

THE SINGLE CRYSTAL STRUCTURE OF AN ORGANIC TETRACATION:

TETRAKIS(4-DIMETHYLAMINOPYRIDINIUM)-*p*-BENZOQUINONE TETRAKIS(TRIFLATE)^{1,2}

Hans Bock*, Sabine Nick and Jan W. Bats

Department of Chemistry, University of Frankfurt,
Niederurseler Hang, 6000 Frankfurt/Main, Germany

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Abstract: The structure of the dark red title salt shows a distorted planar quinone ring with CC bonds of 133, 147 and 153 pm length and distorted pyridine rings twisted by 56° or 63° with ipso angles of 116°; it can be largely rationalized both by structure comparison with other *p*-benzoquinone derivatives or pyridinium salts and by MNDO calculations, which suggest that an extensive delocalization of the four positive charges may contribute to its stability.

Only a few organic molecules M are sufficiently electron-rich to yield on fourfold oxidation their respective tetracations M⁺⁺⁺⁺.²⁻⁵ Frequently, the alternative acid/base reaction route via protonation, alkylation, amination, etc., provides easier access to tetracation salts [MR₄⁺⁺⁺⁺][X⁻]₄.^{2,6,7} Despite their positive charges, however, the molecular polycations [M(R)_n]⁺ⁿ are seemingly not as electron-deficient as the M⁺ⁿ ones and, therefore, structural differences between them provide interesting information.

Stimulated by a literature report,⁷ that fourfold dimethylaminopyridinio substitution of *p*-benzoquinone - readily accomplished by allowing tetrachloro-*p*-benzoquinone to react with 4-dimethylaminopyridine and (H₃C)₃Si-OSO₂CF₃ - lowers its first half-wave reduction potential from -0.40 V by +1.13 V(!) to 0.73 V, we have grown single crystals of the dark red compound and determined its structure⁸ (Figure 1).

In crystalline tetrakis(4-dimethylaminopyridinium)-*p*-benzoquinone tetrakis(triflate), layers of the bulky tetracations are interspersed with two independent and disordered triflate anions and two with rather short contact distances of about 280 pm to the (O)CC bonds of 153 pm length (Figure 1). The intramolecular distances O...N are shorter by 12 or 17 pm than the sum of the frequently used van der Waals radii ($r^{\text{vdW}} \approx 150$ pm; $r^{\text{vdW}} \approx 140$ pm).²

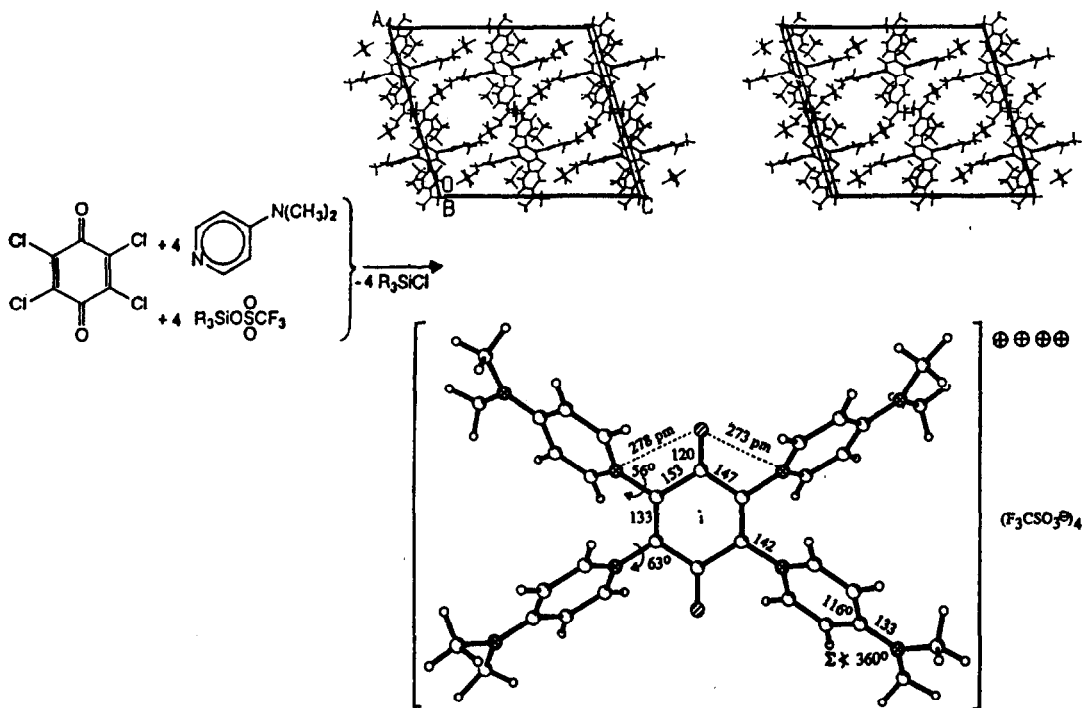


Figure 1. Preparation⁷ and structure of tetrakis(dimethylaminopyridinio)-*p*-benzoquinone tetrakis(triflate): Stereoscopic view of the monoclinic ($C 2/c$) unit cell containing four formula units and the tetracation structure (i = center of inversion, \bullet : O; \oplus : N; cf. text).

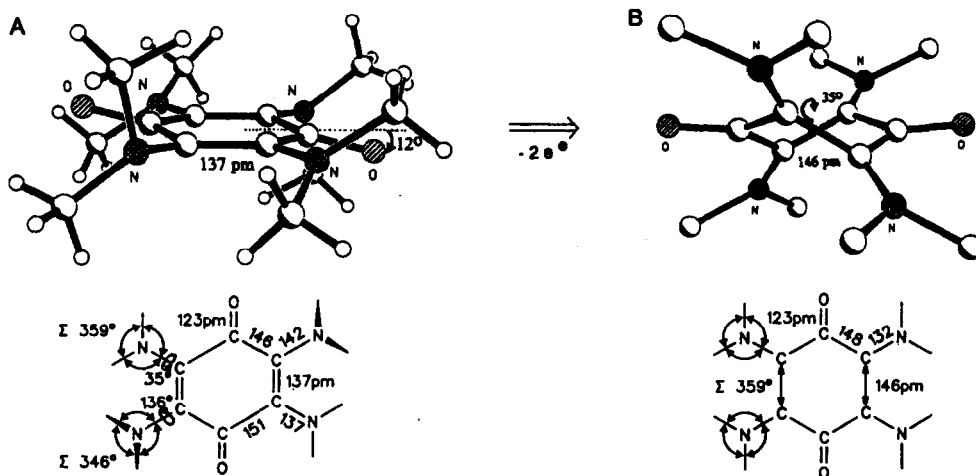
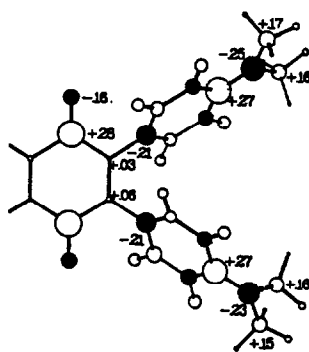
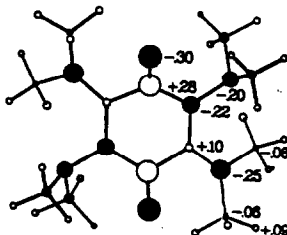


Figure 2. Structures of (A) tetrakis(dimethylamino)-*p*-benzoquinone M and (B) its dication salt $M^{2+}(\text{SbCl}_6^-)_2$, prepared by oxidation with $\text{SbCl}_5/\text{H}_2\text{CCl}_2$.⁹

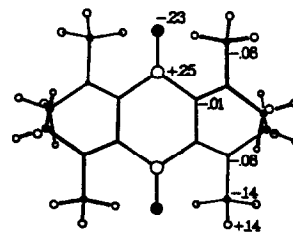
The following structural differences between the quinone tetracation (Figure 1) prepared by acid/base reaction and the related compounds, the sterically overcrowded tetrakis(dimethylamino)-*p*-benzoquinone and its twisted dication generated by twofold oxidation,⁹ (Figure 2) are emphasized: In fourfold dimethylaminopyridinio-substituted *p*-benzoquinone tetracation the skeleton remains planar. For its chain-subunits $O=C=(N^{\delta+})C=C=N^{\delta+}$ two different prototype cyanine-like distortions^{2,8} are feasible: either analogous to the neutral $O=C=C=C=N$ chains (Figure 2: A) or to the positively charged subunits $(N=C=C(O)=C=N)^{\oplus}$ (Figure 2: B). Obviously, the structure parameters determined (Figure 1: (O)C-C 147 pm and 153 pm; C-N^{δ+} 141 pm) more closely resemble the former. This observation suggests that the positive charges are largely delocalized within the dimethylaminopyridine rings twisted by 56° or 63° out of the benzoquinone plane, and thus the substituents do not exert a considerable (N^{δ+}) perturbation. MNDO charge distributions, calculated based on the crystal structure coordinates, support this interpretation (cf.⁹):



(Figure 1)

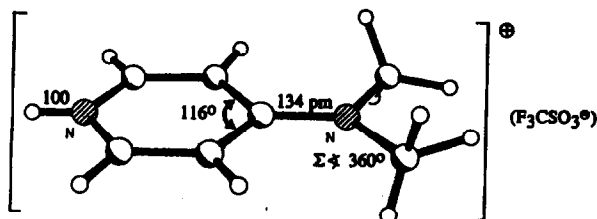


(Figure 2: A)



(Figure 2: B)

Whereas in the twisted dication with stretched C-C bonds (Figure 2: B), the two positive charges reduce the negative ones at the N centers and appear predominantly in the peripheral hydrogens, in both the neutral tetrakis(dimethylamino) derivative (Figure 2: A) and the tetrakis(dimethylaminopyridinio)-substituted *p*-benzoquinone (Figure 1) substantial negative charge is predicted for all N centers. The MNDO charge distributions calculated for the dimethylaminopyridinio substituents also help to rationalize their structural parameters (Figure 1): the dimethylamino groups are fully planarized and connected by rather short NC bonds to the 4-positions of the pyridine rings, which due to the remaining R₂N donor effect close their ipso angles² down to 116°. The very same features are exhibited by the structures of other dimethylamino-substituted pyridinium salts¹¹ such as 4-dimethylaminopyridinium-triflate:¹¹



In summary, the structures of organic polycations prepared by acid/base instead of redox reactions^{2,3} due to the usually smaller differences in total energy involved² often exhibit less severe distortions relative to the neutral molecule. As demonstrated, however, intriguing peculiarities can be found and, therefore, they are well worth further exploration.¹¹

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- A mixture containing each 40 mmoles 4-dimethylaminopyridine and trimethylsilyl trifluoromethylsulfonate and 10 mmoles chloranil in 50 mL of H₂CCl₂ was stirred for 12 h. The red precipitate was recrystallized from aprotic acetonitrile (c_H⁺ < 1 ppm). Structure of C₃₈H₄₀F₁₂N₈O₁₄S₄ (1189.02 g/mole), a = 2315.9(6), b = 935.1(4), c = 2621(1) pm; β = 107.27(3)°; V = 5421(7) × 10⁶ pm³ (293 K); ρ_{calcd.} = 1.457 g/cm³, monoclinic (C 2/c); Z = 4, Enraf-Nonius CAD4-diffractometer, μ(Cu-Kα), 2° < 2θ < 100°, 3006 registered reflections, 2880 independent with I > O (I); slow decomposition, R = 0.116; R_w = 0.102. The higher than usual R values are due to the disordering of two of the triflate counter anions. Direct methods (SHELXS-90), C,F,N,O,S atoms anisotropically refined, the H atoms on calculated positions were isotropically refined using a constant temperature factor. Standard deviations for the tetracation are estimated to be ± 1 pm and ± 1°. For further structural details cf. the report submitted to the Cambridge Crystallographic Data Centre.
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