

## Theoretical Study of Microscopic Molecular Structure of Helicenebisquinone Aggregates

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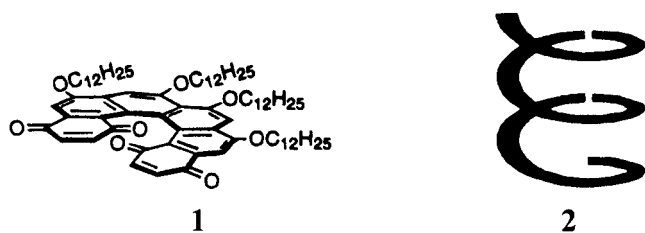
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Molecular level studies of intermolecular interaction forces and microscopic structures are essential to understand molecular aggregates and self-assembly phenomena. Recently, fibrous helicenebisquinone (HBQ) aggregates have been of great interest because of their strongly enhanced nonlinear optical (NLO) properties. The intermolecular interaction force and microscopic structure of HBQ aggregates were proposed to be donor–acceptor interaction and a columnar stack, respectively. However, our present study suggests that the intermolecular interaction force of HBQ aggregates would be the paired hydrogen bonding between quinone moieties, and its molecular structure would be one-dimensional hydrogen bond chain. Though the information from the experiments is somewhat limited, our prediction of molecular level structure is consistent with the experimentally observed macroscopic structure.

## Introduction

Molecular solids with predefined solid-state structures have many important applications for developing new materials.<sup>1</sup> Recently, much efforts in assembling molecular solids has been focused on 1-dimensional aggregates, such as fiber, chain, and columns,<sup>2</sup> as well as 2,3-dimensional aggregates.<sup>3</sup> The study of the origin of these molecular assembling forces is a new field of chemistry that is essential to understand the molecular aggregating phenomena.

## CHART 1



Katz and collaborators synthesized novel nonracemic helical compounds, tetrasubstituted helicenebisquinones (HBQ) **1** (Chart 1), which aggregate spontaneously into macroscopic fibrous structures that show strongly enhanced nonlinear optical properties.<sup>4</sup> However, the structure and the driving force for aggregation of HBQ fiber are not understood well. It was proposed that donor–acceptor interactions between the electron-rich inner rings of one molecule and the electron-poor outer rings of another might stabilize a columnar stack of helical aggregation like structure **2** (Chart 1).<sup>4</sup>

To understand the molecular assembling phenomena of the HBQ fiber, we have investigated the driving force and the structure. Donor–acceptor interactions have provided a new tool for molecular aggregation, self-assembly, discotic liquid crystals, and crystal engineering.<sup>5</sup> For donor–acceptor interaction, electron-rich molecule (A) and electron-deficient molecule (B) are aligned alternatively like {ABABAB} to make a one-

dimensional material. In an X-ray diffraction pattern, Katz et al. could not find a sharp peak for the spacing between planes containing core rings that is usually observed in the diffraction patterns of columnar discotic liquid crystals.<sup>4b</sup> This fact implies that aggregation structure could not be a simple columnar stack. Although structure **2** seems to be feasible in view of the literal meaning of “stack”, the hypothesis that the donor–acceptor interaction can be the driving force of aggregation may raise a question because only one kind of molecule is involved in the HBQ aggregation. Thus, in this study, to give a reasonable explanation to the aforementioned question, we investigated the intermolecular interaction forces and the microscopic molecular structure of the HBQ aggregates.

## Methods

We carried out extensive calculations of the *p*-benzoquinone (PBQ) dimer, 1,4-naphthoquinone (NQ) dimer, and HBQ dimer with and without side chains, using various calculation methods, such as molecular mechanics (MM) with AMBER force field and restrained electrostatic potential (RESP) fitting atomic charges,<sup>6</sup> semiempirical theory AM1,<sup>7a</sup> hybrid density functional theory (B3LYP),<sup>7b,c</sup> and ab initio theory (MP2)<sup>7d</sup> with the 6-31G\* basis set. AM1, B3LYP, and MP2 calculations were carried out using a Gaussian 98 suite of programs,<sup>7e</sup> and MM calculations were done with an AMBER5 package.<sup>7f</sup> In B3LYP and MP2 calculations, the interaction energies were obtained with 50% basis set superposition error (BSSE) correction, because, for mid-size basis sets, the full BSSE correction tends to underestimate the interaction energy due to the underestimation of electron correlation.<sup>8</sup>

## Results and Discussion

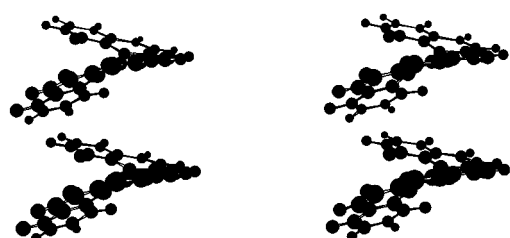
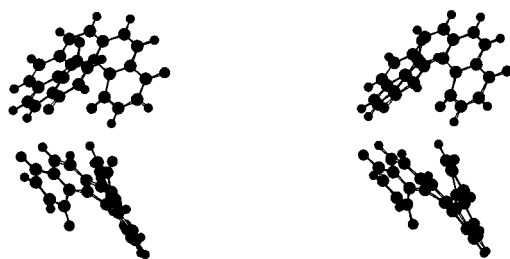
The first step of this study was to find the lowest energy structure of the HBQ dimer. In the beginning, four side chains were truncated with the assumption that the side chains of –OC<sub>12</sub>H<sub>25</sub> have little influence on the binding process. This

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**TABLE 1: Interaction Energies and Structures of the PBQ, NQ, and HBQ Dimers with and without Side Chains by Various Calculation Methods<sup>a</sup>**

complex		this work				other work
		MM	AM1	B3LYP/6-31G*	MP2/6-31G*	
PBQ dimer	$\Delta E$	−3.68	−3.25	−4.63	−5.57	−3.01 <sup>c</sup>
	$r_{\text{OH}}(\text{PBQ})$	2.496	2.264	2.310	2.302	−3.49 <sup>d</sup>
						2.45 <sup>e</sup>
NQ dimer	$\Delta E$	−4.94	−2.73	−3.37	−5.02	2.375 <sup>f</sup>
	$r_{\text{OH}}(\text{NQ})$	2.597	2.341	2.377	2.369	
HBQ dimer no side chains	$\Delta E$	−8.95	−4.30	−7.85		
	$r_{\text{OH}}(\text{PBQ})^b$	1.998	2.328	2.335		
	$r_{\text{OH}}(\text{NQ})^b$	2.030	2.426	2.495		
HBQ dimer with side chains	$\Delta E$	−9.65	−5.80			
	$r_{\text{OH}}(\text{PBQ})^b$	2.162	2.326			
	$r_{\text{OH}}(\text{NQ})^b$	2.062	2.485			

<sup>a</sup> Energies are in kcal/mol; bond lengths, in Å. B3LYP and MP2 binding energies are the median values of binding energies with and without BSSE correction (ref 8). <sup>b</sup> In the HBQ dimer complex, the average value of the two  $r_{\text{OH}}$  distance is given. <sup>c</sup> AM1 result from ref 9(l). <sup>d</sup> B3LYP/D95 result from ref 9(l). <sup>e</sup> In crystalline solid at room temperature from ref 9(m). <sup>f</sup> In crystalline solid at −160 °C from ref 9(n).

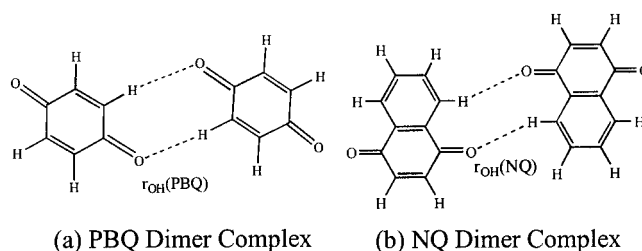
**3: Conjectured Structure (Columnar Stack)****4: Another Possible Conformation Involving Hydrogen Bonds**

**Figure 1.** Two possible HBQ dimers (stereoview).

assumption was verified later by calculating the effects of side chains on the intermolecular interaction.

According to the proposition of Katz and collaborators, we started to investigate the interaction energies by minimizing a columnar stack of helical aggregation like structure 2. The HBQ dimer without  $-\text{OC}_{12}\text{H}_{25}$  side chains, shown in Figure 1, was optimized. During the minimization with AM1, however, we found that structure 3 changed to structure 4, which has two quinone–quinone interactions (Figure 1). Conformer 4 has characteristic hydrogen bonds between quinone moieties of each HBQ. From this result, the origin of HBQ aggregation is likely to be a special type of hydrogen bond of quinone–quinone interaction rather than the donor–acceptor interaction.

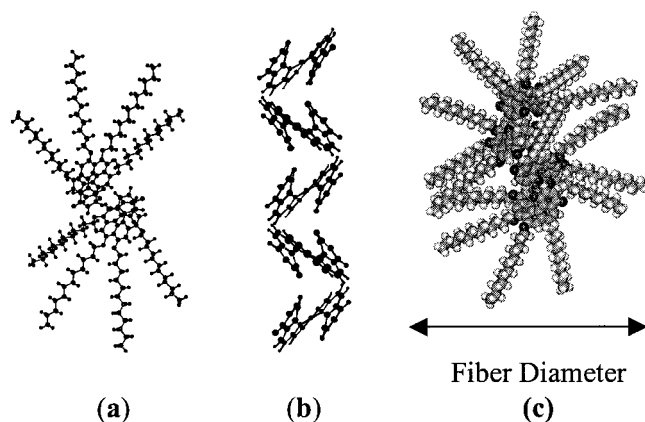
Conformer 4 has two quinone–quinone interactions, both of which have paired hydrogen bonds. The term “paired hydrogen bonds” denotes a kind of intermolecular interaction that one molecule with two atomic sites for hydrogen bonding interacts with the other similar molecule through two hydrogen bonds. Paired hydrogen bonds have been found in a number of experimental and theoretical studies of carboxylic acid dimerization, DNA base pairing, and crystal engineering, in particular, by Desiraju, Steiner, Dannenberg, and their co-workers.<sup>9</sup>



**Figure 2.** Paired hydrogen bonds in PBQ and NQ dimers. At the MP2/6-31G\* level, the angles of  $\angle\text{C}–\text{H}\cdots\text{O}$  in (a) and (b) are 178° and 139°, respectively, and the angles  $\angle\text{C}–\text{O}\cdots\text{H}$  in (a) and (b) are 123° and 137°, respectively.

Two types of paired hydrogen bonds of PBQ and 1,4-naphthoquinone NQ in the HBQ aggregates are shown in Figure 2. Structures and binding energies of the PBQ, NQ, and HBQ dimers with and without side chains predicted by various calculation methods are listed in Table 1. Because B3LYP results are available for PBQ, NQ, and HBQ dimers and they are consistent with MP2 results of PBQ and NQ, the binding energies and structures are discussed based on B3LYP results, unless otherwise specified.

The distance and strength of hydrogen bonding in PBQ clusters and crystalline solid have been of interest to experimental and theoretical chemists.<sup>9</sup> Crystalline PBQ was constructed by infinite and periodic  $\text{C}–\text{H}\cdots\text{O}$  paired and multiple hydrogen bonds. For the PBQ crystalline solid, the structural parameters were obtained by X-ray crystallography by Trotter at room temperature<sup>9m</sup> and by Bolhuis and Kiers at −160 °C.<sup>9n</sup> The hydrogen bond distances of the PBQ dimer in the crystalline solid are 2.375 Å at −160 °C and 2.45 Å at room temperature (Table 1). In the PBQ dimer, the (B3LYP, MP2)/6-31G\* predicted hydrogen bond distances are 2.310 and 2.302 Å, which show good agreement with experimental observation (2.375 Å) in crystalline solid. The difference of temperature (0 K for the calculation and −160 °C for X-ray crystallography) would cause the difference in bond distance. Steiner et al. studied the  $(\text{C}–\text{H}\cdots\text{O})$  paired hydrogen bonded dimer in PBQ with the combined ab initio calculational and statistical investigation.<sup>9f</sup> Their statistical study is based on the organic crystal structures of the Cambridge Structural Database (CSD). According to their report, the mean hydrogen bond distance for the 53 dimers (in centrosymmetric and roughly planar geometry) is 2.47 Å.<sup>9f</sup> Very recently, Dannenberg et al.<sup>9i</sup> carried out extensive semiempirical and ab initio calculations of crystalline PBQ. According to their



**Figure 3.** Structures of AM1-optimized HBQ dimer complex with side chains (a), AM1-optimized HBQ pentamer complex without side chains (b), and MM-optimized HBQ tetramer with side chains (c).

report, AM1 and B3LYP/D95 predicted interaction energies of the PBQ dimer are  $-3.01$  and  $-3.49$  kcal/mol, respectively. In our study, (B3LYP, MP2)/6-31G\* predicted interaction energies of the PBQ dimer are  $-4.63$  and  $-5.57$  kcal/mol, as given in Table 1.

For the NQ system, no theoretical and experimental results of interaction energy and structure of clusters and crystalline solids have been reported. The (B3LYP, MP2)/6-31G\* predicted interaction energies for NQ dimer are  $-3.37$  and  $-5.02$  kcal/mol, respectively. In the NQ dimer, as sketched in Figure 2, the hydrogen bond angles  $\angle C-H\cdots O$  of the PBQ and NQ dimer are  $178^\circ$  and  $139^\circ$ , respectively, at the MP2/6-31G\* level. The hydrogen bonds are almost linearly aligned in the PBQ dimer, but severely bent in the NQ dimer. The bent structure of NQ paired hydrogen bonds is due to the  $sp^2$  type lone pair electrons density lobes of the O atoms attached to the C atom with double bonds. This result can be demonstrated from the bond angle  $\angle C-O\cdots H$  of the PBQ and NQ dimers, which are  $123^\circ$  and  $137^\circ$ , at the MP2/6-31G\* level. Therefore, the linearly aligned  $C-H\cdots O$  hydrogen bonds in the PBQ dimer should be much stronger than the bent hydrogen bonds in the NQ dimer.

For both PBQ and NQ dimers, the  $C-H\cdots O$  hydrogen bond distances ( $r_{OH} = 2.310$  Å in PBQ dimer and  $r_{OH} = 2.377$  Å in NQ dimer at the B3LYP/6-31G\* level) are longer than the standard hydrogen bond ( $\sim 1.9$  Å in water dimer) because of the intrinsic weakness of the  $C-H\cdots O$  hydrogen bond due to weak electronegativity of the carbon atom.

In the HBQ dimer,  $r_{OH}(\text{PBQ})$  (2.335 Å) and  $r_{OH}(\text{NQ})$  (2.495 Å) are slightly longer than those in PBQ and NQ dimers, because each dimer complex moiety is structurally strained by the helix backbone. Because the binding energies of PBQ dimer and NQ dimer were obtained at the geometries that the intermolecular interactions reach the maximum, the sum of these two binding energies would give the upper bound of the binding energy of the HBQ dimer.

We also calculated the HBQ dimer with four dodecyl ( $-OC_{12}H_{25}$ ) side chains to confirm our initial assumption that the side chains do not significantly affect the paired hydrogen bonds in the HBQ dimer. Indeed, we find that the effect is not significant (except for the slight binding energy increase due to partial multiple hydrogen bonds by weak hydrogen bonds between a carbonyl oxygen atom of the quinone moiety and alkyl hydrogen atoms of the side chain), because all the four side chains are positioned outward, as shown in Figure 3a. The central skeletal structure is nearly the same as that of the HBQ dimer without side chains. As listed in Table 1, the AM1

predicted binding energy of HBQ dimer with side chains ( $-5.8$  kcal/mol) is slightly larger than that of the HBQ dimer without side chains ( $-4.3$  kcal/mol). Side chains partially contribute to the stability of HBQ dimer because H atoms of the side chains also form hydrogen bonds with O atoms of NQ moiety in the other HBQ. However, this side chain effect is much smaller than that of the main paired hydrogen bonding between quinone moieties of the HBQ dimer. The results of MM simulations with AMBER parameters and RESP fitting charges are consistent with those of AM1. The MM predicted interaction energy of the HBQ dimer with side chains ( $-9.65$  kcal/mol) is also larger than that of the HBQ dimer without side chains ( $-8.95$  kcal/mol). Because the MM results are consistent with higher levels of calculation for the relatively small HBQ dimer, MM calculation would be a useful approach that can describe a quite large HBQ aggregation system.

As shown in Figure 3b, the one-dimensional chain structure of HBQ aggregates through paired hydrogen bonds is obtained by AM1 calculations. Because each HBQ has four paired hydrogen bonding sites and an HBQ pair has two paired hydrogen bonds, one HBQ molecule may bind two adjacent HBQ molecules linearly. Figure 3c shows the CPK model of MM optimized HBQ tetramer with side chains. Without side chains, its central skeletal structure is practically the same as that in Figure 3b. One-dimensional hydrogen bond chain of HBQ shows a structure similar to one-dimensional infinite acetic acid hydrogen bond chain, which was studied by Dannenberg et al.<sup>9i</sup> The fiber diameter in Figure 3c is  $\sim 38$  Å, which is very close to the experimental value (36 Å) reported by Katz et al.<sup>4</sup> Thus, our predicted structure is consistent with the macroscopic structure observed experimentally with X-ray diffraction, electron diffraction, and transmission electron microscopy. As seen in Figure 3b and c, the molecular structure of the HBQ aggregate would be a one-dimensional hydrogen bond chain, which is quite different from the columnar stack. This result would explain why Katz et al. were not able to find the sharp peak for the spacing between planes containing core rings in X-ray diffraction pattern that is usually observed in the diffraction patterns of columnar discotic liquid crystals.<sup>4b</sup> Actually, they gave a reasonable explanation that the sharp peak for the spacing between planes is absent, possibly because adjacent molecules may fluctuate from exact parallelism. Although the structural deviation of planes from the exact parallelism can cause the absence of the sharp peak, we think that the deviation from the exact parallelism would not be large in the case of well-aligned columnar stack. Thus, our proposed structure of one-dimensional hydrogen bond chain in Figure 3 (b and c) could be an alternative solution to the molecular structure of HBQ aggregates.

## Conclusions

The present study is one of very few theoretical studies on molecular assembling forces. Our results suggest that the intermolecular interaction of HBQ aggregates would be the paired hydrogen bonds between quinone moieties of HBQ rather than donor-acceptor interaction, which was proposed earlier. Paired hydrogen bonds provide enough binding affinity and structural robustness for helical aggregates. Interaction energy for an HBQ dimer is  $-7.9$  kcal/mol at the B3LYP/6-31G\* level. Our results suggest that the molecular structure of HBQ aggregates could be one-dimensional hydrogen bond chain rather than the columnar stack. Based on this one-dimensional hydrogen bond chain, the MM predicted diameter of HBQ fiber of 38 Å, is consistent with the experimental observation of 36 Å.

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