

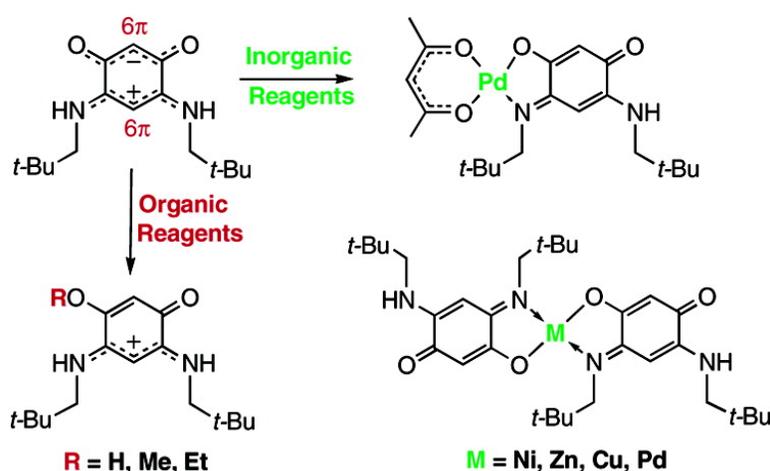
Article

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A $6\pi + 6\pi$ Potentially Antiaromatic Zwitterion Preferred to a Quinoidal Structure: Its Reactivity Toward Organic and Inorganic Reagents

Pierre Braunstein,^{*,†} Olivier Siri,[†] Jean-philippe Taquet,[†] Marie-Madeleine Rohmer,[‡] Marc Bénard,[‡] and Richard Welter[§]

Contribution from the Laboratoire de Chimie de Coordination, UMR 7513 CNRS, Université Louis Pasteur, 4, rue Blaise Pascal, F-67070 Strasbourg Cedex, France, Laboratoire de Chimie Quantique, UMR 7551 CNRS, Université Louis Pasteur, 4, rue Blaise Pascal, F-67070 Strasbourg Cedex, France, and Laboratoire DECMET, UMR 7513 CNRS, Université Louis Pasteur, 4, rue Blaise Pascal, F-67070 Strasbourg Cedex, France

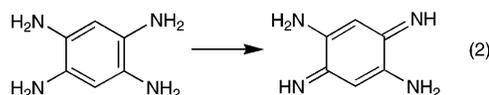
Received April 4, 2003; E-mail: braunst@chimie.u-strasbg.fr

Abstract: A straightforward synthesis of the zwitterionic benzoquinoneminoimine **8** is reported. This molecule is a rare example of a zwitterion being more stable than its canonical forms. It is shown that **8** is best described as constituted of two chemically connected but electronically not conjugated 6π electron subunits. Its reactivity with electrophiles such as H^+ , CH_3^+ , and metal salts leads to the synthesis of new 12π electron molecules **12** (H^+), **14** (CH_3^+), and **20** (Pd^{2+}), respectively, in which one or both 6π electron subsystems localize into an alternation of single and double bonds, as established by X-ray diffraction. The acidity of the N–H protons of **8** can be modulated by an external reagent. Dependent on the electrophile used, the control of the π system delocalization becomes possible. When the electrophile simply adds to the zwitterion as in **12**, **14**, or **15**, there is no more negative charge to be delocalized and only the positive charge remains delocalized between the nitrogen atoms. Furthermore, when a reaction with the electrophilic reagent results in deprotonation, as in **17–21**, there remains no charge in the system to be delocalized. DFT calculations were performed on models of **8**, **12**, **14**, **20**, and on other related zwitterions **9** and **10** in order to examine the influence of the fused cycles on the charge separation and on the singlet–triplet energy gap. An effect of the nitrogen substituents in **8** is to significantly stabilize the singlet state. The dipole moment of **8** was measured to be 9.7 D in dichloromethane, in agreement with calculated values. The new ligands and complexes described in this article constitute new classes of compounds relevant to many areas of chemistry.

Introduction

More than one century ago, Kekulé proposed the 6-fold symmetric structure of benzene for explaining the characteristic differences in physical properties and chemical reactivity between benzenoid and nonbenzenoid compounds.¹ During the following decades, organic chemists were so much involved in this field that the theory of “aromatic character” was broadened to encompass a wider range of molecules. The concept of “aromaticity” was then defined by the Hückel rule on the basis of quantum-mechanical considerations.² According to this rule, an aromatic compound is a fully conjugated, planar monocyclic molecule with $4n + 2\pi$ electrons ($n = 1, 2, 3, \dots$). However, definitions continue to evolve³ and are currently based on experimental and theoretical data while a number of criteria are now accepted to define aromaticity.³ Furthermore, aromaticity is not confined only to planar rings but also exists in three-dimensional systems.^{4–6} “Aromaticity” was often associated

with lower chemical reactivity and higher stability.⁷ For example, the attempt to prepare the two electron oxidation product of benzene, that is, an unsubstituted antiaromatic dication (see below), failed, which provided additional evidence for the stability of benzene toward oxidation (eq 1).^{8,9}



However, a strong ring current throughout the π system does not always guarantee benzene-like reactivity and stability. This

[†] Laboratoire de Chimie de Coordination.

[‡] Laboratoire de Chimie Quantique.

[§] Laboratoire DECMET.

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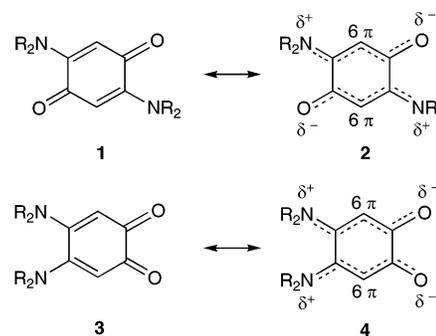
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was observed in the case of substituted benzene compounds. For example, when tetraaminobenzene was prepared by Nietzki, the compound was found to undergo spontaneous oxidation in air at room temperature, yielding the 2,5-diamino-1,4-benzoquinonediimine (eq 2).¹⁰ With 12 π electrons, this molecule is antiaromatic according to Breslow's definition of a planar, conjugated $4n$ π electrons system.¹¹ Since we shall return to the question of antiaromaticity in the course of this and following papers,¹² it is appropriate here to explain what will be understood with this term. The question was again raised recently whether a fundamental difference exists between nonaromatic and antiaromatic cyclic, conjugated $4n$ π electrons systems.¹³ Although he had not considered in his review the six-membered ring systems in this respect, Wiberg concluded that the "smaller $4n$ π species are markedly destabilized if they are planar... When the ring size becomes larger, the antiaromatic character is decreased and is small even for cyclooctatetraene".¹³ Shaik and Hiberty on the other hand reject the classical interpretation of an electronic delocalization initiated by the π electrons and show that the bond length equivalence in a delocalized system is due to the σ backbone.¹⁴

Cyclobutadiene is perhaps the most typical example of antiaromatic molecule, and it is interesting that a closely related, all-metal antiaromatic 4 π system was recently reported with [Al₄]⁴⁺.¹⁵ Its π -HOMO is bonding along the two shorter Al–Al bonds but is antibonding between the two Al₂ pairs, resulting in the rectangular structure and antiaromatic character. This system may therefore be viewed as two 2 π electron systems connected by two σ single bonds. With a $4n$ π electron count of 8, the phenolate anion is however clearly not antiaromatic.¹⁶ Obviously, it is composed of two separate π subsystems, one aromatic (the phenyl ring) and the other nonaromatic (the O⁻ ion). The resulting phenolate retains the aromatic character of the ring. In most cases, however, the π system of exocyclic substituents should be taken into account, since it exerts an influence on the intracyclic delocalization. In most substituted $4n$ π systems, the arrangement of the substituents is compatible with a consistent scheme of bond alternation throughout the system. The molecule then localizes its π electrons and escapes, through a quinoidal structure, the destabilization associated with antiaromatic delocalization. In other, less common cases, a partition scheme of the $4n$ π system not reducible to an alternation of single and double bonds can successfully compete with the canonical quinonoid species. At variance with quinonoids, a single $\pi \rightarrow \pi^*$ excitation in these systems is sufficient to fully restore π delocalization and antiaromaticity. We will term such systems "potentially antiaromatic".

Chart 1

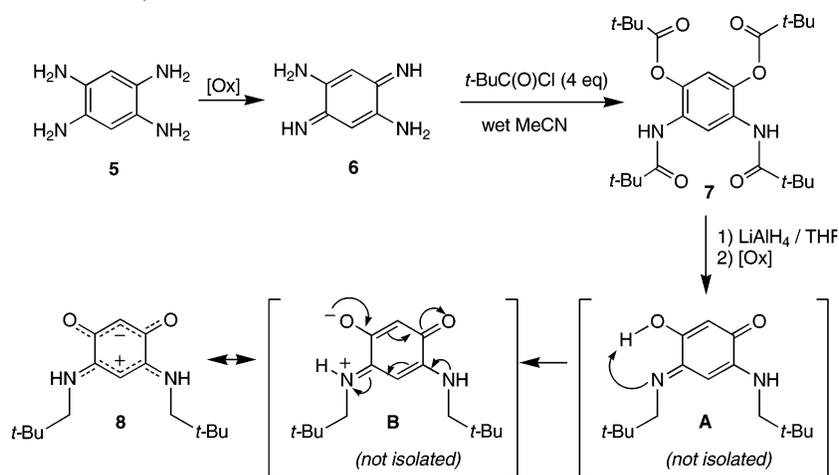
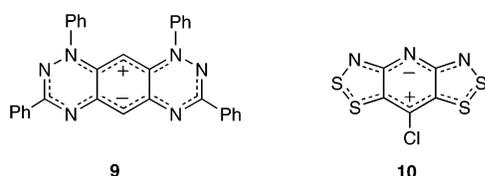


The 2,5-diamino-1,4-benzoquinonediimine shown in eq 2 belongs to the large and important class of quinonoid molecules, defined on a structural basis and displaying specific and remarkable chemical and physical properties.¹⁷ For years, studies on structure/color relationships have typically involved quinones with *N*-substituted amino groups (Chart 1) whose synthesis generally requires substitution at the quinonoid system.¹⁸ Indeed, when a reasonably strong electron donor group is attached to a benzoquinone structure, an intense absorption band in the visible region always appears which can be attributed to an electronic transition involving a transfer of electron density from the donor group to the quinone moiety. For example, aminoquinones such as 2,5-diamino-1,4-benzoquinones **1** represent a color system for which the physicochemical properties can only be fully understood if the molecule is regarded as constituted of a pair of merocyanine structural units coupled via two C–C bonds (see **2**, Chart 1).^{19a} The determination of interatomic distances confirmed the coupling concept by revealing an equalization of bond lengths within the W-like merocyanine subunits with values intermediate between single and double bonds and a stretching of the coupling bonds to the range of C–C σ bonds.^{19b} Similarly, 4,5-diamino-*o*-benzoquinones **3** reveal two coupled merocyanine structural elements involving 6 π electrons as indicated in **4** (Chart 1).²⁰

Quinonemonoimines occupy a central role in many commercial applications, such as color photography²¹ and hair-coloring chemistry.^{22,23} In view of the potential of such molecules as ligands in coordination and organometallic chemistry, we recently developed a versatile access that does not require initial *N*-substitution of the amine before its condensation with benzoquinone.²⁴ This synthesis involved oxidation of tetraaminobenzene **5** into **6** which was then treated with an acyl chloride and water to afford **7** while **5** was acting as a reducing agent (Scheme 1). Reduction of **7** followed by an aerobic workup led to an intermediate **A** which rearranges to **B** by proton migration from the oxygen atom to the more basic

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Scheme 1. Synthesis of Zwitterion **8** Reported in 2002²⁴**Chart 2**

nitrogen site, leading to the first zwitterionic quinonemonoimine **8** constituted by two molecular moieties in which the conjugated π system is fully delocalized (Scheme 1). The situation in **8** represents a novel electronic pattern for N, N, O, O systems since previously known quadrupole merocyanine-type structures **2** and **4** display electronic delocalization exclusively along the N–C–C–O chain of atoms with no occurrence of a zwitterionic structure.

The zwitterion **8** is a planar, 12 π electron system. The theoretical analysis reported below will lead us to envisage this molecule as a potentially antiaromatic system constituted by two 6 π systems facing each other and connected by two C–C σ bonds. It is relevant that recent studies have also reported rare cases of potentially antiaromatic compounds with zwitterionic ground states, such as **9** and **10**, with π electron counts also typical of antiaromaticity ($4n$ with $n = 4$) (Chart 2).^{25,26} In these heterocyclic zwitterions, the charge differentiation also results from the splitting of the π system into two separated subunits.

These conjugated π subsystems are composed of 6 + 10 electrons and linked by two C–C bonds of the central carbon rings and by two single N–N or N–S bonds in the fused heterocycles. The interruption of π delocalization along the fused cycles therefore makes these heterocyclic compounds electronically similar to a single ring with four exocyclic substituents.

Zwitterion **8** appears to be a first choice reagent in organic and coordination chemistry which could give access to new ligands and complexes with a benzoquinonemonoimine-type structure. To our knowledge, no N, N, O, O quinones have so far been used as ligands in the preparation of metal complexes, although they could give access to novel classes of compounds.²⁷

However, the efficiency of the original preparation of **8** was limited by the low yield of the synthesis of **7** owing to the difficult control of the oxidation step, thus limiting the scope of the synthesis of new benzoquinonemonoimines such as **8** and their use as precursors in organic and inorganic chemistry. An improved synthesis was therefore desirable, and this article reports a new and extremely efficient synthesis of **7** and **8**. The high yields obtained with the new procedure have allowed a detailed investigation of the reactivity of **8** and the synthesis of new 12 π electron molecules in which either part of the π system, or all of it, displays an alternation of single and double bonds as a result of electron relocalization. DFT calculations were performed on **8** and on the related zwitterions **9** and **10** in order to examine the influence of the fused cycles on the charge separation and on the singlet–triplet energy gap.^{25,26} We will finally discuss the amount of π delocalization in **8** and related compounds and examine whether these molecules are best described as 12 π electron systems or as constituted of two chemically connected but electronically not conjugated 6 π electron subunits.

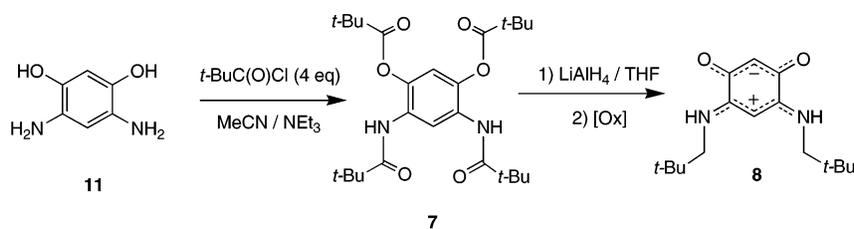
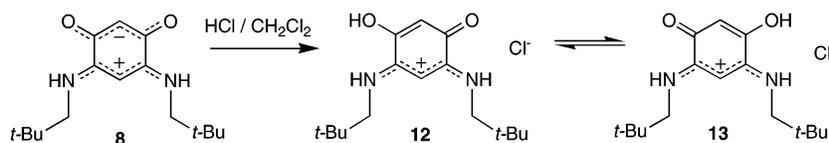
Results and Discussion

Synthesis of Zwitterion 8. We developed a new synthesis of **8** starting from the commercially available diaminoresorcinol **11**·HCl instead of tetraaminobenzene as originally reported.²⁴ Smooth reaction of **11**·HCl with *t*-BuC(O)Cl in CH₃CN and excess NEt₃ afforded **7** in high yield (90%) (Scheme 2), whereas the previously reported synthesis afforded **7** in 25% yield maximum (Scheme 1). Interestingly, ¹H NMR data of compound **7** revealed the presence of two, far apart aromatic signals (6.93 and 8.88 ppm), suggesting that, in solution, one aromatic proton is strongly hydrogen bonded ($\delta = 8.88$ ppm) to the two carbonyl oxygen atoms, while the other is not. Reduction of **7**, followed by an aerobic workup, led to the formation of **8** as a purple solid.²⁴

Reactivity of 8 with Organic Electrophiles. We decided first to use the simplest electrophile and found that protonation of one oxygen atom of **8** occurs easily upon treatment with strong acids such as HCl, affording **12** as a red compound (Scheme 3).

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Scheme 2. New Synthesis of Zwitterion **8**Scheme 3. Reaction of **8** with H⁺

The ¹H and ¹³C NMR data of **12** revealed a higher symmetry of the molecule in solution which is explained by the presence of an intermolecular keto–enolic equilibrium involving two tautomers (**12** and **13**) in solution (Scheme 3).²⁸ Both neopentyl groups become then equivalent on the NMR time scale. Furthermore, a ³J_{HH} coupling of each CH₂ group with one N–H proton was observed, and the N–H proton signal appeared at δ = 8.32 ppm. As expected, both C=C–H protons are downfield shifted with respect to those in **8**. The ¹⁵N NMR spectrum of **12** showed one signal at δ = –261 ppm which is in a range between amine and imine nitrogen atoms²⁹ and therefore consistent with the delocalization of the π system between the two nitrogen atoms, as observed in the case of **8** (δ = –264 ppm). Compound **12**·2CHCl₃ could be isolated as a crystalline solid by slow evaporation of a CHCl₃ solution, and the X-ray analysis confirmed the presence of an OH group. Its structure is shown in Figure 1, and crystallographic data and selected bond lengths are listed in Tables 1 and 2, respectively.

Examination of the bond distances within the O(1)–C(2)–C(1)–C(6)–O(2) moiety revealed an alternation of single and double bonds, whereas the C–C and C–N distances of the N(1)–C(3)–C(4)–C(5)–N(2) moiety show a bond equalization with the positive charge being delocalized between the two nitrogen atoms (Table 2). The C(2)–C(3) and C(6)–C(5) distances of 1.494(4) and 1.527(4) Å, respectively, are consistent

with single bonds and the lack of conjugation between the O–C–C–C–O and N–C–C–C–N moieties. Thus, two conjugated π systems, respectively *without* and *with* delocalization, coexist in **12**·2CHCl₃. In contrast, full delocalization within each of the π subsystems occurred in **8** with delocalization of the positive charge between the nitrogen atoms and of the negative charge between the oxygen atoms (Table 2). Its C–C distances in the range from 1.379(5) to 1.399(5) Å show a remarkable bond equalization. In contrast, the C(2)–C(3) and C(6)–C(5) distances of 1.516(5) and 1.523(5) Å correspond to single bonds and indicate the lack of conjugation between the two “halves” of the ligand (Table 2).²⁴ The Cl(1) atom in **12**·2CHCl₃ is located near the protonated site and interacts with the O(1)–H proton by hydrogen bonding (*d*(O(1)–H···Cl(1)) = 2.192(6) Å).

Formation of a *p*-benzoquinoneminoimine with localized bonding from **12** by removal of the iminium proton did not occur since the O–H group is more acidic than N–H and only compound **8** was recovered upon treatment of **12** with a base such as NEt₃. We then decided to alkylate an oxygen atom of **8** in order to obtain a cationic species susceptible to be deprotonated at the iminium nitrogen. Usual alkylating agents such as methyl iodide did not react with **8**, which is consistent with recent reports on other zwitterions.³⁰ The O-methylation reaction was successful only after treatment with (R₃O)BF₄ reagents (R = Me, Et) in dichloromethane at room temperature which afforded **14** and **15** in high yields (Scheme 4). Compounds **14** and **15** are highly soluble in acetone, dichloromethane, or protic solvents, such as water and alcohols, but insoluble in hydrocarbons.

The ¹H NMR data of **14** revealed coupling of both CH₂ groups with one N–H proton. The ¹⁵N spectrum contains two signals at δ = –245 and –255 ppm consistent with chemically different nuclei, and these chemical shifts are in a range between those of amine and imine nitrogen atoms.²⁹ These values are therefore in agreement with the delocalization of the π system between the two nitrogen atoms, as observed in the case of **8** (δ = –264 ppm). Compound **14**·CH₂Cl₂ could be isolated as a crystalline solid from a solution of dichloromethane/*n*-hexane and analyzed by X-ray crystallography. Its structure is shown

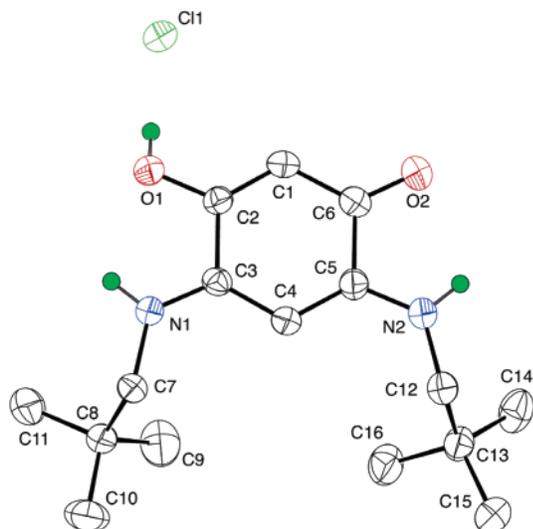


Figure 1. Ortep view of structure of **12** in **12**·2CHCl₃. Thermal ellipsoids are drawn at the 50% level.

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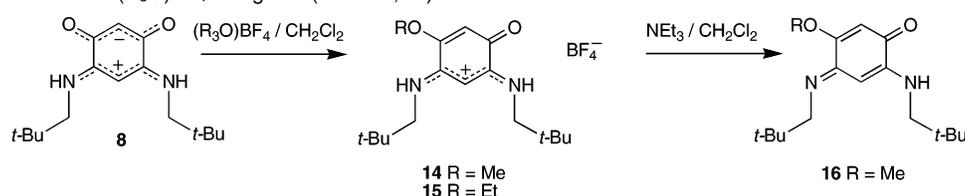
Table 1. Crystal Data and Details of the Structure Determination for Compounds **12**·2CHCl₃, **14**·CH₂Cl₂, and **20**·CH₂Cl₂

crystal data	12 ·2CHCl ₃	14 ·CH ₂ Cl ₂	20 ·CH ₂ Cl ₂
formula	C ₁₆ H ₂₇ N ₂ O ₂ Cl·2CHCl ₃	C ₁₇ H ₂₉ N ₂ O ₂ BF ₄ ·CH ₂ Cl ₂	C ₂₁ H ₃₂ N ₂ O ₄ Pd·CH ₂ Cl ₂
formula weight (g mol ⁻¹)	553.57	465.16	567.81
crystal system	monoclinic	monoclinic	triclinic
space group	<i>P2₁/c</i>	<i>C2/c</i>	<i>P1</i>
<i>a</i> [Å]	12.653(5)	32.358(2)	9.483(5)
<i>b</i> [Å]	11.538(5)	13.502(2)	11.395(5)
<i>c</i> [Å]	18.794(5)	24.127(2)	12.583(5)
α [deg]	90	90	90.876(5)
β [deg]	97.116(5)	116.35(5)	102.760(5)
γ [deg]	90	90	97.566(5)
<i>V</i> [Å ³]	2722.6(18)	9445.8(17)	1313.2(10)
<i>Z</i>	4	16	2
density (calc) [g cm ⁻³]	1.346	1.308	1.436
μ(Mo Kα) [mm ⁻¹]	0.745	0.322	0.938
<i>F</i> (000)	1136	3904	584
crystal size [mm ³]	0.08 × 0.10 × 0.13	0.13 × 0.10 × 0.02	0.15 × 0.12 × 0.10
temperature (K)	173	173	173
radiation [Å]	Mo Kα −0.710 69	Mo Kα −0.710 69	Mo Kα −0.710 69
θ min–max [deg]	2.4, 30.0	2.06, 27.46	2.19, 32.07
data set [<i>h</i> ; <i>k</i> ; <i>l</i>]	−17/17; 0/16; 0/26	−41/37; 0/17; 0/31	−14/14; −16/17; 0/18
tot., uniq. data, <i>R</i> (int)	13853, 7823, 0.045	35013, 10504, 0.036	15068, 9068, 0.040
observed data [<i>I</i> > 2σ(<i>I</i>)]	4243	4649	7686
<i>N</i> reflections, <i>N</i> parameters	7823, 302	10504, 524	9068, 284
<i>R</i> , w <i>R</i> ₂ , GOF	0.0861, 0.2014, 1.128	0.0925, 0.1818, 1.123	0.0365, 0.0929, 1.029
max and avg shift/error	0.01, 0.00	0.01, 0.00	0.00, 0.00
min, max resd. dens. [e/Å ³]	−0.830, 1.125	−0.516, 0.788	−1.017, 0.953

Table 2. Interatomic Distances (Å) Observed in **8**, Its Protonated (**12**), Methylated (**14**), and Palladated (**20**) Derivatives, and Comparison with the Calculated^a Values in Model Compound **8_H** and in the Related Cationic Species **12_H**, **14_H**, and Metalated **20_H**

	8 obsd	8_H calcd	12 ·2CHCl ₃ obsd	12_H calcd	14 ·CH ₂ Cl ₂ obsd	14_H calcd	20 ·CH ₂ Cl ₂ obsd	20_H calcd	A_{Me} calcd
C(1)–C(2)	1.379(5)	1.406	1.337(4)	1.356	1.334(7)	1.361	1.369(2)	1.383	1.364
C(1)–C(6)	1.399(5)	1.406	1.432(5)	1.450	1.427(7)	1.447	1.416(3)	1.425	1.436
C(2)–C(3)	1.516(5)	1.545	1.494(4)	1.490	1.508(7)	1.494	1.500(3)	1.497	1.503
C(3)–C(4)	1.393(5)	1.393	1.405(4)	1.397	1.375(7)	1.397	1.414(2)	1.418	1.431
C(4)–C(5)	1.389(5)	1.393	1.370(4)	1.390	1.382(7)	1.390	1.377(2)	1.378	1.380
C(5)–C(6)	1.523(5)	1.545	1.527(4)	1.538	1.517(7)	1.537	1.525(3)	1.534	1.529
C(2)–O(1)	1.265(4)	1.258	1.330(4)	1.350	1.354(6)	1.341	1.297(2)	1.309	1.334
C(3)–N(1)	1.323(5)	1.325	1.311(4)	1.332	1.328(6)	1.332	1.320(2)	1.321	1.305
C(5)–N(2)	1.320(5)	1.325	1.324(4)	1.322	1.314(6)	1.323	1.333(2)	1.340	1.344
C(6)–O(2)	1.254(4)	1.258	1.224(4)	1.228	1.243(6)	1.230	1.235(2)	1.250	1.245
Pd–O(1)							1.9860(15)	2.055	
Pd–N(1)							1.9952(16)	2.020	

^a Geometries optimized from DFT/BP86 calculations. The subscript H or Me indicates that the neopentyl substituents have been replaced by H or Me, respectively.

Scheme 4. Reaction of **8** with (R₃O)BF₄ Reagents (R = Me, Et)

in Figure 2, and crystallographic data and selected bond lengths are listed in Tables 1 and 2, respectively.

Similarly to **8**, examination of the bond distances within the O(1)–C(2)–C(1)–C(6)–O(2) moiety revealed alternating single and double bonds, whereas the C–C and C–N distances in the N(1)–C(3)–C(4)–C(5)–N(2) moiety show a bond equalization (Table 2). The C(2)–C(3) and C(6)–C(5) distances of 1.508–

(7) and 1.517(7) Å, respectively, correspond again to single bonds and indicate a lack of conjugation between the two “halves” of the ligand. The tetrahedral counterion interacts by hydrogen bonding with the N(1)–H proton; the shortest distance of 2.219(6) Å corresponds to the F(7)⋯H–N(1) interaction. The solid-state structure of **14**·CH₂Cl₂ revealed a complicated network due to the presence of solvent molecules and π–π

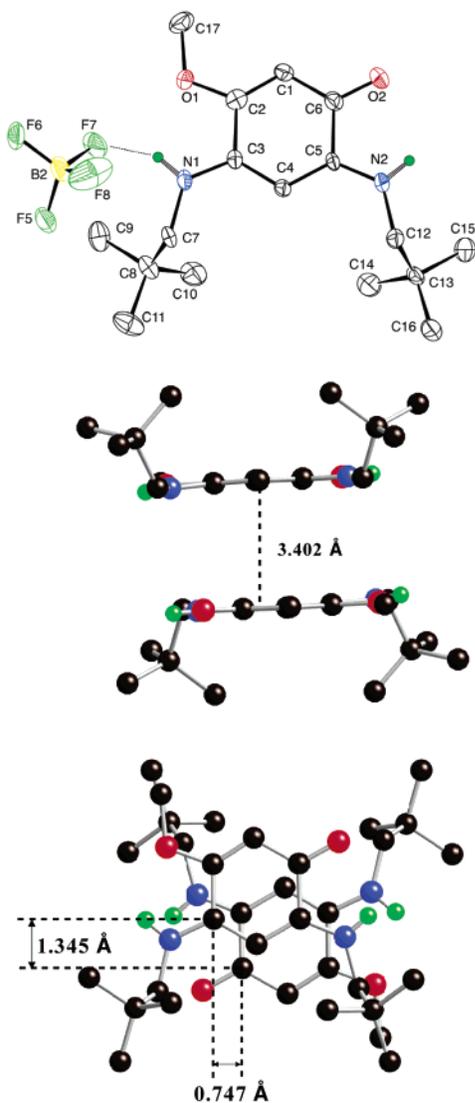


Figure 2. Ortep view (top) of **14** in **14**·CH₂Cl₂ and crystalmaker perspective views (middle and bottom) of the stacking of two cations in the solid state. Thermal ellipsoids are drawn at the 50% level.

interactions between two molecules in a face-to-face arrangement, separated by 3.402 Å (Figure 2).³¹ There is a slippage of 0.747 Å horizontally and 1.345 Å vertically between the centers of two molecules.

Deprotonation of **14** was achieved by treatment with NEt₃ in dichloromethane at room temperature and afforded **16** as a beige compound. Its ¹H NMR data showed two signals at δ = 1.00 and 1.02 ppm corresponding to the methyl protons of the two neopentyl groups. The methoxy protons appeared at δ = 3.82 ppm, and the N–H proton, at δ = 5.41 ppm. Compound **16** is the first member of a new class of *p*-benzoquinonemonoimines.

Reactivity of 8 with Inorganic Electrophiles. Reactions of **8** with inorganic electrophiles were examined in view of the promising features of this ligand in coordination chemistry. Two benzoquinonemonoimines were assembled by reaction of **8** with [Ni(acac)₂], which gave rapidly a green material **17** insoluble in most solvents and poorly soluble in chloroform or dichloromethane (Scheme 5). Compound **17** was fully characterized

(31) Hunter, C. H.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

except by X-ray crystallography since no single crystals suitable for a structure determination were isolated. Formation of a σ bond between the oxygen and the metal center and a dative bond between the nitrogen and the metal center has occurred.

Only one isomer is present in solution, and although the *cis* or *trans* configuration of the isomer could not be determined from the NMR data, the *cis* geometry is likely to be disfavored due to the proximity of the bulky neopentyl groups. Other square planar nickel complexes with N, O ligands were found to adopt the *trans* geometry (centrosymmetric).^{32,33} The ¹H NMR data revealed the presence of two far apart neopentyl CH₃ signals (δ = 1.02 and 1.19 ppm), suggesting that one CH₃ group is closer to the nickel center. Only one N–H signal is observed at δ = 6.45 ppm which is consistent with an aminic proton. Following a similar procedure, we also prepared the zinc and copper analogues **18** and **19** by reaction of **8** with [Zn(acac)₂] and [Cu(acac)₂], respectively. Compound **18** appeared to be unstable in solution unlike its Ni and Cu analogues.

Interestingly, reaction of **8** with palladium bis(acetylacetonate) gave in a stepwise manner the mononuclear complexes **20** and **21** (Scheme 6). The intermediate **20** could be isolated after separation by preparative chromatography, whereas **21**, which precipitated, was recovered by filtration.

The ¹H NMR data of **20** revealed the presence of only one N–H proton. Compound **20**·CH₂Cl₂ could be isolated as a crystalline solid from a solution of dichloromethane/*n*-hexane and analyzed by X-ray crystallography. The structure is shown in Figure 3, and crystallographic data and selected bond lengths are listed in Tables 1 and 2, respectively.

The coordination geometry around the palladium center is square planar. Examination of the bond distances within the O(1)–C(2)–C(1)–C(6)–O(2) and N(1)–C(3)–C(4)–C(5)–N(2) moieties reveals an alternation of single and double bonds, which is consistent with two conjugated but localized π systems (Table 2). The relative lengthening of the N(1)–C(3) bond is due to N-coordination to the metal. The C(2)–C(3) and C(6)–C(5) distances of 1.500(3) and 1.525(3) Å, respectively, correspond again to single bonds and indicate the lack of conjugation between the two π systems. Interestingly, the packing in the solid state is such that two molecules form a centrosymmetric pseudo-dimer with an intermetallic distance of 3.536 Å.

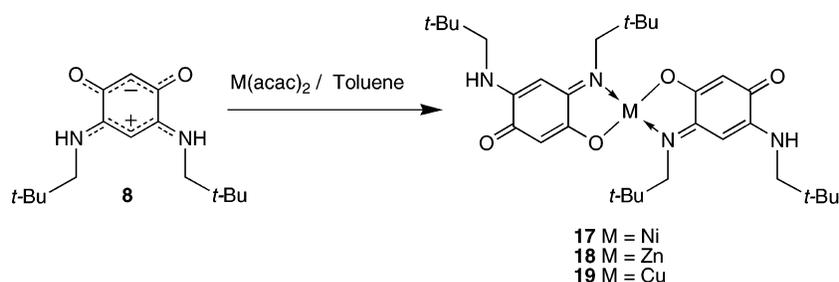
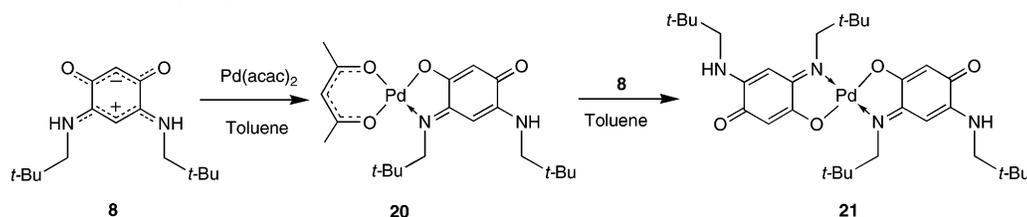
We have found that, depending on the electrophile used, it is possible to control the delocalization of the π system. When the electrophile simply adds to the zwitterion as in **12**, **14**, or **15**, there is no more negative charge to be delocalized and only the positive charge remains delocalized between the nitrogen atoms. Furthermore, when reaction with the electrophilic reagent results in deprotonation, as in **17**–**21**, there remains no charge in the system to be delocalized.

Electronic Spectra

The electronic spectral data are reported in Table 3. The UV–vis absorption spectrum of **8** is characterized by two strong bands at 350 nm (log ϵ = 4.49) and 343 nm (log ϵ = 4.45).²⁴ Sawicka et al. have recently described the first theoretical

(32) Richeter, S.; Jeandon, C.; Ruppert, R.; Callot, H. J. *Chem. Commun.* **2001**, 91.

(33) (a) Richeter, S.; Jeandon, C.; Ruppert, R.; Callot, H. J. *Chem. Commun.* **2002**, 266. (b) Richeter, S.; Jeandon, C.; Gisselbrecht, J.-P.; Ruppert, R.; Callot, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 6168.

Scheme 5. Reaction of **8** with M^{2+} **Scheme 6.** Reaction of **8** with $\text{Pd}(\text{acac})_2$ 

analysis of **8**, and they reported that the first band corresponds to the $\pi \rightarrow \pi^*$ absorption of **8** and the second one could be assigned to a vibrational excitation on top of the electronic transition.^{34a,35} Similarly to the UV–vis absorption spectrum of **8**, that of **12** is characterized by two strong absorptions at 337 and 349 nm which correspond to intraquinone charge transfer. In addition, a weak absorption at 506 ($\log \epsilon = 3.65$) is observed for **12**. In contrast, **14** is characterized by only one strong absorption at 327 nm ($\log \epsilon = 4.26$) for the intraquinone charge transfer, and by the presence of one more band at 503 nm ($\log \epsilon = 3.65$). Similarly, **15** revealed two absorption bands at 328 nm ($\log \epsilon = 4.28$) and 504 nm ($\log \epsilon = 3.73$). Interestingly, the deprotonation of **14** to **16** led to a significant blue shift of the highest energy band ($\Delta\lambda = 18$ nm) and of the lowest energy absorption band ($\Delta\lambda = 48$ nm). The main

Table 3. Electronic Spectra λ (nm) in CH_2Cl_2

	λ (log ϵ)
8	343 (4.45), 350 (4.49)
12	337 (4.35), 349 (4.34), 506 (3.15)
14	327 (4.26), 503 (3.65)
15	328 (4.28), 504 (3.73)
16	311 (4.13), 455 (3.41)
17	333 (sh) (4.45), 485 (4.22), 521 (4.11)
18^a	338 (4.54), 352 (4.56)
19	292 (4.35), 361 (4.70), 376 (4.80)
20	379 (4.25), 395 (4.27), 412 (4.24), 530 (3.24)
21	296 (4.33), 419 (4.62), 444 (4.71)

^a In CHCl_3 .

absorptions can be attributed to the $\pi \rightarrow \pi^*$ transition of the benzoquinone derivatives. The weak absorption band corresponds to an $n \rightarrow \pi^*$ transition originating at the nitrogen lone pair.³⁶

Coordination of a metal center to **8** leads to new absorption bands corresponding to a metal-to-ligand charge transfer (MLCT) for which the extinction coefficients are the most intense. The UV–vis absorption spectrum of **17** shows three bands at 333 ($\log \epsilon = 4.45$), 485 ($\log \epsilon = 4.22$), and 521 nm ($\log \epsilon = 4.11$). Similarly, **21** revealed absorption bands at 296 nm ($\log \epsilon = 4.33$), 419 nm ($\log \epsilon = 4.62$), and 444 nm ($\log \epsilon = 4.71$). By comparison, the UV–vis absorption spectrum of **20** is characterized by three strong absorptions at 379 nm ($\log \epsilon = 4.25$), 395 nm ($\log \epsilon = 4.27$), and 412 nm ($\log \epsilon = 4.24$). We shall come back to these aspects in the theoretical analysis.

Theoretical Calculations

The first theoretical analysis of **8** has been recently published.³⁴ These authors carried out geometry optimizations at the restricted Hartree–Fock level and energy calculations at the MP2 level on the zwitterionic form of **8** and on various tautomers displaying a “canonical” quinonoid structure. This study was mainly focused on the $\text{N}-\text{H}\cdots\text{O}\rightarrow\text{N}\cdots\text{H}-\text{O}$ proton-

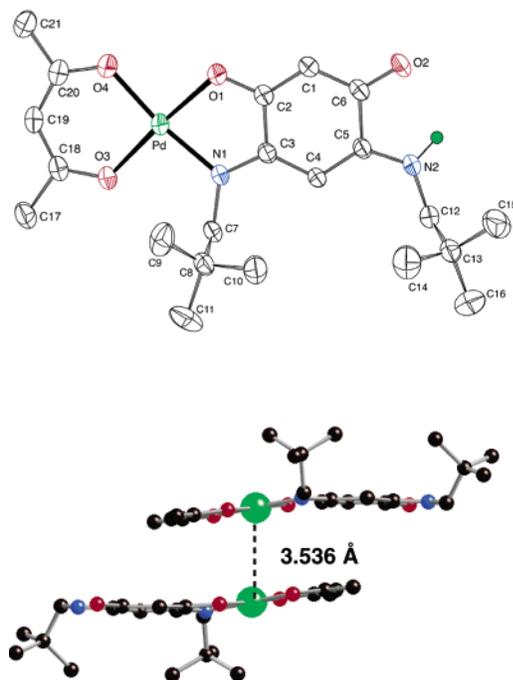


Figure 3. Ortep view (top) of **20** in $20\cdot\text{CH}_2\text{Cl}_2$ (thermal ellipsoids are drawn at the 50% level) and crystalmaker perspective view (bottom) of the staking of two molecules in the solid state.

(34) (a) Sawicka, A.; Skurski, P.; Simons, J. *Chem. Phys. Lett.* **2002**, *362*, 527. (b) Note added in proof: another theoretical analysis of **8** has been performed by Le, H. T.; Nam, P. C.; Dao, V. L.; Veszprémi, T.; Nguyen, M. T. *Mol. Phys.* **2003**, in press.

(35) We thank a referee for his comments.

(36) Zhang, R.; Zheng, H.; Shen, J. *J. Mol. Struct.* **1998**, *446*, 103.

transfer process and showed the zwitterionic form to be more stable than the lowest canonical form (form **A**, see Scheme 1) by 1.42 kcal mol⁻¹, but the kinetic barrier to the proton transfer was estimated to 13.2 kcal mol⁻¹.^{34a} The attachment of an excess electron to the various tautomers was also studied in detail.^{34a} The results we obtain from DFT calculations corroborate this result, since the energy difference between models of **8** and **A**, in which neopentyl substituents have been replaced by methyls, is calculated to be 3.0 kcal mol⁻¹ in favor of the zwitterion. However, in the present theoretical section, we rather concentrate on an analysis of the zwitterionic form of **8**, on the origin of its stability, and on the comparison between **8** and two series of heterocyclic molecules displaying similar properties.

Indeed, several heterocyclic molecules, belonging to the family of polyazaacenes **9** and dithiazoles **10** have been recently characterized, by means of experiment and theory, to have a zwitterionic ground state.^{25,26,37} As for the present benzoquinonemonoimine **8**, the charge differentiation results from the splitting of a potentially antiaromatic π system into two separate subunits (Chart 2). These conjugated π subsystems are composed of 6 + 10 electrons, in heterocyclic zwitterions, compared to 6 + 6 electrons in **8**. Another difference comes from the linking between the π subsystems. In **8**, this link is ensured solely by the carbon-carbon bonds C(2)-C(3) and C(5)-C(6), which display an exclusive σ character in accordance with the observed and calculated bond lengths (Table 2). In **9**, **10**, and related systems, the two C-C bonds of the central carbon rings are supplemented as separators by two single bonds involving heteroatoms of the adjacent cycles. The observed distances, as in the analysis of the DFT calculations, suggest that these four bonds retain a minor π bonding component.^{25,26,37} This implies that the separation between the two π subsystems should be more complete in **8**. We report here some results obtained from DFT/BP86 and DFT/B3LYP calculations. These calculations have been carried out with ADF³⁸ and with Gaussian 98,³⁹ respectively, on **9**, **10**, and on two models of **8** in which the neopentyl substituents have been replaced by H (**8_H**) or CH₃ (**8_{Me}**). DFT/BP86 calculations have also been carried out on a similar model of the Pd complex **20** (**20_H**). Some computed properties directly related to the zwitterionic ground states of these compounds are listed in Table 4.

An important feature, common to **8**, **9**, and **10**, is the π nature of both the HOMO and the LUMO. In all three compounds, the LUMO is delocalized over the whole molecular π system. This orbital has a large weight, with π bonding character, on the lateral C-C bonds of the C₆ or C₅N ring.³⁷ This weight is maximal in **8** (55%), in relation with the smaller extension of the overall π system. Despite this C-C bonding character, the

Table 4. Properties of Hexaazaanthracene **9**, Chloro-bis-1,2,3-dithiazole **10**, Models of **8** (**8_H** and **8_{Me}** and **8_{Et}**; **A_{Me}**, **A_{Et}**, and **A** (Scheme 1)), and Pd Complex **20_H** Calculated at the DFT/BP86 and (except for **A_{Me}** and **20_H**) DFT/B3LYP Levels^a

	BP86						B3LYP					
	<i>q</i>	S-T	μ_S	μ_T	C-C _S	C-C _T	<i>q</i>	S-T	μ_S	μ_T	C-C _S	C-C _T
8_H	±0.42	25.7	7.9	6.1	1.545	1.464	±0.47	23.3	8.0	5.1	1.547	1.461
8_{Me}	±0.46	28.1	8.8	6.7	1.541	1.463	±0.49	25.7	8.6	5.6	1.545	1.462
9	±0.41	23.7	5.0	4.8	1.457	1.423	±0.35	18.9	5.0	4.6	1.461	1.421
10	-0.08	9.7	4.7	3.4	1.470	1.449	-0.61	2.4	4.4	2.8	1.478	1.446
	+0.25 ^b						+0.55 ^b					
A_{Me}	±0.03			5.1	1.503						1.529	
20_H	-0.44			5.8	1.497						1.534	
	-0.11				1.534							

	ab initio MP2 ^{34a}		
	ΔE	μ_S	
8	0	10.0	
8_{Et}	0	10.1	
A	+1.4	4.8	
A_{Et}	+1.0	5.1	

^a The dipole moments of **8_{Et}**, **8**, **A_{Et}**, and **A** in the lowest singlet state (Debye) refer to the SCF calculations of Sawicka et al.^{34a} ΔE (kcal mol⁻¹) represents the relative energies of the corresponding tautomers, **8** and **A** and **8_{Et}** and **A_{Et}**.^{34a} For the other molecules (this work; DFT/BP86 and DFT/B3LYP levels of calculation) are reported the Mulliken charge *q* of the two subsystems in the singlet state (electrons); the dipole moment of the singlet (μ_S) and of the triplet state (μ_T) (Debye); the singlet-triplet energy separation (S-T, kcal.mol⁻¹); and the length of the carbon-carbon bond separating the two π subsystems (C-C_S, singlet ground state; C-C_T, triplet state; Å). $\Delta E(\mathbf{A}_{Me}) = +3.0$ kcal mol⁻¹ with the BP86 functional. ^b The charge of the Cl atom has not been taken into account.

LUMO of **8**, **9**, and **10** is destabilized because of antibonding π interactions with the neighboring heteroatoms, which illustrates the potential antiaromatic character of these molecules. The lowest triplet state always results from an HOMO-LUMO transfer. Populating the LUMO with one electron breaks the separation between the π subsystems and provides the lateral C-C bonds some π bonding character and a shorter bond length (Table 2). The contraction of the lateral C-C bonds in the triplet state is especially important in **8** due to the prominent weight of the C-C π bonding contribution in the LUMO. The high energy of the C-C bonding, C-X antibonding LUMO is directly related to the relative stability of the zwitterionic ground state. It should be emphasized that these systems in the lowest triplet state display semioccupied orbitals with a π delocalized character, illustrated in the spin density distributions (see Supporting Information) rather than behaving like a standard biradical with a localized arrangement of the unpaired electrons.

The properties calculated for **9** and **10** at the B3LYP/6-31G** level closely reproduce the result of previous theoretical investigations.^{25,26,37} Even though the BP86 functional seems to slightly overestimate the S-T energy gap, both series of calculations suggest that the zwitterionic ground state calculated for the models of **8** are most stable in the series, closely followed by **9**. The Mulliken charge separation between the two molecular subsystems appears somewhat dependent upon the chosen basis set, especially for **10**. The zwitterionic character of the considered molecules is more reliably illustrated by the dipole moment, which is also maximal for **8_H** and especially for **8_{Me}**.

Most zwitterionic molecules are in close energetic competition with an isomer not displaying a strong charge separation, which is usually a biradical. Such a low energy biradical, with a localized arrangement of the unpaired electrons, does not exist

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for **8** and **9**. For **10**, the lowest triplet is close in energy to the ground state but displays as for **8** and **9** a π delocalized character, illustrated in the spin density distributions (Supporting Information). The high energy of the lowest triplet state computed for **8** and **9**, and, to a much lesser extent, for **10**, should be related to the fact that populating the LUMO with one electron restores the communication between the two π subsystems and therefore brings back into the molecule the antiaromatic character that was kept away in the zwitterionic form. As investigated by Sawicka et al.,^{34a} a possibility to cancel the charge separation between the molecular moieties without introducing antiaromaticity would consist in transferring a proton from an amino group to the closest quinonic oxygen. This transfer generates a molecule that is assumed to be an undetected intermediate in the synthesis of **8** (intermediate **A**, Scheme 1). DFT/BP86 calculations on intermediate **A**_{Me}, in which the CH₂-*t*-Bu substituents are modeled by CH₃, show that this quinonoid form is destabilized by 3.0 kcal mol⁻¹. This is to be compared with the relative energies of +1.42 and +1.03 kcal mol⁻¹ computed by Sawicka et al. at the ab initio MP2 level for **A** and **A**_{Et}, respectively^{34a} (Table 4). The present calculations point out an important decrease of the dipole moment when going from the zwitterionic form **8**_{Me} (8.8 D) to the quinonic tautomer (5.1 D). The charge separation (± 0.03 e) is close to zero, compared to ± 0.46 e in the zwitterionic form (Table 4). These values are in keeping with the results of Sawicka et al., showing a decrease of the dipole moment from 10.0 D in **8** to 4.8 D in **A** and from 10.1 D in **8**_{Et} to 5.1 D in **A**_{Et}.^{34a} The experimental dipole moment was measured at 9.7 D in dichloromethane at 21 °C, which is consistent with calculated values.

In the optimized geometry of **A**_{Me} (Table 4), both lateral C–C bonds C(2)–C(3) and C(5)–C(6) remain longer than 1.5 Å, at variance with the same bond lengths in the lowest triplet state of **8**_H and **8**_{Me}. The two π subsystems therefore remain largely separated in **A**, but a marked alternation of the bond lengths is initiated in both molecular moieties (Table 2), in agreement with the quinonoid representation of the structure displayed in Scheme 1. A bond alternation, restricted to the RO–C=CH–C=O moiety, was observed in cations **12** and **14** and computed in their models **12**_H and **14**_H. However, this alternation did not affect the diamino system, which remained fully delocalized. Interestingly, a similar, but somewhat weaker bond alternation affecting the whole molecule is observed in the Pd complex **20** and computed in the model **20**_H.

In complex **20**, the Pd^{II} center is coordinated to the deprotonated form of **8**. Despite the nitrogen deprotonation, which cancels the zwitterionic character of the quinoneimine ligand, the two π subsystems remain largely separated, as in **8**. The O–C–CH–C–O moiety retains the same negative charge as in the isolated molecule (–0.44 e). Despite this charge conservation, some bond alternation is observed in this part of the molecule as in the amino-imino moiety. The geometry changes induced by bond alternation are however less important than for the hypothetical intermediate **A**, except for the C(2)–C(3) bond whose length is reduced to 1.500(3) Å. This shortening should be assigned to a slight back-bonding interaction from the occupied orbital of Pd with appropriate symmetry to the LUMO of the ligand which introduces some π bonding character into the C(2)–C(3) bond and reduces the bond length by ~ 0.04 Å with respect to C(5)–C(6). This difference is also

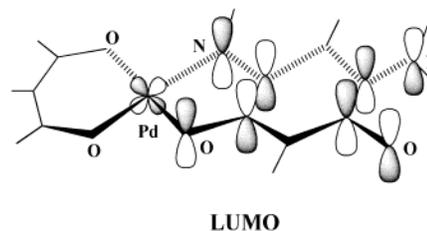


Figure 4. LUMO of **20**.

significant in the X-ray structure (Table 2). The LUMO of complex **20**_H which represents the counterpart to this interaction is displayed in Figure 4.

Protonation or methylation at one oxygen atom of **8** has quite similar effects on the π electronic structure and subsequently on the molecular geometry (Table 2). The π connection between the alkoxide (or methoxy) substituent and the delocalized subsystem next to it is strongly decreased. Therefore, the remaining π subsystem tends to localize, giving rise to a strong bond alternation quite reminiscent of the acrolein structure (Table 2). The net charge of this molecular moiety becomes slightly positive (+0.28 e for the protonated species, +0.30 e for the methylated one). With an unmodified 6 π electron system, the other molecular moiety remains fully delocalized, with an increased positive charge (+0.72 e) and interatomic distances practically unchanged with respect to those calculated in **8**_H. The two π subsystems, localized and delocalized, remain largely disconnected, even though the long C–C distance next to the protonated or methylated oxygen decreases by ~ 0.05 Å to 1.49 Å (Table 2).

Conclusion

We have found that the unusual zwitterionic benzoquinoneiminoamine **8** is a rare example of a zwitterion being more stable than its canonical forms and is best described as constituted of two chemically connected but electronically not conjugated 6 π electron subunits. Its new and straightforward synthesis has allowed a study of its reactivity with electrophiles such as H⁺, CH₃⁺, and metal salts leading to the synthesis of new 12 π electron molecules in which one or both 6 π subsystems localize into an alternation of single and double bonds. We have found that the acidity of the N–H protons of **8** can be modulated by an external reagent and that, depending on the electrophile used, it is possible to control the delocalization of the π system. When the electrophile simply adds to the zwitterion as in **12**, **14**, or **15**, there is no more negative charge to be delocalized and only the positive charge remains delocalized between the nitrogen atoms. Furthermore, when reaction with the electrophilic reagent results in deprotonation, as in **17**–**21**, there remains no charge in the system to be delocalized. DFT calculations were performed on **8** and on the related zwitterions **9** and **10** in order to examine the influence of the fused cycles on the charge separation and on the singlet–triplet energy gap.^{25,26} An effect of the nitrogen substituents in **8** is to significantly stabilize the singlet state. The dipole moment of **8** was measured to be 9.7 D in dichloromethane, in agreement with calculated values. The new ligands and complexes described in this article constitute new classes of compounds relevant to many research areas such as organometallic chemistry, homogeneous catalysis, and color chemistry. The following paper will report new antiaromatic quinonediimines whose

colors and degree of delocalization of their 6 π electron subsystems can be tuned by protonation.¹² In general, quinone-type ligands are also of considerable interest in inorganic chemistry owing to their often unique redox and electron-transfer properties.^{40,41}

Experimental Section

General. ¹H NMR (300 or 400 MHz), ¹³C NMR (75 MHz), and ¹⁵N NMR (40.562 MHz) spectra were recorded on a Bruker AC-300, DPX-400, or ARX-500 instrument. FAB mass spectral analyses were recorded on an autospec HF mass spectrometer, and EI mass spectral analyses were recorded on a Finnigan TSQ 700. Elemental analyses were performed by the "Service de Microanalyse, Université Louis Pasteur (Strasbourg, France)". Preparative chromatography was performed using silica gel with an average particle size of 40 μ m. Solvents were freshly distilled under nitrogen prior to use. 4,6-Diaminoresorcinol was purchased from Across, and trialkyloxonium tetrafluoroborate, from Avocado. All reactions of air- or water-sensitive compounds were performed using standard Schlenk techniques under dry argon atmosphere.

Synthesis of the Zwitterion 8. To a suspension of 4,6-diaminoresorcinol **11** (1.00 g, 4.70 mmol) was added an excess of triethylamine (4 mL) in acetonitrile (150 mL). After the mixture was stirred for 5 min at room temperature, 4 equiv of trimethylacetyl chloride (2.34 mL, 18.80 mmol) were added dropwise to the resulting solution. After the mixture was further stirred at room temperature for 12 h, the solvent was evaporated, the residue was taken up in water, and the insoluble product in suspension was filtered, washed with water, and dried to afford the diamidodiester **7** as a light brown powder (2.08 g, 92%). This latter was reduced as previously described.²⁴ **8** was obtained as a purple solid after crystallization from a mixture of dichloromethane and hexane (0.84 g, 70% yield).

Synthesis of 12. The zwitterion **8** (0.20 g, 0.72 mmol) was dissolved in a mixture of anhydrous CH₂Cl₂-toluene (20 mL/80 mL), and diluted aqueous HCl (ca. 0.5 mL concentrated HCl in 10 mL of toluene) was added dropwise to the solution which resulted in an instantaneous color change to intense violet at room temperature with precipitation of a violet solid. After the solid was filtered and washed with toluene, **12** was obtained quantitatively as a violet powder. ¹H NMR (300 MHz, CDCl₃) δ : 1.05 (s, 18 H, CH₃), 3.27 (d, ³J_{HH} = 6.6 Hz, 4 H, CH₂), 5.41 (s, 1 H, N=C=C-H), 6.26 (s br, 1 H, O=C=C-H), 8.32 (s br, 2 H, N-H). ¹³C NMR (50 MHz, CDCl₃) δ : 27.50 (CMe₃), 33.03 (CMe₃), 55.13 (CH₂N), 82.84 (H-C=C), 102.97 (H-C=C), 155.01 (C=N), 170.02 (C=O). Anal Calcd. for C₁₆H₂₇ClN₂O₂·0.5HCl: C, 57.78; H, 8.18; N, 8.42. Found: C, 58.06; H, 8.38; N, 8.25.

Synthesis of 14 and 15. General Procedure. The zwitterion **8** (0.84 g, 3.01 mmol) was dissolved in anhydrous CH₂Cl₂ (100 mL), and solid trialkyloxonium tetrafluoroborate (0.45 g, 3.01 mmol) was added to the solution. After the solution was stirred at room temperature for 3 h, the solvent was evaporated and the alkylated product was obtained as a red powder by precipitation from a mixture of dichloromethane and hexane.

14: 1.03 g, 90% yield. MS (FAB, 70 eV) m/z : 293 [$M + 1$]⁺. ¹H NMR (300 MHz, CDCl₃) δ : 1.06 (s, 9 H, CH₃), 1.07 (s, 9 H, CH₃), 3.27 (d, ³J_{HH} = 6.7 Hz, 2 H, CH₂), 3.53 (d, ³J_{HH} = 7.1 Hz, 2 H, CH₂), 4.07 (s, 3 H, OCH₃), 5.81 (s, 1 H, N=C=C-H), 5.89 (s, 1 H, O=C=C-H), 7.41 (s br, 1 H, N-H), 8.99 (s br, 1 H, N-H). ¹³C NMR (50 MHz, CDCl₃) δ : 27.28 (CMe₃), 27.44 (CMe₃), 32.80 (CMe₃), 34.15 (CMe₃), 54.87 (CH₂N), 55.81 (CH₂N), 58.35 (OCH₃), 85.12 (H-C=C), 102.66 (H-C=C), 149.86 (C=N), 156.17 (C=N), 160.77 (C-O), 178.61 (C=O). Anal Calcd. for C₁₇H₂₉BF₄N₂O₂: C, 53.70; H, 7.69; N, 7.37. Found: C, 53.41; H, 7.65; N, 7.35.

15: 1.07 g, 90% yield. MS (FAB, 70 eV) m/z : 307 [$M + 1$]⁺. ¹H NMR (300 MHz, CDCl₃) δ : 1.06 (s, 9 H, CH₃), 1.07 (s, 9 H, CH₃), 1.65 (t, ³J_{HH} = 7.02 Hz, 3 H, CH₃), 3.28 (d, ³J_{HH} = 6.66 Hz, 2 H, CH₂), 3.57 (d, ³J_{HH} = 7.05 Hz, 2 H, CH₂), 4.27 (q, ³J_{HH} = 7.02 Hz, 2 H, OCH₃), 5.85 (s, 1 H, N=C=C-H), 5.88 (s, 1 H, O=C=C-H), 7.60 (s br, 1 H, N-H), 8.90 (s br, 1 H, N-H). ¹³C NMR (50 MHz, CDCl₃) δ : 13.49 (CH₃-CH₂), 27.28 (CMe₃), 27.44 (CMe₃), 32.67 (CMe₃), 34.14 (CMe₃), 54.89 (CH₂N), 55.7 (CH₂N), 68.2 (OCH₃), 85.24 (H-C=C), 102.91 (H-C=C), 149.64 (C=N), 156.17 (C=N), 159.84 (C-O), 178.71 (C=O). Anal Calcd. for C₁₈H₃₁BF₄N₂O₂: C, 54.82; H, 7.93; N, 7.11. Found: C, 54.02; H, 7.72; N, 7.00.

Synthesis of 16. The methylated zwitterion **14** (0.20 g, 0.526 mmol) was dissolved in anhydrous dichloromethane (50 mL), and an excess of dry NEt₃ was added to the solution at room temperature resulting rapidly in a color change from red to yellow. After addition of water, the aqueous phase was extracted with dichloromethane. The organic phase was dried on magnesium sulfate and evaporated. The residue was dissolved in pentane, and the solution was filtered and evaporated to afford **16** as a yellow-brown powder (0.06 g, 40% yield). MS (EI, 70 eV) m/z : 292 [M^+]. ¹H NMR (300 MHz, CDCl₃) δ : 1.00 (s, 9 H, CH₃), 1.02 (s, 9 H, CH₃), 2.81 (d, ³J_{HH} = 6.7 Hz, 2 H, CH₂), 3.46 (s, 2 H, CH₂), 3.82 (s, 3 H, OCH₃), 5.41 (s br, 1 H, N-H), 5.52 (s, 1 H, N=C=C-H), 5.77 (s, 1 H, O=C=C-H). ¹³C NMR (50 MHz, CDCl₃) δ : 27.80 (CMe₃), 28.63 (CMe₃), 32.10 (CMe₃), 33.40 (CMe₃), 54.13 (CH₂N), 56.44 (CH₂N), 64.15 (OCH₃), 86.85 (H-C=C), 102.36 (H-C=C), 142.60 (C-N), 154.56 (C-O), 165.45 (C=N), 183.92 (C=O). No satisfactory elemental analysis was obtained despite several attempts owing to the moisture sensitivity of the product.

Synthesis of 17, 18, and 19. General procedure: The zwitterion **8** (0.50 g, 1.80 mmol) was dissolved in anhydrous toluene (100 mL), and 0.5 equiv of [M(acac)₂] (M = Ni, Zn, Cu) (0.9 mmol) was added to the solution. The mixture was then refluxed for 12 h. At room temperature, a crystalline green (Ni) and red (Zn) powder was filtered and washed with cold toluene to afford **17** and **18**, respectively. When M = Cu, the purple solid which precipitated at room temperature was first isolated by filtration and redissolved in anhydrous dichloromethane. The solution was filtered through Celite and evaporated to dryness to afford **19** as a purple solid.

17: 0.45 g, 81% yield. MS (FAB, 70 eV) m/z : 613 [$M + 1$]⁺. ¹H NMR (400 MHz, CDCl₃) δ : 1.02 (s, 18 H, CH₃), 1.19 (s, 18 H, CH₃), 2.73 (s, 4 H, CH₂), 2.88 (d, ³J_{HH} = 6.3 Hz, 4 H, CH₂), 5.20 (s, 2 H, N=C=C-H), 5.31 (s, 2 H, O=C=C-H), 6.45 (t br, 2 H, N-H); ¹³C NMR (50 MHz, CDCl₃) δ : 27.58 (CMe₃), 27.89 (CMe₃), 32.31 (CMe₃), 35.85 (CMe₃), 54.17 (CH₂N), 57.181 (CH₂N), 85.01 (H-C=C), 102.108 (H-C=C), 146.88 (C-N), 168.58 (C-O), 179.88 (C=N), 180.31 (C=O). Anal Calcd. for C₃₂H₅₀N₄NiO₄: C, 62.65; H, 8.22; N, 9.13. Found: C, 62.16; H, 8.22; N, 8.93.

18: 0.45 g, 80% yield. MS (FAB, 70 eV) m/z : 620 [$M + 1$]⁺. ¹H NMR (400 MHz, CDCl₃) δ : 0.965 (s, 18 H, CH₃), 1.02 (s, 18 H, CH₃), 2.94 (s, 4 H, CH₂), 3.32 (d, ³J_{HH} = 6.0 Hz, 4 H, CH₂), 5.30 (s, 2 H, N=C=C-H), 5.69 (s, 2 H, O=C=C-H), 6.80 (br t, 2 H, N-H); ¹³C NMR (50 MHz, CDCl₃) δ : 27.65 (CMe₃), 28.33 (CMe₃), 32.38 (CMe₃), 34.19 (CMe₃), 54.18 (CH₂N), 61.34 (CH₂N), 83.85 (H-C=C), 102.14 (H-C=C), 149.29 (C=N), 164.26 (C-N), 173.23 (C-O), 179.69 (C=O). Anal Calcd. for C₃₂H₅₀N₄O₄Zn: C, 61.98; H, 8.13; N, 9.03. Found: C, 61.67; H, 8.65; N, 8.81.

19: 0.57 g, 91% yield. MS (FAB, 70 eV) m/z : 618 [$M + 1$]⁺. Anal Calcd. for C₃₂H₅₀CuN₄O₄·CH₂Cl₂: C, 56.36; H, 7.45; N, 7.97. Found: C, 55.87; H, 7.45; N, 7.76.

Synthesis of 20 and 21. The zwitterion **8** (0.50 g, 1.80 mmol) was dissolved in anhydrous toluene (100 mL), and 1.5 equiv of [Pd(acac)₂] (0.82 g, 2.70 mmol) were added to the solution. The mixture was then refluxed for 12 h. At room temperature, a crystalline brown powder was formed, isolated by filtration, and washed with cold toluene. The filtrate **A** was kept. The solid was redissolved in dichloromethane. The solution was filtered through Celite and was evaporated to afford **21**

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as a brown powder (0.07 g, 11.7% yield). The filtrate **A** was taken to dryness. The brown residue was dissolved in dichloromethane and purified by preparative chromatography on silica gel (eluant: CH₂Cl₂/MeOH 99/1) to afford **20** as a red crystalline solid (0.36 g, 27% yield).

20: ¹H NMR (300 MHz, CDCl₃) δ: 0.97 (s, 9 H, CH₃), 1.07 (s, 9 H, CH₃), 2.00 (s, 3 H, CH₃), 2.03 (s, 3 H, CH₃), 2.85 (d, ³J_{HH} = 6.3 Hz, 2 H, CH₂), 3.06 (s, 2 H, CH₂), 5.27 (s, 1 H, N=C=C-H), 5.39 (s, 1 H, C-H_{acac}), 5.59 (s, 1 H, O=C=C-H), 6.55 (br t, 1 H, N-H). ¹³C NMR (50 MHz, CDCl₃) δ: 25.45 (CH_{3acac}), 25.69 (CH_{3acac}), 27.49 (CMe₃), 29.00 (CMe₃), 32.16 (CMe₃), 35.73 (CMe₃), 54.04 (CH₂N), 57.36 (CH₂N), 84.79 (H-C=C), 101.37 (H-C≡C_{acac}), 103.80 (H-C=C), 146.55 (C-N), 171.57 (C-O), 179.72 (C=N), 183.50 (C=O), 185.50 (C≡C_{acac}), 189.14 (C≡C_{acac}). Anal Calcd. for C₂₁H₃₂N₂O₄Pd: C, 52.23; H, 6.68; N, 5.80. Found: C, 52.80; H, 6.85; N, 5.30.

21: MS (FAB, 70 eV) *m/z*: 661 [*M* + 1]⁺; ¹H NMR (400 MHz, CDCl₃) δ: 0.99 (s, 18 H, CH₃), 1.08 (s, 18 H, CH₃), 2.87 (d, ³J_{HH} = 6.3 Hz, 4 H, CH₂), 3.22 (s, 4 H, CH₂), 5.24 (s, 2 H, N=C=C-H), 5.47 (s, 2 H, O=C=C-H), 6.48 (br t, 2 H, N-H). ¹³C NMR (50 MHz, CDCl₃) δ: 27.60 (CMe₃), 28.82 (CMe₃), 32.33 (CMe₃), 36.04 (CMe₃), 54.20 (CH₂N), 61.26 (CH₂N), 84.57 (H-C=C), 102.61 (H-C=C), 146.88 (C-N), 170.83 (C-O), 179.92 (C=N), 182.79 (C=O). Anal Calcd. for C₃₂H₅₀N₄O₄Pd·0.5CH₂Cl₂: C, 55.80; H, 7.31; N, 7.96. Found: C, 55.60; H, 7.34; N, 7.93.

Computational Details. Calculations have been carried out first using the formalism of the density functional theory (DFT) within the generalized gradient approximation (GGA), as implemented in the ADF program^{38,42–44} with the so-called BP86 exchange-correlation functional.^{45–47} For first row atoms, the 1s shell was frozen and described by a single Slater function. For complex **20_H**, the frozen core of the Pd atom composed of the 1s to 3sp shells was also modeled by a minimal Slater basis. For hydrogen, carbon, nitrogen, and oxygen, the Slater basis set used for the valence shell is of triple- ζ -quality, supplemented with one p- or d-type polarization function. The 4s and 4p shells of palladium are described by a double- ζ -Slater basis; the 4d and 5s shells by a triple- ζ basis and the 5p shell by a single orbital. No polarization function is added for Pd.^{48,49} Molecular bonding energies are reported with respect to an assembly of neutral atoms assumed isolated and in their ground state. Most geometry optimizations have been carried out without any symmetry constraint, but the optimized structures never

significantly deviate from planarity. The optimization cycles were continued until all of the three following convergence criteria were fulfilled: (i) the difference in the *total energy* between two successive cycles is less than 0.001 hartree; (ii) the difference in the *norm of the gradient* between two successive cycles is less than 0.001 hartree Å⁻¹; (iii) the maximal difference in the *Cartesian coordinates* between two successive cycles is less than 0.01 Å. The geometries of **8_H**, **8_{Me}**, **9**, and **10** were then reoptimized and the energy differences recomputed using the hybrid B3LYP exchange-correlation functional as implemented in *Gaussian 98*.³⁹ The all-electron 6-31G** set of basis functions was then used for all atoms.

Dipole Moment Measurement. The determination of the dipole moment of **8** was achieved in a dichloromethane solution by measuring the variation of the dielectric constant with the concentration.⁵⁰ For this purpose, an HP 16452A Liquid Test Fixture for capacitive measurement connected to a QuadTech 7600 Precision LCR meter was used. The measurement cell was immersed in a thermostatic bath for temperature stabilization with a 0.1 °C precision, and the capacity is investigated with a 1 V, 300 kHz modulated voltage.

X-ray Data. The selected crystals were mounted on a Nonius Kappa-CCD area detector diffractometer (Mo K α , λ = 0.710 73 Å). The complete conditions of data collection (Denzo software) and structure refinements are given in Table 1. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SIR97) and refined against *F*² using the SHELXL97 software. The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.⁵¹

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Supporting Information Available: Crystallographic details for the structure of **12**, **14**, and **20** as cif files (CCDC 201315–201317); total energies, Cartesian coordinates, and (for the triplet states) spin density distribution of hexaazaanthracene (**9**), chlorobis-1,2,3-dithiazole (**10**), models of **8** (**8_H** and **8_{Me}**), cationic systems **12_H** and **14_H**, intermediate **A_{Me}** and Pd complex **20_H** optimized at the DFT/BP86 and (except for **20_H**) DFT/B3LYP levels. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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