Phosphorus Heterocycles

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Facile Synthesis and Properties of 2-λ^5-Phosphaquinolines and 2-λ^5-Phosphaquinolin-2-ones

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Abstract: *Treatment of 2-ethynylanilines with $P(OPh)_3$ gives either 2,2-diphenoxy-2-λ^5-phosphaquinolines or 2-phenoxy-2-λ^5-phosphaquinolin-2-ones under transition-metal-free conditions. This reaction offers access to an underexplored heterocycle, which opens up the study of the fundamental nature of the N=P^V double bond and its potential for delocalization within a cyclic π-electron system. This heterocycle can serve as a carbostyril mimic, with application as a bioisostere for pharmaceuticals based on the 2-quinolinone scaffold. It also holds promise as a new fluorophore, since initial screening reveals quantum yields upwards of 40%, Stokes shifts of 50–150 nm, and emission wavelengths of 380–540 nm. The phosphaquinolin-2-ones possess one of the strongest solution-state dimerization constants for a D–A system (130 M^{-1}) owing to the close proximity of a strong acceptor (P=O) and a strong donor (phosphonamidate N–H), which suggests that they might hold promise as new hydrogen-bonding hosts for optoelectronic sensing.*

The azaphosphinine scaffold has been explored as an analogue of hydrocarbon-based molecules for nearly half a century. The simplest six-membered ring systems, analogous to benzene, are comprised of three structural isomers: 1,4-λ^3-azaphosphinine (**1**) was first made in 1972,[1] followed by the 1,3- (**2**) and 1,2- (**3**) λ^3-azaphosphinine congeners in 1987 (Figure 1 a).[2] Until recently, nearly all azaphosphinines have featured phosphorus atoms formally in the +3 oxidation state,[3] except for one notable example, compound **4**, which has phosphorus in the +5 oxidation state and was prepared in 1991.[4] The pioneering studies of Dewar and Campbell on 1,2-azaphosphinines in the early 1960s, however, met with varying degrees of success.[5] While Dewar was able to prepare the HI salt of **5**, attempts by both groups to isolate the corresponding λ^3-derivatives yielded unstable systems that required isolation as λ^5-phosphonamidates such as **6**. While there have since been a handful of other investigations of 1,2-azaphosphinine structure and reactivity, the difficulty in synthesizing them has precluded rigorous investigations.[6] On the other hand, examination of the fully inorganic variants has proceeded extensively, with cyclotriphosphazenes such as **7** being one of the most studied inorganic heterocycles.[7] For example, the first cyclotriphosphazene was described in 1834 by Liebig, though the exact structure remained contested until the 1860s.[8]

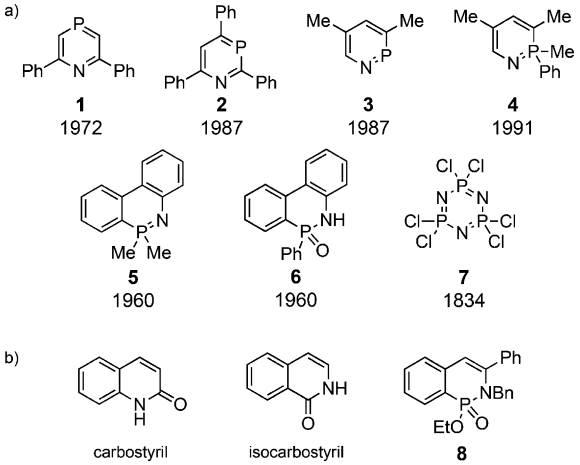

Figure 1. a) Early examples of azaphosphinines. b) Carbostryril and isocarbostyril and their structural similarity to bioisosteres like phosphonamidate **8**.

The choice of substituents on the phosphorous atom can significantly affect the stability and reactivity of the 1,2-λ^5-azaphosphinine scaffold. P–C_{alkyl} and P–C_{aryl} derivatives such as **4** and **5** are very sensitive to oxygen and water and decompose readily upon atmospheric exposure.[4–6] On the other hand, 1,2-λ^5-azaphosphinines with alkoxy and phenoxy groups tend to hydrolyze from their phosphonimidate form (e.g., **4**, **5**) to the considerably more stable phosphonamidate form (e.g., **6**, **8**).

Phosphonates and their analogues have seen extensive use as transition-state mimics for ester and amide hydrolysis. For instance, compound **8** has been explored recently as a bioisostere of isocarbostyril[9] and shows promise in pharmacological applications (Figure 1 b).[10] In addition to the ability of phosphonates/phosphonamidates to act as ester and amide bioisosteres, these compounds have relevance for a number of other health-related uses.[11] As a result, new efficient metal-free reactions to make phosphonate derivatives of common heterocyclic scaffolds, such as the quinolinone substructure, are highly desirable.[12] Herein, we describe a simple synthesis

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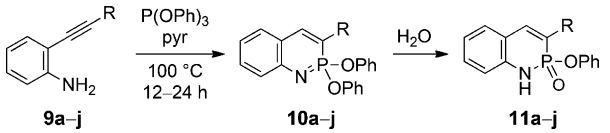
to assemble the 2-λ^5-phosphaquinoline framework in a single step from easily attainable starting materials.

Reaction of $P(OPh)_3$ with 2-ethynylanilines **9a–j**, which are accessible through Sonogashira cross-coupling of known alkynes with 2-iodoaniline, furnished phosphaquinolines **10** (the imidate form; Scheme 1) along with varying amounts of



Scheme 1. Synthesis of 2-phosphaquinolines and 2-phosphaquinolin-2-ones.

phosphaquinolinones **11** (the amidate form), the latter of which arise from the partial hydrolysis of **10** by adventitious water during work-up and purification. The yields in Table 1

Table 1: Reaction scope and yields of isolated product for the azaphosphinine cyclization.

Entry	R	Yield (**10**)	Yield (**11**)
a	3,5-$(CF_3)_2$Ph	–[a]	39%
b	4-CNPh	54%	79%
c	4-(CO_2Et)Ph	54%	74%
d	4-ClPh	–[a]	80%
e	Ph	45%	72%
f	4-MePh	63%	82%
g	4-MeOPh	56%	66%
h	4-(NMe_2)Ph	68%	–[a]
i	*n*-Pen	–[a]	73%
j	2-pyridyl	71%	31%

[a] Not isolable.

reflect our best efforts to rigorously exclude (**10**) or include (**11**) water as part of the overall sequence; nonetheless, **10a**, **d**, **i** were too labile to isolate purely as the phosphaquinoline. This cyclization is tolerant of a variety of electron-rich and electron-poor arenes, as well as alkyl functionality attached at the ethynyl group (Table 1, entry **i**). However, the reaction did not tolerate silyl-protected or terminal alkynes, and nor were ketones stable to the cyclization conditions owing to competing Kabachnik–Fields condensation,[13] all of which resulted in intractable polymers. Interestingly, ethyl ester derivative **10c** does not undergo a "traceless" Staudinger ligation.[14] This and the general stability of the phosphonimidate toward hydrolysis at room temperature once purified lends credence to the idea of increased stability from electron delocalization within the heterocycle.

Single-crystal X-ray diffraction provided the solid-state structures of **10j** (Figure 2) and **11j** (Figure 3a), which allowed us to directly compare the imidate and amidate forms, respectively (Table S1).[15] The P–N bond in **10j** (1.565 Å) is much shorter than the amidate P–N bond in **11j** (1.635 Å) but is similar to the analogous bond in hexaphenoxycyclotriphosphazene (1.575 Å).[16] The imidate structure indicates some π-electron delocalization within the

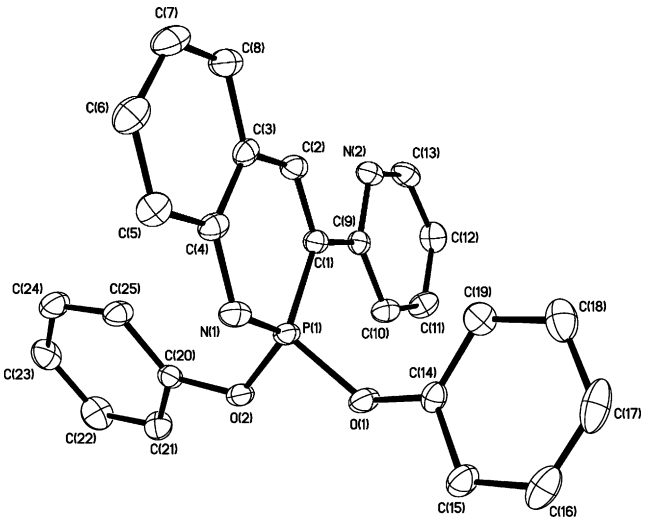


Figure 2. X-ray crystal structure of **10j**.

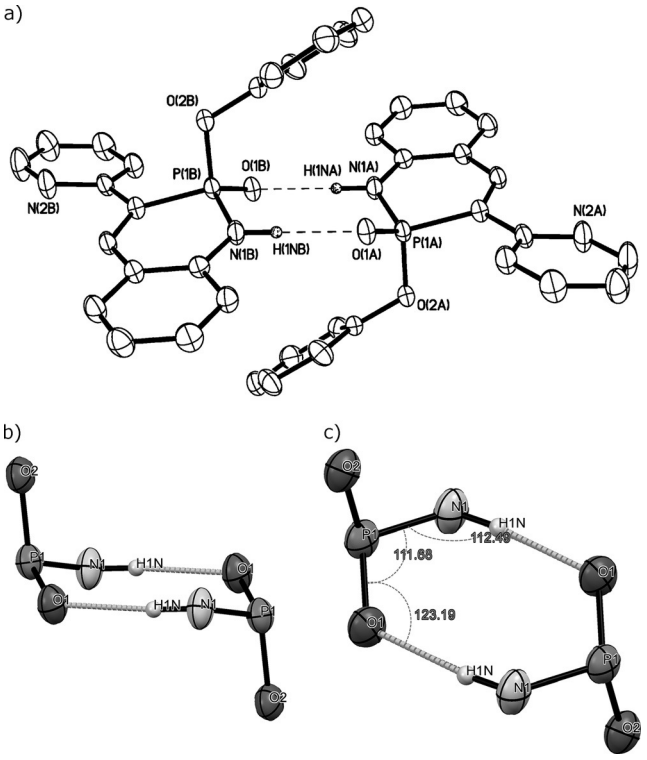


Figure 3. a) ORTEP of the dimer of **11j**. b) An angled view, with C atoms removed for clarity, shows the chair conformation of the H-bonding ring. c) A view from above the ring with relevant bond angles demonstrates their similarity to idealized chair-conformation angles.

heterocycle, with the C(1)=C(2) double bond length (1.367 Å) intermediate between that of benzene and an isolated double bond, whereas the same bond in **11j** (1.341 Å) is nearly identical in length to the corresponding bond in carbostyril (1.343 Å).[17] The azaphosphinine ring in **10j** shows only small deviations from planarity (RMSD 0.014 Å). Analysis of crystal structure and computational models (see the Supporting Information) indicates that the enhanced

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stability of **10j** to hydrolysis is likely due to coplanarity of pyridine and the azaphosphinine ring, held by a weak hydrogen bond between the hydrogen atom on C(2) and the pyridine nitrogen atom. This conformation limits water addition at phosphorus, since attack would likely occur 180° from the P=N bond. Phosphates hydrolyze via an associative mechanism, thus making a dissociative pathway unlikely.[18] Moreover, the S_N2-type displacement that is commonly found for alkyl phosphonates cannot occur with the phenyl substituents within **10**.

Interestingly, the amidate-type structures tend to crystallize as dimers between the two enantiomers, forming a complementary association between the N–H and P=O groups (Figure 3a), with correspondingly short intermolecular distances (N···O 2.837-2.840 Å in **11j**) and nearly linear N-H···O angles (164-174°). This dimer formation is mirrored in solution, since compound **11b** possesses a dimerization constant (K_{dim}) of $130 \pm 4\,M^{-1}$ in $CDCl_3$. This corresponds to an energy of ca. 1.5 kcal mol^{-1} per H bond, which is large compared to *cis* amides such as pyrrolidone or caprolactam, which show dimerization constants in the range 1–5 M^{-1} in $CHCl_3$.[19] Along with phosphonamidates possessing both a stronger hydrogen-bond acceptor (P=O vs. C=O) and a stronger hydrogen-bond donor (P(O)N-H vs. C(O)N-H) than amides, the non-coplanar arrangement of donor/acceptor and lower directional preference of P=O donors allow the pseudo 6-membered ring to adopt a chair conformation and minimize repulsive secondary interactions (Figure 3b,c).[20] As a result, this dimer deviates from the trends noted by Schneider and Sartorius, where each attractive interaction gives −1.88 kcal mol^{-1} of energy to ΔG, and each repulsive secondary interaction gives +0.74 kcal mol^{-1}.[21] Following the same scheme, two repulsive secondary interactions in our dimer yield only +0.76 kcal mol^{-1} of destabilization, roughly half of what is expected.

The 2-phosphaquinolinone scaffold demonstrates a wide range of fluorescent emission wavelengths (383–554 nm), dependent on substitution and protonation state (Figure 4 and Table 2). The fluorescence behavior is similar to that of carbostyril, although somewhat red-shifted (3-phenylcarbostyril ex: 345 nm, em: 410 nm; **11e** ex: 354 nm, em: 427 nm).[22] Significant differences between the azaphosphinine and carbostyril include: 1) a more dramatic solvatofluorescent effect in azaphosphinines (**11b** $CHCl_3$ em: 430 nm, MeCN em: 450 nm, see the Supporting Information), and 2) an easily deprotonated amidate N–H, which yields a red-shifted fluorescent response, with the anion possessing a surprisingly large Stokes shift of 102–151 nm, depending upon substitution. Fluorophores possessing such a large Stokes shift are very useful owing to the lack of overlap between excitation and emission, thus lending promise for their use in imaging/sensing applications.[23] In addition, although the more promising red-shifted derivatives of **11** possess only modest quantum yields (ca. 4–5%) the anions of those fluorophores show quantum yields in the range of 30–40%, thus demonstrating their potential for use as fluorescent tags, especially if the design principles for carbostyril fluorophore development were to be followed to further red-shift emission and increase the quantum yield.[24]

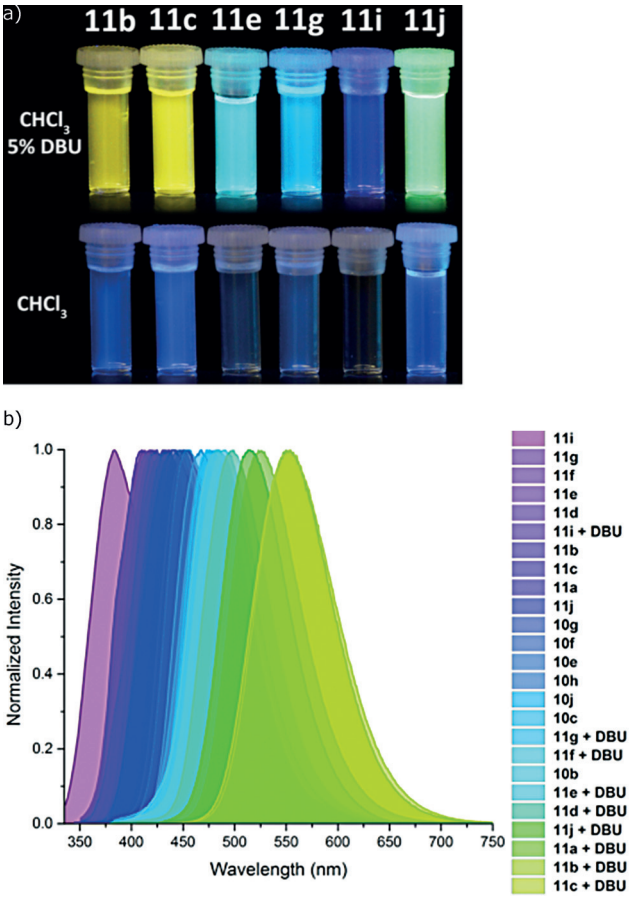

Figure 4. a) Images of the fluorescence of 2-phosphaquinolin-2-ones under neutral and basic conditions. b) Graphical depiction of the differing emissions of 2-phosphaquinolines and 2-phosphaquinolin-2-ones in $CHCl_3$ and upon the addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), demonstrating the emission range from UV to yellow.

Table 2: Fluorescence properties of compounds **10**, **11**, and deprotonated **11**.[a]

Entry	10	11	11 + DBU
a	–	434, 85	523, 128
b	483, 83	430, 81, 4%	554, 137, 41%
c	473, 90	432, 81, 5%	553, 151, 31%
d	–	422, 63	499, 126
e	453, 80	418, 76	491, 127
f	450, 81	413, 72	482, 114
g	447, 78	410, 71	473, 107
h	454, 85	–	–
i	–	383, 65	425, 102
j	467, 79	442, 79	514, 102

[a] Each entry is listed with the emission maximum, Stokes shift (nm), and photoluminescent quantum yield (if present), in that order.

In summary, we present a facile synthesis of 2-λ^5-phosphaquinoline derivatives from 2-ethynylanilines. The ease of preparation and the range of diverse structures that can be readily accessed will permit detailed examination of this rare class of heterocycles, from the fundamental perspective of the study of the delocalization of N=P^V bonds to

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applications of the phosphaquinolinones as carbostyril mimics and as novel switchable fluorophores with high quantum yields and large Stokes shifts in the ON state. In addition, the surprisingly large dimerization constant of **11b**, a system bound by only two hydrogen bonds, hints at potential for the phosphaquinolinones as new hydrogen-bonding scaffolds in supramolecular chemistry. Our group is currently working to expand upon these varied and exciting applications.

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[15] Crystallographic data for **10j**: $C_{25}H_{19}N_2O_2P$, $M = 410.39$, $0.17 \times 0.16 \times 0.12$ mm, $T = 173(2)$ K, Monoclinic, space group $P2_1/c$, $a = 11.0967(14)$ Å, $b = 9.6020(13)$ Å, $c = 19.319(2)$ Å, $\beta = 90.982(4)°$, $V = 2058.2(5)$ Å^3, $Z = 4$, $\rho_{cald} = 1.324$ Mg m^{-3}, $\mu = 0.158$ mm^{-1}, $F(000) = 856$, $2\theta_{max} = 50.0°$, 22128 reflections, 3633 independent reflections [$R_{int} = 0.0525$], $R1 = 0.0428$, $wR2 = 0.0921$ and GOF = 1.024 for 3633 reflections (347 parameters) with $I > 2\sigma$(I), $R1 = 0.0763$, $wR2 = 0.1078$ and GOF = 1.024 for all reflections, max/min residual electron density $+0.290/-0.311$ e Å^{-3}. Crystallographic Data for **11j**: $C_{19}H_{15}N_2O_2P$, $M = 334.30$, $0.12 \times 0.09 \times 0.04$ mm, $T = 223(2)$ K, Triclinic, space group P-1, $a = 8.4050(3)$ Å, $b = 10.5908(4)$ Å, $c = 20.2049(7)$ Å, $\alpha = 103.100-(2)°$, $\beta = 94.314(3)°$, $\gamma = 109.365(2)°$, $V = 1630.36(11)$ Å^3, $Z = 4$, $Z' = 2$, $\rho_{cald} = 1.362$ Mg m^{-3}, $\mu = 1.607$ mm^{-1}, $F(000) = 696$, $2\theta_{max} = 134.32°$, 18307 reflections, 5681 independent reflections [$R_{int} = 0.0529$], $R1 = 0.0544$, $wR2 = 0.1447$ and GOF = 1.050 for 5681 reflections (553 parameters) with $I > 2\sigma$(I), $R1 = 0.0738$, $wR2 = 0.1576$ and GOF = 1.050 for all reflections, max/min residual electron density $+0.742/-0.441$ e Å^{-3}. CCDC 1416795 and 1416794 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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