**2,5,8,11-Tetra-tert-butyl-peri-xanthenoxyanthene and its Dication**

**Spectroelectrochemistry and Model Calculations on a Dioxap-22-\(\pi\)-system**

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Spectroelectrochemistry of 2,5,8,11-tetra-tert-butyl-peri-xanthenoxyanthene 1 yields the UV/VIS spectra of the corresponding radical cation 1\(^+\) and dication 1\(^{2+}\). The bathochromic shift for the dication 1\(^{2+}\) relative to 1 and to the isoelectronic hydrocarbon anthanthrene (2) can be understood by quantum mechanical calculations (\(ab\ initial,\ AM1\)) of model structures.

**Introduction**

2,5,8,11-Tetra-tert-butyl-peri-xanthenoxyanthene 1 has been oxidized at a Pt electrode in dichloromethane (DCM) in two reversible one-electron transfers via the radical cation 1\(^+\) to give the dication 1\(^{2+}\) [1], both being persistent on the time-scale of cyclic voltammetry (CV) (\(v > 5\) mV s\(^{-1}\)). In addition, 1\(^+\) could be synthesized in larger scale by anodic or chemical oxidation of 1 and characterized by ESR and UV/VIS spectroscopy. Electrochemical oxidation of unsubstituted peri-xanthenoxyanthene 1\(^a\) afforded charge-transfer complexes of the corresponding radical cation with the parent hydrocarbon [2]. The dication 1\(^{2+}\), however, when prepared from 1 by oxidation, decomposed already on transferring the sample into the spectrometer.

On the other hand, the spectroscopic investigation of the “heteroaromatic” compound 1 and both of its oxidation products is of interest for the following reasons: (i) 1 is a potential donor for conducting charge-transfer complexes. Heterocycles with S [3], Se [3] or Te [4] as heteroatoms have been intensively investigated in this respect, similar species with oxygen, however, only scarcely [5]. (ii) The dication of the parent molecule (1\(^a\)) is isoelectronic with the aromatic hydrocarbon anthanthrene 2 [6], whose UV/VIS spectrum has been known for a long time [7,8]. We have therefore made efforts to obtain the UV/VIS spectrum of 1\(^{2+}\) by spectroelectrochemical methods, to compare it with that of anthanthrene 2 and to check the experimental results against quantum-mechanical calculations.

![Spectroelectrochemistry of 1, 1\(^+\) and 1\(^{2+}\)](attachment:image)

**Spectroelectrochemistry of 1, 1\(^+\) and 1\(^{2+}\)**

The UV/VIS spectra of the system 1\(^+\)/1\(^{2+}\), as recorded in a potentiodynamic spectroelectrochemical experiment between 320 and 800 nm, are shown in Fig. 1 in the potential region \(-400\) mV < \(E\) < +1400 mV (all potentials are referred to the standard redox couple Fe/Fe\(^{3+}\); Fe = ferrocene). Three characteristic domains can be distinguished. At potentials below ca. 150 mV, the spectrum is that of 1. Between 150 and 500 mV (Fig. 1a), this spectrum converts...
378 G. Frenking et al. ■ 2,5,8,11-Tetra-tert-butyl-peri-xanthenoxanthene and its Dication

Fig. 1. (a) Spectroelectrochemistry of the system 1/1⁺ in the region -400 mV < E < +500 mV (first oxidation wave in the CV; the band at 534 nm grows with increasing potential); (b) spectroelectrochemistry of the system 1⁺/1²⁺ in the region +500 mV < E < +1400 mV (second oxidation wave in the CV; the band at 621 nm grows with increasing potential). The arrows in the spectra indicate increasing or decreasing intensity with more positive potentials, the arrows in the cyclic voltammograms show the potential region where the corresponding spectra were recorded (FOC means Fc/Fc⁺ reference electrode).

into the known one of the radical cation 1⁺ [1]. Finally, above 950 mV a new spectrum (λ_max = 621 nm [log ε = 4.35] with two shoulders at 670 and 730 nm; Fig. 1b) appears, which, according to CV experiments (see insets in Fig. 1), has to be attributed to the dication 1²⁺.

If the potential (after oxidation at +1400 mV) is reverted to the region where 1⁺, and then 1, are persistent, the spectra of the radical cation and of the starting compound, respectively, are observed as before. The oxidation of 1 to 1²⁺ is therefore chemically reversible under the conditions used. This is further confirmed by the occurrence of isosbestic points during variation of the potential.

The absorption of the dication 1²⁺ is more intense than that of 1⁺ and 1; the strongest absorption maximum is shifted bathochromically in passing from 1 to 1⁺ and 1²⁺. The radical cation 1⁺ has an absorption between the bands of 1 and 1²⁺. The most intensive absorption of 1⁺, however, is found in the long-wavelength region at 940 nm (see also [9]). The visible colour varies from yellow (1) through purple (1⁺) to blue (1²⁺) [1].

The spectrum of 1 reveals a vibrational structure as expected for extended aromatic systems: on the long-wavelength side of the band there is a steep rise of the absorption, on the short-wavelength side the intensity gradually declines. This is similar to the spectrum of the unsubstituted peri-xantheno-xanthene 1a [10] and indicates that the molecular structure in the excited state is not much different from that in the ground state [11]. Although the absorption band in the spectrum of 1²⁺ does not show a discernible vibrational structure, the gradual decreasing of the maximum on both sides allows to assume a distinct change of the bonding in the excited state relative to that in the ground state of this dicaticonic species.

Thus, the spectrum of 1²⁺ differs from that of the isoelectronic anthanthrene 2, which shows an unsymmetrical longest-wave length band with a steep edge on the long-wave length side [7, 8]. Moreover, dication 1²⁺ absorbs about 200 nm more bathochromically as 2 (maximum of the band). This may be a consequence of the higher electronegativity of the two O⁺-atoms as compared to that of the corresponding C-atoms in 2.

Quantum Mechanical Calculations

In order to understand the bathochromic shift in the spectrum of 1²⁺ relative to the spectra of 1 and 2, quantum mechanical calculations have been performed. The oxidation of 1 to 1²⁺ formally corresponds to the transition of a 24 π-antiaromatic into a 22 π-aromatic system. A very simple model compound, which can be investigated with ab initio methods with a justifiable calculation expense, is 1,4-dioxin 3. This is an 8 π-system, which would produce the dication 3²⁺, isoelectronic to benzene,
upon oxidation. Figure 2 shows our calculation results for benzene, 3, and 3\(^{2+}\). The geometrical data theoretically predicted for 3 agree well with the experimental ones [12]. The dication 3\(^{2+}\) has shorter C–O- and longer C–C-bonds than 3 itself, which indicates stronger delocalization of the \(\pi\)-electrons over the ring in 3\(^{2+}\). The degenerate \(e\)\(_{1g}\) HOMO and \(e\)\(_{2u}\) LUMO orbitals of benzene split in passing to 3\(^{2+}\) and become energetically lowered. More important is the HOMO-LUMO gap. The energy difference between the frontier orbitals of 3\(^{2+}\) is distinctly smaller as compared to benzene (by 3.52 eV at HF/3-21G, by 2.12 eV at AM1, see Fig. 2). Although a simple HOMO-LUMO calculation cannot be used as quantitative estimate of the excitation energy, the shift of the UV absorption is usually predicted in good agreement with experimental observation. The calculations indicate a bathochromic shift for 3\(^{2+}\) with respect to 3.

Transferability of the results obtained with the model system 3 to 1 was checked by AM1 calculations for 2 and the parent compounds of 1 and 1\(^{2+}\) without tert-butyl groups (1a and 1a\(^{2+}\), Fig. 2). The AM1 calculations also predict a bathochromic shift for 1a\(^{2+}\) relative to 1a and 2, the HOMO-LUMO distance in 1a\(^{2+}\) being distinctly smaller (5.29 eV) than in 2 (6.25 eV) and 1a (6.90 eV). PPP-calculations [10] lead to the same conclusion.

The calculated bond lengths in the oxabenzen unit in 1a (Fig. 2) agree well with the experimental ones for 1 itself [13]. Their changes in passing from 1a to 1a\(^{2+}\) can simply be explained by the coefficients of the respective HOMO, which are collected in Fig. 3. The signs of the coefficients remain unchanged in 1a and 1a\(^{2+}\) for the bonds O\(^1\)-C\(^2\), C\(^2\)-C\(^3\), and C\(^3\)-C\(^4\). Hence, the corresponding bond lengths are scarcely varied on oxidation of 1a to 1a\(^{2+}\) (Figs. 2, 3). In contrast, the coefficients show antibonding interaction for the bonds O\(^1\)-C\(^6\) and C\(^4\)-C\(^5\) in 1a and reversed behaviour in 1a\(^{2+}\). In accordance with this fact, the bonds O\(^1\)-C\(^6\) and C\(^4\)-C\(^5\) are shortened significantly in passing from 1a to 1a\(^{2+}\). The C\(^5\)-C\(^6\)-bond in 1a\(^{2+}\) is substantially longer than that in 1a, since the bonding interaction is weaker in 1a\(^{2+}\) due to distinctly smaller coefficients.

**Conclusion**

The experimental and theoretical results presented in this paper show that the dication 1\(^{2+}\) produced by two-electron oxidation of 1 has a decreased HOMO-LUMO gap as compared to the
neutral molecule 1. The aromatic character of $1^{2+}$ is indicated by its stability and the bond length equilibration expected from the model calculations for $1^{2+}$. Similar observations have been reported for tetraoxaporphyrine [14] and tetraoxaporphycene [15] and their respective dications.

**Experimental Part**

$2,5,8,11$-Tetra-tert-butyl-peri-xanthenoxanthene 1 was synthesized as described earlier [13]. – The spectrotro-electrochemical investigations were performed in dichloromethane with NBu$_4$PF$_6$ as supporting electrolyte ($c = 0.1$ mol L$^{-1}$), substrate concentration: $5 \times 10^{-3}$ mol L$^{-1}$. The potentials refer to ferrocene/ferricenium ion as internal standard [16]. Details of the equipment have been reported elsewhere [17]. – UV/VIS spectra were registered as a function of the potential. For every potential the adjustment of the Nernst equilibrium in the thin-layer electrolytic cell was awaited before running the spectrum.

Quantum-mechanical *ab initio* calculations were performed with the 3-21G basis set [18], semiempirical calculations were done with the AM1 method [19]. The calculations of the force constant matrix of the geometry-optimized structures prove those to be minima on the potential hypersurface (only positive eigenvalues). For all theoretical calculations the program Gaussian 88 [20] was used.

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19. M. J. S. Dewar, E. G. Zocherisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* 107, 3902 (1985). The enthalpies of formation calculated by AM1 are (in kcal mol$^{-1}$): $+21.9$ (benzene); $-29.2$ (3); $+492.6$ (3$^{2+}$); $+99.1$ (2); $+42.5$ (1a); $+466.8$ (1a$^{2+}$).