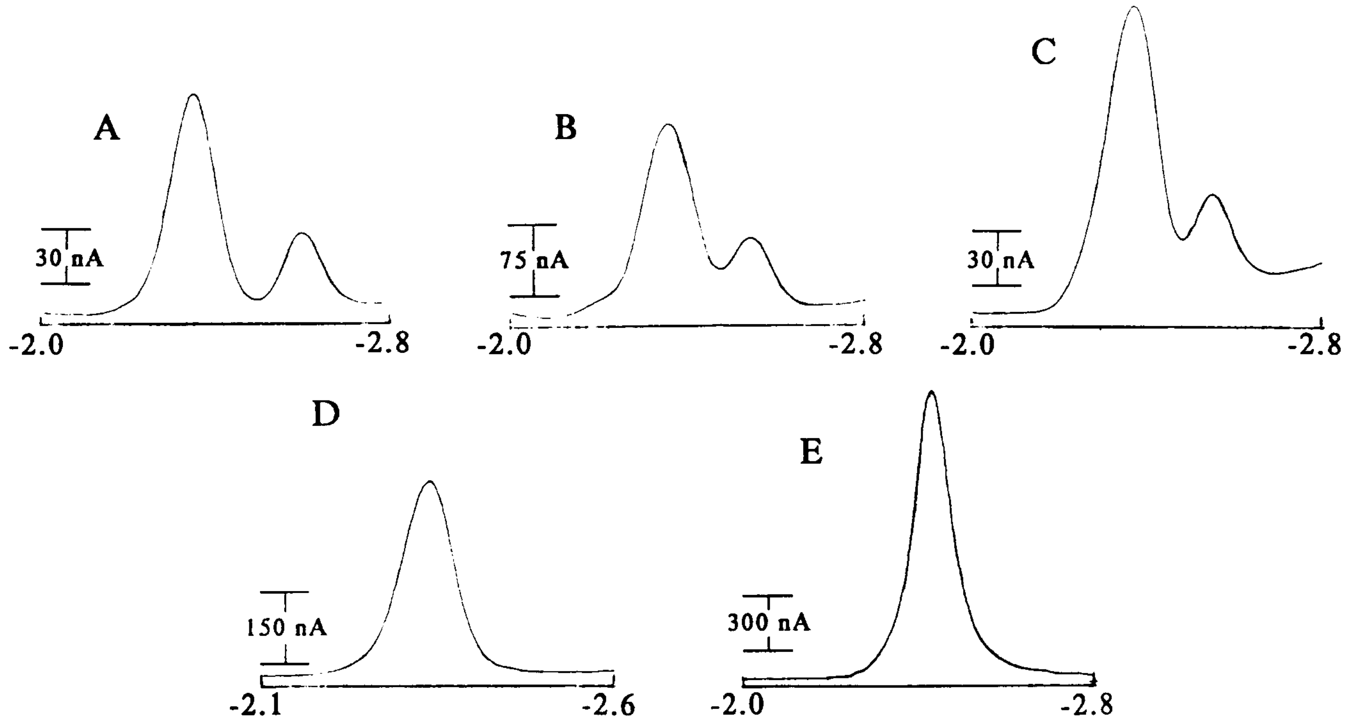

Figure 3. Differential pulse voltammograms of the bis[*n*.1]metacyclophanylidenes ([*n*.1]MCs) and tetra-*m*-tolylethylene (TTE) in 0.1 M tetra-*n*-butylammonium perchlorate-tetrahydrofuran at a Pt disk electrode. Scan rate = 200 mV/s. Concentration of substrates was ca. 1 to 3 mM. A: [4.1]MC; B: [5.1]MC; C: [6.1]MC; D: [7.1]MC; E: TTE. Potentials vs Ag wire quasi-reference electrode.

Table II. Differential Pulse Voltammetric Data[a] for the Bis[*n*.1]metacyclophanylidenes and Tetra-*m*-tolylethylene

cmpd	$E_{DP,1}$ (V ± 2 mV)[b]	$E_{DP,2}$ (V ± 2 mV)[c]	ΔE_{DP} (V ± 2 mV)[d]	width (V ± 5 mV)[e]	$\Delta E_{1/2}$ (V)[f]	$D_d \times 10^4$ (±20%)[g]
[4.1]MC	-2.35	-2.60	-0.25		-0.250	0.59
[5.1]MC	-2.35	-2.53	-0.18		-0.180	9.1
[6.1]MC	-2.35	-2.54	-0.19		-0.185	7.7
[7.1]MC				0.09	-0.035	2600
TTE				0.07	-0.008	7300

[a] Potentials vs Ag wire quasi-reference electrode. [b] Peak potential for the first reduction step. [c] Peak potential for the second reduction step. [d] Difference between first and second peak potentials. [e] Width at half-height of DPV curve. [f] Difference between first and second half-wave reduction potentials calculated from working curve in ref 5. [g] Disproportionation equilibrium constant calculated from eq 4.

torsion affects the electrochemical behavior of TPE, manifested as a difference in redox potentials for reduction to the anion and to the dianion (and hence, as a disproportionation equilibrium constant K_d).

Results

Cyclic Voltammetry. Cyclic voltammetry (CV) was used as a probe to investigate qualitative aspects of the electrochemical behavior of these compounds (Figure 2, Table I). The cyclic voltammetric behavior of [7.1]MC is much like that of TTE: a single reversible wave that by analogy with TPE[3] consists of two reversible one-electron waves separated by less than 50 mV. However, the cyclophanes [4.1]MC, [5.1]MC, and [6.1]MC show two distinct, reversible, one-electron waves. The redox potential for the second wave shifts negative as the tether length decreases. The voltammetric data for [4.1]MC, [5.1]MC, and [6.1]MC, are summarized in Table I. The waveforms of the second reduction steps of [4.1]MC, [5.1]MC, and [6.1]MC are insensitive to scan rate, whereas the cyclic voltammetric waveforms of [7.1]MC and TTE change as scan rate is altered. This is a qualitative indication that the second charge-transfer rate is faster for [4.1]MC, [5.1]MC, and [6.1]MC than for [7.1]MC and TTE.

Differential Pulse Voltammetry. The complex shape of the cyclic voltammetric waveform makes deconvolution of two closely spaced redox waves difficult under the best of circumstances. In our case the task is made even more difficult by additional complications from large uncompensated solution resistances in tetra-*n*-butylammonium perchlorate/tetrahydrofuran. The waveshape analysis problem may be simplified by using differential pulse voltammetry rather than cyclic voltammetry. The waveshape in DPV is nearly symmetric, and the redox potential difference, $\Delta E_{1/2}$, becomes a simple function of the DPV peak width or peak separation.[4]

We acquired DPV data on our compounds (Figure 3, Table II) and utilized the working curves of Richardson and Taube[4] to extract, from DPV peak widths and DPV peak separations, the value $\Delta E_{1/2}$ between the first and second reduction processes. As expected from cyclic voltammetry the DPVs of [4.1]MC, [5.1]MC, and [6.1]MC show two well-separated cathodic waves corresponding to

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formation of the radical anion and the dianion. Potential differences between the first and second cathodic peaks for [4.1]MC, [5.1]MC, and [6.1]MC, and voltammetric widths at half-height for [7.1]MC and TTE are listed in Table II.

The relative heights of the first and second waves are controlled by both thermodynamic and kinetic aspects of the disproportionation reaction.[5] As the disproportionation reaction proceeds, neutral starting material is regenerated, which may then be re-reduced. This leads to a relative increase in the current passed at the first reduction potential. Production of the dianion via homogeneous disproportionation also leads to a relative decrease in the current passed during the second heterogeneous charge transfer.

Discussion

Benzenoid hydrocarbons typically exhibit two reversible, one-electron reduction steps in aprotic solvents, which occur at potentials E_1 and E_2 (eq 1 and 2).[6] Many benzenoid hydrocarbons show a potential difference between E_2 and E_1 ($\Delta E_{1/2}$) of ca. −500 mV.[6] This difference is a function of stabilization by ion-pair formation and solvation and destabilization by electron–electron repulsion.[6]

$$\mathrm{B} + \mathrm{e}^- = \mathrm{B}^- \qquad E_1 \tag{1}$$

$$\mathrm{B}^- + \mathrm{e}^- = \mathrm{B}^{2-} \qquad E_2 \tag{2}$$

The relative stabilities of the radical anion and dianion may be ascertained from the disproportionation equilibrium constant. Subtraction of eq 1 from eq 2 gives the disproportionation equilibrium, eq 3. Its equilibrium constant K_d related to $\Delta E_{1/2}$ by eq 4, where n equals the number of electrons transferred, F is the Faraday constant, R is the gas constant, and T is temperature in Kelvin. Since $\Delta E_{1/2}$ is approximately constant for most benzenoid hydrocarbons, K_d is also constant and the equilibrium represented by eq 3 lies far to the left.

$$2\mathrm{B}^- = \mathrm{B} + \mathrm{B}^{2-} \tag{3}$$

$$K_d = \exp\,[\Delta \mathrm{E}_{1/2} n_1 n_2 F/RT] \tag{4}$$

In contrast, TPE in ethereal solvents gives a $\Delta E_{1/2}$ of less than 50 mV.[3,7,8] In this case, E_2 is shifted to more positive potentials (closer to E_1). Szwarc and co-workers showed that the thermodynamics of disproportionation and ion pairing are directly related.[9c,1011] Large values of K_d reflect strong dianion ion pairing and, conversely, small values of K_d reflect weak dianion ion pairing.

Several authors have suggested that K_d for TPE radical anions is large because of strong ion pairing in the dianion.[9,10] It has also been theorized that the principal structural change on dianion formation is olefinic torsion.[7,9,10a,11] This assumption led to the conclusion that the conformation resulting from 90° torsion of the olefinic bond gives the tightest ion pair.[7,9,10a,11] Olefinic twisting would isolate each electron of the dianion into a noninteracting half of the molecule and thereby decrease $\Delta E_{1/2}$ by reducing electron–electron repulsion. This twisting would also decrease steric repulsion of the *cis*-phenyl groups.[9a,b10a,11]

Olefinic twisting has also been invoked to explain the differences in kinetics of heterogeneous charge transfer for the first and second reduction steps of TPE.[6,7] Grzeszczuk and Smith[7] have obtained heterogeneous charge-transfer rate constants at a dropping mercury electrode for the two reduction steps of TPE in dimethylformamide solution, using Faradaic admittance data and numerous working curves. The second charge-transfer rate constant is approximately 1 order of magnitude *smaller* than the first. The small rate constant for the second reduction step has been attributed to a large structural reorganization in the transition state (rather than a large solvent reorganization).

A spectroscopic and theoretical study by Suzuki and co-workers[11] and earlier theoretical work[12] indicates that substantial geometry changes occur when TPE is reduced to either the radical anion or the dianion. Olefinic twisting in the dianion was assumed to constitute the largest geometry change.

However, an electrostatic model of contact ion pairing described by Streitweiser[13] shows that preferential stabilization of aryl ethylene dianions may be achieved by minimal olefinic torsion. X-ray crystal structures of bifluorenylidene and stilbene dianions determined by Walczak and Stucky[14] show only small increases in olefinic torsion. Recent NMR studies have presented evidence for minimal (ca. 30°) olefinic torsion in TPE^{2-}, $2\mathrm{K}^+$ contact ion pairs in tetrahydrofuran.[15]

We agree that TPE^{2-} is a contact ion pair in ether solvents; however, we disagree with the hypothesis that olefinic torsion is the largest structural change required for contact ion pair formation. Figure 3 and Table II show that the potential of the first reduction wave does not change with tether size, indicating that the structural restrictions imposed by the tethers do not strongly affect the relative energies of the LUMOs.[16] The potential of the second reduction step is, however, a function of tether size. The negative shift of the second reduction step corresponds to a decrease in K_d by more than 4 orders of magnitude from TTE (7.3×10^{-1}) to [4.1]MC (5.9×10^{-5}).[17] Based

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(16) An excellent correlation exists between the first reduction potential and the eigenvalue of the LUMO of benzenoid hydrocarbons, see: Streitweiser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961; Chapter 7.

on our recent work,[1] we suggest that the primary structural response to TPE dianion formation is phenyl ring torsion rather than olefinic torsion. Therefore, phenyl ring torsion dramatically affects ion pairing and, consequently, also affects K_d. The compound with the most restrictive tethers, [4.1]MC, exhibits the lowest tendency for stabilization by ion pairing, while the ion pair stabilization of the cyclophane with the least restrictive tethers, [7.1]MC, is almost indistinguishable from that of simple TTE. The cyclophanes [5.1]MC and [6.1]MC exhibit intermediate stabilization by ion pairing. The hydrocarbon tethers restrict flattening of the phenyl rings and therefore increase the counterion distance. This destabilizes the dianion and causes a decrease in K_d.

The waveform of the second reduction step for [4.1]MC, [5.1]MC, and [6.1]MC is insensitive to scan rate, whereas the shape of the CVs of [7.1]MC and TTE depend on the scan rate. This is a qualitative indication that the second charge-transfer rate is faster for [4.1]MC, [5.1]MC, and [6.1]MC than for [7.1]MC and TTE. Therefore, phenyl ring torsion and the ion-pairing dynamics associated with this torsional motion may be responsible for the slow heterogeneous electron-transfer rate constant for the second reduction step of TPE.[7]

The values of K_d for [5.1]MC and [6.1]MC are equal within experimental error, suggesting that one of these compounds behaves in a manner inconsistent with that expected on the basis of the size of the tether. This anomaly was also observed for the photophysical behavior of [5.1]MC and [6.1]MC.[1] Another interesting aspect of the relative values of K_d in this series is the large increase in going from [6.1]MC to [7.1]MC. This may be an indication that it is [6.1]MC that behaves anomalously.

Conclusions

We examined the cyclic voltammetric and differential pulse voltammetric behavior of the [*n*.1]MC series and TTE. Since the hydrocarbon tethers of the [*n*.1]MCs restrict phenyl ring torsion without affecting olefinic torsion,[1] the differences in electrochemical behavior within this series reflect differences in phenyl ring torsional freedom. The variation in phenyl ring torsion in these compounds manifests itself as a potential difference between the first and second reduction steps. The magnitude of the observed changes is determined by the relative stability of the ion pairs formed by each reduction step. Our findings show that phenyl ring torsion plays an important, if not paramount, role in ion pairing (and therefore K_d) and possibly in heterogeneous electron-transfer rates of TPE.[7]

Experimental Section

The synthesis and characterization of the [*n*.1]MCs and TTE have been described previously.[1] Tetrahydrofuran was distilled from sodium metal and stored under vacuum over lithium aluminum hydride. The supporting electrolyte, tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized from acetone/ether and dried under vacuum prior to use. The electrochemical cell consisted of a Pt disk working electrode (area = 0.020 cm^2), Pt foil counter electrode, and a silver wire quasi-reference electrode. Solutions were prepared by bulb-to-bulb distillation of ca. 3 mL of tetrahydrofuran into an electrochemical cell that contained 200 mg of TBAP (ca. 195 mM). After a background voltammogram was recorded, the substrate was added via a side arm (concentrations approximately 1–3 mM), and an electrochemical measurement was taken. The cyclic voltammetric and differential pulse voltammetric experiments were performed on a Bioanalytical Systems BAS-100 electrochemical analyzer. The differential pulse voltammetric parameters described by Richardson and Taube[4] were used (scan rate = 4 mV/s, pulse amplitude = 10 mV, pulse width = 50 ms, pulse period = 1000 ms). Values of $\Delta E_{1/2}$ were interpolated from the working curves of Richardson and Taube[4] from the DPV peak separation ([4.1]MC, [5.1]MC, and [6.1]MC) or the DPV peak width ([7.1]MC and TTE). Although positive feedback *iR* compensation affected the cyclic voltammetric peak shape, *iR* compensation affected neither the differential pulse voltammetric peak separation nor the peak width.[18]

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Registry No. [4,1]MC, 121080-15-7; [5,1]MC, 121080-16-8; [6,1]MC, 121080-17-9; [7,1]MC, 124482-28-6; TTE, 100200-63-3.

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[17] Values of $K_d > 400$ have been reported for the disodium salt of TPE dianion in tetrahydrofuran and dimethoxyethane.[9] The disodium salt of TPE dianion in tetrahydrofuran is a contact ion pair.[9c] The ion pair of tetra-*n*-butylammonium cations and tetraphenylethylene dianion is probably not a contact ion pair (if indeed the magnitude of K_d is a measure of the structure of the ion pair). The large shielded tetra-*n*-butylammonium counterion will decrease the stability of a contact ion pair relative to a smaller charge-intense ion,[10] and this is probably the reason for the smaller values of K_d observed in the present work. However, since tetra-*n*-butylammonium counterion was used in all of our experiments, changes in K_d are still a function of the ion pairing regardless of the structure.

[18] The large (ca. 100 mV) peak separations observed may be a consequence of large solution resistances caused by ion pairing of the electrolyte since ca. 100-mV peak separations were observed for ferrocene under identical conditions (1 mM ferrocene, Ca. 195 mM TBAP).