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STABLE DICATIONS OF TETRAAMINO-p-BENZOQUINONES

Rudolf Gompper*, Rudolf Binder and Hans-Ulrich Wagner

Institut für Organische Chemie der Universität München Karlstraße 23, D-8000 München 2, West Germany

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 diminium salts are crystalline compounds² 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 0-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:

		H ₂ N O	$-NH_2$ H_2N H_2N H_2N H_2N H_2N H_2N H_2N	$\begin{array}{c} 0 \\ NH_2 \\ H_2N \\ H_2N \\ NH_2 \\ NH_2 \\ H_2N \\ NH_2 \\ NH_2 \\ NH_2 \end{array}$	12 12
номо	NHOMO (eV)	-9.09/-9	9.23 -7.8	-6.79	
H ^O	(singlet)	-30.8 kd	eal/Mol -6.1	90.2	
H ²⁺	(singlet, CI)	451.3 kc	cal/Mol 410.4	494.5	
-	(triplet)	450.8 kg	cal/mol 410.2	483.5	
∆H _f (triplet/singlet)		-0.5 kc	cal/Mol -0.2	-11.0	
ΔH _f (t	criplet ²⁺ /	481.6 ka	eal/Mol 416.3	393.3	
-	singlet	·°)			

Since the donor effect of the amino substituent is reduced when tetrakisdialkylamino-p-benzoquinones are not planar (steric),⁵ we set out to synthesize planar tetraamino-p-benzoquinones. When tetramethoxy-p-benzoquinone (<u>1</u>) is warmed with N,N'-dimethylethylenediamine without solvent, the dark blue tetraamino-p-benzoquinone derivative <u>2</u> 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 B-aminovinylketones. However, alkylation and protonation of <u>2</u>



occur only at nitrogen and the salts <u>3</u> (<u>3a</u>: mp 205-207°C; <u>3b</u>: mp 278-279°C, UV/VIS (CH₃CN): $\lambda_{max} = 467$, 354, 227 nm) are formed. The reaction of <u>2</u> with triflic anhydride affords, instead of an acylation product, the bronze dication salt <u>4</u> (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 <u>5</u> can be prepared in 71% yield from <u>2</u> using nitrosyl or silver tetrafluoroborate (mp 212°C; UV/VIS (CF₃COOH): λ_{max} (lg ϵ) = 590 (4.60), 509 (4.29), 390 (3.65), 331 (4.00), 236 nm (4.25)).

 $\frac{4}{2}$ and $\frac{5}{2}$ are thus the first reported benzoquinone dication salts (the tetrakis-dimethylamino-p-benzoquinone radical cation has been described only recently⁶). Despite their (4n) π electron systems, $\frac{4}{2}$ and $\frac{5}{2}$ are fairly stable in the crystalline state (they decompose slowly in solution). As a solid, $\frac{5}{2}$ provides a singlet ESR spectrum centered at g = 2.0. The spin concentration at 20°C is 3.3 x 10¹⁹ 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 $\text{Et}_4 \text{N}^+\text{BF}_4^-$) 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 ($\Delta E \approx 60$ 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 $\frac{4}{2}$ and $\frac{5}{2}$ were obtained through chemical oxidation, and the radical cation at best in trace amounts.

<u>2</u> can be reduced with zinc/acetic anhydride to afford the air-sensitive electron-rich benzene derivative <u>6</u> in high yield (mp 205-206°C; cyclovoltam-mogram in CH₃CN: two-electron wave at +0.16 V vs SCE, $\Delta E \approx 60$ mV). The oxidation potential of <u>6</u> differs not very much from that of <u>2</u> which underlines the close electronic relationship between tetraaminodihydroxybenzenes and tetraaminobenzoquinones. Surprisingly, the dimethoxy derivative <u>7</u> is formed when <u>1</u> is warmed with an excess of dimethylethylenediamine in water (mp 167-169°C). The oxidation of <u>6</u> with nitrosyl tetrafluoroborate furnishes the violet-blue benzene dication salt <u>8</u> in 61% yield (mp 164-166°C; UV/VIS (aceto-nitrile): 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 aceto-nitrile ($\Delta E \approx 30$ mV; Figure 1c) or at 0.33 V in DMF ($\Delta E \approx 33$ mV) similar to a two-electron wave. It is surprising that with tetrakis-dimethylamino-p-benzo-

quinone 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 $\underline{12}$ (mp (chlorobenzene) $\underline{314}$ - $\underline{315}$ °C) was synthesized through the reaction of chloranil with ethanedithiol (cf. the reaction of 2,3-dichloronaphthoquinone 8). The donor effect of the ethylenedithic 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 <u>13</u> (UV/ VIS (H_2SO_4): λ_{max} (lg ϵ) = 493 (3.07), 387 (4.11), 263 (4.05)).

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References

1.	E.Wasserman,	R.S.Hutton,	V.J.Kuck,	E.A.Chandross,	J.Am.Chem.Soc.	96	(1974))
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- E. Wasserman, K.S. Hutton, V.S. Kuck, E.A. Chandross, J. Am. Chem. Soc. 90 (1974)
 S. Hünig, P. Richters, Chem. Ber. 91 (1958) 442. [1965.
 R. Breslow, P. Maslak, J.S. Thomaides, J. Am. Chem. Soc. 106 (1984) 6453.
 R. Gompper, N. Sengüler, Tetrahedron Lett. 24 (1983) 3567.
 K. Wallenfels, W. Draber, Tetrahedron 20 (1964) 1889.
 H. Bock, P. Hänel, W. Kaim, U. Lechner-Knoblauch, Tetrahedron Lett. 26 (1985)
 D.S. Polcyn, I. Shain, Anal. Chem. 38 (1966) 370. [5115.
 W. E. Hahn, L. Wojciechowski, Rocz. Chem. 41 (1967) 1067 (Chem. Abstr. 68 (1968) 59510y).

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