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Unprecedented zwitterion in quinonoid chemistry†

Olivier Siri and Pierre Braunstein*

Laboratoire de Chimie de Coordination, UMR CNRS 7513, Université Louis Pasteur, 4 rue Blaise Pascal F-67070. Strasbourg Cédex, France. E-mail: braunst@chimie.u-strasbg.fr

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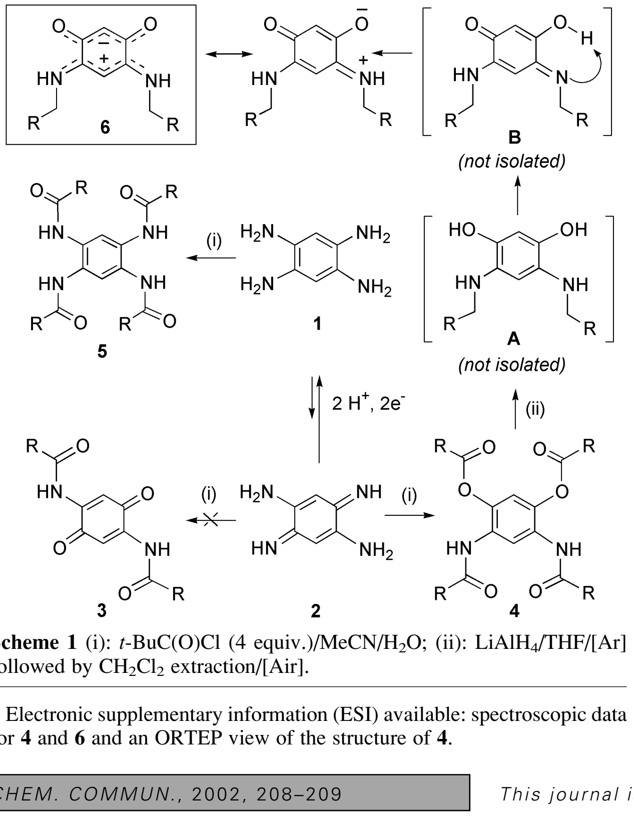
The first 12π-electron zwitterionic structure in quinonoid chemistry is described with the *N,N,O,O* -molecule 6 in which the positive charge is π-delocalized between the nitrogen atoms and the negative charge between the oxygen atoms; depending on the crystallization solvent, a 1D-tape-like H-bonded network can be generated in the solid-state.

Organic molecules with a quinonoid structure constitute a large and important class of compounds with remarkable chemical and physical properties.[1] For years, studies on structure/colour relationships have typically involved *N*-substituted aminoquinones[2] whose synthesis generally requires *N*-substitution of the amine before nucleophilic attack at the quinonoid system. In view of the intrinsic interest in these molecules and related benzoquinoneimines,[3] and their potential as ligands in coordination and organometallic chemistry, a more versatile access than that currently available appears attractive. Herein, we describe (*i*) the first 12π-electron zwitterionic molecule (**6**) in quinonoid chemistry which results from the unexpected one-pot synthesis of the aromatic *N,N,O,O*-system **4** from 1,2,4,5-tetraaminobenzene **1** and (*ii*) the supramolecular H-bonded network based on the '*tête-bêche*' arrangement of these zwitterions in the solid state.

Although compound **1** is known to be readily oxidized in **2**,[4] smooth reaction of **1**·4HCl with RC(O)Cl (R = *t*-Bu) in wet CH_3CN and excess NEt_3 did not afford the *p*-benzoquinone derivative **3**. Instead, the new compound **4** was obtained (25% yield) together with known **5** (72% yield) which results from direct *N*-substitution of **1**[5] (Scheme 1).



Scheme 1 (i): *t*-BuC(O)Cl (4 equiv.)/MeCN/H_2O; (ii): $LiAlH_4$/THF/[Ar] followed by CH_2Cl_2 extraction/[Air].

The ^1H and ^{13}C NMR data of **4** (see ESI)† were consistent with the presence in solution of either a mirror plane or an inversion center, symmetry elements compatible with isomeric structures in which the two oxygen functions would be in mutual *meta* or *para* position, respectively. An X-ray diffraction study established the mutual *meta* relationship between the *N*- and *O*-substituents,[6] and the down,up,up,up-type orientation of the carbonyl functions which implies a lower symmetry than in solution. We are currently investigating the reaction pathways leading to **4**.

Reduction of **4** with $LiAlH_4$, followed by work-up in air, afforded **6** as a purple solid in 70% yield. An X-ray diffraction study on single crystals of **6**·$2H_2O$, obtained from acetone/H_2O, showed a planar molecule, except for the *t*-Bu groups which are both on the same side of the plane (Fig. 1).[6] The C(2)–C(3) distance of 1.517(5) Å corresponds to a single bond and indicates the lack of conjugation between the two halves of the ligand. In contrast, the other C–C distances within the ring, the C–O and C(3)–N(1) and C(5)–N(2) bond distances show a remarkable bond equalization. Delocalization of the 12π-electron system appears therefore confined within two independent subunits of the molecule: the negative charge being delocalized between the oxygen atoms and the positive charge between the nitrogen atoms. Formation of **6** could be explained by reduction of the amido and ester groups of **4** leading to an intermediate **A** (not isolated but related to known molecules[7]) which would be readily oxidized by air during work-up to give **B** (Scheme 1). Proton migration from oxygen onto the more basic nitrogen atoms then results in the zwitterionic benzoqui-

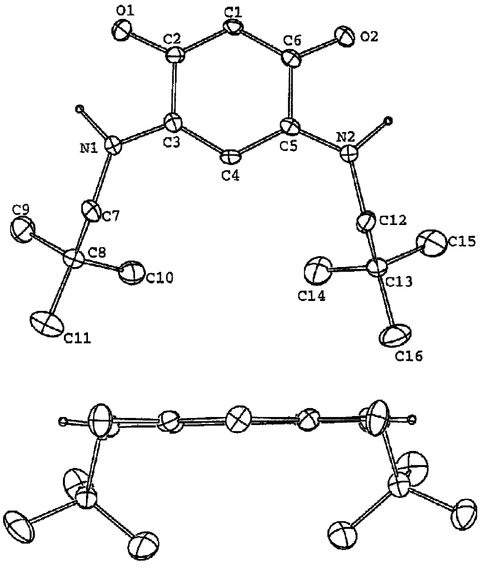


Fig. 1 Top (A) and side (B) views of the structure of **6**·$2H_2O$ in the crystal. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): C1–C2 1.379(5), C1–C6 1.399(5), C2–O1 1.265(4), C2–C3 1.516(5), C3–C4 1.393(5), C3–N1 1.323(5), C4–C5 1.389(5), C5–C6 1.523(5), C5–N2 1.320(5), C6–O2 1.254(4); C2–C1–C6 122.0(4), C1–C2–C3 118.7(3), C3–C2–O1 115.5(4), C5–C6–O2 116.2(3), C2–C3–N1 113.4(3), C6–C5–N2 113.5(3).

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† Electronic supplementary information (ESI) available: spectroscopic data for **4** and **6** and an ORTEP view of the structure of **4**.

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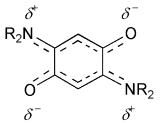
nonemonoimine structure **6**. In contrast to the UV–VIS. absorption spectrum of substituted benzenes like **4** and **5**, that of **6** in CH_2Cl_2 is characterized by two strong absorptions at 350 nm (log ε = 4.49) and 343 nm (log ε = 4.45) which correspond to the intraquinone charge transfers.[8] The situation in **6** represents a novel electronic pattern for *N,N,O,O*-systems since previously known quadrupol-merocyanine-type structures **7** and **8** display electronic delocalization exclusively between nitrogen and oxygen atoms with no occurrence of a zwitterionic structure.[2]



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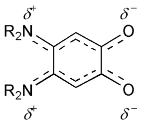

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In the latter cases, theoretical studies have been performed in relation to the coupling effects which occur in polymethine dyes.[9] The molecular symmetry deduced from the ^{1}H and ^{13}C NMR spectra (see ESI†) is clearly explained by the zwitterionic structure of $\mathbf{6}\cdot 2H_2O$ and not by a tautomeric equilibrium as suggested in related systems.[3,10] In the solid state, intermolecular interactions develop between water molecules of solvation and O(1), O(2) and the N(2)H proton. In contrast, crystals of **6** grown from an aprotic solvent such as chlorobenzene showed a '*tête-bêche*' arrangement of the zwitterion,[6] leading to an H-bonded tape-like supramolecular array (Fig. 2). The six-membered rings of two consecutive molecules are almost orthogonal to each other. A change in the orientation of the *t*-Bu groups is observed, which are now situated on opposite sides with respect to the molecular plane. Bond distances in **6** are very similar to those in $\mathbf{6}\cdot 2H_2O$.

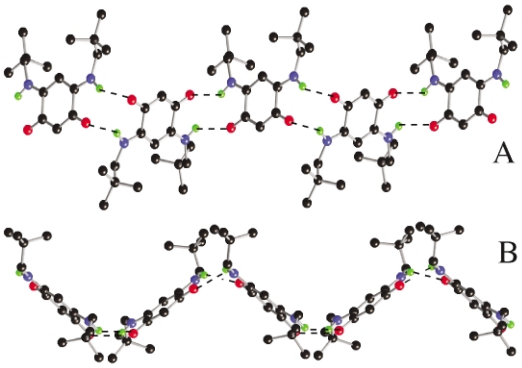

Fig. 2 Views of the supramolecular array generated by **6** in the solid-state: (A) view of the tape running in the projection plane; (B) side view with the tape orthogonal to the projection plane. Colour coding : oxygen, red; nitrogen, blue; hydrogen, green.

The synthesis of the unprecedented zwitterion **6** results from a new strategy for the preparation of substituted aminobenzoquinones. This molecule displays a remarkable delocalization of its 12π-electron system and represents a promising building block in coordination and supramolecular chemistry.[11]

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6 *Crystal data for* **4**: $C_{26}H_{40}N_2O_6$, M = 476.62, triclinic, space group $P\bar{1}$; a = 10.3719(6), b = 11.2034(6), c = 13.8449(8) Å, α = 103.748(5), β = 103.919(5)°, γ = 112.113(5)°, V = 1346.9(4) Å^3, Z = 2, μ(Mo-Kα) = 0.083 mm^{-1}, T = 294 K, 2192 data with $I > 3\sigma(I)$, final R = 0.068, R_w = 0.081, GOF = 1.180. CCDC reference number 149251. An ORTEP plot is provided in the ESI.† *Crystal data for* $\mathbf{6}\cdot 2H_2O$: $C_{16}H_{30}N_2O_4$, M = 314.43, monoclinic, space group $C2/c$; a = 24.998(2), b = 16.728(1), c = 8.8553(6) Å, β = 102.112(5)°, V = 3620.6(4) Å^3, Z = 8, μ(Mo-Kα) = 0.082 mm^{-1}, T = 173 K, 1571 data with $I > 3\sigma(I)$, final R = 0.056, R_w = 0.080, GOF = 1.311. The two N-*H* atoms were located experimentally. CCDC reference number 149253. *Crystal data for* **6**: $C_{16}H_{26}N_2O_2$, M = 278.40, monoclinic, space group $P2_1/c$; a = 12.9221(7), b = 19.696(1), c = 13.3065(8) Å, β = 101.231(5)°, V = 3321.9(7) Å^3, Z = 8, μ(Mo-Kα) = 0.073 mm^{-1}, T = 294 K, 1891 data with $I > 3\sigma(I)$, final R = 0.039, R_w = 0.041, GOF = 1.035. The H atoms were placed in calculated positions. CCDC reference number 149252. All structures were refined using SHELXL-97 with F^2 data sets. See http://www.rsc.org/suppdata/cc/b1/b107828n/ for crystallographic data in CIF or other electronic format.

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