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DFT Calculations and IR Studies on 2-Hydroxy-1,4-naphthoquinone and Its 3-Substituted Derivatives

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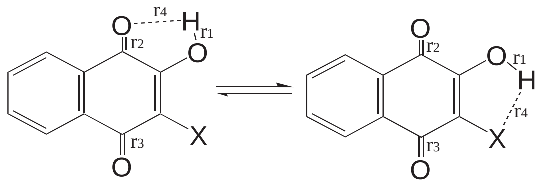
The carbonyl stretching vibrations of the title compounds were studied using DFT calculations at the B3LYP/6-311G** level and the IR spectra in terms of the intramolecular hydrogen bond (H-bond). Two types of H-bond systems were examined: type I in which the H-atom of the OH group points towards to neighboring carbonyl oxygen atom, and type II in which the H-atom points away. The results of the DFT calculations show that the IR spectra of 2-hydroxy-1,4-naphthoquinone (**1**), 3-chloro-2-hydroxy-1,4-naphthoquinone (**2**), 3-bromo-2-hydroxy-1,4-naphthoquinone (**3**), and 2-hydroxy-3-iodo-1,4-naphthoquinone (**4**) in CCl_4, are well explained by the assumption of the two types of H-bond systems.

The hydrogen bond is one of the most important chemical concepts for the explaining chemical properties in many regions.[1] A hydrogen bond forms between two or more molecules (intermolecular H-bond), and sometimes within the molecule itself (intramolecular H-bond). Sometimes, thanks to the hydrogen bond the chemical properties and the structure of the compounds are changed dramatically. Here, we have studied the stretching vibrations of the carbonyl groups via the intramolecular H-bond in **1** and its 3-substituted derivatives. Compound **1** was initially obtained from *lawsonia inermis* as one of the hydroxy-1,4-naphthoquinone derivatives of the natural products, and it has been thought that it has an intramolecular H-bond by some authors (Scheme 1).[2,3] Padhye and Kulkarni reported, on the other hand, that no intramolecular hydrogen bond was found in **1**.[4,5] Compound **1** and its various derivatives have also been studied by many authors from the perspective of its synthesis, structure,[6–8] and pharmacology or biochemistry.[9–11] Compound **1** has also been investigated as an indicator, which shows as a pale yellow color in acidic solutions and brown-red in high pH solutions.[12] The property of the OH group in **1** is different from that of 5-hydroxy-1,4-naphthoquinone (juglone), which is a structural isomer of **1**. For example, the pK_a of juglone is 8.9[13] and similar to that of phenol (pK_a = 9.82),[14] but the pK_a of **1** is smaller than that of phenol as shown in Table 1. This is due to the difference in the intramolecular hydrogen bond in each molecule. Here, we have studied the properties of the intramolecular H-bonds and the carbonyl groups of **1** and its 3-substitute derivatives, i.e., 3-chloro-2-hydroxy-1,4-naphthoquinone (**2**), 3-bromo-2-hydroxy-1,4-naphthoquinone (**3**), 2-hydroxy-3-iodo-1,4-naphthoquinone (**4**), and 2-hydroxy-3-methyl-1,4-naphthoquinone (**5**) from both experimental and theoretical perspectives. The UV–vis and NMR spectra were also measured for compounds **1** to **5**.



Scheme 1.

Table 1. The Results of IR, NMR, and pK_a

Compound	ν/cm^{-1}	$\Delta\nu^{a)}$	δ/ppm	$\Delta\delta^{a)}$	pK_a
1	3411	—	7.38	—	4.40
2	3394	−17	7.66	0.28	2.50
3	3392	−19	7.83	0.45	2.45
4	3388	−23	8.05	0.67	2.35
5	3411	0	7.31	−0.07	5.30

a) The differences from the values of **1**.

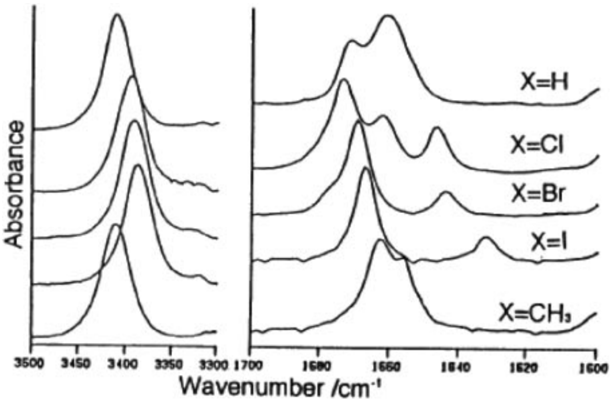


Fig. 1. IR spectra of **1** and its derivatives. The left half is O–H stretching vibration region and the right half is C=O stretching vibration region.

Figure 1 shows the IR spectra of **1**–**5** in CCl_4 in the region of OH stretching vibration (ν(OH)). Compounds **1** and **5** give almost the same frequencies for ν(OH), however, the peak position for **2** to **4** gradually shifts to low frequencies. Table 1 lists the ν(OH) along with the ^{1}H NMR chemical shifts and pK_a values. From these results we see that the properties of the OH proton are all in accordance with our native chemical intuition, i.e., a small pK_a value means that the proton is easily released, and this corresponds to the strength of the OH bond, which leads to a lower ν(OH). Also, a small amount of charge density on the proton leads to lower field chemical shifts. Judging from the OH group behavior, the strength of the interaction between the hydrogen atom of the OH group and the oxygen atom of the neighboring carbonyl group increases from **2** to **4**. Figure 1 shows that the IR spectra of **2**–**4** in the region of 1600–1700 cm^{-1}, which correspond to the C=O stretching

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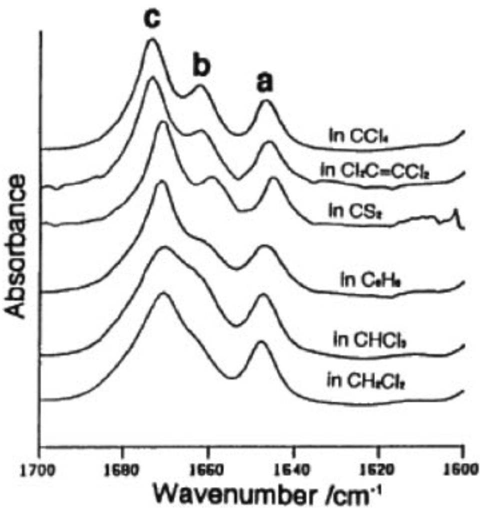

Fig. 2. IR spectra of **2** in various solvents.

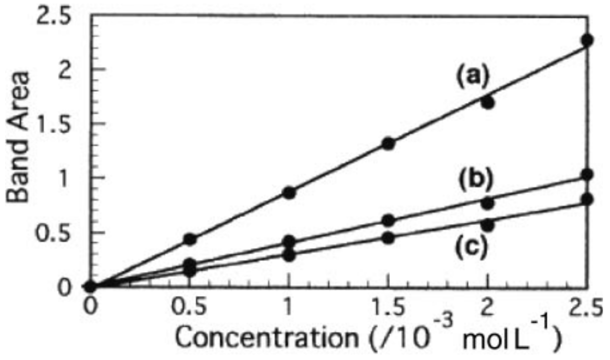

Fig. 3. The relation between the band area and the concentration of **2** in CCl_4. (**a**), (**b**), (**c**) correspond to the bands shown in Fig. 2.

vibrations, are different from those of **1** and **5**. In this region, there are three peaks for **2** and **3**. The IR spectra of **2** shows three clearly distinct peaks, but for **3**, the highest frequency peak appears as a shoulder. We tried to characterize these C=O stretching vibrations and examined the above-mentioned OH proton properties structurally. Figure 2 shows the IR spectra of **2** in various solvents. We define, hereafter, the peak near $1670\,cm^{-1}$ is band **c**, the peak near $1660\,cm^{-1}$ is band **b**, and the peak at $1650\,cm^{-1}$ is band **a**. Interestingly, band **b** became broad or a shoulder in polar solvents. The three peaks observed for **2**–**4** may be considered as a result of Fermi resonance by an overtone or a combination of some vibrational modes. In fact, Jose et al. explained that three peaks for **2** observed in the solid state were due to the Fermi resonance.[15] We may assume, however, taking account of the results of the DFT calculations given below, that these three peaks observed in the region $1600–1700\,cm^{-1}$ all correspond to the C=O stretching vibration modes. Moreover the IR spectra of **2** showed that the absorbance ratios among these three peaks do not depend on the concentration of **2** in the range of the concentrations studied, as shown in Fig. 3. The same results were obtained for **3**. Therefore, we cannot explain the difference in the IR spectra between **2** and **1** or **5** by invoking an intermolecular interaction, such as the formation of a dimer or aggregate.[16] We measured the IR spectra of **2** in the mixed solvents of CCl_4 and CH_2Cl_2, and the results are given in Table 2. The relative absorption intensity of band **a** mainly does not change. However, the relative intensity of band **b** decreases and that of band **c** increases as the polarity of the solvent becomes high. The result of the IR spectra suggests that the existence of two types of conformers. The observed carbonyl stretching frequencies are summarized in Table 3.

Table 2. The Carbonyl Stretching Frequency (ν(C=O)) of the Mixed Solvents ($/cm^{-1}$)

%[a)]	Band **c**	Band **b**	Band **a**
100	1671 (0.76)[b)]	1661 (0.05)	1647 (0.19)
50	1672 (0.70)	1662 (0.10)	1647 (0.20)
20	1673 (0.63)	1662 (0.17)	1646 (0.20)
0	1673 (0.57)	1662 (0.24)	1646 (0.19)

a) The volume percentage of CH_2Cl_2 to CCl_4. b) The values in parentheses are relative intensity.

Table 3. The Observed ν(C=O) of **1** and Its Derivatives ($/cm^{-1}$)[a)]

Compound	Band **c**	Band **b**	Band **a**
1	1672	1661	—
2	1673	1662	1646
3	1677	1669	1644
4	—	1667	1632
5	—	1662	1655

a) We set the highest frequency peak as band **c**, next one band **b** and the lowest one band **a**, respectively. For the compounds **4** and **5**, we could not find the corresponding highest frequency peak, and for **1** we cannot find the lowest one.

The C=O stretching vibration frequencies obtained by the DFT/6-311G** level calculations are given in Table 4 along with the bond lengths and atomic distances (see Scheme 1). The large differences between these bond lengths and atomic distances are not found for the sense of the OH bond. For both type I and II, two C=O groups give a pair of stretching vibration frequency peaks: one is the symmetric vibration mode and the other is the antisymmetric mode for all compounds. The calculated lower frequency peak (symmetric mode) of type II is nearly equal to that of the calculated higher frequency peak (antisymmetric mode) of type I. The IR spectra in the mixed solvents show that the relative intensity of peak **b** decreases and that of peak **c** increases as the polarity of the solvent mixture increases, and the DFT calculations, taking the solvent effects into account, show that the relative intensity of the higher frequency peak of type II increases and that of type I decreases as the polarity of the solvent increases.[17] We may assume that the band **c** belongs to the calculated higher peak of the type II structure, band **a** belongs to the calculated lower peak of the type I structure, and band **b** belongs to both types I and II structures. It is possible that band **a** is the C=C stretching vibration of the quinone ring, and bands **b** and **c** are the carbonyl vibrations from type I only. The calculated frequencies of the C=C stretching mode, however, are all very lower than those of the carbonyl regions. Thus, our assignments agree with that of the IR spectra. For **1**, band **a** could not be found due to the overlap with band **b**, and as the DFT calculations suggest, an equilibrium between the

Table 4. The DFT Calculations of ν(CO)[a)], the Charge Density of H-atom and the Bond Lengths (Scheme 1) of the Compounds **1** to **5**

Compound and Type		Band **c**/cm^{-1}	Band **b**/cm^{-1}	Band **a**/cm^{-1}	q(H)[b)]	$r1$/Å	$r2$/Å	$r3$/Å	$r4$/Å
1	I	—	1669(1.00)	1663(0.02)	0.273	0.977	1.223	1.221	2.003
	II	1700(0.74)	1669(0.63)	—	0.258	0.965	1.212	1.221	—
2	I	—	1682(0.40)	1663(0.55)	0.263	0.977	1.223	1.215	1.995
	II	1699(0.886)	1681(0.63)	—	0.264	0.970	1.212	1.215	2.428
3	I	—	1679(0.39)	1663(0.51)	0.262	0.978	1.223	1.215	1.989
	II	1700(0.90)	1677(0.31)	—	0.252	0.974	1.212	1.216	2.495
4	I	—	1621(0.26)	1609(0.06)	0.376	1.002	1.237	1.243	1.963
	II	1644(0.48)	1624(0.07)	—	0.376	1.011	1.251	1.242	2.661
5	I	—	1661(1.00)	1659(0.13)	0.259	0.976	1.225	1.222	1.989
	II	1693(0.88)	1658(0.63)	—	0.247	0.964	1.214	1.222	—

a) The calculated values are multiplied by the factor 0.967 except **4**. For the molecule **4** we used the basis set 3-21G** and the factor 0.962. The values in parentheses are relative intensity. b) On the H-atom of the hydroxy group.

two conformers may exist for **1** in CCl_4. On the other hand, for compound **5**, the experimental spectra are clearly explained by the calculated results for type I only.

Experimental and Calculations

Compound **1** was obtained commercially (Eastman Kodak), and the four 3-substituted derivatives were synthesized by the method given in the literature.[18] The samples were purified by recrystallization from the appropriate solvents, and the measurements were performed at room temperature. The IR spectra were measured on a Bio-Rad FTS30 spectrometer using a 1 mm solution cell with KBr window. The NMR spectra were obtained in $CDCl_3$ solutions on a JEOL JMN270 spectrometer. The pK_a values were determined from the usual spectrophotometric method by using a Hitachi-Horiba F-7LC pH meter and a Hitachi 228 spectrophotometer. The wavelengths used for the pK_a determination were 450, 465, 480, 485, and 470 nm, which are the maximum absorptions for compound **1** to **5**, respectively, at various pH solutions.

The DFT calculations were performed at the Research Center for Computational Science (Okazaki, Japan) and the Information Center of Hirosaki University by using the program Gaussian 98,[19] at the B3LYP/6-311G** level. The geometrical parameters were optimized for the molecules **1** to **3** and **5**. For the molecule **4**, the B3LYP/3-21G** level calculations were performed.

References

1 G. C. Pimentel, A. L. McClellan, *The Hydrogen Bond*, W. H. Freeman and Company, San Francisco and London, **1960**; *Hydrogen Bonds*, ed. by P. Schuster, Springer-Verlag, Berlin and Tokyo, **1984**; A. Kollman, *Applications of Electronic Structure Theory*, ed. by H. F. Schaefer, III, Plenum Press, New York, **1997**, Vol. 4, Chap. 3.

2 J. H. Richards, S. Walker, *Trans. Faraday Soc.* **1961**, *57*, 399.

3 A. W. Baker, A. T. Shulgin, *J. Am. Chem. Soc.* **1958**, *80*, 5358.

4 S. B. Padhye, B. A. Kulkarni, *J. Phys. Chem.* **1975**, *79*, 927.

5 S. B. Padhye, B. A. Kulkarni, *J. Magn. Reson.* **1974**, *16*, 150.

6 L. F. Fieser, *J. Am. Chem. Soc.* **1948**, *70*, 3165.

7 A. C. Baillie, R. H. Thomson, *J. Chem. Soc. C* **1966**, 2184.

8 L. F. Fieser, *J. Am. Chem. Soc.* **1928**, *50*, 439.

9 S. Subramanian, M. M. C. Ferreira, M. Trsic, *Struct. Chem.* **1998**, *9*, 47.

10 N. Curreli, F. Sollai, L. Massa, O. Comandini, A. Rufo, E. Sanjust, A. Rinaldi, A. C. Rinaldi, *J. Basic Microbiol.* **2001**, *41*, 253.

11 P. J. Jewess, J. Higgins, K. J. Berry, S. R. Moss, A. B. Boogaard, B. P. S. Khambay, *Pest Manage. Sci.* **2002**, *58*, 234.

12 S. S. Saehney, *J. Indian Chem. Soc.* **1977**, *50*, 641.

13 M. G. Ettlinger, *J. Am. Chem. Soc.* **1950**, *72*, 3085.

14 K. C. Joshi, P. Singh, G. Singh, *Z. Natureforsch., B: Chem. Sci.* **1977**, 890.

15 L. S. Prabhumirashi, V. D. Kelkar, C. I. Jose, *Indian J. Phys., B* **1984**, *58*, 570.

16 N. R. Dhumal, A. V. Todkary, S. Y. Rane, S. P. Gejji, *Theor. Chem. Acc.* **2005**, *113*, 161.

17 For the band **c** of **2**, the relative intensities of type I and type II calculated by using B3LYP/6-311G** with the solvent effect are (0.36:0.80), (0.31:0.74) for $\varepsilon = 2.229$ and $\varepsilon = 7.58$, respectively. The Onsager model was used for the solvent effect calculations.

18 2-Hydroxy-3-methyl-1,4-naphthoqinone: F. Radt, *Elsevier's Encyclopedia of Organic Chemistry*, **1952**, Vol. 12B; 3-Chloro-2-hydroxy-1,4-naphthoquinone: F. Radt, *Elsevier's Encyclopedia of Organic Chemistry*, **1952**, Vol. 12B; 3-Bromo-2-hygroxy-1,4-naphthoquinone and 2-hydroxy-3-iodo-1,4-naphthoquinone: F. Kehrmann, B. Mascioni, *Berichte* **1895**, *27*, 345.

19 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98, Revision A.11.2*, Gaussian, Inc., Pittsburgh, PA, **2001**.