

Competitive Hydrogen Bonding in π -Stacked Oligomers**

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During the last decade, there has been a sustained interest in the formation of strongly packed discotic liquid crystals for electronic device applications, such as light-emitting diodes, field-effect transistors, and photovoltaic cells.^[1] Although such materials usually show low carrier mobility (10^{-6} – 10^{-5} cm² V⁻¹ s⁻¹), recent production of well-defined organic crystals with small intermolecular distances gives materials with mobilities^[2] (0.1–1 cm² V⁻¹ s⁻¹) approaching the transverse mobility of graphite (3 cm² V⁻¹ s⁻¹).^[3] In general, the reported intermolecular distance in a semiconducting discotic liquid crystal is around 3.5 Å.^[4] However, a surprisingly short interplanar distance of 3.18 Å has been reported for a discotic mesophase in which cohesion is assured by multiple amide functional groups with the ability to form hydrogen bonds.^[5] Thus, one can significantly decrease the intermolecular distance, leading to improved π – π coupling and enhanced cohesion of the assembly, by exploiting attractive intermolecular interactions such as hydrogen bonding.^[5–7] One clear advantage in exploiting hydrogen bonding for the production of electroactive materials is the probability of creating highly organized, tightly packed, and enforced low-dimensional nanostructures.^[8] Once intermolecular π overlap is increased, one may also expect a radical change in the charge-transport mechanism, where slow charge hopping could be replaced by fast band transport.^[9–10]

Previous work on 1,3,5-benzene triamides, in which the three amide side chains are disposed in a C₃-symmetry, allowed the formation of a hydrogen-bonded intermolecular network, yielding a helical columnar structure.^[8,11] More recent studies have explored hexasubstituted benzene rings in which the presence of alkoxy^[6] and alkyne^[12] substituents in 2,4,6-positions are considered to reinforce hydrogen bonding. The steric effect of such additional 2,4,6-substitution can induce a larger twist angle between the amide groups and the aromatic planes, thereby facilitating intermolecular hydrogen bonding between the amides.^[8,11] It could, however, also induce the opposite trend if the formation of intramolecular hydrogen bonding between amides becomes feasible. This would

ultimately hinder the twisting of the amides and prevent the formation of intermolecular hydrogen bonds. Although a strategic approach for the synthesis of assembled systems based on hydrogen bonding between molecules has been developed during the last years, the influence of intramolecular hydrogen bonds on such a mechanism is not usually considered. In the present work, we report a theoretical study showing the importance of intra- and intermolecular hydrogen bonding in the formation of self-assembled systems and, more specifically, on the creation of highly organized and stable oligomers. Strong intramolecular hydrogen bonding generally prevents the formation of very stable oligomers except where the inter-ring distance is relatively short. In contrast, weak hydrogen bonding facilitates the deformation of the functional groups to form relatively strong intermolecular bonds and stable systems but in which the inter-ring distance is large.

Figure 1 shows four molecules that have the ability to form intra- and intermolecular hydrogen bonds. Molecule **I** was previously studied by our group,^[13] and serves as a model of a large molecule that was experimentally shown^[6] to self-assemble into a helical shape. A similar helical structure has been also reported for molecule **II**.^[11] Molecules **III** and **IV** have not been previously investigated. The substituents were carefully chosen to evaluate different extents of intramolecular hydrogen bonding. Quantum-chemistry density functional theory (DFT) calculations were performed with the GAMESS^[14] software package. We mostly used a double- ζ (6-31G) basis set in conjunction with several functionals

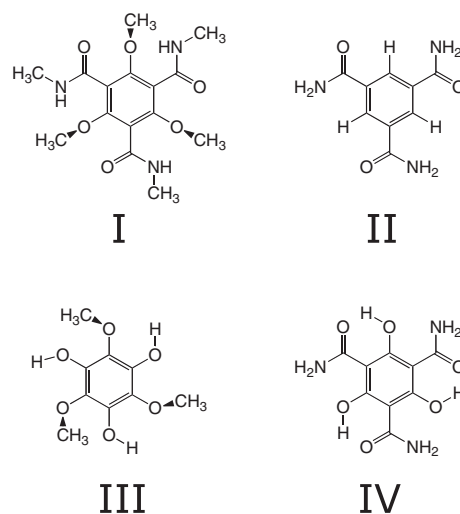


Figure 1. Schematic of molecular species considered in the formation of the small oligoassemblies.

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(VWN,^[15] B3LYP, and PBE). The aim of using different DFT functionals is to extract qualitative trends rather than to quantitatively evaluate electronic properties such as the band gap or dipole moment. This approach also helps to validate the ability of DFT functionals to predict qualitatively coherent properties. Because we were comparing the relative stability of different molecular systems, we did not performed any basis-set superposition error (BSSE) corrections. We have previously shown that DFT/B3LYP and Hartree–Fock methods give a quite appropriate description of the structural and electronic properties of such systems that are mainly directed by hydrogen bonding.^[13] The B3LYP functional is relatively good in describing weak hydrogen bonding,^[16–18] and is reasonably accurate in evaluating the band gap.^[19] On the other hand, Hartree–Fock is in close agreement with B3LYP in describing the cohesive energy of similar types of assemblies. The DFT functionals used here are also known to underestimate π – π dispersion energy^[18,20] by a few kcal mol^{–1} (1 cal \approx 4.19 J) on comparable systems; therefore, the calculated cohesive energies (which include BSSE) can be considered as a lower limit of an assembly's stability.

The main structural properties and the overall stabilities of the dimer assemblies are reported in Table 1. The cohesive energy per molecular unit was evaluated with $\Delta E = (E_{\text{ass}} - nE_{\text{mol}})/(n-1)$, where E_{ass} is the total energy of the assembly, E_{mol} is the total energy of the molecule, and n is the number of molecules in the assembly. Since the calculations were performed at 0 K, the structural parameters reported in Table 1 are more representative of the crystalline than the liquid-crystal phase. In addition, we have previously shown^[13] that structural parameters (ring–ring distance, twist angle) are not drastically affected by the number of units in the assembly. This result suggests that the values obtained for the dimers reasonably describe the structural properties of more extended systems. We first focused on the molecules that contain amide substituents between which intermolecular hydrogen bonding is expected to occur. Previous results support the idea that intermolecular hydrogen bonding in such assemblies depends on the ability of amide groups to twist with respect to the aromatic ring.^[6,8,11]

The results of our calculations on compounds **I**, **II**, and **IV** allow us to make the three following observations: from **I** to **IV** 1) the twist angle decreases, 2) the cohesive energy decreases, and 3) the intramolecular hydrogen bonding with side groups increases. The change in twist angle from the mono-

mer (in parenthesis) to the dimer when going from **I** to **IV** supports our contention that improved intramolecular hydrogen bonding significantly stabilizes a molecule, and makes the amide groups much less able to form intermolecular hydrogen bonds. The decrease in cohesive energy from compound **I** to **II** to **IV** is also consistent with the decreasing twist angle of the amides and, consequently, with the weaker intermolecular hydrogen bonding. It is interesting, however, to note that a low twist angle tends to favor smaller ring–ring separation, but that the resulting systems are less stable. In addition, the ring–ring separation value calculated at VWN (3.58 Å) and B3LYP (3.62 Å) levels for molecule **II** was in excellent agreement with the experimental value of 3.62 Å obtained from X-ray diffraction for this compound.^[11,21]

The case of molecule **IV** is also interesting because it remains practically flat, even in the dimer assembly, because of the several intramolecular hydrogen bonds that hinder the twisting of the substituents. In this specific case, the cohesive energy is in the same range as weakly bonded π -stacked systems such as benzene, naphthalene, and anthracene dimers.^[22] In contrast to these acene dimers, which preferably adopt either displaced, T-shaped, or herringbone-like structures,^[22] molecule **IV** maintains a face-to-face configuration with a relatively small ring-to-ring separation. This result suggests that the presence of intermolecular hydrogen bonds in **IV**, even if very weak, compensates for the π – π interactions that should cause the dimer to adopt a more deformed structure. The existence of the π – π interaction is also important in considering this type of π -stacked system. We have previously demonstrated that such dispersive π – π interactions in a system where benzene rings are perfectly organized into a columnar shape would be very small, and more probably slightly repulsive.^[13] The presence of an intermolecular hydrogen-bonding network suggests that such assembly is more rigid, and would present a higher phase transition temperature than other discotic materials involving only the π – π interaction. Then, even though the determination of structural parameters at higher temperatures ($T > 0$ K) would necessitate a mixture of both quantum-mechanical and statistical-physics methods to be properly addressed, we can predict that the structural parameters of hydrogen-bonded systems should be much less affected by temperature than π – π stacked systems.

Substitution by methoxyl groups is another way of varying the structure and cohesion of the molecular assemblies. The most important effect of adding methoxyl groups is that steric

Table 1. The structural properties of 2-unit oligoassembly.

Species	ring–ring separation (Å)			twist angle [a] [degrees]			helical angle [degrees]			cohesive energy (ΔE) [eV monomer ^{–1}]		
	VWN	B3LYP	PBE	VWN	B3LYP	PBE	VWN	B3LYP	PBE	VWN	B3LYP	PBE
I	4.53	4.54	5.11	68 (48)	71 (45)	81 (53)	28	28	14	0.76	0.63	0.72
II	3.58	3.62	3.94	32 (0)	33 (0)	36 (0)	55	54	56	0.54	0.55	0.45
III	3.92	4.22	4.63	–	–	–	18	21	22	0.23	0.15	0.17
IV	3.63	3.67	4.06	1 (1)	0 (0)	0 (0)	57	59	40	0.16	0.12	0.14

[a] This corresponds to the angle between the amide group and the aromatic plane. Calculated values for the monomers are given between parentheses.

congestion prevents the molecule from adopting a flat conformation. Another important factor is that methoxyls participate in intermolecular hydrogen bonding. These two factors are the main reasons for the large ring–ring separation and the small helical angle observed in compounds **I** and **III**. A comparison of molecules **I** and **II** also gives clear evidence of the effect of methoxyl substitution. In **II**, the ring–ring separation decreases by around 1 Å, the helical angle practically doubles, and the cohesive energy per monomer decreases by nearly 30%. A comparison of cohesive energies among **I**, **II**, and **III** gives a rough estimate of the contribution of the methoxyl groups to the stabilization of the assemblies. Molecule **I** shows intermolecular hydrogen bonds arising from amide and methoxyl groups, giving a cohesive energy of 0.63–0.76 eV, molecule **II**, which has only amide groups gives 0.45–0.55 eV, and molecule **III** with only methoxyls (if one assumes that the OH–OH interaction is negligible) gives 0.15–0.23 eV. This result indicates that methoxyl interactions stabilize the assembly. Furthermore, they increase the ring–ring separation and, consequently, decrease the π -electron coupling.

From these results on the structural stability of small assemblies, we can understand that hexasubstituted benzene rings form stacked assemblies that are 1) strongly bonded (high cohesive energy) and 2) tightly stacked (short interplanar distance). The presence of substituents with a propensity to participate in intramolecular hydrogen bonds make the molecule flatter, the ring–ring separation shorter, and the cohesive energy smaller. In contrast, the presence of substituents that preferably form intermolecular hydrogen bonds are predicted to increase the ring–ring separation, favoring the twisting of substituents, improving the overall dipole moment, and improving the stability of the assembly. A judicious choice of substituents that reflect a balanced competition between intra- and intermolecular bonding is thus required to design assemblies for specific applications.

The electronic structure properties found in Table 2 are consistent with our description of intra- and intermolecular interactions. The drastic difference in the dipole moments of molecules **I**, **II**, and **III** (in parenthesis) compared to their dimers clearly indicates an increasing twist of the substituents in order to form intermolecular hydrogen bonds. The dipole moment of **I** is lower than that of **II** simply because the individual dipoles of the amides and methoxyl groups in **I** are pointing in opposite directions. Hence, the change in dipole moment

Table 2. Variation of electronic properties upon the formation of 2-unit oligoassemblies.

Species	dipole moment [Debye]			band gap [a] [eV]		
	VWN	B3LYP	PBE	VWN	B3LYP	PBE
I	12.7 (3.2)	12.6 (2.6)	15.3 (3.8)	11.5 (12.3)	4.4 (5.3)	2.5 (3.4)
II	14.2 (0.0)	14.2 (0.0)	14.7 (0.0)	10.9 (12.1)	4.0 (5.3)	2.0 (3.1)
III	8.2 (3.4)	8.7 (3.8)	9.1 (4.1)	12.0 (12.8)	5.2 (5.9)	3.4 (4.0)
IV	0.0 (0.0)	0.0 (0.0)	0.0 (0.2)	11.8 (12.2)	4.4 (5.3)	2.5 (3.5)

[a] Calculated values for the monomers are given between parentheses.

upon assembly is a good indicator of the flexibility of the substituents, which is needed to create intermolecular hydrogen bonding. The calculated dipole moments for **IV** demonstrate that intramolecular hydrogen bonding can inhibit the twisting of amides to create intermolecular hydrogen bonds. In contrast to the evaluation of the dipole moment, the calculated values for the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap strongly, but not surprisingly, depends on the DFT functionals used.^[23] Nevertheless, we emphasize that the band gap systematically decreases upon the formation of the dimers (Table 2). Although a decrease in ring–ring separation is the major factor that contributes to decreasing the band gap through an improved π coupling,^[24] it remains difficult to uniquely correlate the changes observed from the monomer to the dimer to this structural parameter. In fact, the calculated band gap also depends on the method used, on the symmetry of the molecules, and on the donor–acceptor nature of the substituents that modulate the π charge density on the ring moiety.^[25]

In order to evaluate the stability of longer oligoassemblies, we investigated the variation of the cohesive energy as a function of the number of molecules in the assembly. Figure 2

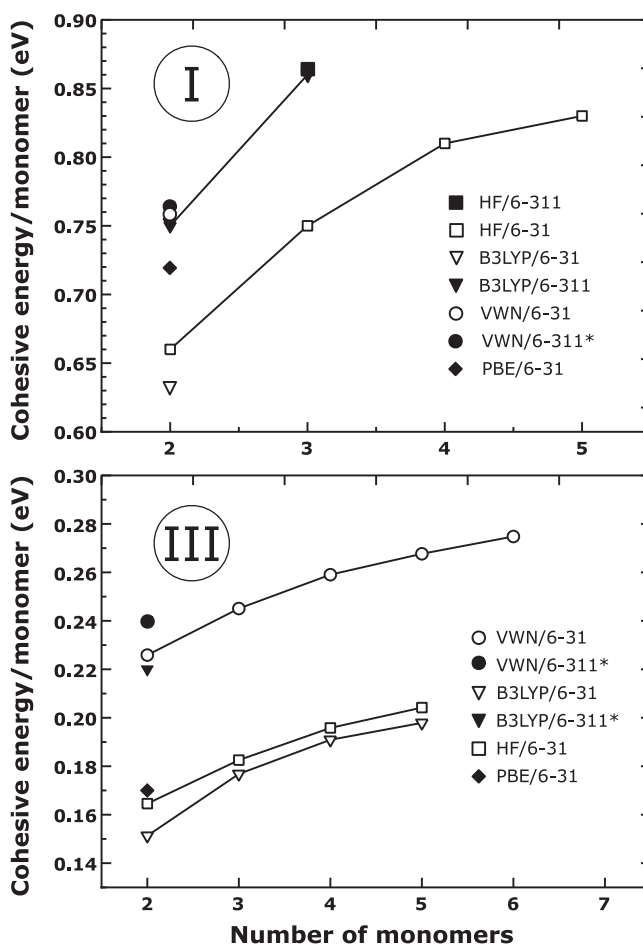


Figure 2. Variation of cohesive energy per monomer as a function of the number of monomers in the **I** and **III** assembly.

shows the increasing stabilities of the systems against the number of monomers calculated using several computational methods. Although we used several different theoretical approaches to evaluate cohesive energies, they remained in a relatively narrow range, and the relative stabilities of the assemblies were similar from one method to another (see also Table 2). From the variation in cohesive energy calculated for molecules **I** and **III**, we can predict that the electronic properties for an assembly containing more than 8–9 molecular units will converge to stable values. This result is in agreement with observations of other similar systems^[10,13] as well as of polymers.^[26] We can expect similar behavior for molecules **II** and **IV** in terms of assembly stabilities. In addition, we want to emphasize that the calculated structural properties for the longer assemblies are very similar to the ones shown in Table 1 for the two-units assemblies.

In conclusion, we have described the importance of intra- and intermolecular hydrogen bonds on the creation of strongly organized assemblies and their physical properties. Molecules with significantly strong intramolecular hydrogen bonds are generally flat, and do not show the conformational flexibility required to form tightly packed oligomers. In contrast, molecules with an elevated molecular flexibility can create strong intermolecular hydrogen bonds, which favor the cohesion of oligomers. However, the molecules are separated by relatively large interplanar distances. Consequently, the π - π coupling that is generally associated with significant charge-transport properties can be tailored through a judicious choice of functional groups.

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