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Chemical bonding in zwitterionic diamino-*meta*-quinonoids and their isomers

Tibor Höltzl,[1,2] Tamás Veszprémi[2] and Minh Tho Nguyen[1]*

[1]Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium
[2]Department of Inorganic Chemistry, University of Technology and Economics, Gellért tér 4, H-1521-Budapest, Hungary

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ABSTRACT: Quantum chemical calculations using molecular orbital (HF) and density functional (B3LYP) methods, in conjunction with the 6-311++G(d,p) basis set, have been applied to investigate the electronic structure of a series of diamino-*meta*-quinonoid molecules, each containing a six-membered ring coupled with two exocyclic C═O bonds situated in a *meta* position, along with two amino substituents (NH_2 and NH—R). The chemical bonding phenomena in these zwitterions and isomers where one or two hydrogens are transferred from N— to O— are analyzed with the aid of the atoms-in-molecules (AIM) approach. The relative energies between zwitterionic and quinonoid isomers in both neutral and ionized states also have been evaluated. Substituents exert a strong effect that in many cases changes the energy ordering. Copyright © 2005 John Wiley & Sons, Ltd.
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KEYWORDS: density functional theory; *ab initio* calculations; diamino-*meta*-quinonoid structures; zwitterion structures; atoms-in-molecules analysis; substituent effects

INTRODUCTION

A quinone is formally derived from a six-membered carbon ring upon coupling with two exocyclic C═O double bonds. Quinones form an interesting family of organic compounds and versatile ligands in coordination and organometallic chemistry owing to their often unique redox and electron transfer and color properties.[1] A wealth of quinone derivatives have thus been available showing typical properties following different substitutions at the remaining ring carbon atoms.[2] Most of the known stable quinonoids were, however, derived from the parent *para*-quinone **I** and *ortho*-quinone **II** (Scheme 1). The *meta*-quinone has been demonstrated to be a transient biradical species having a triplet electronic ground state and a singlet–triplet separation gap at ca. 40 kJ/mol^{-1}.[3] Recently, the first synthesis of a novel type of benzoquinone (**III**), which is formally a diamino derivative of *meta*-quinone, has been reported.[4] Crystal structure analysis clearly showed that molecule **III** features a non-classical structure that is a formal zwitterion consisting of two separated charged subunits.[4,5] Thus, the two amino substituents tend to stabilize strongly the closed-shell singlet configuration, making it the ground electronic state and thereby transforming a biradical into a zwitterion.

The molecular and spectroscopic properties of some simple diamino *meta*-quinone derivatives have been examined in detail in subsequent theoretical studies.[5–9] The essential features of the zwitterions (**III**) have thus been revealed: the system contains two subunits where the positively charged N—C—C(H)—C—N subunit, containing the two amino groups, forms two chemical bonds with the negatively charged O—C—C(H)—C—O subunit; the negative charge amounts to about half of an electron; the parent molecule of **III** is characterized by a tiny but positive electron affinity (0.065 eV)[6], a low ionization energy (7.8 ± 0.3 eV) and a small triplet–singlet energy gap (40 kJ/mol^{-1});[7] and the UV absorption bands centered at 350 and 343 nm recorded for a *tert*-butylamino derivative[4,5] belong to the same electronic transition but with different vibrational states. These absorptions arise qualitatively from $\pi^* \leftarrow \pi$ transitions of electrons in frontier orbitals (LUMO ← HOMO). There has been a discussion[6,8] as to whether the strong absorption band originates from an electronic transition from the ground state to the first singlet excited state, or rather to the second singlet excited state. In our opinion,[8] the latter is likely to be the case. In the parent **III**, the ${}^1A_1 \rightarrow 2{}^1B_2$ excitation is associated with a large oscillator

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**Correspondence to:* M. T. Nguyen, Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium.
E-mail: minh.nguyen@chem.kuleuven.be
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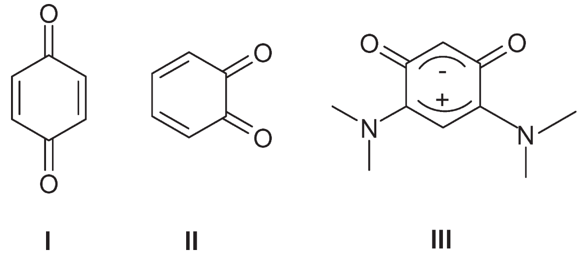


Scheme 1

strength.[8] In addition, there have been different views on its aromaticity. Although the NICS indices indicated that the *meta*-quinonoid **III** is essentially non-aromatic,[7] other charge distribution analyses[5,6] suggested a $6\pi + 6\pi$ potentially anti-aromatic system. It has been suggested that a possible way to cancel the charge separation between the two subunits without introducing anti-aromaticity would be to transfer a proton from an amino group to the nearby quinonic oxygen.[6] In fact, in such an H-transferred isomer the classical quinonoid structure is formed again (as an imine). However, no quantitative information is available yet on these isomers.[7] In a recent paper investigating the charge separation in some 1,2,4,5-tetrasubstituted benzene derivatives, Haas and Zilberg concluded that the charge separation is not related to the aromatic character but to the ease of ionization of the amino group and the large electron affinity of the dioxallyl radical.[9]

In view of the novelty in molecular and electronic aspects of the zwitterions **III** and their potential in synthetic chemistry, we have undertaken a further analysis of their chemical bonding phenomena. The topology of the electron density has been approached using the atoms-in-molecules (AIM) method.[10] In addition, we have evaluated the relative stabilities between the zwitterion and two H-transferred isomers, in both neutral and ionized states, for a series of derivatives substituted at both nitrogen centers.

METHODS OF CALCULATION

Quantum chemical calculations were performed by the Gaussian program package,[11] whereas the AIM2000 V1.0 program[12] was used to determine the topology of electron density. The geometries of the stationary points considered were optimized using MO theory at the Hartree–Fock level with the 6-31+G(d) basis set and also density functional theory (DFT) with the popular hybrid functional B3LYP and the 6-311++G(d,p) basis set. Harmonic vibrational frequencies were computed with the HF/6-31+G* method to determine the character of the stationary points and to evaluate the zero-point energies (ZPE). The B3LYP/6-311++G(d,p) level was used to calculate the charges, bond orders and topological properties of the electron density (ρ) and its Laplacian ($\nabla^2\rho$). The unrestricted formalism (UHF, UB3LYP) was employed for open-shell systems.

RESULTS AND DISCUSSION

We first analyse the topology of zwitterion **III**, comparing it with those of some close reference compounds (Fig. 1). Subsequently, the stability of substituted compounds **III** relative to their hydrogen-transferred isomers **V** and **VI** is discussed (Scheme 2).

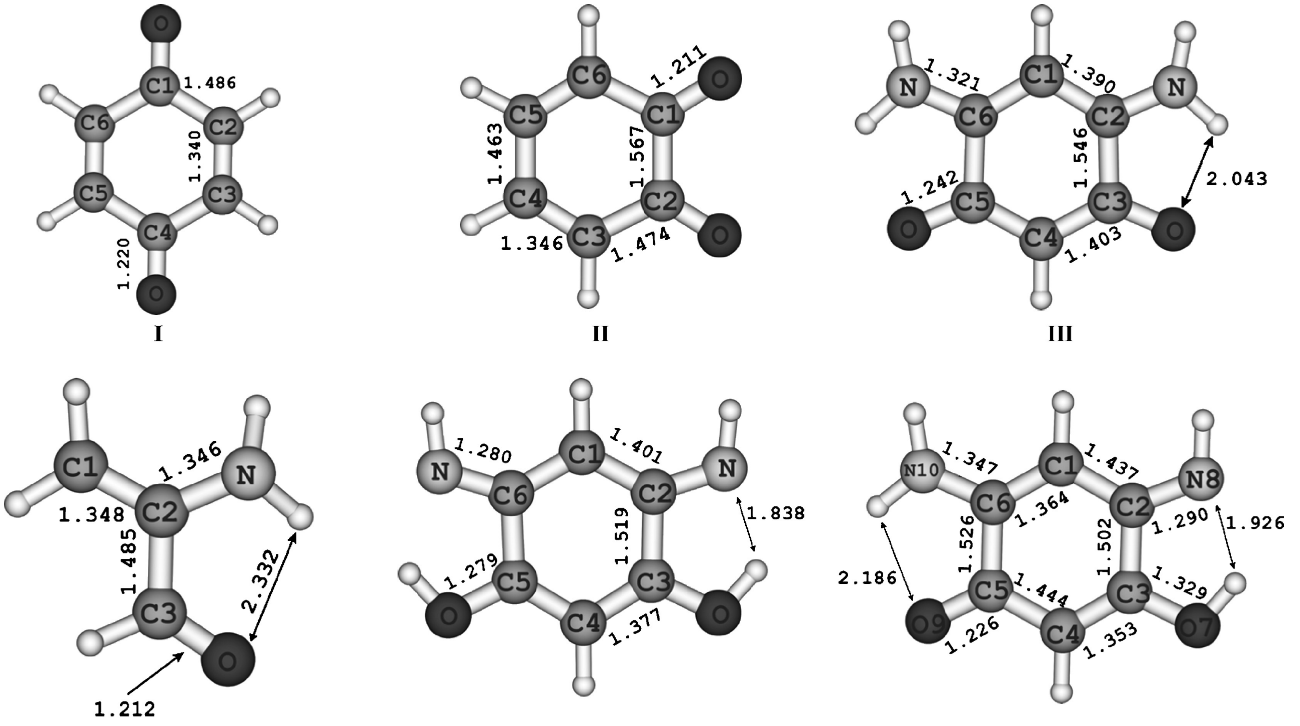
Comparison of the zwitterion with some reference compounds

Selected geometrical parameters of the parent zwitterion **III** and three reference compounds, including *para*-quinone (**I**), *ortho*-quinone (**II**) and 2-aminopropenal (**IV**), are given in Fig. 1. The latter corresponds in fact to a small and open portion of the skeleton of **III**. The molecular geometry of **III** has been examined abundantly in previous studies.[5,8] According to the main resonance structures depicted in Scheme 2, it is expected that in the non-classical structures there are no pure single and double bonds. Although both structures **a** and **b** contain a certain quinonoid form, structure **c** shows a smaller degree of bond alternation. Some properties describing the electron distribution are summarized in Table 1.

Together with the bond lengths (Fig. 1), the Wiberg bond indices[13] (which show the order of a given bond, i.e. the number of electron pairs, denoted hereafter as WI) and ellipticities of the bond critical points (BCPs) determined from AIM calculations (Table 1) characterize the single and double bonds in both the *ortho*- and *para*-quinone. The lengths of single and double bonds in the two compounds are similar, except for the C1—C2 bond in *ortho*-quinone, which is longer than a single bond and associated with a WI of 0.90. This bond is weaker than a single bond owing to the repulsion of the two exocyclic oxo-groups.

The Laplacian, which measures the local curvature of the electron density, is negative for **III** at every BCP (indicated by broken lines in Fig. 2), which means that the electrons are actually concentrated in the internuclear regions.[10,14]

The C1—C2 bond in **III** is about the same as that in benzene. The WI and ellipticities also show that the bond order of the C1—C2 bond in **III** is between 1 and 2. This is also true in the case of the C3—C4 bond of this zwitterion, where the bond order is ca. 1.5. The inter-fragment C2—C3 bond in **III** is longer than a single bond in both *ortho*- and *para*-quinones, the corresponding ellipticity being equal to zero (spherical distribution)

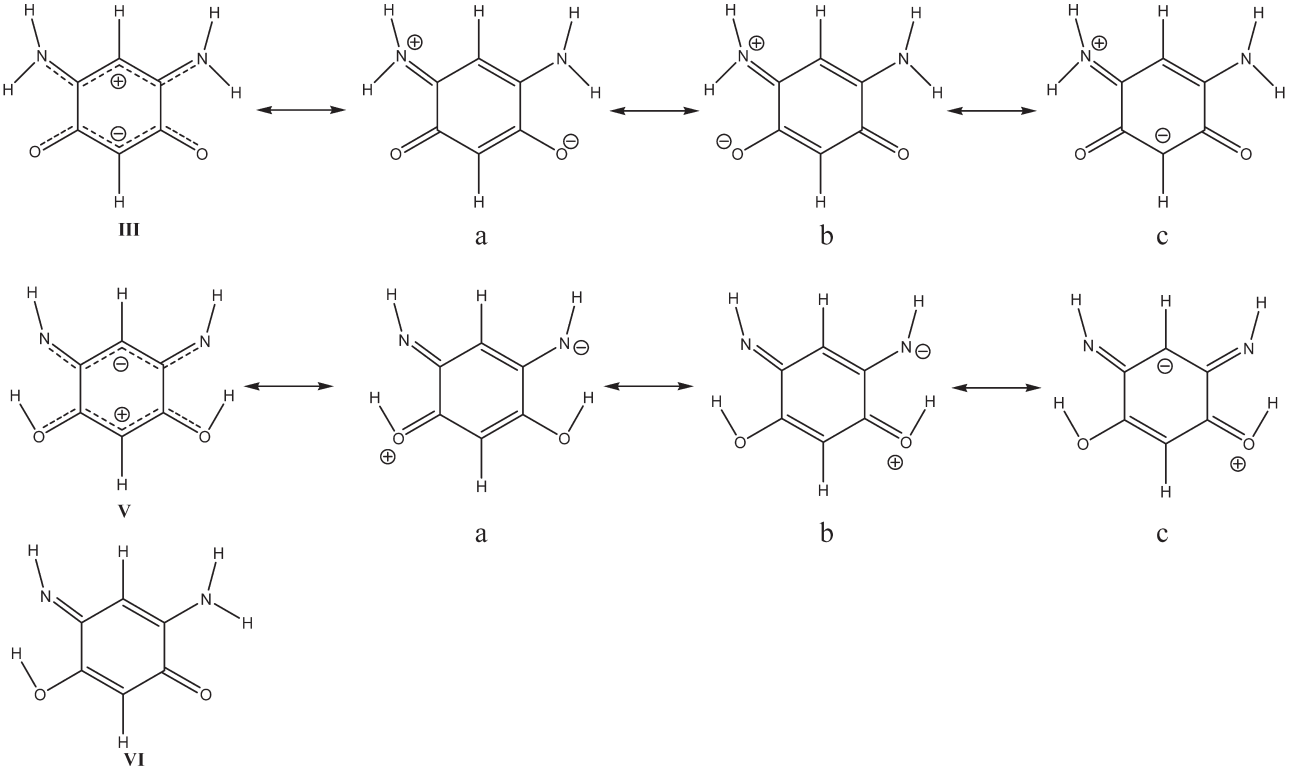


I II III

IV V VI

Figure 1. Bond lengths (in Å) (from B3LYP/6-311++G(d,p) calculations) of aminoquinones and some reference compounds

and the WI to 0.93. The electron density in the BCP is also smaller than in the case of single bonds in quinones **I**, **II** and also in **IV**. The C2—N bond in **III** is shorter than in **IV** by 0.025 Å, which is reflected by the larger electron density and the WI in the BCP of the former. These results are in line with the view that the C2—N bond in **III** has a partial double bond character; the bond order is ca. 1.4. Similarly, the C═O bond turns out to be longer



Scheme 2

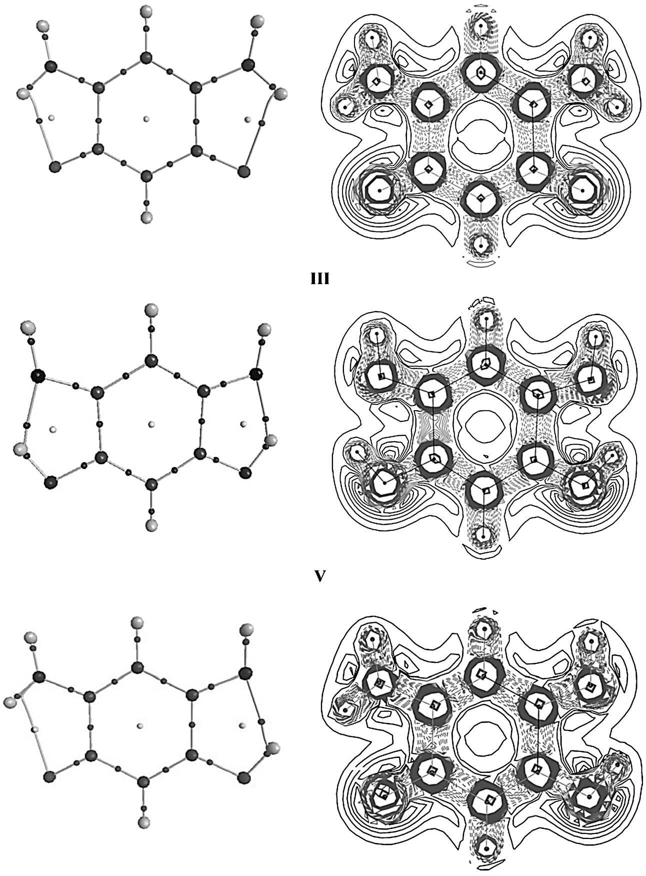
Table 1. Analysis of the electron densities in the zwitterion and reference compounds derived from B3LYP/6-311++G (d,p) calculations

	Bond	Ellipticity	ρ in BCP[a] (a.u.)	$\nabla^2\rho$ in BCP[a] (a.u.)	WI[b] (a.u.)
I	C1—C2	0.27	0.08	−0.17	1.04
	C2—C3	0.28	0.34	−0.25	1.82
	C3—C4	—	—	—	—
	C4—C5	—	—	—	—
	C1—O	0.05	0.40	−0.03	1.75
II	C1—C2	0.07	0.24	−0.13	0.90
	C2—C3	0.10	0.27	0.02	1.07
	C3—C4	0.29	0.34	−0.25	1.77
	C4—C5	0.08	0.27	−0.18	1.12
	C1—O	0.04	0.41	0.00	1.80
III	C1—C2	0.24	0.31	−0.22	1.40
	C2—C3	0.00	0.24	−0.14	0.93
	C3—C4	0.26	0.31	0.00	1.33
	C3—O	0.05	0.38	−0.08	1.55
	C2—N	0.02	0.34	−0.21	1.40
	O…H	0.44	0.03	0.03	0.03
IV	C1—C2	0.32	0.33	−0.24	1.71
	C2—C3	0.11	0.27	−0.17	1.04
	C3—C4	—	—	—	—
	C3—O	0.03	0.41	−0.01	1.80
	C2—N	0.08	0.31	−0.22	1.15
	O—H	—	—	—	0.01
V	C1—C2	0.25	0.30	−0.20	1.30
	C2—C3	0.08	0.26	−0.16	0.98
	C3—C4	0.24	0.32	−0.23	1.39
	C3—O	0.07	0.34	−0.08	1.25
	C2—N	0.15	0.36	−0.26	1.59
	N…H	0.03	0.06	0.03	0.07
VI	C1—C2	0.16	0.29	−0.19	1.16
	C2—C3	0.09	0.26	−0.17	0.99
	C3—C4	0.33	0.33	−0.25	1.60
	C4—C5	0.16	0.29	−0.19	1.15
	C5—C6	0.08	0.25	−0.25	0.96
	C6—C1	0.32	0.32	−0.23	1.56
	C2—N8	0.16	0.38	−0.25	1.72
	C3—O7	0.03	0.31	−0.09	1.13
	C6—N10	0.07	0.32	−0.22	1.26
	C5—O9	0.04	0.40	−0.04	1.68
	N8…H	0.11	0.03	0.03	0.05
	O9—N10	9.79	0.02	0.02	0.02
	O9…H	—	—	—	0.01

[a] The electron density (ρ) and the Laplacian of the electron density ($\nabla^2\rho$) at the bond critical point (BCP).

[b] The Wiberg index, which is defined as the sum of the squares of the corresponding values of the density matrix.

in **III** than in the reference compounds. As a consequence, the WI and the electron density in the BCP are smaller in the case of **III**, in line with the fact that the bond order of the C═O bond is actually <2. However, the ellipticity of the BCPs of all CO bonds almost vanishes, bearing in mind that this value for C═O bonds is consistently close to zero (0.038 in formaldehyde).



III

V

VI

Figure 2. Maximum electron density lines and Laplacians of molecules **III**, **V** and **VI**. The bond critical points are indicated by small black dots in the chemical bonds. These occur where the gradient of electron density vanishes

The correlation between the net charges computed according to different schemes (Mulliken, Bader, NBO; Table 2) is not good. The sum of the charges of the atoms belonging to the upper moiety of molecules was calculated as a measure of charge separation. This was indicated by the quantity 'Sum' listed in Table 2. In any case, the charge separation in **III** is larger than that in **IV**. The dipole moments are also in agreement with this, because **III** has a dipole moment of 8.57 D whereas it is only 2.66 D in **IV**. Experimental measurements[5] on substituted zwitterions also emphasized large dipole moments up to 9.7 D. All these results agree with each other that **III** has the structure shown in Scheme 2 (the scheme indicates only the most important resonance structures, e.g. it is expected that resonance structures that involve a C^+—N electron distribution have much smaller weight than those of C—N^+): positive charge is delocalized between the N—C6—C1—C2—N bonds whereas the negative charge is delocalized between the O—C5—C4—C3—O bonds. Resonance structures could explain the partial double-bond character of bonds C1—C2, C3—C4 and C—N, the decrease of bond order in the case of the C═O bond and the weakness of the C2—C3 bond.

Table 2. Atomic net charges calculated using different schemes (from B3LYP/6-311++G(d,p) calculations)

Molecule	Atom	Mulliken	NBO	Bader
III	C1	0.03	−0.40	−0.01
	C2	0.15	0.29	0.52
	C3	−0.55	0.42	0.87
	C4	0.54	−0.43	−0.07
	O	−0.38	−0.64	−1.14
	N	−0.29	−0.69	−1.13
	H	0.22	0.23	0.06
	H	0.16	0.20	0.01
	H	0.31	0.43	0.46
	H	0.28	0.39	0.41
	Sum[a]	**1.10**	**0.65**	**0.53**
IV	C1	−0.55	−0.41	−0.06
	C2	0.39	0.06	0.39
	C3	−0.08	0.40	0.97
	H	0.11	0.12	0.03
	O	−0.28	−0.54	−1.09
	N	−0.35	−0.80	−1.09
	H	0.14	0.20	0.03
	H	0.12	0.20	0.03
	H	0.26	0.40	0.40
	H	0.24	0.38	0.38
	Sum[a]	**0.25**	**0.02**	**0.08**

[a] The sum of the charge of the positive moiety.

Comparison of III with the H-transferred isomers V and VI

Isomer **VI** shown in Scheme 2 is formally derived from **III** through a 1,4-H-shift from nitrogen to oxygen. The bond lengths and bond orders of **VI** are recorded in Table 1 and Fig. 1. The C1—C2 bond in **III** is longer whereas the ellipticity and WI are smaller than those of the C6—C1 bond in the more classical isomer **VI**. The C2—C3 bond in **III** is similar to the C6—C5 bond in **VI**. The WI values are <1 in both cases due to the high electronegativity of the amino and oxo groups (this effect is related to the case of the C1—C2 bond in *ortho*-quinone **II**).

The double-bond character of the C3—C4 bond in **III** is greater, the bond is shorter and the BCP ellipticity is larger than those of the C4—C5 bond in **VI**. Similarly, the double-bond character of the C6—N bond in **III** is greater than in **VI**. According to the bond lengths and WI values, the double-bond character of the C3—O bond in **III** is smaller than that in **VI**. Overall, these results indicate that in zwitterions **III** the electrons are delocalized in the upper and in the lower side of the molecule (Scheme 2) in such a way that they are not separated in single and double bonds; the bond order is the range between single and double. On the contrary, **VI** has a more classical structure, with well-separated single and double bonds in the typical quinonoid molecule.

In form **V**, the dipole moment is substantially smaller (0.92 D) than that of **III** (8.57 D), indicating that the charge separation is smaller in the first case. The resonance structures of the two molecules are significantly different (Scheme 2). In the first case, the charges of oxygen atoms are partially negative and those of the nitrogens are partially positive. In the second case, the nitrogens are negatively charged and the oxygens are positive. Because oxygen is more electronegative than nitrogen, the charge separation is larger in the first case.

The C1—C2 bond is shorter in **V** than in **VI**. This also holds true for the C6—N, C3—O and C2—C3 bonds, suggesting a larger bond order for these bonds in **VI**. Electrons are apparently more delocalized in the former between oxygen and nitrogen atoms (Scheme 2), in such a way that there is no pure single or double bond. Owing to the delocalization, the bond order of C1—C2, C3—C4 and C3—O will become >1 whereas the bond order of C2—N is <2. Such a charge separation is actually opposite to that of zwitterion **III**. The overall result of this charge redistribution is that **V** has a higher energy than **III**.

Figure 2 shows the maximum electron density lines (which according to AIM theory correspond to the chemical bonds) and the Laplacian maps of structures **III**, **V** and **VI**. In both zwitterionic forms (**III** and **V**) in the neighborhood of all BCPs (except the H-bond) the Laplacian is negative, indicating that the electron concentration is in the bonding region.

On the contrary, in the neighborhood of BCPs for C5—O, C1—C2, C1—C6, C3—C4 and C4—C5 bonds in **VI** the Laplacian is positive due to the large electronegativity of the oxygen and nitrogen atoms that is not compensated by delocalization of the electrons.

Singlet, triplet, radical anion and radical cation states of III and its *N*-methyl-substituted derivatives

Some calculated properties of zwitterion **III** and its *N*-methyl derivatives in different electronic states are recorded in Table 3. In both cases, the singlet electronic state is energetically more stable than the triplet counterpart. The transition from singlet to triplet state results from the transfer of one electron from the HOMO (which is antibonding with respect to C2—N and C3—O) to the LUMO (which is strongly bonding with respect to C2—C3). This causes a decrease in the length of C2—C3 from 1.546 to 1.460 Å and an increase of C2—N from 1.321 to 1.361 Å. A similar effect occurs in the case of the *N*,*N*-dimethyl derivative.

In the anion, the C2—C3 bond is shorter than in the other states but the C2—N and C3—O bonds are longer, no doubt due to a full delocalization of the excess electron.

Calculations for radical cations did not add much to the main conclusions, therefore these results and discussion can be seen in the supplementary material in Wiley Interscience.

Table 3. Structure of different states of **III** (with H and CH_3 substituents on nitrogen atoms)

X	State[a]	Bond length (Å) C1—C2	C2—C3	C3—C4	C2—N	C3—O	7–13	E_{rel} (eV)	Dipole moment(D)
H	(0; 1)	1.390	1.546	1.403	1.321	1.242	2.043	0.00	8.57
	(0; 3)	1.397	1.460	1.439	1.361	1.257	2.289	1.00	5.70
	(−1; 2)	1.392	1.482	1.414	1.390	1.272	2.106	−1.62	6.91
	(+1; 2)	1.395	1.527	1.442	1.316	1.220	2.219	7.56	6.35
CH_3	(0; 1)	1.393	1.545	1.403	1.319	1.243	1.989	0.00	9.28
	(0; 3)	1.401	1.461	1.437	1.356	1.258	2.220	1.13	6.31
	(−1; 2)	1.397	1.482	1.413	1.369	1.275	2.076	−1.37	9.48
	(+1; 2)	1.399	1.524	1.441	1.316	1.222	2.149	9.00	5.79

[a] Charge and multiplicity.

Properties of hydrogen bonds

The characterization of hydrogen bonds could be approached using the AIM model. Accordingly, there are several criteria for detecting hydrogen bonds,[14] from which in our case the most important ones include the BCP and the maximum electron density (MED) line between the atoms. According to Popelier,[14] electron density at the BCP of a hydrogen bond ranges between 0.02 and 0.04 a.u. and the Laplacian at the BCP ranges between −0.15 and −0.02. It has been pointed out[15] that for hydrogen bonds there is a certain linear correlation between the electron density in BCPs of hydrogen bonds and the strength of the hydrogen bonds: the larger the electron density at the BCP, the stronger the hydrogen bond. Thus, for a comparison of the strength of hydrogen bonds in different compounds it could be sufficient to calculate the values of electron density in BCPs This is true also for intramolecular hydrogen bonds, but in this case the relationship is usually non-linear.[16,17] It could be expected that there is a certain extent of intramolecular hydrogen bond between the hydrogen and oxygen atoms in the singlet ground-state **III** and its *N*-methyl-substituted derivative, in fact the Laplacian at the BCP of the O . . . H bond is positive in both cases, which indicates weak hydrogen bonds.

Similarly, weak hydrogen bonds are also present in the anion, and properties of these bonds are comparable with those in the ground state. On the contrary, there are apparently no hydrogen bonds in cation **III**, seemingly due to an increase in the positive charge of the nitrogen atom (cf. resonance structures in Scheme 1S in supplementary material, Wiley Interscience). Following methyl substitution at both amino groups, the hydrogen bonds again emerge in the *N*-methyl-substituted cation **III**. Methyl groups obviously donate an electron to nitrogen atoms, therefore the partial positive charge of the N atoms decreases and this induces the appearance of an H-bond. There are no hydrogen bonds in the triplet state of either the parent or the methyl-substituted **III**.

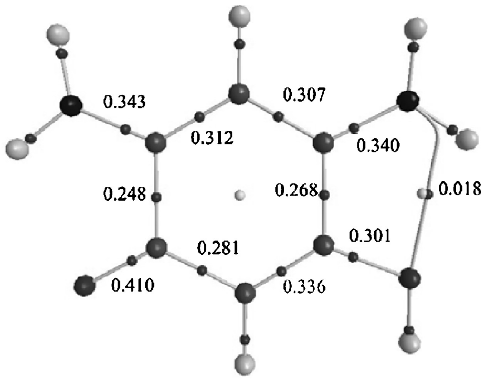
According to the AIM analysis, there is no hydrogen bond in the open molecule **IV**, whereas there is a certain hydrogen bond in the case of **III**. The O . . . H bond distance of 2.042 Å in **III** is considerably smaller than that of 2.332 Å in IV. The Laplacian of the O . . . H BCP in **III** is found to be positive and the associated electron density is small, indicating that there is a very small electron concentration between the oxygen and hydrogen atoms.

If a MED line with a BCP represents the chemical bond, the appearance of new, ‘non-classical’ bonds should be assumed in some molecules investigated. for example, when studying the MED lines between the atoms in Fig. 2 a nitrogen–oxygen bond appears on the left side of **VI**. Similar ‘bonds’ can be found in the protonated form of **III** (**VII** in Fig. 3) and compound **VIII**. Properties of this interaction could be related to a hydrogen bond. Accordingly, the small electron density at the BCP and the positive Laplacian indicate a weak interaction. The high ellipticity associated with the BCP of this non-classical bond is due to the small distance between the BCP and the ring critical point (RCP, indicated by light grey dots in Fig. 2).

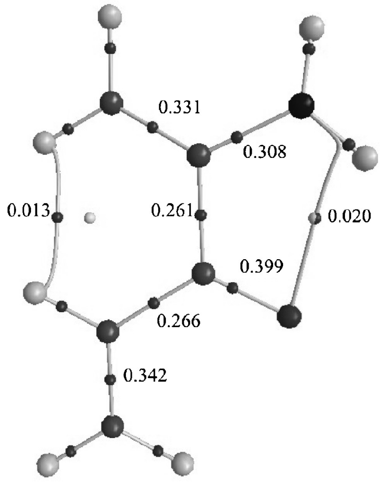
Figure 3 illustrates the electron distribution obtained from an AIM analysis in the model molecule **VIII** (the 3-ethenyl derivative of **IV**). It is of interest to note that some intramolecular dihydrogen bond[14] could be identified here. Properties of this interaction are related to the weak hydrogen bonds, the Laplacian is positive and the electron density is small.

Substituent effects on the properties of III and V

The geometries and some AIM-related properties of zwitterions **III** bearing different substituents on nitrogen atoms (Scheme 3, **IIIs**) are summarized in Table 4. The resulting structures are quite similar except for the N—X and C—N bonds, which are close to the substituent positions. The electron densities at the BCPs of bonds 8—13 in the parent and *N*,*N*-dimethyl-substituted molecule are peculiarly large (0.458 and 1.328 a.u., otherwise it amounts to ca. 0.35 a.u.). The ring exhibits a similar



VII



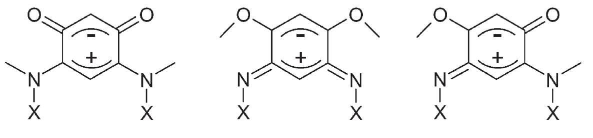
VIII

Figure 3. Electron density (in a.u.) in bond critical points for protonated zwitterion **VII** and 2-amino-3-oxo-pent-(1,4)-diene (**VIII**)

structure in all cases, pointing towards a high stability for this non-classical structure.

Properties of the substituted derivatives of V (Scheme 3, **Vs**) are listed in Table 5. The calculated dipole moment is large when involving an electronegative substituent (the largest value being with the CN group). This is in line with the resonance structures shown in Scheme 2. The geometrical parameters are also similar, but some large differences in ellipticities could be noticed.

Relative energies of the neutral isomers **III**, **V** and **VI** calculated using the B3LYP/6-311++G(d,p)+ZPE level of theory are displayed schematically in Fig. 4. The references are the substituted zwitterion **III**. In most cases, the classical aminoquinone **VI** represents the thermodynamically most stable isomer. Both methyl and silyl groups tend to stabilize **III**, seemingly through a hyperconjugation effect. It can be expected that with a larger alkyl (*t*-butyl) or silyl group at nitrogen the stabilization is even larger. It appears that the nitrogen lone pair of the amino group is responsible for stabilizing **III** through electron delocalization.



IIIs **Vs** **VIs**

Scheme 3

Electronegative substituents consistently stabilize isomer **VI**, therefore it is expected that they provide a possibility for the synthesis of the aminoquinone isomers. Electronegative substituents also stabilize isomer **V**, even though these compounds have higher energy than **VI**, irrespective of the substituents.

The N—H . . . O bonds remain appreciable in all the N-substituted **III** compounds considered, even though the strength of the bond varies. We calculated the values of the electron density at the BCP and at two RCPs that appear within the six-membered ring formed by the N—C2—C3—O—H atoms. The values of the BCP electron densities range between 0.034 (CN substituent) and 0.023 (F substituent). For the RCPs, the densities vary from 0.028 (CN) to 0.023 (F). The H—O distance is shortest (1.901 Å) in the cyano- and longest (2.120 Å) in the fluorine-substituted **III**. As a consequence, the strongest hydrogen bond corresponds to the former and the weakest to the latter.

Correlation between the H . . . O lengths and the electron densities at its BCP is very good; the correlation coefficient amounts to 0.95 with the relationship:

$$\rho(\mathrm{BCP}) = -0.0503\mathrm{d} + 0.1288 \qquad (1)$$

where *d* is the O . . . H distance in angstroms. Correlation is equally good between the bond lengths and the values of electron densities at RCPs issued by the existence of the hydrogen bond. The resulting correlation coefficient is now 0.88 and Eqn (2) could be fitted:

$$\rho(\mathrm{RCP}) = -0.0212\mathrm{d} + 0.0681 \qquad (2)$$

These results point out a simple fact: *the larger the electron density at the BCP and at the RCP, the stronger the hydrogen bond.*

Let us now consider the hydrogen bonds in isomers **V**. The electron densities at RCPs and BCPs related to the hydrogen bonds in its substituted derivatives are uniformly larger than those in **III**. The length of the H . . . N bond is also shorter in the first case, suggesting a somewhat stronger hydrogen bond in **V**. This is due to the partially negative charge of the nitrogen atoms, making it a better acceptor for a hydrogen bond.

The largest value of electron density at the BCP is found with the SiH_3 substituent (0.065) and the smallest is found with fluorine (0.017). Similarly, the shortest H . . . N distance is with SiH_3 (1.654 Å) and the longest is with fluorine (1.934 Å). In the same trend, the largest

Table 4. Geometrical parameters, total energies and dipole moments of *N*,*N*-disubstituted **III** compounds

	Bond length (Å)								
X	C1—C2	C2—C3	C3—C4	C2—N	C3—O	N—X	O—H	Energy (a.u.)	Dipole moment(D)
H	1.390	1.546	1.403	1.321	1.242	1.021	2.043	−492.33573	8.57
CH_3	1.393	1.545	1.403	1.319	1.243	1.449	1.989	−570.97540	9.28
SiH_3	1.391	1.548	1.401	1.331	1.243	1.774	1.931	−1073.80743	8.30
CF_3	1.387	1.551	1.400	1.332	1.241	1.417	1.923	−1166.60658	3.56
F	1.387	1.552	1.402	1.310	1.240	1.367	2.120	−690.69929	7.31
Cl	1.387	1.553	1.401	1.319	1.241	1.703	1.951	−1411.47797	6.31
Br	1.387	1.556	1.401	1.319	1.241	1.856	1.981	−5639.33537	7.14
OH	1.387	1.545	1.403	1.320	1.243	1.385	2.064	−642.69929	7.31
SH	1.387	1.549	1.402	1.330	1.243	1.720	1.973	−1288.71621	7.54
NH_2	1.388	1.545	1.403	1.324	1.244	1.402	2.014	−603.00550	8.31
PH_2	1.390	1.549	1.401	1.331	1.243	1.757	1.930	−1176.27466	7.75
CN	1.385	1.543	1.400	1.341	1.242	1.339	1.901	−676.81227	0.05

electron density at BCP is again identified with SiH_3 (0.039) and the smallest with fluorine (0.026). These results agree with each other, indicating that the hydrogen bond is strongest with SiH_3 and weakest with fluorine.

Correlation is also good between the lengths of hydrogen bonds and the values of electron density at the BCP (correlation coefficient being 0.99):

$$\rho(\mathrm{BCP}) = -0.1149\mathrm{d} + 0.2524 \qquad (3)$$

and between the bond lengths and the values of electron density at the RCP (correlation coefficient being 0.99):

$$\rho(\mathrm{RCP}) = -0.0430\mathrm{d} + 0.1093 \qquad (4)$$

In agreement with the resonance structures shown in Scheme 2, the hydrogen bonds could be stabilized with electron-donor substituents. The larger the electronegativity of a substituent, the weaker the resulting hydrogen bond: the hydrogen bond is indeed stronger with Br than with Cl as substituent, and consistently stronger with Cl than with F. This also holds true for the pair OH/SH: in the latter, the hydrogen bond is stronger than in the former. Again, this is also the case for the NH_2/PH_2-substituted derivatives of **V**.

In **III**, the ellipticity of hydrogen bonds is extremely large, ranging between 0.214 (SiH_3) and 1.067 (F). This is due to the fact that the bond and RCP are situated very close to each other (with a long O—H distance). In **V**, as the N—H bond is getting shorter, the distance between the RCP and the BCP of the hydrogen bond is longer and thereby the ellipticity is lower, in most cases being close to zero.

Discussion of the substituent effects in the case of radical cations of **III**, **V** and **VI** can be found in Supplementary material, Wiley Interscience.

CONCLUSIONS

In the present theoretical analysis, the structure and properties of non-classical diamino-*meta*-quinonoid zwiterions

Table 5. Geometrical parameters, total energies and dipole moments of *N*,*N*-disubstituted **V** compounds

	Bond length (Å)								
X	C1—C2	C2—C3	C3—C4	C2—N	C3—O	N—X	N—H	Energy (a.u.)	Dipole moment(D)
H	1.403	1.514	1.384	1.307	1.296	1.015	1.702	−492.29582	0.92
CH_3	1.406	1.504	1.385	1.308	1.299	1.443	1.716	−576.93490	1.34
SiH_3	1.402	1.525	1.384	1.308	1.290	1.745	1.654	−1073.77236	0.18
CF_3	1.398	1.513	1.383	1.314	1.295	1.397	1.782	−1166.59451	5.11
F	1.399	1.484	1.385	1.315	1.311	1.397	1.934	−690.69886	4.19
Cl	1.400	1.493	1.384	1.318	1.037	1.726	1.853	−1411.47118	2.51
Br	1.400	1.497	1.384	1.317	1.306	1.878	1.841	−5639.32631	2.02
OH	1.403	1.472	1.386	1.320	1.317	1.391	1.923	−642.69343	0.65
SH	1.406	1.479	1.385	1.323	1.313	1.698	1.866	−1288.70142	0.23
NH_2	1.412	1.465	1.387	1.322	1.320	1.369	1.905	−602.98892	1.97
PH_2	1.405	1.499	1.385	1.315	1.303	1.713	1.781	−1176.25674	0.08
CN	1.396	1.496	1.384	1.325	1.302	1.319	1.877	−676.81712	8.30

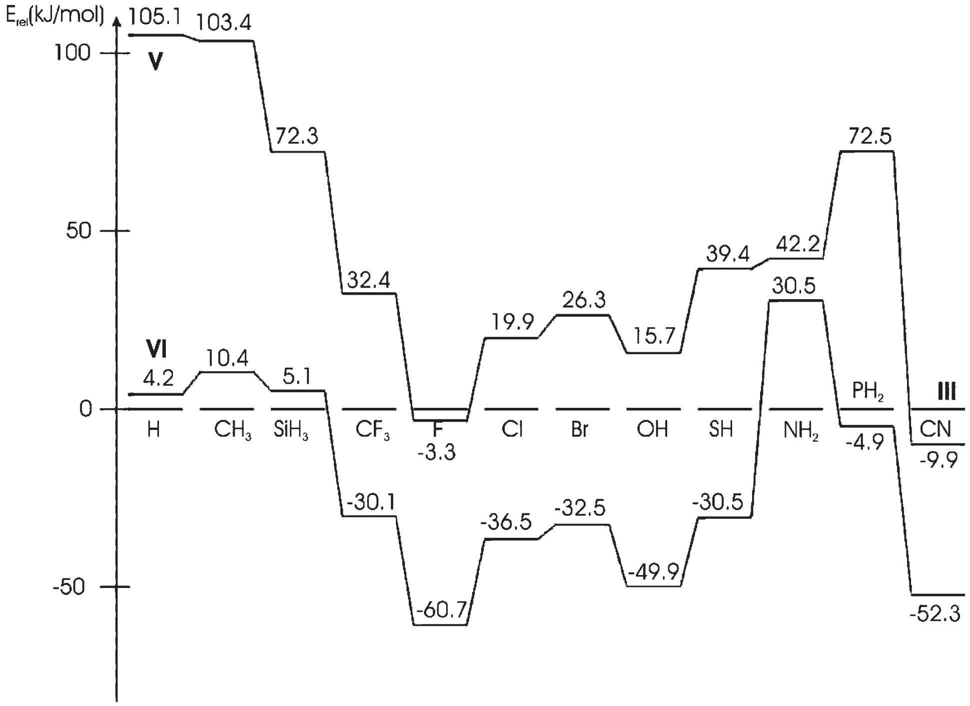


Figure 4. Relative energies of the neutral isomers obtained using B3LYP/6-311++G(d,p)+ZPE calculations

were calculated and compared with those of hydrogen-transferred isomers and another reference compound. Bond orders were approached using Wiberg indices, and the AIM analysis was performed for all molecules. The calculated results consistently show a zwitterionic structure for both isomers **III** and **V** and a more classical structure for isomer **VI**. Structures of the triplet, radical anion and radical cation have been studied. Calculations show that the non-classical zwitterion **III** is a singlet ground state, irrespective of the substituents on both nitrogen centers.

The Substituent effect on the relative stability of the three main isomers was also probed in both neutral and ionized forms (given in Supplementary material, Wiley Interscience). In most cases, the classical amino-quinone **VI** represents the most thermodynamically stable isomer; the least stable is zwitterion **V**. Electropositive groups such as methyl and silyl tend to stabilize the non-classical zwitterionic structure **III**, whereas electronegative substituents favor the substituted isomer **VI**. The latter is disfavored due to the presence of a negative charge on nitrogen and a positive charge on oxygen. Weak hydrogen bonds were also identified in zwitterions.

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