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Electrochemistry

Evidence for a π Dimer in the Electrochemical Reduction of 1,3,5-Trinitrobenzene: A Reversible N_2-Fixation System**

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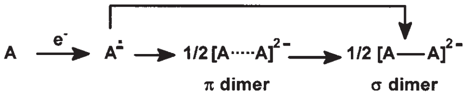
Couplings between two radical anions[1] or two radical cations[2] are common outcomes in electrochemical reactions and give rise to a doubly charged σ-bonded dimeric species. In the case of delocalized π systems such as 9-cyanoanthracene, formation of a π-dimer intermediate before collapse of the two radical anions into a σ-bonded species has been proposed,[2a–b] although the same event has been explained by one-step radical-anion dimerization[2c–d] (Scheme 1).



Scheme 1. Dimerization of the radical anion of 9-cyanoanthracene (**A**).

Moreover, the formation of radical-anion dimers in the solid state, such as that of 7,7,8,8-tetracyanoquinodimethane (TCNQ), is well established.[3] Furthermore, it is known that the nucleophilic aromatic substitution (S_NAr) mechanism involves addition compounds (σ complexes) as intermediates.[4] For this reaction, UV and NMR spectroscopic experiments suggested the existence of a π-complex intermediate prior to σ-complex formation.[5] Definitive evidence was provided by the isolation of the π-complex intermediate in the S_NAr reaction of indole-3-carboxylate with 1,3,5-trinitrobenzene.[6] Thus, the formation of π-dimer intermediates in the σ dimerization of radical anions remains controversial.

In the reduction of 1,3,5-trinitrobenzene (**1**), Bock and Lechner-Knoblauch observed an irreversible wave, which was explained by formation of 1,3-dinitrobenzene and nitrite anion.[7] However, by bulk electrochemical reduction of **1** in acetone, Sosokin et al. isolated the σ-bonded dimer 1,1′-dihydrobis(2,4,6-trinitrocyclohexadienyl) (**3,** Scheme 2) as its tetraethylammonium salt.[8] We report herein on a complete electrochemical (cyclic voltammetry and bulk electrolysis), spectroscopic, and synthetic investigation of the reduction of **1**, providing conclusive evidence for the formation of a π-dimer intermediate prior to formation of the σ dimer and the reaction of this π dimer with N_2 to give an organic N_2-fixation system.

The electrochemical behavior of **1** is definitely different from those of nitrobenzene or dinitrobenzenes (see the Supporting Information).[9] Figure 1a shows that, at low scan rates, **1** has one chemically irreversible reduction wave at -0.56 V versus SCE in acetonitrile (CH_3CN, $0.1\,\mathrm{M}$ $n\mathrm{Bu_4NBF_4}$, Ar atmosphere, 10 °C). The resulting follow-up product is oxidized at $+0.23$ V. This oxidation wave only appears after a first reduction scan. The reduction wave becomes reversible at scan rates higher than $1800\ \mathrm{V\,s^{-1}}$ ($E° = -0.57$ V, $k_s = 0.01\ \mathrm{cm\,s^{-1}}$). Peak-potential analysis of the reduction wave at low and high scan rates indicates a one-electron process. The shape of the voltammograms (peak width) suggests fast electron transfer with kinetic control by chemical reaction.[10] The peak potential is concentration-dependent (22 mV per unit $\log c$) and scan rate-dependent (23 mV per unit $\log v$) in the concentration range 2–10 mM. These cyclic voltammetric data indicate dimerization of the radical anion of **1** through a second-order reaction pathway ([E + C2(A rr)] mechanism) to form **2**, which is responsible for the oxidation wave at $+0.23$ V (Scheme 2).[11] A dimerization rate constant of $k_2 = (1.80 \pm 0.05) \times 10^5\ \mathrm{L\,mol^{-1}\,s^{-1}}$ was determined by simulation of the experimental curves with the DigiSim software.[12]

Dianion **2** was synthesized as its tetraethylammonium salt $(\mathrm{Et_4N})_2$-**2** by bulk electrolysis of **1**. A fresh solution of this salt in CH_3CN ($0.1\,\mathrm{M}$ $n\mathrm{Bu_4NBF_4}$, Ar, 10 °C) shows, at low scan rates, a two-electron process for the characteristic oxidation peak at $+0.23$ V. The characteristic reduction peak of **1** at -0.56 V is observed only after the potential is set above $+0.23$ V (Figure 1b), which means that the oxidation product of **2** is **1**. Furthermore, **1** is recovered in 100 % yield after exhaustive electrolysis of **2** at $+0.40$ V. If the cyclic voltammogram is recorded 5 min after preparing the solution, a new oxidation peak rises at $+0.56$ V, while the height of the peak at $+0.23$ V decreases in comparison with the initial value. In less than one hour, only the peak at $+0.56$ V remains in the cyclic voltammogram, and the peak at $+0.23$ V is no longer visible. This new peak at $+0.56$ V is assigned to **3** (Scheme 2).

The tetraethylammonium salt of dianion **3** was isolated and characterized by aging a solution of **2** in CH_3CN.[13] A freshly prepared solution of the salt of **3** in CH_3CN ($0.1\,\mathrm{M}$ $n\mathrm{Bu_4NBF_4}$, Ar atmosphere, 10 °C) shows, at low scan rates, a

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

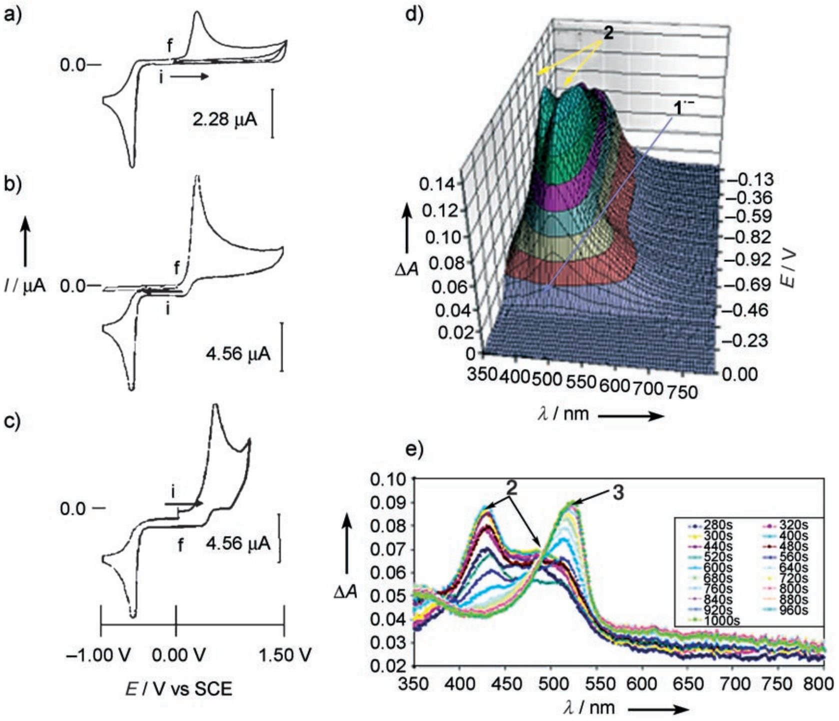
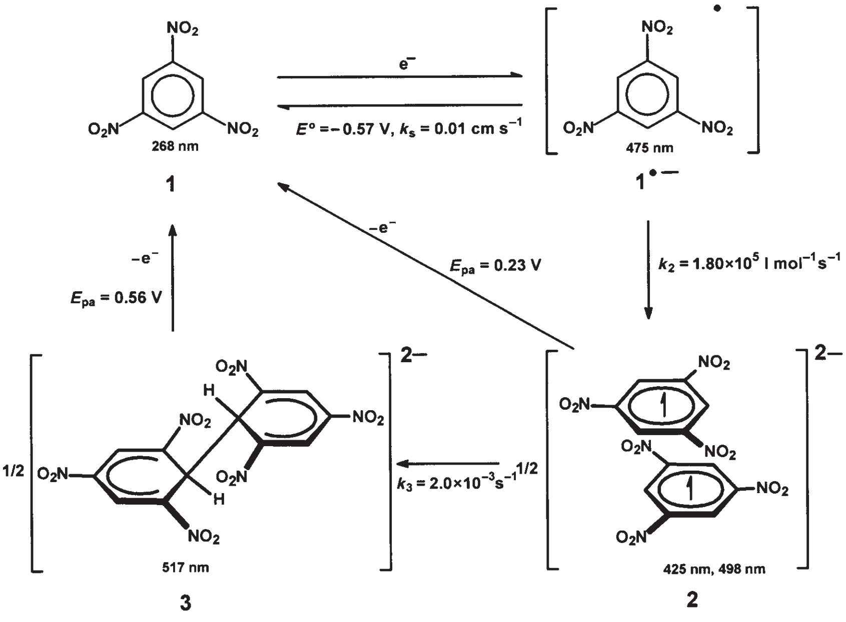


Figure 1. Cyclic voltammetry (CV) at 4.0 mм in CH_3CN with 0.1 м nBu_4NBF_4 at 10 °C. Scan rate 1.0 Vs^{-1}, glassy carbon disk electrode (0.05 mm diameter). a) **1** in the potential range 0.00/1.50/−1.00/0.00 V (two cycles). b) **2** in the potential range 0.00/−1.00/1.50/0.00 V (two cycles). c) **3** in the potential range 0.00/1.00/−1.00/0.00 V. d) Spectrocyclovoltammogram of **1** (0.5 mм) with scan rate 0.1 Vs^{-1} in the potential range 0.00/−1.00/0.00 V; 60 spectra were recorded during the scan.[15] e) In situ UV/Vis spectra during electrolysis of **1** (0.5 mм) at −1.00 V vs. Ag/AgCl in a spectroelectrochemical cell with Pt minigrid as working electrode.[15]



Scheme 2. Detailed mechanism for reduction of **1** under an Ar atmosphere.

two-electron oxidation process for the peak at +0.56 V (Figure 1 c). Again, the characteristic reduction peak of **1** at −0.56 V only arises after the oxidation of **3**, which indicates that **1** is the oxidation product of **3**. This is corroborated by exhaustive electrolysis (+1.30 V) of **3**, which gives **1** in 100 % yield. The oxidation peak of **3** (+0.56 V) is in the range of oxidation potentials found for the σ complexes formed in S_NAr reactions (0.60–1.00 V),[14] whereas **2** is oxidized at a lower potential (+0.23 V), which is consistent with a π dimer.

A potential-step experiment in a UV/Vis–electrochemical cell[15] facilitates measuring the disappearance of **2** by monitoring the absorption band at 425 nm and the appearance of a new band at 517 nm (Figure 1 e; for technical details, see the Supporting Information).[16] From these data, it is possible to deduce that the absorption of **2** (425 and 498 nm) grows rapidly in the beginning, while **1** is totally consumed (about 400 s). Later, the absorption bands of **2** decrease, with concomitant development of the new absorption of **3** (517 nm). Highly accurate kinetic data, gathered by monitoring the appearance of the new absorption band at 517 nm over time, led to $k_3 = 2\times10^{-3}\,s^{-1}$ for the isomerization process **2**→**3** (see the Supporting Information).

The tetraethylammonium salt of dianion **2** was synthesized as a paramagnetic crystalline solid by electrolyzing a solution of **1** in CH_3CN under argon with Et_4NBF_4 as supporting electrolyte.[17] The needle-shaped, conducting crystals grew on a graphite cathode (Figure 2).

X-ray analysis of **2** shows a π-stacked structure in the solid state (Figure 3).[18] The radical-anion units are not parallel to each other; instead, the stack shows a smooth zigzag motif through a short contact (2.48(3) Å) between C2 of one unit and $C4^i$ (i: $-x$, $y+{}^1\!/_2$, $-z+{}^1\!/_2$) of the next. The dihedral angle between the mean planes of two neighboring units is 34.5(8)° and the ring slippage is 1.85(3) Å. This tilted structure could be preserved in solution until the shortest C−C distance collapses to give a σ bond when π dimer **2** evolves into **3.**

Furthermore, **2** is a biradical in solution, as shown by the EPR spectrum of frozen DMF solutions (77 K) of **2** (see the Supporting Information). The spectrum is the result of an $S = 1$ entity having axial symmetry with an isotropic g factor ($g = 2.0075\pm0.0005$) and a zero-field splitting parameter of $D = 323.1\pm0.5$ MHz.[19] The central signal corresponds to a two-photon $\Delta M_s = \pm2$ transition.[20] Moreover, solutions of the paramagnetic species **2** in CH_3CN show fluorescence ($\lambda_{emission} = 608$ nm, $\Phi = 0.25$, irradiation at 428 nm; see the Supporting Information).[21] Neither fluorescence nor an EPR signal was observed for σ complex **3**.

When the electrochemical reduction of **1** is performed in N_2 atmosphere instead of Ar, neither the oxidation waves of **2** (+0.23 V vs. SCE) nor those of **3** (+0.56 V vs. SCE) are observed in the cyclic voltammogram.

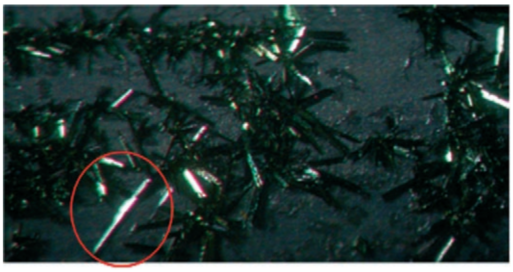


Figure 2. Crystal growing on the graphite electrode surface when electrolysis of **1** is performed at −0.60 V.

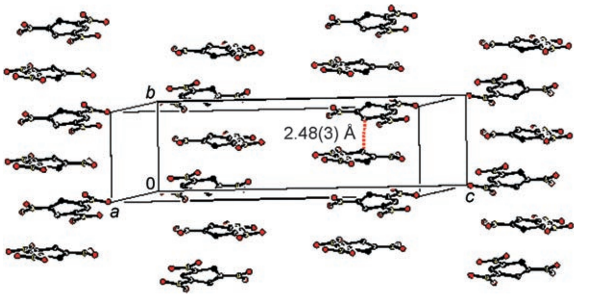


Figure 3. Crystal structure of $(Et_4N)_2$-**2**. The dashed line shows the shortest distance between two aromatic rings C2···C4^i (*i*: $-x, y+{}^1/_2, -z+{}^1/_2$). Tetraethylammonium counterions are omitted for clarity.

However, a new oxidation wave occurs at +1.09 V versus SCE and corresponds to a two-electron transfer process (Figure 4). By analogy with the electrochemical behavior of **1** under Ar, the oxidation wave at +1.09 V can be assigned to dimer **4**. This species was quantitatively formed in solution by electrolysis of **1** at −0.60 V versus SCE (20 mM, CH_3CN, 0.1 M $n$$Bu_4NBF_4$, N_2) after passing 1 F. The electrogenerated species again shows an oxidation wave at 1.09 V versus SCE. The characteristic reduction peak of **1** at −0.56 V is observed only after the potential is set above +1.09 V (Figure 1 a), that is, the oxidation product of **4** is **1**. Furthermore, **1** is recovered in a 100 % yield after exhaustive electrolysis of **4** at +1.20 V (Scheme 3, path B).

To establish whether the new species **4** arises from the reaction of **2** or **3** with N_2, the tetraethylammonium salt of **2** was dissolved in CH_3CN and a flow of nitrogen was immediately passed through the solution and maintained for 10 min. Electrochemical analysis of the resulting solution showed an identical *I–E* curve to that of electrogenerated **4**, that is, a two-electron oxidation wave at +1.09 V. The fact that no difference was observed when N_2 was bubbled through a solution of **3** unequivocally showed that the new product **4** arises from the reaction of biradical **2** with one molecule of N_2 (Scheme 3, path B). Further evidence for this composition was provided by electrospray-ionization mass spectrometry (ESI^-) analysis of an electrogenerated solution of the tetraethylammonium salt of **4**; the peaks at 713.4 $[M-H]^-$, 357.2 $[M]^{2-}$, and 213.0 $[M-28]^{2-}$ show appropriate isotopic distribution.

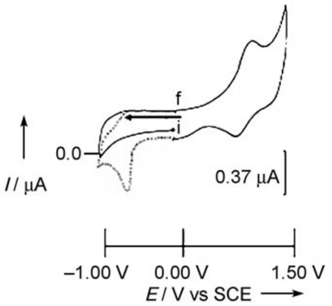
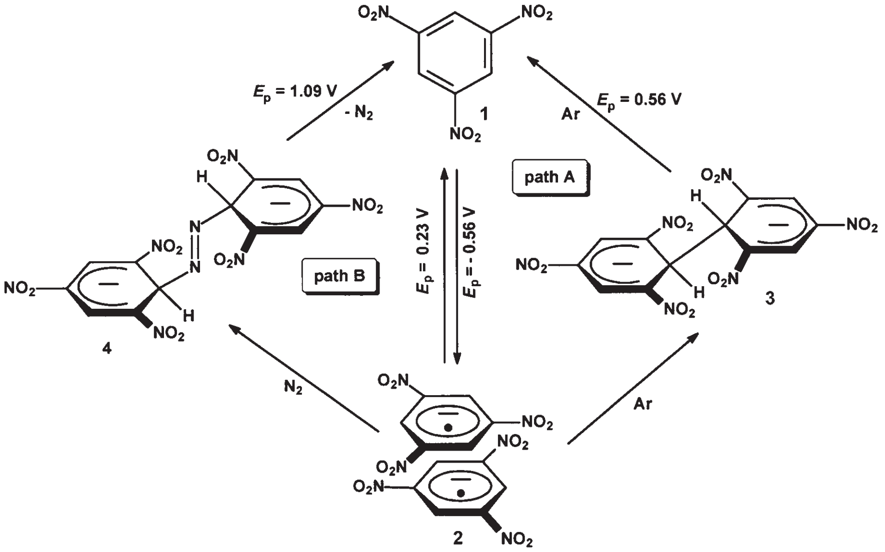


Figure 4. CV of $(Et_4N)_2$-**4** (0.5 mM) in CH_3CN with 0.1 M $n$$Bu_4NBF_4$ at 10 °C. Scan rate 1.0 $V s^{-1}$, glassy carbon disk electrode (∅ 0.5 mm). The potential ranges were 0.00/−1.00/1.50/0.00 V (first scan, solid line) and 0.00/−1.00/0.00 V (second scan, dotted line).

All attempts to isolate a salt of **4** by direct electrochemical reduction of **1** under N_2 failed. However, we were able to isolate single crystals of the tetraethylammonium salt of **4** by exposing the green crystals of the tetraethylammonium salt of **2** to an N_2 flow for one week. This unusual solid–gas reaction at room temperature affords the tetraethylammonium salt of **4** as a red-orange crystalline material. A fresh solution of these crystals in CH_3CN under Ar shows an identical CV to electrogenerated solutions of **4**. The ^1H NMR spectrum of **4** shows two singlets at $\delta = 8.40$ and 6.41 ppm (2:1), which are significantly shifted with respect to those of the σ complex **3** at $\delta = 8.15$ and 5.53 ppm.

The molecular structure of dianion **4** is shown in Figure 5.[22] It consists of two trinitrobenzene units linked by an azo group through two sp^3 carbon atoms (C6 and C12). Thus, the C6−C1, C6−C5, C12−C7, and C12−C11 bonds (av 1.484(3) Å) are longer than the remaining C−C distances in the rings. Furthermore, distances between the sp^2 carbon atoms are consistent with a quinonic structure for the rings, since C1−C2, C4−C5, C7−C8, and C10−C11 are significantly shorter (av 1.358(5) Å) than C2−C3, C3−C4, C8−C9, and C9−C10 (av 1.402(3) Å). The C−N distances are within the normal range, but the N=N distance (1.481(5) Å) is longer than those reported for other azo compounds. Moreover, the angles around the azo fragment are severely distorted: the C6-N14-N13 and C12-N13-N14 angles are only 107.5(3)° and 107.3(3)°, respectively, and the dihedral angle around the N=N bond (C6-N14-N13-C12) is 131.5(4)°. All these structural data indicate significant single-bond character for this azo bond. Interestingly, each of the nitrogen atoms lies within a short, nonbonding distance of two oxygen atoms of two *ortho*-nitro groups (N13···O62 3.046(7), N14···O11 3.028(5) Å). Since the oxygen atoms carry a significant fraction of the negative charge of the dianion, donation from these atoms into the π* bond of the N=N fragment cannot be ruled out. This could be the reason for the observed N=N bond lengthening, as well as the pyramidalization around the N atoms. The close resemblance between the packings of the structures of **2** and **4** suggests that dinitrogen molecules diffuse into solid **2** and bind two neighboring trinitrobenzene radicals without making major changes in the crystal structure or changing the space group. However, the two trinitrobenzene fragments in **4** are no longer related by crystallographic symmetry. Therefore, the volume of the unit cell of **4** (3434(2) $Å^3$) is about twice that of **2** (1646.4(5) $Å^3$). Furthermore, the symmetry elements in the crystal are



Scheme 3. Mechanism for the reversible dimerization of **1** under Ar (path A) or N_2 (path B).

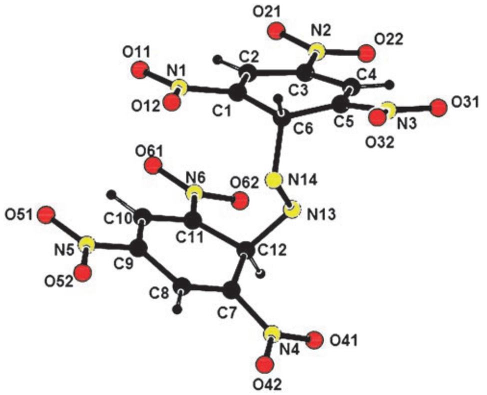


Figure 5. Molecular structure of dianion **4**.[22]

rearranged between **2** and **4**. While in **2** the π stack of trinitrobenzene molecules runs along a 2_1 axis, parallel to the crystallographic *b* axis, the column of azo dimers in **4** is generated by a *c*-glide plane parallel to the *c* axis (Figure 6).

In summary, the radical anion of **1** dimerizes to form biradical π dimer **2**, which forms a π-stacked structure in the solid state. The reversible conversion between the monomeric and dimeric species (**2** and **3**) provides a new example of a molecular switch (Scheme 3, path A) under Ar atmosphere.[23] Whereas there are numerous examples of dinitrogen coordinating to transition metal systems,[24] we have shown for the first time that an organic molecule, namely, **2**, can reversibly bind N_2 at room temperature in an electrochemically controlled process under N_2 atmosphere (Scheme 3, path B). The different behaviors of the reduction product of 1,3,5-trinitrobenzene (**1**) under N_2 or an inert gas such as Ar provides the basis for building sensor devices for dinitrogen.

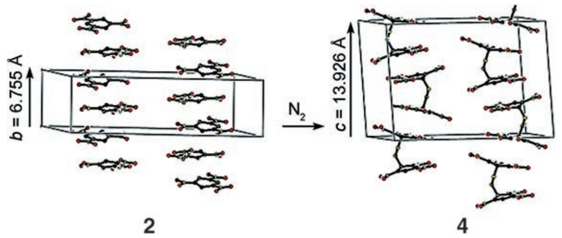


Figure 6. Comparison of the unit cells of the tetraethylammonium salts of **2** and **4**. Cations are omitted for clarity.

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[9] In all scans, nitrobenzene shows a one-electron reversible reduction wave, and dinitrobenzene two successive one-electron reversible reduction waves.

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[12] Simulations were performed by using DIGISIM software, which is commercially available from BAS Corp.

[13] a) The tetraethylammonium salt of 1,1′-dihydro-bis(2,4,6-trinitrociclohexadienyl) dianion (**3**) was isolated and characterized as the same compound previously described by Sosokin et al.[8] Elemental analysis, UV/Vis spectroscopy (517 nm), ^{1}H NMR (the spectrum shows two singlets at $\delta = 8.15$ and 5.53 ppm (2:1), corresponding to the two different kinds of protons). Importantly, no signals were observed by EPR or fluorescence techniques;[13b] b) Investigations by Taylor and Farnham under different environmental conditions showed that the fluorescence quantum yields of σ complexes are about 0.09 (S. Farnham, R. Taylor, *J. Org. Chem.* **1974**, *39*, 2446).

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[16] a) The spectra of **1** and **3** show maximum absorption at 268 and 517 nm, respectively, in accordance with the literature;[4a,8] b) The maximum absorption of **2** was determined in our laboratory.

[17] The tetraethylammonium salt of biradical bis(1,3,5-trinitrobenzene) dianion **2** was obtained by cathodic electrolysis of **1**. Potential-controlled electrolysis at −0.60 V vs. SCE of **1** (20 mM, CH_3CN, 0.1M Et_4NBF_4, Ar, 10°C) quantitatively produces **2** on a graphite working electrode after passage of 1 F. This dark green solid was isolated as a tetraethylammonium salt. Elemental analysis (%) of **2**, calculated for a dimeric structure ($C_{28}H_{46}N_8O_{12}$): N 16.37, C 48.98, H 6.71; found: N 15.94, C 48.60, H 6.72.

[18] a) Crystal structure analysis of $(Et_4N)_2$-**2** ($C_{14}H_{23}N_4O_6$, $M_r = 343.36\ \text{g mol}^{-1}$): A green needle was rapidly mounted under Paratone-8277 on a glass fiber and immediately placed in a cold nitrogen stream at −80°C on a Bruker diffractometer with SMART CCD area detector. Crystal size 0.28 × 0.05 × 0.03 mm; monoclinic, space group $P2_1/c$; $a = 11.657(2)$, $b = 6.7546(14)$, $c = 23.262(4)$ Å, $\beta = 115.988(7)°$, $V = 1646.4(5)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.671\ \text{g cm}^{-3}$; $\mu = 0.109\ \text{mm}^{-1}$; $2\theta_{max} = 56.6°$, $\lambda(\text{Mo}_{K\alpha}) = 0.71073$ Å. 9295 reflections collected (1535 unique reflections, $R_{int} = 0.1131$). Data were corrected for absorption with the SADABS[18b] program. The structure was solved by direct methods and refined (218 parameters) by full-matrix least-squares techniques on F^2 (Bruker-AXS, SHELXTL-NT[18c] version 5.10). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions. The structure was refined to goodness-of-fit and final agreement factors of GoF = 1.211, $R1(I>2\sigma(I)) = 0.1086$, $wR2(\text{all data}) = 0.2376$, residual electron density ±0.39 e$^-$Å^{-3}. CCDC-616742 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif; b) The SADABS program is based on the Blessing method: R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33; c) SHELXTL NT: Structure Analysis Program, version 5.10, Bruker-AXS, Madison, WI, **1995**.

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[21] a) M. A. Muñoz, O. Sama, M. Galán, P. Guardado, C. Carmona, M. Balón, *Spectrochim. Acta Part A* **2001**, *57*, 1049; b) the fluorescence quantum yield of **2** in CH_3CN was determined in relation to the fluorescence quantum yield of *N*′,*N*′′,*N*′′′-triisopropyl-4-oxo-6-isopropyliminio-2*s*-(2*H)*-triazinespiro-1′,2′,4′,6′-trinitrocyclohexadienylide (0.5); c) in CH_3CN, a compound with similar features: R. O. Al-Kaysi, G. Guirado, E. J. Valente, *Eur. J. Org. Chem.* **2004**, 3408.

[22] Crystal structure analysis for $(Et_4N)_2$-**4** ($C_{28}H_{46}N_{10}O_{12}$, $M_r = 714.75\ \text{g mol}^{-1}$) was perfomed on a Nonius Kappa CCD diffractometer. Crystal size 0.16 × 0.07 × 0.05 mm; monoclinic, space group $P2_1/c$; a = 13.131(5), $b = 19.359(5)$, $c = 13.926(5)$ Å, $\beta = 104.043(5)°$, $V = 3434(2)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.382\ \text{g cm}^{-3}$; $\mu = 0.109\ \text{mm}^{-1}$; $2\theta = 54.7°$; $\lambda(\text{Mo}_{K\alpha}) = 0.71073$ Å, $T = 293(2)$ K. 42967 reflections collected (7606 unique reflections, $R_{int} = 0.1286$). The structure was solved by direct methods and refined (452 parameters) by full-matrix least-squares methods on F^2 with the SHELXTL package.[18c] Hydrogen atoms were calculated and placed in idealized positions. The structure was refined to goodness-of-fit and final agreement factors of GoF = 1.023, $R1(I>2\sigma(I)) = 0.1058$, $wR2(\text{all data}) = 0.3592$, residual electron density +0.86 and −0.32 e$^-$Å^{-3}). CCDC-195183 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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