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STABLE DICATIONS OF TETRAAMINO-p-BENZOQUINONES

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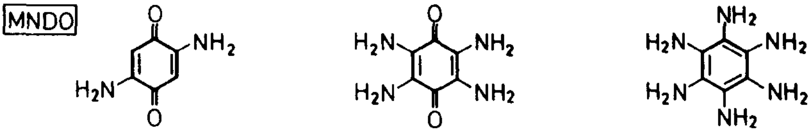
Abstract: N-Peralkyl-tetraamino-p-benzoquinones react with oxidants to form crystalline dication salts. Reductive acylation gives rise to 1,4-bisacyloxy-2,3,5,6-tetraaminobenzenes which can be oxidized to benzene dication salts.

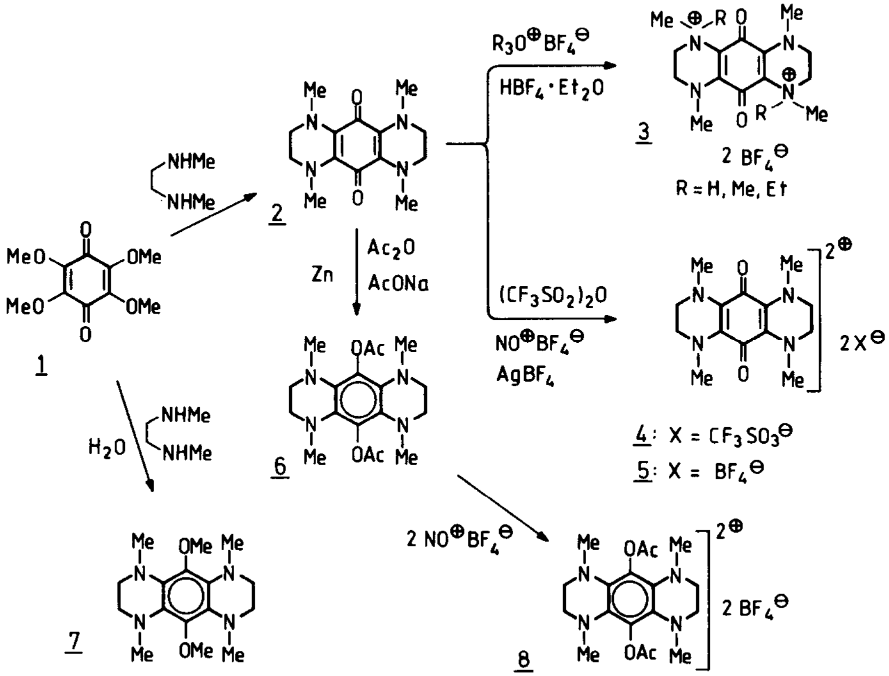
The benzene dication is an antiaromatic 4π electron system. Its hexachloro derivative,[1] possessing a triplet ground state, has been detected in solution. Amino groups exert, as expected, a stabilizing effect on this system. For example, quinone diiminium salts are crystalline compounds[2] with singlet ground states. Recently, a derivative of hexaaminobenzene ("wheel") was synthesized and subsequently oxidized to a dication which had a triplet-ground state in solution.[3]

Benzoquinones can be viewed, in a sense, as derivatives of benzene dications. Since amino groups compensate for the electron-withdrawing effect of the carbonyl groups, tetraaminobenzoquinones are therefore expected to be electron-rich rather than electron-poor compounds. Thus, dialkylaminonaphthoquinones can be O-alkylated.[4] MNDO calculations show that the triplet state of the tetraamino-p-benzoquinone dication has approximately the same energy as the singlet state and that the difference between the heats of formation of tetraamino-p-benzoquinone and its dication is not fundamentally different from that of hexaaminobenzene and its dication:



HOMO/NHOMO (eV)	-9.09/-9.23	-7.83/-8.08	-6.79
H_f^o (singlet)	-30.8 kcal/Mol	-6.1	90.2
H_f^{2+} (singlet, CI)	451.3 kcal/Mol	410.4	494.5
(triplet)	450.8 kcal/mol	410.2	483.5
ΔH_f(triplet/singlet)	-0.5 kcal/Mol	-0.2	-11.0
ΔH_f(triplet^{2+}/ singlet^o)	481.6 kcal/Mol	416.3	393.3

Since the donor effect of the amino substituent is reduced when tetrakis-dialkylamino-p-benzoquinones are not planar (steric),[5] we set out to synthesize planar tetraamino-p-benzoquinones. When tetramethoxy-p-benzoquinone (1) is warmed with N,N'-dimethylethylenediamine without solvent, the dark blue tetraamino-p-benzoquinone derivative 2 is obtained in moderate yield (mp (cyclohexane) 190-192°C; UV/VIS (CH_2Cl_2): λ_{max} (lg ε) = 627 (2.28), 394 (4.05), 235 (sh, 4.02), 232 nm (4.10)). The low carbonyl stretching frequency (1618 cm^{-1}) indicates a high nucleophilicity of the carbonyl oxygen characteristic of ß-aminovinylketones. However, alkylation and protonation of 2



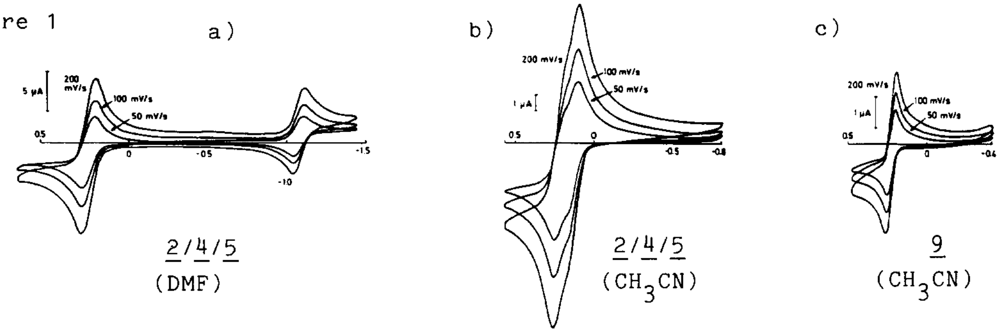
occur only at nitrogen and the salts 3 (3a: mp 205-207°C; 3b: mp 278-279°C, UV/VIS (CH_3CN): λ_{max} = 467, 354, 227 nm) are formed. The reaction of 2 with triflic anhydride affords, instead of an acylation product, the bronze dication salt 4 (mp 194-196°C; UV/VIS (acetonitrile): λ_{max} (lg ε) = 589 (4.39), 514 (4.13), 347 (3.92), 270 nm (4.10)). The corresponding green tetrafluoroborate 5 can be prepared in 71% yield from 2 using nitrosyl or silver tetrafluoroborate (mp 212°C; UV/VIS (CF_3COOH): λ_{max} (lg ε) = 590 (4.60), 509 (4.29), 390 (3.65), 331 (4.00), 236 nm (4.25)).

4 and 5 are thus the first reported benzoquinone dication salts (the tetrakis-dimethylamino-p-benzoquinone radical cation has been described only recently[6]). Despite their (4n)π electron systems, 4 and 5 are fairly stable in the crystalline state (they decompose slowly in solution). As a solid, 5 provides a singlet ESR spectrum centered at g = 2.0. The spin concentration at 20°C is 3.3×10^{19} spins/mol which amounts to a concentration of $5.5\ 10^{-5}$

radicals per molecule. At -160°C, in addition to the singlet spectrum, a weak triplet signal at g = 4 is observed which disappears at higher temperatures. In methanol solution, no triplet signal but a well-resolved multiplet spectrum centered at g = 2.0029 with more than 17 lines is observed (a = 3.88 G). Obviously, the radical species that causes the ESR signal (radical cation of 2?) is present only in very low concentration. There is thus no indication that 5 exists in a triplet state at temperatures higher than -160°C.

The cyclovoltammograms (Figure 1b) of 2 and 4 or 5 (0.001 M in acetonitrile with 0.1 M $Et_4N^+BF_4^-$) exhibit one broad distorted wave typical of two successive oxidation steps (at approximately 0.14 and 0.22 V vs SCE) with a potential separation of approximately 80 mV (cf.[7]). In DMF the two steps coalesce even more, so that one observes only a single wave at +0.25 V (ΔE ≈ 60 mV; Figure 1a). The area of this wave is twice that of the wave at -1.07 V (reduction to the radical anion). The electrochemical results are in accordance with the observation that only the dication salts 4 and 5 were obtained through chemical oxidation, and the radical cation at best in trace amounts.

Figure 1



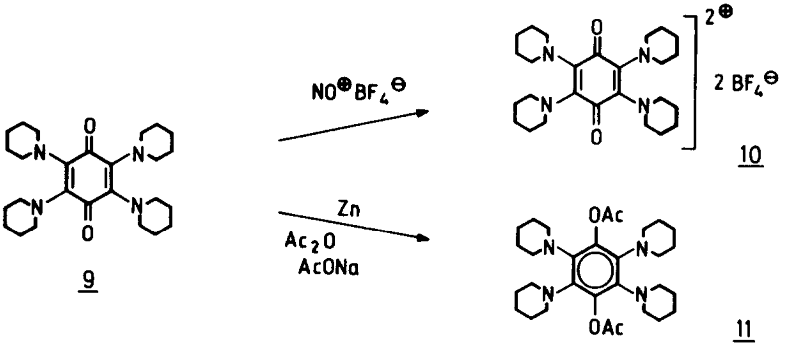
2/4/5 (DMF)

2/4/5 (CH_3CN)

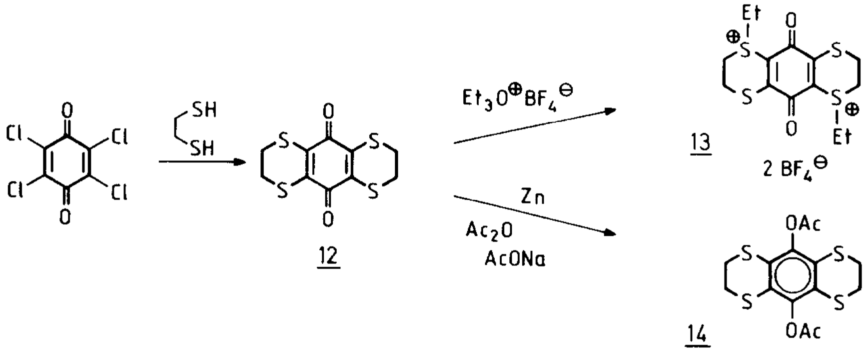
9 (CH_3CN)

2 can be reduced with zinc/acetic anhydride to afford the air-sensitive electron-rich benzene derivative 6 in high yield (mp 205-206°C; cyclovoltammogram in CH_3CN: two-electron wave at +0.16 V vs SCE, ΔE ≈ 60 mV). The oxidation potential of 6 differs not very much from that of 2 which underlines the close electronic relationship between tetraaminodihydroxybenzenes and tetraaminobenzoquinones. Surprisingly, the dimethoxy derivative 7 is formed when 1 is warmed with an excess of dimethylethylenediamine in water (mp 167-169°C). The oxidation of 6 with nitrosyl tetrafluoroborate furnishes the violet-blue benzene dication salt 8 in 61% yield (mp 164-166°C; UV/VIS (acetonitrile): λ_{max} (lg ε) = 631 (2.93), 425 (4.13), 372 (4.35), 253 nm (4.26)).

Likewise, tetrapiperidino-p-benzoquinone (9) reacts with nitrosyl or trimethyloxonium tetrafluoroborate to afford, as green needles, the dication salt 10 in almost pure form (mp 239-241°C; λ_{max} (acetonitrile) = 543 nm). The cyclovoltammogram of 9 exhibits only a single wave at +0.22 V vs SCE in acetonitrile (ΔE ≈ 30 mV; Figure 1c) or at 0.33 V in DMF (ΔE ≈ 33 mV) similar to a two-electron wave. It is surprising that with tetrakis-dimethylamino-p-benzoquinone the electrooxidation stops at the stage of the radical cation.[6] The reductive acylation of 9 gives rise to the colorless diacetoxytetrapiperidinobenzene 11 (mp 296-298°C) which could not be oxidized.



In order to investigate the properties of mercapto analogues of 2, the purple bisethylenedithio-p-benzoquinone 12 (mp (chlorobenzene) 314-315°C) was synthesized through the reaction of chloranil with ethanedithiol (cf. the reaction of 2,3-dichloronaphthoquinone[8]). The donor effect of the ethylenedithio groups is, however, too weak to permit the chemical oxidation of 12 to



a radical cation or a dication. Alkylation gives rise to the bright orange disulfonium salt 13 (UV/ VIS (H_2SO_4): λ_{max} (lg ε) = 493 (3.07), 387 (4.11), 263 (4.05)).

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