Theoretical Study on Some Nitroresorcinols: Intramolecular Hydrogen Bonding

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The intramolecular hydrogen bonding of 2-nitroresorcinol and 4,6-dinitroresorcinol is investigated by both an ab initio method and density functional theory (DFT). We have considered several possible conformations in which the hydrogen bonding is hindered by rotation of the hydroxyl groups in order to see how much molecular structures are affected by hydrogen bonding. The results show that the geometries of the benzene rings in nitroresorcinols are somewhat changed by intramolecular hydrogen bonding. Geometrical parameters calculated from ab initio and DFT calculations at the higher levels of theory are also in good agreement with data of electron diffraction experiments. On the other hand, the planarity of a nitro group is very responsible not only for hydrogen bonding but also for nonbonding interactions between two oxygen atoms in these compounds. We have also estimated the energy of hydrogen bonding by comparing the molecular energies between two different conformers of a given molecule. The magnitude of computed values from both ab initio and DFT methods is about 10 kcal/mol per hydrogen bond.

Introduction

Hydrogen bonding is a very interesting issue because it plays an important role in certain chemical and biochemical processes. Particularly intramolecular hydrogen bonding can greatly have an influence on conformations of a molecular geometry and on equilibria of reactions such as keto−enol tautomerisms and isomerizations. This directional nonbonding interaction between a hydrogen atom and an electronegative atom such as F, O, and N is not so strong since the interaction energy may be about 5−10 kcal/mol. However, it can sometimes affect the overall molecular geometry seriously enough to change the positions of particular atoms participating in intramolecular hydrogen bonding. It is also responsible for the stability of a predominant conformation.

For the past few decades, many experimental and theoretical investigations of intramolecular hydrogen bonding have been performed.[1−20] However, the gas-phase electron diffraction studies for nitrophenol,[11] 2-nitroresorcinol,[12] and 4,6-dinitroresorcinol[13] have been recently done, and these results show that the geometries of benzene rings in these nitroresorcinols somewhat deviate from structures of benzene rings in phenol and nitrobenzene. In nitroresorcinols with hydrogen bonds, an intramolecular hydrogen bond between a hydroxyl group and π-electron system in a nitro group is supposed to make a six-membered ring, which causes the O···H interaction onto the resonance of benzene ring. Hence, Gilli et al.[14−16] suggested that the formation of this intramolecular hydrogen bond was aided by a sort of such resonance. It is now called resonance-assisted hydrogen bonding (RAHB),[14] which was first introduced to describe the hydrogen bonding observed in a number of crystal molecules.

The accumulated results of theoretical studies during the past decade show that ab initio calculations can provide us with reliable information about molecular properties at the ground state. In addition, the incorporation of electron correlation beyond Hartree−Fock (HF) approximations is required to describe the equilibrium geometry for an RAHB system containing the intramolecular hydrogen bonding.[14,17] However, an enormous computational cost beyond HF approximations has still prevented one from computing molecular properties of larger molecules at the higher levels of theory despite a dramatic development in computer hardwares and software algorithms. On the contrary, the density functional theory (DFT) can be an alternative to ab initio methods since it is sufficiently accurate and applicable to any systems of interest, even for larger molecules. DFT is practically a much cheaper technique than conventional ab initio methods especially in terms of electron correlation. The results of previous studies[18−20] indicate that the calculated molecular properties with the DFT methods are in excellent agreement with available experimental data in benzene analogues as well as systems containing the hydrogen bonding.

In this article, we are going to investigate both the molecular structures and characteristics of intramolecular hydrogen bonding for 2-nitroresorcinol and 4,6-dinitroresorcinol in terms of molecular orbitals by an ab initio method as well as the density functional theory. We compare the optimized geometrical parameters with the experimental values and discuss the differences of calculated structural parameters between 2-nitroresorcinol and 4,6-dinitroresorcinol. Finally, we estimate the hydrogen bonding energies of these molecules by comparing the molecular energies among their possible conformers at the various levels of theory.

Computational Details

For nitroresorcinols, calculations are performed on conformers with O-H bonds syn or anti to adjacent nitrogroups. Possible confomers for 2-nitroresorcinol and 4,6-nitroresorcinol are shown in Figure 1 along with numbering of atoms for these two molecules. Three conformers for each molecule are subdivided into three groups: syn−syn conformers with two hydrogen bonds, syn−anti conformers with a single hydrogen bond, and anti−anti conformers with no hydrogen bond at all.

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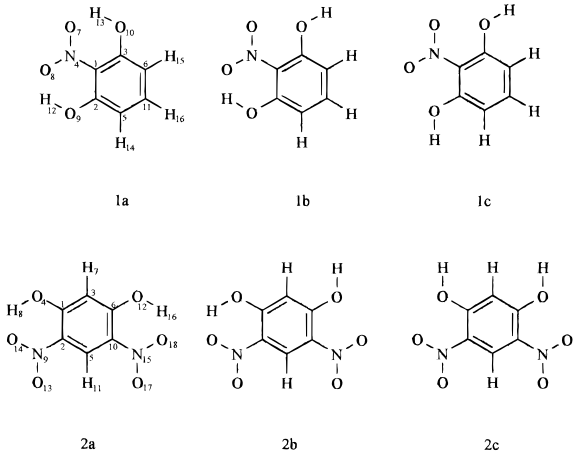

Figure 1. Possible conformers of 2-nitroresorcinol (**1a**, syn−syn form; **1b**, syn−anti form; **1c**; anti−anti form) and 4,6-dinitroresorcinol (**2a**, syn−syn form; **2b**, syn−anti form; **2c**, anti−anti form).

Three conformers—syn−syn, syn−anti, and anti−anti—differ only in the positions of two OH groups.

All calculations in this study are performed with the Gaussian 94 program.[21] The molecular geometries of possible conformers for 2-nitroresorcinol and 4,6-nitroresorcinol are fully optimized at the various levels of theory without geometrical restrictions of any sort whatsoever, and final molecular symmetries result from such calculations. We have carried out the geometry optimization first at the restricted Hartree−Fock (RHF) levels by using 6-31G*, 6-31G**, and 6-311G* basis sets. The effects of electron correlation on the geometry optimization are taken into account intensively by using the Becke's three-parameter hybrid (B3LYP) method[22,23] in the density functional theory with 6-31G* and 6-311G* basis sets along with the second-order Moeller−Plesset (MP2) perturbation theory. The reason is that the B3LYP method using the Lee−Yang−Parr correlation functional[24] provides energetics typically better than the HF method. In addition, the B3LYP results are closer to correlated post-Hartree−Fock approximations such as the MP2 method or better. Vibrational frequency analyses at the RHF/6-31G*//RHF/6-31G* indicate that optimized structures of all conformers are at stationary points corresponding to local minima without imaginary frequencies.

Results and Discussion

Structure of 2-Nitroresorcinol. Although a theoretical study of the molecular structure for 2-nitroresorcinol at the RHF/6-31G*, RHF 6-31G**, and MP2/6-31G* levels was already done by Bock and Hargittai,[5] these geometrical parameters are reproduced and also calculated with the density functional formalism at the B3LYP/6-31G* and B3LYP/6-31G** levels as well. In addition, we have calculated the molecular structure of this molecule with much larger basis set such as 6-311G* at both RHF and B3LYP levels. According to the previous theoretical work and our calculations, adding the polarization functions to hydrogen atoms changes the geometry of the molecule so rarely that we have only considered the effect of polarization functions on heavy atoms. The geometrical parameters of 2-nitroresorcinol are listed in Table 1.

The computed C_1-C_3 bond length is about 0.04 Å longer than other C−C bonds at ab initio and DFT levels. The lengthening of this C−C bond in the benzene ring between two different functional groups can be well rationalized with the resonance structures of this compound shown in Figure 2. At the RHF levels, the molecular parameters calculated with the triply-split valance basis set 6-311G* are about the same as those with the double-ζ basis set 6-31G*. This trend is also found in DFT calculations. Table 1 also shows that the overall structural parameters of the B3LYP/6-31G* level are almost the same as those of the MP2/6-31G* level. It appears that there is a large difference between computed and experimental values especially for the C−O−H bond angles. These computed bond angles are quite sensitive to the effects of electron correlation at the MP2 and B3LYP levels, which is commented on by Bock and Hargittai.[5] The computed angles at both MP2 and B3LYP levels are around 108°, which is well comparable to the experimental value of 116(3)°. The N−O bond lengths also show a slight difference between RHF and MP2 calculations. However, the values at the MP2 and DFT levels are also in good agreement with the experimental bond length.

Structure of 4,6-Dinitroresorcinol. The optimized geometrical parameters of 4,6-dinitroresorcinol at various ab initio and B3LYP levels are summarized in Table 2. The optimized structures at the various levels of theory show that this molecule has a plane of symmetry. This means that all atoms of substituents are located in the same plane of the benzene ring. At the RHF levels, the computed bond lengths are generally a little shorter than those determined from the electron diffraction method. However, the hydrogen bond length is about 0.1 Å longer than the experimental value. As can be seen from Table 2, the computed geometrical parameters at the RHF/6-31G* and the RHF/6-31G** levels are almost the same. These facts are also true for 2-nitroresorcinol. No serious differences of calculated geometrical parameters between double- and triple-ζ basis sets can also be found in Table 2. However, the computed hydrogen bond lengths $H\cdots O(H_8-O_{14})$ and C−O−H bond angles at RHF/6-311G* level are slightly larger than those at the RHF/6-31G* level.

It is also shown in Table 2 that the C−C bonds between two different functional groups are considerably longer than other C−C bonds. These results can be easily explained in term of two quinonoid resonance structures of this system shown in Figure 3. The computed endocyclic angles such as $C_2-C_5-C_{10}$ and $C_1-C_3-C_6$ bond angles are little bit different from those of the experiment. In addition, the computed $C_2-C_1-C_3$ and $C_1-C_3-C_6$ bond angles deviate from the geometry of benzene by about 2°.

When the effects of electron correlation are taken into account at the MP2/6-31G* level, all bond lengths somewhat increase as generally expected. The hydrogen bond length at this level is calculated to be 1.764 Å, which is about 0.06 Å shorter than that calculated at the RHF/6-31G* level. However, this value is very close to the experimental value 1.72(2) Å. On the other hand, as the electron correlation effects are included, the C−O−H bond angles decrease quite sensitively, whereas the other bond angles change slightly. All optimized geometrical parameters at the MP2/6-31G* level are generally in good agreement with experimental values.

The bond lengths at the B3LYP/6-31G* level have some parallels with the results at the MP2/6-31G* level except for the hydrogen bond length (1.705 Å), which is about 0.06 Å shorter than that at the MP2/6-31G* level, but this value is also closer to the experimental value of 1.72(2) Å. The differences of all the bond angles between DFT and MP2 calculations are less than 1°. Therefore, it is certain that the differences of geometrical parameters between two calculations are almost negligible.

In triple-ζ calculations at the B3LYP/6-311G* level, the overall geometrical parameters are not so different from those of double-ζ calculations at the B3LYP/6-31G* level. However, some geometrical parameters, such as the O−H bond lengths, C−O−H bond angles, and hydrogen bond lengths H···O,

TABLE 1: Geometrical Parameters for 2-NItroresorcinol, 1a (Distances, Å; Angles, deg)

parameter	RHF/6-31G*[a]	RHF/6-31G**[a]	RHF/6-311G*	MP2/6-31G*[a]	B3LYP/6-31G*	B3LYP/6-311G*	exptl value[a]
C_1-C_3	1.421	1.421	1.419	1.425	1.435	1.433	1.426(5)
C_3-C_6	1.384	1.384	1.383	1.395	1.395	1.393	
C_6-C_{11}	1.381	1.380	1.379	1.390	1.392	1.388	
C_3-O_{10}	1.323	1.322	1.323	1.351	1.337	1.336	1.354(4)
$O_{10}-H_{13}$	0.952	0.949	0.943	0.984	0.987	0.977	1.038(15)
C_1-N_4	1.439	1.430	1.438	1.439	1.422	1.430	1.449(7)
N_4-O_7	1.203	1.203	1.195	1.253	1.249	1.241	1.239(3)
O_7-H_{13}	1.789	1.783	1.812	1.734	1.691	1.723	1.76(40)
$\angle C_2C_1C_3$	119.80	119.87	119.98	120.16	119.92	120.02	119.1(7)
$\angle C_1C_2C_5$	119.19	119.15	119.07	118.93	118.99	118.90	120.4(5)
$\angle C_2C_3C_{11}$	119.92	119.89	119.96	120.35	120.06	120.12	118.3(5)
$\angle C_5C_{11}C_6$	121.98	122.04	121.93	121.26	121.98	121.93	123.6(6)
$\angle C_3O_{10}H_{13}$	111.13	111.10	112.11	107.56	107.48	108.72	116(3)
$\angle C_1C_3O_{10}$	124.64	124.48	124.92	124.72	123.40	123.80	122.8(7)
$\angle C_3C_1N_4$	120.10	120.06	120.01	119.92	120.03	119.97	120.5(4)
$\angle C_1N_4O_7$	119.33	119.35	119.10	119.73	119.95	119.73	119.3(3)
$\angle O_7N_4O_8$	121.33	121.30	121.79	120.53	120.06	120.56	121.4(5)

[a] Reference 5.

TABLE 2: Geometrical Parameters for 4,6-Dinitroresorcinol, 2a (Distances, Å; Angles, deg)

parameter	RHF/6-31G*	RHF/6-31G**	RHF/6-311G*	MP2/6-31G*	B3LYP/6-31G*	B3LYP/6-311G*	exptl value[a]
C_1-C_2	1.417	1.417	1.415	1.419	1.432	1.429	1.424(5)
C_1-C_3	1.384	1.384	1.383	1.394	1.395	1.392	
C_2-C_5	1.379	1.378	1.377	1.386	1.388	1.384	
C_1-O_4	1.313	1.312	1.312	1.344	1.329	1.328	1.341(4)
O_4-H_8	0.955	0.952	0.946	0.988	0.995	0.981	1.002(9)
C_2-N_9	1.440	1.439	1.446	1.454	1.445	1.453	1.461(4)
N_9-O_{13}	1.187	1.187	1.179	1.238	1.224	1.216	1.225(7)
N_9-O_{14}	1.207	1.208	1.200	1.255	1.252	1.245	1.241(7)
H_8-O_{14}	1.821	1.816	1.847	1.764	1.705	1.743	1.72(2)
$\angle C_2C_1C_3$	118.38	118.38	118.27	117.98	118.42	118.26	119.3(3)
$\angle C_1C_2C_5$	120.23	120.29	120.27	120.91	120.54	120.47	121.6(3)
$\angle C_2C_5C_{10}$	120.66	120.60	120.69	119.88	120.22	120.39	118.0(4)
$\angle C_1C_3C_6$	122.09	122.06	122.24	122.29	121.87	122.12	120.3(4)
$\angle C_2C_1O_4$	124.63	124.50	124.91	124.97	123.46	123.92	123.4(3)
$\angle C_1O_4H_8$	110.73	110.72	111.65	106.98	106.94	108.16	104.5(14)
$\angle C_1C_2N_9$	122.04	121.97	122.03	121.65	121.45	121.58	121.0(2)
$\angle C_2N_9O_{13}$	118.61	118.64	118.58	118.82	119.25	119.18	
$\angle C_2N_9O_{14}$	117.77	117.82	117.51	117.95	117.87	117.53	
$\angle O_{13}N_9O_{14}$	123.63	123.55	123.91	123.23	122.88	123.30	123.7(2)

[a] Reference 13.

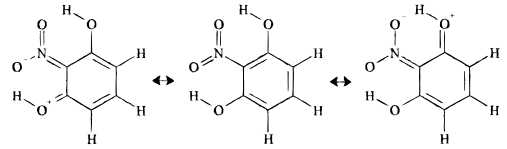

Figure 2. Resonance structures of 2-nitroresorcinol.

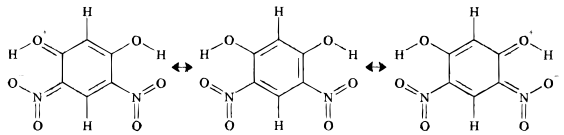

Figure 3. Resonance structures of 4,6-dinitroresorcinol.

somewhat diverge from experimental values as the level of calculations is improving.

In order to analyze the structure of 4,6-dinitroresorcinol more rigorously, some important geometrical parameters between 4,6-dinitroresorcinol and 2-nitroresorcinol are compared. The computed C_1-C_3 bond length between the substituents of 2-nitroresorcinol is slightly longer than the C_1-C_2 bond of 4,6-dinitroresorcinol. In the case of the C−N bond, the bond of 4,6-dinitroresorcinol is a little longer than that of 2-nitroresorcinol for MP2 and B3LYP levels in which electron correlation is taken into account. These discrepancies can be easily understood by making a comparison between their resonance structures in Figures 2 and 3.

The noticeable difference of structural parameters between two nitroresorcinols is found at the O−N−O bond angle. The computed O−N−O bond angle of 4,6-dinitroresorcinol at the MP2 and B3LYP levels is about 3° larger than that of 2-nitroresorcinol, which must be caused by the nonbonding interaction between two oxygen atoms. In other words, 2-nitroresorcinol which has each hydroxyl group on both sides of the nitro group, has far more nonbonding repulsion than 4,6-dinitroresorcinol whose nitro group has only one adjacent hydroxyl group. On the other hand, the computed C−O−H bond angles of 2-nitroresorcinol are slightly larger than those of 4,6-dinitroresorcinol, although considerable discrepancies are found between the computed and experimental angles for both molecules.

Effect of Hydrogen Bonding on the Structure of 4,6-Dinitroresorcinol. In order to investigate how much the molecular structure of 4,6-dinitroresorcinol is affected by intramolecular hydrogen bonding, we are going to compare the geometrical parameters of three possible conformers in 4,6-dinitroresorcinol. They are described as the syn−syn conformer **2a**, the syn−anti conformer **2b**, and the anti−anti conformer **2c** in Figure 1. In syn−anti and anti−anti forms, dihedral angles containing the O−H bonds are rotated up to 180° on the molecular plane so as to prevent the hydrogen bonding partially or fully, and these conformers are fully optimized with such conformations. The vibrational frequency analyses verify that all the optimized conformations are indeed at real stationary points on the potential energy surface.

TABLE 3: Deviation of Geometrical Parameters of both 2b and 2c from 2a for 4,6-Dinitroresorcinol (Distances, Å; Angles, deg)

	2b		2c	
parameter	RHF 6-311G*	B3LYP 6-311G*	RHF 6-311G*	B3LYP 6-311G*
C_1-C_2	−0.010	−0.009	−0.016	−0.018
C_1-C_3	0.007	0.004	0.004	0.005
C_2-C_5	0.008	0.006	−0.000	0.001
C_3-C_6	−0.002	−0.001	0.005	0.005
C_5-C_{10}	−0.008	−0.005	0.001	0.001
C_6-C_{10}	−0.006	−0.008	−0.015	−0.016
C_1-O_4	0.001	0.001	0.009	0.013
O_4-H_8	−0.000	0.002	−0.006	−0.015
C_2-N_9	−0.001	−0.002	0.009	0.019
N_9-O_{13}	−0.001	−0.000	0.011	0.009
N_9-O_{14}	0.001	0.002	−0.018	−0.024
$\angle C_2C_1C_3$	−0.31	−0.46	−0.20	−0.30
$\angle C_1C_2C_5$	−0.09	−0.14	−0.34	−0.59
$\angle C_2C_5C_{10}$	0.34	0.60	0.73	1.22
$\angle C_1C_3C_6$	0.03	0.29	0.16	0.60
$\angle C_2C_1O_4$	0.63	0.60	−4.12	−3.31
$\angle C_1O_4H_8$	−0.24	−0.31	0.24	1.91
$\angle C_{10}C_6O_{12}$	−4.71	−3.92	−4.13	−3.32
$\angle C_6O_{12}H_{16}$	−0.06	1.70	0.22	1.92
$\angle C_2N_9O_{13}$	0.03	0.11	−1.88	−2.34
$\angle C_2N_9O_{14}$	−0.07	−0.03	0.67	0.47
$\angle O_{13}N_9O_{14}$	0.04	−0.09	1.21	1.84
$\angle C_6C_{10}N_{15}$	0.72	1.27	0.68	1.21
$\angle C_{10}N_{15}O_{17}$	−1.87	−2.42	−1.92	−2.38
$\angle O_{17}N_{15}O_{18}$	1.23	1.99	1.19	1.92

The differences of computed geometrical parameters for the syn−syn form **2a** and other two possible conformers **2b** and **2c** at the RHF/6-311G* and B3LYP/6-311G* levels are listed in Table 3. When the hydroxyl groups are rotated to prevent the hydrogen bonding partially or fully in the syn−anti and the anti−anti form, the C−C bonds of the benzene ring are somewhat altered. In the anti−anti form **2c**, the lengths of C_1-C_2 and C_6-C_{10} bonds become shorter than those of the syn−syn form **2a**. These facts indicate that these bonds are more sensitive to the positions of OH groups than other C−C bonds in the benzene ring. On the contrary, the endocyclic bond angles of the benzene ring show almost no change by intramolecular hydrogen bonding.

Table 3 also shows that the O−H and N−O bonds are also very sensitive to a change of conformation. When the hydrogen bonding is totally excluded in the anti−anti form **2c**, these bond lengths somewhat decrease. In addition, the bonds connected between the benzene ring and substituents, such as C−O and C−N, are also sensitive to change in the presence of the hydrogen bonds. The C_1-O_4 and C_2-N_9 bonds of the anti−anti form **2c** are slightly longer than those of the syn−syn form **2a**.

Some bond angles of syn−anti and anti−anti forms apparently deviate from those of the syn−syn form. The bond angles such as $C_{10}-C_6-O_{12}$ and $C_{10}-N_{15}-O_{17}$ around hydroxyl and nitro groups decrease by a few degrees. It also appears in Table 3 that the O−N−O and C−O−H bond angles apparently change with breaking the hydrogen bonds. In the syn−anti form, the geometrical parameters for hydroxyl and nitro groups participated in the hydrogen bonding are almost the same as those of the syn−syn form. These results may reflect that one hydrogen bond of 4,6-dinitroresorcinol does not affect the other hydrogen bond very much, even though all bonds in this molecule are connected by resonance.

The planarity of a nitro group in nitroresorcinols is seriously affected by intramolecular hydrogen bonding. Table 4 shows the torsional angles of nitro groups for three conformers of 4,6-dinitroresorcinol as well as 2-nitroresorcinol. In 2-nitroresorcinol, the torsional angle of the nitro group for **1c** in which the hydrogen bonding is absent is surprisingly going up to 70°. However, in 4,6-dinitroresorcinol, the optimized structures of the syn−anti form **2b** at RHF and B3LYP levels show that the nitro group with no hydrogen bond is rotated by about 20° out of the molecular plane, whereas the other nitro group with the hydrogen bond remains on the same plane of the benzene ring. The torsional rotations of both nitro groups are also found in the optimized structures of the anti−anti form **2c**, in which the angles of torsion for each nitro group are computed to be 24.7° and 20.5° at the RHF/6-311G* and B3LYP/6-311G* levels, respectively. However, these angles of torsion reduce to about 12° at the B3LYP/6-31G* level. A large difference of torsional angles between the B3LYP/6-31G* and B3LYP/6-311G* levels is also found in the syn-anti form **1b** of 2-nitroresorcinol.

The torsional behavior of a nitro group is also appreciably related to the nonbonding interaction between the oxygen atoms of the hydroxyl and the nitro group. The nonbonded O···O distances for the possible conformers of 2-nitroresorcinol and 4,6-dinitroresorcinol are summarized in Table 5. All the computed and experimental values which are in 2.5−2.9 Å are shorter than twice the van der Waals radius 1.5 Å of the oxygen atom. Therefore one can see that there is a considerable nonbonding repulsion between these two oxygen atoms. The intramolecular hydrogen bonding may be a relief to reduce this nonbonding interaction through the delocalization of nonbonded electrons of an oxygen atom. However, if this hydrogen bond is broken by changing the conformation, the torsion of the nitro group may occur to release this nonbonding interaction. It can be shown in Table 5 that the O···O distances of 2-nitroresorcinol and 4,6-dinitroresorcinol are definitely interrelated with the hydrogen bonding. There is a large variation for the torsional angle of the nitro group in the anti−anti form **1c** of 2-nitroresorcinol. It is probably because this nitro group between two hydroxyl groups has much larger nonbonding interaction than the nitro group adjacent to only one hydroxyl group in 4,6-dinitroresorcinol.

These facts can be rationalized with the O···O distances in Table 5. At both RHF and B3LYP levels, the computed O···O distances of the anti−anti form **1c** in 2-nitroresorcinol are at least 0.2 Å much larger than those of the anti−anti form **2c** of 4,6-dinitroresorcinol. Especially these values of 2-nitroresorcinol are not largely different from twice the van der Waals radius of the oxygen atom. These results indicate that the electron densities of these two oxygen atoms, which have been reduced in the presence of the hydrogen bonding, beccome normalized with the breaking of the hydrogen bond. Hence the van der Waals repulsions between both two oxygen atoms of the nitro group and two adjacent hydroxyl groups play an important role for such a large torsion of the nitro group in the anti−anti conformation of 2-nitroresorcinol.

Hydrogen Bond Energy for 2-Nitroresorcinol and 4,6-Dinitroresorcinol. The hydrogen bond energy of each molecule is estimated from the difference of energy between the syn−syn conformer and other conformer such as the syn−anti conformer and the anti−anti conformer.[1,2] Table 6 summarizes the relative energies (kcal/mol) which are computed at various ab initio and B3LYP levels for 2-nitroresorcinol as well as for 4,6-dinitroresorcinol. The relative energies of conformers at a given level of theory are not much dependent upon the basis set. At the RHF levels, the calculated energies of the syn−anti form **1b** and anti−anti form **1c** in 2-nitroresorcinol relative to the syn−syn form **1a** are approximately 8.0 and 15.0 kcal/mol, respectively. However, these energies increase by about a few kcal/mol at the B3LYP levels. In 4,6-dinitroresorcinol, the molecular energies of the syn−anti form **2b** and anti-anti

TABLE 4: Torsional Angles of Nitro Groups (Angles, deg)

	2-nitroresorcinol			4,6-dintitroresorcinol					
				2a		**2b**		**2c**	
	1a	**1b**	**1c**	syn[a]	syn	syn	anti[a]	anti	anti
RHF/6-31G*	0.17	27.01	65.98	0.00	0.00	0.54	21.67	21.45	21.36
RHF/6-31G**	0.11	26.92	65.92	0.05	0.05	0.44	22.50	22.23	22.14
RHF/6-311G*	0.37	28.77	71.68	0.00	0.05	0.55	25.11	24.74	24.66
B3LYP/6-31G*	0.05	0.16	56.09	0.05	0.00	0.17	10.56	11.66	11.64
B3LYP/6-311G*	0.05	11.65	63.65	0.00	0.06	0.37	20.99	20.53	20.50

[a] Nitro groups syn or anti to adjacent OH groups.

TABLE 5: The O···O Distances For 2-Nitroresorcinol and 4,6-Dinitroresorcinol (Distances, Å)

	1a, O_8-O_9	**1b**, O_8-O_9	**1c**, O_8-O_9	**2a**, O_4-O_{14}	**2b**, O_4-O_{14}	**2c**, O_4-O_{14}
RHF/6-31G*	2.568	2.560	2.901	2.605	2.603	2.625
RHF/6-311G*	2.572	2.607	2.968	2.609	2.607	2.644
B3LYP/6-31G*	2.556	2.521	2.815	2.577	2.574	2.605
B3LYP/6-311G*	2.563	2.539	2.898	2.589	2.586	2.636
exptl data	2.558(10)[a]			2.598(6)[b]		

[a] Reference 5. [b] Reference 13.

TABLE 6: Relative Energies (kcal/mol) for 2-Nitroresorcinol and 4,6-Dinitroresorcinol Conformers

	1a	**1b**	**1c**	**2a**	**2b**	**2c**
RHF/6-31G*	0.0	8.07	15.01	0.0	9.46	20.51
RHF/6-31G**	0.0	8.13	15.01	0.0	9.48	20.55
RHF/6-311G*	0.0	7.58	13.92	0.0	9.07	19.87
B3LYP/6-31G*	0.0	10.62	20.91	0.0	11.59	24.57
B3LYP/6-311G*	0.0	10.15	19.11	0.0	11.01	23.53

form **2c** relative to the syn−syn form **2a** at the RHF levels are computed to be about 9.5 and 20 kcal/mol, respectively. These energy differences somewhat increase when the effects of electron correlation are taken into account at the B3LYP levels. These facts can be assigned to the intermolecular nonbonding interactions, which can be correctly reproduced only by the inclusion of electron correlation.[25−27] The magnitude of these relative energies for 4,6-dinitroresorcinol is very close to that of the relative energies of 2-nitroresorcinol. From the results in Table 5, the energy gain per hydrogen bond in these molecules can be estimated to be about 10 kcal/mol.

Conclusion

The molecular structures and intramolecular hydrogen bonding for 2-nitroresorcinol and 4,6-dinitroresorcinol are investigated by an ab initio method and density functional theory. The optimized geometrical parameters at the MP2/6-31G*, B3LYP/6-31G*, and B3LYP/6-311G* levels are in good agreement with experimental values. The computed results show that the resonance-assisted intramolecular hydrogen bonding in these compounds not only affects the geometry of the benzene ring but also changes geometrical parameters of substituents which participate in the intramolecular hydrogen bonding. These facts are also very consistent with the previous experimental results. It is also found that a considerable torsion of a nitro group occurs in the absence of intramolecular hydrogen bonding. This may be ascribed to an increase of the nonbonding electron density of two oxygen atoms with the breaking of hydrogen bond. On the other hand, the energy of intramolecular hydrogen bonding is estimated by making a comparison of molecular energies between two different conformations. In 4,6-dinitroresorcinol, the calculated energy differences between the syn−syn form **2a** and syn−anti form **2b** are 9.07 and 11.01 kcal/mol at the RHF/6-311G* and B3LYP/6-311G* levels, respectively. Although the more detailed investigation is still required for the hydrogen bonding, it is clear that one can use the practically efficient DFT methods instead of expensive post-Hartree-Fock methods to include the effects of electron correlation in the hydrogen bonding. It is also clear that intramolecular hydrogen bonding is a great challenge for DFT.

References and Notes

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