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Disproportionation and Structural Changes of Tetraarylethylene Donors upon Successive Oxidation to Cation Radicals and to Dications

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Abstract

The stepwise (one-electron) chemical oxidation of the tetraphenylethylene donor and its substituted analogues (**D**) can be carried out by electron exchange with aromatic cations or antimony(V) oxidants to selectively afford the cation radical (**D**$^{+\bullet}$) initially and then the dication

(**D**$^{2+}$). The ready interchange of the latter establishes the facile disproportionation (i.e., 2**D**$^{+\bullet} \rightleftharpoons$ **D**$^{2+}$ + **D**) that was originally examined by only transient electrochemical techniques. The successful isolations of the crystalline salts of the tetraanisylethylene cation radical (**1**$^{+\bullet}$) as well as the tetraanisylethylene dication (**1**$^{2+}$) allow X-ray diffraction analysis (for the first time) to quantify the serial changes in the molecular structure upon successive oxidations. Five structural parameters (*d*, *l*, θ, φ, and *q*) are identified as quantitative measures of changes in bond ($\mathrm{C}_\alpha{=}\mathrm{C}_\beta$, $\mathrm{C}_\alpha{-}$anisyl) lengths, dihedral ($\mathrm{C}_\alpha{=}\mathrm{C}_\beta$)/torsional (anisyl) angles, and quinoidal (anisyl) distortion attendant upon the removal of first one-electron and then another electron from the tetraanisylethylene framework. The linear variation of all five parameters in Chart 3 point to a strongly coupled relaxation of tetraanisylethylene (involving simultaneous changes of *d*, *l*, θ, φ, and *q*) to a severely twisted dication. Most noteworthy is the structure of the cation radical **1**$^{+\bullet}$ with *d*, *l*, θ, φ, and *q* values that are exactly one-half those of the dication. The complex molecular changes accompanying the transformation: **D** → **D**$^{+\bullet}$ → **D**$^{2+}$ bear directly on the donor properties and the disproportionation processes of various tetraarylethylenes.

Introduction

Tetraphenylethylene and its ring-substituted analogues are bifunctional electron donors (or acceptors) by virtue of both aromatic and olefinic centers present as either electron-rich (or electron-poor) reservoirs. As such, various tetraarylethylenes have enjoyed widespread application to reaction types as diverse as reduction, oxidation, photocyclization, halogenation, oxygenation, etc.[1,2] Especially noteworthy are the highly hindered electron-rich analogues, which are known to result in intensely colored solutions upon treatment with various electrophiles (Cl_2, Br_2, I_2, and ICl) as well as Brønsted and Lewis acids.[3,4]

Of particular relevance to tetraarylethylenes are the facile disproportionations of the (one-electron) oxidation product, in the form of the tetraarylethylene cation radical on one hand (eq 1)[5] and the anion radical as the reduction product on the other (eq 2).[6] Such interchanges between paramagnetic ion radicals and diamagnetic dications are pertinent to the mechanistic delineation of homolytic (free radical) and electrophilic (ionic) pathways, most certainly as they apply to electron transfer and acid catalysis, respectively.[7]

$$2\ \mathrm{Ar_2C{=}CAr_2}^{+\bullet} \overset{K_{disp}}{\rightleftharpoons} \mathrm{Ar_2C\text{-}CAr_2}^{2+} + \mathrm{Ar_2C{=}CAr_2} \qquad (1)$$

$$2\ \mathrm{Ar_2C{=}CAr_2}^{-\bullet} \overset{K_{disp}}{\rightleftharpoons} \mathrm{Ar_2C\text{-}CAr_2}^{2-} + \mathrm{Ar_2C{=}CAr_2} \qquad (2)$$

The thermodynamics of the redox disproportionation in eq 1 (or eq 2) derives from the corresponding (one-electron) potentials, i.e., $\Delta G^\circ = F, (E^\circ_2 - E^\circ_1)$, where E°_1 and E°_2 refer to the stepwise oxidation (or reduction) of first the tetraarylethylene donor and then the tetraarylethylene cation radical (or anion radical).[8] It is important to note that owing to the overall propeller shape of tetraarylethylenes, their conformation will play an important role in determining these redox properties in oxidation as well as reduction.[9] However, little is definitively known quantitatively about the conformational and/or structural changes that take place when a tetraarylethylene is converted to its cation radical (or anion radical) and thence to the dication (or dianion). Although X-ray crystallographic determination is the most direct approach to molecular structure, it has not been applied to the disproportionation, largely due to the difficulty in growing suitable single crystals of both the cation radical (or anion radical) and the dication (or dianion) of the same tetraarylethylene.[10]

Of the various redox systems extant in the literature, we identify the oxidation/disproportionation of tetraanisylethylene as the potentially most viable for X-ray diffraction analysis. For example, tetraanisylethylene (**1**) can be electrochemically oxidized to its cation radical (**1**$^{+\bullet}$) and to its dication (**1**$^{2+}$) which are both rather persistent in dichloromethane solutions in the presence of 0.2 M supporting electrolyte.[11] Moreover, quantitative analysis of the anodic behavior affords values of the disproportionation constant (see eq 1) in solvents of various polarities.[12] Thus our first task in this study is to confirm the ready redox disproportionation by a wholly chemical method (without the complications of added salt) – ultimately to allow the isolation of crystalline cation-radical and dication salts of tetraanisylethylene for direct X-ray diffraction analysis. To establish the scope of the structural requirements and facilitate the ease of isolation of the one- and two-electron oxidation products, we prepared the series of tetra- and diarylated ethylene analogues identified in Chart 1, where An and Tol are *p*-methoxy- and *p*-methylphenyl groups, respectively.

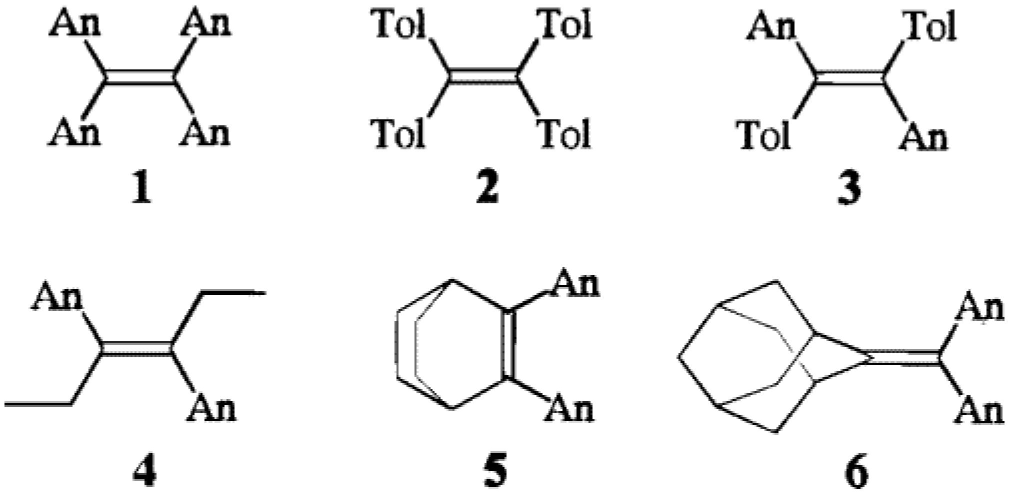


Chart 1. Olefinic Donors

Results and Discussion

The requisite isolation of the various cation radicals and the dications as crystalline salts for X-ray diffraction analysis called for a selective (yet sufficiently powerful) reagent to effect successive one-electron transfers from the tetraarylethylenes in Chart 1, of which we identified three oxidants as follows.

I. Chemical Oxidation of Tetraarylethylenes to Their Cation Radicals and Dications. A. Via Electron Exchange with Aromatic Cation Radicals. The cation radicals of the methano- and ethanoanthrancene derivatives **MA**$^{+\bullet}$ and **EA**$^{+\bullet}$, respectively, are selective organic oxidants with reversible reduction potentials that differ by only 190 mV, as listed in Chart 2.[13] As such, the treatment of tetraanisylethylene (**1**) with 1 equiv of **MA**$^{+\bullet}$ in dichloromethane (under an argon atmosphere at 25 °C) immediately yielded a bright blue solution, the UV−vis spectrum (Figure 1A) of which showed the characteristic twin absorption bands at 560 and 941 nm of tetraanisylethylene cation radical (**1**$^{+\bullet}$).[15] Quantitative spectral analysis of the blue solution (log ε_{560} = 4.28 in Table 1) indicated that the electron exchange in eq 3 was displaced completely to the right. In a similar vein, the treatment of a solution of 2 equiv of **MA**$^{+\bullet}$ at 25 °C with 1 equiv of tetraanisylethylene immediately yielded a dark green solution (Figure 1B) which upon quantitative spectral analysis showed the formation of 1 equiv of tetraanisylethylene dication **1**$^{2+}$ (λ_{max} = 567 nm, log ε_{max} = 4.59) in quantitative yield (eq 4). Indeed the distinctive pair of absorption spectra in Figure 1 indicated that the cation radical (**1**$^{+\bullet}$) and the dication (**1**$^{2+}$) could be generated cleanly via the discrete one- and two-electron transformations in eqs 3 and 4, respectively, without admixture of one with the other.

MA$^{+\bullet}$ **EA**$^{+\bullet}$

E^{o}_{red} 1.11 1.30 (V *vs.* SCE)

Chart 2. Aromatic Oxidants

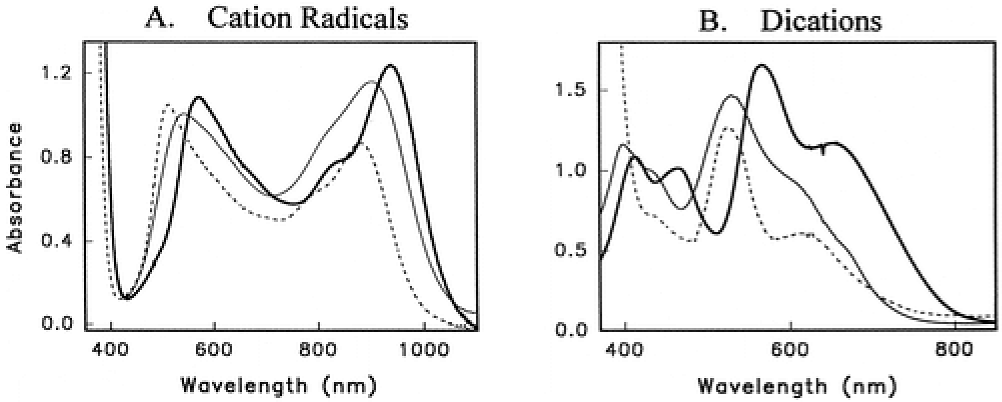
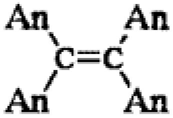
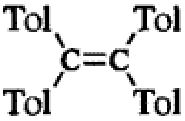
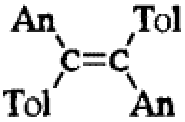
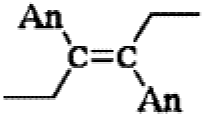
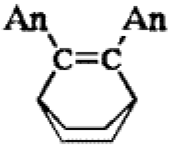
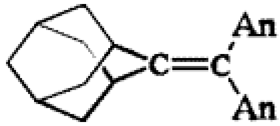


Figure 1 UV−vis absorption spectra of (A) the cation radical and (B) the dication from the oxidation of tetraanisylethylene **1** (─), tetratolylethylene **2** (- - -), and dianisylditolylethylene **3** (- - -) with 1 and 2 equiv of [**EA**$^{+\bullet}$ SbCl$_6^-$], respectively, in dichloromethane at 25 °C.

$$\mathbf{1} + \mathbf{MA}^{+\bullet} \longrightarrow \mathbf{1}^{+\bullet} + \mathbf{MA} \qquad (3)$$

$$\mathbf{1} + 2\,\mathbf{MA}^{+\bullet} \longrightarrow \mathbf{1}^{2+} + 2\,\mathbf{MA} \qquad (4)$$

Table 1. Absorption (UV-Vis) Spectra of Cation Radicals and Dication of Tetraarylethylenes and Related Donors[a]

	Ethylene Donor	Cation Radical nm (log ε)[b]	Dication nm (log ε)[b]
1		560(4.28), 926	567 (4.59), 414[c]
2		516(4.18), 885	515 (- e -), 390[c,d]
3		544(4.17), 904	525 (4.41), 438[c]
4		514(4.09),762(sh), 880	- e -
5		546(4.16), 492(sh), 880	- e -
6		427(1.08), 658, >1100	- e -

[a] In dichloromethane solution at 23 °C, unless otherwise indicated.[b] Extinction coefficient in M^{-1}.[c] See Figure 1 for other peaks.[d] Not stable at room temperature; see text.

The stepwise oxidations of the analogous tetra-*p*-tolylethylene (**2**) and the anisyl/tolyl hybrid (**3**) were only selectively effected by $\mathbf{MA}^{+\bullet}$ at 25 °C. For example, dianisylditolylethylene (**3**) reacted with 1 equiv of $\mathbf{MA}^{+\bullet}$ to produce the cation radical $\mathbf{3}^{+\bullet}$ (λ_{max} = 544 nm) in a manner much like that for tetraanisylethylene in eq 3. However, the electron exchange of tetratolylethylene (**2**) with 1 equiv of $\mathbf{MA}^{+\bullet}$ in dichloromethane proceeded only to 90% conversion (together with 10% unreacted $\mathbf{MA}^{+\bullet}$), as judged by the quantitative spectral analysis of $\mathbf{2}^{+\bullet}$ (λ_{max} = 516 nm, log ε 4.18). Although the incremental addition of another equiv of $\mathbf{MA}^{+\bullet}$ led to the complete conversion of **2** to the cation radical $\mathbf{2}^{+\bullet}$, it was insufficient to effect the further oxidation to the dication $\mathbf{2}^{2+}$. The latter was readily achieved by 2 equiv of the somewhat stronger oxidant $\mathbf{EA}^{+\bullet}$ (vide supra). Solutions of tetraanisylethylene and the hybrid dications $\mathbf{1}^{2+}$ and $\mathbf{3}^{2+}$ (see Figure 1B) prepared in the same manner were stable for several hours at 25 °C.[16] However, treatment of the dianisylethylenes **4−6** with 2 equiv of $\mathbf{EA}^{+\bullet}$ led to highly colored solutions of the corresponding cation radicals (see Table 1) which decomposed rapidly at room temperature.[17] From spectral changes such as these, it was easy to deduce the qualitative trend in redox reactivity of tetraarylethylenes as $\mathbf{1} > \mathbf{3} > \mathbf{2}$ for cation-radical formation and $\mathbf{1} > \mathbf{3} \gg \mathbf{2}$ for dication formation. Moreover, the same monotonic trend pertained to the steady bathochromic shifts of the absorption bands of the tetraarylethylene cation radicals as well as those of the corresponding dications in Figure 1, A and B, respectively.

B. Preparative Isolation of Tetraarylethylene Dications with Antimony Pentachloride. The strongly oxidizing antimony pentachloride[18] proved to be especially suitable for the preparation and isolation of pure tetraarylethylene dications. Thus, the treatment of tetraanisylethylene **1** (1.0 mmol) with antimony pentachloride (4.0 mmol) in anhydrous dichloromethane at −50 °C immediately resulted in a dark green solution from which the crystalline dication salt readily precipitated in quantitative yields upon the slow addition of a mixture of anhydrous ether and hexane (eq 5).[19] The microcrystalline precipitate was filtered under an argon atmosphere and dried in vacuo. A quantitative spectrophotometric analysis of the black solid (after dissolution of a known quantity in anhydrous dichloromethane) showed the characteristic UV−vis absorption spectrum of the dication salt of tetraanisylethylene which was formed in 73% yield according to eq 5. The high purity of the salt was further verified by iodometric titration (see Experimental Section). The same procedure was also used in the preparation of the highly pure dication salt of tetraarylethylene **3**. The dark (red) crystal of the tetratolylethylene dication salt $[\mathbf{2}^{2+}(SbCl_6^-)_2]$ for X-ray crystallography was prepared earlier from $SbCl_5$ at −78 °C (see Supporting Information Available).

$$\mathbf{1} + 3\,SbCl_5 \longrightarrow [\mathbf{1}^{2+}(SbCl_6^-)_2] + SbCl_3 \qquad (5)$$

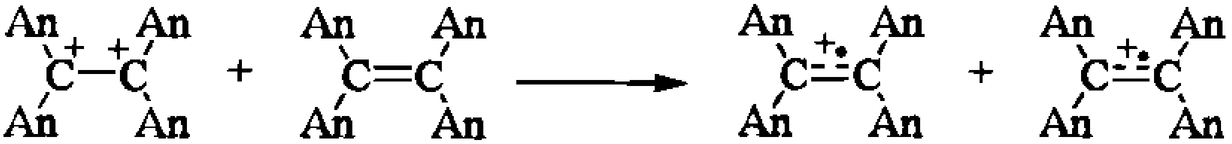
C. Triethyloxonium Hexachloroantimonate for the Preparation of Crystalline Tetraanisylethylene Cation-Radical Salt. A suspension of $[Et_3O^+ SbCl_6^-]$ (1.5 equiv) and tetraanisylethylene **1** was stirred in dichloromethane at 0 °C for an hour, during which the solution took on a dark blue coloration. The UV−vis spectral analysis of the highly colored solution showed the characteristic spectrum with a twin absorption band at λ_{max} = 560 and 941 nm (compare Figure 1) due to the tetraanisylethylene cation radical (vide supra), in essentially quantitative yield (eq 6).[19] The bright blue solution was cooled to −20 °C, and followed by a careful layering with diethyl ether. When the two-phase mixture was allowed to stand undisturbed at −20 °C for a prolonged period, it deposited a well-formed crop of very dark crystals interspersed with colorless crystals of unreacted tetraanisylethylene.[20] A close scrutiny revealed a mixture of two morphological types of essentially the same (indistinguishably dark) color; and manual separation led to (a) isometric prisms of the tetraanisylethylene cation radical salt and (b) long thin plates of the tetraanisylethylene dication salt, both structures of which were established by X-ray crystallography (vide infra). Although a complete determination of the exact stoichiometry was not possible, the (unanticipated) codeposition of cation-radical and dication salts together with unreacted tetraanisylethylene (from a solution consisting of only cation radical) must have arisen from the crystallization-induced disproportionation (eq 7).[21] The treatment of dianisylditolylethylene **3** with [Et_3O^+ $SbCl_6^-$] by the same procedure afforded a quantitative yield of the cation radical ($\mathbf{3}^{+\bullet}$), as determined by quantitative (UV−vis) spectral analysis of the dichloromethane solution. Cooling the solution to 0 °C, followed by a careful layering with toluene, led to dark crystals of the dication salt [$\mathbf{3}^{2+}$ $(SbCl_6^-)_2$], the structure of which was established by X-ray crystallography (vide infra). Curiously, the expected crystals of the cation-radical salt [$\mathbf{3}^{+\bullet}$ $SbCl_6^-$] were not detected. We were also unable to prepare the crystalline salt of the tetratolylethylene cation radical using the [Et_3O^+ $SbCl_6^-$] procedure.[22]

$$2\ \mathbf{1} + 3\ [Et_3O^+\ SbCl_6^-] \longrightarrow 2\ [\mathbf{1}^{+\bullet}\ SbCl_6^-] + 3\ EtCl + 3\ Et_2O + SbCl_3 \qquad (6)$$

$$2\ [\mathbf{1}^{+\bullet}\ SbCl_6^-] \underset{}{\overset{[crystalztn]}{\rightleftharpoons}} [\mathbf{1}^{2+}\ (SbCl_6^-)_2] + \mathbf{1} \qquad (7)$$

II. Electron-Transfer Reactivity of the Tetraanisylethylene Dication ($\mathbf{1}^{2+}$). The ready isolation of the crystalline salt of tetraanisylethylene dication in eq 5 allowed its electron-transfer reactivity toward the parent tetraanisylethylene and other neutral donors to be examined directly, as follows.

A. Redox Conproportionation with Tetraanisylethylene Donor. When a dark green solution of tetraanisylethylene dication was mixed with an equimolar amount of the neutral (colorless) donor, a dramatic color change to bright blue occurred immediately. UV−vis spectral analysis established the simultaneous oxidation of **1** and reduction of $\mathbf{1}^{2+}$ in quantitative yields (eq 8),[23] and the uncluttered character of the electron transfer was established by the pair of well-defined isosbestic points in the UV−vis spectra (Figure 2) when a solution of $\mathbf{1}^{2+}$ was treated with incremental amounts of **1**. [Note the final spectrum remained unchanged upon the addition of **1** beyond 1 equiv.]



(8)

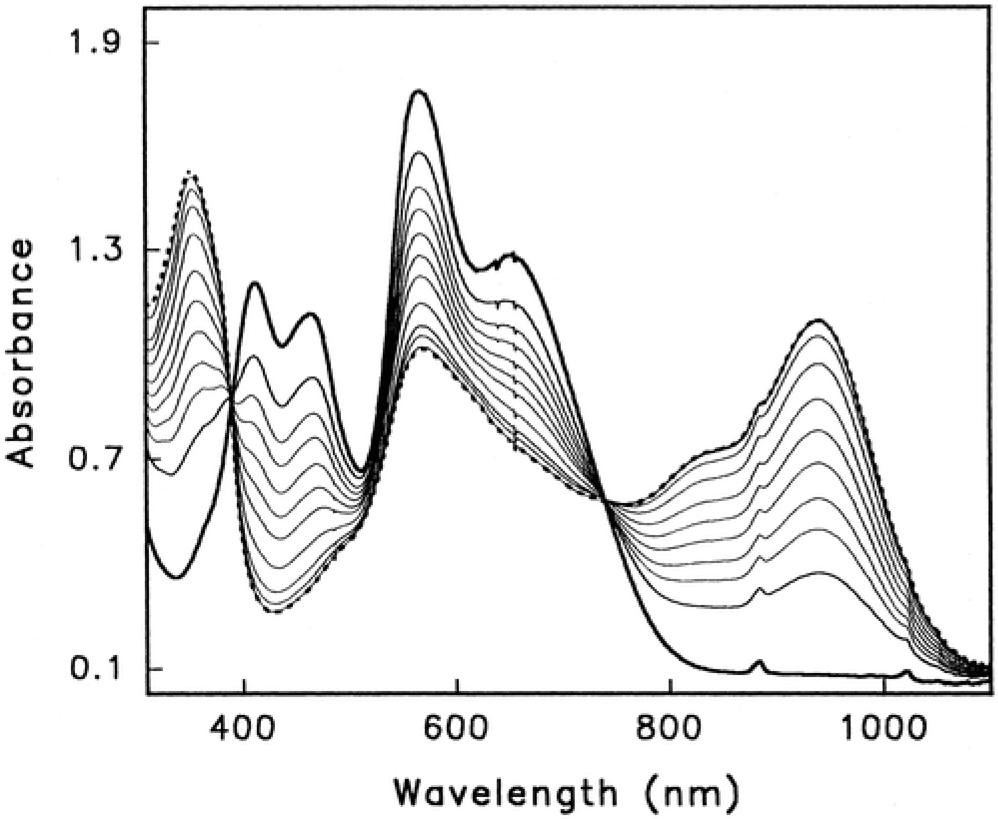
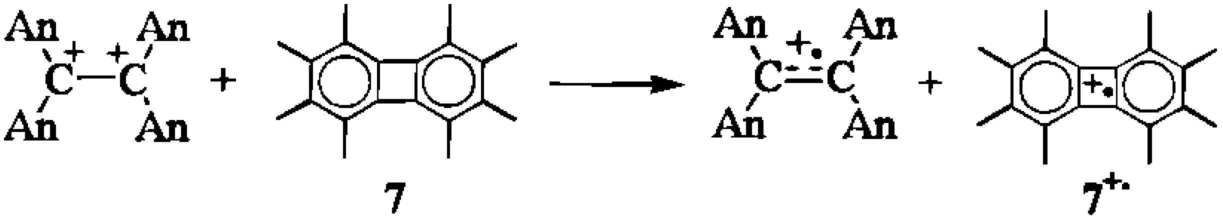


Figure 2 Spectral changes attendant upon the reduction of 4.5 × 10^{-5} M dication $\mathbf{1}^{2+}$ (—) to its cation radical $\mathbf{1}^{+\bullet}$ (- - -) by incremental addition of 1.8 × 10^{-3} M **1** in dichloromethane at 25 °C.

B. Electron Transfer from Octamethylbiphenylene. The treatment of the electron-rich (colorless) donor octamethylbiphenylene (**7**, $E°_{ox}$ = 0.80 V vs SCE) with an equimolar amount of the dication $\mathbf{1}^{2+}$ in dichloromethane resulted in an immediate color change to a dark blue solution, the UV−vis absorption spectrum of which consisted of a broad absorption showing a pair of major bands at λ_{max} = 600 and 930 nm. Spectral subtraction of the tetraanisylethylene cation-radical ($\mathbf{1}^{+\bullet}$) absorption in Table 1 resulted in a well-resolved absorption band with λ_{max} = 602 nm, 550 (sh) and log ε_{602} = 4.08 of the blue octamethylbiphenylene cation radical ($\mathbf{7}^{+\bullet}$).[7] Quantitative comparison of the latter with an authentic spectrum of $\mathbf{7}^{+\bullet}$ (prepared by the oxidation of octamethylbiphenylene with $\mathbf{MA}^{+\bullet}$ as in eq 3) indicated that electron transfer was quantitative, i.e.



(9)

C. Tetrakis-Annelated Cyclooctatetraene as Electron Donor. The oxidation of a colorless solution of the tetrakis-bicyclooctano-annelated cyclooctatetraene[24] (**8**, $E°_{ox}$ = 0.75 V vs SCE) with 1 equiv of tetraanisylethylene dication ($\mathbf{1}^{2+}$) in dichloromethane yielded immediately a dark red solution, the UV−vis spectrum of which showed a nondescript, rather continuous absorption from 500 to 1000 nm. However, spectral subtraction of the tetraanisylethylene cation-radical absorption (see Figure 1A) resulted in the well-defined absorption spectrum shown in Figure 3 with λ_{max} = 745 nm (log ε_{745} = 3.66) and 442 nm (3.09) which coincided with the authentic spectrum of the emerald green cation radical **8**$^{+\bullet}$ generated independently from the oxidation of the cyclooctatetraene **8** and 1 equiv of **MA**$^{+\bullet}$ as in eq 3. It is interesting to note that the intense visible absorption of the cation radical **8**$^{+\bullet}$ derives from the one-electron oxidation of the neutral donor **8** without significant conformational change of its pronounced “tub-shaped” structure.[25]

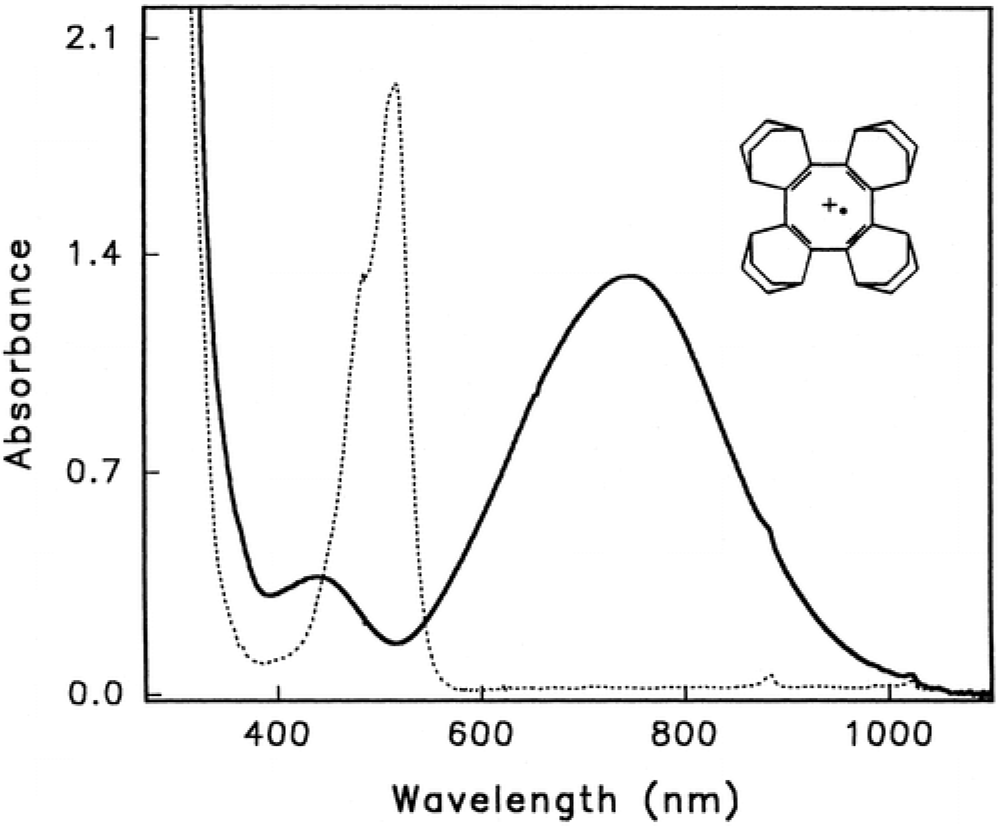
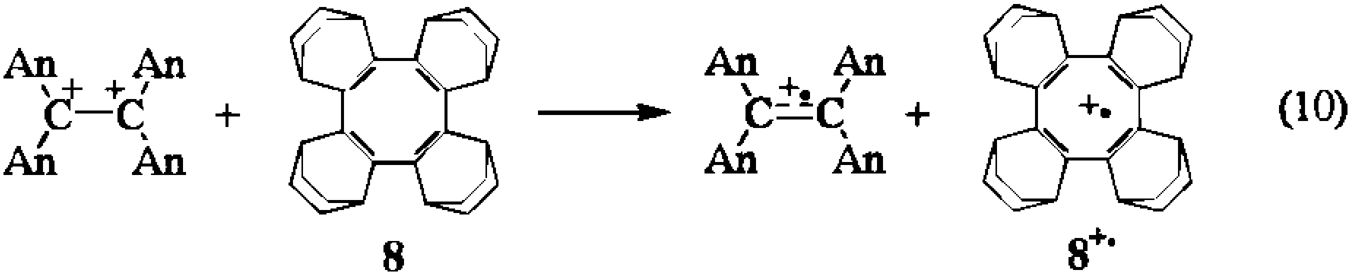


Figure 3 The UV−vis absorption spectrum, of cyclooctatetraene cation radical **8**$^{+\bullet}$ (—) generated by treatment of 0.3 mM **8** in dichloromethane with 1 equiv of [**MA**$^{+\bullet}$ SbCl$_6^-$] (- - -) at 25 °C.



III. Direct Measurement of Cation-Radical Disproportionation. Since the conproportionation of tetraanisylethylene (**1**) with its dication (**1**$^{2+}$) as described in eq 8 was the microscopic reverse of the disproportionation of the cation radical (**1**$^{+\bullet}$) previously reported by

Parker and others in the course of electrochemical (anodic) oxidation of tetraanisylethylene,[12] we carefully measured the magnitudes of the disproportionation constant (see K_{disp} in eq 1) in three solvents of varying polarity in the absence of added salt.

The relative concentrations of the cation-radical $\mathbf{1}^{+\bullet}$ and the dication $\mathbf{1}^{2+}$ were measured in dichloromethane by following the (UV−vis) spectral changes attendant upon the increasing concentrations of tetraanisylethylene cation radical ($\mathbf{1}^{+\bullet}$) generated in situ by oxidation with incremental amounts of the aromatic oxidant $\mathbf{MA}^{+\bullet}$ according to eq 3. Since the resulting changes in the composite spectra (Figure 4) were rather complex (due to the overlapping bands of $\mathbf{1}^{+\bullet}$ and $\mathbf{1}^{2+}$), for clarity they are best considered in two equal segments, i.e., (a) from 0 to 1 equiv (shown by the solid lines) and (b) from 1 to 2 equiv (shown by the dashed lines) of added $\mathbf{MA}^{+\bullet}$. In segment (a), the concentration of cation-radical $\mathbf{1}^{+\bullet}$ (λ_{max} 941 nm) increased steadily, and that of $\mathbf{1}^{2+}$ [λ_{max} 567 nm, 654(sh)] was always minor until 1 equiv of $\mathbf{MA}^{+\bullet}$ was added. In segment (b), the concentration of the dication $\mathbf{1}^{2+}$ increased steadily at the expense of $\mathbf{1}^{+\bullet}$ until 2 equiv of $\mathbf{MA}^{+\bullet}$ was added, at which point all the $\mathbf{1}^{+\bullet}$ was consumed. Most importantly, the composite spectra at the intermediate points (at which ~1 equiv of $\mathbf{MA}^{+\bullet}$ had been added) were identical with those obtained in Figure 2 from the conproportionation of $\mathbf{1}^{2+}$ with **1**. [Note especially the common isosbestic point at 740 nm.] Together, the spectral changes in Figures 2 and 4 thus establish the validity of the reversible character of the redox (disproportionation) interchanges, i.e.

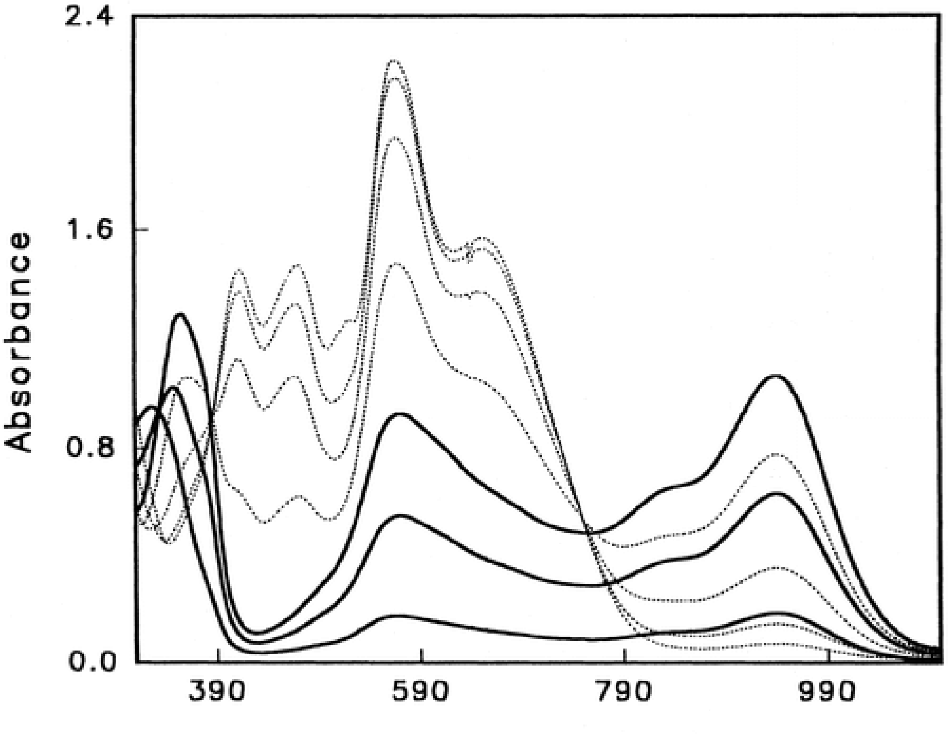
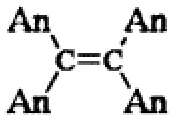
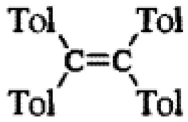
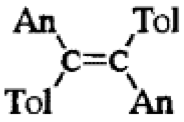


Figure 4 The stepwise oxidation of tetraanisylethylene **1** (6.3×10^{-5} M) with incremental additions of 0 to 1 equiv (—) and 1 to 2 equiv (- - -) of 2.3 mM [$\mathbf{MA}^{+\bullet}$ $SbCl_6^-$] in dichloromethane at 25 °C.

$$2\ \mathbf{1}^{+\bullet} \xrightleftharpoons{K_{disp}} \mathbf{1}^{2+} + \mathbf{1} \qquad (11)$$

It was particularly clear from the spectral results in segment (a) that the cation radical was always the predominant species in dichloromethane solution, i.e., $[\mathbf{1}^{+\bullet}] \gg [\mathbf{1}^{2+}]$. Quantitative analysis of the spectral changes in both segments (a) and (b) afforded the consistent values of the disproportionation constant $K_{disp} = [\mathbf{1}^{2+}][\mathbf{1}]/[\mathbf{1}^{+\bullet}]^2$ listed in Table 2. By contrast, the value of K_{disp} was significantly larger in acetonitrile and intermediate in nitromethane solution.[26] Most importantly, the results in Table 2 largely confirm the values of K_{disp} in dichloromethane and acetonitrile evaluated electrochemically by Parker and co-workers (see Table 2, column 4).[12] Furthermore, the decreasing magnitudes of K_{disp} for dianisylditolylethylene **3** and tetratolylethylene **2** fall in line with their decreasing donor strengths. To quantitatively evaluate the latter, the anodic behavior of the tetraarylethylene donors was examined.

Table 2. Disproportionation Constant (K_{disp}) for Tetraarylethylene Cation Radicals in Different Solvents

Ethylene Donor	Solvent	K_{disp} (Spectral)[a]	K_{disp} (Voltamm.)[b]
1 	CH_2Cl_2	0.002	(9.3×10^{-3})
	CH_3CN	0.90	(0.84)[c]
	CH_2Cl_2/CH_3CN	0.21	(0.26)[c]
2 	CH_2Cl_2	$< 1 \times 10^{-4}$	(2.7×10^{-5})
3 	CH_2Cl_2	7.1×10^{-4}	(6.3×10^{-3})

[a] See Experimental Section.[b] Calculated from the cyclic voltammetric data in Table 3 using the Nernstian expression $K_{disp} = \exp(-0.039\Delta E°)$ at 298 K, where $\Delta E° = E_2° - E_1°$ (mV).[c] Taken from ref 12.

IV. Electrochemical Oxidation of Tetraarylethylene and Related Donors. The various tetraarylethylenes in Chart 1 were oxidized electrochemically at a platinum electrode as 5×10^{-3} M solutions in anhydrous dichloromethane containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. The reversible cyclic voltammograms (CV) of the tetraarylethylenes **1**, **2**, and **3** with two closely coupled reversible one-electron oxidation waves were consistently attained at a scan rate of v = 200 mV s^{-1}; they all showed the anodic/cathodic peak current ratio of i_a/i_c = 1.0 (theoretical) at 25 °C (see Figure 5). The internal calibration of the CV peaks with added ferrocene then yielded the reversible oxidation potential (E°_{ox}) in Table 3 for the production of cation radical via the one-electron redox couple and the dication via the two-electron redox couple (eq 12). The values of first and second oxidation potentials of tetraanisyl and dianisylditolylethylene were separated by only 120 and 130 mV, respectively, whereas tetratolylethylene **3** showed a significantly larger separation of 270 mV.

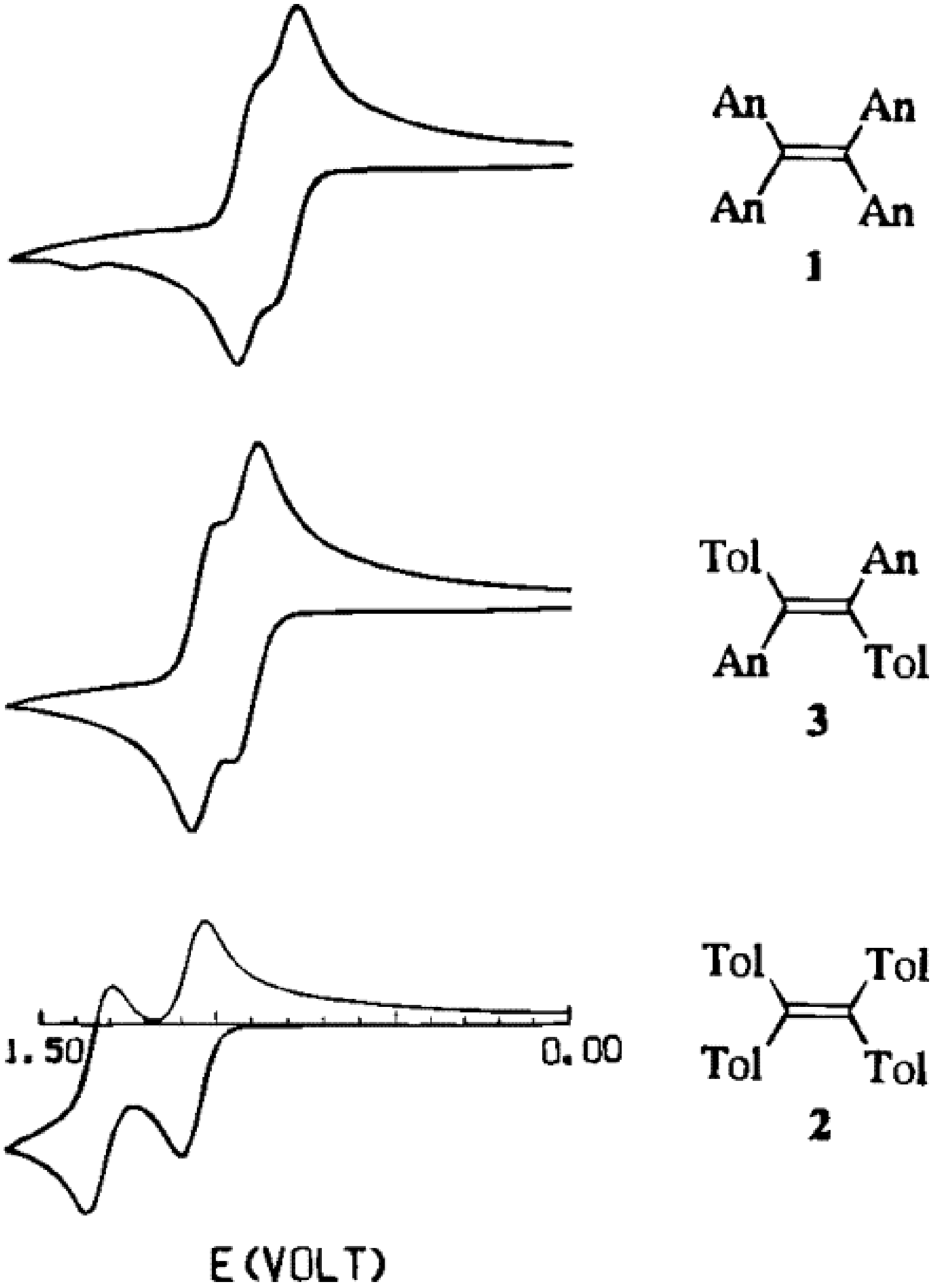
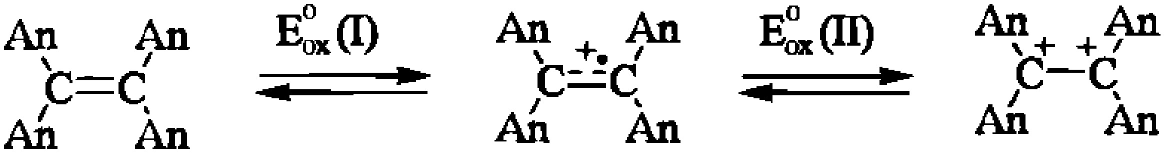
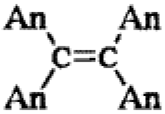
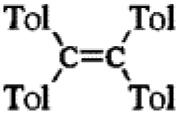
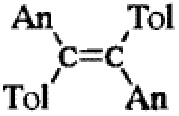
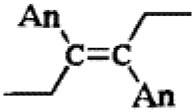
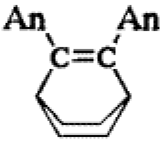
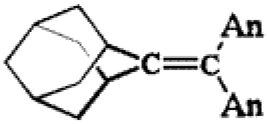


Figure 5 Cyclic voltammograms of 5 mM tetraarylethylenes **1**, **2**, and **3** (as indicated) in dichloromethane containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate at a scan rate of v = 200 mV s^{-1} (25 °C).



(12)

Table 3. Electrochemical Oxidation Potentials of the Tetraarylethylenes and Related Donors[a]

	Ethylene Donor	$E^{0}_{ox}(I)$ (V vs. SCE)	$E^{0}_{ox}(II)$ (V vs. SCE)	Δ (mV) $E^{0}_{ox}(II)$-$E^{0}_{ox}(I)$
1		0.79 (0.90)	0.91 (0.90)	120 (0)[b]
2		1.10 (1.09)	1.37 (1.20)[c]	270 (110)
3		0.89 (0.99)	1.02 (0.99)	130 (0)[d]
4		1.00	1.11	110
5		0.98 (0.96)[e]	1.15	170
6		1.17 (1.17)[e]	1.61[e]	440

[a] In anhydrous dichloromethane (unless otherwise indicated) containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate at a scan rate $v = 200$ mV s^{-1} and 25 °C. Values in parentheses are in acetonitrile. [b] Single reversible CV wave with $E^{c}_{p} - E^{a}_{p} = 65$ mV. [c] Quasi-reversible CV wave at a scan rate $v = 200$ mV s^{-1}. [d] Single reversible CV wave with $E^{c}_{p} - E^{a}_{p} = 88$ mV. [e] Anodic peak potential. Irreversible CV wave at $v = 200$ mV s^{-1}.

The anodic oxidation of the dianisylethylenes **4** and **5** also showed two reversible CV waves that were separated by roughly the same amount as that listed in Table 3 for tetraanisylethylene. In other words, the mere presence of an α, β-pair of anisyl groups was sufficient to confer roughly the same stability to the ethylene dication (relative to the cation radical).[27] The latter was not applicable to the geminally substituted α,α-dianisyl analogue **6** which showed the first reversible redox wave a 1.17 V vs. SCE, but the second anodic wave separated by 440 mV was completely irreversible.[28]

Solvent Effect. We further investigated the electrochemical behavior of 5 × 10^{-3} M solution of tetraanisylethylene in three different solvents. Thus in dichloromethane, two partly overlapped reversible CV waves were observed (vide supra), whereas in the polar acetonitrile and nitromethane only a single reversible wave was observed.[29] Such a pronounced solvent effect on the cyclic voltammograms of **1** is pictorially demonstrated by Osteryoung square-wave voltammograms[30] in Figure 6 (see also Table 3).

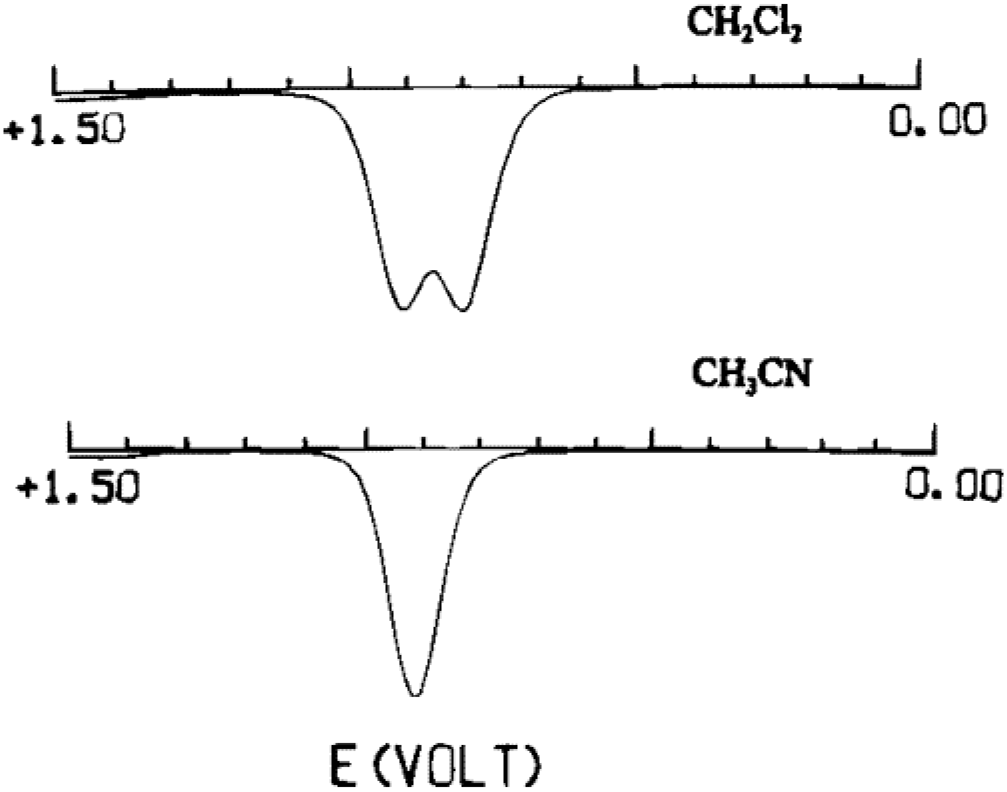
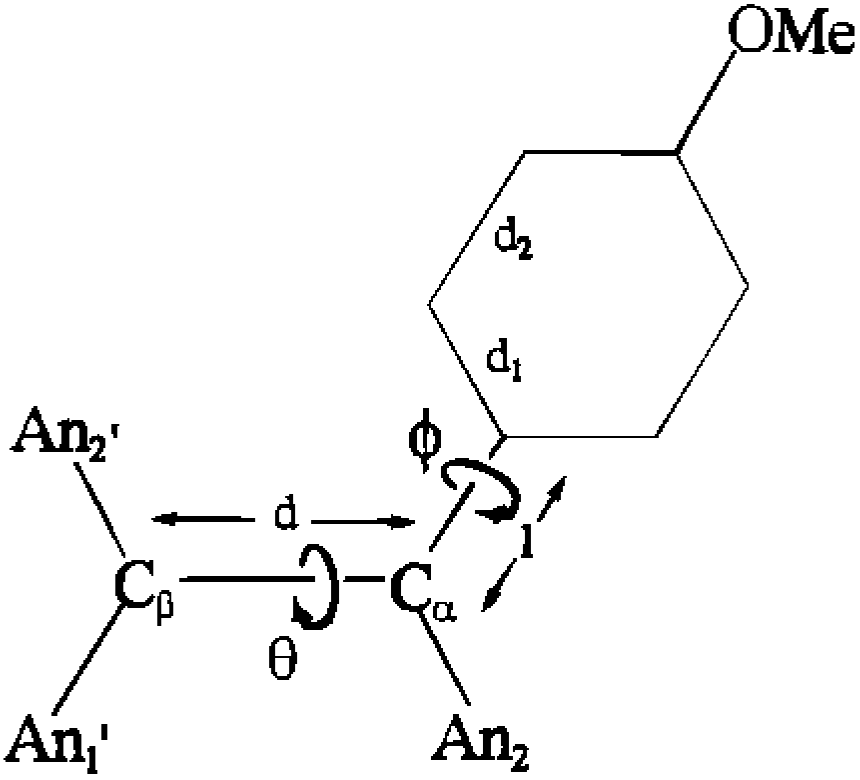


Figure 6 Osteryoung square-wave voltammograms of 5 mM tetraanisylethylene **1** in dichloromethane and acetonitrile containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate at 25 °C.

V. Structural Changes Proceeding from Tetraanisylethylene to Its Cation Radical and Then to Its Dication. The successful isolation of both the tetraanisylethylene cation radical ($\mathbf{1}^{+\bullet}$) and the dication ($\mathbf{1}^{2+}$) as crystalline salts in eq 7 allowed their molecular structures to be directly compared to the molecular structure of the parent donor (**1**) by X-ray diffraction analysis. As such, we are now able (for the first time) to establish the precise changes in molecular structures upon the stepwise oxidation of an electron-rich olefin donor. For convenience, let us first characterize the tetraanisylethylene framework in terms of the five (principal) parameters: d, l, θ, φ, and q that are applicable to the defining structure **9**. We then measure the distinctive changes in the ethylenic bond length (d), the bond to the anisyl group (l), the olefinic planarity (θ), the anisyl coplanarity (φ), and the quinoidal distortion (q) upon successive electron removals from tetraanisylethylene to effect the serial transformation: **1** $\xrightarrow{-e}$ **1**$^{+\bullet}$ $\xrightarrow{-e}$ **1**$^{2+}$ as follows.

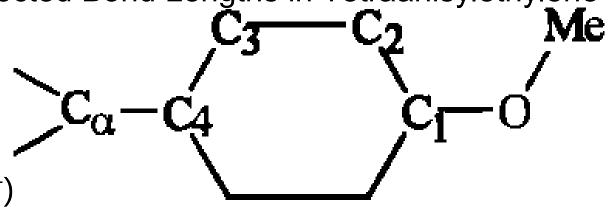


9

A. Changes in Bond Lengths. Ethylenic Bond (*d*). The progressive increase in the ethylenic (C_α−C_β) bond length from 1.359 Å in tetraanisylethylene (**1**) to 1.417 Å in the cation radical (**1**$^{+\bullet}$) and to 1.503 Å in the dication (**1**$^{2+}$) is illustrated in Figure 7.

Anisyl Bond (*l*). Such a significant increase in the (C_α−C_β) bond is accompanied by a concomitant shortening of the bond to the anisyl group (l = C_α−C_4) from 1.492 Å, to 1.460 Å and to 1.411 (1.435) Å in **1**, **1**$^{+\bullet}$, and **1**$^{2+}$, respectively. Moreover, the C−C bonds within the anisyl groups also showed distinctive changes, and the elongation of bond length d_1 at the expense of d_2 was especially notable (see Table 4).

Table 4. Selected Bond Lengths in Tetraanisylethylene (**1**), Its Cation Radical (**1**$^{+\bullet}$), and Its Dictation (**1**$^{2+}$)



Bond	**1**	**1**$^{+\bullet}$	**1**$^{2+\ a}$
Me−O	1.425	1.436	1.451 (1.437)
O−C_1	1.372	1.357	1.330 (1.346)

$C_1{-}C_2$	1.391	1.399	1.413 (1.405)
$C_2{-}C_3$	1.387	1.380	1.362 (1.373)
$C_3{-}C_4$	1.397	1.413	1.434 (1.420)
$C_4{-}C_\alpha$	1.492	1.460	1.411 (1.435)
q(%)[b]	11	37	80 (51)

[a] For the An_1 group, the value for An_2 in parentheses (see text). [b] See footnote 33.

B. Changes in Dihedral and Torsional Angles. Olefinic Planarity (θ). The perspective views along the ethylenic ($C_\alpha{-}C_\beta$) bonds of tetraanisylethylene, its cation radical, and its dication in Figure 8 underscore the increasing deviation from planarity at the olefinic center, with the overall dihedral angle increasing from θ = 4° in **1**, to θ = 31° in $\mathbf{1}^{+\bullet}$, and to θ = 62° in $\mathbf{1}^{2+}$.

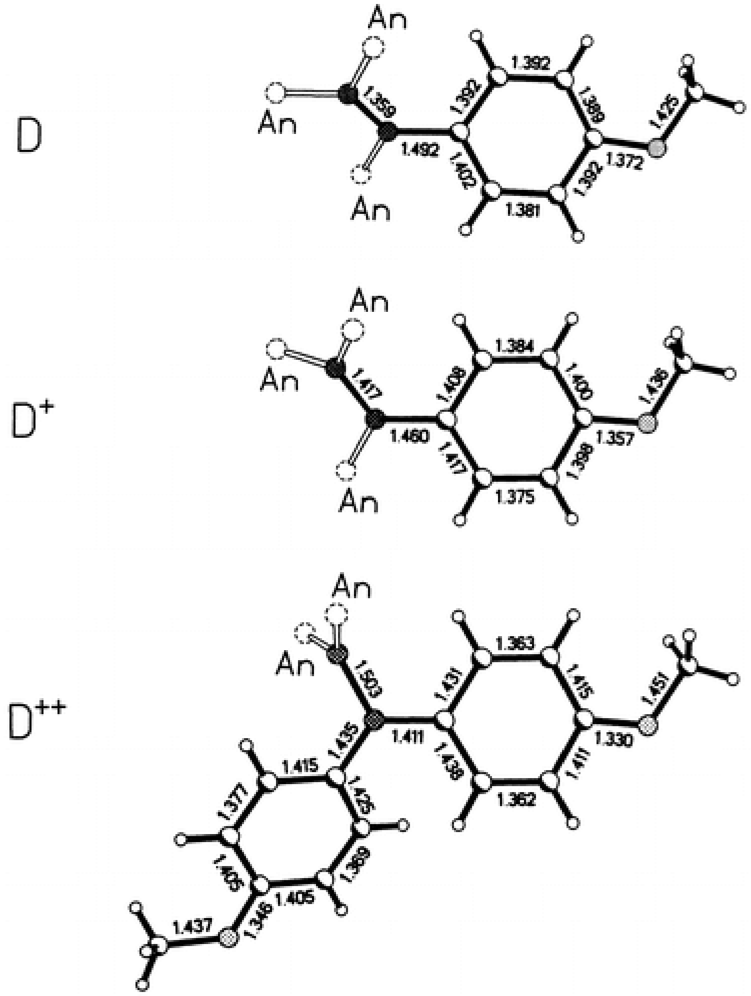


Figure 7 Progressive changes in C−C bond lengths in **D** = tetraanisylethylene (top) upon oxidation to its cation radical (middle) and then to its dication (bottom). [Note that the four An groups in **D** and $\mathbf{D}^{+\bullet}$ are equivalent, but only two pairs are equivalent in $\mathbf{D}^{2+}$].

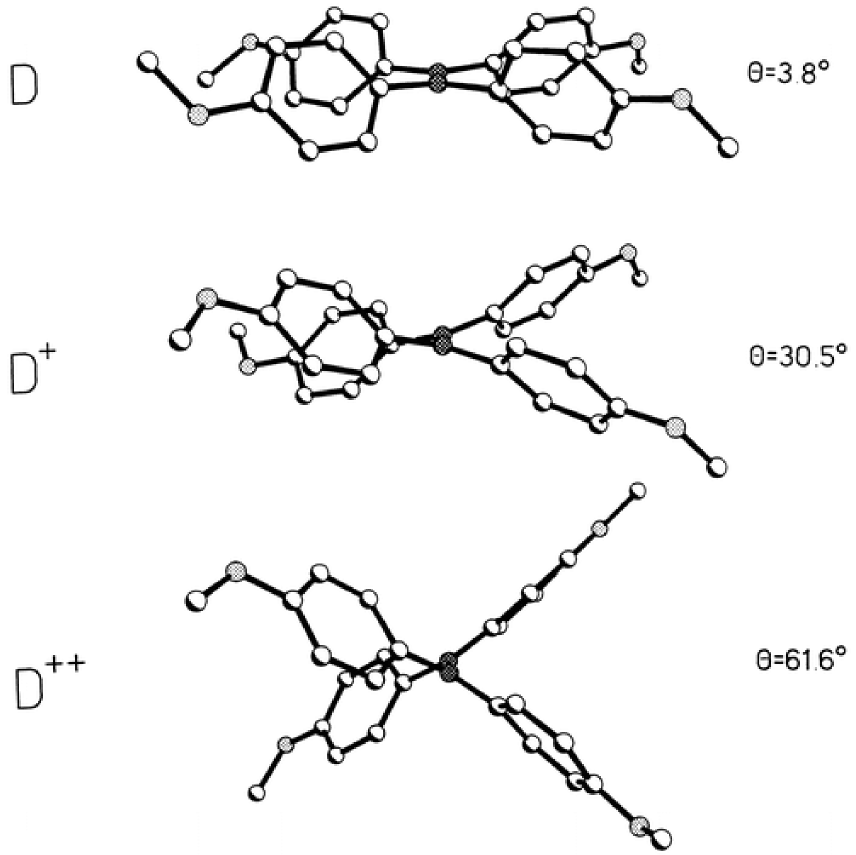


Figure 8 Linear increase in the dihedral (ethylenic) angles θ in tetra-anisylethylene (top), its cation radical (middle), and its dication (bot-tom). The latter shows the inequivalency of An_1 and An_2 in the dication.

Anisyl Coplanarity (φ). The conformation of an anisyl group relative to the ethylenic (C_α−C_β) bond, as described by its torsional angle φ, progressively decreases from tetraanisylethylene (φ = 52°) to its cation radical (φ = 33°) and to its dication (φ = 19°).[31] It is important to note that all four torsional angles in tetraanisylethylene are the same (within ±5°) to describe a neutral molecule with overall D_2 (local) symmetry. Although the same is also true of the cation radical $\mathbf{1}^{+\bullet}$, the dication $\mathbf{1}^{2+}$ has only a decreased symmetry of C_2 and exists in essentially a bisected conformation (θ = 62°). As a result, the *geminal* anisyl groups in the dication are inequivalent, with one anisyl group An_1 more coplanar than An_2 with φ = 19 and 28°, respectively, as illustrated in Figure 9.

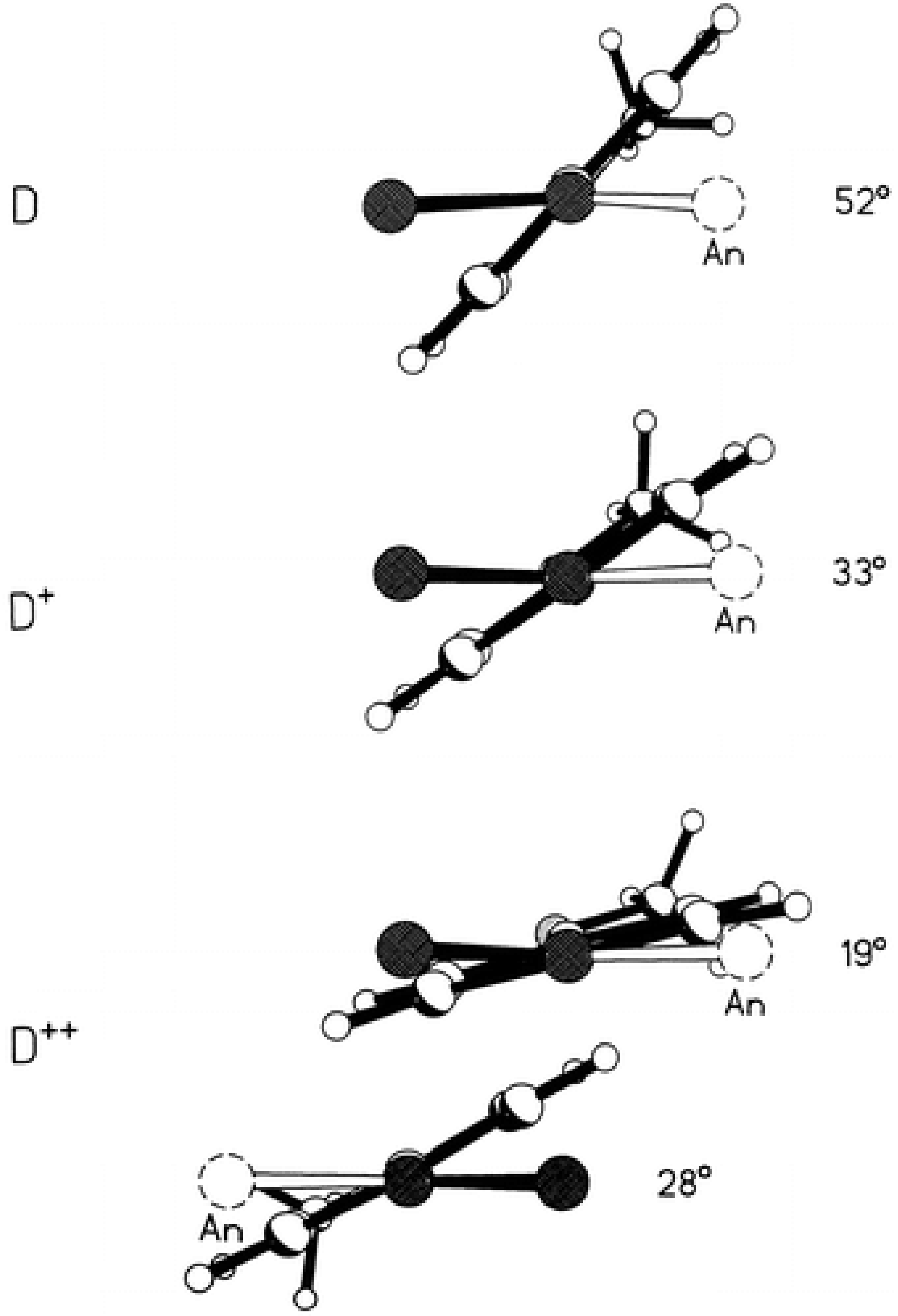
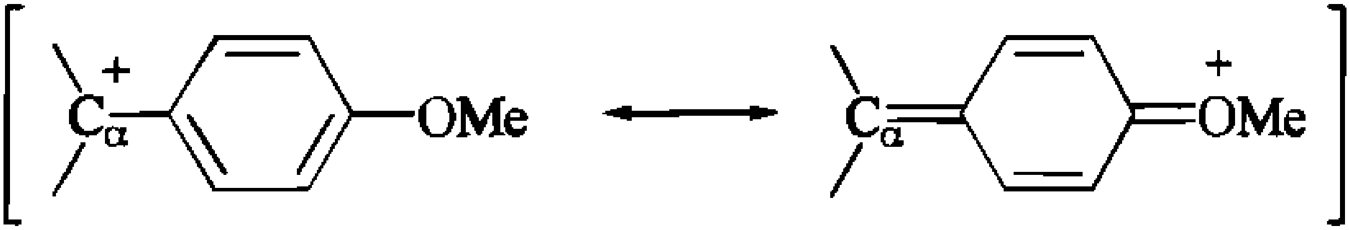


Figure 9 Progressive increase in the anisyl coplanarity (φ) as tetraanisylethylene (top) is successively oxidized to the cation radical (middle) and to the dication (bottom). [Note the difference between φ for An_1 and An_2 in **D**$^{2+}$ is presented in a displaced perspective].

C. Increase in Quinoidal Distortion (*q*). Bond lengths of the anisyl group show selective (progressive) changes attendant upon the conversion of tetraanisylethylene to its cation radical and then to the dication, as listed in Table 4. Indeed, these substantial alterations in the principal bond lengths within the anisyl group (as a result of electron removal) are associated with the increasing contribution from the quinoidal structure **10**. As such, we select changes in the aromatic C_3−C_4 bond relative to the C_2−C_3 bond (see Table 4) as the most sensitive indicator of the quinoidal distortion of the anisyl group. The quinoid parameter *q* in Table 4 increases monotonically with each electron removal in the order[32] **1** < $\mathbf{1}^{+\bullet}$ < $\mathbf{1}^{2+}$. By taking tetraanisylethylene as the reference point, we find that all four anisyl groups in its cation radical $\mathbf{1}^{+\bullet}$ have essentially the same values of q = 32−39%. However, the situation in the dication ($\mathbf{1}^{2+}$) is quite different, and the inspection of the anisyl bond lengths in Table 4 quickly reveal that the (relatively) coplanar anisyl group An_1 suffers substantially more quinodal distortion (q = 82 and 83%) than An_2 (q = 37 and 40%).



10

VI. Stereoelectronic Significance of the Structural Changes of Tetraanisylethylene Upon Successive (One-Electron) Oxidations. The profound molecular alterations of the tetraanisylethylene donor (**1**) attendant upon successive electron removals to generate its cation radical ($\mathbf{1}^{+\bullet}$) and then its dication ($\mathbf{1}^{2+}$) in Figures 7, 8, and 9 are most readily evaluated by a direct comparison of the quantitative changes in the structural parameters *d*, *l*, θ, φ, and *q*, as illustrated in Chart 3.[33] Most striking is the consistent linear change (within experimental error) that all the structural parameters experience on proceeding from the neutral donor to the cation radical and then to the dication, irrespective of the magnitudes of the slopes or their algebraic sign. In other words, the structural parameters *d*, *l*, θ, φ, and *q* are mutually interdependent, and they all relate to a single change in structure, which corresponds to the simultaneous (i) lengthening of the ethylenic bond, (ii) tightening of the anisyl bonding, and (iii) flattening of the anisyl coplanarity. Since this complex change also directly relates to the increasing quinoidal distortion of the anisyl groups, the convoluted change can be largely envisioned as a desire for maximum delocalization of positive charge over a pair of *vicinal* anisyl groups in the illustrative structure **11**. It is particularly noteworthy that this stereoelectronic change is also directly coupled to the increasing orthogonality of the equivalent (An_1−C_α−An_2) and ($An_{1'}$−C_β−$An_{2'}$) moieties about the central C_α−C_β bond toward the bisected conformation. Indeed, the fact that the energy for such a complex structural change to cation radical (i.e., $\mathbf{1} \rightarrow \mathbf{1}^{+\bullet}$) represents one-half that required for dication (i.e., $\mathbf{1} \rightarrow \mathbf{1}^{2+}$) is a most notable result.

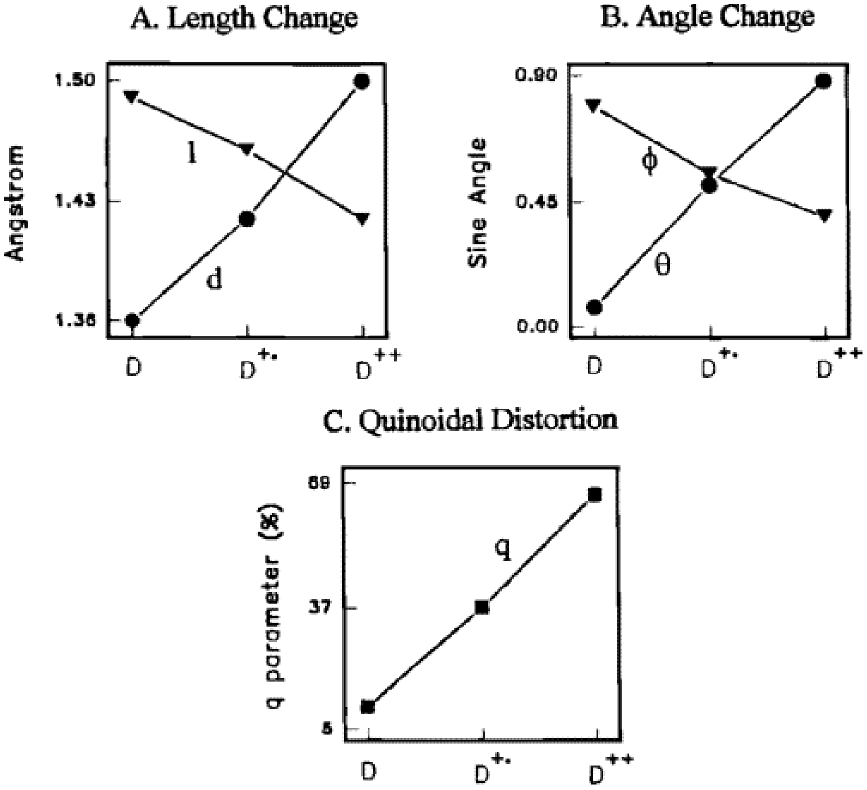
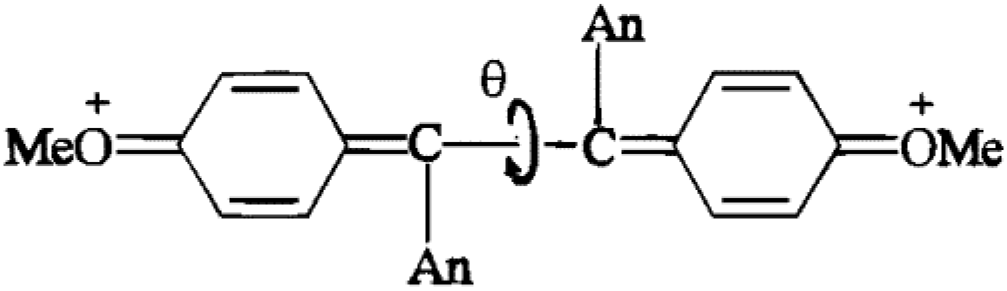


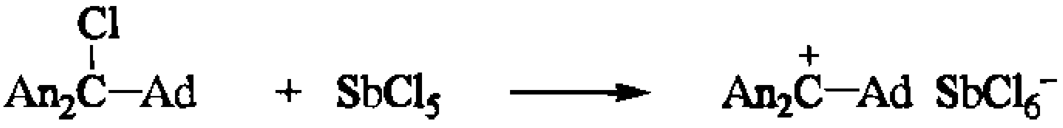
Chart 3. Structural Parameters



11

VII. Mechanistic Implications of the Structural Changes on Donor Strengths and Disproportionation. The linear changes in Chart 3 of all the structural parameters attendant upon the conversion of tetraanisylethylene to its cation radical and then to the dication precisely parallel the energy changes for effecting a pair of successive electron removals, as given by reversible oxidation potentials of E°_{ox}(I) ≃ $\mathbf{E}^\circ_{\mathrm{ox}}$(II) in acetonitrile solution (see Table 3 and Figure 6).[29] As such, we conclude that the energy changes in the cation radical and dication are also linear in this rather polar solvent; they lead to the disproportionation constant K_{disp} of essentially unity in Table 2. However in dichloromethane, the second oxidation potential is shifted slightly positive (Table 3), most likely due to a significantly lower gain in the solvation energy of the dication in the less polar solvent.[34]

In the successive transformations: **1** → $\mathbf{1}^{+\bullet}$ → $\mathbf{1}^{2+}$, the two halves of tetraanisylethylene undergo a significant rotation about the C_α−C_β bond, first by θ = 31° and then to an overall θ = 62°. The latter relates to a more or less distonic dication $\mathbf{1}^{2+}$ consisting of an orthogonal pair of equivalent (positively charged) An−C−An moieties. To quantitatively evaluate the latter, we prepared the dianisyl monocation $\mathbf{12}^{+}$ as a crystalline salt via an oxidative solvolysis (eq 13).[35] Indeed, X-ray diffraction analysis of the cation $\mathbf{12}^{+}$ revealed that only one anisyl group (An_1) was almost coplanar with the C_α−Ad bond (φ = 18°) and suffered significant quinodal distortion (*q* = 74%),[35b,c] and both structural parameters were essentially those observed in tetraanisylethylene dication (Chart 3). This structural similarity of $\mathbf{12}^{+}$ and $\mathbf{1}^{2+}$ indicates that only one anisyl group is sufficient to effectively stabilize an α-cationic center, as illustrated in structure **11**. Such a conclusion also follows from the enhanced electron-donor properties of the hybrid dianisylditolylethylene **3**, with values of $E°_{ox}$(I) and $E°_{ox}$(II) in Table 3, which are essentially the same as those of tetraanisylethylene. Furthermore, the latter analysis even extends to the 1,2-dianisylethylenes **4** and **5** with values of $E°_{ox}$(I) and $E°_{ox}$(II) which are only slightly shifted positive (Table 3, entries 4 and 5).



$$An_2\overset{\overset{Cl}{|}}{C}{-}Ad + SbCl_5 \longrightarrow An_2\overset{+}{C}{-}Ad\ SbCl_6^- \qquad (13)$$

$\mathbf{12}^{+}$

Anisyl stabilization of the cationic charge (as described in structure **11**) does not extend well to the *p*-tolyl group since both $E°_{ox}$(I) and $E°_{ox}$(II) in tetratolylethylene are significantly more positive and the separation Δ in Table 3 is substantially larger than those in the dianisyl-containing **1**, **3**, **4**, and **5** (but not **6**)[36]. However, a modicum of tolyl stabilization is apparent in the tetratolylethylene dication $\mathbf{2}^{2+}$, as indicated by the structural parameters: *d* = 1.502 Å, *l* = 1.423 Å, φ = 24.1°, and *q* = 59% in relation to those in either the tetraanisylethylene dication $\mathbf{1}^{2+}$ or the hybrid $\mathbf{3}^{2+}$.[37]

The rather expanded dihedral angle θ = 77° in tetratolylethylene dication $\mathbf{2}^{2+}$ relative to either tetraanisylethylene dication $\mathbf{1}^{2+}$ (θ = 62°) or dianisylditolylethylene dication $\mathbf{3}^{2+}$ (θ = 56°) indicates that the delocalization of two positive charges (as in **11**) is not a strong requirement for the attainment of a bisected conformation in these dications. Although it may be tempting to attribute the bisected conformation of tetraarylethylene dications to steric repulsion of the large aryl groups, it is noteworthy that a variety of other ethylenic dications with different substituents all exist in twisted conformations with large dihedral (θ) angles.[38] Indeed, theoretical calculations of the simple (unencumbered) ethylene dication predict a bisected structure with structural parameters θ = 90° and *d* = 1.46 Å.[39] Significant twisting of the ethylenic bond also pertains to the ethylene cation radical measured in the gas phase[40] and confirmed by theoretical calculations.[41] Since the same elongation and twisting of the ethylene bond have also been observed in the tetraphenylethylene dianion (*d* = 1.49 Å, θ = 56°),[42] the progressive change from a planar to a bisected conformation may simply reflect the increasing trend for the minimization of Coulombic repulsion.[43]

Summary and Conclusions

The successful isolation of tetraanisylethylene (**1**), its cation radical ($\mathbf{1}^{+\bullet}$), and its dication ($\mathbf{1}^{2+}$) as crystalline salts allows X-ray diffraction analysis to establish the structural changes upon the successive removal of one then two electrons from the ethylenic donor. The linear changes in the structural parameters (d, l, θ, φ, and q as described in Chart 3) coincide with the incremental (linear) change in the energy requirement for electron removal, as indicated by values of the reversible oxidation potentials $E^\circ_{ox}(\mathrm{Ia}) \simeq E^\circ_{ox}(\mathrm{II})$ in acetonitrile solution. The coplanarity (φ) and quinoidal distortion (q) of the anisyl substituents are especially useful measures of the delocalization (and stabilization) of positive charge in order to reduce the values of E°_{ox} and lead to increased disproportionation (K_{disp}) in eq 1. Structural analysis also indicates that a single anisyl substituent on an ethylenic carbon (as in various α,β-dianisylethylenes) is sufficient to confer an optimal cationic stabilization of an ethylenic donor **D** in its oxidative conversion to cation radical ($\mathbf{D}^{+\bullet}$) and then to its dication ($\mathbf{D}^{2+}$).

Experimental Section

The olefinic and aromatic electron donors 1,1,2,2-tetrakis(4-methoxyphenyl)ethylene (**1**),[3c] 1,1,2,2-tetrakis(4-methylphenyl)ethylene (**2**),[1d] 3,4-bis(4-methoxy-phenyl)-hex-3-ene (**4**),[45] 2,3-bis(4-methoxyphenyl)bicyclo-[2.2.2]oct-2-ene (**5**),[46] 4,4'-dimethoxybenzhydrylidene-adamantane (**6**),[1d] octamethylbiphenylene (**7**),[47] and tetrakis(bicyclo[2.2.2]octano)cyclooctatetraene (**8**)[24] have been described previously. The McMurry coupling of 4-methoxy-4'-methylbenzophenone with titanium tetrachloride and zinc dust in tetrahydrofuran afforded 1,2-bis(4-methylphenyl)-1,2-bis(4-methoxyphenyl)ethylene (**3**) in 91% yield. Bis(4-methoxyphenyl)-1-adamantylmethyl chloride (**12**) was prepared from the reaction of Grignard reagent derived from *p*-bromoanisole and ethyl 1-adamantylcarboxylate to yield bis(4-methoxyphenyl)-1-adamantylmethyl alcohol which was in turn converted to bis(4-methoxyphenyl)-1-adamantylmethyl chloride in excellent yield (92%), by treatment with excess thionyl chloride. Procedures for the oxidation of tetraarylethylenes **1−3** and dianisylethylenes **4−6** to the corresponding cation-radical (and dication) salts with aromatic cation-radical salts [$\mathbf{EA}^{+\bullet}$ $\mathrm{SbCl_6^-}$] (λ_{max} = 486 nm, log ε_{486} = 3.66 $\mathrm{M^{-1}\,cm^{-1}}$) and [$\mathbf{MA}^{+\bullet}$ $\mathrm{SbCl_6^-}$] (λ_{max} = 518 nm, log ε_{518} = 3.86 $\mathrm{M^{-1}\,cm^{-1}}$) in dichloromethane, preparative oxidation of tetraarylethylenes with [$\mathrm{Et_3O^+}$ $\mathrm{SbCl_6^-}$] and antimony pentachloride for the isolation and crystallization of dication (and cation-radical) salts, oxidation of electron-rich donors **1**, **7**, and **8** with tetraanisylethylene dication salt [$\mathbf{1}^{2+}$ $(\mathrm{SbCl_6^-})_2$], measurements of cation-radical disproportionation constant, and isolation and X-ray crystallography of single crystals of various dication salts, cation-radical and carbenium salts (discussed above), and neutral tetraarylethylenes are described in detail in the Supporting Information Available.

Acknowledgment

We thank the National Science Foundation and Robert A. Welch Foundation for financial support.

Supporting Information Available

Materials and instrumentation used, synthesis of **3** and **12**, the detailed procedure for the oxidation of donors **1−6** with **MA**$^{+\bullet}$ (and/or **EA**$^{+\bullet}$) and donors **1**, **7**, and **8** with the dication salt (**1**$^{2+}$), the measurement of the disproportionation constants, preparative isolation and crystallization of the dication and cation-radical salts, as well as the X-ray crystal structure data for **1**, [**1**$^{+\bullet}$ $SbCl_6^-$], [**1**$^{2+}$ ($SbCl_6^-$) ($Sb_2Cl_7^-$)·1.7CH_2Cl_2], [**2**$^{2+}$ ($SbCl_6^-$)$_2$], [**3**$^{2+}$ ($SbCl_6^-$)$_2$], **3**, and [**12**$^{+}$ $SbCl_6^-$] (68 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

PDF ja6931.pdf (1.51 MB)

ja6931a.pdf (0.98 MB)

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7 For a recent discussion of the mechanistic ambiguity, see: Rathore, R.; Kochi, J. K. *Acta Chem. Scand*. **1998**, *52*, 114.

8 (a) $E°_1$ and $E°_2$ refer to the reversible one-electron oxidation (or reduction) of tetraarylethylene and its cation radical (or anion radical), respectively. (b) When ΔG is expressed in electron volts, the Faraday constant F is unity. (c) Any ion-pairing effects are ignored (d) For anion radicals, compare: Muzyka, J. L.; Fox, M. A. *J. Org. Chem*. **1991**, *56*, 4549. Fry, A. J.; Hutchins, C. S.; Chung, L. L. *J. Am. Chem. Soc*. **1975**, *97*, 591. See also Garst et al. in ref 2a.

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10 There are no reports extant in which the cation-radical and dication structures of the same donor are available for direct comparison.

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12 Svanholm, U.; Jensen, B. S.; Parker, V. D. *J. Chem. Soc., Perkin Trans. 2* **1974**, 907.

13 Prepared as the crystalline hexachloroantimonate salt via the $SbCl_5$ oxidation of 9,10-dimethoxy-1, 4: 5,8-dimethano-1,2,3,4,5,6,7,8-octahydroanthracene (**MA**) and 9,10-dimethoxy-1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthracene (**EA**).[14]

14 Rathore, R.; Kochi, J. K. *J. Org. Chem*. **1995**, *60*, 4399.

15 Compare Buck et al. in ref 4a.

16 Red solutions of tetratolylethylene dication (**2**$^{2+}$) in dichloromethane were not persistent at room temperature. The crystalline salt [**2**$^{2+}$ $(SbCl_6^-)_2$] was prepared at −78 °C and handled without allowing the temperature to rise (see Experimental Section).

17 Note, however, that the dication **4**$^{2+}$ was not kinetically persistent (probably due to the presence of labile α-protons on the ethyl groups).

18 Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem*. **1976**, *13*, 155.

19 For the stoichiometry of the donor oxidation with antimony(V) oxidants, see: Rathore, R.; Kumar, A. S.; Lindeman, S. V.; Kochi, J. K. Submitted for publication.

20 See Experimental Section in Supporting Information Available for details.

21 The dication actually crystallized from solution as the complex salt [**1**$^{2+}$, $SbCl_6^-$, $Sb_2Cl_7^-$] described in the Supporting Information Available.

22 Although Et_3O^+ $SbCl_6^-$ effectively oxidized tetratolylethylene **2**, we were unable to isolate the crystalline salt of **2**$^{+\bullet}$ from the dark purple solution.

23 Note, however, that the analogous 1-adamantyl-dianisylcarbinyl cation **12**$^+$ generated from the corresponding chloride by treatment with $SbCl_5$ was not an effective oxidant of tetraanisylethylene (as in the conproportionation exchange in eq 8).

24 Komatsu, K.; Nishinaga, T.; Aonuma, S.; Hirosawa, C.; Takeuchi, K.; Lindner, H. J.; Richter, J. *Tetrahedron Lett*. **1991**, *32*, 6767. For an efficient alternative synthesis of **8**, see: Rathore, R.; Lindeman, S. V.; Kumar, A. S.; Kochi, J. K. *J. Am. Chem. Soc.*, in press.

25 See: Nishinaga, T.; Komatsu, K.; Sugita, N. *J. Am. Chem. Soc.* **1993**, *115*, 11642.

26 The peculiar CV behavior of tetraanisylethylene in nitromethane is subject to further study.

27 As indicated by the separation $\Delta \sim 120$ mV that is the same as that in tetraanisylethylene.

28 At a CV scan rate as high as $v = 2$ V s^{-1}. Note also the monocation **12**$^+$ formed in eq 13 is a poor electron-transfer agent.[23]

29 Although E°_{ox}(I) and E°_{ox}(II) for tetraanisylethylene in acetonitrile are not distinguished in Table 3, the difference of $E^\circ_{ox}(\mathrm{II}) - E^\circ_{ox}(\mathrm{I}) = 10$ mV has been evaluated by Phelps and Bard[11a] by digital simulation of the cyclic voltammetric data.

30 Osteryoung, J. G.; Osteryoung, R. A. *Anal. Chem*. **1985**, *57*, 101A.

31 For the anisyl group An_1 and $\varphi = 29°$ for the orthogonal anisyl group An_2 (vide infra).

32 The quinoidal distortion was evaluated as the difference between bond length d_1 and d_2 (see **9**) relative to that in various quinomethane structures with averaged values of $d_1' = 1.444(2)$ Å and $d_2' = 1.354(2)$ Å (by searching more than 50 compounds in the Cambridge data files); i.e., $q(\%) = 100\,(d_1 - \mathrm{d}_2)/(d_1' - d_2')$.

33 The structural parameters l, φ, and q for **D** = tetraanisylethylene in Chart 3 are plotted as values averaged over all four anisyl groups.

34 Based on the potentials in Table 3 which are referenced to ferrocene as the common internal standard with $E^\circ_{ox} = 0.43$ and 0.37 V vs SCE in dichloromethane and acetonitrile, respectively.

35 (a) Where Ad = 1-adamantyl. (b) As described in the Experimental Section, the other anisyl group (An_2) in **12**$^+$ is substituted with a 3-chloro substituent. (c) The structural parameters are: (An_1) d_1 = 1.415 Å, d_2 = 1.356 Å or q_1 = 74%, φ_1 = 18.2° and (An_2) d_1 = 1.387 Å, d_2 = 1.368 Å or q_2 = 22%, φ_2 = 63.7°.

36 Note that 1,1-dianisyl substitution as in **6** is not sufficient to stabilize the dication (Table 3, entry 6).

37 It is noteworthy that the structural parameters in **3**$^{2+}$ confirm the significant coplanarity (φ = 18.2°) and quinoidal distortion (q = 83%) of the anisyl group, certainly by comparison with those of the tolyl group (φ = 36.5° and q = 39%). The other structural parameters for **3**$^{2+}$ are d = 1.502 Å, θ = 56.0°; for the anisyl groups, l = 1.401 Å, d_1 = 1.437 Å, d_2 = 1.363 Å, φ = 18.2°, q = 83%; and for the tolyl group, l = 1.453 Å, d_1 = 1.412 Å, d_2 = 1.377 Å, φ = 36.5 deg, q = 39%.

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