atoms achieve 18 VE when one formally postulates a Fe–Fe double bond. As expected, in the transition from **4** to **7** a considerable shortening occurs of the Fe–P distances (Fe–P 2.29 and 2.10 Å (av), respectively; multiple bond contributions). In **7** the angles at the P atoms (Fe-P-Fe 72.80(2), 73.06(2)°) are considerably smaller than those at the Fe atoms (P-Fe-P 107.06(3), 106.99(3)°). The almost ideally eclipsed Cp‴ five-membered rings (Figure 2) deviate only slightly (2.3°) from a parallel orientation and are arranged almost orthogonal (91.5, 89.2°) to the four-membered ring.

Experimental Section

4: Compound **3** (970 mg, 1.19 mmol) was dissolved in decalin (ca. 150 mL) and heated under stirring to 190 °C (reflux). After about 45 min the CO bands of the starting material **3** were no longer visible by IR spectroscopy.[5] The solvent was removed under vacuum. The red-brown residue was dissolved in dichloromethane (ca. 10 mL) and the solution was treated with silylated silica gel (ca. 2 g). The mixture was transferred to a column (20 × 2 cm) filled with silica gel and petroleum ether. At −20 °C (cryostat) a pale green fraction, which contained **5** (60 mg, 12 %), was eluted with petroleum ether. Compound **6** (370 mg, 44 %) was obtained as the second, dark red fraction with petroleum ether/toluene (20/1). Compound **4** (150 mg, 18 %) was eluted as a dark green solution with petroleum ether/toluene (10/1), and was recrystallized from hexane.

7: A dark green solution of **4** (150 mg, 0.22 mmol) in toluene (ca. 120 mL) was photolyzed at room temperature (150-W mercury high-pressure lamp). After 4.5 h the band for the bridging CO ligand of the starting material was no longer detected in the IR spectrum of the reaction mixture. The solvent was removed under vacuum, and the residue was taken up in heptane. A pale brown insoluble solid was separated on a frit; owing to its poor solubility this could not be characterized further. Compound **7** (90 mg, 63 %) was obtained as a yellow-brown powder from the eluate, and was recrystallized from hexane.

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[6] Spectroscopic data of compounds **4** and **7**: ^{31}P NMR (167.97 MHz, C_6D_6, 85 % H_3PO_4 external; $T = 298$ K): **4**: $\delta = 776.3$ (s, 2P); **7**: $\delta = 1406.9$ (s, 2P); ^{1}H NMR (200.13 and 400.14 MHz, C_6D_6, C_6D_5H internal; $T = 298$ K): **4**: $\delta = 4.61$ (s, 2H), 1.34 (s, 18H), 1.13 (s, 9H); **7**: $\delta = 6.59$ (s, 2H), 1.37 (s,18H), 1.29 (s, 9H); IR (toluene): **4**: $\tilde{\nu}(CO) = 1761$ cm^{-1} (vs).

[7] Crystal structure data of **4** [**7**]: $C_{35}H_{58}Fe_2OP_2$ [$C_{34}H_{58}Fe_2P_2$], $M_r = 668.5$ [640.4], monoclinic [monoclinic], space group $P2_1/n$ [$P2_1/n$], $a = 14.15624(13)$ [11.7825(8)], $b = 14.1991(10)$ [10.4476(4)], $c = 18.171(2)$ Å [28.5310(17)], $\beta = 99.277(12)°$ [91.156(8)], $V = 3604.7(6)$ Å^3 [3511.4(3)], $Z = 4$ [4], $\rho_{calcd} = 1.232$ g cm^{-3} [1.211], $T = 293(2)$ K, $\theta = 2.04–26.08°$ [2.95–25.68], 25078 [46082] measured reflections, 7016 [6644] independent reflections ($R_{int} = 0.1449$ [0.0504]), $R1 = 0.0465$ [0.0373], $wR2 = 0.0687$ [0.0996] ($I > 2\sigma(I)$); $R1 = 0.1500$ [0.0451], $wR2 = 0.0889$ [0.1043] (all data); diffractometer: Siemens P4 [Stoe IPDS]; structure solution: direct methods; program: SHELXS-97 [SIR 92 (A. Altomare, G. Cascarano, G. Giacovazzo, A. Gualiardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435)]; structure refinement: full-matrix least-squares methods against F^2; program: SHELXL-97 (G. M. Sheldrick, Universität Göttingen, **1997**); data/parameters: 7016/379 [6644/361]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-163506 (**4**) and CCDC-163507 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Evidence for σ Dimerization During Anodic Redox Switching of 1,3,5-Tripyrrolidinobenzene: A New Molecular Switch**

Jürgen Heinze,* Christian Willmann, and Peter Bäuerle

The dimerization of radical ions of conjugated aromatic systems has been discussed in the literature for more than 20 years.[1–10] In the case of radical cations, experimental data have led many authors to postulate the formation of weakly reacting π dimers. This assumption, however, is not able to fully explain the experimental results. In the case of radical anions, by contrast, the formation of covalently bonded σ dimers is generally accepted.[2, 11–18] This controversy over the σ or π dimerization of radical ions is unresolved primarily as a consequence of the widely held view that because of coulombic repulsion between charged molecules only weak reactions are possible. This argument overlooked and overlooks first the presence of the counterions, which drastically diminish repulsion, and second that even in moderately polar solutions the level of coulombic interactions is low compared to the gas phase.

Interpretations of the measurements of radical cations in connection with the π-dimer hypothesis are based almost exclusively on the results for UV/Vis spectra obtained at different temperatures. Contrary to expectations, in UV spectra dimerization is usually detected in the short-wave

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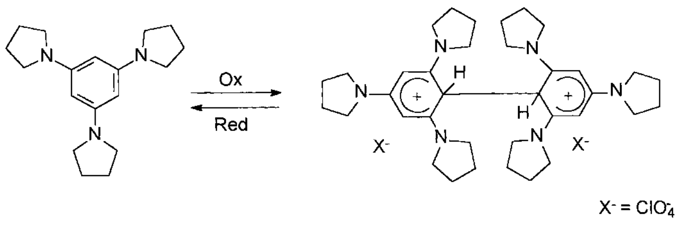
dimer bands. Thus, normal charge-transfer interactions cannot be used to interpret such "π dimerizations"; instead, typical solid-state phenomena, such as the Davydov shift, are used.[19, 20] Further support for the π-dimer hypothesis came from electrochemical studies using cyclic voltammetry, which apparently indicated reversible redox processes without follow-up reactions. However, in none of these examples were fast-scan experiments conducted for different concentrations or at different low temperatures.

In the meantime, more recent electrochemical investigations on oligomeric thiophenes, polyenes, and other aromatic compounds provide conclusive proof that the dimerization of their radical cations leads to the formation of covalent σ bonds,[21–26] as has been shown for radical anions.[11–18] These reactions are obviously driven by the strong tendency for unpaired electrons to couple, forming a σ bond.

In the past, the π-dimer hypothesis was particularly popular in connection with the coupling of radical cations of aromatic amines.[27–29] The publications of Effenberger et al. prove that this is not necessarily compelling. Indeed, by oxidizing 1,3,5-tripyrrolidinobenzene (**1**), they succeeded in isolating a dimeric σ complex **2**[30–34] [Eq. (1)] and, by using X-ray structure analysis, were able to unequivocally prove the existence of the σ bond in the solid state.



1 **2** (1)

For compound **1**, there are no electrochemical data on the formation of σ dimers during redox switching. As structural data unequivocally prove the formation of dicationic σ dimers after the oxidation of **1**, electrochemical measurements should also provide incontrovertible evidence for the dimerization mechanism in solution.

Herein we shall report cyclic voltammetric and spectroscopic investigations into the oxidation of **1** and the reduction of the dimeric σ complex **2**. We shall demonstrate that, after the formation of radical cations, **1** spontaneously reacts to form the dimeric σ complex **2**, which after reduction "reversibly" dissociates to generate **1** again.

In normal voltammetric experiments, the oxidation of **1** at about $E_{p1}^{a} = +0.3$ V versus Ag/AgCl at room temperature is an irreversible process (Figure 1a). The resulting follow-up product is reduced only at about $E_{p1}^{c} = -1.0$ V, which indicates the high stability of this product. Another oxidation step takes place at about $E_{p2}^{a} = +0.8$ V, and the corresponding reduction at about $E_{p2}^{c} = -0.15$ V (Figure 1b). The peak current value of the second oxidation step is exactly half of the current value of the first oxidation step. The conclusion to be drawn from the cyclic voltammogram data, which are in perfect agreement with the chemical findings, is the formation of a dimer at the radical cation level. Nothing is known about the nature of the follow-up reaction after the second redox step. But it does include an oxidation step involving the transfer of one electron, followed by another chemical reaction. At present, this second redox step serves only as further evidence for the formation of the σ dimer **2**, however, it will be the focus of future research. The large difference between the redox potential of the monomer **1** and that of the dicationic dimer **2** is characteristic of both carbocations and carbanions and the corresponding radical ions. Even simple molecular orbital considerations[35] but also AM1 and PM3 calculations show that the dimer in its charged state is considerably more stable than the monomeric radical cation.

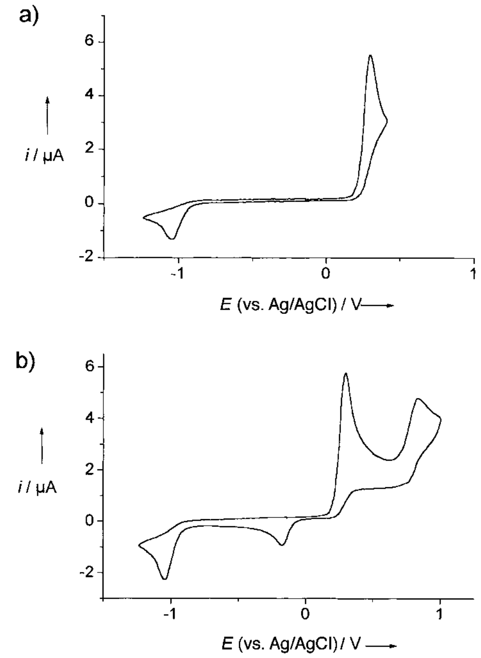


Figure 1. Cyclic voltammograms of **1** in CH_3CN/0.1 M $TBAPF_6$; $v = 0.2$ V s^{-1}; $T = 293$ K; $c = 1.2 \times 10^{-3}$ M: a) to 0.5 V, b) to 1.0 V.

To provide further evidence for dimerization, we carried out voltammetric experiments on the σ complex **2**, present as a salt, under the same conditions as for **1** (Figure 2a, b). As can be seen in Figure 2a, the characteristic oxidation peak at 0.3 V appears only in a second cycle, that is, only after the cathodic wave has been passed at −1.0 V, and the reduction of **2** and the associated cleavage into the starting monomer **1**. Repeating the experiment at a higher potential, it is possible to observe the above-mentioned oxidation peak at about +0.8 V for the oxidation of the dicationic dimer of **2**. Similarly, in a second cycle the peak for the oxidation of the monomer **1** at +0.3 V appears (Figure 2b). Finally, Figure 2c shows the result of the simultaneous voltammetric measurement of **1** and **2** in acetonitrile. That the only peaks to appear are the oxidation peaks previously established at +0.3 V and +0.8 V and the corresponding reduction peaks at +0.15 V and −1.0 V is clear evidence that after the formation of the radical cations, **1** is irreversibly dimerized to the σ complex **2**, after which **2** is reduced again at about −1.0 V and then dissociates into **1** (Scheme 1).

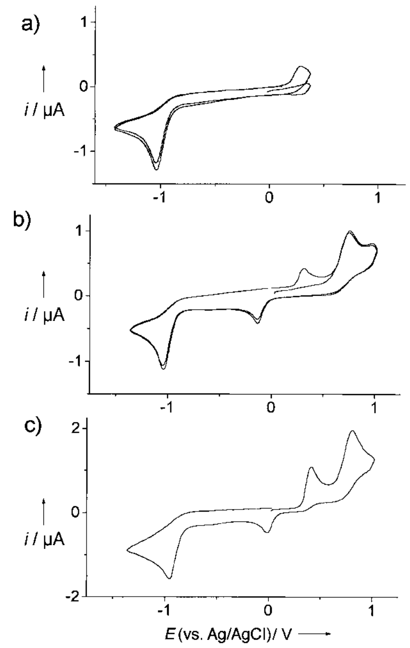
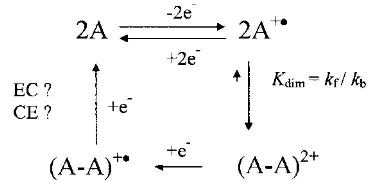


Figure 2. Cyclic voltammograms in $CH_3CN/0.1\,M\,TBAPF_6$; $v = 0.2\,V\,s^{-1}$, $T = 293$ K; a), b) cyclic voltammograms of **2**, $c(\mathbf{2}) = 2.75 \times 10^{-4}\,M$; c) cyclic voltammogram of **1** and **2**, $c(\mathbf{1}) = 2.23 \times 10^{-4}\,M$; $c(\mathbf{2}) = 2.275 \times 10^{-4}\,M$.



Scheme 1. Mechanism of the oxidation and reduction of **1**; E = electrochemical step, C = chemical step.

As further proof of this scheme, UV absorption spectra of both **1** and **2** were measured in a spectro-electrochemical cell.[36] Figure 3a shows a spectrum for **1** with an unpolarized electrode, with maximum absorption at 244 nm, this agrees with the spectrum of **1** in the literature.[37–39] If a potential of +0.4 V is applied, monomer **1** is oxidized, and the resulting spectrum shows main absorption maxima at 261 nm, 346 nm, and 430 nm, which agrees with the spectra for the dimeric σ complex **2**.[31] If the potential is changed to −1.1 V, the σ dimer **2** is reduced and one obtains, as expected, the spectrum of the starting species **1**. Figure 3b compares the spectra of **2** (open circuit conditions) and **1** after the oxidation at +0.4 V. The identical spectra are further evidence for the assumption that the radical cations formed on the oxidation of **1** react to form the dimeric σ complex **2**. The spectra of **2** after reduction at −1.0 V and of **1** (open circuit conditions) are also identical, which clearly demonstrates that the dicationic σ dimer **2** is reduced again to **1** at −1.0 V (Figure 3a, b).

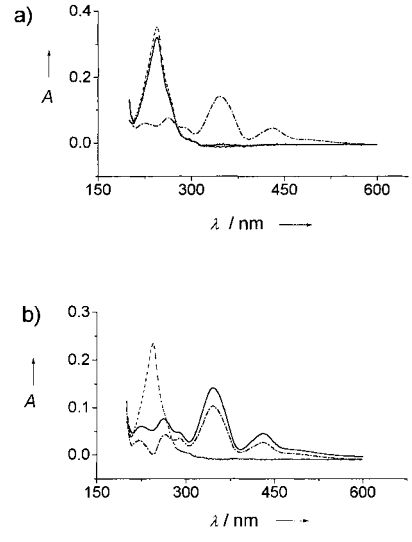


Figure 3. UV measurements of **1** and **2** in a spectro-electrochemical cell,[36] in $CH_3CN/0.1\,M\,TBAPF_6$, $c(\mathbf{1}) = 1.1 \times 10^{-3}\,M$, $c(\mathbf{2}) = 5.1 \times 10^{-4}\,M$; a) **1** at 0 V (——), **1** at 0.4 V (-·-·), **1** at −1.1 V (----); b) **1** at 0.4 V(——), **2** at 0 V (-·-·), **2** at −1.0 V (----).

As the results presented here show, the oxidation of **1** at room temperature and medium concentrations ($c = 1.3 \times 10^{-3}\,M$) is irreversible. The resulting radical cations dimerize to form the σ complex **2**. However, reversible processes are very frequently observed in other dimerization reactions of radical ions,[20–25] that is, the dimer is formed and dissociates within the time scale of the experiment. Consistent with this finding, in voltammetric experiments at room temperature, with slow scan rates, and at low concentrations only the monomeric radical ion is found. Normally, the equilibrium constants for these dimerizations range from 10^2 to $10^7\,M^{-1}$, and the rate constants reach values of up to $10^5\,M^{-1}\,s^{-1}$.

As we can also assume a dynamic dimerization equilibrium in the presence of the radical cation of **1**, we carried out experiments at low concentrations ($1.9 \times 10^{-4}\,M$), increased temperatures, and higher scan rates. Clearly, at 50 °C in acetonitrile and a scan rate of $10\,V\,s^{-1}$, the reduction of the radical cation formed from **1** can already be observed in the reverse scan. At $200\,V\,s^{-1}$, the dimerization proceeds only slowly (Figure 4). The conclusion is that the equilibrium constant of the dimerization falls as the temperature rises, while the rate constant for the dissociation of the dimers rises significantly faster than the rate constant for the dimerization.

A quantitative analysis of the data for the scan rates in the range from $0.2\,V\,s^{-1}$ to $10\,V\,s^{-1}$ at room temperature was carried out with the help of digital simulation (Digisim, Bioanalytical Systems). Figure 5 presents the results of these simulations for reaction Scheme 1 with two very different scan rates. In the oxidation range the agreement between the experimental and simulated data is excellent. The values were as follows: equilibrium con-

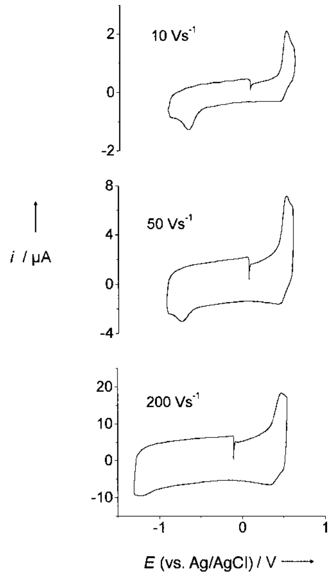


Figure 4. Cyclic voltammograms of **1** in $CH_3CN/0.1\,M$ $TBAPF_6$, $T = 323$ K, $c = 1.9 \times 10^{-4}\,M$.

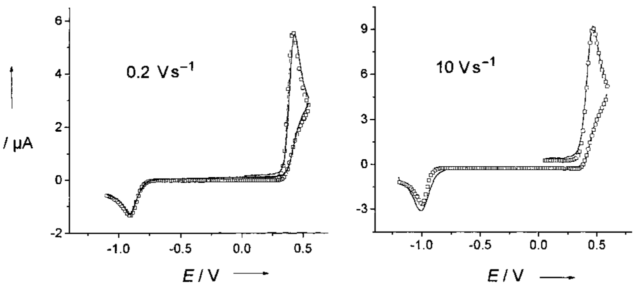


Figure 5. Experimental (——) and simulated (Digisim; □) cyclic voltammograms for the oxidation of **1** at scan rates of $v = 0.2$ (left) and $10\,\mathrm{V\,s^{-1}}$ (right). The simulated data were approximated to the experimental results for the oxidation of **1** in $CH_3CN/0.1\,\mathrm{M}\,TBAPF_6$, $c = 1.2\ 10^{-3}\,\mathrm{M}$, $T = 298\,\mathrm{K}$. Disc elelctrode: $d = 1$ mm (left), $d = 0.5$ mm (right).

stant $K_{eq} = 3.3 \times 10^{11}\,\mathrm{M}^{-1}$, rate constants for formation $k_f = 4.3 \times 10^{6}\,\mathrm{M}^{-1}\mathrm{s}^{-1}$, and breakdown $k_b = 1.3 \times 10^{-5}\,\mathrm{s}^{-1}$ of the dimer. Measurements and simulations at various temperatures provided a rough estimate for the activation energy of $E_A = 29\,\mathrm{kJ\,mol^{-1}}$. This, in turn, indicates a diffusion-controlled reaction, as in other radical-ion coupling processes.[21–23]

The quantitative analysis shows that the dimerization takes place, as assumed, between the radical cations (RR coupling) and not, as often postulated for irreversible processes, between the neutral species and radical cations (RS coupling). It is also noteworthy that the dimerization step is, in principle, chemically reversible. After reduction of the dimer the starting species is regenerated. The switching between the monomeric and dimeric system can be repeated many times without any decomposition of the system.[40] This is a new example of a redox-controlled molecular switch.[26]

Regarding the elimination of protons in the formation of conducting polymers, it is of note that under the given experimental conditions no protons were eliminated from **2**. Owing to the electron-donating amino nitrogens, the acidity of the dimer is so weak that rearomatization from the dicationic σ dimer to the neutral biphenyl cannot take place and can be achieved only after the addition of strong bases. A similar tendency can be observed in the formation of conducting oligomers and polymers, for example, polythiophene, where the stability of σ intermediates formed during coupling increases with the length of the growing chain.

Experimental Section

Compounds **1**[41] and **2**[32] were synthesized according to the literature. The cyclic voltammetric experiments were performed under an argon atmosphere with a three-electrode arrangement: a platinum disc electrode $d = 1$ mm (or 0.5 mm) as working electrode, platinum wire as the counter electrode, and a silver wire as pseudo reference electrode. The potentials were determined relative to the cobaltocinium/cobaltocene redox pair and are given in relation to Ag/AgCl. Solutions of $0.1\,\mathrm{M}$ $TBAPF_6$ ($TBA = Bu_4N^+$) in acetonitrile were used as electrolytes. The UV/Vis spectra were recorded in a spectro-electrochemical cell that we built ourselves which combines cyclic voltammetry and UV/Vis spectroscopy.[36]

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