A Generalized Resonance Model for Substituted 1,4-Benzoquinones

Marco Nonella[†]

Biochemisches Institut der Universität, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Received: March 5, 1999

Resonance effects are known to affect vibrational spectra and electrochemical properties of substituted quinones. On the basis of the results of density functional calculations performed on several singly substituted 1,4-benzoquinones, we propose an extended resonance model which can account for the most prominent substituent effects onto the force constants of carbon−carbon and carbon−oxygen bonds. The calculations show that the two proposed resonance mechanisms are closely coupled. This interplay of the two effects renders a quantitative prediction of force constants of substituted 1,4-benzoquinone difficult. We nevertheless can give some simple rules which in many cases can give a good estimate for expected force constant changes upon substitution of 1,4-benzoquinone.

Introduction

Quinones play an important role in electron-transfer processes of photosynthetic bacterial reaction centers.[1−3] Mesomeric resonance effects have long been considered to play an important role on carbonyl frequencies and redox potentials of substituted 1,4-benzoquinone.[4] A quantitative model for the prediction of carbonyl infrared frequencies of substituted quinones had been postulated several years ago.[5] The frequency change of carbonyl vibrations found upon addition of a substituent had been attributed to the mesomeric effect introduced by this substituent in the case of the carbonyl group in meta position (distal C═O bond) and to steric and inductive effects caused by the substituent in the case of the carbonyl bond in ortho position (proximal C═O bond). Our computational investigations of 1,4-benzoquinone[6] and of methoxy- and methyl-substituted *p*-benzoquinones[7,8] allowed us to study quantitatively the effects of different substituents and different substituent orientations on structure, force constants, and vibrational frequencies.

In the case of 2-methoxy-1,4-benzoquinone[9] we have found two stable, planar conformers which differ in their orientation of the methoxy group as shown in Figure 1. We have analyzed the more stable conformer, conformer **a**, which has its methoxy group pointing away from the proximal carbonyl group. The changes in the force constants of bonds R2, R3, and R10 could be readily explained with the resonance structure depicted in Figure 3. At that stage, however, we were not able to explain the strengthening of bond R7 and the weakening of bond R1. We have also investigated how the C═O and C═C force constants change upon rotation of the methoxy group. Upon a rotation by 90°, we found a reduction of the force constant of the proximal carbonyl group and an increase of the force constants of the distal carbonyl group as well as of the carbon−carbon double bond C2═C3. The findings for bonds R2 and R10 were consistent with a breakdown of resonance effects resulting from the out-of-plane rotation of the methoxy group. Upon further rotation of the methoxy group and thus upon transforming conformer **a** into conformer **b**, the force constants of the carbon−carbon double bond and of the distal carbonyl

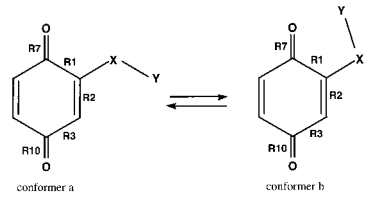

Figure 1. Stable conformers of 2-methoxy-1,4-benzoquinone (X = O, Y = CH_3), 2-methyl-1,4-benzoquinone (X = CH_2, Y = H), 2-ethyl-1,4-benzoquinone (X = CH_2, Y = CH_3), 2-hydroxy-1,4-benzoquinone (X = O, Y = H), and 2-hydroxymethyl-1,4-benzoquinone (X = CH_2, Y = OH).

group decreased again which is in line with the resonance model depicted in Figure 3.[5,9] The force constant of the proximal carbonyl group C1═O7, however, continued to decrease. While the simple resonance model of Figure 3 could well explain the behavior of the force constants R2 and R10 during the rotation of the methoxy group, it fails to predict the observed changes of the force constant of R7.

In the case of 2,3-dimethoxy-1,4-benzoquinone[9] we have found a stable conformation with both methoxy groups oriented in the ring plane and pointing toward the corresponding proximal carbonyl group. This structure had been postulated to be stabilized through the formation of weak internal hydrogen bonds. Our calculations predicted vibrational frequencies for this planar conformer which clearly disagree with all available experimental data. We have explained these findings with a destabilization of the planar structure due to the formation of hydrogen bonds with solvent molecules or with amino acids or other cofactors in a protein. Such external hydrogen bonds can be expected to be energetically more favorable than the proposed internal hydrogen bonds.

A more detailed analysis of the bond lengths of unsubstituted 1,4-benzoquinone suggested, that resonance effects are already present in the unsubstituted molecule.[9] Such resonance structures weaken carbon−carbon and carbon−oxygen double bonds and strengthen carbon−carbon single bonds. Some of these resonance structures are depicted in Figure 4a, **1**−**5**. This suggestion led us to extend the resonance model in our investigation on methyl substituted 1,4-benzoquinones[8] by including the resonance structure depicted in Figure 4b, **6′**. Besides the previously

[†] Present address: Institut für Medizinische Optik, Ludwig-Maximilians-Universität, Oettingenstrasse 67, D-80538 München, Germany.

10.1021/jp9907847 CCC: $18.00
Published on Web 08/18/1999

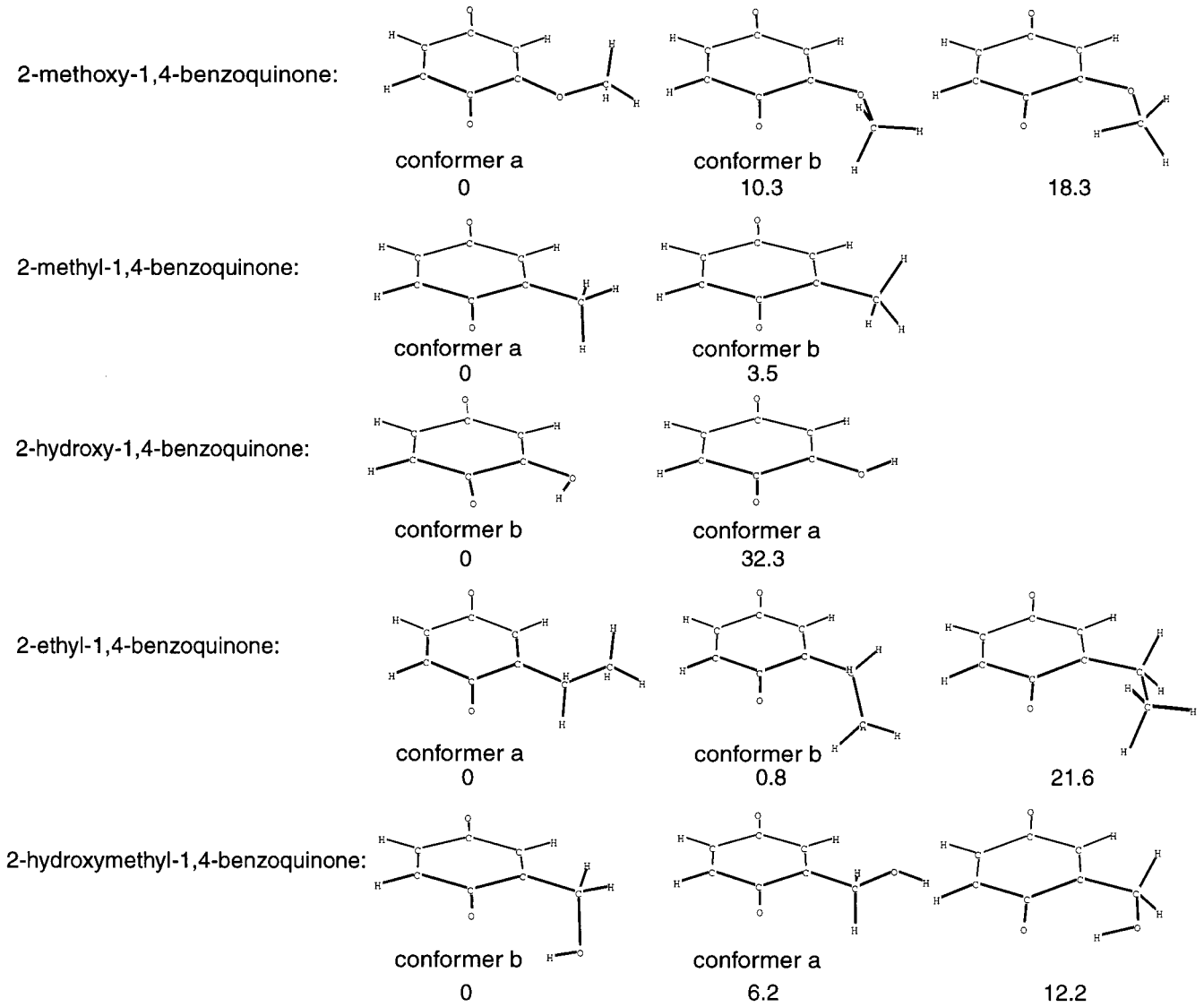

Figure 2. Minimized structures of 2-methoxy-1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone, 2-hydroxy-1,4-benzoquinone, and 2-hydroxymethyl-1,4-benzoquinone. For every molecule, conformers **a** and **b** are denoted in the figure and the relative energies of the conformers are given in kJ/mol.

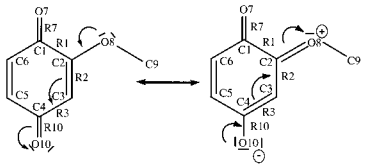

Figure 3. Simple resonance model which can explain the most dominant effects on structure and force constants upon methoxy substitution of 1,4-benzoquinone.

discussed weakening of bonds R2 and R10 and strengthening of bond R3, resonance structure **6′** also explains the strengthening of bond R7 and the weakening of bond R1. All substituent effects on the force constants of the CC and CO bonds we have found in conformer **a** of 2-methoxy-1,4-benzoquinone could thus be explained with the extended resonance model in Figure 4b. The reduction of the force constant of bond R7 upon rotation of the methoxy group of 2-methoxy-1,4-benzoquinone from conformer **a** to conformer **b**, however, could still not be understood with this model.

For 2-methyl-1,4-benzoquinone, we found an increase of the force constants of bonds R1 and R3 and a decrease of the force constants of bonds R2, R7, and R10. While the effects on bonds R1, R2, R3, and R10 could be explained with the electronic resonance effect, we had, in agreement with the literature,[5] to postulate a steric effect in order to explain the weakening of bond R7. This same steric effect could also be taken to explain the observed decrease of the force constant of the proximal C═O bond in conformer **b** of 2-methoxy-1,4-benzoquinone.

On the basis of additional computational investigations, we propose in this contribution a more general resonance model for substituted 1,4-benzoquinones which can account for all substituent effects without having to introduce a not-well-defined sterical effect. We could moreover derive some simple empirical rules which allow a rough prediction of how force constants are expected to change upon addition of a substituent to 1,4-benzoquinone.

Methods of Calculation

Density functional calculations were carried out with the program GAUSSIAN94.[10] The Becke exchange functional,[11] combined with the gradient corrected correlation functional of Perdew,[12] was applied (denoted as BP86). The 6-31G** basis set[13] was chosen for all calculations.

The quantum chemically derived Cartesian force constant matrixes were then read into the program GAMESS[14] which

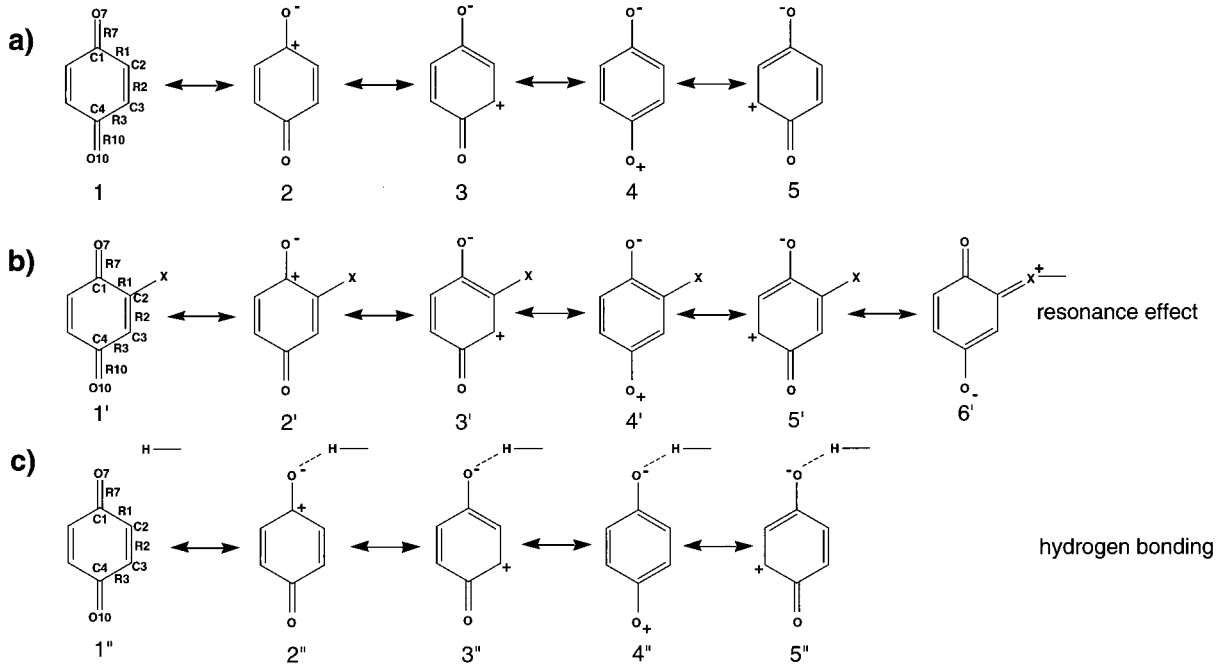

Figure 4. (a) Resonance structures which account for CC and CO bond lengths in 1,4-benzoquinone. (b) Extended resonance model which can additionally explain substituent effects on bond lengths and stretching force constants of bonds R1 and R7 (resonance effect). (c) Resonance structures due to the formation of internal hydrogen bonds as proposed in the present contribution (hydrogen bonding).

was employed to compute normal modes, force constants of internal coordinates and total energy distributions in order to assign the normal vibrations.[15,16] The set of internal coordinates chosen for this process basically corresponds to the one applied in earlier studies on benzene[17] and *p*-benzoquinone.[18] Valence coordinates and internal coordinates are defined in the corresponding references.[8,9]

The definition of the conformers **a** and **b** is given in Figure 1. Y can be an atom (a proton in 2-methyl- and 2-hydroxyl-1,4-benzoquinone) or a group (CH_3 in 2-methoxy- and 2-ethyl-1,4-benzoquinone or OH in 2-hydroxymethyl-1,4-benzoquinone). In conformer **a** Y points away from the proximal carbonyl group and disables strong internal hydrogen bonding while in conformer **b** Y points toward the carbonyl group and strong internal hydrogen bonding is possible. On the basis of our findings in 2-methoxy-1,4-benzoquinone, all molecules were first constrained to C_s symmetry during minimization. One imaginary frequency had been found in the planar conformers **b** of 2-ethyl-1,4-benzoquinone and 2-hydroxymethyl-1,4-benzoquinone. These two molecules were therefore additionally minimized without applying symmetry constraints. The resulting structures still exhibit internal hydrogen bonding; the C═O H interactions are, however, weaker than in the planar structures. All minimized structures are shown in Figure 2. Conformers **a** and **b** of each molecule are denoted in the figure, and the relative energies of the conformers are given in kJ/mol. Structural parameters discussed in this contribution are depicted in Figure 3. Molecular structures have been visualized using the program MacMolPlot.[19]

Results and Discussion

Two stable conformations had been determined in the case of 2-methoxy-1,4-benzoquinone. Both conformations are planar. In the more stable conformer (conformer **a**), the methoxy group is pointing away from the carbonyl group in ortho position, while in the second conformer (conformer **b**), sterical interactions between methoxy and carbonyl groups are believed to cause the higher energy. The calculated force constants of CC and CO bonds of both conformers are listed in Table 1. With a more detailed resonance model which is based on the mesomeric resonance structures of the unsubstituted 1,4-benzoquinone but also includes the dominant additional resonance structure attributable to the substituent at position 2 (see Figure 4b), the force constants found for conformer **a** can be well understood. Resonance structure **6′** which is caused by the substituent strengthens bonds R7 and R3 and weakens bonds R1, R2, and R10. This resonance structure thus explains the previously not understood significant strengthening of R7. The vibrational frequencies determined with this set of force constants agree well with experimental vibrational frequencies. The more stable conformer **a** therefore most likely corresponds to the structure which is found in solution.[9] Conformer **b**, however, is a possible stable conformation in 2,3-disubstituted quinones.[9,20,21] Even though the same resonance effects should be effective as in conformer **a**, a considerably smaller force constant of bond R7 is predicted in conformer **b** than that in conformer **a**. This force constant is even smaller than the corresponding force constant in 1,4-benzoquinone. We explain this significant weakening of bond R7 by introducing internal hydrogen bonding which, compared to 1,4-benzoquinone, stabilizes resonance structures **2**−**5**, yielding structures **2″** to **5″** depicted in Figure 4c. We refer to this mechanism in the following as hydrogen bonding. Resonance structures **2″**−**5″** make clear that the proposed internal hydrogen bonding cannot only explain the significant weakening of bond R7 compared to 1,4-benzoquinone but also weaker effects such as the strengthening of bonds R1 and R3 and the weakening of bonds R2 and R10. Analysis of the resonance structures shown in Figure 4 leads us to summarize the expected effect of a substituent on the force constants of the bonds R1, R2, R3, R7, and R10 as presented in Table 2. The two mechanisms thus affect the force constants of bonds R2, R3, and R10 in the same direction while they are of opposite sign for bonds R1 and R7. This explains the larger force constants for bonds R1 and R3 and the smaller force constants for bonds R2, R7, and R10 in conformer **b** of 2-methoxy-1,4-benzoquinone compared to its more stable conformer. We will,

TABLE 1. Selected Calculated Force Constants (mdyn/Å) of Conformers a and b of 2-Methoxy-1,4-benzoquinone, 2-Methyl-1,4-benzoquinone, 2-Ethyl-1,4-benzoquinone, 2-Hydroxy-1,4-benzoquinone, and 2-Hydroxymethyl-1,4-benzoquinone

	2-methoxy-1,4-benzoquinone		2-methyl-1,4-benzoquinone		2-ethyl-1,4-benzoquinone		2-hydroxy-1,4-benzoquinone		2-hydroxy-1,4-benzoquinone		1,4-benzoquinone[c]
parameter	conformer **a**[a]	conformer **b**	conformer **a**[b]	conformer **b**	conformer **a**	conformer **b**	conformer **a**	conformer **b**	conformer **a**	conformer **b**	
R1	4.029	4.002	4.167	4.208	4.174	4.173	4.051	4.539	4.286	4.407	4.309
R2	7.978	7.957	8.405	8.343	8.353	8.358	8.122	8.178	8.438	8.430	8.687
R3	4.675	4.866	4.412	4.450	4.437	4.431	4.676	4.818	4.444	4.368	4.309
R7	11.725	11.338	11.364	11.331	11.378	11.338	11.739	11.149	11.302	11.002	11.400
R10	11.174	11.028	11.321	11.307	11.332	11.339	11.212	11.151	11.346	11.401	11.400

[a] Reference 9. [b] Reference 8. [c] Reference 6.

TABLE 2. Summary of the Effect of Resonance Effects and Hydrogen Bonding on Selected Force Constants

parameter	no resonances	resonances in 1,4-benzoquinone	resonance effect because of substituent	hydrogen bonding
R1	C−C	+[a]	−	+
R2	C═C	−	−	−
R3	C−C	+	+	+
R7	C═O	−	+	−
R10	C═O	−	−	−

[a] + refers to a strengthening of a bond and − refers to a weakening.

in the following, however, demonstrate that the two mechanisms are not independent of each other and thus not simply additive.

In the case of methyl-substituted 1,4-benzoquinone,[8] only a weak resonance effect can be expected which should be of similar size in both conformers **a** and **b**. The differences of the corresponding calculated force constants are, indeed, small. The force constant of the proximal carbonyl group is considerably smaller in 2-methyl-1,4-benzoquinone than that in conformer **a** of 2-methoxy-1,4-benzoquinone. This can be explained with the much weaker resonance effect a $-CH_3$ group causes compared to that which can be expected of an −OY group. It is, however, even slightly smaller than the corresponding force constant in 1,4-benzoquinone. Even though the resonance effect is weak it should still result in an increase of the force constant of the bond C1═O7. The calculated decrease of this force constant is thus consistent with the suggested internal hydrogen bonding which, in the case of the methylated quinone, is certainly weak but exists in both conformers. We find that hydrogen bonding is slightly stronger in conformer **b** than in conformer **a**. Conformation **b** is the more stable conformation in 2,3-dimethyl-1,4-benzoquinone and in duroquinone which both show C═O stretching frequencies at lower energy than they are found in molecules having methyl groups in conformation **a**.[8] These experimental findings are thus in agreement with our model.

Inspection of the force constants of 2-methoxy-1,4-benzoquinone leads us to believe that bond R7 is more strongly affected by internal hydrogen bonding than by the resonance effect. The behavior of bonds R1 and R2 does not seem to be clearly predictable. In 2-methoxy-1,4-benzoquinone hydrogen bonding introduces a small reduction of the force constant of R1. On the other hand, the slightly stronger internal hydrogen bonding in conformer **b** of 2-methyl-1,4-benzoquinone slightly increases the same force constant. In both molecules, bond R2 seems to be only little affected by hydrogen bonding. We find a small decrease of the force constant of R2 of 0.062 and 0.021 mdyn/Å in 2-methyl- and 2-methoxy-1,4-benzoquinone, respectively. We assume that the two mechanisms, i.e., resonance effect and hydrogen bonding, are not independent and that smaller effects such as those found for bonds R1 and R2 cannot be predicted unambiguously.

Although hydrogen bonding generally stabilizes a molecular structure, conformer **b** of 2-methoxy-1,4-benzoquinone is less stable than conformer **a**. Also in 2-methyl-1,4-benzoquinone we have stated that a stronger internal hydrogen bond is found in the slightly less stable conformer **b** than in conformer **a**. To explain these findings we have in a recent contribution compared the structures of a planar 2-methoxy-3-methyl-1,4-benzoquinone and a complex of 3-methyl-1,4-benzoquinone with methanol.[21] We have found that the C═O H distance in 2-methoxy-3-methyl-1,4-benzoquinone is more than 0.6 Å shorter than the distance in the complex. Sterical constraints thus cause the formation of nonideal, too short hydrogen bonds which raise

the energy but might on the other hand increase the weight of resonance structures **2″**−**5″** in Figure 4c.

To confirm our model we have carried out calculations on 2-hydroxy-1,4-benzoquinone and 2-hydroxymethyl-1,4-benzoquinone which are expected to form stronger internal hydrogen bonds in conformation **b** than those in the previously discussed molecules. While 2-hydroxy-1,4-benzoquinone is expected to show a strong hydrogen bonding and a strong resonance effect, internal hydrogen bonding should be clearly dominant in conformer **b** of 2-hydroxymethyl-1,4-benzoquinone. As in the case of 2-methoxy- and 2-methyl-1,4-benzoquinone we find two stable conformations for both molecules corresponding to conformers **a** and **b** in Figure 1. The calculated force constants are listed in Table 1.

In conformer **a** of 2-hydroxy-1,4-benzoquinone we find an increase of the force constants of bonds R7 and R3 and a decrease of the force constants of bonds R1, R2, and R10 compared to the force constants of 1,4-benzoquinone. These effects are thus correctly predicted by the resonance model shown in Figure 4b. As should be expected, the resonance effect caused by the oxygen atom of the substituent is of similar size in conformers **a** of 2-methoxy-1,4-benzoquinone and 2-hydroxy-1,4-benzoquinone which results in similar force constants. In conformer **b** of 2-hydroxy-1,4-benzoquinone strong internal hydrogen bonding reduces the force constants of bonds R7 and R10 and increases those of bonds R1 and R3. All these effects are correctly predicted by the proposed hydrogen bonding in Figure 4c. The force constant of bond R2, however, is only weakly affected by this combination of strong hydrogen bonding and strong resonance effect. This finding supports the previously made suggestion that the two resonance mechanisms are not independent.

Only a weak resonance effect can be expected in 2-hydroxymethyl-1,4-benzoquinone. For conformer **a** which also lacks strong internal hydrogen bonds, the calculated force constants are similar to those calculated for the two conformers of 2-methyl-1,4-benzoquinone. In conformer **b**, however, we find a strong internal hydrogen bond, which, according to Figure 4c and Table 2 results in an increase of the force constants of bonds R1 and R3 and a decrease of the force constants of bonds R2 and R7. No effect on bond R10 is, however, found. In the case of the symmetry constrained planar structure of conformer **b**, even stronger effects are found. Here, the calculated force constants are 4.555, 8.174, 4.508, 10.755, and 11.240 mdyn/Å for bonds R1, R2, R3, R7, and R10, respectively. These findings thus support the suggestion made above that short hydrogen bonds which are caused by sterical constraints might raise the weight of resonance structures **2″**−**5″**. Since hydrogen bonding is clearly dominant in this molecule, our calculated force constants are in good agreement with the predicted effects on the force constants upon hydrogen bonding as summarized in Table 2.

Several times above we have stated that resonance effect and hydrogen bonding are most likely not independent. As soon as resonance effect and hydrogen bonding occur simultaneously the net effect on a force constant is not simply the sum of effects expected by either resonance or hydrogen bonding. This is nicely illustrated when we compare 2-methoxy-1,4-benzoquinone and 2-ethyl-1,4-benzoquinone (the force constants of the latter molecule are also included in Table 1). In conformation **a** the strong resonance in 2-methoxy-1,4-benzoquinone increases the force constant of R7 by 0.325 mdyn/Å and reduces that of R10 by 0.226 mdyn/Å. A comparable resonance effect can also be expected in conformer **b**. If that assumption is correct, internal hydrogen bonding caused by the methoxy substituent reduces the force constant of R7 by 0.39 mdyn/Å and increases that of R10 by 0.15 mdyn/Å. In conformer **a** of 2-ethyl-1,4-benzoquinone, the force constants of both carbonyl bonds are only slightly affected due to a weak resonance effect and weak hydrogen bonding. A methyl group is not expected to differ dramatically from a methoxy group with respect to its ability of forming hydrogen bonds. Nevertheless the C═O force constants of both conformers of 2-ethyl-1,4-benzoquinone differ only very slightly, i.e., the hydrogen bond formed by the methyl group is considerably weaker than that formed by the methoxy group. The calculations thus suggest that a strong resonance effect allows for a strong internal hydrogen bonding in the case of conformer **b**. Hydrogen bonding therefore tends to compensate for the resonance effect.

Density functional methods have shown to very accurately predict force constant changes caused by addition of a substituent to 1,4-benzoquinone. However, for many cases it would be desirable to have some simple empirical rules for the prediction of such force constant changes. Although the previously discussed coupling of the two mechanisms makes this task difficult we can give the following crude rules.

(R1) The force constant decreases by 0.25 mdyn/Å upon −OY substitution in conformation **a** (pure resonance effect). Upon $-CH_2$ OH substitution in conformation **b**, the force constant increases by 0.1 mdyn/Å (almost pure hydrogen bonding). Upon $-CH_2$ Y (Y = H, CH_3) substitution the force constant decreases by 0.1−0.2 mdyn/Å. Compared to conformer **a**, an increase by 0.15 or 0.5 mdyn/Å is found upon hydrogen bonding with an −OH group forming either a five- or six-membered ring.

(R2) The force constant is generally reduced upon substitution (see also Table 2). Upon −OY substitution a reduction of 0.5−0.7 mdyn/Å is found independent of the substituents conformation. Upon $-CH_2-OH$ or $-CH_2-CH_3$ substitution in conformation **a**, the force constant decreases by about 0.3 mdyn/Å. Upon $-CH_2-OH$ or $-CH_2-CH_3$ substitution in conformation **b**, a decrease of 0.25−0.5 mdyn/Å can be expected.

(R3) The force constant generally increases upon substitution (see also Table 2). An −OY substitution in conformation **a** causes an increase of 0.4 mdyn/Å. Upon $-CH_2$ Y substitution in conformation **a**, the force constant increases by 0.15 mdyn/Å. A large increase of 0.55 mdyn/Å can be expected upon −OY substitution combined with −OH or −CH hydrogen bonding.

(R7) The force constant increases by 0.3 mdyn/Å upon −OY substitution and stays nearly unaffected upon $-CH_2$ Y substitution in conformation **a**. Upon $-O-CH_3$ substitution, the force constant of conformer **b** is 0.4 mdyn/Å smaller than that of conformer **a**. Upon −O−H or $-CH_2-OH$ substitution, the force constant of conformer **b** is 0.3−0.6 mdyn/Å smaller than that of conformer **a**.

(R10) The force constant is generally reduced upon substitution (see also Table 2). An oxygen atom connected to the ring such that no hydrogen bonds can be formed reduces the force constant by 0.2 mdyn/Å. An oxygen atom connected to the ring combined with any type of hydrogen bonding reduces the force constant by 0.25−0.35 mdyn/Å. A $-CH_2$ Y substituent forming a hydrogen bond within a five-membered ring reduces the force constant by 0.01 mdyn/Å. A larger reduction of 0.1−0.15 mdyn/Å is found when the hydrogen bond is formed within a six-membered ring.

These rules can only give some rough predictions of expected force constant changes upon addition of a substituent to 1,4-benzoquinone. Note that due to the coupling of the two

mechanisms, we can in some cases only predict the effect of hydrogen bonding in conformer **b** compared to that in conformer **a** and not compared to that in the unsubstituted 1,4-benzoquinone. The most certain predictions are clearly those for structures which exhibit either a dominant resonance mechanism (−OR substituted ring in conformation **a**) or dominant internal hydrogen bonding (−CR_2 OH substitution in conformation **b**). In molecules which show a strong resonance effect combined with internal hydrogen bonding, on the other hand, the two effects are so strongly coupled that force constant changes compared to unsubstituted 1,4-benzoquinone cannot be predicted reasonably.

To provide some information about a more direct observable than force constants we close this paragraph with a short discussion of selected bond lengths of the molecules discussed above. Calculated bond lengths are listed in Table 3. A strong resonance effect as found in conformers **a** of 2-methoxy-1,4-benzoquinone or 2-hydroxy-1,4-benzoquinone elongates bonds R1, R2, and R10 and shortens bonds R3 and R7 compared to 1,4-benzoquinone. Strong internal hydrogen bonding as it is found in conformer **b** of 2-hydroxymethyl-1,4-benzoquinone elongates predominantly the bond length of the CO double bond R7 in agreement with its decreased force constant. Despite the found increase of the force constant of bond R1 upon internal hydrogen bonding, we find compared to conformer **a** of this molecule only a slight elongation of this bond. This can most likely be attributed to sterical interactions attributable to the formation of a six-membered ring upon hydrogen bonding. This explanation is supported by a widening of the HO−$C(H_2)$-ring angle from 109.5° in conformer **a** to 118.3° in conformer **b**. Bonds R7 and R10 are generally lengthened upon hydrogen bonding except in the methyl and ethyl substituted quinone where they occasionally stay unchanged. Double bond R2 is elongated in all molecules except in 2-hydroxy-1,4-benzoquinone, and single bond R3 is shortened in all cases upon internal hydrogen-bond formation. Although the alterations of bond lengths due to the resonance effect and internal hydrogen bonding are often very small nearly all structural changes are in agreement with the rules given in Table 2.

Conclusions

In this contribution we have presented a model which allows a qualitative prediction of how the force constants of the CC and CO bonds of 1,4-benzoquinone are affected upon addition of a substituent. Using density functional methods we have demonstrated that substituent effects on the vibrational spectrum of 1,4-benzoquinone can be explained by a superposition of two resonance mechanisms. One of these resonance mechanisms is caused by an electronic interaction of the substituents p-orbital with the delocalized π-system of the quinone ring. A second type of resonance mechanism only occurs when internal hydrogen bonds between the substituent the proximal carbonyl group can be formed. This second effect efficiently reduces the force constant of the proximal carbonyl group and is the main source for findings which had previously been attributed to a not-well-defined steric effect.

The two resonance mechanisms have found to be closely coupled. A strong resonance effect increases the electron density of the proximal carbonyl bond and thereby enhances its potential as a hydrogen-bond acceptor. Upon hydrogen bonding, the very same bond is however weakened such that the strengthening of the proximal carbonyl bond attributable to a strong resonance effect is basically neutralized by an enhanced internal hydrogen bonding. Although the interference of the two mechanisms

TABLE 3. Selected Calculated Bond Lengths of Conformers a and b of 2-Methoxy-1,4-benzoquinone, 2-Methyl-1,4-benzoquinone, 2-Ethyl-1,4-benzoquinone, 2-Hydroxy-1,4-benzoquinone, and 2-Hydroxymethyl-1,4-benzoquinone

	2-methoxy-1,4-benzoquinone		2-methyl-1,4-benzoquinone		2-ethyl-1,4-benzoquinone		2-hydroxy-1,4-benzoquinone		2-hydroxymethyl-1,4-benzoquinone		1,4-benzoquinone[c]
parameter	conformer **a**[a]	conformer **b**	conformer **a**[b]	conformer **b**	conformer **a**	conformer **b**	conformer **a**	conformer **b**	conformer **a**	conformer **b**	
R1	1.515	1.512	1.504	1.507	1.505	1.504	1.513	1.507	1.496	1.499	1.490
R2	1.369	1.372	1.361	1.362	1.361	1.362	1.366	1.366	1.359	1.359	1.355
R3	1.471	1.463	1.483	1.482	1.483	1.483	1.470	1.465	1.482	1.485	1.490
R7	1.233	1.239	1.240	1.240	1.240	1.240	1.233	1.245	1.241	1.246	1.239
R10	1.242	1.244	1.240	1.241	1.241	1.241	1.242	1.243	1.240	1.239	1.239

[a] Reference 9. [b] Reference 8. [c] Reference 6.

makes the formulation of general rules about how a substituent affects the force constants of the CC and CO bonds of 1,4-benzoquinone difficult, we have been able to give some rough estimates for such effects. In some cases and because of the interplay of the two mechanisms, such rules cannot be formulated relative to 1,4-benzoquinone but only relative to the other conformer.

Acknowledgment. The author thanks Jacques Breton, Eliane Nabedryk, Jean-René Burie, Claude Boullais, and Paul Tavan for numerous interesting discussions on the vibrational spectra of quinones and J. Robert Huber for critically reading the manuscript. Computing time has been provided by the Rechenzentrum der Universität Zürich and by the Centro Svizzero di Calcolo Scientifico (CSCS) in Manno. Support by the Swiss National Foundation (Project 31-49630.96) is gratefully acknowledged.

References and Notes

(1) Kirmaier, C.; Holten, D. *Photosynth. Res.* **1987**, *13*, 225.
(2) Parson, W. W. In *New Comprehensive Biochemistry: Photosynthesis*; Amesz, J., Ed.; Elsevier: Amsterdam, 1987; p 43.
(3) Boxer, S. G.; Goldstein, R. A.; Lockhart, D. J.; Middendorf, T. R.; Takiff, L. *J. Phys. Chem.* **1989**, *93*, 8280.
(4) Flaig, W.; Beutelspacher, H.; Riemer, H.; Kälke, E. *Liebigs Ann. Chem.* **1968**, *719*, 96.
(5) Meyerson, M. L. *Spectrochim. Acta* **1985**, *41*, 1263.
(6) Nonella, M.; Tavan, P. *Chem. Phys.* **1995**, *199*, 19.
(7) Nonella, M. *J. Mol. Struct. (THEOCHEM)* **1996**, *362*, 7.
(8) Nonella, M. *J. Phys. Chem.* **1996**, *100*, 20148.
(9) Nonella, M.; Brändli, C. *J. Phys. Chem.* **1996**, *100*, 14549.
(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Gaussian, Inc.: Pittsburgh, PA, 1995.
(11) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(12) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
(13) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; deFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.
(14) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J, H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
(15) Pulay, P.; Török, F. *Acta Chim. Hung.* **1965**, *47*, 273.
(16) Keresztury, G.; Jalsovszky, G. *J. Mol. Struct.* **1971**, *10*, 304.
(17) Pulay, P.; Fogarasi, G.; Boggs, J. E. *J. Chem. Phys.* **1981**, *74*, 3999.
(18) Liu, R.; Zhou, X.; Pulay, P. *J. Phys. Chem.* **1992**, *96*, 4255.
(19) Bode, B. M.; Gordon, M. S. *J. Mol. Graphics Model.* **1999**. In press.
(20) Boullais, C.; Nabedryk, E.; Burie, J.-R.; Nonella, M.; Mioskowski, C.; Breton, J. *Photosynth. Res.* **1998**, *55*, 247.
(21) Nonella, M.; Boullais, C.; Mioskowski, C.; Nabedryk, E.; Breton, J. *J. Phys. Chem.* **1999**, *103B*, 6363.