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Hydrogen bonds in the phenol-formaldehyde-*ortho*-naphthoquinondiazide-water system

Valeria Chernuha *, Dmitriy Fomichev, and Sergei Zelentsov

Lobachevsky State University of Nizhni Novgorod
* Correspondence: valeria.chernuxa@yandex.ru

Abstract: Hydrogen bonds are formed in the phenol-formaldehyde-*ortho*-naphthoquinondiazide-water system. In our work quantum-chemical calculations were made using the HF/3-21G ++ theory level and it was found out that phenol-formaldehyde forms three types of hydrogen bonds: between its hydroxyl group and carbonyl group of *ortho*-naphthoquinondiazide, between its hydroxyl group and water and between its hydroxyl groups intramolecularly forming a "circle-like" structure, and this type of bonds prevails.

Keywords: phenol-formaldehyde, *ortho*-naphthoquinondiazide, hydrogen bonds, photoresist

1. Introduction

Naphthoquinondiazides are light-sensitive substances that are used in photolithography as a component of photoresists. The other component is a polymer, for example phenol-formaldehyde resin. These substanses form hydrogen bonds, which inhibit the dissolution of the photoresist until the light irradiation [1], [2], [3].

2. Materials and methods

All calculations described in this paper were performed in the North-West Chemistry software package [4]. The HF/3-21G ++ theory level was chosen because of the large amount of atoms, which makes the computations to take a lot of time.

3. Results

In Fig.1 a model of tetramer of phenol-formaldehyde resin is shown. There are two intramolecular hydrogen bonds. Their lengths were calculated and placed in Table 1.

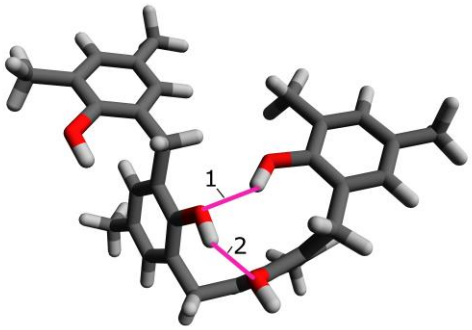

Figure 1. The model of the phenol-formaldehyde tetramer: white atoms - H, gray atoms - C, red atoms - O, pink lines - hydrogen bonds.

Table 1. The lengths of hydrogen bonds from Fig.1.

Bond	Length, Å
1	2,063
2	1,737

There is a model of pentamer phenol-formaldehyde resin shown in Fig.2. It forms a structure like a half of a circle by intramolecular hydrogen bonds. Similar bonds can be found in polyalcohols [5]. Their lengths can be found in Table 2.

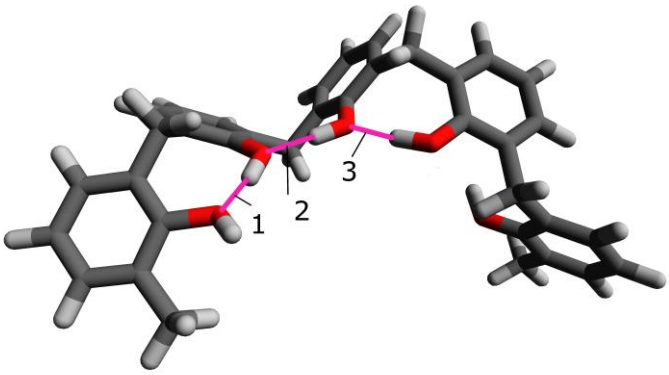

Figure 2. The model of the pentamer phenol-formaldehyde resin: white atoms - H, gray atoms - C, red atoms - O, pink lines - hydrogen bonds.

Table 2. The lengths of hydrogen bonds from Fig.2.

Bond	Length, Å
1	1.636
2	1.592
3	1.639

In Fig.3 a model of the tetramer of phenol-formaldehyde resin accompanied by 5 water molecules is presented. Table 3 contains the lengths of hydrogen bonds formed in this system. It can be seen from the figure that hydrogen groups of tetramer tend to form hydrogen bonds with water molecules.

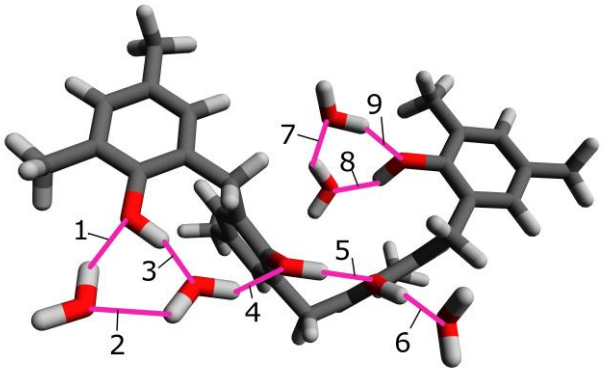

Figure 3. The model of the phenol-formaldehyde tetramer with water: white atoms - H, gray atoms - C, red atoms - O, pink lines - hydrogen bonds.

Table 3. The lengths of hydrogen bonds from Fig.3.

Bond	Length, Å
1	1.871
2	2.118
3	1.610
4	1.822
5	1.637
6	1.274
7	1.918
8	1.689
9	1.784

In Fig.4 a model of phenol-formaldehyde pentamer with water molecules can be seen (initially there were 5 water molecules added; the ones which didn't form hydrogen bonds with phenol-formaldehyde resin during the optimization are not shown in the picture). Their lengths are shown in Table 4.

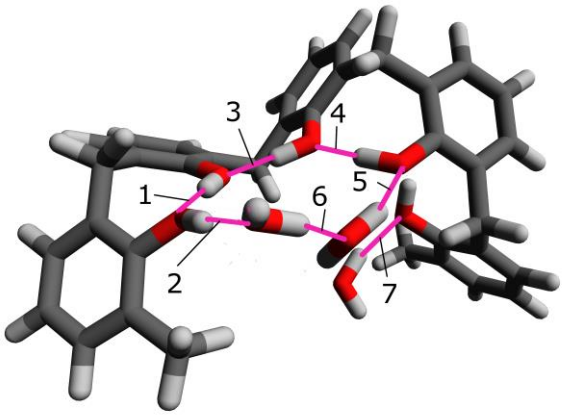

Figure 4. The model of the phenol-formaldehyde pentamer with water: white atoms - H, gray atoms - C, red atoms - O, pink lines - hydrogen bonds.

Table 4. The lengths of hydrogen bonds from Fig.4.

Bond	Length, Å
1	1.517
2	1.566
3	1.545
4	1.552
5	1.931
6	1.575
7	1.848

In Fig.5, there is a model of interaction of the phenol-formaldehyde pentamer and the *ortho*-naphthoquinondiazide molecule. The pentamer forms a "half-a-circle-like" structure. Diazide group is in its center of this structure, but no hydrogen bonds were detected with this group [1]. Although the *ortho*-naphthoquinondiazide carbonyl group forms a hydrogen bond with terminal hydroxyl group of the phenol-formaldehyde resin. It looks like an *ortho*-naphthoquinondiazide fragment closes that "circle". The lengths are placed in Table 5.

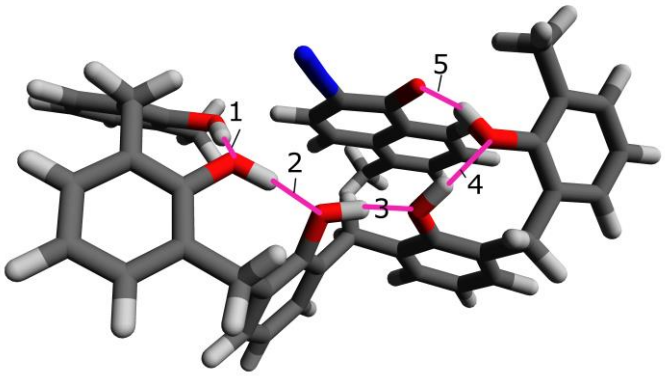

Figure 5. The model of the *ortho*-naphthoquinondiazide with the phenol-formaldehyde pentamer: white atoms - H, gray atoms - C, red atoms - O, blue atoms - N, pink lines - hydrogen bonds.

Table 5. The lengths of hydrogen bonds from Fig.5.

Bond	Length, Å
1	1.686
2	1.613
3	1.566
4	1.627
5	1.641

Fig.6 contains a model from Fig.5, but some water molecules were added (water molecules which did not form hydrogen bonds with any non-water molecules are also not shown). It can be seen that only the two of five initially added water molecules formed hydrogen bonds in this system. The lengths of the hydrogen bonds are shown in Table 6.

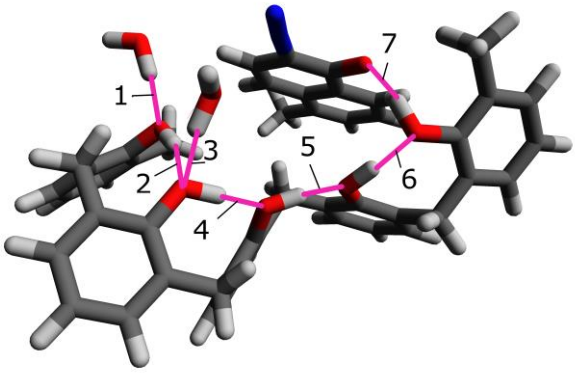

Figure 6. The model of *ortho*-naphthoquinondiazide with phenol-formaldehyde pentamer and water: white atoms - H, gray atoms - C, red atoms - O, blue atoms - N, pink lines - hydrogen bonds.

Table 6. The lengths of hydrogen bonds from Fig.6.

Bond	Length, Å
1	1.695
2	1.762
3	1.863
4	1.564
5	1.569
6	1.621
7	1.560

4. Discussion

The results of this work let us to make a conclusion that phenol-formaldehyde resin together with *ortho*-naphtoquinonediazide compound is less liable to form hydrogen bonds with water than phenol-formaldehyde resin itself. It is more liable to form hydrogen bonds with *ortho*-naphtoquinonediazide compounds than with water molecules.

In our further work we are planning to calculate energies of hydrogen bonds. We are also planning to continue quantum-chemical calculations using the higher theory level.

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