Dithienophosphate-Based Phosphinamides with Intriguing Self-Assembly Behavior

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Abstract: A new, highly adaptable type of phosphinamide-based hydrogen bonding is representatively demonstrated in π-conjugated phosphate materials. The rotational flexibility of these intermolecular P=O–H–N hydrogen bonds is demonstrated by X-ray crystallography and variable-concentration NMR spectroscopy. In addition to crystalline compounds, phosphinamide hydrogen bonding was successfully introduced into the self-assembly of soft crystals, liquid crystals, and organogels, thus highlighting the high general value of this type of interaction for the formation of organic soft materials.

Organometallic compounds, that is, organic species exhibiting B, Si, P, Se, or Te atoms in their scaffold, have recently experienced a surge in growth as potential building blocks for electronic materials. Phospholes, in particular, possess unique electronic and structural features that have made them a particularly intriguing research focus. In this context, we introduced self-assembled phosphole lipid biomimics in 2011. These amphiphilic materials display unique opto-electronic and mechanical features, and their self-assembly is governed by a fine balance of intermolecular ionic, van der Waals, and π-stacking interactions. To further develop the supramolecular self-assembly toolbox of phosphate-based building blocks, it would be desirable to expand the interaction portfolio to include intermolecular hydrogen bonding. Hydrogen bonding plays an important role in diverse fields ranging from biochemistry to materials science. Hydrogen bonding of primary and secondary amides, in particular, is a versatile motif that can be found in various natural or synthetic materials. For example, it is crucial for the formation of secondary structures of peptides, such as α-helix or β-sheet structures, but also for the superior functional performance of materials such as Kevlar.

Phosphinamides have received some attention as a hydrogen-bonding motif, the incorporation of the “PONH” building block was shown to induce unique effects on the self-assembly of such systems. Herein, we demonstrate the synthetic value and self-assembly validity of the phosphinamide functional group with our π-conjugated phosphate system to develop new soft functional materials.

The new phosphinamide species was synthesized by the postfunctionalization of chlorophosphole 3, which is accessible by a three-step protocol from the dibromomethylphosphine precursor S1 (Scheme 1). By closing the phosphole ring with an amino(dichloro)phosphate, we obtained phosphate species 1, which can readily be further functionalized. Cleavage of the P–N bond in an aqueous medium provided us with phosphonic acid 2. From this acid precursor, 3 was obtained by chlorination with thionyl chloride. Treatment of 3 with a series of primary alkyl amines finally afforded the corresponding phosphinamides 4a–d and trisopropylsilyl (TIPS)-decorated 4c-TIPS in good yields (Scheme 1).

Since dithienophospholes are commonly strongly emissive, the photophysical properties of the newly synthesized phosphinamides 1, 4a–d, and 4c-TIPS were tested both in...
Table 1: Photophysical data of the new phosphinamides.

| Compound | $\lambda_{\text{abs}}$ [nm]$^a$ | $\log e$ $^a$ | $\lambda_{\text{em-
solid}}$ [nm]$^a$ | $\eta_{\text{PL, soln.$^b$}}$ [%]$^a$ | $\lambda_{\text{em-
solid}}$ [nm] | $\eta_{\text{PL, soln.$^b$}}$ [%]$^a$ |
|-----------|------------------|------|-----------------|------------------|------------------|------------------|
| 1         | 358              | 3.77 | 447             | 45               | 462              | 27               |
| 4a        | 355              | 3.77 | 448             | 57               | 439              | 22               |
| 4b        | 356              | 3.83 | 448             | 61               | 431              | 13               |
| 4c        | 357              | 3.77 | 450             | 62               | 445              | 10               |
| 4d        | 357              | 3.78 | 450             | 58               | 444 (435)$^a$    | 11 (19)$^a$     |
| 4c-TIPS   | 372              | 4.04 | 458             | 63               | 469              | 49               |

$^{[a]}$The absorption wavelength was measured for a solution in dichloromethane ($\varepsilon = 1.0 \times 10^{-1}$ M). $^{[b]}\varepsilon$ is the molar absorption coefficient ($\varepsilon$ cm$^{-1}$).

The solid-state emission spectra revealed that 4a-d each experience a hypsochromic shift upon going from the solution to the solid state. The absorption coefficient for the parent P-phenyl dithienophosphole ($\varepsilon = 4.33$; 338 nm)$^{[6]}$ DFT calculations at the B3LYP/6-31+G(d) level of theory$^{[7]}$ revealed that this relationship was due to the residence of both the HOMO and LUMO on the backbone of the compounds, in complete agreement with the frontier orbitals of the P-phenyl relative.

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Figure 1. Crystallographic packing of 1. Note the antiparallel alignment of the conjugated phosphate backbone.

Figure 2. Crystallographic packing of 4a. Intermolecular N–O distance: 2.9 Å. Note the parallel alignment of the conjugated phosphate backbone. a) Hydrogen-bonded column viewed along the butyl chain; b) hydrogen-bonded column viewed from the side.
system, owing to the distinctive bonding pattern of the tetracoordinated P center, this conjugation is considerably impeded. What results is the greater rotational freedom about the P=O bond and thus flexible hydrogen bonding. Importantly, however, supramolecular π-stacking is also present in the solid-state structures of both 4a and 4c. The cooperative effects of the H-bonding and the π-stacking in these compounds ultimately lead to the formation of the linear “head-to-tail” assembly in the solid state. However, one question remains: What if the π-stacking were suppressed and the self-assembly process solely governed by H-bonding? To answer this question, we designed compound 4c-TIPS. With the bulky TIPS group appended to the periphery of the backbone, the potential for π-stacking is removed. X-ray crystallography of 4c-TIPS revealed that instead of ordering in a linear fashion, 4c-TIPS adopts an edge-on motif in the solid state, with the only intermolecular interactions of note being H-bonding (Figure 5); the resulting H-bonded “head-to-head” dimer has similar bond angles to those of its organic carboxamide cousins (dihedral angle PO-NH: 17°; Figure 4, 4c-TIPS).

Although X-ray crystallography offers useful insight into the nature of the H-bonding in a static manner, the flexible nature of the newly synthesized phosphinamides compelled us to also study the unprecedented H-bonding in a dynamic manner, that is, in solution. For this purpose, 4c was representatively chosen for its intermediary dihedral H-bonding angle; variable-concentration (VC) NMR experiments were performed in CDCl₃. The results were fitted by the use of a program developed by Thorarinson (see the Supporting Information). The dimerization constant of 4c was determined to be 0.8 M⁻¹. This value is close in magnitude to the dimerization constant of cis amides and approximately two orders of magnitudes lower than the value reported for a related cyclic phosphaquinolinone by Haley and co-workers (Table 2). As the Haley dimer was restricted in the cis conformation, the lower dimerization constant in our phosphinamide species can be attributed to the rotational flexibility of the P–N bond. Our X-ray crystallographic and NMR spectroscopic results indicate significant rotational flexibility of the P–N bond in phosphinamides 4a, c and 4c-TIPS in H-bond formation. Such flexi-

![Figure 3](image-url)  
**Figure 3.** Crystallographic packing of 4c. Intermolecular N···O distance: 2.8 Å. Note the zigzag pattern of the hydrogen bonding.

![Figure 4](image-url)  
**Figure 4.** Dihedral angles between the P=O and N–H moieties in 4a, 4c, and 4c-TIPS, as based on the X-ray crystallographic data.

![Figure 5](image-url)  
**Figure 5.** Crystallographic packing of 4c-TIPS. Intermolecular N···O distance: 2.8 Å. a) Hydrogen-bonded dimer viewed from the top; b) hydrogen-bonded dimer viewed from the side.

| Compound                  | K [M⁻¹]¹   |
|---------------------------|------------|
| ε-caprolactam              | 1.4–1.8    |
| Haley phosphaquinolinone   | 130        |
| 4c                        | 0.8        |

¹ Dimerization constant.  
² Measured for a solution in CHCl₃.  
³ Measured for a solution in CDCl₃.

Table 2: Dimerization constants for amides and phosphinamides. [10, 11]
bility is unknown for classic amide H-bonds, such as those commonly found in peptides.

To capitalize on this unique driving force for self-assembly in the soft-materials realm, the mesogenic versions of the corresponding crystalline compounds 4a,d of the mesogenic versions 4b,d of the corresponding crystalline compounds 4a,c were synthesized by treating chlorophosphole 3 with amines that were appropriately functionalized with long disorder-inducing alkyl chains. Monoalkylated 4b exhibits soft-crystalline features at elevated temperatures, as determined by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and powder X-ray diffraction (PXRD). Although crystalline features were preserved in 4b, all attempts to grow single crystals were unsuccessful. However, on the basis of the POM patterns and the formation of H-aggregates in both 4a and 4b, it is inherently plausible that 4b self-assembles into a smectic mesophase, similar to the structure of 4a in the single crystal (Figure 6a). Owing to the presence of multiple extended alkyl chains, the mesophase behavior of 4d tends to be more on the “softer” liquid-crystalline (LC) side. Correspondingly increased disorder was observed by POM (more uniform domains features), DSC (broader thermal transitions), and PXRD (broad “humps” instead of sharp peaks; see the Supporting Information). Similar to 4b, the combined observation of H-aggregates and the POM pattern lead us to also propose a smectic assembly pattern for 4d (Figure 6b). More rigorous studies toward the detailed supramolecular organization of the mesophases for both 4b and 4d are currently under way.

Besides the observed LC self-assembly, 4d was also able to form an organogel with n-heptane at low concentrations (Figure 6c). Fluorescence emission spectra were collected from the gel (Table 1), and H-aggregation was also observed. The presence of H-bonding in the organogel was moreover confirmed by IR spectroscopy and further indirectly asserted by the complete dissolution of the gel upon the addition of a small amount of methanol as a H-bond donor (see the Supporting Information). The morphology of the xerogel was studied by scanning electron microscopy (SEM), and both fiber bundles and sheetlike microstructures were observed (Figure 6d).

In conclusion, we have synthesized a new class of phosphole-containing conjugated phosphinamide compounds via the synthetically valuable chlorophosphole 3. Single-crystal X-ray crystallography and VC NMR spectroscopy demonstrated the capacity for a new type of rotationally flexible hydrogen bonding of the compounds in both the crystalline state and solution. Mesogenic versions of the crystalline compounds were found to display soft-crystal or liquid-crystal properties at elevated temperatures as a proof of concept. Compound 4d was also shown to form an organogel with hydrogen-bonding components. Furthermore, several of the new phosphinamides studied formed H-aggregates as a result of the unique H-bonding-directed self-assembly, thus demonstrating the considerable and general value of this structural element for the development of self-assembled soft materials. Detailed studies to expand the scope of this intriguing new supramolecular interaction are currently under way in our laboratory.

Acknowledgments

We thank S. Mulmi and Dr. C. Reus for their assistance in collecting PXRD and SEM data, and C. Vonnegut for helpful discussions with regard to the VC NMR studies. Financial support by the NSERC of Canada and the Canada Foundation for Innovation (CFI) is gratefully acknowledged. We also thank Alberta Innovates—Technology Futures for graduate scholarships (Z.W. and B.S.G.).

Keywords: hydrogen bonds · phosphinamides · phosphorus heterocycles · self-assembly · soft materials

How to cite: Angew. Chem. Int. Ed. 2016, 55, 3481–3485
Angew. Chem. 2016, 128, 3542–3546

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Received: December 2, 2015
Published online: February 2, 2016